# A2 Chemistry: Rates, Equilibrium and pH

## rate of reaction

* Rate of reaction - the change in concentration of a reactant or product per unit time. The units of rate are **moldm-3s-1**
* Square brackets are used to represent the concentration of a reactant or product in moldm-3 e.g. [CO2]
* The rate of a reaction can be found by measuring the gradient of the tangent to the curve in a concentration-time graph
* Gradient = **change in y ÷ change in x**
* Initial rate - the change in concentration of a reactant/product per unit time at the start of the reaction when **t = 0**

## measuring reaction rates

* In acid and base reactions, we measure pH changes by carrying out titrations or by using a pH meter
* In reactions that produce gases, we measure the change in volume or pressure or the loss in mass of reactants
* For reactions that produce visual changes, we measure the formation of a precipitate or a colour change using a colorimeter

## orders and the rate equation

### orders

* In a chemical reaction, some particles have an energy greater than the activation energy - these particles can react
* The greater the concentration
	+ the larger the number of collisions per second
	+ the faster the reaction
* The order with respect to a reactant is the power to which the concentration of the reactant is raised in the rate equation
* For a reactant A, **rate α [A]x** where x = order with respect to A
* **Zero order** with respect to A:
	+ rate α [A]0 = 1
	+ the rate is unaffected by changing the concentration of A
* **First order** with respect to B:
	+ rate α [B]1
	+ the rate increases by the same number of times that [B] increases
* **Second order** with respect to C:
	+ rate α [C]2
	+ if [C] increases by x times, rate increases by **x2** times

### the rate equation and the rate constant, k

* The rate equation for a reaction A + B 🡪 C is given by **rate = k[A]m[B]n** where m is the order wrt A and n is the order wrt B
* k is the rate constant which links the rate of reaction with the concentrations raised to the powers of their orders
* The overall order of reaction is the sum of the individual orders **m + n**

### units of rate constants

* The units of k depend on the overall order of the rate reaction
	+ **Zero order**: rate = k[A]0, rate = k, k is measured in **moldm-3s-1**
	+ **First order**: rate = k[A], k = rate/[A], units of k = moldm-3s-1/moldm-3, k is measured in **s-1­**
	+ **Second order**: rate = k[A]2, k = rate/[A]2, units of k = = moldm-3s-1/(moldm-3)2, k is measured in **dm3mol-1s-1**
	+ **Third order**: rate = k[A]2[B], k = rate//[A]2[B], units of k = = moldm-3s-1/(moldm-3)3, k is measured in **dm6mol-2s-1**

## half-lives

* The **half-life** of a reactant is the time taken for the **concentration** of the **reactant** to **reduce by half**
* **Zero order** reactions
	+ concentration decreases at a constant rate - graph is a **straight line**
	+ half-life **decreases** with time
* **First order** reactions
	+ concentration **halves** in equal time intervals
	+ half-life is **constant**
	+ the half-life is independent of the concentration
* **Second order** reactions
	+ concentration decreases **rapidly** but the rate of decrease then slows down
	+ half-life **increases** with time

## orders from rate-concentration graphs

* **Zero order**
	+ the rate is **unaffected** by changes in concentration
* **First order**
	+ the rate **increases** at the same rate as [A]
* **Second order**
	+ the rate increases by **x2** with a concentration increase of x

### initial rates

* A clock reaction measures the time from the start of the reaction until there is a **visual** **change** (preferably sudden) e.g.
	+ appearance of a **precipitate**
	+ **disappearance** of a solid
	+ a change in **colour**
* During a clock reaction, you are measuring the time for the initial part of the reaction to take place
* To a good approximation, the **initial rate** is proportional to **1/t**
* You carry out a series of clock reactions, varying each reactant in turn
* You then plot a graph of initial **rate** against initial **concentration** for each reactant and determine orders

## initial rates and the rate constant

* To calculate k from orders, deduce the **rate** **equation** and use one the concentrations from one of the experiments shown

### the rate constant, k

* Reaction rate depends on both the **rate constant** and the **concentrations** of the reactants present in the rate equation
* The **larger** the value of **k**, the **faster** the reaction
* Rate increases with temperature
	+ the concentrations of the reactants do not change
	+ the **rate** **constant** must **increase**
	+ for many reactions, the rate **doubles** for each **10oC** increase in temperature

## rate-determining step

* A reaction mechanism is a series of steps that together make up the overall reaction
* The rate-determining step is the slowest step in the reaction mechanism of a multi-step reaction
* This affects the whole process - reactants can become products only as fast as they can get through this slow step
* If a reactant appears in the rate equation, that reactant is involved in the rate-determining step
* The order wrt the reactant tells you how many particles of the reactant are involved in the rate-determining step
	+ e.g. rate = k[NO2]2 tells us there are 2 molecules of NO2 in the rate-determining step
* Intermediates are generated and consumed in the reaction
* They do not appear in the overall equation and are typically short lived

## the equilibrium constant

* Dynamic equilibrium is established when
	+ the rate of the forward reaction is equal to the rate of the reverse reaction
	+ the concentrations of reactants and products remain the same (stop changing)

### the equilibrium law

* The equilibrium law tells us the relative proportions of reactants and products present at equilibrium
* For the equilibrium aA + bB ⇌ cC + dD, Kc = $\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}$
* Kc is the equilibrium constant in terms of concentrations and can only be used in dynamic equilibrium
* Homogeneous equilibria - when all species have the same physical state

### units of kc

* Worked out like the rate constant
* $\frac{\left[NO\_{2}\right]^{2}}{\left[N\_{2}O\_{4}\right]}$ = $\frac{(moldm^{-3})^{2}}{moldm^{-3}}$ = moldm-3

## calculations using kc

* Kc = $\frac{[C]^{c}[D]^{d}}{[A]^{a}[B]^{b}}= \frac{products}{reactants}$
* Concentrations must always be in moldm-3
* If you are given amounts, you must use concentration = $\frac{moles}{volume}$
* H2 + I2 ⇌ 2HI

|  |  |  |  |
| --- | --- | --- | --- |
| Component | H2 ­(g) | I2 (g) | HI (g) |
| Initial amount (mol) | 0.60 | 0.40 | 0 |
| Amount reacted (mol) | 0.6 - 0.28 = 0.32 | 0.32 (same as H2) | 0.32 +0.32 = 0.64 |
| Equilibrium mol | 0.28 | 0.4 - 0.32 = 0.08 | 0.64 - 0 = 0.64 |

Pink = given in the question

* Always divide by volume to find concentrations, if the question asks for them

## the equilibrium position and kc

* When Kc > 1, the reaction is product favoured and the equilibrium lies to the right
* When Kc < 1, the reaction is reactant-favoured and the equilibrium lies to the left
* An increase in temperature shifts the position of equilibrium in the endothermic direction
* A decrease in temperature shifts the position of equilibrium in the exothermic direction

## the equilibrium constant kc and the rate constant k

### concentration and pressure

* K­c is only affected by temperature - it is unaffected by concentration and pressure
* If concentration of products doubles, Kc halves, so the system shifts to the right to increase the Kc value back to its original
* By using the Kc equation, you can see that
	+ to increase Kc, increase the moles of product - shift equilibrium right
	+ to decrease Kc, increase the moles of reactant - shift equilibrium left

### the presence of a catalyst

* Catalysts affect the rate of a chemical reaction but not the position of equilibrium
* They speed up the rate of the forward and the reverse reaction so equilibrium is reached more quickly

### the importance of compromise

* A large value of the rate constant k means a fast reaction
* k increases with temperature
* Increasing the temperature increases the rate constant but can reduce Kc if the reverse reaction is endothermic
* Decreasing the temperature decreases the rate constant but can increase Kc if the forward reaction is exothermic
* Compromise conditions rely on a balance between Kc and k

## the road to acids

### arrhenius’s theory

* An Arrhenius acid dissociates when dissolved in water to form hydrogen ions, H+
* An Arrhenius base dissociates when dissolved in water to form hydroxide ions, OH­-
* ­­This theory was restricted to solutions in water and to soluble bases

### the bronsted-lowry theory

* A Bronsted-Lowry acid is a proton donor
* A Bronsted-Lowry base is a proton acceptor
* This model allowed for solvents other than just water and insoluble bases such as ammonia

## the role of h+ in reactions of acids

* Monobasic acids can each release 1 proton e.g. HCl, HNO3
* Dibasic acids can each release 2 protons e.g. H2SO4
* Tribasic acids can each release 3 protons e.g. H3PO4

### acid-base reactions

* Aqueous acids take part in typical acid-base reactions with carbonates, bases and alkalis
* The aqueous acid is neutralised and water is formed as one of the products
* All acids have the same ionic equation for each type of reaction
* Reactions with carbonates where M = group 2 metal
	+ 2H+ + MCO3 🡪 M2+ + CO2 + H2O
	+ acid + carbonate 🡪 salt + carbon dioxide + water
* Reactions with bases where M = group 2 metal
	+ 2H+ + MO 🡪 M2+ + H2O
	+ acid + base 🡪 salt + water
* Reactions with alkalis
	+ H+ + OH- 🡪 H2O
	+ acid + alkali 🡪 salt + water
* The reaction of an acid with a metal is a redox reaction so does not fit in with the acid-base model (M = group 2 metal)
	+ 2H+ + M 🡪 M2+ + H2
	+ acid + metal 🡪 salt + hydrogen

## conjugate acid-base pairs

* An acid will release a proton only if there is something (a base) that will accept it
* Acids often release protons when they are added to water as water molecules accept protons
* The hydronium ion (H3O+) is formed
* H+ ions cannot exist independently in aqueous solutions as bare protons will attract negative electrons very strongly

### acid-base pairs

* An acid-base pair is a pair of two species that transform into each other by gain or loss of a proton

## what is ph?

* pH = -log[H+ (aq)]
* [H+ (aq)] = 10-pH
* The pH scale is logarithmic - the difference between each successive whole number pH value is a factor of 10
* A low pH means a large [H+ (aq)]
* A high pH means a small [H+ (aq)]
* A pH change of 1 changes [H+(aq)] by 10 times

## strong and weak acids

* A strong acid is an acid that completely dissociates in solution
* A weak acid is an acid that partially dissociates in solution

### the acid dissociation constant, ka

* An equilibrium constant that measures the extent of acid dissociation
* The units are always moldm-3
* A large Ka value indicates a large extent of dissociation - the acid is strong
* A small value of Ka indicates a small extent of dissociation - the acid is weak
* For a acid HA: Ka = $\frac{[H^{+}][A^{-}]}{[HA]}$

### ka and pKa

* Values of Ka can be made more manageable if expressed in a logarithmic form called pKa
* pK­a = -logKa
* Ka = 10-pKa

## calculating ph for strong and weak acids

* For a strong acid, [H+ (aq)] = [HA (aq)]
* For a weak acid, [H+ (aq)] = [A-(aq)] so [H+][A-] can be written [H+ (aq)]2
* ­To find Ka for a weak acid, we need to measure the pH and know the concentration of the acid

## the ionisation of water

* The ionic product of water, Kw is defined as Kw = [H+ (aq)][OH- (aq)]
* At 25oC, Kw = 1.00 x 10-14mol2dm-6
* Kw controls the balance between [H+] and [OH-] in all aqueous solutions
* In water and neutral solutions, [H+] = [OH-]
* In acidic solutions, [H+] > [OH-]
* In alkaline solutions, [H+] < [OH-]
* At 25oC, Kw = [H+] x [OH-] must always be equal to 1 x 10-14mol2dm-6
* To find [OH-] from pH, divide Kw by [H+]
* If H+ increases, OH falls until Kw is reached again - this decreases the pH
* If H+ decreases, OH rises until Kw is reached again - this increases the pH

### stretch and challenge

* At 25oC, the pH of water is 7 and [H+ (aq)] = 10-7 moldm-3
* As temperature increases, Kw also increases
* More H2O molecules dissociate, increasing H+ and OH- concentrations
* pH of neutrality decreases due to higher concentration of H+ ions
* At body temperature, pH of neutral water is 6.81
* Water is still neutral as [H+ (aq)] = [OH- (aq)]

## ph values of bases

* Strong bases (alkalis) dissociate completely in water
* Strong bases tend to be hydroxides of the metals in groups 1 and 2
* To work out the pH of a strong base we need to know [H+ (aq)] and this depends on:
	+ the concentration of the base
	+ the ionic product of water, Kw (1 x 10-14 mol­2dm-6) (only needed in method 1

### method 1 - using kw

* [OH- (aq)] = concentration of a strong base
* [H+ (aq)] = $\frac{K\_{w}}{[OH- (aq)]}$ from ionisation of water equation
* The pH can then be calculated using pH = -log[H+ (aq)]

### method 2 - using poh

* [OH- (aq)] = concentration of a strong base
* pOH = -log[OH-]
* 14 - pOH = pH

## buffer solutions

* A buffer solution is a mixture that minimises pH changes on addition of small amounts of acid or base
* A buffer solution contains:
	+ a weak acid, HA
	+ its conjugate base A- (normally in the form of a salt)
* In a buffer system:
	+ the weak acid dissociates partially (large amounts of HA are left)
	+ the salt dissociates completely, generating the conjugate base (large amounts of A- are formed)
* The buffer solution contains large ‘reservoirs’ of the weak acid and its conjugate base

### how does a buffer act?

* The buffer solution minimises pH changes by using the equilibrium: HA (aq) ⇌ H+ (aq) + A- (aq)
* The weak acid, HA, removes added alkali
* The conjugate base, A- removes added acid
* On addition of an acid:
	+ [H+ (aq)] is increased
	+ H+ (aq)HHHh + A- (aq) 🡪 HA (aq)
	+ overall equilibrium shifts to the left, removing most of the H+ ions
* On addition of an alkali:
	+ [OH- (aq)] is released
	+ H+ (aq) + OH- (aq) 🡪 H2O (l)
	+ HA dissociates
	+ the equilibrium shifts to the right to restore the H+ ions that have reacted
* The buffer cannot remove all of any added acid or alkali but pH changes are minimised

## ph values of buffer solutions

* The pH of a buffer solution depends on:
	+ the Ka of the buffer system
	+ the concentration ratio of the weak acid and its conjugate base
* [H+ (aq)] = Ka x $\frac{[HA \left(aq\right)]}{[A^{-}(aq)]}$ (from Ka equation)
* Then use pH = -log[H+ (aq)]

### the carbonic acid-hydrogencarbonate buffer system

* Healthy human blood plasma has to have a pH between 7.35 and 7.45
	+ too acidic - acidosis
	+ too alkaline - alkalosis
* The carbonic acid-hydrogencarbonate ion buffer is the most important buffer system in the blood
	+ carbonic acid H2CO3 acts as the weak acid
	+ HCO3- ions act as the conjugate base
* H2CO3 ⇌ H+ + HCO3-
* Increase in H+
	+ removed by HCO3- ions
	+ equilibrium shifts to the left to remove most of the H+ ions
* Increase in OH-
	+ H+ + OH- 🡪 H2O
	+ removed by H2CO3
	+ equilibrium shifts to the right to restore most of the H+ ions
* Acid dissociation constant for this system is 4.3 x 10-7 moldm-3
* H­2CO3 🡪 CO2 (aq) 🡪 CO2 (g) in lungs 🡪 exhaled

## http://img.sparknotes.com/figures/3/3a5994498f24d59f5d5d762b40844a2a/sasb.gifneutralisation - titration curves

* The equivalence point is the point in a titration at which the volume of one solution has reacted exactly with the volume of the second solution
* Acid base titration pH curves can be plotted (volume of base/acid added against pH)
* The pH is measured by a pH meter or the pH is data logged continuously
* There are three sections to a titration curve:
	+ a slight rise in pH
	+ a sharp rise in pH (equivalence point at the centre of the vertical section)
	+ a slight rise in pH

### choosing the indicator

* An acid-base indicator (HIn) is a weak acid
* An indicator has one colour in its acid form (HIn) and a different colour in its conjugate base form (In-)
* When there are equal amounts of the weak acid and the conjugate base:
	+ [HIn] = [In-]
	+ the indicator is at its end point
* Most indicators change colour over a range of about 2 pH units
* An indicator is chosen so the pH value of the end point is as close as possible to the titration’s equivalence point
* Strong acid-strong base = methyl orange/phenolphthalein
* Strong acid-weak base = methyl orange
* Weak acid-strong base = phenolphthalein
* Weak acid-weak base = no indicator suitable - pH changes slowly through the equivalence point

## neutralisation - enthalpy changes

* Standard enthalpy change of neutralisation, ∆H~~o~~neut is the energy change that accompanies the neutralisation of an aqueous acid by an aqueous base to form one mole of H2O under standard conditions
* Acid + Base 🡪 Salt + Water
* Ionic equation: H+ (aq) + OH- (aq) 🡪 H2O (aq)
* Ions that do not take part in the reaction are called spectator ions

### calculating enthalpy change of neutralisation

* Work out the energy change: Q = mc∆T
* Work out the amount in mol that reacted (moles = concentration x volume)
* Scale the quantities to match the molar quantities needed to form one mole of H2O
* Work out the enthalpy change for neutralisation to form one mole of H2O in kJmol-1