RATES OF REACTION

FACTORS AFFECTING THE RATE OF A CHEMICAL REACTION

TEMPERATURE

THE HIGHER THE TEMPERATURE THE FASTER THE RATE OF REACTION

Particles are moving faster – have greater kinetic energy.

So there are more collisions per second

AND

MORE OF THE PARTICLES HAVE ENERGY GREATER OR EQUAL TO Ea and so more of the collisions THAT are occurring lead to a successful reaction.

When explaining temperature you need BOTH of these important ideas!!

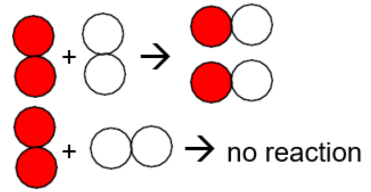
Measuring rates of reaction.

- Collect gas in a syringe or water filled measuring cylinder: record volume of gas at time intervals
- Measure loss of mass over time e.g. $CaCO_3$ & acid in a flask standing on a digital balance
- Time how long for a coloured chemical to appear or disappear

Collision theory:

For a reaction to occur

- The reactants must collide!!!!
- They must collide with the correct orientation

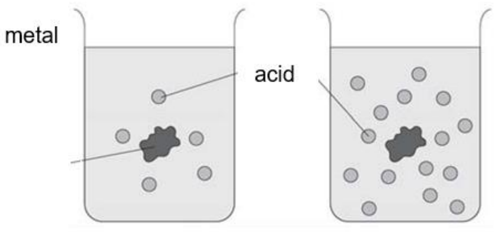


They must collide with energy greater or equal to Ea (the activation energy) for that reaction

Anything that brings about more effective collisions per unit time will increase the rate of the reaction. “effective” – leading to a reaction. “collisions per unit time”? This just means how FREQUENTLY the particles collide, eg the number of collisions per second.

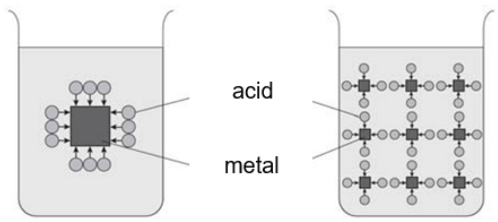
CONCENTRATION

The higher the concentration of a reactant (or reactants), the more particles per unit volume will collide per second.



SURFACE AREA

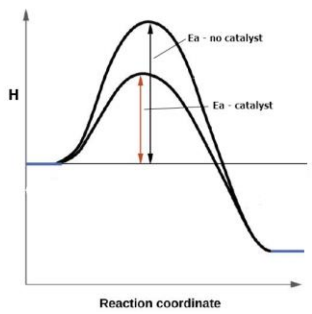
Consider a solid substance in a solution, e.g. magnesium metal in hydrochloric acid. When the solid is broken up, more ACID particles can collide with each piece in the same time.



Increase in collision frequency

CATALYSTS

Provide an alternative pathway for a reaction with a lower Ea (so more molecules have the required energy to react and so the rate is faster). Are NOT used up in the process. Don’t alter ΔH for a reaction.



EQUILIBRIUM

Le Chatelier's Principle

"When a change is applied to a system in dynamic equilibrium, the system reacts in such a way as to oppose the effect of the change".

When a chemical equilibrium is REACHED:

- reaction is dynamic - it is moving forwards & backwards
- the rates of forward & backward reactions are equal
- both reactants & products are present
- concentrations of reactants & products remain constant

Equilibrium can only occur in a closed system, one in which nothing can be added or removed. For gases, the container must be sealed.

The equilibrium sign ⇌ does not imply equal proportions of react & products, but that rates of forward & reverse reactions are equal.

Kc is known as the Equilibrium Constant

Consider: $aA + bB \rightleftharpoons cC + dD$ eg $N_2 + 3H_2 \rightleftharpoons 2NH_3$

$$Kc = \frac{[C]^c.[D]^d}{[A]^a.[B]^b}$$

Product(s) is/are ON TOP!!!

$$Kc = \frac{[NH_3]^2}{[N_2].[H_2]^3}$$

[ ] denotes the equilibrium concentration in mol L^{-1}

Kc is AFFECTED by a change of temperature but is NOT AFFECTED by changes in concentration, a change of pressure OR adding a catalyst.

CONCENTRATION

K_c is not affected by changes in any concentration (at constant temperature). To maintain the constant the composition of the equilibrium mixture changes

left		right
A + B	⇌	C + D

increase [A] or [B] equilibrium moves to right

increase [C] or [D] equilibrium moves to left

decrease [A] or [B] equilibrium moves to left

decrease [C] or [D] equilibrium moves to right

CATALYSTS

Do not affect the position of equilibrium but equilibrium is reached quicker.

PRESSURE

Increase pressure (decrease volume) – equilibrium moves to side with FEWER GASEOUS MOLECULES

Decrease pressure (increase volume) – equilibrium moves to side with MORE GASEOUS MOLECULES

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

Increase in pressure favours NH3 production (4 mol of gas → 2 mol of gas will decrease pressure of system).

No change will occur when equal numbers of gaseous molecules appear on both sides.

Altering the temperature affects the rate of both backward & forward reactions but to different extents. The equilibrium moves producing a new equilibrium constant. The direction of movement depends on the sign of ΔH.

TEMPERATURE

An increase in temperature favours the reaction that absorbs heat (endothermic reaction). A decrease in temperature favours the reaction that releases heat (exothermic reaction).

Look at a thermochemical equation e.g.

$$4NO(g) + 6H_2O(l) \rightleftharpoons 4NH_3(g) + 5O_2(g) \quad \Delta H = +1170 \text{ kJ}$$

The reaction producing NH_3 and O_2 is endothermic and so it would be favoured by an increase in temperature.

Kc is affected by temperature. If Kc increases (bigger products ÷ smaller reactants) when the temperature is increased then the forward reaction is endothermic. +ΔH.

Determining the position of equilibrium from equilibrium constants

Value of *K*	Reactants or products favoured
< 0.001	reactants
between 0.001 and 1000	mixed, comparable amounts of reactants & product
> 1000	products

ACIDS & BASES

Brønsted-Lowry definitions

Acids are proton donors
Bases are proton acceptors

Acid-base conjugate pairs differ by a proton
e.g. HA / A-, H_3O^+ / H_2O, NH_4^+ / NH_3, H_2O / OH^-, HCO_3^- / CO_3^{2-}
Species that can act as acid or base are called amphiprotic e.g. H_2O and HCO_3^-

pH

pH = - log $[H_3O^+]$
$[H_3O^+] = 10^{-pH}$
[ ] = concentration in mol L^{-1}
Kw = ionic product of water = 1×10^{-14}
$2H_2O \rightleftharpoons H_3O^+ + OH^-$ (or $H_2O \rightleftharpoons H^+ + OH^-$)
$[H_3O^+]\ [OH^-] = 10^{-14}$

NB when entering 2.34×10^{-5} into calculator, do 2.34 EXP $^{-5}$ (don't x 10 as well)

pH of some salt solutions

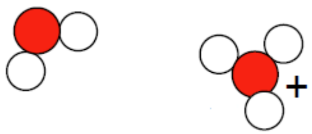
NH_4Cl, ammonium chloride, dissolved in water has a pH < 7. It dissolves $NH_4Cl(s) \rightarrow NH_4^+ + Cl^-$. The NH_4^+ ion then reacts with a proton donor with water
NH_4^+ + H2O $\rightleftharpoons NH_3 + H_3O^+$: H_3O^+ is now > OH^- which makes pH < 7
CH_3COONa, sodium ethanoate, dissolved in water has a pH > 7. $CH_3COONa\ (s) \rightarrow CH_3COO^- + Na^+$. The CH_3COO^- then reacts with water.
CH_3COO- + $H_2O \rightleftharpoons CH_3COOH + OH^-$
OH^- is now > H_3O^+which makes pH > 7

Strong and weak acids and bases

Strong acids – fully ionised / dissociated OR react completely with water; use → in equations
e.g. HA + $H_2O \rightarrow H_3O^+$ + A
Weak acids – partially ionised / incomplete reaction with water; use ⇌ in equations
e.g. HA + $H_2O \rightleftharpoons H_3O^+ + A^-$

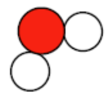
Strong base – $NaOH \rightarrow Na^+ + OH^-$
Weak base – $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

Strong Acids



Fully ionised in water
Low pH as high concentration of H_3O^+
React faster than same concentration of weak acid as more H_3O^+ available for collision at any one time. Good electrical conductors as a high conc. of ions (BOTH H_3O^+ and A^-) to carry current
In diagram below there is no HA – is 100% ionised

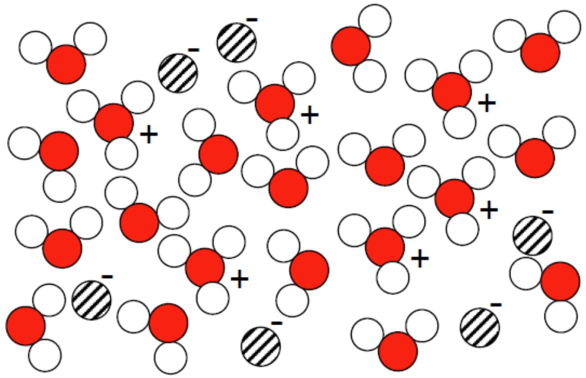
Weak Acids

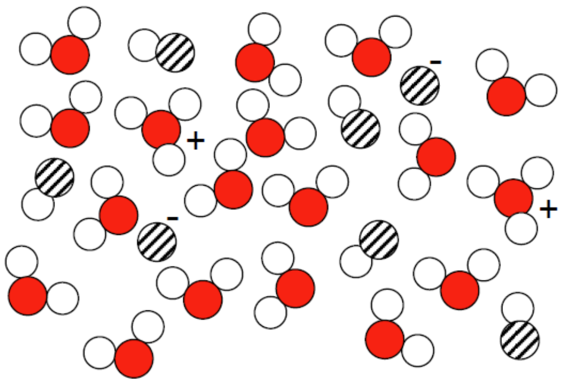


Partially ionised in water
Not such a low pH as lower concentration of H_3O^+ than the strong acid
React slower than same concentration of strong acid as less H_3O^+ available for collision at any one time. Poor electrical conductors as very low conc. of ions (H_3O^+ and A^-) to carry current
In diagram below it is mainly HA.

Stuff you should know from level 1…

pH < 7 = acid, pH 7 = neutral, pH > 7 = basic or alkaline. An alkali is a soluble base.
Litmus: Red litmus: stays red in acid, turns blue in alkali. Blue litmus: turned red in acid, stays blue in alkali
Universal Indicator: Red – yellow (acid), green (neutral), blue-purple (alkali)
Acid + metal → salt + hydrogen
Acid + base → salt + water
Acid + carbonate → salt + water + carbon dioxide





pH in (much) more detail…

pH calculations

Remember that [ ] = concentration, and has the units mol L^{-1}. pH of course has NO units!

Turning H_3O^+ into pH

pH = - log [H_3O^+]

E.g. 1. what is the pH if [H_3O^+] = 3.45×10^{-3} mol L^{-1}

pH = - log 3.45×10^{-3}

Enter as: (-) log 3 . 4 5 EXP (-) 3, and then EXE

Turning pH into H_3O^+

[H_3O^+] = 10^{-pH}

E.g. 2. what is the [H_3O^+] if the pH is 4.55

[H_3O^+] = $10^{-4.55}$

Enter as: SHIFT LOG (-) 4 . 5 5, and then EXE

K_w, the ionic product for water

Water self ionises to a very small extent - $2H_2O \rightleftharpoons H_3O^+ + OH^-$

(or $H_2O \rightleftharpoons H^+ + OH^-$)

[H_3O^+] [OH^-] = 10^{-14} = K_w

Kw = 1×10^{-14}

This is useful when you are asked to calculate [OH-] when you know the [H_3O^+] or [H_3O^+] when you know the [OH-]

K_w = [H_3O^+] [OH^-], so [H_3O^+] = K_w / [OH^-], and of course [OH^-] = K^w / [H_3O^+]

E.g. 3. what is the [OH^-] when [H_3O^+] is 1.76×10^{-8}

[OH^-] = K_w / [H_3O^+]

Enter as: SHIFT LOG (-) 14 ÷ 1 . 7 6 EXP (-) 8, and then EXE

Answers to examples

1. 2.46
2. 2.82×10^{-5} mol L^{-1}
3. 5.68×10^{-7} mol L^{-1}
4. 11.8

But what about [OH^-] to pH? Or pH to [OH^-]?

You need to do it in 2 steps.

There are TWO different ways! They (should) give you the same answer! You only need to know one way.

[OH-] to pH

E.g. 4. what is the pH if [OH^-] = 6.35×10^{-3} mol L^{-1}

Method 1.

Find [H_3O^+], then find pH

[H_3O^+] = Kw / [OH^-]

pH = - log [H_3O^+]

Method 2.

Find pOH, then find pH

pOH = - log [OH^-]

pH = 14 – pOH

Don't round numbers along the way…. Keep all in calculator until the final answer and then write it to 3 s.f.

pH to [OH-]

This is merely the reverse. Either

first calculate [H_3O^+], then [OH^-], OR

first calculate pOH, then [OH^-]   [OH^-] = 10^{-pOH}

Note: Some newer calculators have replaced EXP button with $x10^x$ (which of course does exactly the same thing!)