OCR (A) Chemistry A-level

Module 5: Physical Chemistry and Transition Elements

Notes

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18.1 orders, rate equations and rate constants

- Reaction rates measured by observing changes in quantities reactants/products over time
- rate =change in conc÷time, units=mol dm^{-3} s^{-1}, [A]=concentration A
- rate for particular reactant= rate [A]^n. if n=0, 0 order with respect to reactant, changing concentration has no effect on overall rate. If n=1, 1st order with respect to reactant, if conc x2, overall rate x2. If n=2, 2nd order with respect to reactant, if conc x2, rate x4
- Rate equation: rate=k[A]^n[B]^m
- Rate constant k = proportionality constant
- Overall order=sum of orders with respect to each reactant

18.2 concentration-time graphs

- Continuous monitoring: continuous measurements taken during the course of a reaction. Can be used to plot conc-time graph
- In colorimeter wavelength of light passing through a coloured solution is controlled using a filter & the amount of light absorbed is measured
- Analysis by colorimetry:
    - Reaction of propane + iodine with an acid catalyst ($CH_3COCH_3 + I_2 \rightarrow CH_3COCH_2I + H^+ + I^-$)
    - Iodine used up: orange-brown colour fades, measured precisely by colorimeter
    - Carry out: prepare standard solutions of known conc I_2, select complementary colour filter (for I_2=green/blue, colorimeter will usually tell you), zero colorimeter with water, measure standard absorbance, plot calibration curve of absorbance against concentration, carry out propane and iodine reaction and take absorbance readings at timed intervals, use calibration curve to measure concentration, plot graph conc-time to determine order
- Concentration-time graphs: 0 order=straight line, -ve gradient, gradient equals k, 1st order= downward curve with decreasing gradient, 2nd order= downward curve steeper at start, tails off more slowly
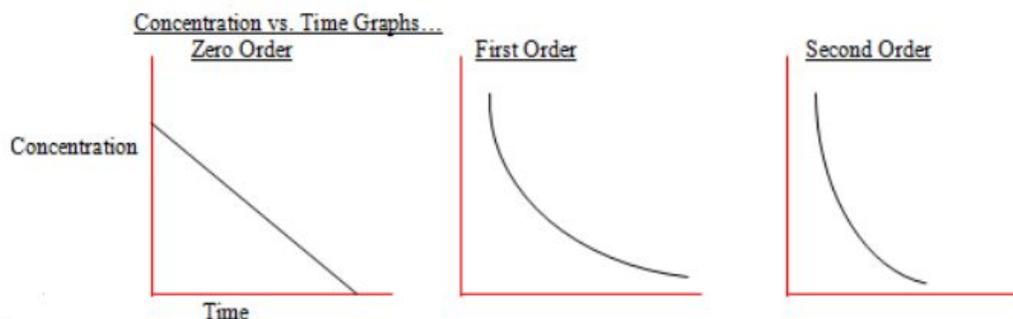
- Half-life: time taken for half of a reactant to be used up
- 1st order reactions, half-life is constant→ exponential decay

- To calculate K for 1st order reaction: from rate (calculate gradient tangent conc-time graph to get rate, sub into rate equation) & from half-life (k=ln2÷t$_{1/2}$)
- Many drugs break down by exponential decay, so those with shorter half-life used for quick effect, those with longer half-life for longer effect

18.3 rate-concentration graphs and initial rates
- 0 order: horizontal straight line, 0 gradient, y-intercept=k
- 1st order: straight line through origin, gradient=k
- 2nd order: upward curve, increasing gradient, plot graph rate-conc^2 (grad=k)

Rate vs. Time Graphs...
Zero Order   First Order   Second Order

Rate

Concentration
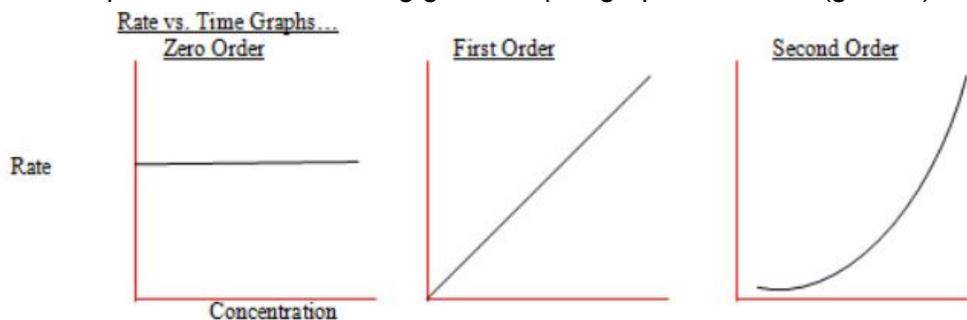
- Initial rate: instantaneous rate at the start of a reaction when time=0, found by measuring gradient at t=0 conc-time graph
- Clock reaction: a convenient way of obtaining initial rate with single measurement
- Iodine clock:
  - Several experiments with different concentrations of one reactant, all other reactant concentrations are kept constant
  - Colour change is delayed by adding a small amount another chemical (e.g. $Na_2S_2O_3$) removes iodine as it forms
  - Colour change: colourless→ blue-black (if starch is added, orange-brown if not)
  - Measure time for blue-black to appear, initial rate is proportional to 1/t (provided no significant change in reaction between t=0 to colour change), plot graph 1/t against concentration
  - Carry out further experiments changing concentration of other reactants then order with respect to each reactant can be determined
- How accurate? In a shorter time period, the less the rate changes so the more accurate the rate measurement is. Reasonably accurate provided less than 15% reaction has taken place

18.4 rate determining step
- A reaction can only take place when particles collide, for many reactions this is very unlikely, especially when lots of particles would have to collide simultaneously, so some reactions are more likely to happen in different steps
- Rate-determining step: slowest step in a multi-step reaction sequence
- Reaction mechanism: series of steps that make up an overall reaction
- Hydrolysis of haloalkanes can be investigated experimentally to find a reaction mechanism

18.5 rate constants and temperature
- When temperature increases, these factors contribute to increased rate & rate constant:
    - Shifts boltzmann distribution to right increasing proportion of molecules exceeding Ea
    - Particles move faster and collide more frequently
- With increasing temperature, increased frequency is comparatively small compared to increase in proportion of molecules exceeding Ea, so change in rate is mostly due to Ea
- $k=Ae^{-Ea/RT}$, A=pre-exponential factor (takes into account frequency of collisions with correct orientation, essentially gives rate if no Ea), $e^{-Ea/RT}$=exponential factor (represents proportion of molecules that exceed Ea + have sufficient energy to react), R=gas constant, T=temp (Kelvin)
- To determine Ea + A graphically: plot graph x axis=1/T, y axis=lnK, use ln(k)= - Ea/RT + Ln(A). gradient=-Ea/R, y intercept=lnA

19.1 the equilibrium constant Kc
- Homogenous equilibria: contains equilibrium species all in the same state/phase
- Heterogeneous equilibria: contains equilibrium species that have different states/phases. Kc only uses gases or aqueous since concentration of solids/liquids is essentially constant
- From experimental results:
    - Mix equal moles of carboxylic acid and alcohol with half moles of HCl as a catalyst in flask
    - Add same mole of HCl to another flask as a control
    - Stopper flasks + leave for week to reach equilibrium
    - Carry out titration of mixture with a standard solution of NaOH & repeat with control to determine amount acid catalyst used
    - Determine equilibrium amount carboxylic acid (mol control-mol eq)
    - Determine equilibrium amounts of each component from equation
    - Find concentrations & then find Kc

19.2 the equilibrium constant Kp
- Mol fraction: the proportion by volume of a gas to the total volume of the gases in a mixture
- Sum of mole fractions in mixture=1
- Partial pressure: contribution that a gas makes towards the total pressure
- Sum of partial pressures=total pressure
- Amount of oxygen that can dissolve in blood is proportional to partial pressure of oxygen breathed in. As oxygen dissolves it combines with haemoglobin allowing much more to dissolve. At high altitude, the body produces more haemoglobin, but partial pressure of oxygen may be so small that little may dissolve, so people use oxygen tanks + breathe pure oxygen
- Units for partial pressure: kPa, Pa or atm, same must be used for all
- Only gases used in Kp

19.3 controlling the position of equilibrium
- k=1→ eq halfway between products/reactants, k=100→ eq well in favour of products, k=10^{-2}→ eq well in favour of reactants
- Temperature is the only condition which causes k to change its value
- Exothermic reaction, increase temp:
  - Kp decreases so system no longer in equilibrium, ratio for Kp is now greater than Kp
  - Partial pressure of products must decrease & of reactants must increase
  - Position of equilibrium shifts towards left, new equilibrium reached where Kp ratio= new Kp
- Endothermic reactions, increasing temp:
  - Kp increases, so system is no longer in equilibrium, ratio of Kp now less than Kp
  - Partial pressure of products must increase & partial pressure of reactants must decrease
  - Position equilibrium shifts to right, new equilibrium reached where Kp ratio= new Kp
- Increasing concentration reactant:
  - Ratio of Kc now less than Kc, so system not in equilibrium
  - Concentration of product must increase & of reactant must decrease
  - Equilibrium position shifts right, new equilibrium is established where Kc ratio=restored
- Increasing pressure (if power is greater on top than bottom):
  - Ratio for Kp is now greater than Kp, the system is no longer in equilibrium
  - Partial pressure of products must decrease and of reactant must increase
  - Equilibrium shifts to left & new equilibrium is established where Kp ratio=restored
- If the moles of gaseous reactants=products, then ratio=k with changing pressure
- Catalysts affect rate chemical reaction, not the position of equilibrium. Speed up forwards + reverse reactions by same factor so equilibrium is reached faster but position is not changed

20.1 Bronsted-Lowry acids and bases
- Previous models describing acids/bases:
  - Early: acids= sour, alkalis from plant ashes
  - 1754 'base' + acid→solid
  - 1832 role of hydrogen: acids contain hydrogen, can be replaced by a metal
  - 1884 Arrhenius model: acids release H^+, bases release OH^- ions (in aq solution)
  - 1923 Bronsted-Lowry model (central role protons)
- Bronsted Lowry acid=proton donor, Bronsted-Lowry base=proton acceptor
- Conjugate base pair: contains 2 species interconnected by transfer of a proton
- In aqueous solution, dissociation doesn't take place unless water is present. Water gains proton→ H_3O^+ (hydronium ion-active ingredient in any acid)
- Neutralisation acid by alkali written as: $H_3O^+ + OH^- \rightarrow 2H_2O$ // $H^+ + OH^- \rightarrow H_2O$

- mono/di/tribasic (or mono/di/tri protic) refers to total number of hydrogen ions in acid that can be replaced per molecule in an acid-base reaction (organic acids don't replace H's from carbon chain)
- When acids react with metals, carbonates, metal oxides, alkalis- H^+ is the active ingredient, which can be shown by ionic equations
- Spectator ions: ions that do not change during the reaction
- Ionic equation for acids reacting with alkalis= $H^+(aq) + OH^- (aq) \rightarrow H_2O (l)$

20.2 the pH scale and strong acids

- Soren Sorenson's method of measuring pH relied on measuring hydrogen ion concentration using an electrochemical cell. Now pH meters are used for accuracy, but they are based on same principle. Indicator paper is cheaper and easier but less accurate.
- Low [H+] high pH, high [H^+] low pH
- Change by 1 of pH is equal to x10 [H^+]
- pH is used rather than [H^+] because the values are a lot more manageable
- Show pH to 2dp unless told otherwise

20.3 the acid dissociation constant Ka

- Ka changes with temp
- Larger value Ka→ greater dissociation→ greater acid strength
- Stronger acid, larger Ka, smaller pKa & weaker acid, smaller Ka, larger pKa
- Wines often contain sulfurous acid (H_2SO_3) as preservative. In the 1st dissociation it acts as weak acid ($H_2SO_3 \rightleftharpoons H^+ + HSO_3^-$) & 2nd dissociation is far weaker ($HSO_3^- \rightleftharpoons H^+ + SO_3^{2-}$)
- For dicarboxylic acids, they dissociate H^+s one at a time
- Alcohol groups do not dissociate (-OH group is much less acidic than COOH)

20.4 the pH of weak acids

- Ka can be determined experimentally by: preparing a standard solution of a weak acid of known concentration, then measuring its pH using a pH meter
- Approximations:
  - The dissociation of water is negligible, $[H^+]_{eqm} \sim [A^-]_{eqm}$. But if ph>6,the dissociation is significant compared to the dissociation of the weak acid, meaning the approximation breaks down for weak acids or dilute solutions
  - The concentration of the acid is much greater than H^+ conc at equilibrium. $[HA]_{eqm}=[HA]_{start}-[H^+]_{eqm}$ is approximated to $[HA]_{eqm}=[HA]_{start}$. Not justified for stronger weak acids with $Ka>10^{-2}$ or for very dilute solutions

20.5 pH and stronger bases

- Ionic product of water: the ions in water (H^+ and OH^-) multiplied together
- The value of Kw at 25°C sets up neutral point in the pH scale
- On dissociation, water is neutral (it has the same number H^+ and OH^- ions)
- Kw essentially controls the concentrations of H^+ and OH^- in aqueous solutions
- Acidic: [H+]>[OH-], neutral: [H+]=[OH-], alkaline: [H+]<[OH-]
- For whole number pH's, concentration indices of [H+] and [OH-] add up to -14

21.1 buffer solutions

- Buffer system: a system that minimises pH changes when small amounts of acid/base are added. Contains a weak acid and a conjugate base
- Preparation from a weak acid and its salt:
  - When the acid is added to water, it partially dissociates: $HA \rightleftharpoons H^+ + A^-$
  - The salt provides the conjugate base. It completely dissolves when added to water: $ANa + aq \rightarrow A^- + Na^+$
- Preparation by partial neutralisation weak acid:
  - The weak acid is partially neutralised by the alkali→ conjugate base
  - Some weak acid is left over, so you are left with a mixture containing the weak acid and salt of the weak acid
- Added acid→ [H+] increases→ H^+ reacts with A→ equilibrium shifts left, removing most H^+ ions
- Added alkali→ [OH⁻] increases→ $H^+ + OH^- \rightarrow H_2O$→ HA dissociates, shifting equilibrium right to restore H^+ ions
- A buffer is most effective when [HA]=[A⁻] because this means: pH of the buffer is same as pKa for HA & operating pH is over approx 2 pH units centered at pH/pKa

21.2 buffer systems in the body
- Blood plasma needs to have a pH between 7.35 to 7.45
- pH below 7.35→ acidosis (fatigue, shortness breath, shock, death)
- pH above 7.45→ alkalosis (muscle spasms, light headedness, nausea)
- carbonic acid-hydrogen carbonate buffer system:
  - $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$
  - Added acid→ [H+] increases→ H^+ reacts with HCO_3→ equilibrium shifts left, removing H^+
  - Added alkali→ [OH⁻] increases→ $H^+ + OH^- \rightarrow H_2O \rightarrow H_2CO_3$ dissociates, shifts equilibrium to the right to restore H^+ ions
  - The body produces far more acidic materials. Prevents building up H_2CO_3 by converting it to CO_2 which is exhaled

21.3 neutralisation
- pH meter: electrode (dipped into solution), connected to meter displaying reading
- Using a pH meter:
  - Add a measured volume of acid to a conical flask (with pipette) + place electrode in
  - Add aqueous base to burette + add $1cm^3$ at a time, swirl contents each time + record pH + total volume added
  - When pH starts to change rapidly, add base dropwise until it changes less rapidly
  - Add base $1cm^3$ at time until pH changes very little for a few additions
  - Graph of pH against volume added is plotted
- Alternative: could attach pH meter to datalogger + use magnetic stirrer. Aqueous base is added slowly & curve is plotted automatically

- pH titration curve for acid against base or base against acid:

Base added to acid   Acid added to base
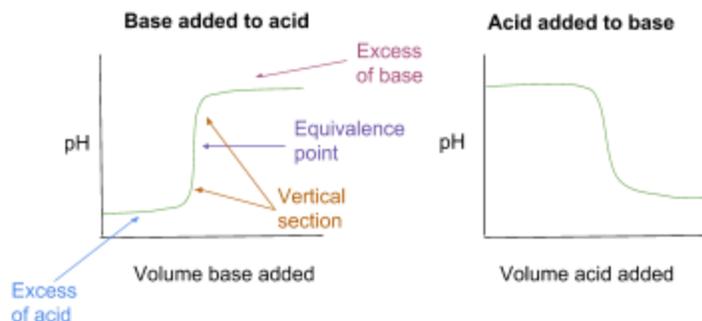
- Vertical section: pH increases rapidly on the addition of a small volume of base. acid/base concentration is similar
- Equivalence point: the volume of one solution that exactly reacts with the volume of the other solution (at the centre of the vertical section)
- Acid-base indicator: weak acid with distinctively different colour to conjugate base (e.g. methyl orange: weak acid is red, conjugate base is yellow, end point colour between two so orange)
- In a titration where a strong base is added to strong acid, indicator is initially the weak acid colour since there is a high conc H^+
- As basic solution added: $OH^- + H^+ \rightarrow H_2O$, weak acid dissociates, equilibrium shifts to right, colour changes to end point colour then to conjugate base colour
- If acid is added to a basic solution: H^+ reacts with conjugate base, equilibrium shifts to left, colour changes first to end point colour then to weak acid when equilibrium shifts left
- At end point: [HA]=[A-], so Ka=[H+] & pKa=pH
- Sensitivity depends on indicator itself + eyesight. Most change over about 2 pH
- Must use an indicator with the colour change coinciding with the vertical section of the pH curve. Ideally end point + equivalence point coincide
- No indicator is suitable for weak acid-weak base titration as there is no vertical section + even at steepest requires several cm^3 to pass through 2 unit pH range
- Curves are different for titrations with different strength acids/bases:
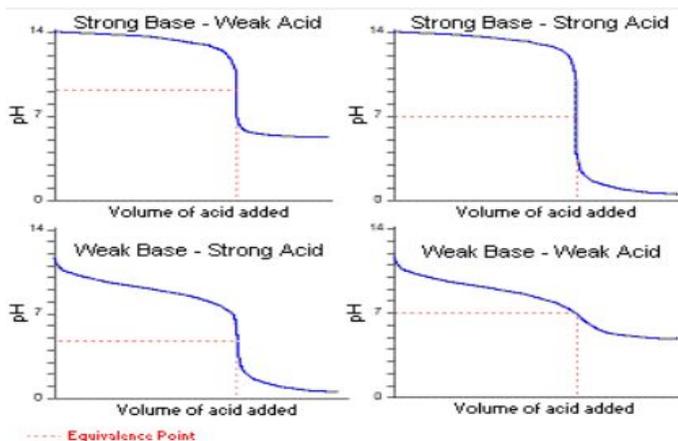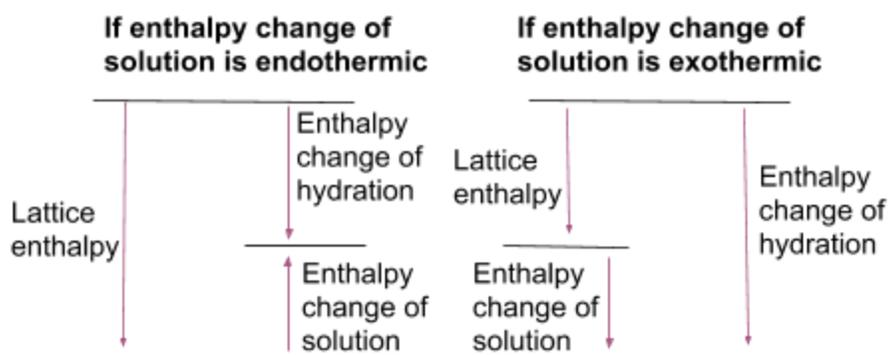

22.1 lattice enthalpy

- Lattice enthalpy: the enthalpy change that accompanies the formation of one mole of an ionic compound from its gaseous ions under standard conditions (always exothermic)
- Cannot be measured directly so must be calculated indirectly using Born-Haber cycle
- Standard enthalpy change of formation $\Delta_f H$: the enthalpy change that takes place when one mole of a compound is formed from its elements under standard conditions in standard states
- Standard enthalpy change of atomisation $\Delta_{at} H$: enthalpy change that takes place for formation of one mole of gaseous atoms from the element in its standard states under standard conditions (endothermic process because bonds are being broken)
- Ionisation energies are endothermic (energy is required to overcome the attraction between a negative electron + positive nucleus)
- First electron affinity $\Delta_{EA} H$: enthalpy change when one electron is added to each atom in one mole of gaseous atoms to form one mole 1- gaseous atoms (1st affinities are exothermic- electron added is attracted towards nucleus, 2nd are endo- negative ion repels electron away)

22.2 enthalpy changes in solution

- Standard enthalpy change of solution $\Delta_{sol} H$: enthalpy change that takes place when one mole of a solute dissolves in a solvent (can be exo/endothermic- depending on relative sizes lattice enthalpy or enthalpy changes of hydration)
- Experimental determination enthalpy change of solution:
  - Weigh out a sample of an ionic solid
  - Pour distilled water into plastic cup inside of a beaker. Measure the temperature of the water
  - Tip all the ionic solid into the water, stir with a thermometer until has all dissolved + temperature no longer changes
  - Use $q=mc\Delta T$ (use mass of water), calculate moles, calculate $\Delta_{sol} H$
- Dissolving process: ionic lattice breaks up forming gaseous ions, water molecules attracted to + surround ions (enthalpy change of hydration)
- Enthalpy change of hydration: the enthalpy change that accompanies the dissolving of gaseous ions in water to form one mole of aqueous ions

- A cold pack is activated by breaking seal between chemical/water compartment. Chemical dissolves, cooling the pack

22.3 factors affecting lattice enthalpy and hydration

- Factors affecting lattice enthalpy:
  - Down a group: ionic radius increases. Attraction between ions decreases, lattice energy becomes less negative, melting point decreases
  - Across a period from metal side: increasing charge (more attraction), decreasing size (more attraction)
  - Across period from nonmetal side: increasing charge (more attraction), increasing size (less attraction)
  - Lattice enthalpy=good indicator of melting point, but other factors (packing of ions) may need to be considered
- Factors affecting hydration:
  - Down group: ionic radius increases, attraction between ion and water molecules decreases, hydration energy less negative
  - Across a period: ionic charge increases, attraction with water increases, hydration energy more negative
- To dissolve an ionic compound in water, attraction between ions in lattice must be overcome (equal to lattice energy). Water molecules are attracted to ions, surrounding them and releasing energy (=hydration enthalpy)
- If sum hydration enthalpies>magnitude lattice enthalpy, overall the reaction is exothermic, so compound *should* dissolve

22.4 entropy
- Entropy: dispersal of energy within the chemicals making up the chemical system (units $J\ K^{-1}\ mol^{-1}$)
- Generally: solids have the smallest entropy, gases have the greatest
- At 0K there is no energy and all substances have entropy of 0. If a system becomes more random, energy spreads out more so entropy is positive
- Going from solid→liquid→gas melting/boiling increases the randomness of particles, energy is spread out more and ΔS positive
- If more moles of gas are produced: disorder of particles increases, energy is spread out more, so ΔS is positive
- Standard entropy: the entropy of one mole of a substance under standard conditions (+ve)
- Entropy change of a reaction: ΔS= ΣS(products) - ΣS(reactants)

22.5 free energy
- Feasibility/spontaneity : whether a reaction is able to happen and is energetically feasible
- Free energy change ΔG: overall energy change during a chemical reaction. Made up of enthalpy change and entropy change.
- ΔG= ΔH - TΔS (t=temperature in K, ΔS= entropy change of system $KJ\ K^{-1}\ mol^{-1}$), to be feasible ΔG<0, so feasibility depends on ΔH and TΔS
- Endothermic processes can be shown to be feasible at room temp using ΔG
- Many reactions with ΔG<0 don't take place because of very large activation energy→ very slow rate (ΔG doesn't take into account kinetics/rate). Catalysts can be used to overcome the activation energy

23.1 redox reactions
- Oxidising agent takes electrons from species being oxidised + contains reduced species & reducing agent adds electrons to species being reduced + contains species oxidised
- Redox reaction Cu/Ag^+: copper wire suspended in silver nitrate. Crystalline deposits of silver metal produced & pale blue solution gets deeper with time because Cu^{2+} is produced
- Writing redox equation from half equation: balance electrons, cancel electrons, cancel same species
- Writing redox equation from oxidation numbers: balance changes in oxidation numbers, balance with $H_2O/H^+/OH^-$

23.2 manganate (VII) redox titrations
- MnO_4^- ions reduced, other chemical used=reducing agent
- Procedure:
  - Standard solution of $KMnO_4$ added to burette
  - Add measured volume of solution being analysed to flask with excess dilute H_2SO_4 (to prove H^+ for reduction MnO_4^-). $KMnO_4$ self indicating
  - End point when first permanent pink colour
  - Repeat until you get 2 concordant titres. Measure from top not bottom of meniscus (deep purple so too difficult to see, the difference is still the same)
- Can be used for analysis of: Fe^{2+} or $(COOH)_2$ (or anything which reduces MnO_4 to Mn^{2+})
- Analysing % purity iron (II) compound:
  - $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$
  - Prepare a standard solution of an iron compound, titrate against $KMnO_4$ + record results
  - Calculate moles of MnO_4^-, determine mol Fe^{2+} (remember to scale up e.g. x10 if only 1/10 used in titration), find mass, calculate % purity (mass÷mass impure sample)
- For $(COOH)_2$, added to conical flask with H_2SO_4 then heat to 60°C + titrated hot
- $KMnO_4$ can be replaced with other oxidising agents (e.g. acidified dichromate $H^+/Cr_2O_7^{2-}$)

23.3 iodine/thiosulfate redox titrations
- $S_2O_3^{2-}$ oxidised, I_2 reduced: $2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$
- Can be used to determine: ClO^- content bleach, Cu^{2+} content copper (II) compounds, Cu content copper alloys
- Procedure:
  - Standard solution of $Na_2S_2O_3$ added to burette
  - Solution of oxidising agent being analysed is added to conical flask with excess KI (oxidising agent reacts with iodine ions to produce iodine ($\rightarrow$ yellow-brown)
  - Titrate with $Na_2S_2O_3$. Iodine colour fades gradually$\rightarrow$ starch indicator added when iodine has faded to pale straw (blue-black $\rightarrow$colourless)
- Analysis of household bleach: ClO^- reacted with I^- and H^+ to form I_2 (by adding KI and HCl to conical flask), then titrated
- Analysis of copper: copper (II) salts are dissolved in water to produce Cu^{2+}, insoluble copper (II) compounds reacted with acids to form Cu^{2+} ions (brass/bronze nitric acid
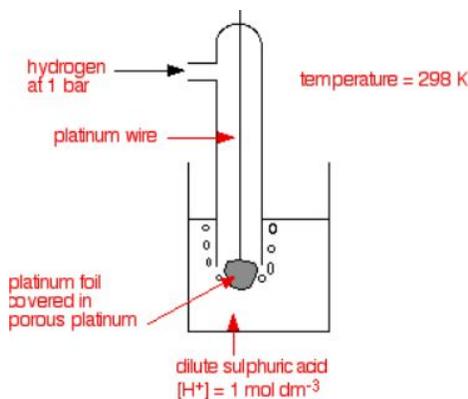
used). Cu^{2+} react with I^- (from KI) to form I_2 and white ppt of CuI (overall a brown coloured mixture)

23.4 electrode potentials

- Voltaic cell: converts chemical energy into electrical energy. Made by connecting 2 different half cells, allowing electrons to flow (not made by mixing cells- would produce heat energy)
- Half cell: contains the species present in a redox half equation
- metal/metal ion: phase boundary where metal in contact with its ions, equilibrium is set up
- Half cell written so forward reaction shows reduction
- In an isolated half cell, there is no net transfer of electrons into/out of the metal
- ion/ion half cell: ions of same element in different oxidation states. Inert metal electrode (Pt) used
- Negative electrode: more reactive metal, loses electrons. Positive electrode: less reactive metal, gains electrons
- Standard electrode potential E: tendency to be reduced and gain electrons. Use half cell with $H_2(g)$ and solution of H^+, Pt electrode with standard conditions

hydrogen at 1 bar
temperature = 298 K
platinum wire
platinum foil covered in porous platinum
dilute sulphuric acid
$[H^+] = 1$ mol dm^{-3}

- Standard electrode potential of standard hydrogen electrode= 0V
- Two electrodes connected by wire to allow flow of electrons. 2 solutions connected by salt bridge (allows ions to flow). Typically contains concentrated solution of electrolyte which doesn't react with either solution (e.g. filter paper soaked in aq KNO_3)
- More -ve E value: greater tendency to lose electrons + undergo oxidation. More +ve E value: greater tendency to gain electrons + undergo reduction
- Measuring standard cell potentials:
    - Prepare 2 standard half cells (ion/ion half cell must have same concentration)
    - Connect to voltmeter using wires
    - Prepare salt bridge (soak strip filter paper in saturated aq KNO_3) + connect to solutions
    - Record standard cell potential from voltmeter
- Electrons will flow from more to less negative half cell
- E_{cell}=E(positive electrode) - E(negative electrode)

## 23.5 predictions from electrode potentials

- Strongest reducing agent= most negative + most likely to be oxidised. Strongest oxidising agent= most positive + most likely to be reduced (will be on right of equation if written as standard form)
- When writing overall equations: keep the reduction equation the same way round, write the oxidation one reversed
- Limitations of predictions using E values:
  - Reactions can have very high activation energies so very slow reaction rates
  - Value of electrode potential will be different from standard value if concentration isn't 1 mol dm^{-3}. If conc>1: equilibrium shifts right, removes electrons, E less -ve. If conc<1, equilibrium shifts left, increases electrons in system, E more -ve
  - Actual conditions may not be standard, which affects the value of E. standard potentials are for aqueous equilibria, many reactions aren't aqueous

23.6 storage and fuel cells

- cells/batteries require 2 electrodes with different electrode potentials
- Primary cells: non-rechargeable, electrical energy produced by oxidation/reduction at electrodes. Used for low current long-storage devices e.g. clocks or smoke detectors. Most are alkaline based on Zn/MnO_2
- Secondary cells: rechargeable, cell reaction can be reversed during re-charging so chemicals in cells are regenerated. E.g. lead-acid (cars), nickel-cadmium/ nickel-metal hydride (radios, torches) and lithium-ion/lithium-ion polymer (laptops, mobile phones)
- Lithium-ion/lithium-ion polymer cells:
  - can be regular shape, or can have flexible solid polymer as salt bridge so can be made into many shapes
  - charges/discharges: Li^+ move between electrodes, electrons move through wires. -ve electrode: graphite coated with lithium metal, +ve electrode: metal oxide
  - Limitations: can become unstable at high temperatures, can ignite devices, hard to recycle since lithium is very reactive
- Fuel cells:
  - use energy from reaction of fuel with oxygen to create voltage
  - Fuel + oxygen flow into cell, products flow out, electrolyte remains
  - Can operate continuously if fuel + oxygen continue to be supplied
  - Don't have to be recharged
  - Hydrogen fuel cells produce only water & fuel cells with hydrogen rich fuels e.g. methanol are being developed
  - A hydrogen fuel cell has an alkali electrolyte or an acid electrolyte
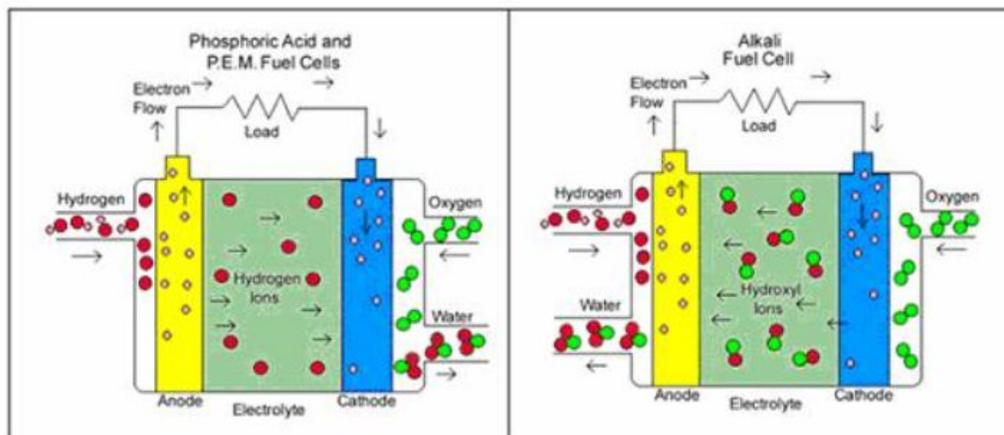
24.1 d-block elements

- Sc-Zn, highest energy subshell=3d, electrons are added to 3d
- Metallic: high melting/boiling point, shiny, conduct electricity/heat
- Iron- construction + tool production, copper- electrical wires + water pipes, titanium- aerospace (great strength) + joint replacements/cosmetic dentistry, copper/silver/nickel/zinc- coinage
- Chromium + copper fill $4s^1$ rather than $4s^2$ since Cr gets half full + Cu full d subshell→ greater stability
- Fill 4s before 3d and when forming an ion, lose 4s before 3d
- Transition elements: d-block elements that form at least 1 ion with a partially filled d-orbital
- Sc only forms Sc^{3+} (empty d orbital) + Zn only forms Zn^{2+} (full d orbital)→ not transition elements
- Transition metals characteristic properties: form compounds w/ different oxidation states, form coloured compounds, elements/compounds can act as catalysts
- Common oxidation states + colours:
    - Sc: +3
    - Ti: +2->+5 (+3=purple)
    - V: +2->+5 (+2=purple, +3=green, +4=blue, +5=yellow)
    - Cr: +2->+6 (+2=blue, +3=green, +6=orange) (common=+3/+6)
    - Mn: +2->+7 (+2=pink, +4=red, +6=green, +7=purple)
    - Fe: +2->+6 (+2=pale green, +3=pale yellow) (common=+2/+3)
    - Co: +2->+5 (+2=bright pink, +3=green)
    - Ni: +2->+4 (+2=green)
    - Cu: +1->+3 (+2=blue)
    - Zn: +2
- Species with transition element in highest oxidation state are often strong oxidising agents

- Coloured compounds (dissolve in water to form coloured solutions):

- ○ Potassium dichromate (VI)=bright orange
  - ○ Cobalt (II) chloride=pink/purple
  - ○ Nickel (II) sulfate=green
  - ○ Hydrated copper (II) sulphate=blue
- Haber process uses finely divided iron catalyst
- Contact process ($2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$)- catalysed by vanadium (V) oxide $V_2O_5(s)$
- Hydrogenation vegetable fats (margarine manufacture)- nickel catalyst
- Decomposition hydrogen peroxide ($2H_2O_{2(aq)} \rightarrow O_{2(g)} + 2H_2O_{(l)}$), manganese (IV) oxide $MnO_2(s)$ catalyst
- Zinc metal + acids catalysed by Cu^{2+} ions
- Homogeneous catalysts e.g. $S_2O_8^{2-}(aq) + 2I^- \rightarrow 2SO_4^{2-}$ (aq) + I_2 (aq) is catalysed by Fe^{2+} (aq) ions. Blue-black colour forms if starch is added, reached more quickly with Fe added. Eq for catalyst: $S_2O_8^{2-} + Fe^{2+} \rightarrow 2SO_4^{2-} + Fe^{3+}$, $Fe^{3+} + 2I^- \rightarrow I_2 + Fe^{2+}$

**24.2 the formation and shapes of complex ions**
- Complex ion formed when 1+ molecules/negative ions (ligands) bond to a central metal ion. Can form with elements other than transition metals
- Ligand: molecule/ion that donates pair of electrons to central metal ion to form coordinate bond
- Coordination number: number of coordinate bonds attached to central metal ion
- Monodentate ligand: a ligand that is able to donate one pair of ions to a central metal ion
- Common monodentate: H_2O: (neutral), $:NH_3$ (neutral), $:Cl^-$ (-1), $:CN^-$(-1), $:OH^-$(-1)
- Bidentate ligands: ligands that can donate 2 lone pairs e.g. 1,2-diaminoethane (en) & ethanedioate (oxalate) ion
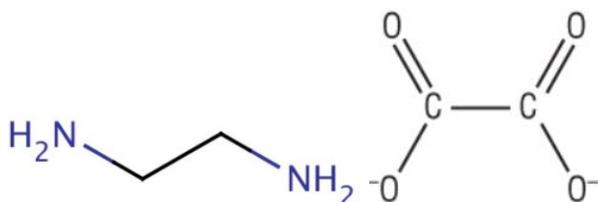
- Coordination number 6→ octahedral (90°, e.g. $[Mn(H_2O)_6]^{2+}$), 4→ tetrahedral (most common, 109.5° e.g. $[CoCl_4]^{2-}/[CuCl_4]^{2-}$) or square planar (occurs in transition metals with 8 electrons in highest energy d-subshell- Pt (II), Pd (II), Au (III), 90°, e.g. $[Pt(NH_3)_4]^{2+}$

24.3 stereoisomers in complex ions
- octahedral (with 4 of one ligand (or 2 bidentate)+ 2 of other)/square planar (with no more than 2 identical ligands)→ cis-trans
- Cis- identical groups adjacent (90°), trans- identical groups opposite (180°)
- Optical isomerism- complexes with 2+ bidentate ligands
- In medicine: cis-platin attacks tumours + can shrink them by forming a platinum complex inside a cell, this binds to DNA & prevents it replicating, eventually leading to systematic cell death, but it leads to kidney damage so clinical trials are happening to find Pt based drugs without side effects
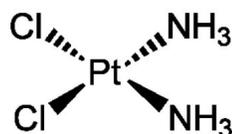
24.4 ligand substitution and precipitation

- Ligand substitution: a reaction in which one ligand in a complex ion is replaced by another ligand
- Ligand substitution of aqueous Cu (II) ions w/ ammonia: excess ammonia is added dropwise, 1st pale blue ppt $Cu(OH)_2$ is formed from pale blue solution, $Cu(OH)_2$ dissolves to dark blue solution. Eq: $[Cu(H_2O)_6]^{2+}(aq) + 4NH_3(aq) \rightarrow [Cu(NH_3)_4(H_2O)_2]^{2+}(aq) + 4H_2O$ (l)
- Ligand sub aq Cu (II) ions with excess of chlorine: blue→ green→ yellow (no intermediate just mix of two colours) $[Cu(H_2O)_6]^{2+}$ (aq) + 4Cl⁻ (aq) $\rightleftharpoons$ $[CuCl_4]^{2-}$ (aq) + 6H₂O (l). product= tetrahedral, Cl ions larger so fewer can fit. If water is added to the yellow solution, more dilute/pale blue solution is formed compared to the original
- Reaction of aqueous Cr (III) ions: $KCr(SO_4)_2 \cdot 12H_2O$ dissolved in water→ $[Cr(H_2O)_6]^{3+}$ formed (pale purple solution). When chromium (III) sulphate dissolves in water→ $[Cr(H_2O)_5SO_4]^+$ (green solution)
- Reaction of Cr (III) ions with excess ammonia: violet solution 1st→ grey-green ppt $Cr(OH)_3$, then→ $[Cr(NH_3)_6]^{3+}$ purple solution. Equation: $[Cr(H_2O)_6]^{3+}$ (aq) + 6NH₃ (aq)→ $[Cr(NH_3)_6]^{3+}$ (aq) + 6H₂O (l)
- Haemoglobin contains 4 protein chains, each with a haem molecule with an Fe^{2+} central ion, oxygen bonds to haemoglobin forming oxyhaemoglobin The oxygen is released to body cells when required, CO_2 is carried back then released by exhalation.
- Carbon monoxide bonds to Fe^{2+}→ carboxyhaemoglobin, carbon monoxide binds more strongly than oxygen and so the bond is irreversible, if concentration is too high, oxygen transport is prevented
- Precipitation reaction: when two aqueous solutions containing ions react to form an insoluble ionic solid
- Precipitation reactions with aqueous NaOH:
  - Cu^{2+}: blue solution→ blue ppt, insoluble in excess NaOH
  - Fe^{2+}: pale green solution→ green ppt, insoluble in excess NaOH, turns brown on surface in air (iron (II)→ iron (III))
  - Fe^{3+}: pale yellow solution→ orange-brown ppt, insoluble in excess NaOH
  - Mn^{2+}: pale pink solution→ light brown ppt, darkens on standing in air, insoluble in excess NaOH
  - Cr^{3+}: violet solution→ grey-green ppt, soluble excess NaOH→ dark green solution ($Cr(OH)_3$(s) + 3OH⁻ (aq) $\rightarrow$ $[Cr(OH)_6]^{3-}$ (aq)
  - overall equations: M^{a+} (aq) + aOH⁻ (aq) $\rightarrow$ $M(OH)_a$ (s) (where M is the transition element, and a is its charge)
- Precipitation reactions with ammonia: in first stage precipitation reaction takes place: $Cu^{2+}\rightarrow Cu(OH)_2$, $Cr^{3+}\rightarrow Cr(OH)_3$, same for Fe^{2+}, Fe^{3+}, Mn^{2+}. no further reaction for last 3 so precipitates don't dissolve

24.5 redox and qualitative analysis

- MnO_4^-(purple)+ $8H^+$ + $5Fe^{2+}$ → Mn^{2+}(colourless) + $5Fe^{3+}$ + $4H_2O$ -titration, acid conditions
- $2Fe^{3+}$(orange-brown)+ $2I^-$ → $2Fe^{2+}$(pale green) + I_2(brown)- colour change obscured by I_2
- $Cr_2O_7^{2-}$(orange) + $14H^+$ + $3Zn$ → $2Cr^{3+}$(green) + $7H_2O$ + $3Zn^{2+}$. With an excess of zinc, Cr ions are reduced further because zinc is a powerful reducing agent: Zn + $2Cr^{3+}$(green)→ Zn^{2+} + $2Cr^{2+}$ (pale blue)
- $3H_2O_2$ + $2Cr^{3+}$ + $10OH^-$ → $2CrO_4^{2-}$ + $8H_2O$ (H_2O_2 is a powerful oxidising agent)
- $2Cu^{2+}$ (pale blue) + $4I^-$ → $2CuI$ (white ppt) + I_2 (brown)
- Disproportionation: Cu_2O + H_2SO_4 → Cu (brown solid) + $CuSO_4$ (blue solution) + H_2O

Calculations

rate

- rate= change in concentration ÷ time
- units=mol dm^{-3} s^{-1}
- there are 4 ways to calculate the rate constant:
  - rate equation: rate=$k[A][B]^2$ (rearrange to get k)
  - use initial rate experiment table
  - work out half life (from concentration-time graph), k=(ln2) ÷ $t_{1/2}$
  - use arrhenius equation k=$Ae^{-Ea/RT}$, ln(k) = ln(A) - Ea/RT

Kc and Kp

- to calculate Kc:
  - work out moles at equilibrium
  - calculate concentration using volume
  - calculate Kc
    - units
- to calculate Kp:
  - work out moles at equilibrium
  - partial pressure= mole fraction x total pressure
  - calculate Kp
  - units

acids and bases

- pH = -log[H^+]
- strong acid: [H^+] = [HA]   (for dibasic x2)
- weak acid: [H^+] = √(Ka x [HA])
- strong base:
  - Kw=[H^+][OH^-]
  - rearrange to: [H^+] = Kw ÷ [OH^-]
    - at 25°C, Kw= 1 x 10^{-14}

- ■ [OH⁻]= same as the concentration of the base, if there are 2OH ions x2
  - weak base:
    - ○ $p(OH^-)$ = -log[OH⁻]
    - ○ pH = 14 - $p(OH^-)$

buffers
- pH of a buffer system: $[H^+]$ = Ka x $([HA] \div [A^-])$
- pKa = -log(Ka)
- method one to make a buffer:
  - ○ weak acid + salt
  - ○ to calculate pH:
    - ■ calculate concentration (use total volume) of HA (weak acid) and A⁻ (salt)
    - ■ use equation above: $[H^+]$ = Ka x $([HA] \div [A^-])$
    - ■ pH = -log[H⁺]
- method two to make a buffer:
  - ○ weak acid (excess) + alkali (neutralisation → salt + acid)
  - ○ to calculate pH:
    - ■ concentration of A⁻ = concentration of alkali
    - ■ moles of HA= original moles - moles of salt formed
    - ■ calculate concentration of HA from moles
    - ■ use equation above: $[H^+]$ = Ka x $([HA] \div [A^-])$
    - ■ pH = - log $[H^+]$
- ratio of a buffer= $[A^-] \div [HA]$ = Ka ÷ $[H^+]$ OR use pH= pKa + log ($[A^-] \div [HA]$)

enthalpy + entropy
- from a born haber cycle: ΔH_{LE}= ΔH_F - (all others added together)
- ΔH_{sol} = Q ÷ moles, (Q=mcΔT)
- Gibb's free energy: $\Delta G = \Delta H - T\Delta S$
  - ○ ΔG in KJ mol⁻¹
  - ○ ΔH in KJ mol⁻¹
  - ○ T in K
  - ○ ΔS calculated by doing S(products) - S(reactants)
- $\Delta G \leq 0$ → feasible reaction

redox and electrode potential
- redox calculations: write redox equation → use molar ratio → titration calculations
- electrode potential: $E^\ominus_{cell}$ = $E^\ominus_{positive}$ - $E^\ominus_{negative}$
- $\Delta G^\ominus$ = -nFE$^\ominus_{cell}$
  - ○ n= number of moles
  - ○ F= faraday constant (96,500 C mol⁻¹)
  - ○ $E^\ominus_{cell}$ = $E^\ominus_{positive}$ - $E^\ominus_{negative}$