Chem bonding

- VSEPR:
    - There are 4 electron densities around the central O atom, giving rise to a tetrahedral electron-pair geometry to minimise repulsion.
    - In X ion, there are 3 bps and 1 lp around O atom. In Y molecule, there are 2 bp and 2 lp around O atom. Since Y has one more lp around O atom and the strength of electron-pair repulsion decreases in the following order: lp-lp>lp-bp>bp-bp, the Y bond angle is smaller in Y
    - Around I atom, there are 5 electron pairs. To minimise repulsion, the e-pair geometry is trig bipyramidal. Since there are 4 bs and 1 lp, shape is see-saw
- Melting points
    - Si has giant molecular structure. Highest mp bc a lot of heat energy required to break the extensive network of relatively strong Si-Si covalent bonds
    - S has lower mp bc less energy required to overcome the weaker id-id attractive forces among S_8 molqs than breaking covalent bonds
    - P has lowest mp bc id-id forces present are even weaker than those in S since the P_4 molqs have fewer es and hence a smaller e cloud size than that of the S_8 molq
        - Between metals: X^{2+} has a larger ionic size and thus lower charge density. Hence the metallic bond strength is relatively weaker in X as compared to Y. Hence less energy is required to break the electrostatic forces of attraction during the melting process
- Electrical conductivity
    - SiO_2 has giant covalent structure with strong covalent bonds between atoms, resulting in high mp. It conducts electricity poorly as there are negligible charged particles in the molten state
    - P_4O_6 does not conduct electricity as there are no charged particles in the molten state
    - Al_2O_3 has a giant ionic lattice structure with strong electrostatic forces of attraction between its cations and anions, resulting in high mp. It conducts electricity in themolten state as its ions become mobile
- Bond length
    - One bonding electron involved in bond x compared to 2 in bond y, hence bond x is longer
    - Ge is below Si in Group 7 with a bigger atomic size, hence orbitals of Ge will be more diffuse. Overlap of the atomic orbitals of Ge and O will be less effective than those of Si and O. covalent bonds are weaker
- As carbon chain length increases, the id-id interactions in alcohol become stronger and the energy released from the formation of H bonding between alcohol and water is insufficient to overcome the stronger intermolecular forces of attraction between the alcohol molecules
- Nucleon number is the total number of protons and neutrons in the atomic nucleus
- Electrons will be deflected towards the positively charged electrode (anode) and protons will be attracted towards the negatively charged electrode (cathode).due to its relative smaller mass, electrons will have a greater angle of deflection than protons
- Fluorine is a Period II element that cannot expand its octet configuration while chlorine can expand its octet due to availability of vacant low-lying 3d orbitals. Fluorine is more electronegative than oxygen, thus it is too electronegative to donate its lone pair of electrons to form dative covalent bonds with oxygen atom

To compare boiling points

- Metals: metallic bond → charge density (including Si (group 4))
- Non-Metals: covalent bond → bond length (atomic radius, diffuse =)
- Ionic bonds: lattice energy → charge density
- Simple Covalent: id-id → electron cloud size
- Giant Covalent: effectiveness of orbital overlap→ atomic radius

Coordination number

- Coordination number of an ion in an ionic crystal lattice structure is the number of its nearest oppositely charged neighbouring ions surrounding it
- Cs+ has a much larger ionic size than Na+ and K+ ions, thus more Cl- ions could be packed around this larger Cs+ ion

Ideal gas law

- Pressure differs from calculation: due to presence of H bonding between molecules, resulting in lower pressure than expected
- Difference between ideal gas and real gas
  - Gases consist of small particles of negligible volumes. The particles are widely separated and can move anywhere in the container
  - The gas particles exert no attractive forces on each other
  - Collisions between the gas particles are perfectly elastic. Ie there is no loss of kinetic energy upon collision

Energetics

Definitions

- Bond energy of a X-Y bond is the average amt of energy required to break 1 mole of X-Y bonds in the gaseous state to form X(g) and Y(g) atoms
- Entropy: a measure of the degree of disorder in a system. The greater the disorder, the larger is the entropy
  - Increase in number of particles, increase in number of ways of arrangement and energy distribution of the particles, hence entropy is more positive
  - Negative → protein chain folds via various side-chain interactions (e.g. hydrogen bonding, ionic interactions) into a tertiary structure which is less disordered
  - Mixing of 1 mole of Cl_2 and 1 mole of N_2 occurs and the number of ways of arrangement of the particles increases, increase in disorderliness occurs
  - Increase in temperature causes the broadening of the Maxwell-Boltzmann energy distribution of the particle. Thus there are more ways of arranging energy quanta/distributing energy
  - Entropy decreases because of the formation of an ordered solid lattice
- Lattice energy: the energy released when 1 mole of an ionic solid is formed from its constituent gaseous ions under standard conditions of 298K and 1atm
- Enthalpy change of combustion: energy evolved when one mole of methanol is completely burnt in excess O_2 under standard conditions
- Enthalpy change of hydration of an ion is the enthalpy change when 1 mole of gaseous ions is hydrated under standard conditions of 298K and 1atm
  - deltaH sol: (deltaH hyd (neg)) – (LE (neg))
-

- Assume that S and H do not change with temperature
- Reaction is endothermic since drop in temp. Reaction has positive entropy since gas and liquid are formed from two solids, system is more disordered. Hence rxn is not spontaneous at low temp, but spontaneous at high temp.
- If H is exo and S is positive, G is negative at all temp, reaction is spontaneous at all temp
- Calculated value did not account for energy absorbed and energy given out… reactants are not in gaseous state
- **Lattice energy**

    - LE: effect of increase in charge product outweighs that of interionic distance
    - Lattice energy of MgO is defined as the enthalpy change when one mole of MgO is formed from gaseous Mg2+ ions and O2- ions at 1atm and 298K
    - The electrostatic attraction between doubly charged ions in MgO is stronger than the singly charged ions in sodium halides. In addition, the ionic radii of Mg2+ and O2- are smaller than that of Na+ and the halide ions. Since LE… thus LE of MgO is considerably larger than those of sodium halides
    - Difference in theoretical LE and calculated LE of BeO: theoretical LE assumes pure ionic character. But Be2+ ion is small and highly charged, hence it ahs high polarising power → BeO exhibits covalent character → attraction is stronger, so observed value is more exothermic
    - The theoretical LE assumes 100% ionic character for the compound. However, there is considerable covalent character in AgI than in AgF since the electron cloud of I-is larger and more polarisable than F-, hence, the model used to calculate the theoretical value of the LE of AgI is unsuitable
- When temperature increases, entropy increases. There is an increase in disorder as particles have more kinetic energy on average and there are more ways to distribute the larger number of quanta of energy
- Q=mc(deltaT) → deltaH = q/n
- Energy cycle, born haber cycle
- Delta G must be converted to Joules if calculating using R
- Reaction to form SO3 could have a high activation energy, hence not kinetically feasible. Hence V2O5 catalyst is required in the Contact process
- **Ionic bonds**
    - The cationic radii of the Group 2 metal cations increases from Mg2+ to Ba2+ while the other variables like the charges of the ions and the anionic radius of SO42- remain constant. This results in the decreasing magnitude of LE.
- **Delta H hydration**
    - The higher the charge density of M2+, the stronger polarising power of the M2+, the more exothermic deltaH hydration is. As the charge of M2+ is the same and the ionic radius of M2+ increases from Mg2+ to Ba2+ thus charge density decreases Mg2+ to Ba2+. Hence, delta H hydration becomes less exothermic from Mg2+ to Ba2+.
- Bond energies are average values. Enthalpy change of vaporization is not included in the calculations as the physical state of ethanol is liquid at standard conditions
- **Delta H solution**
    - Solubility of Group II hydroxides depends on how exothermic enthalpy change of solution is. Since deltaH solution = deltaHhyd – LE and cationic radius ofM2+ increases down the group, deltaHhyd and LE decrease dwn the group. Since anionic radius of OH- is much smaller than the cationic radius of M2+, the decrease in magnitude of delta H hyd is smaller than the decrease in magnitude of LE. Hence, deltaH solution of M(OH)2 becomes more exothermic down the group
- The enthalpy change of combustion of ethanoic acid is expected to be less exothermic than that of ethanal. C-O and O-H bonds which do not exist in ethanal, are strong and have to be broken during the combustion of ethanoic acid. Additional energy will have to be expended, leading to a less exothermic enthalpy change of combustion
- **Sources of error of calorimetry**
  There may be incomplete combustion, leading to a less exothermic enthalpy of combustion obtained in the experiment. Heat loss to environment or container. Temperature change is smaller than the actual value

Entropy and Gibbs Free Energy

- **Entropy of reaction** will increase as gaseous molecules are produced from orderly solid reactants or there is increase in amount of gaseous particles in the system. Reaction proceeds with an increase in disorder
- **Difference in theoretical and calculated value** Because the bond energies given in the Data booklet are only average energies
- **Feasibility:** since H is negative and S is positive, G will always be negative for all temperature range, hence reaction is spontaneous.
- **Assumption**
  S is constant at all temperatures

- **Entropy from diamond to graphite is positive**
  the layered structure of graphite has more disorderliness due to the presence of delocalised electrons as well as mobility of the panes of interconnected hexagonal rings of carbon atoms held by weak instantaneous dipole-induced dipole interactions. Diamond has a giant covalent structure where the carbon atoms are bonded to one another by network of strong covalent bonds that is more orderly and fewer number of ways of arrangement of the carbon atoms
- **Not actually spontaneous**
  The activation energy required for the conversion of diamond into graphite is very high as hybridisation of C changes from sp3 to sp2 and some strong C-C bonds will have to be broken. Hence the reaction is very slow at room temperature and essentially does not occur
- **Change in state:** from solid to aqueous results in an increase in the randomness/disorderliness in the arrangement of the particles
- **Decrease in entropy when compounds dissolve to form aqueous ions**
  this could be a more orderly arrangement of H2O molecules when the aqueous ions are formed
- Delta G=0 at boiling point

Kinetics

Graphical methods

- Intra-expt: limiting reagent (determine half life)
- Inter-expt: excess reagent (initial rate method, draw tangent)
- Rate constant dependent on temp, pressure, surface area of reactant, presence of catalyst. **Does not depend on concentration!**
- All graphs obtained are straight line with negative gradient: rxn is zero order wrt limiting
- Rate = gradient , always positive

Definitions

- Order of reaction: The order of reaction wrt a particular reactant is the power to which the concentration of that reactant is raised in the rate equation
- Rate constant: The rate constant k is a constant of proportionality in the rate equation. It is constant for a particular reaction at a given temperature
- Half-life: The half-life of a reaction is the time taken for the concentration of a reactant to fall to half its initial value

Orders of reaction

- By comparing experiments 1 and 3, when volume of iodine is halved, rate remains the same. Hence reaction is zero order with respect to iodine
- By comparing experiments 1 and 2, when volume of propanone increases by 2 times, rate increases by 2 times. Hence, rate is directly proportional to concentration of propanone, and the reaction is first order with respect to propanone
- By comparing experiments 3 and 4, when concentration of NO is doubled while rest remains the same, initial rate of reaction quadruples. Hence the initial rate of reaction is directly proportional to square of [NO], it is second order with respect to NO.
- Since HCl is a catalyst in the reaction, zero order
- At low [sucrose], reaction is first order wrt sucrose due to availability of active sites on enzyme for binding. As [sucrose] increases, more active sites and enzyme molecules are occupied by sucrose molecules. Hence, reaction is no longer first order wrt sucrose (mixed order). At high [sucrose], all active sites of enzyme molecules will be occupied by sucrose molecules and become saturated. Further increase in [sucrose] will no longer increase the reaction rate. Hence, reaction is zero order wrt to sucrose.

Mechanism

- **Reaction is unlikely:** This reaction involves the collision of 3 particles at the correct orientation and sufficient energy, which is statistically very highly unlikely.

- **Small value of k:** The small value of k is due to a high activation energy which arises due to the collision between 2 negatively charged particles
- **Exothermic reaction:** The reaction involves the forming of highly stable N2 and H2O molecules (or formation of strong N---N bond and O-H bonds) from highly unstable NO molecule.

Experimental techniques

- Addition of large amount of cold water: To quench the reaction at the specified times by rapidly lowering the temperature of the reaction mixture
- At the end point, the yellow solution of I2 decolourises
- By measuring the change in colour intensity of the orange Br2(aq). Let conc of Br be directly proportional to colour intensity. Plot a graph of colour intensity against time. Gradient of graph at any instant is the rate of reaction
- **Which step fits the data**
    - Mechanism A fits the observed kinetic data. The slow step, and also the rate-determining step in the proposed mechanism, is a bimolecular elementary reaction between propanone and the acid. The rate equation for this reaction is of the form: rate = k'[x][y] which is similar to the experimentally determined rate equation. The reaction is zero order with respect to iodine, so iodine is only involved in the fast step (which is not rate-determining). On the other hand, the rate-determining step in mechanism B involves a bimolecular elementary reaction between propanone and iodine. The rate equation is of the form: rate =k'[x][z],which is dissimilar to the experimentally determined rate equation. Since the rate is found to be independent of [z], mechanism B is inconsistent with the observed kinetic data.
    - If the reaction between propanone and bromine proceeds by a similar mechanism, bromine is not involved in the rate-determining step of the reaction mechanism. The reaction is therefore zero order wrt bromine. Consequently, rate of reaction is expected to be identical to that of the reaction between propanone and iodine under the same experimental conditions.
    - Slow step is the rate determining step. This is because the same rate equation as that in e) is obtained if step B is the rate determining step and this is shown below. Intermediate species are broken down to their reactants
    - Mechanism B is consistent with rate equation. The molecularity of the reactants in the slow step is 2 with respect to NO and 1 with respect to H2. It is consistent with the experimentally-determined order of reaction with respect to each reactant
    - The reaction is first order wrt NO, hence step 1 which involves only 1 molecule of NO is the slowest step

Catalyst

Autocatalytic reaction

1) The given reaction is an autocatalytic reaction with the H+ ions produced from the dissociation of x actng as the autocatalyst. Initially, the reaction is slow as there is no catalyst. The reaction rate then increases as the H+ ions produced act as the catalyst. Towards the end of the reaction, the concentrations of the reactants are very low, so the reaction rate decreases even though there is an adequate supply of catalyst
2) Rxn involves autocatalysis where X is the autocatalyst (reactant). The rate of reaction gradually increases at first as the autocatalyst produced catalyses the reaction. However, the rate decreases subsequently as X decreases.

Heterogeneous catalyst

Platinum acts as a heterogeneous catalyst in the decomposition of NH3 into N2 and H2. At very low pressures, the active sites on the catalyst surface area are not saturated with ammonia molecules. Hence, the rate of decomposition of ammonia only depends on the partial pressure of ammonia and the reaction Is first order with respect to ammonia. At moderate or high pressures, most, if not all the active sites present on the platinum surface are taken up by ammonia molecules. Consequently, any increase in the partial pressure of ammonia has no effect on the rate of decomposition. The reaction is zero order with respect to ammonia. In this case, the limiting factor is the availability of active sites for the decomposition reaction

A catalyst provides an alternative pathway with lower activation energy. For eg the SO_2 and O_2 mt olecules are adsorbed onto the surface of the catalyst; they are brought into close proximity at the correct orientation, as well as weakening the bonds within SO_2 and O_2 molecules. Thus more molecules have energy higher than activation energy can participate in the reaction. This speeds up the reaction

Factors affecting rate

- **Pressure:** When pressure is increased, the particles are brought closer together and hence frequency of collision of molecules increases. The frequency of effective collision also increases
- **Temperature:**
  - When temperature increases, average kinetic energy of particles increases. Greater proportion of particles will possess energy greater than or equal to the minimum amount of energy, Ea, for a successful collision to occur. Also, as average kinetic energy of molecules increase with higher temperature, molecules travel faster and hence collide more often. Frequency of effective collisions increases, rate of reaction increases
- **Catalyst**
  - A catalyst provides an alternative reaction pathway of lower activation energy. As a result, there is a greater number of molecules having energy greater than or equal to the lowered activation energy, which is shown by the larger shaded area in the Maxwell-Boltzmann distribution curve. This leads to an increase in the frequency of effective collisions and therefore increases the rate of reaction. Lower activation rate also results in the reaction having a larger rate constant, and hence, the reaction rate is increased.
- **Concentration**
  - When concentration increases, rate increases → increased number of molecules, increased frequency of effective collisions
- **Activation Energy**
  - Molecules with stronger bonds have lower reaction rates due to increased amount of energy required to break the stronger bonds

Chem Equilibria

- N_2O_4 (pale yellow) and NO_2 (dark brown) → when pressure is increased, mixture turns dark brown immediately, then gradually fades
  - When equilibrium mixture is suddenly compressed in a gas syringe, conc of N_2O_4 and NO_2 increase due to the reduced volume. Compression of the gas also results in an increase in pressure. The position of the equilibrium shift left to decrease pressure by producing fewer gas molecules. The mixture becomes paler as N_2O_4 decreases.
- Kc=Kp when number of gaseous products = gaseous reactants
- Kc value is extremely large implying that the forward reaction is effectively complete

Haber process

- 500degC: by LCP, low temp will cause system to react in way to increase temp. Exothermic forward reaction is favoured and position of equilibrium shifts to the right to produce more products. However at low temp, rate of reaction is slow, system will take a long time to reach equilibrium. Hence optimal temp of 500degC and a catalyst is used to ensure that both yield and rate are high

Electrochemistry

- Enot cell only when in standard conditions
- Use reduction potential to deduce feasibility via Ecell values. If >0 reaction is energetically/ thermodynamically feasible under standard conditions
- Reactions with copper
  - Blue solution of $CuSO_4$ fades, pink deposit of Cu forms, rod of metal M dissolves

- Since EH2O is less negative than E Ca, H2O will be preferentially reduced at the cathode instead of Ca2+. No Ca metal obtained
- When concentration of products increases, POE shifts left, hence reduction potential decreases (becomes less positive)
- When calculating nF, follow the number of moles of electrons in the original half equation
- To measure Enot
  - Set up the electrochemical cell as shown above. Read off the Ecell value on the voltmeter. The greater the Ecell value, the greater the difference in electrode potentials of the two half cells. Monitor the direction of the flow of electrons to identify the electrode that is positively charged. The electrode that is more positively charged will contain the stronger oxidising agent in its half cell
- The addition of CN- causes formation of XCN3- and XCN4- complexes. Enot(XCN3-/XCN4-) is +0.36V which is less positive than Enot(X2+/X3+) that is +0.77V. Hence XCN3- has weaker oxidizing power than Fe3+ under standard conditions. In addition, Enot(XCN3-/XCN4-) is less positive than Enot(I2/I-) that is +0.54V. hence position of equilibrium in b) shifts to decrease the oxidising power of XCN3-
- Methanol has a more efficient storage (by volume or by weight) compared to hydrogen gas. Hydrogen gas is volatile and explosive, thus requires high pressure storage system but not methanol.

Adv/Disadv of using Ni-Cd battery

- Adv: rechargeable
- Disadv: Cadmium is toxic/higher cost

Predicting reactions

1) Write half-equations
2) Write full balanced equation, calculate E cell, determine whether feasible

Observations

- Fe2+ → Fe3+ : pale green solution of Fe2+ solution turns to pale yellow solution of Fe3+

Purification of copper

An electrolytic method is used to purify copper industrially. The impure copper to be purified is used as the anode while pure copper is used as cathode. The electrodes are immersed in an electrolyte of copper(II) sulfate solution. During electrolysis, Cu is oxidised at the anode and enters the solution as Cu2+ (aq) while Cu2+ in the electrolyte is reduced to Cu at the pure copper cathode. As the reaction proceeds, the impure copper anode decreases in size while the pure copper cathode increases in size, with pure copper plating out onto the cathode, thus purifying copper.

Zn will be oxidised preferentially over Cu since its reduction potential is more negative than that of Cu. Hence Zn will be oxidised to Zn2+ followed by Cu to Cu2+. However, Zn2+ will remain in the electrolyte as reduction of Cu2+ to Cu at the cathode is preferred. Ag will be deposited as anodic sludge and will not undergo any redox reaction as its reduction potential is more positive than that of Cu, so Ag will not be oxidised

Reaction of Cu+ and I-

- Although the Ecell is negative, the reaction will proceed as the conditions are non-standard. There is formation of the insoluble CuI which drives the reaction. The precipitation would extract Cu+ ions from the solution, leaving only a low [Cu+] ions, causing equilibrium position in Cu2+ + e→ Cu+ to shift to the right

Ionic equilibria

- Amt of Acid: amt of base → 1:1
- Second and third Ka are too close, hence titration curve cannot show a distinct sharp rise for the subsequent equivalence points
- When soil becomes too acidic, the excess H+ ions are removed by the large reservoir of the conjugate base of vanillic acid present, regulating pH of soil

When temp increase, Kw value increases
Self-ionisation of water is an endothermic process. As temperature increases, equilibrium position shifts right to absorb the heat added, hence higher concentration of H+ and OH-. (pure water: [H+]=[OH-])

Water is still neutral since [H+]=[OH-] and the concentrations of both H+ and OH- increase to the same extent

Weak polyprotic acids (multiple Ka values)
Successive Ka values become smaller because successive dissociations involve acidic species that are increasingly more negatively charged, making the donation of positively charged H+ ion increasingly difficult

When calculating pH of weak acid
Assumptions: [H+] from self-ionisation of water is negligible and ignored (common ion effect). Dissociation of H+ from acid << [acid]
<u>If extremely dilute acid:</u> contribution of H+ ions from self-ionisation of water is not negligible (need to add H+ from water)

Strength of pKa values
A stronger acid has a smaller pKa value. The conjugate base of maleic acid formed is further stabilised by the formation of an intramolecular hydrogen bond between the unionised –COOH group and the –COO- group which are in close proximity to each other. Thus, pK1 of maleic acid is smaller as it would dissociate to a greater extent due to stability of the conjugate base.

Relationship between Kb and Ka

Larger the Ka of an acid, the smaller the Kb of its conjugate base → stronger the acid, weaker the basicity of its conjugate base (strong acids have weak conjugate bases, weak acids have strong conjugate bases)

Better indicator of acid strength?
Ka: constant at constant T, independent of [acid]→ Ka of stronger acid is always higher than Ka of a weaker acid regardless of concentration. pH varies with [acid] as pH of stronger acid may be higher than pH of weaker acid if concentration is different. For pH and a, 2 acids have to be at same concentration for them to be a good indicator of acid strength.

Salt undergoes hydrolysis if
its anion is a conjugate base of weak acid and/or its cation is a conjugate acid of a weak base

Salt pH
Salt produced at equivalence point is a relatively strong conjugate acid of a weak base. The hydrolysis of the salt produces H+. Hence the equivalence pH is below 7.

Indicator
Working range must coincide with the region of rapid pH change at the equivalence point

Phenolphthalein and bromothymol blue are both weak acids. Small amounts are used so that it will not affect the accuracy of the end point titre value. If larger amounts are used, a larger titre value will be obtained

Buffer

- A buffer solution resists pH change when small amounts of acid or base is added. Large reservoir of the acid and its salt enable the buffer to cope with the addition of small amounts of H+ and OH- added to the buffer
- pH change when NaOH added to buffer is much smaller since buffer resists changes in pH when small amounts of acid or base is added. However, water does not have a conjugate acid like NH4+ to remove OH- ions, hence pH changes is more significant

By LCP, presence of CH3COO- ions suppresses the dissociation of CH3COOH such that the equilibrium position of reaction 1 is very much to the eft. Buffer solution hence contains a large reservoir of weak acid and a large reservoir of base.

When H+ added, presence of large reservoir of CH3COO- ions in solution ensures that nearly all added H+ ions are removed. Hence [H+] of solution changes very little, pH kept approx. constant.

When OH- added, presence of large reservoir of CH3COOH molecules in solution ensures nearly all OH- ions are removed. Hence [OH-] changes very little, pH approx. constant.

Max buffer capacity

When component concentrations are equal→ when [salt]/[acid] = 1 for acidic buffer; [salt]/[base]=1 for alkaline buffer
when pH=pKa/ pOH=pKb

Effective buffer range: pKa+/-1

Use of indicators

SA-SB: phenolphthalein, thymol blue, methyl orange, screened methyl orange (4-10)
SA-WB: methyl orange, screened methyl orange (3.5-6.5)
WA-SB: phenolphthalein, thymol blue
WA-WB: no suitable indicator

Suitable indicator: when the working range of indicator coincides with region of rapid pH change at the equivalence point

Titration curves

- Initial pH
- pH of solution when half-neutralised
- pH of solution at equivalence point (salt hydrolysis)
- final pH of solution (must include volume of acid + base)

Solubility

Common ion effect affecting solubility

- Write reversible equations
- NaOH dissociates to give OH- ions which increases [OH-]. Due to common ion effect, position of equilibrium 1 shifts to the left as according to LCP. Hence solubility in aq NaOH is lower than that in water.
- In solution Z, the [Ba2+] is higher due to the additional Ba2+ ions from barium hydroxide. By LCP, with higher [Ba2+], the equilibrium position will shift left, thus decreases the solubility of barium iodate in solution Z.
- When conc HCl is added, [Cl-] is high and a soluble complex PbCl42- is formed, thus [Pb2+] is lowered and the ionic product falls below the Ksp of PbCl2 thus the ppt of PbCl2 dissolves

When added to NaF

There will be common ion effect due to the increase in [F-]. By LCP, position of equilibrium will shift left to decrease [F-]. The solubility of SrF2 is reduced. The solubility product of SrF2 is not affected as it is only dependent on temperature

Common ion effect

- The added NaCl dissolves in the solution and dissociates completely. Thus the [Cl-] in the solution increases momentarily. This causes the equilibrium position of the above reaction to shift left in accordance to Le Chatelier's principle. This leads to the precipitation of some AgCl and a decrease in the [Ag+]. Hence solubility of AgCl decreases in the presence of NaCl due to common ion effect, where Cl- is the common ion.

Solubility of sparingly soluble salts of weak acids in aqueous solution of a strong acid

When dilute hydrochloric acid is added, it yields H+ ions. Since PO43- is a relatively strong conjugate base, it combines with H+ ions to establish the equilibrium shown below, forming H3PO4, a weak acid. The reaction of H+ with PO43- ions to form H3PO4 causes the [PO43-] to decrease such that the ionic product momentarily falls below the Ksp value. To counteract the decrease, the equilibrium position of reaction shifts to the right ie Ca3PO42 dissolves. With more HCl added, the equilibrium position of reaction 2 shifts right and this in turn causs the equilibrium position of reaction o shift right. With sufficient dilute HCl added, all the solid Ca… dissolves. When this happens, the ioni product will be less than Ksp and no Ca… exists.

Selective precipitation and dissolution of metallic hydroxides

Aqueous ammonia, being a weak base, undergoes partial dissociation in aqueous solution. When NH3 is added to a solution containing Mg2+ ions, it increases [OH-] in the solution. At that instant, the ionic product, [Mg2+][OH-] momentarily exceeds the Ksp of Mg(OH)2 and consequently Mg(OH)2 is precipitated. IN the case of a mixture of NH3 and NH4Cl, the ionisation of NH3 to form OH- s suppressed by a relatively high [NH4+] since NH4Cl undergoes complete dissociation. The equilibrium position of reaction shifts to the left such that [OH-] in the solution which is low at any time, is made even lower. When this mixture is added to the solution containing Mg2+ ions, [OH-] in the solution increases but is still too low to make the ionic product exceed Ksp of Mg(OH)2. Hence no ppt results.

Selective ppt of metallic sulphides

When H2S is bubbled into an acidic solution of Zn2+ or Pb2+ ions, the relatively high [H+] suppresses the dissociation of H2S due to common ion effect. The equilibrium position of reaction shifts to the left and the [S2-] is reduced below its already low value in the solution. In this case, [S2-] is so low such that the ionic product does not exceed the Ksp of ZnS. Therefore, no ppt occurs

However, the Ksp of PbS is much lower than that of ZnS such that the low [S2-] present is still high enough to make the ionic product exceed the Ksp value. Hence PbS is ppt in acidic medium.

When H2S is bubbled into an alkaline solution of Zn2+ or Pb2+ ions, the OH- ions present will react with the H+ ions from H2S, causing the equilibrium position of reaction to shift to the right. Consequently, the [S2-] in an alkaline medium will be relatively higher than in the case of acidic medium. Therefore, the ionic products of both ZnS and PbS exceed the respective Ksp values. Hence pptn of both sulphides occurs in the alkaline medium.

Solubility product and complex ion formation

- Solubility of sparingly soluble salt in aq solution is increased if a reagent added reacts with one of its ions to form a complex ion
- Complex ion: contains a central metal ion linked to one or more surrounding ions or molecules (ligands) by dative covalent bonds

When aqueous ammonia is added, a complex ion, [Ag(NH3)2]+ is formed and the following equilibrium is established. The formation of Ag… decreases the concentration of uncomplexed Ag+ ions in the solution and momentarily makes the ionic product less than the Ksp of AgCl. To counteract the decrease in [Ag+], the equilibrium position of reaction shifts right, resulting in the dissolution of AgCl. With more aqueous ammonia added, the equilibrium position of reaction shifts right. This in turn causes the equilibrium position of reaction to shift right. With sufficient NH3 added, all the AgCl eventually dissolves.

When NH3 is added to Cu2+, the [OH-] in the Cu2+ solution is momentarily increased and this makes the ionic product of Cu(OH)2 exceed the Ksp of Cu(OH)2. Therefore, a ble ppt of Cu(OH)2 is formed and the following equilibrium is established. When excess NH3 is added, the complex ion [Cu]NH3)4]2+ is formed and the following equilibrium is established. The formation of Cu… decreases the [Cu2+] and momentarily makes the ionic product of Cu(OH)2 less than the Ksp of Cu(OH)2. To counteract the decrease in [Cu2+], the equilibrium position of reaction 1 shifts left, resulting in the dissolution of Cu(OH)2 ie blue ppt dissolves. With more NH3 added, the equilibrium position of rection 2 shifts right. This in turn causes the equilibrium position of reaction 1 to shift left. With sufficient NH3 added, all the Cu(OH)2 eventually dissolves to form the deepblue solution containing Cu….

When dilute HCl is added, the Cl- ions from the complete dissociation of HCl exerts a common on ffect and causes the equilibrium position of reaction 1 to shift left. Hence some PbCl2 solid forms. However, if concentrated HCl is added to the solution, the high[Cl-] present leads to the formation of the complex ion [PbCl4]2- and the following equilibrium is established. The formation of this complex ion reduces the [Pb2+] in the solution and momentarily causes the ionic product to be les than the Ksp of PbCl2. To counteract the decrease in [Pb2+], the equilibrium position of reaction shifts to the right, solid PbCl2 dissolves. As more concentrated HCl added, the equilibrium position of reaction 2 shifts right. This in turn causes the equilibrium position f reaction 1 to shift right. Hence PbCl2 will dissolve completely if sufficient conc HCl is added

Delta S

results in a decrease in entropy of the system ie from a more disordered aqueous solution to a less disordered solid formed