Group 2

Exceptions

Li decomposes on heating in the same way as Group 2 nitrates

$2LiNO3(s) \longrightarrow Li2O(s) + 2NO2(g) + \frac{1}{2}O2(g)$

Li+ has the smallest ionic radius among all the Group I cations. Hence, it has the highest charge density and strongest polarising power. Its charge density and polarising power is similar to the Mg2+ ion and is strong enough to distort the electron cloud of the NO2 – ion to such an extent that the covalent bonds within NO2 – is greatly polarised and "LiNO2" is not thermally stable. Thus, the decomposition of LiNO3 does not stop at LiNO2, but continues till Li2O is formed.

Thermal decomposition temperature is lower for BeCO3 than BaCO3

Since Be2+ has a much smaller cationic radius than Ba+, the charge density and polarising power of Be2+ will be much higher. Hence Be2+ will be able to distort the electron cloud of CO32- to a greater extent, leading to a greater extent of weakening of the CO bond, and a lower temperature required for the thermal decomposition

Aluminium nitrate vs Mg(NO3)2

Al3+ has a smaller ionic radius and a larger charge. Thus Al3+ has a higher charge density and greater polarising power, distorting the electron cloud of NO3- anion to a larger extent.

Thermal Stability

Oxides tend to be more stable than the nitrates, carbonates or hydroxides of a metal because

the electron cloud of O2- is less distorted since O2- ion is relatively small. Stronger lattices formed with the smaller O2- ion since O2- ion has a greater charge density, and so is more strongly attracted to the cation in the crystal.

High temperature to react with Nitrogen

N≡N bond is very strong and requires a large amount of heat energy to break it. Hence a high temperature is needed for the reaction to take place.

Decomposition of magnesium amide

$3Mg(NH2)2(s) \longrightarrow Mg3N2(s) + 4NH3(g)$

Favourable at high temp because: For the given decomposition reaction, $\Delta S > 0$. This is because the reaction produces a gaseous product (NH3), making the products more disordered than the solid reactant. $\Delta S > 0 \Rightarrow -T\Delta S < 0$ $\Delta G = \Delta H - T\Delta S$ • Since $\Delta H > 0$ and $-T\Delta S < 0$, $\Delta G < 0$ only if T is large such that $\Delta H < T\Delta S$. • Hence the decomposition reaction is favourable at high temperatures.

MgNO3 decomposes at lower temperature than BaNO3

The Mg2+ ion has a smaller ionic radius than the Ba2+ ion. Thus, the Mg2+ ion has a higher charge density, and consequently, a stronger polarising power than the Ba2+ ion. The more polarising Mg2+ ion distorts the electron cloud of the NO3 – anion to a larger extent and hence polarises the covalent bonds within the NO3 – anion to a greater extent. Thus, less thermal energy is required to decompose Mg(NO3)2 than Ba(NO3)2. Hence Mg(NO3)2 decomposes at a lower temperature than Ba(NO3)2.

Decomposition of Zinc Nitrate

The ionic radius of Mg2+ (0.065 nm) is smaller than that of Zn2+ (0.074 nm). Hence, with the same charge, Zn2+ has a lower charge density, and hence, weaker polarising power than Mg2+. As a result, Zn2+ distorts the electron cloud of NO3 – ion in Zn(NO3)2 to a smaller extent. The N–O covalent bond is polarised to a lesser extent as compared to that in Mg(NO3)2. Therefore, more heat energy is needed to decompose Zn(NO3)2. Hence, Zn(NO3)2 will decompose at a higher temperature than Mg(NO3)2.

Decomposition of magnesium iodate

2Mg(IO3)2(s) ⟶ 2MgO(s) + 2I2(g) + 5O2(g)

Z(IO3)2 is Ca(IO3)2. This is because its rate of thermal decomposition is the fastest.
X(IO3)2 is Sr(IO3)2. This is because its rate of thermal decomposition is slower than Ca(IO3)2.
Y(IO3)2 is Ba(IO3)2. This is because it does not undergo thermal decomposition.

Note: • Calculation needs to be made for at least one of the iodates(V) and then reasoning can be made to deduce the identities of the given iodates(V).

The thermal stability of the given iodates(V) increases in the following order: Z(IO3)2 < X(IO3)2 < Y(IO3)2 i.e. Ca(IO3)2 < Sr(IO3)2 < Ba(IO3)2
The cationic radius increases from Z2+ to X2+ to Y 2+ . This causes the charge density and polarising power of the cations to decrease from Z2+ to X 2+ to Y2+ . Hence, the extent of distortion of the electron cloud of the IO3 – anion decreases from Z(IO3)2 to X(IO3)2 to Y(IO3)2. The extent of polarisation of the covalent bonds in IO3 – ion also decreases from Z(IO3)2 to X(IO3)2 to Y(IO3)2. Hence, the amount of heat energy required for decomposition increases from Z(IO3)2 to X(IO3)2 to Y(IO3)2. Therefore, thermal stability increases from Z(IO3)2 to X(IO3)2 to Y(IO3)2.

Group 1 vs Group 2

Group 1 metal ions have a lower charge and bigger size than Group 2 metal ions. Group 1 metal ions have a lower charge density and polarising power than Group 2 metal ions. Thus, Group 1 metal ions will distort the large electron cloud of CO32- to a smaller extent, hence are more thermally stable.

Entropy change similar for decomposition of nitrates

upon decomposition, each mole of Group 2 nitrates release the same amount of gaseous molecules, hence the numerical value of the entropy change is very similar

Compound	**Uses**
MgO	As a refractory lining material
MgSO4	As a laxative, as a fertiliser
MgSO4 (anhydrous)	As a drying agent, as an anti-inflammatory agent
Mg(OH)2	To treat acid indigestion, constituent in toothpaste
CaSO4	To make plaster, blackboard chalk, used in concrete, cement
CaCO3	Use in blast furnace in iron extraction
CaCO3/Ca(OH)2/CaO	As fertiliser for correcting acidity (liming)
BaSO4	As barium meal in xray diagnostic work e.g. to detect stomach ulcers
BaCO3	As rat poison

Concrete and plaster containing barium salts are used as building materials to protect against radiation

Physical Properties

Fixed oxidation number

Alkaline earth metals display a fixed oxidation number of +2 because they have two s-electrons in their valence shell and the loss of both valence electrons would result in the formation of an ion with

a stable noble gas configuration and a charge of 2+.
They do not exhibit an oxidation state of +1 because the second ionisation energy is not significantly much larger than the first ionisation energy and the formation of a 2+ ion results in a more stable ionic compound with a more exothermic lattice energy than that of a 1+ ion.
The alkaline earth metals do not exhibit an oxidation state of +3 because the third ionisation energy is extremely high as it involves the removal of an electron from an inner principal quantum shell and such an electron is closer to the nucleus and is held strongly by the nucleus.
Hence, the alkaline earth metals all have a fixed oxidation number of +2 in their compounds.

BeCl2 more volatile than MgCl2 (lower b.p.)
BeCl2 is covalent in nature. In the liquid state, BeCl2 exists as simple non-polar, covalent molecules with instantaneous dipole–induced dipole interactions between its molecules. Boiling BeCl2 involves supplying heat energy to overcome these intermolecular forces. On the other hand, MgCl2 has a giant ionic structure with ionic bonds (i.e. electrostatic forces of attraction between the oppositely charged Mg2+ and Cl – ions) present in its solid lattice and in its liquid state. Boiling MgCl2 involves supplying heat energy to break ionic bonds. Since the instantaneous dipole–induced dipole forces in BeCl2 are significantly weaker than the ionic bonding in MgCl2, less heat energy is required to convert BeCl2 from the liquid to the vapour state. Hence BeCl2 has a lower boiling point and is more volatile.

Lattice energy of MgNO3 and BaNO3
Mg2+ has the same charge as Ba2+ , but Mg2+ has a smaller ionic radius than Ba2+ Hence, the numerical value of the lattice energy of Mg(NO3)2 is larger than that of Ba(NO3)2.

Lattice energy of MgNO3 and MgO
O 2– has a larger charge than NO3 – . O 2– has a smaller ionic size than NO3 – . Both factors (i.e. charge and ionic size) make the numerical value of the lattice energy of MgO larger than that of Mg(NO3)2.

Solubility of sulfates vs solubility of hydroxides
LE: As the cationic radius increases down the group, inter-ionic distance increases (OR L.E. proportional to q+.q-/r++r-. thus the strength of electrostatic forces of attraction between the M2+ and SO42- ions decreases. Hence, the magnitude of LE decreases.

deltaH(hydration): As the cationic radius increases down the group, the charge density of the cation decreases, and hence deltaH(hyd) becomes less exothermic

deltaH(soln) = deltaH(hyd) – LE
For Group 2 sulfates, the size of the cation is much smaller than that of the anion SO42-, thus the decrease in LE is less significant than the decrease in deltaH(hyd). Hence solubility decreases down the group.

Conversely, the size of the OH- anion is much smaller than that of the SO42- anion, thus the decrease in LE is more significant than the decrease in deltaH(hyd). Hence solubility increases down the group.

*LE and Hyd are both negative, but in the equation it is –(-LE), so LE is positive. Decrease in Hyd or LE means smaller magnitude i.e. more positive value e.g. -234 → -80

Basicity/Reaction with water

BeO is amphoteric, oxides of other alkaline earth metals are basic

BeO is a metallic oxide and hence has ionic character and is expected to be basic. It displays basic character when it reacts with acids. $BeO(s) + 2H^+(aq) \longrightarrow Be^{2+}(aq) + H_2O(l)$.
However, Be^{2+} has the smallest ionic radius among the Group II cations and hence has the highest charge density and the strongest polarising power. It distorts the electron cloud of the O^{2-} ion to such an extent that the bonding in BeO has significant covalent character. As such, BeO acquires acidic character and can react with bases. $BeO(s) + 2OH^-(aq) + H_2O(l) \longrightarrow [Be(OH)_4]^{2-}(aq)$.
Hence being an ionic oxide with significant covalent character, BeO is amphoteric in nature.

The oxides of the all the other alkaline earth metals (i.e. MgO, CaO, SrO and BaO) are predominantly ionic and hence basic. They display their basic character when they react with water to give OH^- ions or react with acids. $MO(s) + H_2O(l) \longrightarrow M^{2+}(aq) + 2OH^-(aq)$ $MO(s) + 2H^+(aq) \longrightarrow M^{2+}(aq) + H_2O(l)$

Increase in pH values of solutions of Group 2 Oxides in water

The pH values of solutions formed when the oxides of Group II are separately shaken with water increase from magnesium to barium. This is because each oxide reacts with water to give its hydroxide, and the solubility of these hydroxides increases down the group, giving rise to an increase in the concentration of hydroxide ions down the group.

Reaction with cold water

Q2a Magnesium sinks in water and reacts slowly with cold water to form magnesium hydroxide and hydrogen gas. Some bubbles of hydrogen gas will be observed. A white precipitate of $Mg(OH)_2$ may be observed since $Mg(OH)_2$ is relatively insoluble in water. $Mg(s) + 2H_2O(l) \longrightarrow Mg(OH)_2(s) + H_2(g)$

Calcium sinks in water and reacts steadily with water to give rapid effervescence of hydrogen gas. A white precipitate of $Ca(OH)_2$ forms gradually as $Ca(OH)_2$ is sparingly soluble in water. $Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(s, aq) + H_2(g)$

Barium is more reactive towards water than calcium. It sinks in water and reacts vigorously with water to give rapid effervescence of hydrogen gas and barium hydroxide solution. Since $Ba(OH)_2$ is more soluble in water than $Ca(OH)_2$, a white precipitate of $Ba(OH)_2$ is not observed unless a bigger piece of Ba is used for reaction. $Ba(s) + 2H_2O(l) \longrightarrow Ba(OH)_2(aq) + H_2(g)$

Barium peroxide in water

BaO_2 reacts with water to form barium hydroxide and hydrogen peroxide. $BaO_2 + 2H_2O \longrightarrow Ba(OH)_2 + H_2O_2$ Under acidic conditions, hydrogen peroxide acts as an oxidising agent and oxidises the iodide ions to form iodine. $H_2O_2 + 2H^+ + 2I^- \longrightarrow 2H_2O + I_2$

Mg_3N_2 in water

The white suspension is $Mg(OH)_2$. $Mg_3N_2(s) + 6H_2O(l) \longrightarrow 3Mg(OH)_2(s) + 2NH_3(g)$

$MgO \rightarrow Mg(OH)_2 \rightarrow MgSO_4$

The solid remaining after heating $Mg(NO_3)_2$ is MgO.
$Mg(NO_3)_2(s) \longrightarrow MgO(s) + 2NO_2(g) + ½O_2(g)$ When water is added to MgO, very little of it dissolves to form a weakly alkaline solution of magnesium hydroxide. Unlike BaO, MgO has very poor solubility in water because of its highly exothermic lattice energy.
$MgO(s) + H_2O(l) \longrightarrow Mg(OH)_2(s)$ $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$
With the addition of sulfuric acid, both MgO and $Mg(OH)_2$ react to form a colourless solution of

magnesium sulfate. $Mg(OH)_2(aq) + H_2SO_4(aq) \rightarrow MgSO_4(aq) + 2H_2O(l)$ $MgO(s) + H_2SO_4(aq) \longrightarrow MgSO_4(aq) + H_2O(l)$

Reaction with oxygen

Heating calcium with oxygen

A sample of calcium metal is held by a pair of tongs and strongly heated in air using a Bunsen flame. The sample can also be heated and then transferred to a gas jar filled with oxygen gas. Observations: The reaction usually starts only after heating the calcium metal for a short while (because of the layer of protective oxide). The metal burns with a brick red flame and a white solid (CaO) is obtained after the reaction is complete.

Others

Obtaining Noble gases from air

Air is a mixture of gases consisting mostly of N_2 (78%) and O_2 (21%) and the rest of the gases are CO_2, H_2O and the noble gases. CO_2 can be removed from air by passing the air sample into aqueous NaOH (which removes CO_2 as Na_2CO_3). H_2O is next removed by passing the same air sample through concentrated H_2SO_4 (dehydrating agent). By burning Mg in air, O_2 is removed due to formation of MgO. Further reaction with magnesium at high temperature removes nitrogen leaving the noble gases behind.

CaC_2O_4

$CaC_2O_4(s) \longrightarrow CaO(s) + CO(g) + CO_2(g)$

Sodium hydroxide

reacts with CO_2 and NO_2 (acidic gases)

Gp2

- Ionic radius of M2+ increases down the gp. As inter-ionic distance increases, the attractions become weaker.
- Nitrate anion is larger than M2+ ion while the size of an oxide anion is comparable to than that of an M2+ ion. As such, the lattice energy of gp2 nitrates only changes slightly down the group while the change in LE of oxides is more significant
- Enthalpy change of thermal decomp are increasingly endothermic down the group, implying that increasing amounts of heat have to be supplied in order for the nitrate to decompose
- Ba reacts vigorously with cold water, producing bubbles of hydrogen. Ba reacts explosively with O_2, burns in oxygn with a pale green flame, white solid of BaO formed.
- Reactivity of gp2 elements increases down the group
    - Sum of the first and second IE of Gp 2 elements decreases down the grp, resulting in increasing ease of losing electrons down the grp
    - As indicated by increasingly negative values of E, the reducing power of grp 2 elements increases down the grp. Increasingly negative E values indicate the increasing tendency for the backward reaction to occur
- Finely powdered Ca metal has a large surface area which increases its rate of reaction with water vapour in the air to produce hydrogen gas. The heat produced causes hydrogen gas to combust spontaneously with oxygen gas in the air, causing explosions. This generates more water which spark off further explosive reactions with finely powdered Ca metal

- When reacting with water vapour/steam, CaO is produced, not Ca(OH)2. Both produce H2
- BaCO3 will decompose at a higher temp. Ba2+ has a larger ionic radius compared to Ca2+, resulting in lower charge density. Ba2+ therefore has weaker polarising power, hence weakening the covalent bonds withing X ions to a smaller extent as compared to Ca2+, resulting in higher thermal decomp temperature

Group 7 common answers

X2

Reaction with Hydrogen

Cl2 vs Br2

Chlorine reacts more quickly and explosively with hydrogen gas than the reaction between bromine and hydrogen gas in the presence of ultraviolet light.

Cl2 vs F2

Fluorine reacts more quickly and vigorously with hydrogen gas under room temperature and pressure in the dark but hydrogen does not react with chlorine in the dark.

Disproportionation

Disproportionation: Cl2(g) + 2NaOH(aq) → NaCl(aq) + NaClO(aq) + H2O(l)

When heated, NaClO undergoes further disproportionation.
3NaClO(aq) → 2NaCl(aq) + NaClO3(aq)

Cyanogen

Cyanogen disproportionates in cold aqueous sodium hydroxide. (CN)2(g) + 2OH– (aq) → CN– (aq) + CNO– (aq) + H2O(l)

Redox

Cl2 with Fe2+

Observation: pale green solution of Fe2+ turns to pale yellow due to the formation of Fe3+
When NaOH is added: a reddish brown ppt of Fe(OH)3 is formed, which is insoluble in excess NaOH

I2 with KI

Observation: Black crystals of I2 dissolves to form brown solution due to the formation of the complex I3 –.

Na2S2O3 with I2

From (2), S2O3 2– reacts with I2, thus reducing [I2(aq)]. By Le Chatelier's Principle, position of eqm (1) shifts to the left, reducing [I3 –], until all I2 is reacted with S2O3 2– . Observation: Brown solution is decolourised. (Note: S4O6 2– (aq) is colourless)

AgCl and NH3

NH3(aq) will react with free Ag+ to form the soluble silver diammine complex, [Ag(NH3)2] + and this results in the lowering of [Ag+].
By Le Chatelier's Principle, position of equilibrium (1) shifts right causing more AgCl(s) to dissolve.
When the ionic product of AgCl becomes smaller than its Ksp, all the white ppt of AgCl dissolves.
Observation: White ppt of AgCl dissolves in excess aqueous ammonia to form a colourless solution.

AgBr dissolves in NaCN
AgBr(s) ⇌ Ag+ (aq) + Br– (aq) -----------------------(3)
Upon adding NaCN, the free Ag+ reacts with the strong CN– ligand to form the stable [Ag(CN)2] – complex. Ag+ (aq) + 2CN– (aq) ⇌ [Ag(CN)2] – (aq)
This lowers [Ag+] and by Le Chatelier's Principle, position of equilibrium (3) shifts to the right causing more AgBr(s) to dissolve. When the ionic product of AgBr becomes smaller than its Ksp, all the cream ppt of AgBr dissolves.

AgCN dissolves in NH3
Ag+ (aq) + CN– (aq) ⟶ AgCN(s) -------------(1)
AgCN (s) ⇌ Ag+ (aq) + CN– (aq) --------------(2)
Ag+ (aq) + 2NH3(aq) ⇌ [Ag(NH3)2] + (aq) -----(3)
Upon the addition of NH3(aq), a soluble silver diammine complex [Ag(NH3)2] + is formed. This causes [Ag+ (aq)] to decrease. By Le Chatelier's principle, the position of equilibrium (2) will shift to the right, causing more AgCN(s) to dissolve. When the ionic product of AgCN becomes smaller than its Ksp, all the white ppt of AgCN dissolves.

Distinguishing test
AgCl is soluble in NH3 but AgI is not.

Decomposition of AgCl
Sunlight likely catalysed the decomposition of silver chloride/redox reaction between the Ag+ and Cl- ions to form silver metal and chlorine gas. Silver metal atoms are likely to be formed in nanoclusters in the range of 70nm, producing the purplish colouration

Physical properties

Boiling point
Boiling point increases in the order: HCl < HBr < HI.
Explanation: HCl, HBr and HI have simple molecular structures with both instantaneous dipole–induced dipole (id–id) and permanent dipole–permanent dipole (pd–pd) interactions. Boiling involves overcoming these intermolecular forces of attraction.

From HCl to HI,
- size of the electron cloud increases
- ease of distortion of the electron cloud of increases
- id–id interactions become stronger and more energy is required to break the intermolecular forces of attraction
- hence, boiling point of HX increases in the order: HCl < HBr < HI

HF has an unexpectedly higher boiling point than HCl, HBr and HI.
- HF has a simple molecular structure with intermolecular hydrogen bonding, which is much stronger than the intermolecular van der Waals' forces of attraction in HCl, HBr and HI

pH
Acid strength increases in the order: HF < HCl < HBr < HI
Explanation: The acidity of the hydrogen halides depends on the strength of the H–X bond.
- The weaker the H–X bond, the greater the ease of breaking the H–X bond, the higher the concentration of H3O + in the solution. Thus, the more acidic the hydrogen halide in aqueous solution.

- Since bond dissociation energy decreases in the order: H–F >> H–Cl > H–Br > H–I, acidity increases in the order: H–F << H–Cl < H–Br < H–I

Decomposition

The reaction can be carried out by inserting a hot wire (or glass rod) into a test tube containing the gas or by heating.
The extent of the given decomposition reaction increases down the group. (can use bond energy to calculate deltaH)

The decomposition reaction becomes less endothermic down the group; less heat is required to bring about the decomposition of the hydrogen halide, i.e the ease of decomposition increases down the group.

Thermal stability

The thermal stability of the hydrogen halides decreases down Group VII. Thermal stability is related to the H–X bond strength.
Down Group VII,

- the valence orbitals of a halogen become more diffuse and this results in less effective orbital overlap between the 1s orbital of H and the p orbital of the halogen.
- Differences in electronegativity between H and the halogens also decrease. This leads to a decrease in bond polarity
- a weaker H–X bond is formed
- less endothermic bond dissociation energy
- HX is less thermally stable Bond dissociation energy decreases in the order: H–F > H–Cl > H–Br > H–I

To break HX bond: reaction can be carried out by inserting a hot wire or glass rod into a test tube containing the gas or by heating

Decomposition reaction becomes less endothermic down the group, hence the extent of the reaction increases down the group.

Solubility

Organic solvent vs aqueous solvent

Bromine is non-polar, so it dissolves better in a non-polar solvent like ether. However, the salt is ionic in nature and is insoluble in a non-polar solvent.

Solubility of iodine in cyclohexane

both cyclohexane and iodine have simple molecular structures, are non-polar and have van der Waals’ forces of attraction between their molecules. When iodine dissolves in cyclohexane, the energy released from the vdW forces formed between iodine and cyclohexane is enough to overcome the vdW forces between iodine molecules and the vdW forces between cyclohexane. On shaking with cyclohexane, I_2 will dissolve in the colourless cyclohexane to form a violet organic layer. Brown colour of aqueous layer fades

Oxidising strength

As can be observed from the less positive E o (standard electrode potential) values from Br_2 to I_2, the oxidising strength of the halogens decreases down the group.
In the reaction between bromine and thiosulfate, bromine, a stronger oxidising agent than iodine is able to oxidise sulfur such that the average oxidation state of sulfur increases from +2 to +6

$$4Br_2 + S_2O_3^{2-} + 5H_2O \longrightarrow 8Br^- + 2SO_4^{2-} + 10H^+$$

In the reaction between iodine and thiosulfate, iodine, a weaker oxidising agent is able to oxidise sulfur such that the average oxidation state of sulfur increases from +2 to +2.5.
I2 + 2S2O3 2− ⟶ 2I – + S4O6 2–

OR
• Down the group, the E Ɵ value becomes less positive. • A less positive value of E Ɵ suggests that the reduction of X2 to X– (aq) is less energetically favoured / feasible. • The less likely a halogen is reduced, the weaker its oxidising power is. • Thus, the oxidising power of halogens decreases down Group VII.

Reaction of NaX with conc H2SO4

Conc H2SO4 is an oxidising agent and will oxidise HX to X2 (for HBr and HI only)

NaCl: White fumes of HCl are observed
NaBr: White fumes of HBr are observed. Upon oxidation of HBr, reddish brown Br2 vapour is observed. Acidic and pungent SO2 gas is produced too
NaI: White fumes of HI are observed. Upon oxidation of HI, violet I2 vapour is observed and yellow solid of sulfur may be observed after prolonged reaction with excess conc sulfuric acid

NaCl vs NaI
Ease of oxidation of X – to X2 increases down the group
Reducing power of X – increases down the group

Reaction of NaCl with concentrated H2SO4: NaCl(s) + H2SO4(l) ⟶ NaHSO4(s) + HCl(g)
Observation: Steamy white fumes of HCl are formed.

Reaction of NaI with concentrated H2SO4:
NaI(s) + H2SO4(l) ⟶ NaHSO4(s) + HI(g)
8HI(g) + H2SO4(l) ⟶ H2S(g) + 4I2(s) + 4H2O(l)
Observation: Black crystals / violet vapour are formed. Colourless, pungent gas turned moist blue litmus red.

Explanation: HI is a stronger reducing agent than HCl. Hence, the oxidation state of S decreases from +6 in H2SO4 to –2 in H2S (decrease of 8 units). On warming the reaction, most HI produced would be oxidised by concentrated H2SO4 to give shiny black I2 crystals. H2SO4 is then reduced to H2S (SO2 gas may be formed depending on temperature and concentration of reactants used).

Observations HI with conc H2SO4
violet vapour of iodine, trace white fumes of HI, and a pungent hydrogen sulfide will be evolved

Need to cool the beaker: so that iodine vapour can be deposited as a solid

With KI: when I2 is in contact with I-, the reddish-brown I3- would be formed

Gp7

- Br2: red-brown (hexane), pale yellow (aq)
- I2: violet (hexane), brown (aq) [hexane is less dense than water]
- In the presence of oxidising acid like conc H2SO4, ease of oxidation of halides increases down the group. As HCl is not easily oxidised to Cl2, it wil react wth alcohols to give chlorolkanes. However, most HI produced would be oxidised by conc H2SO4 to give shiny black I2 crystals. Without HI, alcohols are not converted to iodoalkanes

- Ease of hydrolysis increases from chloro to bromo to iodoethane as the size of the halogen atom, X increases in size from chlorine to bromine to iodine. Thus, the valence orbitals become more diffused and the effectiveness of the overlap between the orbitals of carbon and X atom decreases. The C-X bond strength decreases and becomes more easily broken

TM common answers

Physical properties

Definition of Transition element:
a transition element is a d-block element that forms at least one ion with partially filled d orbitals

Ionisation energies (removing e from d subshell vs e from s subshell)
the second electron removed from Mn is a 4s e while the second e removed from chromium is a 3d e. since a 3d e is closwer to the nucleus and has lower energy, more energy is required to remove it, casing second IE to be higher than that of Mn

TM vs Group II

Atomic radius: TM smaller than Gp II
Both Fe and Cu have more protons than Ca and hence have higher nuclear charge than Ca. Fe and Cu also have more electrons than Ca but the increase in shielding effect is minimal. These additional electrons in Fe and Cu (i.e. 3d electrons) are added to an inner sub-shell but provide relatively poor shielding (when compared to 3s and 3p electrons) for the outermost 4s electrons because they are d electrons occupying highly diffuse orbitals. The valence 4s electrons in Fe and Cu experience a greater effective nuclear charge and are attracted more strongly to the nucleus than those in Ca, resulting in Fe and Cu having a smaller atomic radius

OR
Rhodium has more protons than strontium and so has higher nuclear charge than strontium. Although rhodium has more electrons than strontium, the increase in shielding effect is minimal. The additional electrons in rhodium (ie 4d electrons) are added to an inner sub-shell but provide relatively poor shielding (when compared to 4s and 4p electrons) for the outermost 5s electrons because they are d electrons occupying highly diffuse orbitals. The valence 5s electrons in Rh experience a greater effective nuclear charge and are attracted more strongly to the nucleus than those in strontium, resulting in rhodium having a smaller atomic radius

Density: TM greater than GpII
Since relative atomic mass of Fe and Cu are higher than that of Ca while atomic radius of Fe and Cu are smaller than that of Ca, density of Fe and Cu are significantly greater than that of Ca.

Oxidation states: TM – variable; GpII – fixed
Fe and Cu are first row transition metals with the general valence electronic configuration 3dx 4sy . Due to the close similarity in energy between the 3d electrons and the 4s electrons, Fe and Cu can make use of different number of these electrons in bond formation (ionic or covalent) when they form compounds and hence they have a tendency to vary in their oxidation states.

Calcium, an s-block element, has the electronic configuration 1s2 2s2 2p6 3s2 3p6 4s2 . It can only exist in the +2 oxidation state by losing 2 valence electrons to form Ca2+ .
Ca does not exhibit +1 oxidation state where it exists as Ca+ . This is because the lattice energy of an ionic compound in which calcium exists as Ca+ would be much less exothermic compared to an ionic

compound in which calcium exists as Ca2+. Since the 2nd ionization energy of Ca is not very high (as the second electron is removed from the valence 4s sub-shell), calcium loses the two valence electrons to form Ca2+ in its ionic compounds which have much more exothermic lattice energy.
+3 oxidation state of Ca is also not favourable due to the very high 3rd ionization energy required to remove the third electron from the inner quantum shell, n =3. Hence, too much energy is needed for its formation, which is not offset by the more exothermic lattice energy of ionic compounds containing Ca3

Metallic bonding

As shown in the diagram, Ca has a giant metallic lattice structure with a regular array of positively charged Ca2+ ions surrounded by a 'sea of delocalised electrons'. Metallic bonding arises from the electrostatic forces of attraction between the metal cations held in the lattice and the delocalised electrons.

Boiling point: TM greater than GpII

Fe has a significantly higher melting point than Ca due to its stronger metallic bonding. The stronger metallic bonding in Fe arises because both the 3d and 4s electrons of Fe can contribute to the 'sea' of delocalised electrons (due to the small energy difference between these electrons). For Ca, only the two valence 4s electrons can contribute to the 'sea' of delocalised electrons.
In addition, the contribution of more electrons for delocalisation makes the iron cations in the lattice smaller and more highly charged, resulting in stronger electrostatic attraction between these cations and the delocalised electrons than in the case between calcium ions and the delocalised electrons. Hence Fe has a higher melting point than Ca.

Electrical conductivity: TM greater than GpII

3d and 4s electrons are close in energy. Cu has an electronic configuration of [Ar]3d9 4s1 . Both the 3d and 4s electrons of copper are delocalised while calcium has only the valence 4s electrons for delocalisation. With more delocalised electrons to act as mobile charge carriers, electrical conductivity of copper is much greater than that of calcium.

Thermal stability: TM compounds less stable than GpII compounds

The temperature of decomposition of a nitrate depends on the charge density of the cation as a cation with higher charge density has greater polarising power, thus distorting the electron cloud of the nitrate ion to a greater extent, causing the nitrate to decompose at a lower temperature.
Since the charge of Cu2+ and Ca2+ are the same but Cu2+ has a smaller ionic radius, Cu2+ has higher charge density than Ca2+ . Thus, Cu2+ has higher polarising power, distorting the electron cloud of nitrate ion to a greater extent so that copper(II) nitrate decompose at a lower temperature than calcium nitrate.

Between TM atomic radius

The atomic radii of Fe and Cu are almost constant because the increase in effective nuclear charge from Fe to Cu is minimal. This, in turn, occurs because in traversing elements in the first-row transition metals which Fe and Cu are members of, each 'additional electron' enters the penultimate 3d sub-shell where it provides some shielding between the nucleus and the outer 4s shell of electrons, and essentially offsets the increase in nuclear attraction due to each 'additional proton' in the nucleus.

Nuclear charge increases from Fe to Cu. However, additional electrons are being added to the inner 3d subshell. As such, there I an increase in shielding effect caused by the increasing number of electrons from Fe to Cu. Hence, effective nuclear charge remains fairly constant from Fe to Cu.

Catalysis

Definition

Catalysis is the phenomenon in which the rate of a reaction is increased by the addition of a small amount of substance termed a catalyst. A catalyst increases the reaction rate by providing an alternative reaction pathway with lower activation energy. ‘Heterogeneous catalysis’ refers to catalysis in which the catalyst is in a different physical phase compared to the reactants. Most commonly, the catalyst is a solid and the reactants are gases

Examples

Iron is used as a heterogeneous catalyst in Haber Process in the manufacture of ammonia.
Nickel is used as a heterogeneous catalyst for hydrogenation of unsaturated fats in the manufacture of margarine.

Suitability of transition metals as catalysts

As TM compounds contain TM ions which have empty d orbitals which are able to accept the lone pair of e from reactant species, and hence allow their adsorption onto the TM compounds

$S_2O_8^{2-}$ and I^-

Reaction is feasible but because of the reaction is between two negatively charged ions that repel one another, the activation energy is high, hence, reaction is slow when uncatalysed.

Role of Fe^{2+}

The Fe^{2+} ion acts as a homogeneous catalyst and increases the rate of the reaction by enabling it to proceed via an alternative reaction pathway, with lower activation energy and which involves the following steps:

Step I $Fe^{2+}(aq) + \frac{1}{2}S_2O_8^{2-}(aq) \longrightarrow Fe^{3+}(aq) + SO_4^{2-}(aq)$ E^{θ}_{cell} = (2.01– 0.77) = +1.24 V > 0 V
Step II $Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2(aq)$ E^{θ}_{cell} = (0.77 – 0.54) = +0.23 V > 0 V

- Each of these steps involves reaction between oppositely charged species and is therefore expected to occur more readily than the uncatalysed reaction.
- The activation energy for each of these steps is relatively lower than that of the uncatalysed reaction and therefore reaction rate is increased.
- The Fe^{2+} catalyst reacted to form an intermediate (Fe^{3+}) but is regenerated at the end of the reaction

Haber Process (Iron catalyst)

Iron acts as a heterogeneous catalyst in the reaction between gaseous nitrogen and hydrogen in the Haber Process.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$s
In this reaction, Fe(s) provides sites on which $N_2(g)$ and $H_2(g)$ can be adsorbed. The adsorption is possible because Fe(s) possesses a partially filled 3d sub-shell. It has empty low-lying vacant 3d orbitals to accept electron pairs from reactant molecules and also provide 3d electrons to form bonds with reactant molecules. The adsorption leads to an increase in reaction rate • it weakens the covalent bonds in N_2 and H_2 thus reducing the activation energy for the reaction. • It increases the concentration of the reactant molecules at the Fe surface – hence, the reactant molecules to come into close contact with proper orientation for reaction. Once formed, NH_3 molecules can easily desorb from the Fe surface so that the active sites are exposed for further reaction. (regeneration of catalyst)

Reduction potential of homogeneous catalyst must be between the reduction potential of the reactants

Gold wire

A catalyst is a substance that provides an alternative pathway with lower activation energy, remaining chemically unchanged at the end of the reaction. A heterogeneous catalyst is one that is in a different phase as the reactants.

Adsorption: the gold wire provides active sits whereby N_2O molecules may be adsorbed. The adsorption weakens N-O bonds so that the N_2O molecules are more reactive

Reaction: the N_2O molecules on the gold surface are in close proximity and the correct orientation so that they can readily react together

Desorption: the products, N_2 and O_2, formed diffuse away from the surface of the catalyst and the active sites become available again.

Complex formation

Complex ion definition

A complex ion is a charged species which consists of a central metal ion/atom linked to surrounding ions or molecules (ligands) by dative covalent bonds.

Ligand edta used to slow down reaction

The deterioration can be slowed down since edta forms a stable complex with Fe^{2+} (or any other catalysing cation) present in the organic substance. Such a complex formed (e.g. $[Fe(edta)]^{2-}$) is more stable than the original cation (which probably exists as an aqua complex). Being more stable, the complex ion with edta ligand would therefore be less readily involved in any redox reaction in the deterioration process.

$FeCl_3$ is acidic

In an aqueous solution of $FeCl_3$, the Fe^{3+} ion exists as $[Fe(H_2O)_6]^{3+}$. Being highly charged and small in size, the Fe^{3+} ion has high charge density and hence strong polarising power. The strongly polarising Fe^{3+} distorts the electron cloud of the H_2O ligands and enables $[Fe(H_2O)_6]^{3+}$ to become a proton donor and to undergo appreciable hydrolysis. The following equilibrium is established:

$[Fe(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Fe(OH)(H_2O)_5]^{2+}(aq) + H_3O^+(aq)$

The presence of a slight excess of H_3O^+ ions in the solution causes the solution to be acidic i.e. the pH is less than 7.

Redox reactions

Relevant data: $Fe^{3+} + e^- \rightleftharpoons Fe^{2+}$ $E^{\theta} = +0.77$ V

$\frac{1}{2}I_2 + e^- \rightleftharpoons I^-$ $E^{\theta} = +0.54$ V

$[Fe(CN)_6]^{3-} + e^- \rightleftharpoons [Fe(CN)_6]^{4-}$ $E^{\theta} = +0.36$ V

When $FeCl_3(aq)$ is added to $KI(aq)$, the following redox reaction occurs.

$Fe^{3+}(aq) + I^-(aq) \longrightarrow Fe^{2+}(aq) + \frac{1}{2}I_2(aq)$ E^{θ} cell = (0.77–0.54) = +0.23 V > 0

The Fe^{3+} ion is strong enough an oxidising agent to oxidise the I^- ion to I_2 as indicated by the positive E^{θ} value. Hence a brown solution of I_2 is obtained.

When $K_3[Fe(CN)_6]$ (aq) is added to $KI(aq)$, there is no reaction.

$[Fe(CN)_6]^{3-} + I^-(aq) \rightarrow [Fe(CN)_6]^{4-}(aq) + \frac{1}{2}I_2(aq)$ E^{θ} cell = (0.36–0.54) = –0.18 V < 0

The negative E^{θ} value indicates that the reaction is energetically not feasible under standard conditions. Unlike $Fe^{3+}(aq)$, $[Fe(CN)_6]^{3-}$ is not strong enough an oxidising agent to oxidise I^- to $I_2(aq)$.

The CN^- ligand has stabilised the +3 oxidation state relative to the +2 oxidation state of Fe. The difference in oxidising power between Fe^{3+} (i.e. $[Fe(H_2O)_6]^{3+}$) and $[Fe(CN)_6]^{3-}$ can be attributed to their different charges. It is easier for the positively charged Fe^{3+} ion to accept an electron than for the negatively charged [Fe(CN)6] 3– to do so since there will naturally be repulsion between like charges in the latter case.

Oxidation of Fe2+

An acidified solution of Fe2+ ions can be oxidised by O2 in the air to form Fe3+ ions as indicated by the positive EO cell value above. However, this reaction is kinetically slow since it involves the loss of an electron from a positively charged Fe2+ ion which is energetically demanding.

The dirty green precipitate of Fe(OH)2 that is obtained from the reaction between NaOH(aq) and Fe2+ ions can be oxidised by O2 in the air to form the brown Fe(OH)3 as indicated by the positive E O cell value above. Unlike reaction (1), this reaction involves the loss of an electron from the neutral Fe(OH)2. Hence it occurs rapidly as compared to losing an electron from a positively charged Fe2+

Number of dative bonds

since there is 1 lone pair of e on each N atom in X, one X molecule can form 2 dative covalent bonds with the central Co3+ in the complex. With 3 X bonded to 1 Co3+ in the complex, there will be a total of 6 dative bonds formed between the ligands and Co3+. Hence, the formula of the complex is [CoX3]3+ and the shape of the complex is octahedral

Ligands which contain 2 groups that each have at least a lone pair of e which can be donated to the central metal ion in a complex, forming 2 dative covalent bonds.

Stronger ligands

edta ligand stabilises Fe(III) relative to Fe(II) to a larger extent than water ligand. Hence E value is less than +0.77V/decreases

The higher the concentration of a particular complex ion present in an aqueous solution, the more stable the complex frmed, hence the ligand will form a stronger bond with Ni2+

Coloured complexes

Cu2SO4 is a white powder

Cu2SO4 is a white powder because it reflects all the incident white light that falls on it. Since Cu(I) has a d 10 configuration and hence a fully filled d sub-shell, there is no d–d transition to bring about colour.

When water is added

When Cu2SO4 is treated with water, a disproportionation reaction occurs leading to the formation of pink-coloured copper and blue CuSO4 solution. CuSO4(aq) is blue because it contains the blue [Cu(H2O)6] 2+ ions. The reaction is energetically feasible under standard conditions as the Eθ cell value calculated below is greater than 0 V.

Zn(II) is white

Zn(II) ions have fully filled 3d subshells/orbitals. Hence d electrons cannot be promoted from a lower energy level to a higher energy level, d-d transition does not occur.

Explanation for colour

G contains CuF6 3– with the a central Cu(III) which has electronic configuration [Ar] 3d8 .

- presence of F– ligands causes the splitting of the five 3d orbitals in Cu3+ ion into two sets of slightly different energy levels.
- Since these 3d orbitals are partially filled, electrons from the lower-energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the

higher-energy d orbitals. (d-d transitions)

- The colour observed is the complement of the colour absorbed.

OR

In a compound, the iron ions have partially filled 3d orbitals. In the presence of ligands, the d orbitals in Fe ions are split into 2 sets of different energy levels. Since the 3d orbitals are partially filled, the electrons from the lower energy d orbitals can absorb energy corresponding to certain wavelengths from the visible spectrum and get promoted to the higher energy d orbitals. Such d-d transitions are responsible for the colour observed. The colour observed is the complement of the colour absorbed

Explanation for different colours

different ligands have different ligand strength and thus the d orbitals are split to different extents. NH_3 ligand results in a larger E and shorter wavelength absorbed. Thus $[Co(NH_3)_6]^{3+}$ is yellow-brown. F^- ligand results in smaller E and longer wavelength absorbed. Thus $[CoF_6]^{3-}$ appears blue.

Or

different ligands have different capacities of splitting the d orbitals of a particular TM cation. The longer the wavelength absorbed, the smaller the splitting of the d-orbitals

Haemoglobin

Function of haemoglobin

Haemoglobin (denoted by Hb) acts as a transporter of oxygen in the human body. It carries out this function by having the oxygen molecule acting as a ligand forming a dative covalent bond to Fe(II) in its haem group. The resulting compound formed is called oxyhaemoglobin and it travels in the blood to places in the human body which requires oxygen. The H_2O ligand replaces the O_2 ligand when the oxygen is released to the oxygen-starved sites in the human body. $Hb\text{-}O_2 + H_2O \rightleftharpoons Hb\text{-}OH_2 + O_2$

Ligand exchange

In haemoglobin, a H_2O molecule acts as a ligand and forms a dative covalent bond with Fe(II) in the haem group. When converted into oxyhaemoglobin, a ligand exchange reaction occurs with the H_2O ligand being replaced by the O_2 ligand. There is no redox reaction and hence no change in the oxidation number of Fe(II) in the haem group.

Toxicity of CO

The interaction between CO and haemoglobin is that of a co-ordinate bond formed between the carbon atom of CO and the iron(II) in the haemoglobin. The CO acts as a monodentate ligand and donates the lone pair of electrons on the C atom into a vacant low-lying orbital in Fe(II) to form a co-ordinate bond. CO is so much more toxic than CO_2 probably because the CO-haemoglobin complex is more stable than the CO_2-haemoglobin complex. In other words, the CO ligand is so much stronger than the CO_2 ligand in that it forms a stronger co-ordinate bond to Fe(II) such that it is very difficult for O_2 or H_2O ligand to replace it. This renders the haemoglobin ineffective in transporting oxygen and will result in death of the victim concerned.

Toxicity of CN-

CN^- ion. It also forms a very stable complex with haemoglobin. It does so by donating a lone pair of electrons from the carbon atom to a vacant low-lying orbital in Fe(II) of haemoglobin to form a strong co-ordinate bond. This renders the haemoglobin ineffective in performing its oxygen-transporting function.

Mass action effect

By using pure O_2, the equilibrium position of the reaction: $Hb\text{-}CO + O_2$ $Hb\text{-}O_2 + CO$ is shifted right due to the very high concentration of O_2. The formation of Hb-O_2 means that haemoglobin resumes its role as a transporter of oxygen and hence the patient can be revived. Note: The pure oxygen administered does not oxidise CO to CO_2. It displaces CO by a mass action effect.

Transition metals

- Able to form at least one stable ion with a partially filled d-subshell
- Give electronic configuration
- Difference in colours
    - Different ligands split the five 3d orbitals of the Ni^{2+} ion into two sets of slightly different energy levels but to different extents. Hence X and Y ions absorb different wavelengths of light from the visible spectrum for d-d transitions (promotion of e from the lower energy d orbitals to higher energy d orbitals). Consequently diff colours corresponding to the complements of diff colours absorbed, are observed for the 2 diff complex ions.
- Qualitative analysis
    - Test: add NaOH dropwise till excess to each sample in a test tube. For the cation in A, a grey-green ppt forms which is soluble in excess NaOH to form a dark green solution. For the cation in C, a red-brown ppt forms which is insoluble in excess NaOH
- Due to presence of partially filled d subshells in transition metals, reactant moleculescan form weak interactions with the surface of the catalyst. The H_2 and O_2 molecules adsorb onto the surface of the Pt catalyst. The adsorption increases the surface concentration of H_2 and O_2 on the Pt surface and weakens the covalent bonds in H_2 and O_2 for reaction. After reaction, the product desorbs from the surface, allowing more reactants to adsorb
- Upon exposure to air, Fe^{2+} was oxidised to Fe^{3+}. Fe^{3+} underwent hydrolysis in aqueous solution, producing H^+ ions which caused the pH of the solution to decrease
- Co:
    - Water: pink
    - Carbonate: purple ppt
    - $CoCl_4^-$: Cl^- ligand is bigger than H_2O, hence only 4 Cl^- can surround Co^{2+}
- Si has available d orbitals that can incorporate the H_2O ligand forming a 5-coordinate ntermediate whereas C can only form the transition state in a Sn2 mechanism as it does not have available d-orbtials to incorporate the H_2O ligand
- A catalyst is a substance that provides an alternative pathway with lower activation energy, remaining chemically unchanged at the end of the reaction. A heterogeneous catalyst is one that is in a different phase as the reactants. Adsorption: the gold wire provides active sites whereby N_2O molecules may be adsorbed. The adsorption weakens the N-O bonds so that the N_2O molecules are more reactive. Reaction: the N_2O molecules on the gold surface are in close proximity and the correct orientation so that they can readily react together. Desorption: the products, N_2 and O_2, formed diffuse away from the surface of the catalyst and the active sites become available again.
- Without the catalyst, the reaction has a high activation energy due to collisiosn between ions of the same charge. In the presence of catalyst, collisions between ions of the same charge are avoided hence it lowers the activation energy
- Iron which is a transition metal possesses variable oxidation states due to the small energy level difference between the 3d and 4s electrons. This results in different numbers of 3d and 4s electrons lost to form stable ions and compounds of different oxidation states

- Pale blue ppt of $Cu(OH)_2$ is formed initially in blue solution. When excess NH_3 is added, pale blue ppt dissolves to give a deep blue solution of $[Cu(NH_3)_4(H_2O)_2]^{2+}$. When eqm is shifted to the right to produce the deep blue complex, eqm 2 shifts left causing the $Cu(OH)_2$ ppt to dissolve
- $CuO + 2NH_3 \rightarrow H_2O + Cu(NH_3)_2$
  Colour of final solution is dark blue due to presence of NH_3 molecules that could act as ligands to the Cu^{2+} ion in this solvent as easily as it does in aqueous medium. Hence a similar complex is generated, resulting in formation of complex of the same dark blue colour
- Due to presence of both $Cu(h_2O)_6^{2+}$ and $CuCl_4^{2-}$, the resultant solution appears pale yellowish-green. In presence of excess water ligands or dilution wth water, ligand exchange occurs as water ligands replaces Cl^- ligands due to mass action effect. Addition of conc H_2SO_4 does not produce such colour changes as there are no chloride ions to act as ligands to give the $CuCl_4^{2-}$ complex

Periodicity

- High charge density of Al^{3+} polarises e cloud of surrounding anions strongly to form covalent bonds
- Al burns in excess O_2 with an intense white flame to produce Al_2O_3
- S burns in excess O_2 upon gentle heating with a pale blue flame to produce SO_2
- **$SiCl_4$ hydrolyses in water but not CCl_4**
  Carbon atom is small, Cl groups around the atom are bulky and prevent oxygen from approaching the atom due to repulsion of negative charges of lone pairs. Carbon does not have an empty orbital to accept a lone pair from the water molecule. However, silicon atom is bigger and has empty 3d orbitals available to accept a lone pair from the water molecule.
    - C does not have low-lying vacant orbitals to accommodate the lone pair from water during hydrolysis
- $Al^{3+} + 3OH^- \rightarrow Al(OH)_3$
  $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^-$
- P_4 burns in oxygen in a white flame. $P_4 + 5O_2 \rightarrow P_4O_{10}$

Acidity of oxides across the period

- Across the period, the oxides become less basic and more acidic. Al_2O_3 is amphoteric as it is an ionic oxide with covalent character. The covalent character is due to the high charge density of Al^{3+} that polarise and distort the electron cloud of O^{2-}

Comparing ionic radii

Na^+ and Si^+ are smaller than P^{3-} and Cl^- as the latter two have one more filled principal quantum shell as compared to the former 2, thus the valence electrons are frther away from the nucleus.

Si^{4+} is smaller than Na^+. both ions are isoelectronic hence both have similar shielding effect. But S^{4+} has more protons, hence greater nuclear charge. Effective nuclear charge of Si^{4+} is greater than Na^+ thus the valence electrons of Si^{4+} experience greater attraction to the nucleus and is smaller. Cl^- is smaller than P^{3-} for the same reason

Boiling points

More energy is required to break the stronger covalent bonds in Si as compared to the metallic bonds in Na between Na^+ and its delocalised sea of electrons, thus Si has a higher boiling point.

$AlCl_3$

When only a few drops of water are added to the solid, steamy white fumes of HCl are evolved and together with the formation of $Al(OH)_3$