

Section 13 Periodicity

13,1.1

Periodic trends in oxides

- a) Bonding:: Difference in electronegativity between O and period 3 element determines whether electrons are shared or lost...so if it is high we have ionic, low is covalent. So Na, Mg and Al form ionic oxides and the rest are covalent. However SiO₂ has a giant covalent structure due to the need for Si to have 4 bonds and it is too large for double bonds.
- b) Boiling point depends on the forces holding the particles together. The giant ionic structures of the metal oxides give them high boiling points. Since Na is less tightly attracted to the oxide ion, its melting point is lower than the others (but still high) Giant covalents always have massive bpt due to the need to break strong covalent bonds to form a gas. The simple moleculars always have low bpt since only INTERMOLECULAR FORCES need to be broken. They are almost all polar, so differences in bpt depends on M_r ..ie van der waal forces
- c) Solubility in water: Since in order to dissolve, the molecules/ions have to be about as attracted to water as they are to themselves, this too depends on forces of attraction...so low lattice energy of ionics = high solubility. Thus sodium oxide dissolves well, but magnesium oxide is only slightly soluble and aluminum oxide tends not to dissolve at all. The simple molecular ones dissolve since they are polar and they actually react with water.
- d) Since ionics have the O²⁻ ion which is a powerful base, then IF it dissolves well, the solution is highly basic $O^{2-} + H_2O \rightarrow 2OH^-$. The molecular oxides react to form acids: $SO_3 + H_2O \rightarrow H_2SO_4$ with the H attached to a group of very electronegative atoms...thus the bond is VERY polar and weak and H⁺ is easily given off. To get to the acid WITH THE EXCEPTION OF P just add one water to the oxide and if possible, divide by two.
 $P_4O_{10} + 6H_2O \rightarrow 4H_3PO_4$ and a similar stunt with P₄O₆ gives 4H₃PO₃.
- e) Metalloid oxides are AMPHOTERIC ie can act as acids or bases. The classic one here is Al₂O₃, which in its hydrated form would be [Al(OH)₃(H₂O)₃] When it acts as a base it forms salt + water as any metal oxide will and you can write: $Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$. For the acidic, you can write any of several forms. I prefer [Al(H₂O)₃(OH)₃] $\rightarrow [Al(H_2O)_2(OH)_4]^{1-} + H^+$ or you could go $Al(OH)_3 + OH^- \rightarrow Al(OH)_4^{1-}$. this is the aluminate ion and in some books you will see it

written as AlO_2^{1-} and in this case they have just removed as many waters as they can from either of the complexes above to leave this ion...so it is a simplification. GOOD NEWS : I cannot find this in the syllabus, so just know that Al_2O_3 is amphoteric

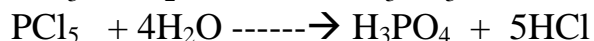
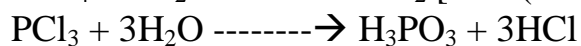
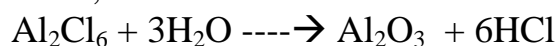
- f) Electrical conductivity: The ionics conduct well in the molten or dissolved state, giant covalents are very poor conductors and simple moleculars are non-conductors. Rationale : In order to conduct electricity the material must have EITHER free moving (delocalised) electrons, which is what metals and graphite have OR mobile ions...which molten or dissolves ionics have . The covalent oxides all have their valence electrons in orbit and so they are not free to migrate. Thus they do not conduct

13,1.2

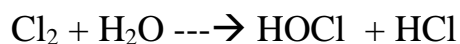
Chlorides

Formulae	NaCl	MgCl_2	Al_2Cl_6	SiCl_4	PCl_5 and PCl_3	Cl_2
Bonding	ionic	ionic	←simple molecular-----→			
Bpt	High	higher	low-----getting lower----→			
Solubility	good	good	reacts violently-----→ mild reaction			
In water						

The trends are for the same reasons as the oxides, but note the molecular formula of aluminum chloride shows it is covalent. The reactivity of the molecular chlorides with water is due to the highly positive period 3 element and a weak polar covalent bond to the Cl. They react to form the oxide (or acid) + HCl,



Chlorine itself reacts mildly with water and in its reaction we can see how the whole process occurs. The H of a water is attracted to one of the Cl's and forms HCl. The remnants of the water(-OH) attach on to the other Cl to produce chloric I acid (HOCl).



In the reactions mentioned before this one, the -OH ends are attracted to each other and break off to give water + the oxide with Al and Si. With the chlorides of P, only one water is ejected and we are left with the acid.

13 2 Transition metals

In order to be classified as classic T-metal, the element **MUST** form more than one ion that **MUST** contain a partially filled d sub-shell...Zn and Sc are not classic T-metals.

E config: : all are $4s^2 3d^n$ EXCEPT Cr and Cu, which stabilise their 3d by going $4s^1 3d^5$ or $4s^1 3d^{10}$

When an ion is formed , the 4s electrons are lost first, since they are on the outside...no ion will contain 4s electrons. The most stable ion will be the one with the most stable arrangement of electrons in its 3d orbitals...preferably with a half filled d shell $3d^5$ as found in Mn^{2+} and Fe^{3+} . If not this then the x-y-z symmetry of d^3 is likely. The usual ionic charges are +2 and +3, although Cu forms the +1 and +2 Note that no ion attains the stability of the inert gases and thus all ions are **PARTIALLY** stable..just some are more stable than others

You should be able to appreciate why Fe and Cr both preferentially have an ion with a 3+ charge...but do not attempt to understand why Cu prefers the 2+ to the 1+, as even I cannot easily explain that!

The IB wants you to know that T-metals will all show a +2 oxidation state. As well as various other oxidation states. I do not know why...almost all non-metal elements have variable oxidation numbers but **ONLY** T-metals have variable ionic charge.

Now this is yet another thing we will do later on, so for now I just want you to think of it as being exactly the same as an ionic state and treat it as electrons lost or gained. So, accepting for now that oxidation state = ionic state, we can predict which state various T metals would prefer:

Cr = $[Ar] 4s^1 3d^5$. So we should predict that the +1 state makes sense with the stability of the half filled d subshell.Pity really as this is **WRONG**. However we should also predict +3 as this would give us $3d^3$ and x,y,z symmetry in the d subshell. This is correct..it is the common ion of Cr. We should also predict +6 as this would be “the inert gas structure” and this is also correct.

Mn = [Ar] 4s² 3d⁵ . Thus we should predict the +2 (half filled d subshell) and the +4 (x,y,z symmetry) and the +7(inert gas structure). And all are true (Hooray!)

T-metals forms complex ions with ligands such as CN¹⁻, H₂O, Cl¹⁻, NH₃ et cetera.

Ligands are species that either have a negative charge, or have a highly electronegative atom with a lone pair of electrons on it. [Note : all -ve ions have lone electron pairs as well]

The highly charged metal ion attracts the lone electron pair of the ligand and forms something called a **dative covalent bond** with it. A dative covalent bond differs from the classic covalent bond as follows:

The classic covalent bond is formed when two atoms share 2 electrons between them, with each donating one of its own electrons to form the shared pair. Example = Cl₂

The dative bonds also has two shared electrons, BUT they both come from the same atom. This is also called a Lewis acid /base reaction, where the acid is defined as the electron pair acceptor(The T-metal) and the ligand is the base...the lone pair giver. (See acid base theory notes in Topic 9).

The complex ion is drawn in square brackets and the overall charge is determined by adding up the T-metal charge and the ligands. So for example if you have Fe³⁺ and six CN¹⁻ then you have a total charge of +3 -6 = -3...[Fe(CN)₆]³⁻

The number of ligands is usually double the charge on the ion or 6. For example [Cu(NH₃)₄]²⁺

Others you need to know are those formed by

- a) Ag¹⁺ and NH₃
- b) Fe³⁺ and water
- c) Cu²⁺ and chloride

Note all these obey the rule “ # of ligands is double the charge on the T-metal” ...so you can do them!

note Al^{3+} and a few other highly charged metal ions can do this. If you are just starting periodicity do not worry about the technical language above...you should understand it when we have done topics 4,14 and 18

T-metal ions are coloured. In order to be coloured , they MUST have a partially filled d shell AND have ligands that split the d shell up into two levels. Anhydrous copper II sulfate is WHITE, hydrated copper II sulfate is BLUE. Here the absence of the ligand water means that the d subshell is not split into 2 levels and so the chemical is not colored

So the upper 3d level must NOT be full and an electron can be promoted from the lower 3d level to it. Now electron promotion requires a photon from within the visible spectrum, so reflected light no longer contains all the photons of white light and so we perceive a colored substance.

Compounds with Sc^{3+} , Zn^{2+} or Cu^+ are all white solids (as far as we are concerned...do NOT ask why copper I oxide is red) and colorless in solution due to either [Ar] or [Ar] $3d^{10}$ as mentioned before.

Color thus depends on the charge on the T-metal ion and the ligand as both with affect the degree of splitting of the d subshell.

T-metals are good catalysts, ie they speed up reactions without being used up/ changedthis really goes back to the ability to form several ions and means that an ion can easily lose or gain an electron without undergoing a massive change in stability. However if an electron is gained or lost from a typical molecule there is a big change in stability.....so the reaction occurs and the t-metal ion will typically change charge ...and as the process nears completion it will revert to its original charge (which it must do as a catalyst)

One great little demo of this that I will probably attempt concerns Co^{2+} . This will catalyse the decomposition of hydrogen peroxide. However Co^{2+} is pink and as the reaction gathers momentum, you see the pink color change to a muddy brown and then to green before fading back to brown and eventually pink. Co^{3+} is green and so what has happened is : $\text{Co}^{2+} \leftrightarrow \text{Co}^{3+} + e$

Think of this extra electron going onto the peroxide molecule. However once it has joined the molecule, there is no way to “balance the books” and have each atom with its desired # of valence electrons. So it falls apart and as it does this it releases an electron which is picked up by the most +ve thing around, Co^{3+} .and thus Co^{2+} is reformed!

Why won't other metal ions act as catalysts? Well firstly they exist with just one definite charge and so the only thing they can do is gain electrons. However it takes a lot of energy to do this (that is why the reverse process...getting metal atoms to lose electrons is so easy) and so the reaction cannot be speeded up as MORE energy is required than before!

Common catalysts

- a) Fe in the Haber process for producing ammonia
- b) V as V_2O_5 in the contact process for making sulfur trioxide
- c) Ni in the conversion of alkenes to alkanes
- d) Manganese IV oxide in the decomposition of hydrogen peroxide
- e) H^+ in esterification
- f) Pt in catalytic converters

Hwk Questions

Test

- 1) When the ions 1 = P^{3-} , 2 = Mg^{2+} , 3 = Cl^- and 4 = Na^+ are arranged in order of increasing size the order is a) 2,3,4,1 b) 4,2,3,1 c) 2,4,3,1 d) 2,1,3,4
- 2) Which of the following reacts with chlorine to produce a covalent chloride?
1 = Mg 2 = Al 3 = P a) 1 only b) 3 only c) 2 and 3 only d) 1 and 2 only
- 3) Which of the following will form more than one different ion? A) Mg b) Sc c) Cu d) Zn
- 4) Which has the lowest first ionization energy? A) Na b) Li c) Cl d) Ar
- 5) When acidified silver ions are added to a solution, a white solid is formed that goes somewhat purple in sunlight. The ion present in the solution is probably a) Sulfate b) fluoride c) Bromide d) Chloride
- 6) Iodine will react with which of the following I = chloride 2 = bromide 3 = fluoride
a) 1 only b) 1 and 2 only c) 1,2 and 3 d) none of them.

7) Account for the fact that

a) The second ionization energy of Mg is less than that of Na and Al (4)

b) P^{3-} is bigger than Cl^{1-} and a lot bigger than Na^+ (3)

10) Give the electronic configuration of Mn, Mn^{2+} and Mn^{3+} and deduce and explain which is the commonest ion of Mn (4)

11) A) Mn^{3+} is wine red in aqueous solution, yet Sc^{3+} produces a colourless solution. Explain (3)

b) Define the term "ligand". Identify two common ligands. (2)

c) The complex ion $[\text{Fe}(\text{CN})_6]^{4-}$ exists Determine the charge on the Fe. (1)

12) a) Give an equation to represent the reactions of i) Na_2O and ii) SO_2 with water. For each one state whether the solution produced would be acidic, basic or neutral. (3)

b) Which would be expected to be more soluble in water, Na_2O or MgO ? Explain at the molecular level. (2)

Test

- 1) When the ions 1 = Al^{3+} , 2 = Mg^{2+} , 3 = Cl^- and 4 = K^+ are arranged in order of increasing size the order is a) 1,2,3,4, b) 2,4,3,1 c) 3,2,4,1 d) 1,2,4,3
- 2) Which equation is the second ionization energy for Na? A) $\text{Na}_{(s)} \rightarrow \text{Na}^{2+} + 2 e$
b) $\text{Na}_{(g)} \rightarrow \text{Na}^{2+}_{(g)} + 2 e$ c) $\text{Na}^+_{(s)} \rightarrow \text{Na}^{2+}_{(g)} + e$ d) $\text{Na}^+_{(g)} \rightarrow \text{Na}^{2+}_{(g)} + e$
- 3) When NH_3 acts as a ligand with Cu^{2+} , then what is formed? A) Copper metal and the ammonium ion b) $[\text{Cu}(\text{NH}_3)_4]^{2+}$ c) $[\text{Cu}(\text{NH}_3)_4]$ d) CuNH_4^{1+}
- 4) Which oxide of the following period 3 elements would produce the most basic solution? A) Mg b) Al, c) Si d) Cl
- 5) Which pair of reactants would produce the most violent reaction? A) Li + Cl b) Li + Br c) Na + Cl d) Na + Br
- 6) Bromine will react with which of the following 1 = chloride 2 = bromide 3 = Iodide
a) 1 only b) 1 and 2 only c) 3 only d) none of them.
- 7) Account for the fact that atomic radius decreases across a period, but increases down a group (3)
- b) The following are successive ionization energies for an element from period 3: 760; 1690; 5200; 6500; 8000; 10,000. (all in kJmol^{-1})
Deduce which element is likely to have such ionization energies and explain your answer.
(3)
- c) Explain why the general increase in ionization energies across period 3 is broken at Al and S(3)

8)

a) Deduce the most likely formula of the complex ion formed when Fe^{3+} and the cyanide ligand, CN^{-} combine(1)

b) Name another ligand that could combine with Fe^{3+} to produce a complex ion. (1)

9) When magnesium reacts with chlorine a crystalline solid is produced that dissolves passively in water, yet when aluminum is reacted with chlorine gas, a powder is produced that reacts violently in water. Explain this difference in terms of bonding. (2)

Answer EITHER Q9 OR Q10

9a) Give an equation for the reaction of Na with water. Would the reaction of K with water be more or less violent? Explain at the molecular level. (3)

b) Give the formula of an ionic and a covalent chloride from period 3. Predict which one of your two compounds would react with water and give an equation for this reaction(3)

10a) Explain why a solution of CuCl_2 is a blueish green color, yet CuCl is white. (4)

b) Why do most transition metals form more than one ion, with one of these being the +2 ion and the other, usually the +3 ion? (2)

TEST 3

- 1) The complex ion $[\text{Co}(\text{NH}_3)_5 \text{Br}]^{2+}$ exists . What is the charge on the cobalt ion? A) +3 b) +2 c) +1 d) +6
- 2) Down Group I Which of the following increases?
i) Density ii) Atomic radius iii) Electronegativity
a) i only b) ii only c) i and ii only d) ii and iii only
- 3) Which of the following is the most stable oxidation state of Mn? A) +3 b) +4 c) +5 d) +6
- 4) When silicon (IV) chloride reacts with water , what is produced? A) Si and HCl b) HOCl and SiH_4 c) HCl and $\text{Si}(\text{OH})_4$ d) Cl_2 and $\text{Si}(\text{OH})_4$.
- 5) Which of the following compounds is most likely to be covalent? a) NaF b) FeCl_3 c) Mn_2O_7 d) KBr
- 6) Which of the following is not the formula of an oxide of a period 3 element? A) Na_2O b) Al_2O_3 c) Cl_2O d) SO
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7a) Define the term “ionization energy” and give equations for the first ionization of Na and the 4th ionization energy of P (3)

b) Explain why ionization energy decreases down group VII (2)

8) Account for the trend in reactivity down Group VII (3)

9a) The oxide of aluminum is ionic, but the chloride is covalent. Account for this fact. (1)

b) Why is aluminum oxide very insoluble in water yet sodium oxide is highly soluble? (2)

Answer EITHER Q 10 or Q11

10a) Give the electronic configuration of Nickel and Ni^{2+} . (2)

b) Account for the fact that a solution of Ni^{2+} is pale green, but when ammonia is added it turns blue. (2)

c) Why can Nickel form +2 or a +3 ion whereas Mg only forms a +2 ion? (2)

11) Give the formulae of the oxides of the following period 3 elements: Na, Mg, Al, Si and S (2)

b) For each oxide state whether it would form an acidic, basic or neutral solution when added to water. (2)

c) Give balanced equations for the reaction of the oxides of Na and Mg with water. (2)