

**DEPARTMENT OF CHEMISTRY
FOURAH BAY COLLEGE
UNIVERSITY OF SIERRA LEONE**

CHEM 221

INORGANIC CHEMISTRY IV

(Unit 1 only)

CREDIT HOURS	2.0
MINIMUM REQUIREMENTS	Pass in CHEM 122
REQUIRED FOR	Honours

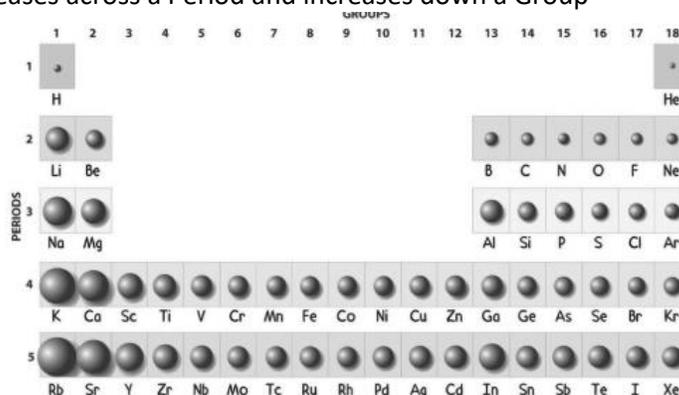
UNIT 1 – FURTHER ATOMIC STRUCTURE AND BONDING

Course Outline:	What are the main trends in the properties of the atoms in Groups 13 – 18 of the Periodic Table? How and why does metallic character change in these elements? What is the inert pair effect and what causes it?
Lesson 1:	Trends in the Periodic Table, with emphasis on Groups 13 – 18; ionisation energies, atomic size, metallic character
Lesson 2:	Inert pair effect; oxidation numbers in Groups 13 – 18; ionic and covalent bonding in compounds
Lesson 3:	Boron, Aluminium and their Compounds – Structure and Physical Properties
Lesson 4:	Boron, Aluminium and their Compounds – Chemical Properties
Lesson 5:	The Chemistry of Thallium and its Compounds
Lesson 6:	The Chemistry of Carbon and Silicon
Lesson 7:	The Chemistry of Tin and Lead
Lesson 8:	The Chemistry of Nitrogen and Phosphorus
Lesson 9:	The Chemistry of Sulphur, Oxygen, the Halogens and The Noble Gases
Lesson 10:	The position of hydrogen in the Periodic Table

Lesson 1 – A Review of Trends in the Periodic Table

a) Ionisation Energy, Electron Affinity and Atomic Size

- The ionisation energies of atoms increase across a Period (with some exceptions) and decrease down a Group
- The electron affinities of atoms increase across a Period (with some exceptions) and decrease down a Group
- The size of atoms decreases across a Period and increases down a Group



- Explanation:
 - nuclear charge increases across a Period which increases the attraction between the nucleus and the outer electrons
 - electrons are shielded from the nuclear pull by electrons in inner shells; the number of shells does not change across a Period, so the shielding also stays the same
 - the nuclear charge increases down a group, but the number of shells also increases so the shielding increases; the effect of extra shielding outweighs the effect of extra nuclear charge
 - when the effect of ionisation energy and electron affinity are combined, the trend is consistent; it becomes easier to lose electrons and harder to add electrons as you move from left to right across a Period

b) Electronegativity and Bonding

- The ability of an atom to attract bonding electrons is known as electronegativity; electronegativity increases across a Period and decreases down a Group; atoms with high electronegativity are **electronegative** and atoms with low electronegativity are **electropositive**
- Atoms on the left-hand side and at the bottom of the Periodic Table (ie electropositive atoms) do not hold on to bonding electrons strongly; these atoms can give up their valence electrons; when bonding with other identical atoms (ie in the elemental form), the valence electrons will become delocalised and there will be an attraction between the lattice of cations and the delocalised electrons; this is known as **metallic bonding**; elements which contain atoms bonded together by metallic bonding are known as **metals**; metals have **giant metallic** structures

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- Atoms on the right-hand side and at the top of the Periodic Table (ie electronegative atoms) hold on to bonding electrons strongly; these atoms are not able to lose their valence electrons and will tend to gain or share electrons; when bonding with identical atoms (ie in elemental form) the valence electrons will become shared and **covalent bonds** will be formed; elements which contain atoms bonded together by covalent bonding are known as **non-metals**; non-metals can have **giant covalent** or **simple molecular** structures; noble gases form no bonds at all with each other and exist as free atoms; they are also classified as non-metals and their structure is described as **simple atomic**
- In some elements, the bonding between the atoms varies between covalent and metallic; sometimes metallic properties increase with temperature and in other cases the elements can have metallic and non-metallic allotropes; these elements have properties in between those of metals and non-metals and are known as **metalloids** or **semi-metals** (B, Si, Ge, As, Sb, Te)

Period	Group			
	13	14	15	16
2	B metalloid	C non-metal	N non-metal	N non-metal
3	Al metal	Si metalloid	P non-metal	P non-metal
4	Ga metal	Ge metalloid	As Metalloid	As non-metal
5	In metal	Sn metal	Sb Metalloid	Te metalloid
6	Tl metal	Pb metal	Bi Metal	Po metal

- All bonds except those between the same atoms have some ionic character and some covalent character; we describe them as “ionic” or “covalent” depending on which of these two extremes the bonding resembles more closely:
 - If all bonds are considered covalent, the ionic character of the bond can be estimated based on the difference in electronegativity between the two atoms; the greater the difference in electronegativity, the greater the ionic character in the bond
 - If all bonds are considered ionic, the covalent character the bond can be estimated based on the polarizing power of the cation and the polarizability of the anion; the more polarizing the cation and the more polarizable the anion, the greater the covalent character in the bond

Lesson 2 – Oxidation Numbers and the Inert Pair Effect

- The oxidation number of an atom depends on how many electrons it is able to gain, lose or share
- Taking electrons away requires energy, and the more electrons are removed, the more energy is required; however removing more electrons allows more covalent bonds to be formed and creates more highly charged ions which form stronger bonds, so there is an energy benefit to forming higher oxidation numbers
- The oxidation number adopted by an atom is the one which provides the best balance between the energy needed to remove electrons and the energy released when bonds are formed
- Metals can form cations; the maximum oxidation number represents the loss of all valence electrons (+3 for Group 13, +4 for Group 14, +5 for Group 15 and +6 for Group 16); in practice, however, cations with a charge of greater than +3 are very highly polarising and tend to form covalent bonds
- Non-metals in Groups 15 and 16 can form anions; the minimum oxidation number represents the gain of enough electrons to fill the outer shell (-3 for Group 15 and -2 for Group 16); atoms in Groups 13 and 14 do not form stable anions; they are highly polarisable and tend to form covalent bonds
- Most compounds of the elements in Groups 13 – 16 contain covalent bonds, due to the high polarising power of the cations and the polarizability of the anions; atoms in Groups 13 and 14 share up to 3 and 4 electrons respectively, resulting in maximum oxidation numbers of +3 and +4 respectively; atoms in Group 15 and Group 16 only have 3 and 2 unpaired electrons and this limits the maximum oxidation numbers to +3 and +2 respectively in Period 2 (N and O) (although N can increase its oxidation number to +5 by forming dative bonds)
- Atoms in Groups 15 and 16 other than N and O can increase their valency by promoting paired electrons from s and p orbitals into empty low energy d-orbitals; this requires energy but creates more unpaired electrons and so allows more covalent bonds to be formed; Group 15 atoms can exist in the +5 oxidation state by doing this, and Group 16 atoms can exist in the +4 and +6 oxidation states
- In general, it becomes easier to remove and promote electrons on descending the group; however the bonds formed are generally weaker so it is not always easy to predict which oxidation numbers will be the most stable; this requires a closer look at the trends in ionisation energies:

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- The following table shows some ionisation energies of the atoms of Group 13 – 16; the first column shows the energy needed to remove the p electrons; the second column shows the energy required to remove the s-electrons

13	1 st IE	2 nd IE + 3 rd IE	14	1 st IE + 2 nd IE	3 rd IE + 4 th IE
B	801	6087	C	3439	10844
Al	578	4562	Si	2366	7588
Ga	579	4942	Ge	2329	7713
In	558	4526	Sn	2121	6873
Tl	589	4849	Pb	2166	7165

15	1 st – 3 rd IE	4 th IE + 5 th IE	16	1 st IE - 4 th IE	5 th IE + 6 th IE
N	8836	16920	O	17472	24316
P	5827	11231	S	8176	15508
As	5481	10880	Se	10104	14473
Sb	4869	9663	Te	8967	12488
Bi	4779	9773			

Although there is a general decrease down a group, the change is small between Periods 3 and 6, showing that it does not in fact become significantly easier to remove electrons on descending the group; this is due to the fact that the d and f electrons do not provide as much shielding to the p-electrons as might be expected

The most important exception is that between Periods 5 and 6 in Groups 13, 14 and 15; in all three Groups, the energy required to remove the last two valence electrons (the s electrons) (in Tl, Pb and Bi) is anomalously high; this is due to the fact that the s-electrons are very poorly shielded by the 5d and 4f electrons, making them much harder to remove; as a result, the 6s electrons in Tl, Pb and Bi are generally not involved in bonding and the preferred oxidation numbers of these three atoms is +1, +2 and +3 respectively; this is known as the **inert pair effect**

- In is most stable in the +3 oxidation state; Indium (I) compounds are unstable and are good reducing agents
- Sn is most stable in the +4 oxidation state; Tin (II) compounds are unstable and are good reducing agents
- Sb is most stable in the +5 oxidation state; Antimony (III) compounds are unstable and are good reducing agents
- Tl is most stable in the +1 oxidation state; Thallium (III) compounds are unstable and are good oxidising agents
- Pb is most stable in the +2 oxidation state; Lead (IV) compounds are unstable and are good oxidising agents
- Bi is most stable in the +3 oxidation state; Bismuth (V) compounds are unstable and are good oxidising agents

Questions

1.	(a)	Explain why metallic character increases down Group 14
	(b)	Explain why sulphur can form tetravalent and hexavalent compounds but oxygen cannot
	(c)	Explain why tin (II) compounds are good reducing agents but lead (II) compounds are not

Lessons 3 and 4 – Group 13 Elements and their Compounds

(a) Structure and Bonding in B and Al

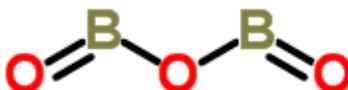
- Aluminium is a metal; the $3+$ ion and relatively small size of aluminium makes the metallic bonding relatively strong; aluminium has a relatively high melting point and is also fairly strong; aluminium has a low density compared to other metals of reasonable strength, as its RAM of 27.0 is relatively low
- Boron is a semimetal and exists in various different allotropes, most of which are based on layers of planar boron atoms similar to graphite; it is an unstable electron deficient structure and impurities tend to form within the layers; elemental boron is a good absorber of neutrons; boron-10 and boron-11 are both stable isotopes and boron-10 can absorb neutrons to become boron-11

(b) Structure and Bonding in Compounds of B and Al

- Boron forms covalent compounds; many of which are electron deficient
- Aluminium forms ionic (Al_2O_3 and AlF_3) and covalent (AlCl_3 , AlH_3) compounds; many of the covalent compounds are electron deficient

(i) Oxides

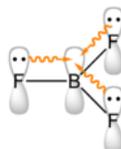
- Boron oxide B_2O_3 is a giant covalent oxide with a complex structure based on the molecular unit below:



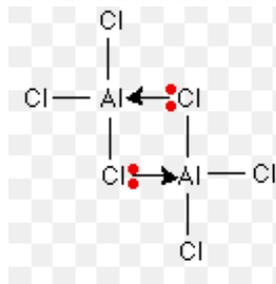
- Aluminium oxide Al_2O_3 is an ionic oxide

(ii) Halides

- BF_3 is a simple molecular electron deficient halide; the B-F bond is stronger and shorter than expected due to π -bonding between the lone pair on the F atom and the empty orbital in the B atom; this happens to a lesser extent in BCl_3 and BBr_3

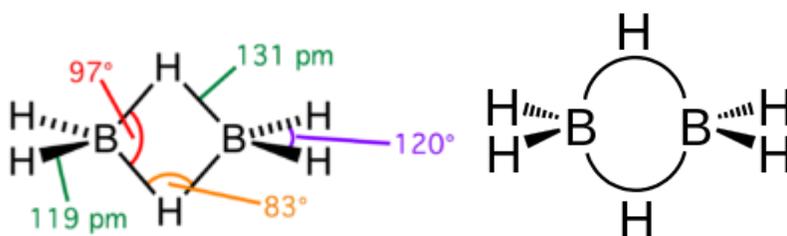


- AlF_3 is an ionic compound; AlCl_3 and AlBr_3 are simple molecular structures; AlCl_3 has a complex structure in the solid state but in the liquid and vapour states it exists as the dimer Al_2Cl_6 :



(iii) Hydrides

- Diborane B_2H_6 has a simple molecular dimeric structure which involves bridging H atoms in a 3-atom 2-electron system sometimes known as a “banana bond”



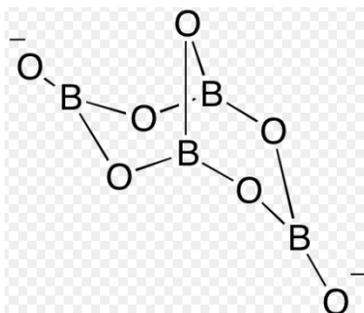
- Alane AlH_3 has a more complex polymeric structure, again involving bridging H atoms
- Both compounds are more stable when they have an extra H^- ion to form BH_4^- and AlH_4^- ; both of these species are important reducing agents in organic chemistry

(iv) Nitrides

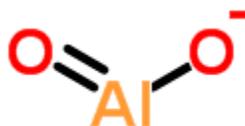
- Boron and aluminium both form stable nitrides (BN and AlN); BN has a layered giant covalent structure similar to graphite; AlN has a structure with some ionic and some covalent characteristics

(v) Oxoanions

- Both boron and aluminium form stable oxoanions and hydroxoanions known as borates and aluminates respectively
 - The simplest borate is BO_3^{3-} ; but the most stable borate is $B_4O_7^{2-}$; the compound $Na_2B_4O_7$ is known as borax and is very common



- Boron also form the stable acid boric acid (H_3BO_3)
- Aluminium tends to form hydroxoanions, the most stable of which is $Al(OH)_4^-$; but it also forms the stable aluminate AlO_2^-

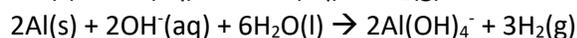
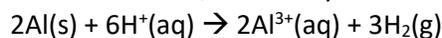


(c) Reaction of B and Al with non-metals

- Boron and aluminium reacts readily with oxygen and halogens
- Boron does not react directly with other elements; aluminium can react with nitrogen and hydrogen directly under certain conditions
- Diborane can be manufactured by the reaction of BCl₃ with LiH: $6\text{LiH} + 2\text{BCl}_3 \rightarrow \text{B}_2\text{H}_6 + 6\text{LiCl}$; AlH₃ is prepared by a similar method; excess LiH is more likely to produce NaBH₄ or LiAlH₄

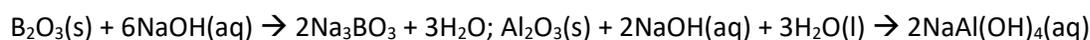
(d) Reaction of B and Al with acids, alkalis and water

- Both B and Al are oxidised in aqueous conditions; Al can form both cations and oxoanions so reacts with both acids and alkalis; B can only form oxoanions so reacts with alkalis only; neither react with pure water

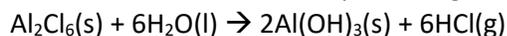


(e) Reactions of oxides, halides and hydrides of B and Al

- B₂O₃ is acidic and reacts with alkalis to form borates such as Na₃BO₃ and NaB₄O₇; Al₂O₃ is amphoteric and reacts with acids to form salts and with alkalis to form aluminates:

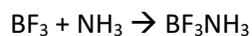


- All the halides of boron and aluminium except the ionic AlF₃ are readily hydrolysed, due to the availability of empty orbitals on the central atoms:



The ionic fluoride is likely to form the hydrated $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ ion when it is dissolved in water

- The covalent halides are also good Lewis acids and form dimers with Lewis bases such as NH₃:



- The hydrides of boron and aluminium, in particular LiAlH₄ and NaBH₄ are good reducing agents; the H⁻ ion is oxidised to H₂

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(f) Extraction of B and Al

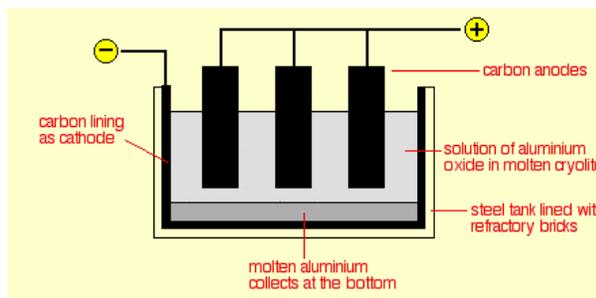
- The commercial extraction of aluminium from its main ore bauxite (Al_2O_3) is a hugely important industrial process:
 - Aluminium oxide is amphoteric so bauxite is dissolved in hot sodium hydroxide to remove impurities:

$$\text{Al}_2\text{O}_3(\text{s}) + 2\text{NaOH}(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \rightarrow 2\text{NaAl}(\text{OH})_4(\text{aq})$$
 - The sodium aluminate solution is cooled and seeded with $\text{Al}(\text{OH})_3$, under which conditions it precipitates:

$$\text{NaAl}(\text{OH})_4(\text{aq}) \rightarrow \text{Al}(\text{OH})_3(\text{s}) + \text{NaOH}(\text{aq})$$
 - The aluminium hydroxide is heated until it turns into the pure oxide:

$$2\text{Al}(\text{OH})_3(\text{s}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 3\text{H}_2\text{O}(\text{g})$$
 - The pure aluminium oxide is then electrolysed; it is dissolved in molten cryolite (Na_3AlF_6) in order to reduce the melting point and electrolysed at $900\text{ }^\circ\text{C}$ using graphite electrodes

$$2\text{Al}_2\text{O}_3(\text{cry}) \rightarrow 4\text{Al}(\text{l}) + 3\text{O}_2(\text{g})$$
 - The graphite anode reacts with oxygen under these conditions; as a result the anode needs to be regularly replaced



- Boron cannot be extracted electrolytically as it does not form ionic compounds; impure boron can be obtained by the reduction of boron oxide with Mg but the boron produced is contaminated with Mg_3B_2 ; pure boron is obtained by reacting BCl_3 with H_2 : $2\text{BCl}_3 + 3\text{H}_2 \rightarrow 2\text{B} + 6\text{HCl}$

Questions

1.	Describe the structure and bonding in the following species:	
	(a)	Boron fluoride
	(b)	Aluminium chloride
	(c)	Diborane
	(d)	Borax
2.	(a)	Write equations for the reactions of Al and Al_2O_3 with acids and alkalis
	(b)	Explain why BF_3 gives white fumes when added to water but AlF_3 does not
	(c)	Write an equation to show how B_2H_6 and NaBH_4 can be prepared in the laboratory
3.	(a)	Describe in detail how aluminium is extracted from its main ore, bauxite
	(b)	Explain why boron cannot be extracted in the same way and explain briefly how pure boron is prepared commercially.

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(g) Thallium and Its Compounds

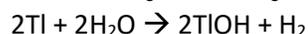
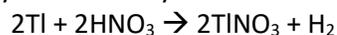
- The Chemistry of Thallium is dominated by the inert pair effect; its electronic configuration is $[\text{Xe}]4f^{14}5d^{10}6s^26p^1$, but the $6s^2$ electrons are not generally promoted or removed and the most stable oxidation number of thallium is +1:



Thallium (III) compounds exist but are very strong oxidising agents

(i) Thallium (I)

- The Tl^+ cation forms weak metallic bonds in the elemental state and thallium is a soft metal with a low melting point (300°C); the metal tarnishes in air to form a layer of Tl_2O and reacts slowly with water to form TlOH ; it can be stored under oil; the metal dissolves readily in sulphuric and nitric acids to form Tl_2SO_4 and TlNO_3 respectively but only reacts slowly with HCl due to the limited solubility of TlCl



- The hydroxides and carbonates of thallium (TlOH and Tl_2CO_3) show high thermal stability, typical of the alkali metals (Group 1); Tl_2O and TlOH are both basic; TlCl , TlBr and TlI are photosensitive (similar to AgCl and AgBr)

(ii) Thallium (III)

- Thallium (III) compounds are strongly oxidising and generally show low thermal stability: Tl_2O_3 decompose to give Tl_2O and O_2 ; TlCl_3 and TlBr_3 decompose to give TlX and X_2
- TlI_3 is a thallium (I) compound containing the triiodide ion (I_3^-)
- Tl_2O_3 and $\text{Tl}(\text{OH})_3$ are amphoteric; demonstrating that higher oxidation states generally have higher electronegativities
- TlH_3 does not exist due to the inability of the large Tl orbitals to overlap with the $1s$ orbitals on H

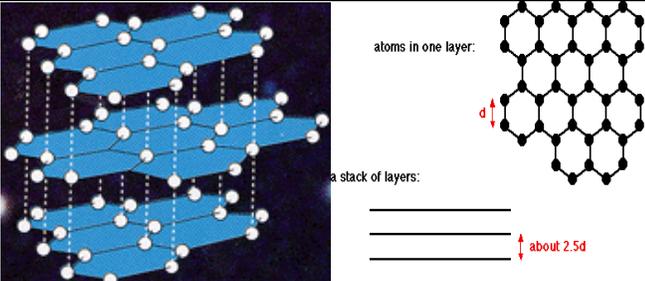
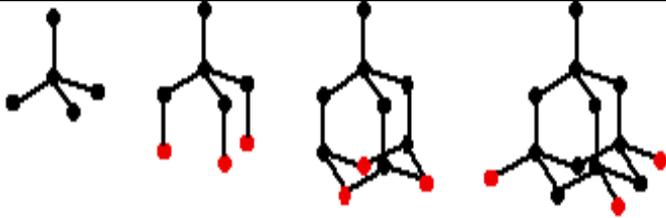
Questions

1.	Despite being in Group 13 of the Periodic Table, thallium shows many chemical properties characteristic of alkali metals. Explain why and give three examples.
2.	Explain, using examples, why thallium (III) compounds are strongly oxidising.
3.	Explain why Tl_2O is basic but Tl_2O_3 is amphoteric.
4.	Describe some similarities in the chemistry of thallium and silver.

Lesson 5 – Group 14: The Chemistry of Carbon and Silicon

(a) Structure and Bonding in Elements

- Carbon forms two stable allotropes; graphite and diamond

Graphite	Diamond
sp^2 hybridisation – trigonal planar (hexagonal)	sp^3 hybridisation – tetrahedral
2D giant covalent (layered) – Van der Waal's forces between layers	3D giant covalent
1 electron per atom delocalised due to multiple overlap of p-orbitals	No delocalised electrons
 <p>atoms in one layer:</p> <p>a stack of layers:</p> <p>↑ about 2.5d</p>	

- Graphite has a high melting point but is soft and a good conductor of electricity; it is used in pencils, electrodes and as a solid state lubricant; diamond has a high melting point but is hard and a poor conductor of electricity; it is used in jewellery and in drills

- Silicon has a structure similar to diamond; it does not form an allotrope similar to graphite as the p-orbital overlap is much less good

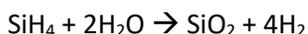
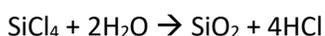
(b) Structure and Bonding in Compounds

- CO_2 has a simple molecular structure due to the ability of C and O to form strong π -bonds with each other; the C=O bond strength more than twice the C-O bond strength, which favours double bond formation
- SiO_2 has a giant covalent structure; the Si and O atoms cannot form strong π -bonds with each other and single bonds are preferred, leading to a tetrahedral giant covalent structure
- In limited oxygen, carbon can also form CO; this structure is unusually stable due to the strong π -bond formation between C and O; there is no equivalent oxide for silicon
- Both C and Si form stable oxoanions, CO_3^{2-} and SiO_3^{2-} ; CO_3^{2-} is stabilised by C=O bond formation; SiO_3^{2-} tends to form polymeric structures based on the tetrahedral SiO_4 unit commonly found in rocks
- Both form tetrahedral hydrides and halides (CH_4 , SiH_4 , CCl_4 , $SiCl_4$); in CH_4 the C is more electronegative than H but in SiH_4 the Si is more electropositive than H
- The C-C bond is the strongest single covalent bond between two identical atoms (other than H-H); as a result carbon has a much greater tendency to catenate (form chains) than any other atom, and this gives rise to the huge number of carbon-chain compounds generally classified as “organic compounds”

(c) Chemical Properties of the Elements and Compounds

- C and Si both react with oxygen and halogens to form the oxides and halides (CO_2 , SiO_2 , CCl_4 , SiCl_4)
- C and Si do not react directly with hydrogen; methane and silane are formed from carbides and silicides:
 $\text{Mg}_2\text{Si} + 4\text{HCl} \rightarrow \text{SiH}_4 + 2\text{MgCl}_2$
 $\text{Mg}_2\text{C} + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{MgO}$

- SiCl_4 and SiH_4 are much more reactive than CH_4 and SiCl_4 ; CCl_4 and CH_4 do not react with water at room temperature but SiCl_4 reacts violently and SiH_4 is also hydrolysed:



The main reason for the difference in reactivity of the halides and hydrides of carbon and silicon is the availability of empty 3d orbitals in silicon which can readily accept electron pairs from Lewis bases/nucleophiles; carbon does not have any low energy empty orbitals and therefore no bonds can be formed with C until the C-H or C-X bonds have been broken

Other reasons for the high reactivity of SiCl_4 and SiH_4 include:

- Si-X bonds are weaker than C-X bonds, due to the larger size of the Si atom
- Si is the more electropositive atom in SiH_4 and so attracts Lewis bases and nucleophiles; the C atom in CH_4 does not attract nucleophiles

(d) Extraction of carbon and silicon

- If high purity is not required, silicon is extracted by reacting SiO_2 with C: $\text{SiO}_2 + 2\text{C} \rightarrow \text{Si} + 2\text{CO}$; high purity silicon is produced by the thermal decomposition of SiHCl_3 : $2\text{SiHCl}_3 \rightarrow 2\text{Si} + 3\text{Cl}_2 + \text{H}_2$
- Graphite is found naturally; coke is the material most commonly used as a reducing agent; it is formed by heating coal in the absence of air

Questions

1.	Describe briefly the differences in the structures of diamond and graphite. Discuss the different properties of diamond and graphite and relate these differences to their different structures. Explain why silicon does not form an allotrope analogous to graphite.
2.	Describe the structures of SiO_2 and CO_2 and account for any differences. Explain why the physical properties of SiO_2 and CO_2 are so different. Explain why carbon forms a stable monoxide (CO) but silicon does not.
3.	Explain why carbon forms an infinite number of chain compounds but silicon only forms a few.
4.	Explain why SiCl_4 hydrolyses rapidly on exposure to water but CCl_4 does not.

Lesson 6 – Group 14: The Chemistry of Tin and Lead

(a) Properties of the elements

- Tin and lead are soft, malleable metals
- They can form compounds in the +2 and +4 oxidation state; the existence of the +2 oxidation state is due to the inert pair effect; in tin the +4 oxidation state is more stable than the +2 oxidation state, and the +2 oxidation state is therefore reducing; in lead the +2 oxidation state is more stable than the +4 oxidation state; the +4 oxidation state is therefore oxidising
- Tin and lead do not react with water but reacts with acids, alkalis, oxygen and halogens to form a variety of Sn (II) and Sn (IV) compounds:
 - tin and lead react with acids to form tin (II) and lead (II) compounds; $\text{Sn} + 2\text{H}^+ \rightarrow \text{Sn}^{2+} + \text{H}_2$
 - tin reacts with alkalis to form stannate (IV) compounds: $\text{Sn} + 2\text{NaOH} + 4\text{H}_2\text{O} \rightarrow \text{Na}_2\text{Sn}(\text{OH})_6 + 2\text{H}_2$
 - lead reacts with alkalis to form plumbate (II) compounds: $\text{Pb} + 2\text{NaOH} + 2\text{H}_2\text{O} \rightarrow \text{Na}_2\text{Pb}(\text{OH})_4 + \text{H}_2$
 - tin reacts with oxygen to form SnO_2 (although it forms a stable oxide layer) and with chlorine to form SnCl_4 ; lead reacts with oxygen to form PbO and with chlorine to form PbCl_2
 - the reaction of lead with chlorine, HCl and H_2SO_4 is limited by the low solubility of PbCl_2 and PbSO_4

(b) Properties of the compounds

- Tin (IV) oxide and lead (IV) oxide are amphoteric:
 - SnO_2 can react with acids to make tin (IV) salts: $\text{SnO}_2 + 4\text{H}^+ \rightarrow \text{Sn}^{4+} + 2\text{H}_2\text{O}$ (the Sn^{4+} ion is only stable in strongly acidic conditions)
 - PbO_2 also reacts with acids but to produce lead (II) salts and oxygen: $2\text{PbO}_2 + 4\text{H}^+ \rightarrow 2\text{Pb}^{2+} + 2\text{H}_2\text{O} + \text{O}_2$
 - SnO_2 and PbO_2 react with alkalis to make stannate (IV) and plumbate (IV) salts: $\text{SnO} + \text{H}_2\text{O} + 4\text{OH}^- \rightarrow \text{Sn}(\text{OH})_6^{2-}$
- SnF_4 is mainly ionic but all the other tin (IV) halides are covalent and hydrolysed in water; lead does not readily form lead (IV) halides; SnCl_2 is a useful reducing agent in organic chemistry; PbO_2 is a useful oxidising agent and can oxidise chloride ions to chlorine: $\text{PbO}_2 + 4\text{HCl} \rightarrow \text{PbCl}_2 + \text{Cl}_2 + 2\text{H}_2\text{O}$
- PbO_2 reacts with Pb in acidic conditions to produce PbSO_4 : $\text{PbO}_2 + 2\text{H}_2\text{SO}_4 + \text{Pb} \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$; this reaction is used in car batteries ($\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2\text{e}^-$, $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$)

(c) Extraction

- Tin is extracted by reducing its main ore SnO_2 with carbon
- Lead is extracted from its main ore PbS first by roasting it to give PbO : $2\text{PbS} + 3\text{O}_2 \rightarrow 2\text{PbO} + 2\text{SO}_2$; the PbO is then reduced to lead by reaction with carbon

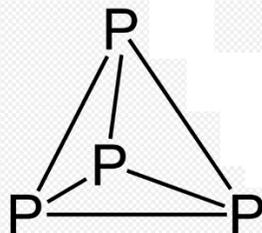
Questions

1.	Discuss the relative stability of the +2 and +4 oxidation states of lead and tin. Illustrate your answer with suitable equations.
2.	Write the half-equations for the reactions taking place in the lead-acid battery.

Lesson 7 – Group 15: The Chemistry of Nitrogen and Phosphorus

(a) Elements

- Nitrogen exists as the N_2 molecule with a triple bond between the N atoms; the p-orbital overlap is good and the triple bond is very strong ($N \equiv N$: 941 kJmol^{-1}); the N-N bond is 418 kJmol^{-1} and N-N bond only 163 kJmol^{-1}); the weakness of the N-N bond is due to repulsion between the p-electrons
- The P-P bond is stronger than the N-N bond, despite its greater length; however the P=P bond is much weaker than the N=N bond and P therefore forms single bonds only with itself, resulting in a number of allotropes:



white phosphorus (P_4) has a strained structure; red phosphorus has an amorphous polymeric structure and black phosphorus has a structure similar to graphite

(b) Oxides

- Oxides of nitrogen are unstable; many are radicals and/or stabilised by resonance:

- N_2O : stabilised by resonance: $N \equiv \overset{+}{N} - O^- \longleftrightarrow ^- N = \overset{+}{N} = O$
 produced by thermal decomposition of NH_4NO_3 : $NH_4NO_3 \rightarrow N_2O + H_2O$

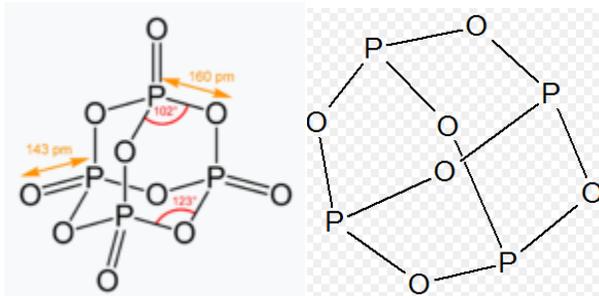
- NO : free radical, electron deficient, bond order 2.5, stabilised by resonance
 produced by oxidation of ammonia or by reduction of nitric acid:
 $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$; $3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$



- NO_2 : stabilised by resonance: $^- O - \overset{+}{N} = O \longleftrightarrow O = \overset{+}{N} - O^-$
 produced by oxidation of NO in air: $2NO + O_2 \rightarrow 2NO_2$
 coexists as dimer N_2O_4

- N_2O_5 ; produced by thermal dehydration of nitric acid: $2HNO_3 \rightarrow N_2O_5 + H_2O$

- P can react with air to produce either P_4O_6 or P_4O_{10} , depending on the amount of available oxygen and the temperature:



(c) Oxoacids and oxoanions

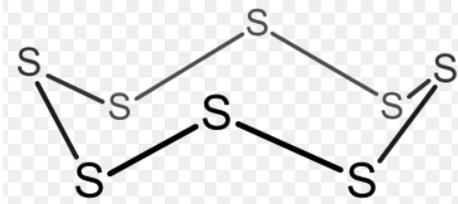
- N forms two stable acids: HNO_3 and HNO_2
 - HNO_3 is related to N_2O_5 : $\text{N}_2\text{O}_5 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_3$
it is a strong acid and forms stable NO_3^- ions
it is produced commercially in three stages: oxidation of ammonia; oxidation of NO and then oxidation of NO_2
 - HNO_2 is formed by acidifying NO_2^- salts; it is a weak acid
 NO_2^- salts are formed by thermal decomposition of KNO_3 or NaNO_3 : $2\text{NaNO}_3 \rightarrow 2\text{NaNO}_2 + \text{O}_2$
 - NO_2 disproportionates in water to form HNO_3 and HNO_2
- P forms two stable acids: H_3PO_4 and H_3PO_3 ; formed from their respective oxides:
 $\text{P}_4\text{O}_6 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_3$ $\text{P}_4\text{O}_{10} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{PO}_4$
 - H_3PO_4 is a weak tribasic acid used to make phosphate (V) salts
 - H_3PO_3 is a weak dibasic acid

(d) Other compounds

- Both form hydrides: phosphine (PH_3) and ammonia (NH_3)
- Nitrogen forms halides in the +3 and -3 oxidation state; phosphorus forms halides in the +3 and +5 oxidation state

Lesson 8 – Group 16: The Chemistry of Oxygen and Sulphur**(a) Elements**

- Oxygen exists as the O_2 molecule with a double bond between the O atoms; the p-orbital overlap is good and the double bond is very strong ($\text{O}=\text{O}$: 498 kJmol^{-1}); the O-O bond is 142 kJmol^{-1} ; the weakness of the O-O bond is due to repulsion between the p-electrons
- Oxygen can also form O_3 in the stratosphere
- The S-S bond is stronger than the O-O bond, despite its greater length; however the S=S bond is much weaker than the O=O bond; the strength of S-S means sulphur has a strong tendency to catenate and can form a number of allotropes; the most stable is S_8 :

**(b) Oxides**

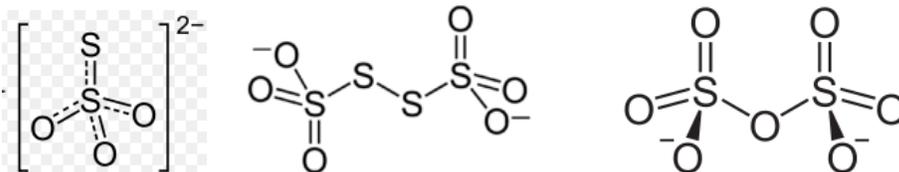
- S reacts with oxygen to form SO_2 : $\text{S} + \text{O}_2 \rightarrow \text{SO}_2$
 SO_2 reacts reversibly with oxygen to form SO_3 (Contact process): $2\text{SO}_2 + \text{O}_2 \rightarrow \text{SO}_3$
S does not form a stable oxide in the +2 oxidation state

(c) Oxoacids and oxoanions

- Sulphur's ability to catenate combined with its ability to form reasonably strong single and double bonds with oxygen means that a wide variety of oxoanions and acids are possible:
- SO_2 dissolves in water to form the weak acid sulphurous (IV) acid (H_2SO_3) and reacts with alkalis to form the sulphite (IV) ion SO_3^{2-} ; $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$; $\text{SO}_2 + 2\text{OH}^- \rightarrow \text{SO}_3^{2-}$
- SO_3 dissolves in water to form the strong acid sulphuric (VI) acid (H_2SO_4) and reacts with alkalis to form the sulphate (VI) ion SO_4^{2-} ; $\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$; $\text{SO}_3 + 2\text{OH}^- \rightarrow \text{SO}_4^{2-}$
 SO_3 dissolves in concentrated sulphuric acid to form the disulphuric acid $\text{H}_2\text{S}_2\text{O}_7$; this dissolves in water to give sulphuric acid: $\text{H}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4$; this reaction is less exothermic than the direct combination of SO_3 with water and is used in the commercial preparation of sulphuric acid; it can exist in anionic form as the disulphate ion $\text{S}_2\text{O}_7^{2-}$ ($2\text{KHSO}_4 \rightarrow \text{K}_2\text{S}_2\text{O}_7 + \text{H}_2\text{O}$)
- SO_3^{2-} is a reducing agent and is readily oxidised to SO_4^{2-} ; SO_4^{2-} ions are not oxidising in aqueous solution but concentrated H_2SO_4 is a good oxidising agent
- S disproportionates in alkali to form the $\text{S}_2\text{O}_3^{2-}$ (thiosulphate) ion; the same ion can be formed by heating SO_3^{2-} with S: $4\text{S} + 6\text{OH}^- \rightarrow 2\text{S}^{2-} + \text{S}_2\text{O}_3^{2-} + 3\text{H}_2\text{O}$; $\text{S} + \text{SO}_3^{2-} \rightarrow \text{S}_2\text{O}_3^{2-}$

Thiosulphate has the same structure as sulphate (VI), with one of the O atoms replaced with an S

- $\text{S}_2\text{O}_3^{2-}$ disproportionates in acidic conditions to produce S and SO_2 : $\text{S}_2\text{O}_3^{2-} + 2\text{H}^+ \rightarrow \text{S} + \text{SO}_2 + \text{H}_2\text{O}$
- $\text{S}_2\text{O}_3^{2-}$ can be oxidised by mild oxidising agents to tetrathionate $\text{S}_4\text{O}_6^{2-}$: $2\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2\text{e}^-$; this reaction is used in iodine-thiosulphate titrations:



- Oxidation of sulphate (VI) oxoanions can lead to peroxydisulphate compounds (eg $\text{S}_2\text{O}_8^{2-}$)

(e) Other compounds

- Both form hydrides: water (H_2O) and hydrogen sulphide (H_2S); H_2S is formed by the acidification of metal sulphides: $\text{eg CuS} + 2\text{H}^+ \rightarrow \text{H}_2\text{S} + \text{Cu}^{2+}$
- Sulphur forms chlorides in the +1 and +2 oxidation state (S_2Cl_2 and SCl_2) but it forms a hexafluoride (SF_6)

Lesson 9 – Groups 17 and 18: An Overview of the Chemistry of the Halogens and Noble Gases

- F-F bond (159 kJmol^{-1}) weaker than Cl-Cl (243 kJmol^{-1}) bond due to repulsion between lone pairs; first electron affinity of F lower than that of Cl for the same reason; however F has the highest electronegativity
- HF is a weak acid; the other acids are strong acids; this is due to the very high strength of the H-F bond
- All halogens except F can expand their octet and form oxoanions and oxoacids with oxidation numbers +1, +3, +5 and +7, eg HClO, HClO₂, HClO₃, HClO₄; the oxides are more complex with various radical oxides existing, eg ClO₂
- Inter-halogen compounds are often formed with the formula XY_n, where n = 1, 3, 5 or 7, and X is the less electronegative of the two halogens: n > 3 only when Y = F and n = 7 only in IF₇
- Helium, Neon, Argon and Krypton form no known stable compounds; Xe can expand its octet and form three stable fluorides: XeF₂, XeF₄, XeF₆ and some moderately stable oxides: XeO₂, XeO₃, XeO₄

CHEM 221 – INORGANIC CHEMISTRY IV

Questions

1.	Explain why the structures of elemental nitrogen and elemental phosphorus are so different.
2.	Draw the structures of four oxides of nitrogen. Explain why nitrogen forms so many oxides.
3.	Draw the structures of the two oxides of phosphorus. Explain why the oxides of phosphorus and nitrogen are so different, despite N and P being in the same group.
4.	Outline the main stages in the industrial preparation of nitric acid, indicating how the oxidation number of the nitrogen changes in each stage.
5.	Explain why nitrate (III) salts are reducing agents but nitrate (V) salts are oxidising agents. Write a half equation for the oxidation of a nitrate (III) ion and the reduction of a nitrate (V) ion.
6.	Explain why phosphorus can exist in the -3, +3 and +5 oxidation states. Other than the oxides, give two examples of phosphorus compounds in each oxidation state.
7.	Explain why the structures of elemental oxygen and elemental sulphur are so different.
8.	Explain why sulphur can form so many different oxoanions. Draw the structures of four different anions of sulphur, each with a different oxidation number, and state the oxidation number in each oxoanion.
9.	Outline the main stages in the industrial preparation of sulphuric acid, indicating how the oxidation number of the sulphur changes in each stage.
10.	Explain why sulphur can form compounds in the -2, +2, +4 and +6 oxidation states. Give the formula of the most stable hydride, chloride, oxide and fluoride of sulphur. Suggest why the H, O, Cl and F stabilise different oxidation numbers of S.
11.	Account for the +1, +3, +5 and +7 oxidation states shown by chlorine
12.	Explain the low bond dissociation enthalpy of fluorine
13.	Describe the structure and bonding in two compounds of xenon
14.	Explain why H-F is a much weaker acid in water than the other hydrogen halides.

Lesson 10 – The Chemistry of Hydrogen

- Hydrogen is the only atom in the Periodic Table which cannot conveniently be placed in a Group; it has one electron in its outer shell – suggesting it should be placed in Group 1 – it displays some but not all of the properties of the alkali metals; it is one electron short of a full outer shell – suggesting it could be placed in Group 17 – it displays some but not all of the properties of the halogens
- The position of He could also be questioned - two electrons in its outer shell could place it in Group 2 – however its physical and chemical properties closely resemble that of the other noble gases and do not resemble Group 2 at all – so it is reasonable to place it in Group 0
- Arguments for placing hydrogen in Group 1 of the Periodic Table include:
 - it has one electron in its outer shell
 - it can form a stable +1 ion (H^+) in aqueous solution
 - it cannot form any compounds with oxidation number greater than 1
 - it can behave as a reducing agent when it reacts with non-metals
 - it is less electropositive than lithium, so placing it above Li in the Periodic Table is consistent with the trend in reactivity and reducing properties of the alkali metals
- Arguments against placing hydrogen in Group 1 of the Periodic Table include:
 - it cannot form a stable +1 ion (H^+) other than in aqueous solution; all non-aqueous compounds of hydrogen are covalent
 - it is not a metal
- Arguments for placing hydrogen in Group 17 of the Periodic Table include:
 - It requires one electron for a full shell
 - it can form a stable -1 ion (H^-) in the solid state
 - it cannot form any compounds with oxidation number less than -1
 - it can behave as an oxidising agent when it reacts with metals
 - it is a diatomic gas
- Arguments against placing hydrogen in Group 17 of the Periodic Table include:
 - it cannot form a stable -1 ion (H^-) in aqueous solution; H^- reacts with water to produce hydroxide ions and hydrogen: $H^- + H_2O \rightarrow H_2 + OH^-$
 - it is less electronegative than fluorine, so placing it above F in the Periodic Table is inconsistent with the trend in reactivity and oxidising properties of the halogens
- Hydrogen is therefore usually placed on its own in the Periodic Table, in terms of its electronegativity it lies between B and C

Questions

1.	Suggest reasons for and against the inclusion of hydrogen as a main group element of the Periodic table
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