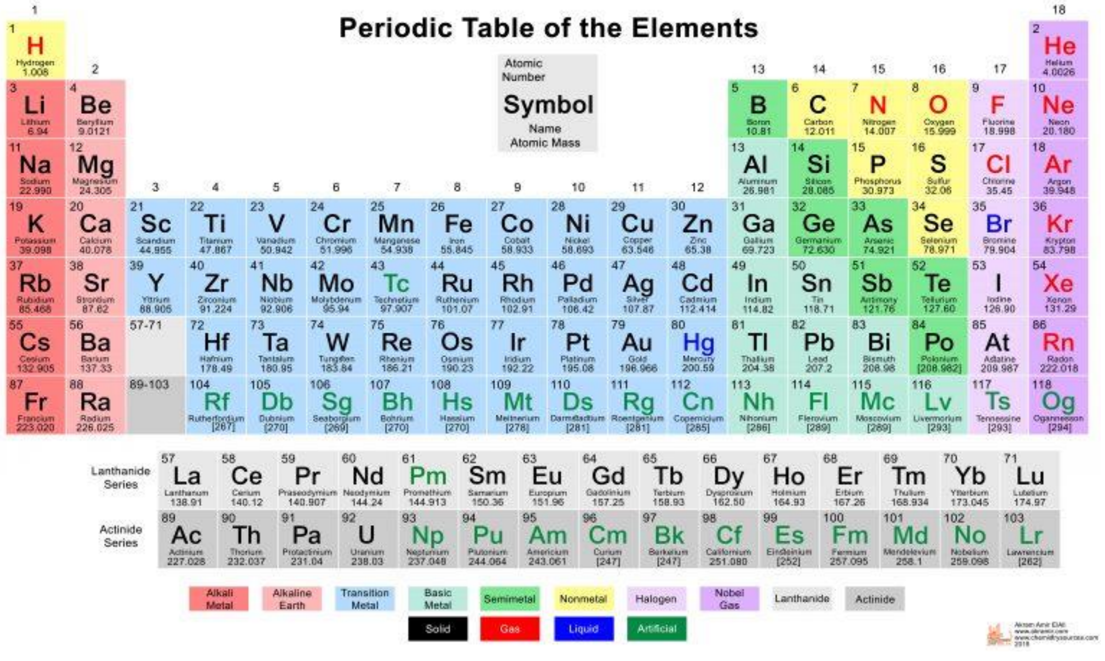
University of Baghdad
College of Science for Women
Department of Chemistry

Inorganic Chemistry

Second Year
Second Semester
2022-2023

Dr. Sahar Sabeeh Hassan



Periodic Table of the Elements

Atomic Number
Symbol
Name
Atomic Mass

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H Hydrogen 1.008																	2 He Helium 4.0026
3 Li Lithium 6.94	4 Be Beryllium 9.0121											5 B Boron 10.81	6 C Carbon 12.011	7 N Nitrogen 14.007	8 O Oxygen 15.999	9 F Fluorine 18.998	10 Ne Neon 20.180
11 Na Sodium 22.990	12 Mg Magnesium 24.305											13 Al Aluminum 26.981	14 Si Silicon 28.085	15 P Phosphorus 30.973	16 S Sulfur 32.06	17 Cl Chlorine 35.45	18 Ar Argon 39.948
19 K Potassium 39.098	20 Ca Calcium 40.078	21 Sc Scandium 44.955	22 Ti Titanium 47.867	23 V Vanadium 50.942	24 Cr Chromium 51.996	25 Mn Manganese 54.938	26 Fe Iron 55.845	27 Co Cobalt 58.933	28 Ni Nickel 58.693	29 Cu Copper 63.546	30 Zn Zinc 65.38	31 Ga Gallium 69.723	32 Ge Germanium 72.630	33 As Arsenic 74.921	34 Se Selenium 78.971	35 Br Bromine 79.904	36 Kr Krypton 83.798
37 Rb Rubidium 85.468	38 Sr Strontium 87.62	39 Y Yttrium 88.906	40 Zr Zirconium 91.224	41 Nb Niobium 92.906	42 Mo Molybdenum 95.94	43 Tc Technetium 97.907	44 Ru Ruthenium 101.07	45 Rh Rhodium 102.91	46 Pd Palladium 106.42	47 Ag Silver 107.87	48 Cd Cadmium 112.414	49 In Indium 114.82	50 Sn Tin 118.71	51 Sb Antimony 121.76	52 Te Tellurium 127.60	53 I Iodine 126.90	54 Xe Xenon 131.29
55 Cs Cesium 132.905	56 Ba Barium 137.33	57-71	72 Hf Hafnium 178.49	73 Ta Tantalum 180.95	74 W Tungsten 183.84	75 Re Rhenium 186.21	76 Os Osmium 190.23	77 Ir Iridium 192.22	78 Pt Platinum 195.08	79 Au Gold 196.966	80 Hg Mercury 200.59	81 Tl Thallium 204.38	82 Pb Lead 207.2	83 Bi Bismuth 208.98	84 Po Polonium [208.982]	85 At Astatine 209.987	86 Rn Radon 222.018
87 Fr Francium 223.020	88 Ra Radium 226.025	89-103	104 Rf Rutherfordium [267]	105 Db Dubnium [270]	106 Sg Seaborgium [269]	107 Bh Bohrium [270]	108 Hs Hassium [270]	109 Mt Meitnerium [278]	110 Ds Darmstadtium [281]	111 Rg Roentgenium [281]	112 Cn Copernicium [285]	113 Nh Nihonium [286]	114 Fl Flerovium [289]	115 Mc Moscovium [289]	116 Lv Livermorium [293]	117 Ts Tennessine [293]	118 Og Oganesson [294]

Lanthanide Series	57 La Lanthanum 138.91	58 Ce Cerium 140.12	59 Pr Praseodymium 140.907	60 Nd Neodymium 144.24	61 Pm Promethium 144.913	62 Sm Samarium 150.36	63 Eu Europium 151.96	64 Gd Gadolinium 157.25	65 Tb Terbium 158.93	66 Dy Dysprosium 162.50	67 Ho Holmium 164.93	68 Er Erbium 167.26	69 Tm Thulium 168.934	70 Yb Ytterbium 173.045	71 Lu Lutetium 174.97
Actinide Series	89 Ac Actinium 227.028	90 Th Thorium 232.037	91 Pa Protactinium 231.04	92 U Uranium 238.03	93 Np Neptunium 237.048	94 Pu Plutonium 244.064	95 Am Americium 243.061	96 Cm Curium [247]	97 Bk Berkelium [247]	98 Cf Californium 251.080	99 Es Einsteinium [252]	100 Fm Fermium 257.095	101 Md Mendelevium 258.1	102 No Nobelium 259.098	103 Lr Lawrencium [262]

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Course Structure:-

1- **Nitrogen & The (VA) Group Elements (1-4 weeks)**
2- **Oxygen& The (VIA) Group Elements (5-7 weeks)**
3- **Mid-term written exam (8)**
4- **Halogens (VIIA) Group (9-11 weeks)**
5- **solid state (12)**
6- **Noble Gases (13-14)**
7- **Written exam 2 (15)**

References :-

1- **Advance Inorganic Chemistry, Taro Saito, 2004.**
2- **Basic Inorganic Chemistry , F. A. Cotton, G. Wilkinson, P. L. Gaus, Third Edition.**
3- **Inorganic Chemistry , Shriver& Atkins, p. Atkins, T. Overton, J. Rourke, M. Weller, F. Armstrong, M. Hagerman Fifth Edition ,W. H. Freeman and Company New york, 2010.**
4- اساسيات الكيمياء غير العضوية ترجمة د. محمد ابراهيم غزالي و أ. حسني حسن يحيى قسم الكيمياء كلية العلوم – جامعة الملك سعود 2012.

Nitrogen & The (VB) Group Element

The electronic structure & the oxidation state

Element	Electronic state	Oxidation state
N	$[He]2S^2 2P^3$	-III,-II,-I,0,I,II,III,IV,V
P	$[Ne]3S^2 3P^3$	The most III , V
As	$[Ar]3d^{10}4S^2 4P^3$	Abundant III, V
Sb	$[Kr]4d^{10}5S^2 5p^3$	Stable III, V
Bi	$[Xe]4f^{14}5d^{10}6s^2 6p^3$	III, V

Why there arise negative oxidation state for N?
Because of the difference in the EN between H=2.1 & N=3.0.
Example :-NH_3 (N -III), N_2H_4 (-II), NH_2OH(-I) ,N_2 (0), N_2O (+I), NO (+II), HNO_2(+III), NO_2(+IV) & HNO_3(+V).

Nitrogen can fill the outer shell to be 8es by:

1.Gains 3es forming N^{3-} (Nitrides of alkaloids elements)

2.Forming single covalent. Bonds (e.g.NH_3) or multiple (e.g. N≡N).

3.Forming covalent. bonds with loosing e, e.g. $[NH_4]^+$.

4.Forming covalent. bonds with gaining e, e.g. NH_2^- amide.

There will be stable nitrogen compounds, the outer shell of nitrogen is incomplete (e.g.NO or NO_2) each N contains one unpaired e. They have paramagnetic properties.

Nitrogen forms multiple bonds differing from the other gr. elements, so it likes C & O. The bond (N-N) is weaker than that in (C-C) because of the repulsion of the non – bonding electrons on the Nitrogen atoms.

Abundance of Nitrogen in Nature :-

It forms 78% by volume of the air around the earth crust. Nitrogen separated by fractional distillation of the liquefied air (B.P. of N_2=-195.8˚C), it contains traces of Ar. It has two isotopes N^{14} & N^{15} ($N^{14}/ N^{15} = 272$)

$N_2 \longrightarrow 2N$ ΔH= 944KJ/ mole (High to break N≡N bonds)

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- The most important reactions of N_2 at room temperature is will Li forming lithium nitride, this reaction increases with increasing temp. specially in presence of catalyst
- N_2 Compounds:-

  -NH_3 -NO -Mg_3N_2

  $N_2 + 3H_2 \longrightarrow 2NH_3$

  $N_2 + O_2 \longrightarrow 2NO$

  $N_2 + 3Mg \longrightarrow Mg_3N_2$

Nitrides

Nitrides produce by the reaction of N_2 with another element in which N_2 is the more EN.

These compounds are three types:-

1- **Ionic:-**

e.g. Li_3N , nitrides of earth alkaloids .They produce by the direct reaction of the element and nitrogen , they have N^{-3} and hydrolyze by water forming Ammonia and hydroxide.

$Li_3N + 3H_2O \longrightarrow NH_3 + 3LiOH$

2- **Covalent**:-

Covalent nitrides like BN, AlN , which have high melting .points. and like carbon in their crystalline structure , can be formed. BN have two forms, like diamond in one form and like graphite in the other. Also there are volatile nitrides like S_4N.

3- **Transition Element Nitrides:-**

They are like their iodides and carbides. Mostly nitrogen takes place in the cavities produced because of the packing of the metal's atoms. These nitrides are non-stoichiometric, nitrogen ratio is less in these compounds. They conduct electron current, chemically inactive and their melting points are very high e.g. VN (m.p.2570˚c).

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Nitrogen and Hydrogen Compounds:-

1- Ammonia NH_3 (gas):-

The most one of these compounds, boils at -33.5˚c ,melts at -77˚c.

Preparation

a- **In Laboratory :-** From the reaction of ammonium salts with strong base:-

$\mathbf{NH_4X + OH^- \longrightarrow NH_3 + H_2O + X^-}$

b- **In Industry:-** A very important produce millions of tons. According to **Haber Bosch Method** by the direct reaction of N_2 and H_2 in presence of a catalyst and at high pressure (300 atm. Pres.) and temperature of 400- 550 ˚c:-

$N_2 + 3H_2 \longleftrightarrow 2NH_3$ $\Delta H = -45$ KJ/ mol, K25=103at m^{-1}

(N_2 from air, H_2 from water or hydrocarbons they are very cheap sources to produce NH3 for fertizers).

The structure of NH3 in pyramid  , nitrogen atom on the top while hydrogen atoms are at the corners of the triangle below nitrogen atom.

Properties of NH_3

1- Ammonia considered as a solvent like water (polar) also because of their self-ionization .

$2NH_3 \longleftrightarrow NH_4^+ + NH_2^-$ $K_{25} = 10^{-30}$

$2H_2O \longleftrightarrow H_3O^+ + OH^-$ $K_{25} = 10^{-14}$

acides bases

2- Ammonia strongly dissolves in water (727 l in one of H_2O at 15 ˚c), pH of the basic solution (10-11) .

$NH_3 + H_2O \longleftrightarrow NH_4^+ + OH^-$ (There are hydrogen bonds)

3- Ammonia burns with air giving N_2 and H_2O gases.

$4NH_3 + O_2 \longrightarrow 2N_2 + 6H_2O$

4- Ammonia can be oxidized by O_2, using Pt as catalyst giving nitrite oxide (used in HNO_3 industry)

$4NH_3 + 5O2 \longrightarrow 4NO + 6H_2O$

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Compounds of Ammonia

1- Ammonium Salts

They are like K and Rb salts in their solubility and crystal structure. This is due to their near values of the radii of Rb^+ , K^+ and NH_4^+ ions.

$NH4^+$ ion is a weak acid compared with H_3O^+. Its structure is Tetrahedral (sp3 hybridization).

Note:- Vigorous heating of these salts produces an explosion (that is why they used in explosives).

2- Hydrazine N_2H_4

Prepared by oxidation of NH_3 by hypochloric acid or sodium hypochlorite

$2NH_3 + OCl \longrightarrow H_2N - NH_2 + H_2O + Cl^-$

Enthalpy of formation Δ=50 KJ/ mol.

Hydrazine is stable (although its ΔH is +), liquid , colorless, melts at 1.8 ˚c and boils at 114˚c , behave as a base because it can accept one or two protons from acids producing two types of salts ($N_2H_5^+$ and $N_2H_6^{+2}$), but it is less basicity than NH_3. Salts that contain $N_2H_6^{+2}$ are stable in acidic medium only (hydrolysis).

$N_2H_6^{+2} + H_2O \longleftrightarrow N_2H_5^+ + H_3O^+$

Hydrazine used against corrosion in low concentration in electricity stations and as fuel for rockets because of the large energy produced through the burning.

$N_2H_4 + O_2 \longrightarrow N_2 + 2H_2O \qquad \Delta H = -622$ KJ/ mol

Hydrazine in structure like H_2O_2 ,the two NH_2 groups does not rotate around the bond they are fixed as gauche shape,

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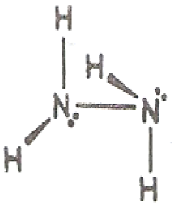


The relation between the chemistry of N_2H_4 and NH_3 is as that between H_2O and H_2O_2 .

Hydrazine behave as an oxidizing agent with strong reducing agent and as a reducing agent toward the strong oxidation agents, so it like H_2O_2.

3- Hydroxyamine NH_2OH:-

Prepared from reducing of nitrates or nitrides by SO_2. It is a solid , white substance, malting point 33 °c, unstable so that we find it as salts like $(NH_3OH)_2SO4$ and $(NH_3OH)Cl$.

Hydroxylamine less basic than ammonia.

$NH_2OH + H_2O \longleftrightarrow NH_3^+OH + OH^-$ K25= 6.6×10-9

It behaves as oxidation – reducing agent as hydrazine, but is used as a reducing agent.

4- Hydrazoic acid HN_3:-

Prepared by oxidation of hydrazine using a strong oxidizing agent like HNO_2 in an acidic medium :-

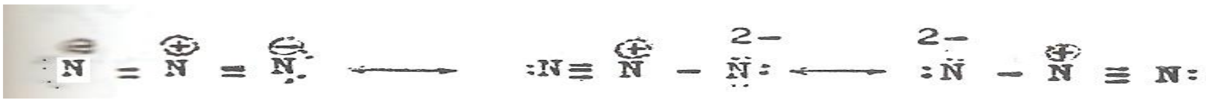
$N_2H_5+ + HNO_2 \longrightarrow HN_3 + H_3O^+ + H_2O$

HN3 is a colorless liquid, boils at 37°c , high explosed .Weak salts are called azides (Explosives).

$3NaNH_2 + NaNO_3 \longrightarrow NaN3 + 3NaOH + NH_3$

Sod.amide   azide

Ionic azides are relatively stable because of the resonance energy of the azide ion .



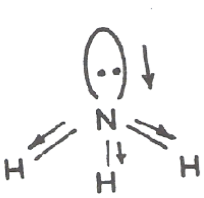
Nitrogen and Halogens Compounds:-

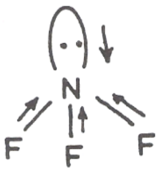
The most known pure compounds are :- NF_3 , N_2F_2, N_2F_4 and NCl_3. Compounds of Br_2 and I_2 with nitrogen are complexes , e.g. $NBr_3.6NH_3$, $NI_3.6NH_3$.

NF_3:- Prepared from F_2 with NH_3:-

$4NH_3 + 3F_3 \longrightarrow NF_3 + 3NH_4F$

It's a stable gas, colorless, odorless , m.p.-207˚c , b. p. -129˚c .It has the same structure as NH_3 , pyramid, but differs in many properties, it behave as Lewis base, having a dipol moment (D= 0.23) lower than that of NH_3 (D= 1.47) ,this is because of the direction of the dipoles of the three bonds in ammonia and NF_3 :-





D in the same direction D is in the opposite direction

(D of the non-bonding and of the bonding electrons)

NCl_3

$N_2 + 3Cl_2 \longrightarrow 2NCl_3$

It is a deep yellow oil (b. p. 71˚c), decomposes with explosion when contacts impurities O_2 by stirring or exposuring to UV light.

$2NCl_3 \longrightarrow N_2 + 3Cl_2$ $\Delta H = - 55$ Kcal/mol

Dissolve in the polar solvents, hydrolysis by water as :-

$NCl_3 + 3H_2O \longleftrightarrow NH_3 + 3HOCl$

Bromine and iodine complexes (with N_2) are unstable highly explosive materials.

Nitrogen Oxides:-

a- **Nitrous Oxide N_2O**

Prepared by thermal decomposition of NH_4NO_3 at 250-260˚c, N and O atoms are on the straight line

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$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2H_2O$

N_2O is relatively inactive at room temperature.

b- Nitric Oxide NO

Prepared by many methods, one of them by reduction of HNO_3 by Cu or reduction of nitrates by I_2:

$8HNO3 + 3Cu \longrightarrow 3Cu(NO_3)_2 + 4H_2O + 2NO$

$2NaNO_3 + 2NaI + 4H_2SO_4 \longrightarrow 2NO + 4NaHSO_4 + I_2 + 2H_2O$

1.NO simultaneously oxidized by O_2 to NO_2,also by strong oxidizing agents like KMO_4 forming HNO_3,

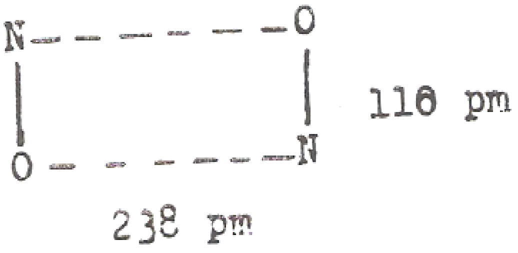
2.reduced in acidic medium to N_2O (SO_2 as a reducing agent) and gives NH_2OH if Cr^{2+} is used as a reducing agent

The paramagnet properties of NO can be explained according to (MOT) because of the un-paired electron in the π^* orbital against the antibonding electron .The outer 11 electron are distributed as the following :-

$\sigma 2S^2, \sigma^* 2S^2, \sigma 2S^2, \pi 2P^4, \pi^* 2P^1$

NO lose the π^* electron easily forming NO^+ ion which forms some salts e.g. $NO^+[BF_4]^-$and $NO[ClO_4]$.

NO molecules bonded together in the liquid and solid state by weak bonds forming dimers.



c- **Nitrogen Trioxide N_2O_3**

It presents only in the solid state, decomposes at its melting point (-110˚c) to NO and NO_2.

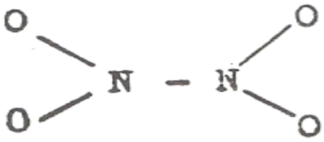
d- **NO_2 and N_2O_4 Oxide**

NO_2 is brown in color with paramagnetic properties, always in equilibrium with N_2O_4 (colorless with diamagnetic properties), this equilibrium effected by heat:-

$$2NO_2 \longleftrightarrow N_2O_4$$

The equilibrium can be shifted to the right hand side in the solid state, while shifted to the left hand side in the liquid and gas state.NO_2 increased in the mixture with increasing temperature exceeding 90% at 100˚c.

N2O4 has 3 isomers (structures) which are similar, the most stable one that contains the N-N bond:-



The structure of NO_2 is bent , The angle is 134˚ bigger than that of O_3 (117˚) of NO^-_2(116˚), the reason for that is the presence of an electron in SP^2 orbital (atomic nonbonding) of nitrogen, while such orbital contains 2e in O_3 and NO^-_2 cases.

It is well known that one electron occupies less space than that occupied by two electrons.

NO_2 and N_2O_4 formed by the thermal 1.decompostion of the metal nitrates O_2 by 2.oxidizing NO and also by 3. Reducing of HNO_3. They are toxic gases, react with water to give HNO_3 and HNO_2.

e- N_2O_5 Oxide

This one considered as a nitric acid anhydride, prepared by dehydration of HNO_3 by P_4O_{10}

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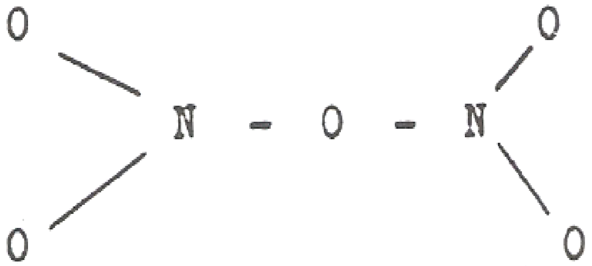
$4HNO_3 + P_4O_{10} \longrightarrow 4HPO_3 + 2N_2O_5$

Phosphorous pentaoxide

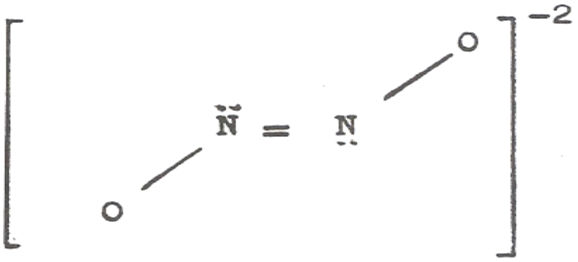
It is crystals (colorless, relatively unstable), hydrolyses in the solid stste to $NO_2^+NO_3^=$, while in the gas state it has a planar structure:-



Oxo Acid of Nitrogen

1- **Hyponitrous acid $H_2N_2O_2$**

It is a weak acid (pH≈7), unstable white crystals, decomposed to NM2O and water. It's salts are prepared by reduction of nitrites by sodium amalgam, the free acid is prepared by acidifying the silver hyponirite (difficulty dissolve in water), which is a reducing agent, the hyponitrite ion has a trans structure:-



2- **Nitrous acid HNO_2:-**

It is not known in it's free form, it's solutions prepared by the action of acids on nitrites or by dissolving N_2O_3 in water, it decomposes by heat in these solutions.

$3HNO_2 \longrightarrow HNO_3 + 2NO + H_2O$

HNO_2 is an oxidizing agent versus reducing agent, e.g. I^-, Fe^{2+} and $C_2O_4^{-2}$.

It is a reducing agent against some of the oxidizing agents.

$NO_3^- + 3H+ +2e \longrightarrow HNO_2 + H_2O \quad E^\circ = 0.94V.$

HNO_2 is used in organic chemistry to prepare diazonium salts and the nitrites derivatives are those in which NO_2 group is bonded through oxygen atom (RONO) white nitro derivatives are when NO_2 gr.is bonded through nitrogen atom.

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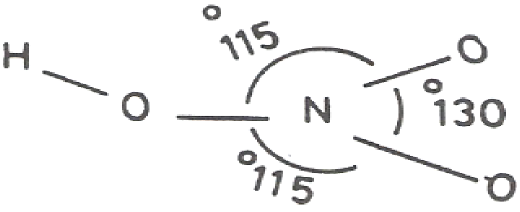
Also NO_2 bonded in the inorganic complexes by one of the two method before when it reacts as a ligand.

3- Nitric acid HNO_3

Liquid, colorless, m. p. -41.6˚c, b.p.83˚c.It is one of the most important acid, planar in structure



HNO_3 is prepared in industry by ammonia oxidation with O_2, using Pt as a catalyst. This reaction produces an intermediate compound. NO_2 or N_2O_4 which gives a mixture of HNO_2 and HNO_3 by dissolving in H_2O.

HNO_2 oxidizes by O_2 to HNO_3.

Pure nitric acid (without water) is prepared from the reaction of KNO_3 with concentration H_2SO_4 (100%) at 0˚c.It separated by vacuum distribution, it has a high degree of self-ionization

$$2HNO_3 \longleftrightarrow H_2NO_3^+ + NO_3^-$$

$$H2NO_3^+ \longleftrightarrow H_2O + NO_2^+$$

$$2HNO_3 \longleftrightarrow NO_2^+ + NO_3 + H_2O$$

HNO3 is completely ionized in water into NO_3^- and N_3O^+

It is an oxidizing agent, it's power increased with increased temperature. Metals are oxidized (except Ir, Rh, Pt and Au) by acid giving nitrates and H_2 .

Al , Fe and Cu react with HNO_3 forming a layer of oxide which protect them from reaction.

This behavior is important to carry and transform HNO_3 acid in containers manufacture of these element.

A mixture of HNO_3 and HCl by volume((3:1) can dissolve Au and Pt (this called aquaregia). The extra ability of oxidation of this mixture is belong to Cl2 and NOCl which form according to the equation:-

$$HNO_3 + 3HCl \longrightarrow NOCl + Cl_2 + 2H_2O$$

Nitrate ion has a planar structure, the ion (NO_3^-) is more stable than acid, because of the resonance energy:-

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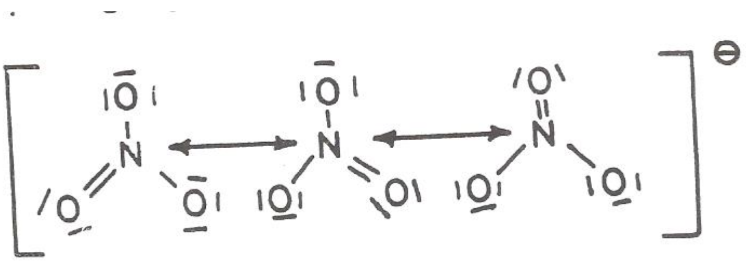


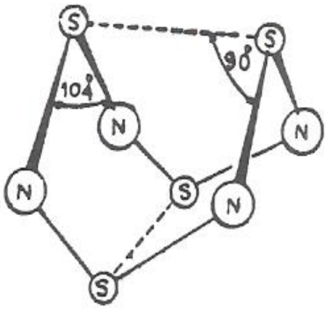
All metal nitrates dissolve in water, some of them can be produced (or prepared) without water of crystallization which sublimate by heating in vacuum, without decomposition , while at high temperature the alkaloid nitrates decompose into nitrite and O2, others form oxides and oxygen, e.g. :-

$2NaNO_3 \longrightarrow 2NaNO_2 + O_2$

$2Pb(NO_3)_2 \longrightarrow 2PbO + 4NO_2 + O_2$

Nitrogen and Sulfur Compounds:-

Nitrogen forms with sulfur a lot of nitrides, one of the most important (known) is S_4N_4 which can be prepared by the reaction of SCl_2 or S_2Cl_2 with NH_3.S_4N_4 is orang crystal, melts at 187˚c, exploses by knocking. Its structure is like a cage:-



The nonbonding electrons on N_2 form Pπ-dπ bonds with d orbitals of sulfur atoms (the vacant orbitals).

P, As, Sb and Bi:-

Properties:-

There are big differences between the chemistry of nitrogen and these elements in spite of the same electronic configuration of the outer shell they have .The reason of that is ,the 1.nitrogen atom does not have d orbitals while the above elements have d orbitals, also 2. the max. coordination no. of nitrogen is (4) while others can use vacant

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d orbitals to form bonds which increase the number of electrons in their valance shells. Nitrogen can form double and triple bonds type (p-p).

Table giving the properties of the VB group elements which change systematically from P to Bi, some properties change in a disorder system like the tendency of some penta oxides to react as oxidizing agents.

Element	Atomic No.	Atomic Wight	Boiling point	Atomic radii (pm)	EV	EN
N	7	14	-195.8	74	14.5	3.0
P	15	31	280.5	110	11.0	2.1
As	33	75	610	121	10.0	2.0
Sb	51	121.75	1380	141	8.64	1.8
Bi	83	209	1450	152	8	--

Phosphorous likes nitrogen (to be covalent character) in its compounds, while others like to form ionic compounds (increasing) from As to Bi, e.g. BiF3 is ionic.

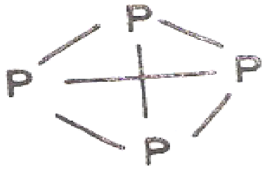
Acidic and basic properties change for the group V. elements (specially oxides) from acidic for P to basic for Bi. Oxidation state of these elements are trivalent or pentavalent, the stability of the trivalent oxidation state increases from P to As, Bi (III) is stable, but Bi_2O_5 (Bi V) is difficult to prepare and is the least stable oxide in this group.

Occurance in Nature:-

P is present as phosphate in many minerals like Apatite $Ca_5(PO_4)$ (Cl, OH, F), As, Sb and Bi are rarely present in their elemental from mostly they present as sulfides.

a- **Phosphorous:-**

Prepared by reduction of phosphate rocks by coke and silica in an electrical furnaces, it evaporate as P_4 molecules, condensed under water forming white phosphorous:



(P4 molecule)

$$2Ca_3(PO_4)_2 + 6SiO_2 + 10C \longrightarrow P_4 + 6CaSiO_3 + 10CO$$

Phosphorous has three allotropic forms ,white ,red and black, each form has many shapes (at least 11 shapes). White phosphorous presents in the liquid and

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solid states (P_4), it's structure is tetrahedral, the distance P-P is equal to 221 pm and the P-P-P angle is 60°.

The total energy of the P_4 bonds (6 bonds) is less than the total energy of six (P-P) bonds have the same length of the bond (P-P) in P_4, so that the bonds of P_4 molecule are weak and easy to break, which explain the activity of white phosphorus.

Black phosphorous has double layers (coupled) in which each P atom bonded to other three atoms. It can be prepared in its crystalline form by heating the white phosphorous under high pressure at 220-370 °c, in presence of Hg as catalyst.

Red phosphorous produced from heating the white type for many hours at 400°c. The activity of phosphorous depends on its form, the white is more active it burns when exposes to air so it must kept under water, white the black and red phosphorous are stable in air, the black one is the less stable.

b- **As, Sb and Bi:-**

We can prepare them by reduction of their oxides using carbon or hydrogen , a yellow form for As and Sb can be produced as As_4 and Sb_4 by fast condensation of the vapors, the yellow form can be converted to the stable state, for Sb at -90°c, which is bright and gaseous appearance.

As, Sb and Bi are used with many metals to manufacture alloys, e.g. Sb(20%) with Pb form the alloy of typing letters, Bi with Pb and Sn form low melting point alloys.

Compounds:-

1- **Hydrides:-**

All the group V elements form hydrides (MH_3), each one prepared from the reaction of MCl_3 and the metal hydride (to be wanted):-

$$4PCl_3 + 3LiAlH_4 \longrightarrow 4PH_3 + 3LiCl + 3AlCl_3$$

Phosphine and Arsine are prepared by the reaction of phosphides and arsenides of the metals with acids. SbH_3 and BiH_3 are unstable with temperature. Generally the stability of hydrides decrease of the bond energy in the same direction.

E N-H= 391, E P-H=322, E As-H =247, E Sb-H=255 KJ/ mol

2-**Phosphine PH_3:-**

The pH_3 structure is pyramid, the HPH angle in 93.7° less than HNH in NH_3 and close to the angle formed because of the overlapping of P-orbitals of

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phosphorous with S-orbital of hydrogen (90˚) without hybridization of SP_3 for P. So that the non-bonding two electrons in phosphorous atom has the S character and they are distributed in a spherical shape around the nucleus of this atom (P), which retard the contribution of phosphine by these electrons to behave as a Lewis base on the contrary of NH_3 in which the HNH angle (107˚) and the nitrogen atom is hybridized (SP^3) and the nonbonding pair of electrons is present in the hybridized SP^3 orbital which directed from nitrogen to one corner of the tetrahedral shape of NH_3, that make it easy for NH_3 to give (donate) these electron to be a strong Lewis base.

The tendency of the hydrides as Lewis bases decreases decrease from

N ⟶ Bi. Phosphonium salts can be prepared by reaction of phosphine with strong acids,

$PH_3 + HI \longrightarrow PH^+{}_4I^-$

$PH_4^+ + H_2O \longrightarrow PH_3 + H_3O^+$

Arsine AsH_3

Very toxic compound, easily hydrolyse by heat to its components, As precipitated as a mirror, this character is used to detect As, this test is called Marsh test. Stibine SbH_3 likes arsine AsH3 but it is less stable. All hydrides are reducing agents (strong), burn when contact air forming oxides.

Halides

Group V elements form two types of halides, trihalides (MX_3) and penta (MX_5).

a- MX_3

MX_3 of P, As, Sb and Bi (except PF_3) are prepared from halogens with enough (or excess) quantity of the metals while PF_3 is prepared by the reaction of ZnF_2 with PCl_3.

$2PCl_3 + 3Zn\ F_2 \longrightarrow 2PF_3 + 3ZnCl_2$

Trihalides are mostly covalent from which one can conclude that they have relatively low boiling and melting points. The ionic character of these halides increase from P to Bi and for the central atom from I to F.

Salts	Milting point.	Boiling Point.	Color	Salts	Milting point.	Boiling Point.	Color
PF_3	-151.5	-101.15	colorless	AsI_3	141	400	Red
PCl_3	-111.8	74	colorless	SbF_3	290	319	colorless
PBr_3	-40	175	colorless	SbI_3	170	410	red
PI_3	81	----	Red	$BiBr_3$	218	453	----
AsF_3	-5.95	63	colorless	BiI_3	440	500	violet red

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MX_3 molecule have a pyramide structure in the gas state, hydrolyse easly in water to give HX and $M(OH)_3$:- e.g.

$$PCl_3 + 3H_2O \longrightarrow P(OH)_3 + 3HCl$$

SbX_3 and BiX_3 in water form SbO^+ and BiO^+ ions. SbF3 and AsF3 are used as fluorinating agents (Source of Flurine).

b- MX_5 pentahalides

The well-known are PF_5, AsF_5, SbF_5, BiF_5, PCl_5, PBr_5 and $SbCl_5$.

PCl_5 in the gas state have triganal bipyramide structure while the solid is composed of $[PCl_4]^+$ $[PCl_6]^-$ ions by transforming Cl ion in PCl_5 molecules to another molecule.

PBr_5:- In the solid state is of $PB_4{}^+Br^-$ structure PCl_5 liquid, yellow in color (milting point 6˚c, boiling point 79˚c), SbF_5 and $SbCl_5$ are strong Lewis acids.

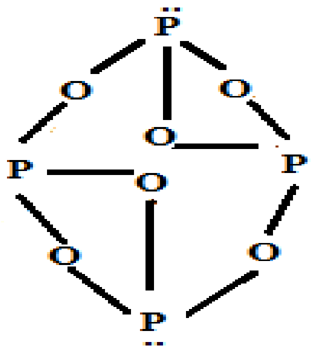
Oxides:-

The group V elements have two types of oxides, tri and pentvalent oxides (+3 and +5), their basic properties increase with increasing the atomic no. P and As oxides are acidic, Sb oxides are amphoteric, while Bi oxides are basic.

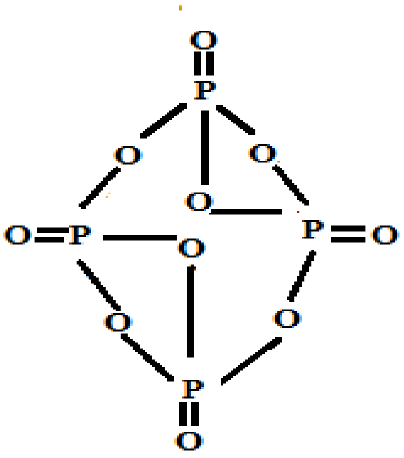
a- Phosphorous oxides:-

They are prepared from the reaction of phosphorous vigorously with O_2, their formation depends on the O_2 quantity and P reacted. Increasing O_2 give P_2O_5 while increasing P gives P_2O_3.

Phosphorous atoms in P_4O_{10} are occupying the corners of the tetrahedral shape while 6 oxygen atoms are at the sides (edges) of the tetrahedral, the other 4 oxygen atoms are bonded to P atoms along with the three axis. The 12 formed bonds between oxygen and phosphorous atoms are single ones, some others are double as in the structures:-



P_4O_6



P_4O_{10}

These bonds are produced from the overlapping of (Pπ-dπ) between the nonbonding electrons of oxygen with the vacant d orbitals of phosphorous atoms. P_2O_3 structure (P_4O_6 is one of its forms) likes the structure of P_4O_{10} except the presence of the other 4 oxygen atoms.

P2O5 is strong absorb water due to the tendency of p- atom to accept electrons (in P_4O_{10}), electrophilic.

According to that, the P_2O_5 is used in drying of gases and organic compounds which do not react with it, also it does not absorb water from most of the anhydrous oxo acids and convert them to anhydrides.

P_2O_5 converts HNO3 to N_2O_5 and H_2SO_4 to SO_3. P_4O_{10} dissolve in water forming phosphoric acid:-

$P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

P_2O_3 (or P_4O_6) trioxide forms phosphorous acid with water:-

$P_4O_6 + 6H_2O \longrightarrow 4P(OH)_3 \longleftrightarrow H_3PO_4$

b- **Oxides of As, Sb and Bi**

- As_4O_6 produced from burning of As in oxygen (air) it's structure like P_4O_6, dissolves in many organic solvent and water forming Arsenous acid. As_2O_5 (pentaoxide) produced not from the direct reaction of As with O2, but by oxidation of As by HNO_3, then dehydration of Arsenic acid produced.

  $As_4O_{10} + 6H_2O \longrightarrow 4H_3AsO_4$ (dissolving the oxide in water)
- Antimony trioxide Sb_2O_3 :-Prepared from the reaction of Sb and O_2. The structure of Sb_4O_6 likes P_4O_6 and As_4O_6 does not dissowe in water dissolves in HCl acid and in bases forming antimonates solutions

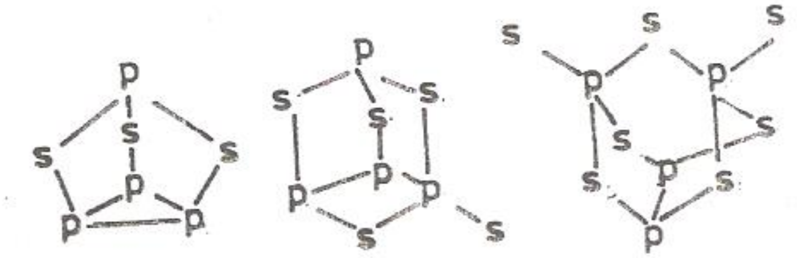
- Sb_2O_5 prepared from Sb+HNO_3 reaction, losing O_2 to give Sb_2O_3 (trioxide)
- The only known oxide for Bi is Bi_2O_3 which is a yellow powder, dissolves in acids forming Bi salts $Bi(OH)_3$ precipitated from Bi-salt solution by adding (-OH). This oxide behaves as a base is its reactions.

Sulfides:-

- Phosphorous can combine with sulfur if a mixture of them heated over 100^oc giving many phosphorous sulfides depending on the ratio of P and S, e.g.:- P_4S_3, P_4S_5, P_4S_7, P_4S_{10} which are covalent compounds, yellow in color, can be melted and distilled with decomposition.

  P_4S_3 is used in match manufacturing, dissolves in organic solvents like benzene and CS_2. P_4S_{10} likes P_4O_{10} in structure.

  Some sulfides structures:-



Phosphorous sulfides burn in air giving P_4O_{10} and SO_2, hydrolyses in water to give oxo acids and H_2S.

- Arsenic when melt with sulfur form As_4S_3, As_4S_4, As_2S_3 and As_2S_2. Arsenic sulfides do not hydrolyses in water to H_2S and oxo compounds.
- Antimony with sulfur form compounds of the general formula (Sb_2S_3) and (Sb_2S_5) which have a polymeric structure, prepared from (1) direct reaction of Sb with S or (2) reaction of H_2S with antimonates and antimonites BiS_3 (deep brown) produced from Bi (III) with H_2S.

Oxohalides:-

Phosphorous oxides POX_3 (X= F, Cl or Br) are the most important oxohalides of the group V elements. POCl3 prepared from

1- PCl_3 and oxygen reaction or by

$$2PCl_3 + O_2 \longrightarrow 2POCl_3$$

2- PCl_5 and P_4O_{10} reaction

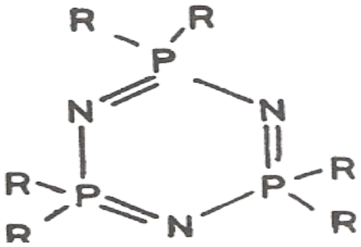
$$6PCl_5 + P_4O_{10} \longrightarrow 10POCl_3$$

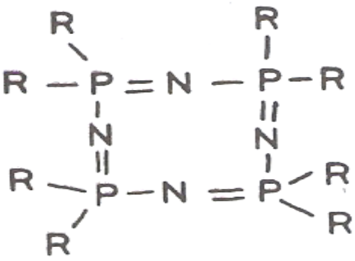
POX_3 has a distorted tetrahydral structure, P atom in the center and the O and the 3X atoms are at the corners. Also X_3PS compounds are known .

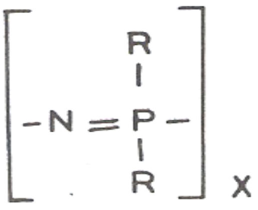
Compounds of P and N

Phosphor does not react directly with nitrogen, but oxides and sulfides react with ammonia at high temperature to form P_3N_5, P_2N_3 and PN which have a polymeric structure. A lot of compounds containing N-P bonds are known, two types of these bonds, P-N and P=N are known. Phosphazenes are important compounds. of (N and P) which are cyclic or chain compounds. They are 3parts:

1- Cyclic trimer compounds.
2- Cyclic tetramer compounds.
3- Oligmer and high polymer.







Bonds between (P and N) in phosphasines are equal in length and their bond order is 1.5, but they are mostly represented as P-N or P=N.

Organic Derivatives

There are a large number of organic derivatives of the group V elements which can be prepared in many methods, the simpler one is the reaction of halide or oxohalide of the element with Grignard reagent. Compound of the R_3MO types are stable, while R_3M types are easily oxidize. e.g. Me_3P burns when exposed to air oxygen.

R_3M (R=alkyl or phenyl, M=P As or Sb) form complexes with transition elements in which the atom (M) donates its nonbonding electron pair, while the (d) orbital in the valance shell of this atom (which is vacant) will accept electrons from the transition element. This type of ligand called (π-acid ligand), also R_3M form salts when react with alkyl or aryl halide –RX:

$$R_3M + R^{-}X^{-} \longrightarrow [R_3MR^{-}]^{+}X^{-}$$

These salts are called according to M atom, e. g. $(C_6H_5)_4\,As^+\,Cl^-$ compound. is called , tetraphenyl arsenium chloride.

Antimony only forms R_5M compounds of (t bp), aryl compounds are more stable than alky compounds. Antimony has derivatives of R_4Sbx, R_3Sbx_2 , where X=OH, OR or X or NO_3^- or ClO_4^- etc.

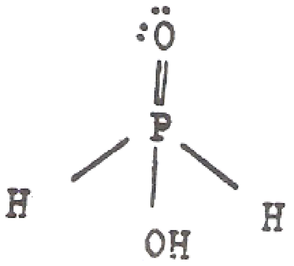
Oxo acids:

Phosphorous oxo acids :

a- Hypophosphorous acid:

$Ba(H_2PO_2)_2+H_2SO_4 \longrightarrow 2H[H_2PO_2]+Baso_4$

It is a colorless crystals , m. p. $26.5c^o$, the structure is:

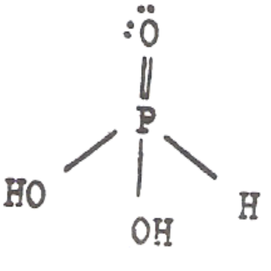


monobasic acid (can lose H^+ to give $[H_2PO_2]$ ion)

as referred to it by (nmr) spectrum

b- **Phosphorous acid H_3PO_3**

Is prepared from PCl_3 or P_4O_6 reaction with cold water. The pure acid melts at $70C^o$ (PK_a=1.8) it's structure is:



dibasic acid (can lose two H^+ to form $[HPO_3]^{-2}$ ion)

This acid and its salts are strong reducing agents.

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C-Phosphoric acid H_3PO_4

The most of the phosphorous compounds, prepared from H_2SO_4 with phosphate rocks or from P_4O_{1O} with water reaction. This acid is tribasic, has three types of salts, M_3PO_4, M_2HPO_4 and MH_2PO_4. The free acid is solids, melts at 42.35 C°.

d-Pyrophosphoric acid $H_4P_2O_7$

produced as:

$H_3PO_4 + H_3PO_4 \longrightarrow H_4P_2O_7 + H_2O$ (m.61C°)

Two molecules of phosphoric acid .

Phosphates:

A proximately all the metal elements have phosphates which used as fertilizers, e.g. Ammonium phosphate.

Other phosphate type is the condensed which are of three types:

1- Linear poly phosphate (e.g. $M_4P_2O_7$) (PnO_{3n+1})
2- Cyclic poly phosphate $(P_nO_{3n})^n$-,e.g. Trimeta phosphate $M_3P_3O_9$ and $M_4P_4O_{12}$ tetra…
3- Long chain metaphosphate , e.g. KPO_3.

Oxo acids of As, Sb and Bi

Examples:

$As(OH)_3$ Arsenous acid.

H_3AsO_4 Arsenic acid.

H_7SbO_6 Antimonic acid (not know as free , but in solution).

Antimony salts are called Antimonite and Antimonate.

Bismothate are not known as pure but by the reaction of Cl_2 $Bi(OH)_2$ in strong basic solutions or by heating of Na_2O_2 with Bi_2O_2 to give $NaBiO_3$.

Bismothates are strong oxidizing agents.

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Oxygen

These elements have six electrons in the outer shell, e. g. :-

$_8O$: $1S^2$ $2S^2$ $2P^4$

Oxygen forms compounds with all elements, except He , Ne , and may be Ar. It combines directly with other elements, except halogens and some nobel gases, this takes place either at normal temperatures or high.

Oxygen is the more found element, forms 50% by weight of the earth crust e.g. in water and silica which are the main components of earth .

Oxygen is one of the second period, the outer shell saturated by 8 electrons by one of the following methods:

1. Gaining 2 es forming oxide ion (O^{2-}).
2. Forming two single covalent bonds as in (R-O-R) or double bond as in (O=C=O).
3. Gaining electron in addition to form single covalent bond (OH^-).
4. Forming 3 or 4 covalent bonds as in ($R_2^-OH^+$).

Oxides:

The oxygen di compounds are called oxides, differ in their properties due to the nature of the bond bonding oxygen with other element, some of the compounds are ionic and covalent , others are between ionic and covalent properties.

Oxide ion formation from the molecular oxygen needs a lot energy u 1000KJ/mole.

$1/2\ O_2 \longrightarrow O_{(g)}$ $\Delta H=248$ KJ/mol.

$O_{(g)} \xrightarrow{+2e} O^{2-}{}_{(g)}$ $\Delta H=752$ KJ/mol.

Also the formation of ionic oxides need another quantity of ene. to atomize the element atoms. A large no. of the ion oxides are stable in a high degree , this is because of the net ene. value of these compounds. and to the small size of ion $(oxide)^{-2}$, so for this reason the bond is covalent as in BeO and B_2O_3, also compounds. of C, N, P and S with oxygen are molecular. compounds.

Hydroxide ion:

It can be prepared in the aqueous solutions of oxides and peroxides of metals of high electropositive because of the hydrolysis reactions :

$O_{(s)}^{2-} + H_2O \longrightarrow 2\,^{-}OHaq. \qquad K > 10^{22}$

$O_2^{2-} + H_2O \longrightarrow HO_2^{-} + OH^{-}$

$2O_2 + H_2O \longrightarrow O_2 + HO^{-}_2 + OH^{-}.$

In the solid state hydroxide ion presents as a separated unit in the metal and alkaloid earth hydroxides, produced from the solvation of these ionic hydroxides in water (aquation).

$M^{+-}OH_{(s)} + nH_2O \longrightarrow M^{+}_{(aq)} + H_3O^{+}(aq).$

These materials are strong bases , while when the M-O bond is covalent, so the dissociation takes place in different degrees as:

$MOH + nH_2O \longleftrightarrow MO^{-}_{(aq)} + H_3O^{+}(aq)$

So that water is on acid, while hydroxide is amphoteric when the above dissociation probability is occur.

When a strong acid is present, dissociation of ^{-}OH is:

$M\text{-}O\text{-}H + H^{+} \longleftrightarrow M^{+} + H_2O$, when base ,

$M\text{-}OH + {}^{-}OH \longleftrightarrow MO^{-} + H_2O$

The formation of H_2O from H^{+} and ^{-}OH is being complete.

$H^{+} + {}^{-}OH \longleftrightarrow H_2O \qquad K_{15^{o}} = 10^{14}$

Hydroxide ion has the ability to form bridges between the metal atoms e. g. : Ferric ion :-

$[Fe(H_2O)_6]^{+3} \longrightarrow [Fe(H_2O)OH]^{+2} \longrightarrow [(H_2O)_4Fe(OH)_2Fe\,(H_2O)_4]^{+4}$

$pH < 0 \qquad\qquad 0 < pH < 2 \qquad\qquad \sim 2 < pH < \sim 3$

$\xrightarrow{+XH^{+}}$ colloidal $Fe_2O_3.XH_2O \xrightarrow{-yH^{+}} Fe_2O_3.ZH_2O$ (ppt)

$\sim 3 < pH < \sim 5 \qquad\qquad pH \sim 5$

Stereochemistry of Oxygen and Structures

There present 4 orbitals in the covalency layer of oxygen, so it has 2,3 and 4 (as max) coordination number.

a- The Coordination no.

Most of oxygen compounds contain oxygen atom bonded by two covalent bonds, so two lone pairs of electrons are left in the covalence shell, e.g. H_2O, ROH, R-OR and most of the covalent oxides. When the oxygen is bonded by two single bonds the group X-O-X will be bent and the angle is about 104.5° (H_2O) or 111° ($(CH_3)O$). The bond X-O is

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sigma type only, when X atom as group has d orbital able to overlap with the lone pairs of electrons on oxygen, so the bond X-O has some π character which cause shorting of the X-O distance and also the angle X-O-X will be larger, in $(C_6H_5)_2O$ is 124° and in quartz O-Si-O (124°) and in $H_3Si\text{-}O\text{-}SiH_3$ (> 150°) .

b- The Coordination no. 3:-

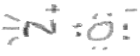
It happens when oxygen is connected with other by three covalent bonds, so the molecules is pyramide, e. g. oxonium ions H_3O^+, $H_2{}^+OH$, $ROH_2{}^+$ and R_3O^+.

$H_2O + H^+ \longrightarrow H3O_+$ as in $NH_3 + H^+ \longrightarrow NH_4{}^+$ (Addition of H+).

Oxygen is less basic than nitrogen, so that oxonium ions are naturally less stable.

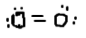
c- Coordination no. 4

There are some known compounds (although oxygen is rarely bonded with 4 covalent bonds). e. g. : complexes : $Mg_4OBr_6.4C_4H_{10}O$ and $M_4O(OOCR)_6$, M=Zn or Be.

d- In addition to above aminono oxides  has a single bond or the bond X-O is double as in ketones (σ and π bonds).

Occurrence of O_2 in Nature

Oxygen has three isotopes: ^{16}O : 99.76%, ^{17}O: 0.37% and ^{18}O: v.v. low%. It is possible to get some samples in which the concentration of H_2O^{18} is 97% and H_2O^{17} is 4%.

Oxygen has two states O_2 which is the more stable, and the second is O_3. O_2 has paramagnetic properties. O_2 state has a high decomposition energy = 496KJ/ mol. According to (VBT), the structure of O2 is  which can be explained the high decomposition energy, but this does not explain the paramagnetic properties. The MOT give the correct answer of this structure by: $(\sigma_1)^2$ $(\sigma_{x/2})^2$ $(\pi_1)^4$ $(\sigma_3)^2$ $(\pi^*{}_2)^2$ and $(\sigma_1)^2$ $(\sigma_{x/2})^2$ $(\sigma_3)^2$ $(\pi_1)^4$ $(\pi^*{}_2)^2$, hance the bond order = 8-4/ 2=2, in the same time there are two lone electrons in $\pi^*{}_2$ which explain the paramagnetic properties of the molecule and then the color of O_2 (pale blue) in liquid and solid state.

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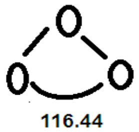
Ozon O_3

O_3 is prepared by electrical discharge on O_2, in which 10% concentration O_3 can be produced , also O_3 in small amounts can be formed by electrical analysis of dilution H_2SO_4 acid and also in some reactions that give the atomic oxygen. Lastly O_3 is formed by the action of UV radiation on O_2 in the higher layer of atmospheric.

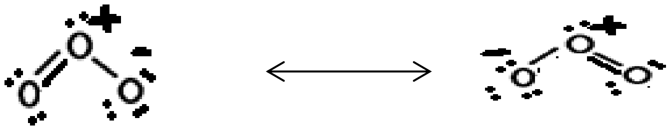
The higher concentration of O_3 is reached at 25 Km. above the ground, so that the earth can be protected from the excess UV radiation.

The formation reaction of O_3 from O_2 endothermic

$O_3 \longleftrightarrow 3/2\ O_2$ $\Delta H = -142$ KJ/ mol , although it decomposes slowly at 250 °c without catalyst or UV.



The bond O-O is single in HO-OH , it's length 149Pm, in O_2= 12 Pm (double bond), while in O_3, the O-O bonds have a lot of the double bond character, so according to the resonance principle, the O3 molecule has the canonical forms



Chemical Properties of O_2 &O_3

The chemical activity of O_3 differs than that of O_2, it is well known that O_2 combines with most element but at high temperature, in the meantime O_3 reacts at normal temperature with materials that O_2 doesn't react with e.g.:

$$O_3 + 2KI + H_2O \longrightarrow I_2 + 2KOH + O_2$$

This reaction is used in the quantitative determination of O_3 by titration of I_2 and knowing its quantity. The activity of O_3 (high) compared to O_2 is due to the high energy a company to its reaction as an oxidizing agent :-

$$O_2 + 4H^+ + 4e \longrightarrow 2H_2O \qquad E^o= +1.229V$$

$$O_3 + 2H^+ + 2e \longrightarrow H_2O + O_2 \qquad E^o= +2.07V$$

The average decomposition of O3 extremely reduce in the alkaloid solutions. The half-life time ($t_{1/2}$) of its decomposition in 1N NaOH solution is ≈2 minutes at 25 °c increases to 40 minutes in 5N and to 83 hours in 20N, also it seems that O_3^- ion is more stable in alkaline solutions.

The ability of some materials for simultaneous oxidation in aqueous solution belongs to O_2 dissolved, e.g.; Cr^{+2} ion doesn't oxidize in pure water, while it is rapidly oxidize if water is saturated with O_2, also Fe^{+2} oxidizes slowly in acidic medium of rapidly in basic medium in presence of O_2.

The average of simultaneous oxidizing of many bio materials increases with presence of transition elements ions (ascorbic acid in presence of Cu^{+2}) in which Cu_{+2} reduced to Cu^+ which simultaneous oxidizes to Cu^{+2} in presence of dissolved O_2 and so on …

Oxygen Compounds:-

The most important compounds of oxygen are peroxides, super oxides and ozonides.

1- **Hydrogen peroxide H_2O_2**

It can be prepared by:-

a- Electrical analysis of H_2SO_4 solution or the acidic solution with ammonium sulfates, using Pt electrodes and high current:-

$2HSO_4^- \longrightarrow S_2O_8^{-2} + 2H^+ + 2e$

$S_2O_8^{-2} + 2H^+ \longrightarrow H_2S_2O_8$ peroxo disulfuric acid.

Analysis process takes place at low temperature to prevent hydrolysis of the produced acid at the moment of formation.as :-

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$

The current stop and the temperature increase when the concentration of $H_2S_2O_8$ reach a certain concentration, hence the acid gives H_2SO_5 which itself hydrolyze to give H_2O_2 as in equation :-

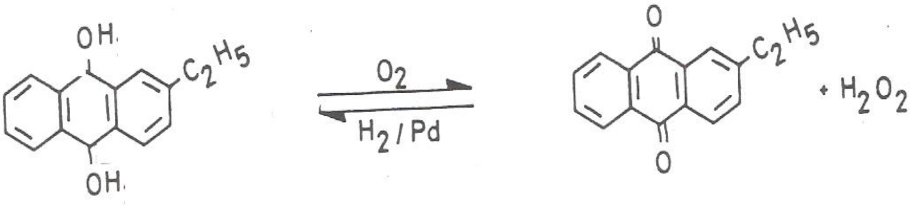
$$H_2SO_5 + H_2O \longrightarrow H_2O_2 + H_2SO_4$$

The produced H_2O_2 is distilled under reduced pressures. The solution concentration is increased by vacuum distant to reach 28-35% by weight. The Vacuum distant is repeated in presence of Na per phosphate (to prevent the

..

catalytic effect) to reach 90-99% concentration of the H_2O_2 solutions of some ions.

b- H_2O_2 prepared in a large scale by simultaneous oxidation of methyl ethyl 2-ethyl antraquinol in a continuous cycle, in which H_2 is used to reduce the produced quinone using Pd as catalyst, then Hydrogen oxide is extracted from the organic liquid by the counter current method. The used materials in this preparation are H_2, air and water which are cheaper than in (a).



H_2O_2 Properties

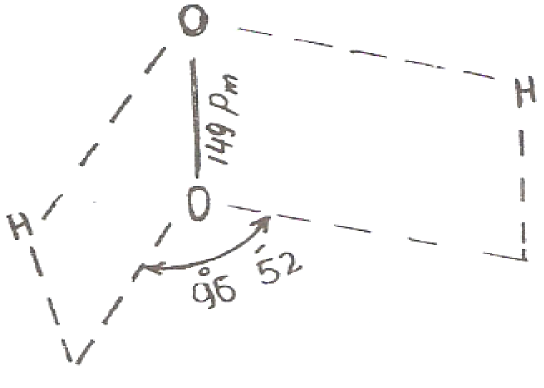
Pure H_2O_2 is a syrupy liquid, pale blue in color, b.p.152.1°c, F.P. -0.89. It likes water in many properties, e.g. dielectric constant (d) of H_2O_2 =93, it's solution 65% in water has d=120, so H_2O_2 and it's solution in water are excellent ionizing solvents, but it's easy to dissociate and its power as an oxidizing agent limits it to be used as a solvent.

$2H_2O_2 \rightleftharpoons 2H_2O + O_2 \qquad \Delta H = -99\ KJ/\ mol$

*H_2O_2 is more acidic than water in its dilute solutions.

$H_2O_2 \rightleftharpoons H^+ + HO_2^- \qquad K_{20} = 1.5\times10\text{-}2$

*H_2O_2 molecule is not a linear but have the following structure:-



In the liquid state H_2O_2 molecules aggregate by hydrogen bonds larger than what happens in water, it's behavior as an oxidizing agent can be summarize by :-

$H_2O_2 + 2H^+ + 2e \rightleftharpoons 2H_2O \qquad E^o= 1.77V$

$O_2 + 2H^+ + 2e \rightleftharpoons H_2O_2 \qquad E^o = 0.68V$

$HO_2^- + H_2O + 2e \rightleftharpoons 3OH^- \qquad E^o = 0.87V$

..

From these equations, it is clear that H_2O_2 is a strong oxidizing agent in acidic medium and basic, reacts with most anhydrides of the organic acids forming (per acids) e.g. peracetic acid which can be commercially prepared by reaction of H_2O_2 (50%) with acetic acid in presence of H_2SO_4 as a catalysis at 45-60. It doesn't react as a reducing agent unless there is a strong oxidizing agent like $KMnO_4$ or Cl_2 or Ce^{+4}. The released O_2 in these reaction (using H_2O_2) is formed from peroxy hydrogen, not from water, so that the above oxidizing agents cannot break the O-O bond, but remove es only.

In case of Cl_2

as oxidizing agent, it believes that that the reaction taken place according to these equations:-

$Cl_2 + H_2O_2^{18} \longrightarrow H^+ + Cl^- + HO^{1818}OCl$

$HO^{1818}OCl \longrightarrow H^+ + Cl^- + O_2$

Peroxides:-

Some of them are ionic containing the (O_2^{-2}) ion, e.g. alkali methal, Ca, Sr and Ba peroxides.

Sodium peroxide can be prepared in air, firstly to get Na_2O then Na_2O_2. It is a yellow powder, highly like water, doesn't decompose till 500ºc.

Peroxides react with water giving H_2O_2, they are oxidizing agents (strong). The reaction of these ionic oxides are useful with (CO_2) to generate O_2 in the closed system ,e, g. submarines which stay under water surface for long times.

$M_2O_2 + CO_2\ (g) \longrightarrow M_2CO_3 + ½\ O_2$

Magnesium forms with lanthanides peroxides that have a moderate properties between ionic and covalent, while Zn, Cd and Hg peroxide are covalent.

Super peroxides MO_2

Oxygen reacts (under atmospheric pressure) have an orange color, their general formula is MO_2. It is not possible to prepare NaO_2 by the same way, but from the reaction of Na_2O_2 + O2 at 500ºc, pressure 300 atm. LiO_2 yet not prepared.

These oxides are paramagnetic materials which explain the presence of O_2^- ion, also they are strong oxidizers, react strongly with water:-

$2O_2^{-2} + H_2O \rightleftharpoons O_2 + HO_2^- + {}^-OH$

$2HO_2^- \rightleftharpoons O_2 + 2OH$ slow reaction.

Ozonides:-

Can be prepared from O_3 gas with solid Cs, Rb or KOH:-

$3KOH_{(s)} + 2O_3 \rightleftharpoons 2KO_{3\,(s)} + KOH.H_2O_{\,(s)} + ½\ O2_{(g)}$

KO_3 crystalline, orange red, slowly decomposition to KO_2 and O_2.

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S,Se,Te and Po:-

Table give some properties of these elements

Element	Electronic confirmation	m. p. ºC	b. p. ºc	E.N
S	[Ne]$3s^2\ 3p^4$	119	444.6	2.44
Se	[Ar] $3d^{10}\ 4s^2\ 4p^4$	217	684.8	2.48
Te	[Kr]$4d^{10}\ 5s^2\ 5p^4$	450	990	2.01
Po	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^4$	254	962	1.76

It is clearly seen that the electronic configuration of these elements is less by 2e than the noble gases, except Po, all elements are non-metals can from covalent compounds. The outer shell saturated by the following :-

1- Gaining 2e to form S^{-2}, Se^{-2}, Te^{-2} (although these ions are present only in salts of the higher elements of electropositive (Alkali and earth alkaloid metals).

2- Forming two covalent bonds as in H_2S, R_2S, SCl_2,

3- Forming ionic groups have one covalent bond and one negative charge as RS^-.

4- Forming group have 3 covalent bonds and one positive charge as R_3S^+.In these compounds, the covalent lance is divalent. These elements have oxidation number of 4 and 6 connecting by 4, 5 or 6 bonds, Te forms TeF_8^{-2} where the coordination no=8.

Examples of some compounds of these elements:

Covalency	No. of bonds	Structure	Examples
2	2	Bent	H_2Te, Me_2S
	3	Pyramid	Me_3S^+
	4	Square Planar	$Te[Se(NH_2)_2]_2Cl_2$
4	2	Bent	So_2
	3	Pyramid	SO_3^{-2}, SF_3^+, OSF_2
	4	Square Planar	Me_3SO^+
	6	Octahedral	$SeBr_6^{-2}$, PoI_6^{-2}
6	3	Trigonal Planar	$SO_{3\ (g)}$
	4	Tetrahedral	SeO_4^{-2}, SeO_2Cl_2
	5	T. b. p.	SO
	6	Octahedral	SeF_6

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Properties of the group elements:-

There is a big difference between the chemistry of oxygen and sulfur, while the properties of the elements from S ⟶ Po are grading, the properties of these elements differ from oxygen due to the following reason :-

1- Decrease in the EN from Se to Po lowering the ionic properties in their compounds, also the action of hydrogen bonding, although there present a weak hydrogen bond type S----H-S in sulfur compounds.

2- Because they have (d) orbital (not oxygen and sulfur) which used to form additional bonds, so that their coordination no. not limited by 4(max.) and the covalence 2 as in oxygen.

3- Only sulfur tends to form chains, so that it forms a lot of compounds not known in case of O, Se, and Te. e. g. polysulfides, sulfanes(XSn), X= H or CN. Polysulfuric acid HO_3SSnSO_3H and their salts.

The metallic properties and the tendency to form complexes and the decomposition of the compounds of high oxidation state (positive) are due to the increase of size and decomposition of EN from S → Po.

Occurrence (Abundance) in Nature

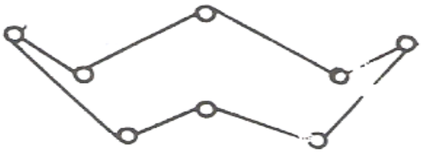
S as an element is found as in Almishraq (Iraq) and also as H_2S, SO_2 sulfides and sulfates of metals, e. g. $CaSO_4$, $CaSO_4.2H_2O$.

Se and Te are present as impurities in the sulfur ores, while Po is present in a very little amounts (~ 0.1 mgm/ ton) in some ores.

It can be produced by Bi irradiation in the nuclear reactors :-

$209\ Bi(n,8)Bi^{210} \longrightarrow {}^{210}Po + \beta_1$ separated by sublimation

Structure of Sulfur:-



Rhombos Sulfur

1- All the polymerized sulfur contains:-
   - a- Sulfur cycles of 6, 8, 10 or 12 atoms of S then they called (cyclo hexa sulfur), cycloocta …….ete.
   - b- Chains of S atoms called (chain sulfur), the most familiar one is the cyclic containing 8 atoms of sulfur which has three shapes, Rhombos sulfur the more stable one as large yellow crystals (in volcanoes) , monoclinic and prismy sulfur. The prismy one can be prepared by converting the Rhombos one at 955ºc also by slow polymerization of S from it's solution in alcoholic ammonium sulfide.

2- Liquid Sulfur:-

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Transparent yellow liquid, not viscous, can be produced from molten sulfur. It's viscosity increases by forming the chain type because of the breaking of chains during heating. The viscosity become maximum at 200ºc.

Dicompounds of Group VI Elements

1- Hydrides :- e.g. H_2S, H_2Se, H_2Te, H_2Po.

They are highly toxic compounds, have bad odors. Their stability decrease(and the strength of bond) from H_2S to H_2Po ,while H2S and H2Se are stable (thermodynamically) , H_2Te and H_2Po are not stable.

Their solutions in water are very weak acidic, but their chemical activity increases (also $K_{dissoc.}$) with increasing of the atomic no. of elements.

2- Sulfanes:- e. g. H_2S_2 to H_2S_6 can be prepared in their pure from, all are liquids, viscosity increases with increase chain length.

3- Metal Chalconides :- These come from the direct reaction of most elements with S, Se, Te and for somehow Po. e. g. Hg reacts with S at room temperature to give mercury chalconide.

4- Ionic Sulfides:- Prepared from reaction between only alklai and earth alkaloid metals with sulfur. As there is O_2^- ion, also S_2^- ion is there has paramagnetic properties.

5- Halides:- e. g. S_2F_2, S_2Cl_2, S_2Br_2, SF_4, SCl_2, SF_6, $SeCl_2$, $TeCl_4$, $TeBr_4$, TeF_6……ete.

6- Oxides:- S_2O, SO (unstable), SO_2, SeO_2, TeO_2 ….

7- Oxoacids:- S, Se and Te from oxoacids. e. g. H_2SO_3, H_2SO_4……

$2H_2SO_4 \longleftrightarrow H_3SO_4^+ + HSO_4^-$ selfionization

8- Oxohalides:- Only S and Se from such compounds :-

a- Thionyl and selinyl halides; SOX_2, $SeOX_2$, SOFCl, $SOBr_2$……ete.

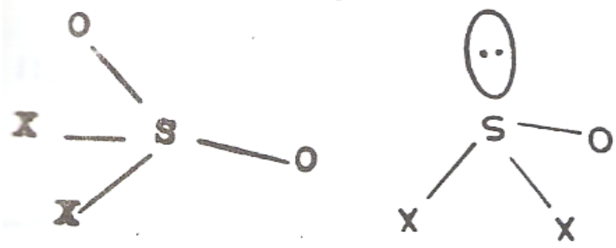
b- Sulfuric halides : SO_2X_2 and only SeO_2F_2 for Se.

c- No. of oxofluoride and oxochloride of S (complexes).

$SOCl_2$

$PCl_5 + SO_2 \longrightarrow SOCl_2 + POCl_3$

Thionyl halides have a pyramide structure



Sulfuric halide have a distorted tetrahedral

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Group VII elements :- Halogen

The group that contains, ^{9}F,^{17}Cl, ^{35}Br, ^{53}I, and ^{85}As (Astatine) elements is called halogen element group. This name means in Greek salts, the electronic configuration of the outer shell (covalence) is ns^2 np^5, so we call it as group VII. Astatine is produced in very few amounts from the radiation degradation processes as an intermediate element with short life, no details are know about.

General properties of the group elements:-

The electronic configuration of them refers that they need one electron to be like the closer Nobel gas, which means their extreme tendency to gain an e forming ionic halides as NaCl or their contribution by es forming covalent halides, e. g. HCl, also their presence as diatomic molecules can be explained from ns^2np^5.

These elements (except fluorine) show positive oxidation no. in their compounds with O2 as in the following examples:-

Element	$^{9}F_2$	$^{17}C_{l2}$	$^{35}Br_2$	$^{53}I_2$
Color	Pale yellow (g)	Green (g)	Reddish brown (l)	Violet (s)
M. P. ºC	-288	-101	-7	113
B. P. ºC	-188	-35	59	183
Ionization pot.(ev)	17.4	13	11.8	10.4
E. affinity (ev)	-3.6	-3.8	-3.5	-3.2
EN.	4	3	2.8	2.5
Energy of bond KJ/ mol	154.8	242.7	192.5	150.2
Radius of atom (pm)	72	99	114	113

It is very clear that the properties are systematically ranging among the group (from F to I) e. g. Ionization potential . Decomposition while the radius increases. These element have a high ionization potential coming directly after that of the nobal gases, the metallic character increase through the group (from F to I).

Halogens are present in the normal conditions as diatomic molecules bonded by a covalent bond (single), also there are van der walls forces bonding the molecules in the liquid and solid state.

Iodine molecule is the largest molecule of the group VII elements in size, it has the largest no. of electrons which make its polarization easy, so it has large van der walls forces that explain why Iodine is a solid in normal conditions and has a high m. p. compared to the other elements in the group.

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The elements of the 2nd period, where the F is found deviate from their group elements in many properties because of the small size of their atoms, higher EN, they doesn't have d orbitals which mean they are not able to en large their covalency shell, e. g. maximum no. of electrons in the outer shell is (8es) and they cannot form more than 4 bonds.

It is easy to break F-F bond in (F_2) because of the decomposition energy of the molecule which is due to the repulsion between the two atoms of the molecule and their non-bonding electrons.

Chlorine has higher decomposition energy that the other elements because the non-bonding electrons form with (d) orbitals (vacant) in the neighboring atom what called ($p\pi$-$d\pi$) bond which increases the strength of Cl-Cl bond, while the large size of Br and I decrease the possibility of ($p\pi$-$d\pi$) bonds formation, so that the decomposition energy of their molecule is less than that of chlorine.

Occurrence in Nature

Mostly the group VII elements are present as halides, like NaCl, KCl, CaF_2, Na_3AlF_6. Salts of bromine and iodine are present in sea's water, also iodine is present in small quantities in chilli nitrate ($NaNO_3$).

Methods of preparation

1- **F_2:-** The more active element and the stronger oxidizing agent, cannot be prepared in aqueous solution because it oxidizes water.

$$2F_2 + 2H_2O \longrightarrow 4HF + O_2$$

Fluorine can be prepared by electronic analysis of the fluorides melts inside Cu-containers or alloys of Cu- Ni, because it forms an isolating layer of fluoride when react with them prevent the reaction to continue and then protect the containers.

a- $2K[HF_2] \longrightarrow H_2 + 2KF + F_2$

Also we can get fluorine from the fluorides decomposition by heat:-

b- $AuF_3 \longrightarrow AuF + F_2$

2- **Cl_2:-** Is prepared by the electronic analysis of NaCl

$$2NaCl + H_2O \longrightarrow H_2 + Cl_2 + 2NaOH$$

also by oxidation of HCl (conc.) by one of the strong oxidizing agents, e. g. $KMnO_4$, $K_2Cr_2O_7$, PbO_2, MnO_2:

$MnO_2 + 4HCl \longrightarrow [MnCl_4] + 2H_2O$

$\hookrightarrow MnCl_2 + Cl_2$

3- **Br_2:-** Prepared by oxidation of bromide to Br_2 using Cl_2

$Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$ or in Lab. As :-

$MnO_2 + 2KBr + 2H_2SO_4 \longrightarrow Mn\ SO_4 + Br_2 + K_2SO_4 + 2H_2O$

4- **I_2:-**By oxidizing of iodide by Cl2

$Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$

Industrially by reducing iodides present in chilli salt using sodium bisulfite:-

$2IO_3 + 5HSO_3^- \longrightarrow I_2 + 5SO_4^{-2} + 3H^+ + H_2O$

Laboratory prepared in a similar way as in Cl_2 and Br_2 by oxidation iodide using $Cr_2O_7^{-2}$:

$Cr_2O_7^{-2} + 14H^+ + 6I^- \longrightarrow 2Cr^{+3} + 3I_2 + 7H_2O$

Compounds of halogens with hydrogen :-

Halogens give hydrogen halides when react with hydrogen ,the strength of reaction decomposition from (F to I). e. g. hydrogen chloride HCl and HF in industry are prepared from hot conc. H_2SO_4 with NaCl, CaF_2

$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl$

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

The products HCl and HF are easily separated from the reaction liquid, because they are in the gaseous state. It is not possible to prepare HBr and HI by the same way because H_2SO_4 oxidize Br^- and I^- into Br_2 and I_2

$2NaBr + 2H_2SO_4 \longrightarrow Br_2 + SO_2 + Na_2SO_4 + 2H_2O$

but they are prepared by the reaction between their salts and phosphoric acid

$NaBr + H_3PO_4 \longrightarrow HBr + NaH_2PO_4$

$NaI + H_3PO_4 \longrightarrow HI + NaH_2PO_4$

Hydrogen halides (HX) can be produced from H2O and P reaction :-

$PX_3 + 3H_2O \longrightarrow 3HX + H_3PO_3$

Hydrogen halides dissolve strongly in water, their solution in water are called Hydrohalic acids.

e. g. Hydrofluoric acid, the bond H-F is strong can pared with H-Cl or H-Br or H-I, because it is totally ionized in water forming stronger acids than HF, which is relatively weak acid.

Hydrogen halides are similar in their physical properties and to a large extent in their chemical properties, they are colorless gases have a sharp and bad smell HF, m. p. =19.5°c which is considered high due to the tendency of F to form hydrogen bonds because of its high EN.

Hydrofluoric acid reacts with glass forming tetra fluoro silicon (SiF_4), this is because of the presence of SiO_2 in glass structure.

$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

For this reason HF is kept in plastic containers.

Halides and their preparation

There are many halides and many different methods for preparation : e. g. :

- Ionic halides, $CuCl_2$, $PbCl_2$, $SnCl_2$, $SbCl_3$……etc.
- Molecular halides, BeF_2, $BeCl_2$ …..
- Organic halides, halide complexes, oxohalides, $POCl_3$, $VOCl_3$, …..etc.

Preparation Methods

1- Direct reaction between halogens and elements:-

$2Fe + 2Br_2 \longrightarrow 2FeBr_3$

$Sn + 2Cl \longrightarrow SnCl_4$

$S + 3F_2 \longrightarrow SF_6$

2- Reaction of halides compounds with oxides:-

$UO_2 + CCl_4 \longrightarrow UCl_4 + CO_2$

3- Fluorides are prepared from HF or ZnF_2 with chlorides:-

$CrCl_3 + 3HF \longrightarrow CrF_3 + 3HCl$

..

$PCl_3 + 3ZnF_2 \longrightarrow 2PF_3 + 3ZnCl_2$

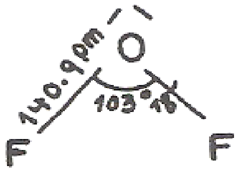
Compounds of oxygen and halogens:-

Compounds of F_2 with O_2 are called oxygen fluorides because the EN of (F) is larger than that of oxygen, while others are called halogen oxides.

a- Oxygen fluorides OF_2:- prepared by passing F_2 in 2% NaOH solution

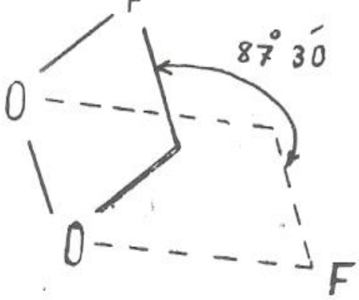
$2F_2 + 2{}^{-}OH \longrightarrow F_2O + 2F^{-} + H_2O$

It is a pale yellow gas, toxic, relatively unactive, its structure like water.



OF₂ reacts with water giving HF.

$OF_2 + H_2O \longrightarrow HF + O_2$



O_2F_2 : it's structure is
Unstable, decomposes into
O_2 and F_2 at -50 °c, strong oxidizing agent.

b- Chlorine oxides: very active, unstable, tends to explode under different conditions e. g. Cl_2O is prepared:-

$2Cl_2 + 2HgO \longrightarrow HgCl_2\text{-}Hg + Cl_2O$

Reddish yellow gas at room temperature, dissolve in water forming HOCl which forms with molecular chlorides oxohalides:-

$TiCl_4 + Cl_2O \longrightarrow TiOCl_2 + 2Cl_2$

ClO_2 :- Highly explosive and active, oxidizing agent, it's structure is angular. Other oxides are like Cl_2O_6, Cl_2O_7 .

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c- Bromine oxides:- unstable, prepared by O_2 with Br_2 reaction under electrical discharging at low temperature e. g. Br_2O white solid material, unstable above 80ºc, keep in ozone atmosphere.

d- Iodine oxides:- e. g. I_2O_5, which crystals, it is an oxidizing agents.

Oxohalo acids:-

Fluorine doesn't form such acids. The most important example are oxochloro acids, HOCl, HOBr, HOI (oxidation no. +1), $HClO_2$(+3).

Negative ions of such acid, e. g. (ClO^-) from by losing protons. Negative ions are more stable than acids due to their gaining (accepting) resonance energy, e. g. ClO^-_2:-

Inter halogen cpds.

These can be produced by the reaction of halogens themselves xx^-n, where (n) is an odd no., e. g. ICl, ICl_3, IBr, BrF, …..etc.

Fluorides are very active, react strongly with water and organic cpds. Sometimes the activity causes explosion.

The activity is following the order:-

$ClF_3 > BrF_5 > IF_7 > ClF > BrF_3 > IF_5 > BrF$

The structure of these cpds can be deduced by help of (VSEPR) theory, the tetra cpds, e. g. XF_3 have the structure:-

Three bonding pairs and two non-bonding pairs of es.

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Pseudo halogens:-

They are molecules formed from elements of high (EN), like halogen in their properties, from ions called pseudo ions which like halides ions in behavior : example:- cyanogene $(CN)_2$, Thiocyanogene $(SCN)_2$, .(OCN^-) etc.

The common properties with halogens are:-

1- Volatile materials form from two radicals combination:-

$x^{\cdot} + x^{\cdot} \rightarrow x_2$ $\quad x =$F, Cl, …..,CN, SCN.

2- Forms salts when combine with metals (contains x^-)

3- Salts of Ag^I, Hg^I and Pb^{II} dissolve in water, e. g. AgCl, $HgCl_2$, $PbCl_2$, AgCN, AgN_3 etc.

$Ag+ + N_3^- \longrightarrow AgN_3$

$Pb^{+2} + 2CN^- \longrightarrow Pb(CN)_2$

4- Halogens and pseudo halogen forms acids of type :-

HX; HF, HCl, HCN, HSCN

5- Pseudo halogens form inter cpds., and also with halogens, e. g. ClCN, ClN_3, BrCN.

6- Pseudo ions form complexes as halides ions:-

e. g. $[Zn(NCS)_4]^{-2}$

7- They form covalent pseudo halides like covalent halides when hydrolyze in water e. g. $Si(OCN)_4$, $SiBr_4$.

All halocyanogenes are known and can be prepared by the reaction of halogen and cyanide, they are volatile cpds. Their structure is linear:-

X-C-N

The Solid State

Experimental evidence on structure .
What is the structure?

Structure (of solids) refers to the arrangement of the atoms, ions or molecules which compose them.

The structure (arrangement) of a solid may be:-

- Ordered one of the crystal or,
- Random one one of amorphous material.

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Crystal are probably never perfectly ordered nor amorphous material completely random.

Structure and type of Solids:-

There are many ways to classify solids, but the broadest categories are:-

1- Crystalline Solids, those with a highly regular arrangement of their components, and

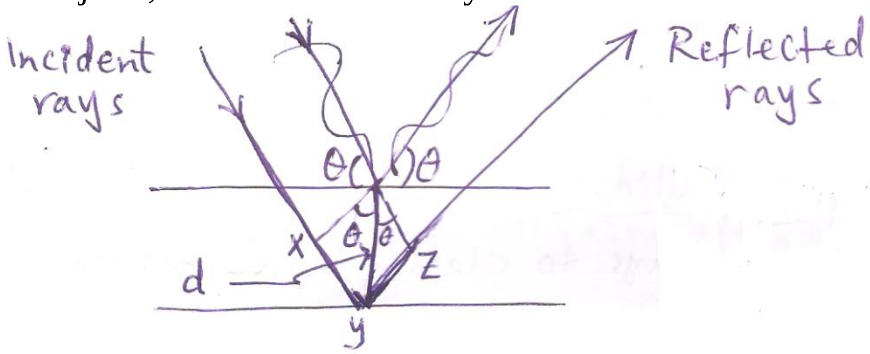
2- Amorphous Solids, those with considerable disorder in their structures.

The positions of the components in a crystalline solid are usually represented by a lattice, a three dimensional system of points designating the positions of the components (atoms, ions or molecules) that make up the substances.

The smallest repeating unite of the lattice is called the unit cell. There are many important non crystalline (amorphous) materials, an example is common glass, which is best pictured as a solution in which the components are "frozen in place". Although glass is a solid (it has a rigid shape), a great deal of disorder exists in the structure.

X-ray Diffraction :-

Diffraction occurs when an electromagnetic radiation is scattered from a regular array of objects, such the ions in a crystal of NaCl.



Reflection of X-rays of wavelength λ from a pair of atoms in two different layers of crystal.

Xy + yz = nλ…………………(1), where n is an integer and λ is the weavelength of X-ray , then

Xy + yz = 2dsin θ……………..(2), where d is the distance between the atoms, and θ is the angle of incident and reflection .

Combining equation 1 and 2 gives:-

nλ = 2d sin θ ………………..(3) Bragg's low.

The X-ray analysis of crystals is carried out by using a computer – controlled instrument called " the diffractometer".

X-ray produce diffraction patterns when passed through crystals, the diffraction is due to construction (because of) interferences when the wave of parallel beams are in phase and to destructive interferences when the waves are out of phase.

Bragg investigated the reflection of monochromatic beams of X-rays from surfaces of crystals such as NaCl and ZnS. He found that, for a particular salt, there were certain angles between the incident beam and the surface which gave rise to strong reflection.

There is an interaction occurs between x-rays and the extra- nuclear electrons of atoms or ions.

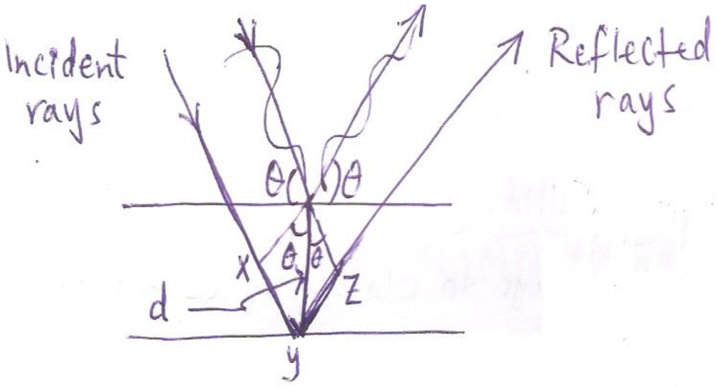
$n\lambda = 2d \sin \theta$ Bragg’s equation

λ= wavelength of the x-ray

n= a small hole no.

d= distance between two layers

θ= angle of diffraction



place of atoms or ions in crystals.

EX.

x-ray of W.L.1.54A° were used to analyze an aluminum crystal, a reflection was produced at θ= 19.3°, assuming n=1, calculate the distance (d) between the planes of atoms producing this reflection?

Solution

Using Bragg,s equation:-

$n\ \lambda = 2d \sin \theta$

$$\therefore d = \frac{n\lambda}{2\sin\theta} = \frac{1 \times 1.54A^{\circ}}{2 \times 0.3305}$$

$= 2.33A^{\circ} = 233$PM (picometer)

Type of crystalline solids

There are many different type of crystalline solids, e. g. although both sugar and salt dissolve readily in water, the properties of the resulting solutions are quite different.

The salt solution readily conducts an electric current, whereas the sugar solution. does not . This behavior arises from the nature of the components in these two solids.

NaCl is an ionic solid; it contains Na^+ and Cl^- ions. When solid NaCl dissolves in the polar water, Na^+ and Cl^- ions are distributed through the resulting solution and are free to conduct electric current. Table sugar (sucrose), on the other hand, is composed of neutral molecules that are dispersed throughout the water when solid dissolve. No ions are present, the resulting solution does not conducting electricity.

Methods of XRD

X-rays; photons of high energy and short wavelengths in the order of tenths of angstroms to several angestroms.

There are two methods:-

a- Powder Method:-

In this method a monochromatic beam of x-rays is used to fall on a powder of small crystals, or crystal fragments, to deduce Bragg's angles and hence structure.

The finely divided material compressed or held in the form of a rod, is rotated in a beam of near monochromatic x-rays and the diffractions from it are recorded on a photographic film, which will give then angle (θ) and intensities (I) with great precision.

b- **Single Crystal Method:-**

A single crystal is fixed in a narrow beam of monochromatic x-rays gives diffractions which may be recorded as dark spots on a photographic plate. Provided the geometry of the system is known, the Bragg's angle may be found and the structure deduced. This method, now provides the most powerful means of determining structure.

Neutron diffraction:-

The diffraction of x-rays and electrons is due to interaction with orbital electrons of the atoms they encounter. The diffraction of neutrons springs from:-

a- Nuclear Scattering:

It happens by an interaction with protons or neutrons in the nucleus depending on the nuclear size and nuclear structure.

b- Magnetic Scattering:-

It arises from interactions between the magnetic moment of the neutron and that of the atom, or ion under test.

Structure and Properties:-

The properties of solid depend on:-

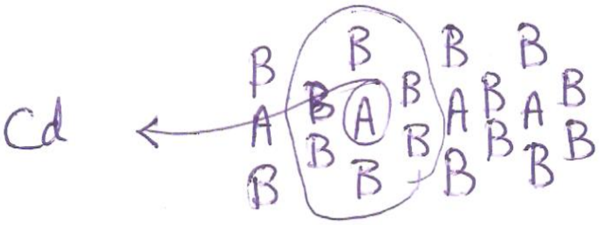
1- The number and kind of atoms composing it.
2- The arrangement of these atoms.

Examples:-

1- Solid CO_2, O=C=O like AB_2, B-A-B Each carbon atom (as separate molecules). Is connected to two oxygen atoms

2- As an infinite layer, CdI_2

Each Cd atom has six iodine atoms.



3- In various three dimensional structure, e. g. CaF_2, has cubic crystal with one of these arrangement, every Ca atom has eight fluorine atoms. Therefore the chemical of formula a solid should be considered in relation to its crystal structure.

Even two solids are similar in formula as PCl_5 and PBr_5, they differ structurally; why?

PCl5 has equal numbers of PCl^+_4 ions and PCl^-_6ions .While PBr_5 has equal number of PBr^+_4 ions and Br^- ions.

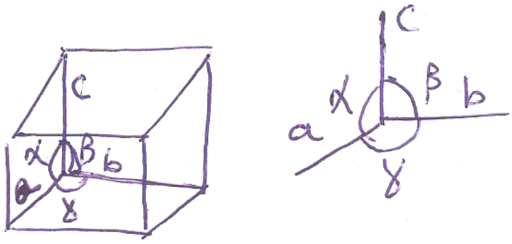
The Unit Cell

A crystalline solid is composed of atoms (or ions) packed regularly in a three dimensional arrangement. There is a pattern has many points that define a regular lattice. By taking a suitable no. of translations (steps) along each lattice of three suitable directions, one can find many points.

The unit cell means a block of different points. The nature of the solid is determined by the size, shape and content of its unit cell.

The size and shape is defined by length (a, b, c) of three intersecting edges and the angle (α, β, γ) between them.

Unit Cell



There are seven types of unit cell, and therefore seven simple or primitive lattices with one unit of pattern at each cell corner.

These types are:-

1- Cubic 2- Monoclinic 3- Triclinic 4- Tetragonal 5- Hexagonal 6- Orthorhombic 7- Rhombohedral.

Crystallization Water

Salt hydrates hold water molecules as :-

1- Co-ordinated water, e.g. $[Co(H_2O)]Cl$, $[Be(H_2O)4]SO_4$.

..

2- Anion water, e. g. (not common),
$CuSO_4.5H_2O \longrightarrow CuSO_4.3H_2O \longrightarrow CuSO_4.H_2O$

3- Lattice water, e. g. Alums
Where six of water molecules are coordinated round the 3+ cation (Al^{+3}) and other six are arranged at a much greater distance about the unipositive cation (K^+).Water is not associated directly with either anion or cation.

4- Zeolite water : water here cannot be removed stepwise, e. g. CaCO3.6H2O, water found between the layers of a crystal lattice.

Crystal Growth

Reaction between solids effected by two factors:-

1- The mean length of diffusion path.

2- The slow rate of diffusion through the solids.

Tammann's Rule:-

A significant reaction will not occur until the thermodynamic temperature is two-thirds (2/3) of the melting point of the lower melting solid.

Group 18- The Noble Gases

..

Table 17.1 Electronic structures

Element	Symbol		Electronic structure
Helium	He		$1s^2$
Neon	Ne	[He]	$2s^2\ 2p^6$
Argon	Ar	[Ne]	$3s^2\ 3p^6$
Krypton	Kr	[Ar]	$3d^{10}\ 4s^2\ 4p^6$
Xenon	Xe	[Kr]	$4d^{10}\ 5s^2\ 5p^6$
Radon	Rn	[Xe]	$4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$

NAME OF GROUP AND THEIR ELECTRONIC STRUCTURES

The elements of Group 18 have been called 'the inert gases' and 'the rare gases'. Both are misnomers, since the discovery of the xenon fluorides in 1962 shows that xenon is not inert, and argon makes up 0.9% by volume of the atmosphere. The name 'noble gases' implies that they tend to be unreactive, in the same way that the noble metals are often reluctant to react and are the least reactive metals.

Helium has two electrons which form a complete shell $1s^2$. The other noble gases have a closed octet of electrons in their outer shell ns^2np^6. This electronic configuration is very stable and is related to their chemical inactivity. These atoms have an electron affinity of zero (or slightly negative), and have very high ionization energies – higher than any other elements. Under normal conditions the noble gas atoms have little tendency to gain or lose electrons. Thus they have little tendency to form bonds, and so they exist as single atoms.

with S, and absorbing the SO_2 in NaOH solution. This gave a small volume of unreactive gas.

Ar is quite abundant and can be recovered by fractional distillation of liquid air (see under 'Nitrogen', Chapter 14). Ar constitutes 0.93% by volume of air (i.e. 9300 ppm). It originates in the air mostly from electron capture (β+ decay) of potassium:

$$^{40}_{19}\mathrm{K} + ^{0}_{-1}\mathrm{e} \rightarrow ^{40}_{18}\mathrm{Ar}$$

World production of Ar is over 700 000 tonnes/year.

The other noble gases are much less abundant. The abundance of He in the atmosphere is only about 5 ppm by volume and recovery from air would be very expensive. A cheaper source is from natural gas deposits, where the hydrocarbons are liquified, leaving He gas. The He has been produced by radioactive decay, and trapped underground. The richest source is in southwest USA, where the natural gas contains 0.5–0.8% He. This provides most of the world's supply of He. Other natural gas deposits containing appreciable amounts of He have been found in Algeria, Poland, the USSR and Canada. World production was 18 800 tonnes in 1993.

The non-radioactive noble gases are all produced industrially by fractional distillation of liquid air. This gives large amounts of dinitrogen and dioxygen, and only a small amount of the noble gases. (The dioxygen is mainly used for steel making.) Of the noble gases, Ar is obtained in the largest amounts, and it is the cheapest.

Rn is radioactive and is produced by the decay of radium and thorium minerals. A convenient source is ^{226}Ra, and 100 g of radium yields about 2 ml of radon per day:

$$^{226}_{88}\mathrm{Ra} \rightarrow ^{222}_{86}\mathrm{Rn} + ^{4}_{2}\mathrm{He}$$

The most stable isotope ^{222}Rn is itself α active and has a half life of only 3.8 days, so only tracer studies have been made.

USES OF THE ELEMENTS

The largest use of Ar is to provide an inert atmosphere for metallurgical processes. This includes welding stainless steel, titanium, magnesium and aluminium, and in the production of titanium (Kroll and IMI processes). Smaller amounts are used in growing silicon and germanium crystals for transistors, and in electric light bulbs, fluorescent lamps, radio valves and Geiger–Müller radiation counters.

Helium has the lowest boiling point of any liquid, and it is used in cryoscopy to obtain the very low temperatures required for superconductivity, and lasers. It is used as the cooling gas in one type of gas cooled nuclear reactor, and as the flow-gas in gas–liquid chromatography. It is also used in weather balloons and airships. Though H_2 has a lower density and is cheaper and more readily available than He, H_2 is highly flammable. Thus on safety grounds He is used in preference to H_2 in airships. He is much less dense than air. One cubic metre of He gas at atmospheric

continued overleaf

pressure can lift 1 kg. Helium is used in preference to dinitrogen to dilute dioxygen in the gas cylinders used by divers. This is because dinitrogen is quite soluble in blood, so a sudden change in pressure causes degassing and gives bubbles of N_2 in the blood. This causes the painful (or fatal) condition called 'bends'. Helium is only slightly soluble so the risk of 'bends' is reduced.

Small amounts of Ne are used in neon discharge tubes which give the familiar reddish orange glow of 'neon' signs. The other gases are also used in discharge tubes to give different colours.

PHYSICAL PROPERTIES

The elements are all colourless, odourless monatomic gases. The enthalpy of vaporization is a measure of the forces holding the atoms together. The values are very low because the only forces between the atoms are very weak van der Waals forces. The enthalpy of vaporization increases down the group as the polarizability of the atoms increases.

Table 17.2 Physical properties of the noble gases

	First ionization energy (kJ mol^{-1})	Enthalpy of vaporization (kJ mol^{-1})	Melting point (°C)	Boiling point (°C)	Atomic radii (Å)	Abundance in atmosphere (% volume)
He	2372	0.08		−269.0	1.20	5.2×10^{-4}
Ne	2080	1.7	−248.6	−246.0	1.60	1.5×10^{-3}
Ar	1521	6.5	−189.4	−186.0	1.91	0.93
Kr	1351	9.1	−157.2	−153.6	2.00	1.1×10^{-4}
Xe	1170	12.7	−111.8	−108.1	2.20	8.7×10^{-6}
Rn	1037	18.1	−71	−62		

Because the interatomic forces are very weak, the melting points and boiling points are also very low. The boiling point of He is the lowest of any element, only four degrees above absolute zero.

The atomic radii of the elements are all very large, and increase on descending the group. It must be noted that these are non-bonded radii, and should be compared with the van der Waals radii of other elements rather than with covalent (bonded) radii.

The noble gases are all able to diffuse through glass, rubber and plastic materials, and some metals. This makes them difficult to handle in the laboratory, particularly since glass Dewar flasks cannot be used for low temperature work.

SPECIAL PROPERTIES OF HELIUM

Helium is unique. It has the lowest boiling point of any substance known. All other elements become solids on cooling, but cooling only produces helium liquid. It only forms a solid under high pressure (about 25 atmospheres). There are two different liquid phases. Helium I is a normal liquid, but helium II is a superfluid. A superfluid is a most unusual state of matter. Normally atoms are free to move in a gas, can move in a more restricted way in a liquid, and can only vibrate about fixed positions in a solid. As the temperature decreases, the amount of thermal motion of atoms decreases, and gases become liquids, and eventually solids. When the temperature of helium gas is lowered to 4.2 K it liquifies as helium I. Rather surprisingly the liquid continues to boil vigorously. At 2.2 K, the liquid suddenly stops boiling (which with normal materials is when a solid is formed). In this case helium II is formed. This is still a liquid because the interatomic forces are not strong enough to form a solid, but thermal motion of the atoms has actually stopped. Helium I is a normal liquid, and when it changes to helium II at the λ-point temperature, many physical properties change abruptly. The specific heat changes by a factor of 10. The thermal conductivity increases by 10^6 and becomes 800 times greater than for copper. It becomes a superconductor (i.e. shows zero electrical resistance). The viscosity becomes effectively zero and 1/100th of that of gaseous hydrogen. It spreads to cover all surfaces at temperatures below the λ-point. Thus *the liquid can actually flow up the sides of the vessel* and over the edge until the levels on both sides are the same. The surface tension and compressibility are also anomalous.

CHEMICAL PROPERTIES OF THE NOBLE GASES

The noble gases were isolated and discovered because of their lack of reactivity. For a long time it was thought that they really were chemically inert. Before 1962, the only evidence for compound formation by the noble gases was some molecular ions formed in discharge tubes, and clathrate compounds.

Molecular ions formed under excited conditions

Several molecular ions such as He_2^+, HeH^+, HeH^{2+} and Ar_2^+ are formed under high energy conditions in discharge tubes. They only survive momentarily and are detected spectroscopically. Neutral molecules such as He_2 are unstable.

Clathrate compounds

Clathrate compounds of the noble gases are well known. Normal chemical compounds have ionic or covalent bonds. However, in the clathrates atoms or molecules of the appropriate size are trapped in cavities in the crystal lattice of other compounds. *Though the gases are trapped, they do not form bonds.*

If an aqueous solution of quinol (1,4-dihydroxybenzene) is crystallized under a pressure of 10–40 atmospheres of Ar, Kr or Xe, the gas becomes trapped in cavities of about 4 Å diameter in the β-quinol structure. When the clathrate is dissolved, the hydrogen bonded arrangement of β-quinol breaks down and the noble gas escapes. Other small molecules such as O_2, SO_2, H_2S, MeCN and CH_3OH form clathrates as well as Ar, Kr and Xe. The smaller noble gases He and Ne do not form clathrate compounds because the gas atoms are small enough to escape from the cavities. The composition of these clathrate compounds corresponds to 3 quinol : 1 trapped molecule, though normally all the cavities are not filled

The gases Ar, Kr and Xe may be trapped in cavities in a similar way when water is frozen under a high pressure of the gas. These are clathrate compounds, but are more commonly called 'the noble gas hydrates'. They have formulae approximating to $6H_2O : 1$ gas atom. He and Ne are not trapped because they are too small. The heavier noble gases can also be trapped in cavities in synthetic zeolites, and samples have been obtained containing up to 20% of Ar by weight. Clathrates provide a convenient means of storing radioactive isotopes of Kr and Xe produced in nuclear reactors.

CHEMISTRY OF XENON

The first real compound of the noble gases was made in 1962. Bartlett and Lohman had previously used the highly oxidizing compound platinum hexafluoride to oxidize dioxygen.

$$PtF_6 + O_2 \rightarrow O_2^+[PtF_6]^-$$

The first ionization energy for $O_2 \rightarrow O_2^+$ is $1165\,kJ\,mol^{-1}$, which is almost the same as the value of $1170\,kJ\,mol^{-1}$ for $Xe \rightarrow Xe^+$. It was predicted that xenon should react with PtF_6. Experiments showed that when deep red PtF_6 vapour was mixed with an equal volume of Xe, the gases combined immediately at room temperature to produce a yellow solid. They (incorrectly) thought the product obtained was xenon hexafluoroplatinate(V), $Xe^+[PtF_6]^-$. The reaction has since been shown to be more complicated, and the product is really $[XeF]^+[Pt_2F_{11}]^-$.

$$Xe[PtF_6] + PtF_6 \xrightarrow{25\,^\circ C} [XeF]^+[PtF_6]^- + PtF_5 \xrightarrow{\text{heat } 60\,^\circ C} [XeF]^+[Pt_2F_{11}]^-$$

Soon after this it was found that Xe and F_2 reacted at 400 °C to give a colourless volatile solid XeF_4. This has the same number of valency electrons as, and is isostructural with, the polyhalide ion $[ICl_4]^-$. Following these discoveries there was a rapid extension of the chemistry of the noble gases, and in particular of xenon.

The ionization energies of He, Ne and Ar are much higher than for Xe, and are too high to allow the formation of similar compounds. The ionization energy for Kr is a little lower than for Xe, and Kr does form KrF_2. The ionization energy of Rn is less than for Xe, and Rn might be expected to form compounds similar to those of Xe. Rn is radioactive, has no stable isotopes, and all the isotopes have short half lives. This has limited work on radon compounds, and only RnF_2 and a few complexes are known.

Table 17.3 Structures of some xenon compounds

Formula	Name	Oxidation state	m.p. (°C)	Structure
XeF_2	xenon difluoride	(+II)	129	linear (RnF_2 and $XeCl_2$ are similar)
XeF_4	xenon tetrafluoride	(+IV)	117	square planar ($XeCl_4$ is similar)
XeF_6	xenon hexafluoride	(+VI)	49.6	distorted octahedron
XeO_3	xenon trioxide	(+VI)	explodes	pyramidal (tetrahedral with one corner unoccupied)
XeO_2F_2		(+VI)	30.8	trigonal bipyramid (with one position unoccupied)
$XeOF_4$		(+VI)	−46	square pyramidal (octahedral with one position unoccupied)
XeO_4	xenon tetroxide	(+VIII)	−35.9	tetrahedral
XeO_3F_2		(+VIII)	−54.1	trigonal bipyramid
$Ba_2[XeO_6]^{4-}$	barium perxenate	(+VIII)	dec. >300	octahedral

Xe reacts directly only with F_2. However, oxygen compounds can be obtained from the fluorides. There is some evidence for the existence of $XeCl_2$ and $XeCl_4$, and one compound is known with a Xe—N bond. Thus there is quite an extensive chemistry of Xe. The principal compounds are listed in Table 17.3.

Xenon reacts directly with fluorine when the gases are heated at 400 °C in a sealed nickel vessel, and the products depend on the F_2/Xe ratio.

$$\begin{array}{lll} & \nearrow & 2:1 \text{ mixture} \rightarrow XeF_2 \\ Xe + F_2 & \rightarrow & 1:5 \text{ mixture} \rightarrow XeF_4 \\ & \searrow & 1:20 \text{ mixture} \rightarrow XeF_6 \end{array}$$

The compounds XeF_2, XeF_4 and XeF_6 are all white solids. They can be sublimed at room temperature, and can be stored indefinitely in nickel or Monel containers. The lower fluorides form higher fluorides when heated with F_2 under pressure. The fluorides are all extremely strong oxidizing and fluorinating agents. They react quantitatively with hydrogen as follows:

$$XeF_2 + H_2 \rightarrow 2HF + Xe$$

$$XeF_4 + 2H_2 \rightarrow 4HF + Xe$$
$$XeF_6 + 3H_2 \rightarrow 6HF + Xe$$

They oxidize Cl^- to Cl_2, I^- to I_2 and cerium(III) to cerium(IV):

$$XeF_2 + 2HCl \rightarrow 2HF + Xe + Cl_2$$
$$XeF_4 + 4KI \rightarrow 4KF + Xe + 2I_2$$
$$SO_4^{2-} + XeF_2 + Ce_2^{III}(SO_4)_3 \rightarrow 2Ce^{IV}(SO_4)_2 + Xe + F_2$$

They fluorinate compounds:

$$XeF_4 + 2SF_4 \rightarrow Xe + 2SF_6$$
$$XeF_4 + Pt \rightarrow Xe + PtF_4$$

XeF_2 is now commercially available and is quite widely used in synthe organic chemistry. It can oxidize and fluorinate the 'hetero element' in organometallic compound, but does not attack the alkyl or aryl groups.

$$CH_3I + XeF_2 \rightarrow CH_3IF_2 + Xe$$
$$C_6H_5I + XeF_2 \rightarrow C_6H_5IF_2 + Xe$$
$$(C_6H_5)_2S + XeF_2 \rightarrow (C_6H_5)_2SF_2 + Xe$$

If XeF_2 is mixed with anhydrous HF its reactivity is greatly increase possibly due to the formation of XeF^+.

$$Pt + 3XeF_2/HF \rightarrow PtF_6 + 3Xe$$
$$S_8 + 24XeF_2/HF \rightarrow 8SF_6 + 24Xe$$
$$CrF_2 + XeF_2/HF \rightarrow CrF_3 + Xe \rightarrow CrF_4 + Xe$$
$$MoO_3 + 3XeF_2/HF \rightarrow MoF_6 + 3Xe + 1\tfrac{1}{2}O_2$$
$$Mo(CO)_6 + 3XeF_2/HF \rightarrow MoF_6 + 3Xe + 6CO$$

The fluorides differ in their reactivity with water. XeF_2 is soluble in wate but undergoes slow hydrolysis. Hydrolysis is more rapid with alkali.

$$2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$$

XeF_4 reacts violently with water, giving xenon trioxide XeO_3.

$$3XeF_4 + 6H_2O \rightarrow 2Xe + XeO_3 + 12HF + 1\tfrac{1}{2}O_2$$

XeF_6 also reacts violently with water, but slow hydrolysis by atmospheri moisture gives the highly explosive solid XeO_3.

$$XeF_6 + 6H_2O \rightarrow XeO_3 + 6HF$$

With small quantities of water, partial hydrolysis occurs, giving a colourless liquid xenon oxofluoride $XeOF_4$. The same product is formed wher XeF_6 reacts with silica or glass:

$$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$$
$$2XeF_6 + SiO_2 \rightarrow XeOF_4 + SiF_4$$

XeO_3 is an explosive white hygroscopic solid. It reacts with XeF_6 and $XeOF_4$.

$$XeO_3 + 2XeF_6 \rightarrow 3XeOF_4$$

$$XeO_3 + XeOF_4 \rightarrow 2XeO_2F_2$$

XeO_3 is soluble in water, but does not ionize. However, in alkaline solution above pH 10.5 it forms the xenate ion $[HXeO_4]^-$.

$$XeO_3 + NaOH \rightarrow \underset{\text{sodium xenate}}{Na^+ [HXeO_4]^-}$$

Xenates contain Xe(+VI) and they slowly disproportionate in solution to perxenates (which contain Xe(+VIII)) and Xe.

$$2[HXeO_4]^- + 2OH^- \rightarrow \underset{\text{perxenate ion}}{[XeO_6]^{4-}} + Xe + O_2 + 2H_2O$$

Several perxenates of Group 1 and 2 metals have been isolated, and the crystal structures of $Na_4XeO_6 \cdot 6H_2O$ and $Na_4XeO_6 \cdot 8H_2O$ have been determined by X-ray crystallography. The solubility of sodium perxenate in 0.5 M NaOH is only 0.2 grams per litre, so precipitation of sodium perxenate could be used as a gravimetric method of analysis for sodium. Perxenates are extremely powerful oxidizing agents, which will oxidize HCl to Cl_2, H_2O to O_2, and Mn^{2+} to MnO_4^-. With concentrated H_2SO_4 they give xenon tetroxide XeO_4, which is volatile and explosive.

Xenon fluoride complexes

XeF_2 acts as a fluoride donor and forms complexes with covalent pentafluorides including PF_5, AsF_5, SbF_5 and the transition metal fluorides NbF_5, TaF_5, RuF_5, OsF_5, RhF_5, IrF_5 and PtF_5. These are thought to have the structure

$$XeF_2 \cdot MF_5 \qquad [XeF]^+ [MF_6]^-$$

$$XeF_2 \cdot 2MF_5 \qquad [XeF]^+ [M_2F_{11}]^-$$

and

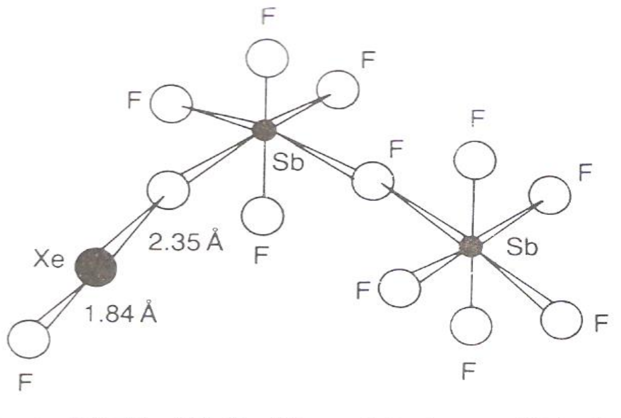


Figure 17.1 Structure of $XeF_2 \cdot 2SbF_5$. (From Mackay and Mackay, *Introduction to Modern Inorganic Chemistry*, 4th ed., Blackie, 1989.)

$$2XeF_2 \cdot MF_5 \qquad [Xe_2F_3]^+ [MF_6]^-$$

The structures of some of the XeF_2 complexes in the solid state are known. In the complex $XeF_2 \cdot 2SbF_5$ (Figure 17.1) the two Xe–F distances differ greatly (1.84 Å and 2.35 Å). This suggests the formulation $[XeF]^+ [Sb_2F_{11}]^-$. However, the Xe–F distance of 2.35 Å is much less than the van der Waals (non-bonded) distance of 3.50 Å. This suggests that one fluorine atom forms a fluorine bridge between Xe and Sb. In fact the structure is intermediate between that expected for the ionic structure, and that for the fully covalent bridge structure.

XeF_4 forms only a few complexes, for example those with PF_5, AsF_5 and SbF_5. XeF_6 can act as a fluoride donor, forming complexes such as:

$XeF_6 \cdot BF_3$
$XeF_6 \cdot GeF_4$
$XeF_6 \cdot 2GeF_4$
$XeF_6 \cdot 4SnF_4$
$XeF_6 \cdot AsF_5$
$XeF_6 \cdot SbF_5$

XeF_6 may also act as a fluoride acceptor. With RbF and CsF it reacts as follows:

$$XeF_6 + RbF \rightarrow Rb^+[XeF_7]^-$$

On heating, the $[XeF_7]^-$ ion decomposes:

$$2Cs^+[XeF_7]^- \xrightarrow{50^\circ C} XeF_6 + Cs_2[XeF_8]$$

STRUCTURE AND BONDING IN XENON COMPOUNDS

The structures of the more common xenon halides, oxides and oxoions are given in Table 17.4 (on page 647). The nature of the bonds and the orbitals used for bonding in these compounds are of great interest and have been the subject of considerable controversy.

XeF_2

XeF_2 is a linear molecule with both Xe–F distances 2.00 Å. The bonding may be explained quite simply by promoting an electron from the 5*p* level of Xe to the 5*d* level. The two unpaired electrons form bonds with fluorine atoms. The five electron pairs point to the corners of a trigonal bipyramid. Of these, three are lone pairs and occupy the equatorial positions, and two are bond pairs and occupy the apical positions. The atoms thus form a linear molecule (Figure 17.2).

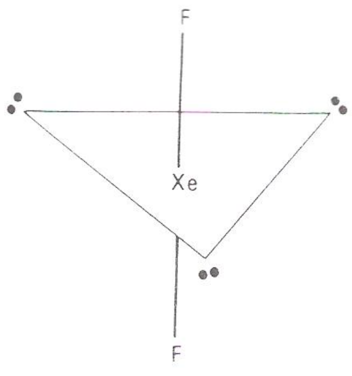
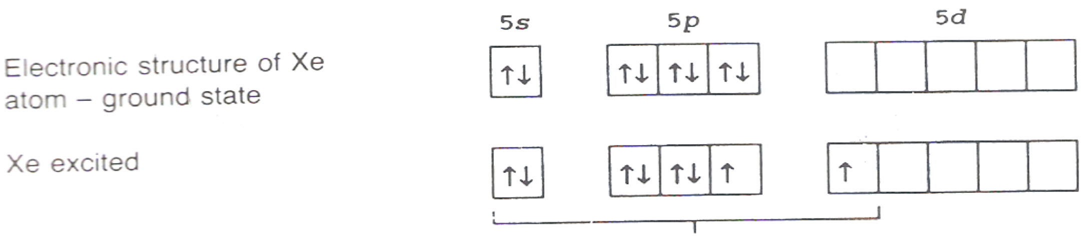


Figure 17.2 XeF_2 molecule.



two unpaired electrons form bonds with fluorine atoms
five electron pairs – trigonal bipyramid

This explains the observed structure, but an objection is that the 5*d* orbitals of Xe appear to be too large for effective overlap of orbitals. The maximum in the radial electron distribution function for a 5*d* orbital in a Xe atom occurs at a distance of 4.9 Å from the nucleus. It has been noted in Chapter 4 in the section 'The extent of *d* orbital participation in molecular bonding' that highly electronegative atoms like fluorine cause a large contraction in the size of *d* orbitals. If this contraction is big enough, the valence bond explanation will suffice.

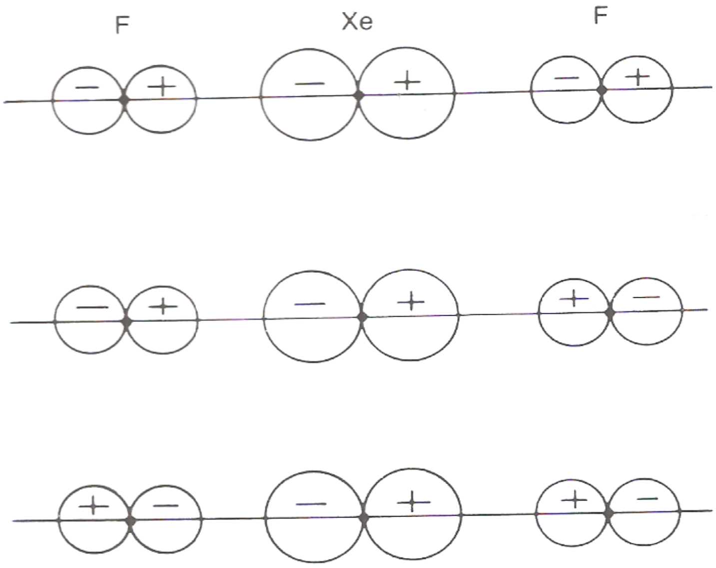
A second objection is over the mixing of orbitals (sp^3d hybridization). Mixing is only effective between orbitals of similar energy, and the Xe 5*d* orbitals would seem too high in energy to contribute to such a scheme of hybridization. (The difference in energy between a 5*p* and a 5*d* level is about 960 kJ mol^{-1}.)

The molecular orbital explanation involving three-centre bonds is more acceptable. The outer electronic configurations of the atoms are

Assume that bonding involves the $5p_z$ orbital of Xe and the $2p_z$ orbitals of the two F atoms. For bonding to occur, orbitals with the same symmetry must overlap. These three atomic orbitals combine to give three molecular orbitals, one bonding, one non-bonding and one antibonding. This is represented in a simple way in Figure 17.3. The original three atomic orbitals contained four electrons (two in the Xe $5p_z$ and one in each of the F $2p_z$). These electrons will occupy the molecular orbitals of lowest energy. The order of energy is:

bonding MO < non-bonding MO < antibonding MO

Thus two electrons occupy the bonding MO, and this pair of electrons is responsible for binding all three atoms. The remaining two electrons occupy the non-bonding MO. These electrons are situated mainly on the F atoms, and confer some ionic character. The bonding may be described as three-centre, four-electron σ bonding. A linear arrangement of the atoms gives the best overlap of orbitals, in agreement with the observed structure. These bonds should be compared with the three-centre two-electron bonds described for B_2H_6 (see Chapter 12).



Antibonding (orbitals have wrong symmetry for overlap on both left and right hand sides, indicated by + and − signs)

Non-bonding (the Xe 5*p* orbital has no net contribution to bonding, since the bonding effect on the right hand side is cancelled by the antibonding effect on the left hand side)

Bonding (orbitals on both the left and right hand sides have correct symmetry for overlap)

Figure 17.3 Possible combinations of atomic orbitals in XeF_2.

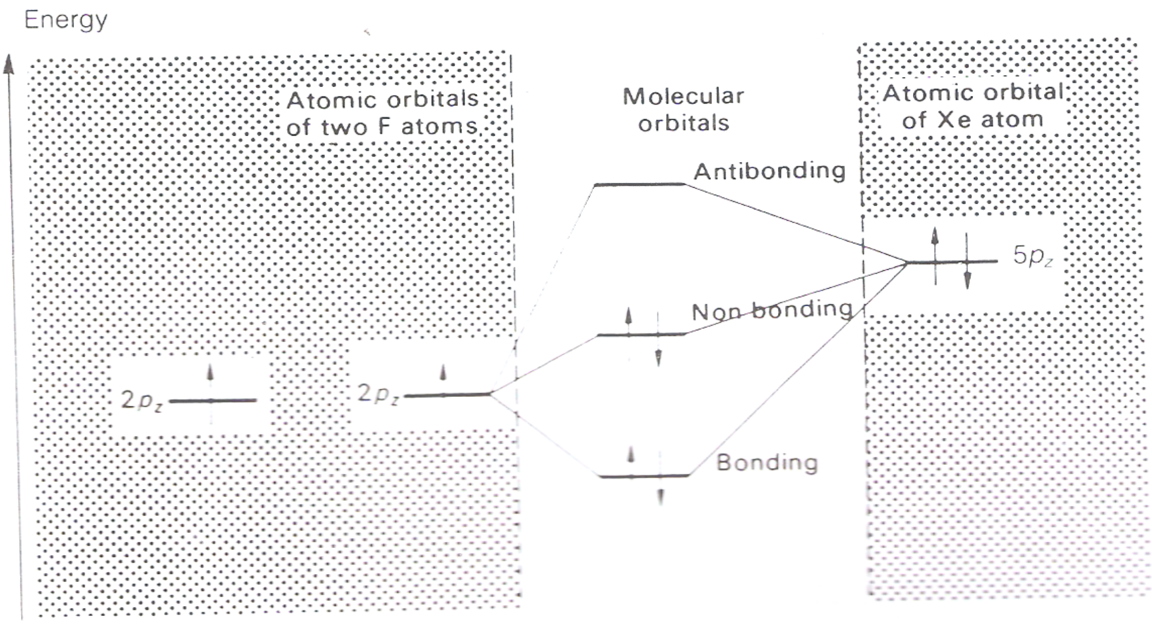
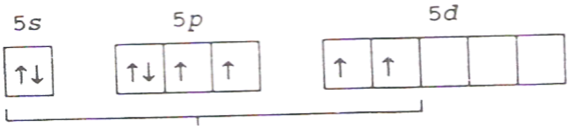


Figure 17.4 Molecular orbitals in XeF_2.

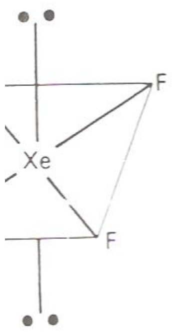
XeF_4

The structure of XeF_4 is square planar, with Xe–F distances of 1.95 Å. The valence bond theory explains this by promoting two electrons as shown:



Electronic structure of
Xe – excited state

four unpaired electrons form bonds to four fluorine atoms
six electron pairs form octahedral structure
with two positions occupied by lone pairs



7.5 XeF$_4$ molecule.

The problem of whether the size of the xenon 5*d* orbitals will allow effective overlap, or their energy will allow mixing and hybridization, is the same as in XeF$_2$. The molecular orbital explanation of XeF$_4$ is similar to that for XeF$_2$. The Xe atom bonds to four F atoms. The xenon 5p_x orbital forms a three-centre MO with 2*p* orbitals from two F atoms just as in XeF$_2$. The 5p_y orbital forms another three-centre MO involving two more F atoms. The two three-centre orbitals are at right angles to each other, thus giving a square planar molecule.

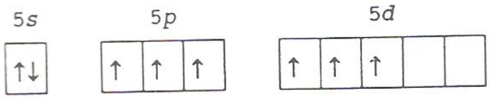
Table 17.4 Possible explanation of structures

Formula	Structure	Number of electron pairs	Number of lone pairs	VSEPR explanation of structure
XeF_2	linear	5	3	five electron pairs form trigonal bipyramid with three lone pairs in equatorial positions
XeF_4	square planar	6	2	six electron pairs form an octahedron with two positions occupied by lone pairs
XeF_6	distorted octahedron	7	1	pentagonal bipyramid, or capped octahedron with one lone pair
XeO_3	pyramidal	7	1	three π bonds so the remaining four electron pairs form a tetrahedron with one corner occupied by a lone pair
XeO_2F_2	trigonal bipyramid	7	1	two π bonds so remaining five electron pairs form trigonal bipyramid with one equatorial position occupied by a lone pair
$XeOF_4$	square pyramidal	7	1	one π bond so remaining six electron pairs form an octahedron with one position occupied by a lone pair
XeO_4	tetrahedral	8	0	four π bonds so remaining four electron pairs form a tetrahedron
XeO_3F_2	trigonal bipyramid	8	0	three π bonds so remaining five electron pairs form a trigonal bipyramid
$Ba_2[XeO_6]^{4-}$	octahedral	8	0	two π bonds so remaining six electron pairs form an octahedron

XeF_6

The structure of XeF_6 is a distorted octahedron. The bonding in XeF_6 has caused considerable controversy which is not completely resolved. The structure may be explained in valence bond terms by promoting three electrons in Xe:

Electronic structure of xenon – excited state



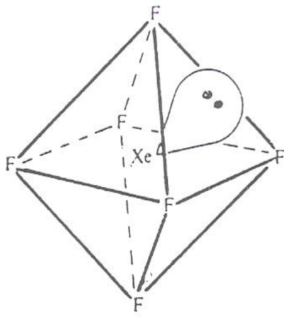


Figure 17.6 Capped octahedron.

The six unpaired electrons form bonds with fluorine atoms. The distribution of seven orbitals gives either a capped octahedron or a pentagonal bipyramid (as in IF_7). (A capped octahedron has a lone pair pointing through one of the faces of the octahedron.) Since there are six bonds and one lone pair, a capped octahedron would give a distorted octahedral molecule. The molecular orbital approach fails with XeF_6, since three three-centre molecular orbital systems mutually at right angles would give a regular octahedral shape.

The vibrational spectrum of gaseous XeF_6 indicates C_{3v} symmetry, i.e. an octahedron distorted by the lone pair at the centre of one triangular face. The structure of the molecule rapidly fluctuates between structures where the lone pair occupies each of the eight triangular faces. In various non-aqueous solvents, xenon hexafluoride forms a tetramer Xe_4F_{24}. Solid xenon hexafluoride is polymorphic. Except at very low temperatures it contains tetramers, where four square pyramidal XeF_5^+ ions are joined to two similar ions by means of two bridging F^- ions. The XeF distances are 1.84 Å on the square pyramidal units and 2.23 Å and 2.60 Å in the bridging groups.

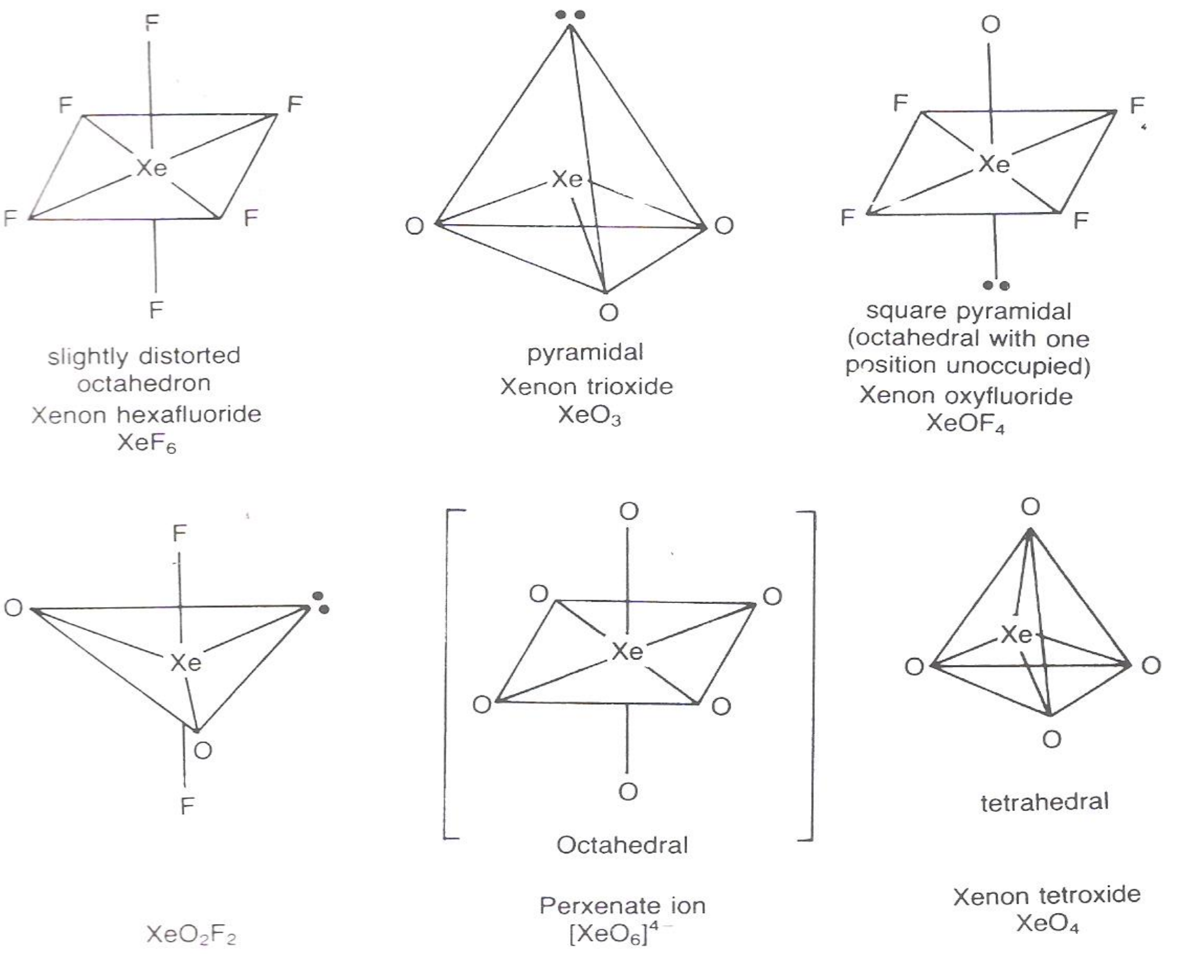
The shapes of oxygen containing compounds of Xe are correctly predicted by the valence bond method. (Electrons in π bonds (double bonds) must be subtracted before counting the number of electron pairs which determine the primary shape of the molecule.)

VALEDICTION

For many years the noble gases were thought to be completely unreactive. This was associated with the concept that an octet of electrons is the only stable arrangement. The octet rule has done much to help the understanding of why atoms react, how many bonds they will form, and the shape of the periodic table. The discovery of the noble gas compounds has shown that though the 'octet' arrangement is very stable, it can be broken, and that there are other stable arrangements of electrons.

Two important points emerge:

1. Only the heavier noble gases (Kr, Xe and Rn) form these compounds. This is related to their lower ionization energies.
2. Compounds are only formed with electronegative ligands.



slightly distorted octahedron
Xenon hexafluoride
XeF_6

pyramidal
Xenon trioxide
XeO_3

square pyramidal
(octahedral with one position unoccupied)
Xenon oxyfluoride
$XeOF_4$

XeO_2F_2

Octahedral
Perxenate ion
$[XeO_6]^{4-}$

tetrahedral
Xenon tetroxide
XeO_4

Figure 17.7 Structures of some xenon compounds.

The discovery of the noble gas compounds led to a flurry of practical work attempting the synthesis of new compounds. There was also much theoretical work attempting to explain the structure and bonding in these compounds. This involved calculations on large computers on the extent of *d* orbital participation in bonding by elements in the *s*- and *p*-blocks. These conclusions may be summarized as follows:

1. In compounds of high coordination number with elements of high electronegativity, such as PF_5, SF_6, IF_5 and XeF_6, the *d* orbitals appear to be significantly involved in σ bonding. (These compounds may all be described without using *d* orbitals if three-centre bonds are formed.)
2. In compounds with elements of low electronegativity such as H_2S and PH_3, the *d* orbital population is very low (1–2%). However, this small contribution considerably improves the agreement between the observed and calculated values for the dipole moments and the energy levels.
3. The use of *d* orbitals makes a very significant contribution to π bonds, for example $p\pi-d\pi$ bonding in the phosphates and oxoacids of sulphur, and in PF_3.