8. Chemistry of p-block elements,group 16,17 and 18

1. **p-Block elements:** Elements belonging to groups 13 to 18 of the periodic table are called p-block elements.

2. **General electronic configuration of p-block elements:** The p-block elements are characterized by the ns^2np^{1-6} valence shell electronic configuration.

3. **Representative elements:** Elements belonging to the s and p-blocks in the periodic table are called the representative elements or main group elements.

4. **Inert pair effect:** The tendency of ns^2 electron pair to participate in bond formation decreases with the increase in atomic size. Within a group the higher oxidation state becomes less stable with respect to the lower oxidation state as the atomic number increases. This trend is called 'inert pair effect'. In other words, the energy required to unpair the electrons is more than energy released in the formation of two additional bonds.

5. **Nitrogen family:** The elements of group 15 – nitrogen (N), phosphorus (P), arsenic (As), antimony (Sb) and bismuth (Bi) belong to configuration is ns^2np^3.

6. **Oxygen family:** Group 16 of periodic table consists of five elements – oxygen (O), sulphur (S), selenium (Se), tellurium (Te) and polonium (Po). Their general electronic configuration is ns^2np^4.

7. **The halogen family:** Group 17 elements, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At), belong to halogen family. Their general electronic configuration is ns^2np^5.

8. **Group 18 elements:** Helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn) are Group 18 elements. They are also called noble gases. Their general electronic configuration is ns^2np^6 except helium which has electronic configuration $1s^2$. They are called noble gases because they show very low chemical reactivity.

GROUP 15 ELEMENTS

9. **Atomic and ionic radii:** Covalent and ionic radii increase down the group. There is appreciable increase in covalent radii from N to P. There is small increase from As to Bi due to presence of completely filled d or f orbitals in heavy elements.

10. **Ionisation energy:** It goes on decreasing down the group due to increase in atomic size. Group 15 elements have higher ionisation energy than group 14 elements due to smaller size of group 15 elements. Group 15 elements have higher ionization energy than group 16 elements because they have stable electronic configuration i.e., half filled p-orbitals.

11. **Allotropy:** All elements of Group 15 except nitrogen show allotropy.

12. **Catenation:** Nitrogen shows catenation to some extent due to triple bond but phosphorus shows catenation to maximum extent. The tendency to show catenation decreases down the group.

13. **Oxidation states:** The common oxidation states are +3, +5, –3. The tendency to show –3 oxidation state decreases down the group due to decrease in electronegativity which is due to increase in atomic size.

    The stability of +5 oxidation state decreases whereas stability of +3 oxidation state increases due to inert pair effect.

    Nitrogen shows oxidation states from –3 to +5.

    Nitrogen and phosphorus with oxidation states from +1 to +4 undergo oxidation as well as reduction in acidic medium. This process is called disproportionation.

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

14. **Reactivity towards hydrogen:** All group 15 elements from trihydrides, MH_3. Hybridisation - sp^3

    The stability of hydrides decrease down the group due to decrease in bond dissociation energy down the group.

    $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

    Boiling point: $PH_3 < AsH_3 < NH_3 < SbH_3 < BiH_3$

    Boiling point increases with increase in size due to increase in van der Waals forces. Boiling point of NH_3 is more because of hydrogen bonding.

    Bond angle: NH_3 (107.8°) > PH_3 (99.5°) > AsH_3 (91.8°) ≈ SbH_3 (91.3°) > BiH_3 (90°)

    Electronegativity of N is highest. Therefore, the lone pairs will be towards nitrogen and hence more repulsion between bond pairs. Therefore bond angle is the highest. After nitrogen, the electronegativity decreases down the group.

    Basicity decreases as $NH_3 > PH_3 > AsH_3 > SbH_3 < BiH_3$.

This is because the lone pair of electrons are concentrated more on nitrogen and hence the basicity will be maximum in the case of NH_3. It will decrease down the group as the electronegativity decreases down the group.

The reducing power of hydrides increases down the group due to decrease in bond dissociation energy down the group.

15. **Reactivity towards oxygen:** All group 15 elements from trioxides (M_2O_3) and pentoxides (M_2O_5).

    Acidic character of oxides decreases and basicity increases down the group. This is because the size of nitrogen is very small. It has a strong positive field in a very small area. Therefore, it attracts the electrons of water's O-H bond to itself and release H^+ ions easily. As we move down the group, the atomic size increases. Hence, the acidic character of oxides decreases and basicity increases as we move down the group.

16. **Reactivity towards halogen:** Group 15 elements form trihalides and pentahalides.

    Trihalides – covalent compounds and become ionic down the group.

    sp^3 hybridisation , pyramidal shape

    Pentahalides - sp^3d hybridisation, TBP shape

    They are lewis acids because of the presence of vacant d – orbitals.

    $PCl_5 + Cl^- \rightarrow [PCl_6]^-$

    PCl_5 is ionic in solid state and exist as $[PCl_4]^+ \ [PCl_6]^-$

    In PCl_5, there are three equatorial bonds and two axial bonds. The axial bonds are longer than equatorial bonds because of greater repulsion from equatorial bonds.

    Nitrogen does not form pentahalides due to absence of *d*- orbitals.

17. **Reactivity towards metals:** All elements react with metals to form binary compounds in –3 oxidation state.

18. **Anomalous behaviour of nitrogen:** The behaviour of nitrogen differs from rest of the elements.

    Reason:

    i. It has a small size.

    ii. It does not have d – orbitals

iii. It has high electronegativity

iv. It has high ionization enthalpy

19. **Dinitrogen:**

Preparation:

$$NH_4Cl(aq) + NaNO_2\ (aq) \xrightarrow{\text{heat}} N_2(g) + 2H_2O(l) + NaCl(aq)$$

$$(NH_4)_2\ Cr_2O_7 \xrightarrow{\text{heat}} N_2 + 4H_2O + Cr_2O_3$$

$$Ba(N_3)_2 \xrightarrow{\text{heat}} Ba + 3\ N_2$$

Properties:

It is a colouless, odourless, tasteless and non – toxic gas. It is chemically un-reactive at ordinary temperature due to triple bond in

$N \equiv N$ which has high bond dissociation energy.

20. **Ammonia:** Ammonia molecule is trigonal pyramidal with nitrogen atom at the apex. It has 3 bond pairs and 1 lone pair. N is sp^3 hybridised.

Preparation:

Haber's process:

$$N_2\ (g) + 3H_2\ (g) \rightleftharpoons 2\ NH_3\ (g) \qquad \Delta_f H^o = -\ 46.1\ kJ\ mol^{-1}$$

$Pr\,essure = 200\,x\,10^5\,Pa$

$Temperature = 773\ K$

Catalyst is FeO with small amounts of K_2O and Al_2O_3

21. **Nitric Acid:**

a. Ostwald Process:

$$4NH_3 + 5O_2 \xrightarrow[500\ K,\,9bar]{Pt\,/\,Rh gauge} 4NO + 6H_2O\ ......(i)$$

$$2NO + O_2 \rightleftharpoons 2NO_2\ ......(ii)$$

$$3NO_2\ (g) + H_2O(l) \rightarrow 2HNO_3\ (aq) + NO(g)\ ......(iii)$$

NO thus formed is recycled and the aqueous HNO_3 can be concentrated by distillation upto ~ 68% by mass. Further concentration to 98% can be achieved by dehydration with concentrated H_2SO_4.

Nitric acid is strong oxidizing agent in the concentrated as well as in the dilute state.

22. **Phosphorus:**

a. It shows the property of catenation to maximum extent due to most stable P – P bond.

b. It has many allotropes, the important ones are :

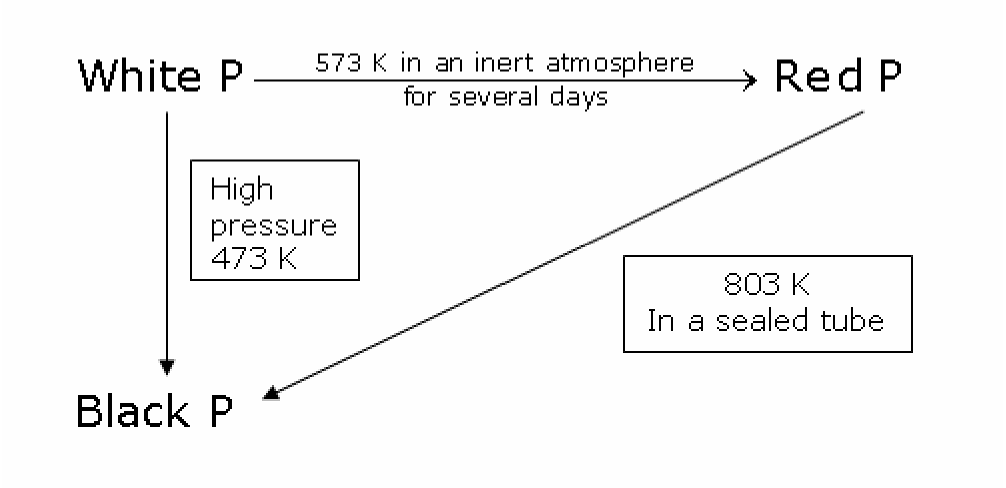
   i. White phosphorus

   ii. Red phosphorus

   iii. Black phosphorus

White phosphorus	Red phosphorus	Black phosphorus
Discrete tetrahedral P_4 molecules	Polymeric structure consisting of chains of P_4 units linked together	Exists in two forms - α black P and β black P
Very reactive	Less reactive than white P	Very less reactive
Glows in dark	Does not glow in dark	-
Translucent waxy solid	Has an iron grey luster	Has an opaque monoclinic or rhombohedral crystals
Soluble in CS_2 but insoluble in water	Insoluble in water as well as CS_2	-
It has low ignition temperature, therefore, kept under water	-	-

Preparation:



23. **Phosphine:**

Preparation:

i.

$$\underset{\text{(calcium phosphide)}}{Ca_3P_2} + \underset{\text{(water)}}{6H_2O} \rightarrow \underset{\text{(calcium hydroxide)}}{3Ca(OH)_2} + \underset{\text{phosphine}}{2PH_3}$$

$$Ca_3P_2 + 6HCl \rightarrow 3CaCl_2 + \underset{\text{(phosphine)}}{2PH_3}$$

ii.

$$P_4 + 3NaOH + 3H_2O \rightarrow \underset{\text{(sodium hypophosphite)}}{3NaH_2PO_2} + \underset{\text{(phosphine)}}{PH_3}$$

Phosphine is highly poisonous, colourless gas and has a smell of rotten fish.

24. **Chlorides of Phosphorous:**

PCl_3	PCl_5
Colourless oily liquid	Yellowish white powder
$P_4 + 6Cl_2 \rightarrow 4PCl_3$ $P_4 + 8SOCl_2 \rightarrow 4PCl_3 + 4SO_2 + 2S_2Cl_2$	$P_4 + 10Cl_2 \rightarrow 4PCl_5$ $P_4 + 10SO_2Cl_2 \rightarrow 4PCl_5 + 10SO_2$
Is hydrolysed in the presence of moisture $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$	$PCl_5 + H_2O \longrightarrow POCl_3 + 2HCl$ $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$
$3CH_3COOH + PCl_3 \rightarrow 3CH_3COCl + H_3PO_3$	$3CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$
$3C_2H_5OH + PCl_3 \rightarrow 3C_2H_5Cl + H_3PO_3$	$C_2H_5OH + PCl_5 \rightarrow C_2H_5Cl + POCl_3 + HCl$
Pyramidal shape, sp^3 hybridisation	TBP geometry, sp^3d hybridisation
-	$2Ag + PCl_5 \rightarrow 2AgCl + PCl_3$ $Sn + 2PCl_5 \rightarrow SnCl_4 + 2PCl_3$

Source : http://ciseche10.files.wordpress.com/2013/12/8-chemistry-of-p-block-elements-group-1617-and-18.pdf