V-JEE INSTITUTE

CHEMISTRY - XII

P Block Elements-Solution

Name :......................

Time : 6 hr

Total Marks = 95

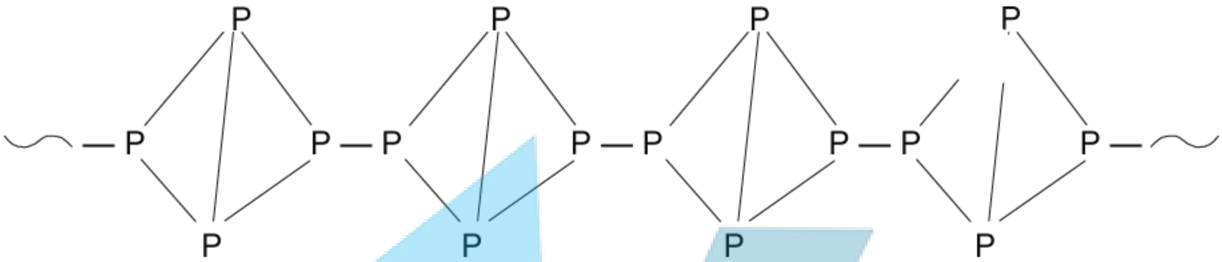
Date: 23/10/2017

S1. (a) $2NaI(aq) + Cl_2(g) \longrightarrow 2NaCl(aq) + I_2(g)$

(b) $SiO_2 + 6HF \longrightarrow H_2SiF_6 + 2H_2O$

(c) $I_2 + 10HNO_3$ (conc.) $\longrightarrow 2HIO_3 + 10\ NO_2 + 4H_2O$

S2. (a)

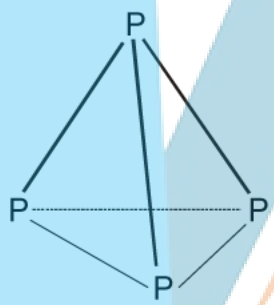


Red Phosphorous

Structure – Tetrahedral Polymeric

Hybridization – sp^3

(b)



White phosphorous

Shape – P_4 of tetrahedron

Hybridazation – sp^3

S3. (a) $H_2O > H_2S > H_2Se > H_2Te$

(b) $H_2O > H_2S > H_2Se > H_2Te$

(c) $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

S4. (a) M – F > M – Cl > M – Br > M – I

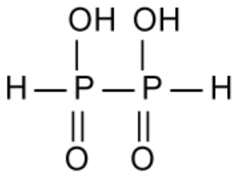
(b) $Cl_2O > ClO_2 > Cl_2O_6 > Cl_2O_7$ (decreasing order)

(c) $ClO > ClO_2^{\ominus} > ClO_3^{\ominus} > ClO_4^{\ominus}$

S5. (a) $H_2SO_4 > H_2SO_3 > H_2S_2O_3 > H_2SO_5$

(b) $HClO_4 > HClO_3 > HClO_2 > HClO$

(c) $NH_3 > PH_3 > ASH_3 > SbH_3 > BiH_3$

S6. (a)


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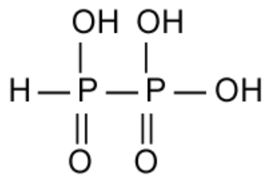
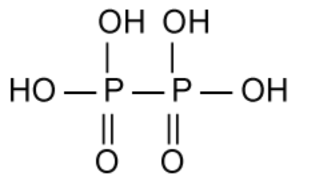


(c)


S7. Isostructural noble gas molecules:

(a) $IBr_2^{\ominus}$: XeF_2

(b) $ICl_4^{\ominus}$: XeF_4

(c) $BrO_3^{\ominus}$: XeF_3

S8. Aerosols such as chlorofluorocarbons (CFC's) depletes the O_3 layer by supplying Cl free radical which convert O_3 to O_2 in the following sequence of reactions :

$$\underset{\text{Freon}}{Cl_2CF_2\,(g)} \xrightarrow{hv} \bullet Cl\,(g) + \bullet CClF_2\,(g)$$

$$\bullet Cl(g) + O_3\,(g) \longrightarrow ClO\bullet\,(g) + O_2\,(g)$$

$$ClO\bullet\,(g) \longrightarrow Cl\bullet\,(g) + \bullet O\,(g)$$

$$ClO\bullet\,(g) + \bullet O\,(g) \longrightarrow \bullet Cl\,(g) + O_2\,(g)$$

S9. (a) ***Electronic configuration:*** All these elements have the common ns^2np^4 (n = 2 to 6) valence shell electronic configuration.

$$_{8}O = [He]2s^2\,2p^4;\quad _{16}S = [Ne]\,3s^2\,3p^4;\quad _{34}Se = [Ar]\,3d^{10}\,4s^2\,4p^4$$

$$_{52}Te = [Kr]\,4d^{10}\,5s^2\,5p^4 \quad \text{and} \quad _{84}Po = [Xe]\,4f^{14}\,5d^{10}\,6s^2\,6p^4$$

Hence, it is justified to place them in Group 16 of the periodic table.

(b) ***Oxidation states:*** They need two more electrons to form dinegative ions and acquire the nearest inert gas configuration. Thus, the minimum oxidation state of these elements should be –2. Oxygen, sulphur being electronegative show an oxidation state of –2. Other elements of this group, being more electropositive than O and S, do not show negative oxidation states. Since these elements have six electrons in the valence shell, therefore, at the maximum they can show an oxidation state +6. Other positive oxidation states shown by these elements are +2 and +4. However, due to the absence of *d*-orbitals, oxygen does not show oxidation states of +4 and +6. Thus, on the basis of minimum and maximum oxidation states, these elements are justified to be placed in the same group.

(c) ***Formation of hydrides:*** All the elements complete their respective octets by sharing two of their valence electrons with 1*s*-orbital of hydrogen to form hydrides of the general formula EH_2, i.e., H_2O, H_2S, H_2Se, H_2Te and H_2Po. Thus, on the basis of formation of hydrides of the general formula EH_2, these elements are justified to be placed in Group 16 of the period table.

S10. (a) $$NH_4NO_3\,(s) \xrightarrow{\text{Heat}} N_2O(g) + 2H_2O(l)$$

(b) $$N_2O + 2NaNH_2 \longrightarrow NaN_3 + NH_3 + NaOH$$

(c) $$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$$

S11. These xenon fluorides are obtained by direction reaction between Xe and F_2, under different conditions as shown below :

$$\underset{\text{(Excess)}}{Xe\,(g)} + F_2 \xrightarrow{673\text{ K, 1 bar}} (g)\ XeF_2\,(s)$$

$$\underset{(1:5\text{ ratio})}{Xe\,(g) + 2F_2\,(g)} \xrightarrow{873\text{ K, 7 bar}} XeF_4\,(s)$$

$$\underset{(1:20\text{ ratio})}{Xe\,(g) + 3F_2\,(g)} \xrightarrow{573\text{ K, 60 – 70 bar}} (g)\ XeF_6\,(s)$$

S12. (a) $Mg_3N_2 + 6H_2O \longrightarrow 3Mg(OH)_2 + \underset{\text{Ammonia}}{2NH_3}$

(b) $I_2 + 10HNO_3\,(\text{conc.}) \longrightarrow \underset{\text{Iodic acid}}{2HIO_3} + \underset{\text{Nitrogen dioxide}}{10NO_2} + 4H_2O$

(c) $Cu + 4HNO_3\,(\text{conc.}) \longrightarrow \underset{\text{Copper nitrate}}{Cu(NO_3)_2} + 2NO_2 + 2H_2O$

S13. Consider the reaction of a divalent metal (M) with oxygen. The formation of M_2O and MO involves the following steps:

$$M(g) \xrightarrow{\Delta_i H_1} M^{\oplus}\,(g) \xrightarrow{\Delta_i H_2} M^{2\oplus}\,(g)$$

$\Delta_i H_1$ and $\Delta_i H_2$ are first and second ionisation enthalpies of the metal M.

$$O\,(g) \xrightarrow{\Delta_{eg} H_1} O^{\ominus}\,(g) \xrightarrow{\Delta_{eg} H_2} O^{2\ominus}(g)$$

$\Delta_{eg} H_1$ and $\Delta_{eg} H_2$ are first and second electron gain enthalpies

$$2M^{\oplus}(g) + O^{\ominus}(g) \xrightarrow{\text{Lattice energy}} M_2O(s)$$

$$M^{2\oplus}(g) + O_2^{\ominus}(g) \xrightarrow{\text{Lattice energy}} MO\,(s)$$

Although $\Delta_i H_2$ is much more than $\Delta_i H_1$ and $\Delta_{eg}H_2$ is much higher than $\Delta_{eg}H_1$, yet the lattice energy of formation of MO (s) due to higher charges is much more than that of M_2O (s). In other words, formation MO is energetically more favourable than M_2O. It is due to this reason that oxygen forms preferably oxides having the $O_2^{\ominus}$ species and not $O^{\ominus}$.

S14. Industrial preparation of ammonia (Haber's process). Haber's process involves the direct combination of dihydrogen with dinitrogen to form ammonia as follows:

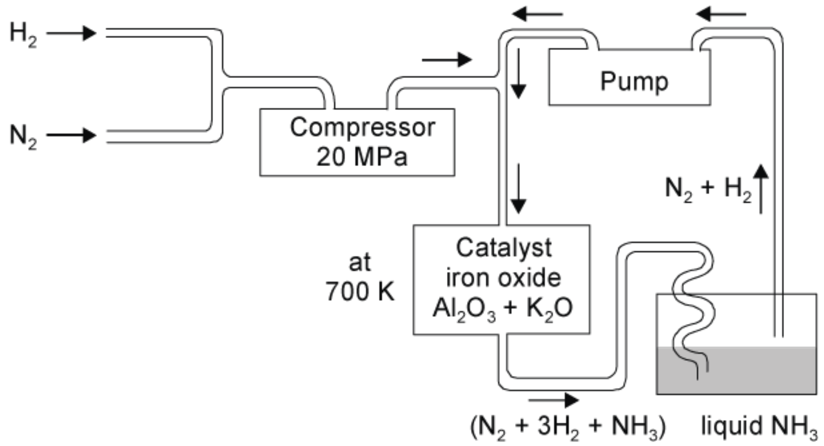
$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) : \Delta H = -46.1\ \text{kJ/mol.}$$

This reaction is reversible, exothermic and is accompanied by decrease in volume. Therefore, the most favourable conditions for maximum yield according to Le Chatelier's principle are:

(a) ***Low temperature:*** The optimum temperature has been found to be nearly 700 K.

(b) ***High pressure:*** The optimum pressure is nearly 200 atm.

(c) ***Catalyst:*** Finely divided iron with molybdenum as promoter is used as catalyst. The flow chart for the production of ammonia is shown.



S15. Ostwald's Process: In this process, conversion of ammonia to nitric acid is done through the following steps.

Step 1: *Oxidation of ammonia to nitric oxide.* Ammonia is oxidized by air in the presence of Pt catalyst to give nitric oxide.

$$\underset{\text{from air}}{4NH_3(g) + 5O_2(g)} \xrightleftharpoons[\text{500 K. 9 bar}]{\text{Pt. Rh guauge catalyst (9 : 1)}} 4NO(g) + 6H_2O(g) : \Delta H = -90 \text{ kJ}$$

Step 2: *Oxidation of NO to NO$_2$.* The nitric oxide is oxidized to nitrogen dioxide (NO_2) by air at temperature below 100°C.

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

Step 3: *Formation of nitric acid.* Nitrogen dioxide dissolves on water to give HNO_3.

$$3NO_2(g) + H_2O(l) \longrightarrow 2HNO_3(aq) + NO(g)$$

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.

S16. (a) HF > HCl > HBr > HI

(b) HI > HBr > HCl > HF

(c) $I^{\ominus} < Br^{\ominus} < Cl^{\ominus} < F^{\ominus}$

(d) HF < HCl < HBr < HI

(e) HF > HCl > HBr > HI

S17. (a) $Au + HNO_3 + 4HCl \longrightarrow H[AuCl_4] + NO + 2H_2O$

(b) $Pb(s) + 4O_3(g) \longrightarrow PbSO_4(s) + 4O_2(g)$

(c) $2Se_2Cl_2 \xrightarrow{\Delta} SeCl_4 + 3Se$

(d) $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$

(e) $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$

S18. (a) $XeF_4 + O_2F_2 \longrightarrow XeF_6 + O_2$

(b) $2XeF_2(s) + 2H_2O(l) \longrightarrow 2Xe(g) + 4HF(aq) + O_2(g)$

(c) $XeF_4 + PF_5 \longrightarrow [XeF_3]^{\oplus} [PF_6]^{\ominus}$

(d) $XeF_4 + SbF_5 \longrightarrow [XeF_3]^{\oplus} [SbF_6]^{\ominus}$

(e) $XeF_6 + NaF \longrightarrow Na[XeF_7]$

S19. (a) $P_4 + 3KOH + 3H_2O \longrightarrow \underset{\text{Phosphine}}{PH_3} + 3KH_2PO_2$

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

(c) $Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$

(d) $POCl_3 + 3H_2O \longrightarrow H_3PO_4 + 3HCl$

(e) $3HgCl_2 + 2PH_3 \longrightarrow Hg_3P_2 + 6HCl$

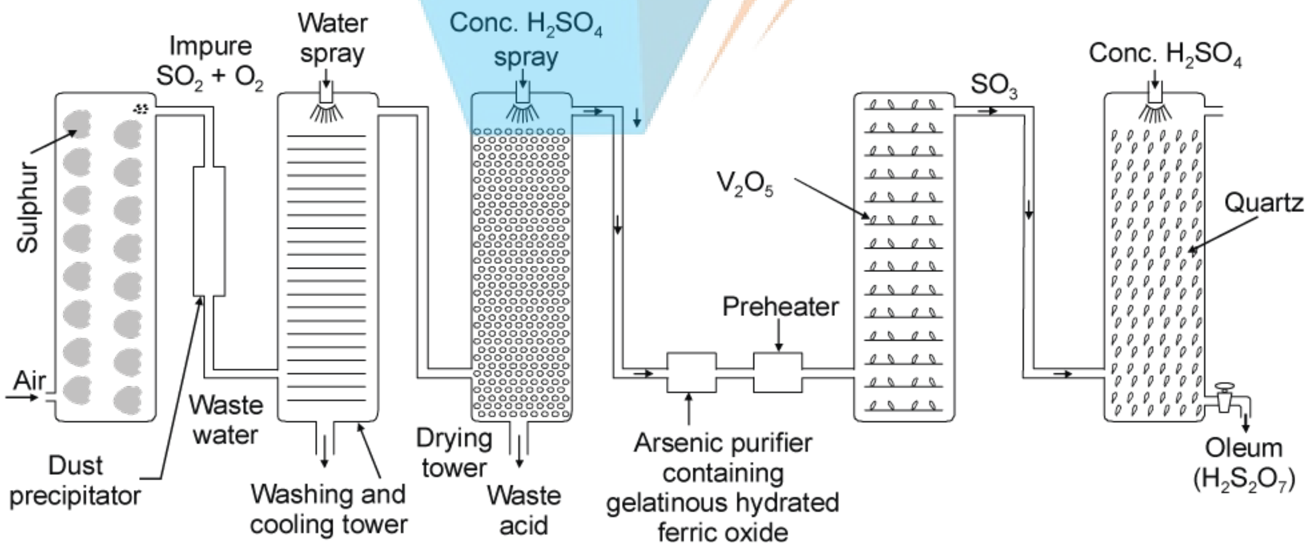
S20. Manufacture of sulphuric acid by contact process involves three steps:

(a) Burning of sulphur in air to generate SO_2.

(b) Conversion of SO_2 to SO_3 by oxidation with air in the presence of V_2O_5 as catalyst.

(c) Absorption of SO_3 in H_2SO_4 to obtain oleum $H_2S_2O_7$.

A flow diagram for the manufacture of H_2SO_4 is given below:

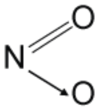
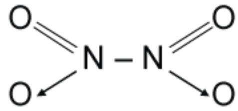


SO_2 produced by burning of sulphur is freed from dust and other impurities.

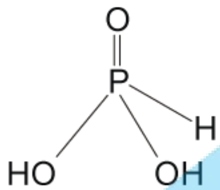
The plant is operated at a pressure of 2 bar and a temperature of 720 K. These are the optimum conditions for the conversion of SO_2 to SO_3, according to Le Chatelier principle.

SO_3 produced in the catalyst converter is absorbed in concentrated H_2SO_4 to produce oleum. Oleum is diluted with water to obtain H_2SO_4 of desired concentration.

Sulphuric acid obtained as above is 96-98% pure.

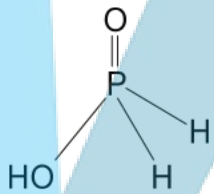
S21. (a)  has one unpaired electron, therefore, it is unstable and forms dimer, i.e., N_2O_4 whose structure is 

(b) H_3PO_3 has three H atoms and therefore, it is expected to be tribasic. However, in its structure, two hydrogen atoms are joined through oxygen atoms and are ionisable. The third H atom is linked to P and is non-ionisable.



$$H_3PO_3 \rightleftharpoons HPO_3^{2\ominus} + 2H^{\oplus}$$

(c) H_3PO_2 has one P = O, one P — OH and two P — H bonds as. Phosphorous has +1 oxidation state.



Since two H atoms are bonded directly to P atom which impart reducing character to the acid.

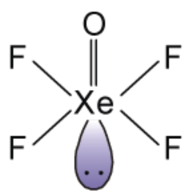
S22. (a) (i) $$Xe(g) + 2F_2(g) \xrightarrow[7\ \text{bar}]{873\ \text{K}} XeF_4(s)$$
1 : 5

(ii) $$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl.$$

(b) (i) Due to high electronegativity of oxygen, the O — H in H_2O forms strong intermolecular H — bonds. While other hydrides of group of 16 like H_2S do not form H — bonds. So, water has high stability as compared to H_2S.

(ii) It is because white phosphorus is a discrete P_4 molecule whereas red phosphorus is polymeric.

(c) Structure $XeOF_4$.



S23. (a) $2KClO_3 \xrightarrow[\Delta]{MnO_2} 2KCl + 3O_2$

MnO_2 lower the B.P. of $KClO_3$

(b) $P_4 + 3\,NaOH + 3H_2O \longrightarrow \underset{\text{Sodiumhydrophosphite}}{3\,NaH_2PO_2} + \underset{\text{phosphine}}{PH_3}$

(c) Oxygen Floride OF_2 oxygen has +2 oxidation state. Hydrogen peroxide H_2O_2 oxygen has –1 oxidation state.

(d) Oxygen is smaller in size and has ability to form $P\pi - P\pi$ multiple bond, and satisfy its octate forming (O $=$ O) O_2 molecule.

While S is bigger in size and has not ability to form $P\pi - P\pi$ multiple bond, satisfy its octate by forming (Puckered shape) S_8 molecule.

(e) F is highly electronegative hence F unpair the paired electron of sulphate to form SF_6 while H is electropositive in respect to sulphur and it cannot unpair to paired electron of sulphur to expained S oxidation state.

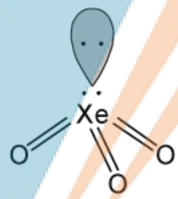
S24. (a) Due to sterically protection of six F atom, which donot allow to water molecules to attack on sulphur and due to steric repulsion of F at SF_6 thermodynamically unstable.

(b) Due to higher electron-density on F, the bond length of F–F increase due to electron-electron repulsion and B.d.E. decrease while Cl is bigger in size and has less electron-density and has not electron-electron repulsion in Cl_2 and bond length is comparatively shorter than F_2.

(c) Shape of XeO_3

Hybridization sp^3

Shape - Bent pyramidal



(d) $XeF_6 + KF \longrightarrow K^{\oplus}[XeF_7]^{\ominus}$

(e) $H_2O > H_2Te > H_3Se > H_2S$

S25. (a) Xe is noble gas, its ionization energy is much higher. F is highly electronegativity element it can unpair the paired electron of Xe to form covalence bond.

(b) XeF_2 is prepared in Lab in Nickel tube at 673 and 1 bar pressure.

$$Xe + F_2 \xrightarrow[\text{673 K, 1 bar}]{\text{Nickel tube}} XeF_2$$

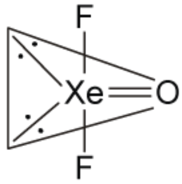
XeF_4 is prepared in Lab in nickel tube at 673 K and 7 bar pressure.

$$Xe + 2F_2 \xrightarrow[\text{673 K, 7 bar}]{\text{Nickel tube}} XeF_4$$

(c) $XeOF_2$

hybridization – sp^3d

shape – T–shape

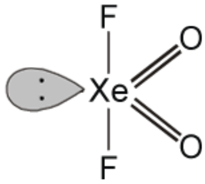


$XeOF_2$

XeO_2F_2

hybridization — sp^3d

shape — see-saw shape



XeO_2F_2