TOPIC : p-BLOCK ELEMENT (NITROGEN & OXYGEN FAMILY)
EXERCISE # 1

SECTION (A)

2 Melting point $\propto$ heat of atomization $\propto$ strength of metallic bond
Strength of metallic bond depends on number of mobile electrons per atom and size of atom.

3 $H_3\overset{3+}{P}O_3 \longrightarrow H_3\overset{5+}{P}O_4 + \overset{3-}{P}H_3$

4 Has one lone pair of electrons on central atom which they can donate to lewis acid and the order of basicity is :

$$NH_3 > PH_3 > AsH_3 > SbH_3$$

5 Nitrogen exhibits oxidation states in the range – 3 to + 5.

6 (2) Statement is correct .

7 The basic strength of the hydrides of group 15 elements down the group decreases with decrease in the electronegativity of the central atom according to Drago's rule.

9. From top to bottom in group 15, reducing character of hydrides increases due to decrease in thermal stability.

10. In nitrogen family all the elements show +5 oxidation state.

11. Oxidation state of molecular sulphur S_8 is zero
Oxidation state of sulphur in $S_2F_2 = 2x + 2(-1) = 0$; $2x = +2$ or $x = 1$
Oxidation state of sulphur in $H_2S = 2(+1) + x = 0$ or $x = -2$.

12. Allotropes differ in their crystal structures and physical properties but have same chemical properties.

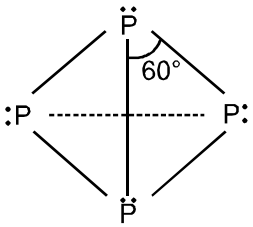
13. Black phosphorus is thermodynamically most stable form of phosphorus as it is a highly polymerised form of phosphorus. Hence it is least reactive.

14. The difference of electronegativities between nitrogen (V) and oxygen is least as compared to that of in the other oxides. On moving down the group acidic strength decreses.

15. Sb_4O_6 reacts with NaOH forming arsenite as well as HCl forming $SbCl_3$.

16. Down the group the X–H bond length increases with increase in size of atom. So bond dissociation energies decrease and thererfore, thermal stability decrease. Hence the correct decreasing order is $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$.

18.



19. $P_4 \xrightarrow[\text{low tempt. / sun light}]{250^\circ C \text{ or}}$ Red phosphorus.

SECTION (B)

1. $(NH_4)_2\ Cr_2O_7 \xrightarrow{\Delta} N_2 + 4H_2O + Cr_2O_3$

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

4. $4Zn + 10HNO_3 \longrightarrow 4Zn\ (NO_3)_2 + 5H_2O + N_2O$
Cu and Pb give NO with dilute HNO_3 and Au is not attached by dilute HNO_3.

5. $Fe^{2+} + 5H_2O + NO \longrightarrow [Fe(H_2O)_5NO]^{2+}$

6. $2Pb\ (NO_3)_2 \xrightarrow{673\ K} 2PbO + 4NO_2 + O_2$
$NaNO_3$ and KNO_3 gives their nitrites and O_2 where as NH_4NO_3 gives N_2O.

7. $H_2N_2O_2$ (two replaceable hydrogen) and thus form two series of salts.

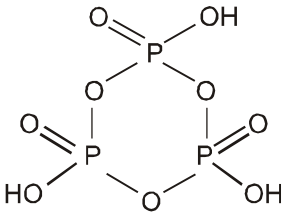
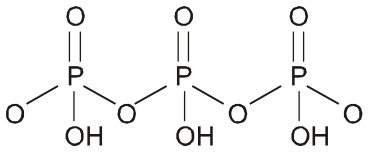
8. $P_4 + 2OHNO_3$ (concentrated) $\longrightarrow 4H_3PO_4 + 2ONO_2 + 4H_2O$.

9. Gold dissolves only in aquaregia.

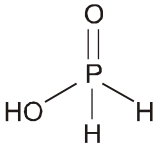
10. $4HNO_3 + P_4O_{10} \xrightarrow{250\ K} 4HPO_3 + N_2O_5$ (anhydride of HNO_3)

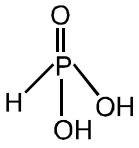
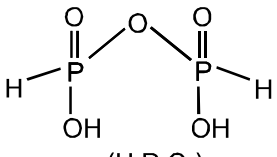
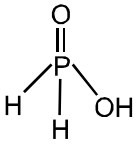
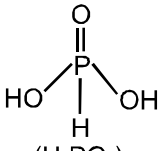
11. White phosphorus glows in dark and the phenomenone is known as chemiluminescnce.

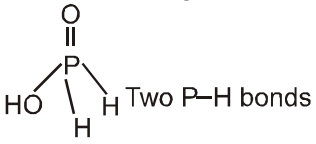
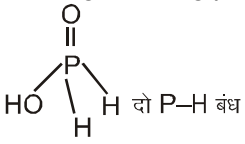
12. $P_4O_{10} + 6H_2O \longrightarrow 4H_3PO_4$

13.  ; 

14. Boiling point : NH_3 = 238.5 K , SbH_3 =254.6 K (due to higher mol. wt)

16. 
It has one replaceable hydrogen.

17.  (H_3PO_3) ;  $(H_4P_2O_5)$;  (H_3PO_2) ;  (H_3PO_4)

18. Acids containing P–H bonds have strong reducing properties.



SECTION (C)

1. (3) Increases from O to Te with increasing atomic number.

2. S and O-non-metals ; Po-metal ; Te and Se semi-metals.

9. Bond dissociation enthalpy decreases down the group with increasing H–E bond length with increasing size of atoms from O to Te.

15. Stability (Mono clinic < Rhombic)
Monoclinic and Rhombic sulphur have same puckered ring structure but they differs in crystalline structure.

16. KO_2 exists as K^+ and O_2^- ; so it is superoxide.
$2KO_2 + 2H_2O \longrightarrow 2KOH + H_2O_2 + O_2$

17. As water has H-bonding due to the presence of highly electronegative oxygen but H_2S does not (electronegativity of sulphur is low).

18. Factual

19. Most abundant element is earth crust is oxygen

SECTION (D)

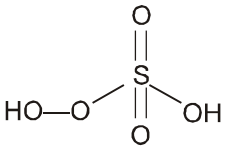
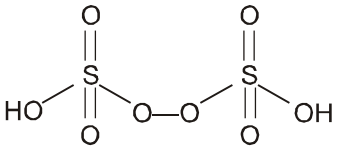
4. $AgNO_3 \xrightarrow{\Delta} Ag + NO_2 + ½O_2$; $2BaO_2 \xrightarrow{800°C} 2BaO + O_2$.
$Pb(NO_3)_2 \xrightarrow{\Delta} PbO + 2NO_2 + 1/2O_2$

7. There is ozone layer high above the earth atmosphere which prevents the UV rays of the sun reaching the earth surface.

8. $2Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + SO_2 + SO_3$

9. SO_2 acts as reducing agent only in presence of strong oxidising agent.

10. Lead chamber process, $2SO_2 + O_2$ (air) $+ 2H_2O + NO$ (catalyst) $\longrightarrow 2H_2SO_4 + NO$.

13.  ; 

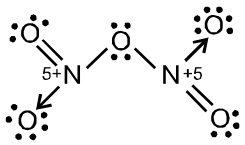
15. By absorbing UV radiations not γ-radiations.

17. $5O_3 + I_2 + H_2O \longrightarrow 2HIO_3 + 5O_2$

18. Mn is in +6 oxidation state and can be oxidised to +7, remaining salts can not be oxidised as central atoms are in their highest oxidation states.

20. $\overset{-1}{2HI} + \overset{+6}{H_2SO_4} \longrightarrow \overset{0}{I_2} + \overset{+4}{SO_2} + 2H_2O$
Thus H_2SO_4 oxidises HI to I_2.

EXERCISE # 2

1. 

Nitrogen uses three p-orbitals and one s-orbital for making bonds as it does not have d-orbital.

2. It is 2nd period element which does not contain d-orbitals.

3. $Al_2O_3 + 3C + N_2 \longrightarrow 2AlN + 3CO$
$2AlN + 3H_2O \longrightarrow Al(OH)_3 + NH_3$

4. $4NH_3 + 5O_2 \xrightarrow[800°C]{Pt} 4NO + 6H_2O$ (Ostwald's process of mfg. HNO_3).

5. $2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

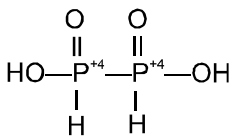
7. (1), (2) and (4) are correct statements. (3) red phosphours is insoluble in H_2O as well as CS_2.

8. $3CuSO_4 + 2PH_3 \longrightarrow Cu_3P_2 + 3H_2SO_4$

9. (1) It is slightly soluble in water ; the aqueous solution being neutral.
(2) The solution of PH_3 in water decomposes in presence of light giving red phosphorus and H_2.
(3) Phosphonium compounds are obtained when anhydrous phosphine reacts with anhydrous halogen acids (not in aqueous solution).
(4) Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

10. The spontaneous combustion of phosphine is technically used in Holme's samples. Containers containing calcium carbide and calcium phosphide are pierced and thrown in the sea when the gases evolved burn and serve as a signal.

11. $P_4O_6 + 6H_2O \longrightarrow 4H_3PO_3$
$P_4O_{10} + H_2O$
$H_3PO_3 + Br_2$, heat in a sealed tube.
White P_4 + Alkali

12. 

13. $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$

14. $P_4 + 3OH^- + 3H_2O \longrightarrow PH_3 + 3H_2PO_2^-$

15. All statements are correct.

16. (1) Neutralisation reaction
(2) Addition reaction
(3) SO_2 reduces Fe^{3+} to Fe^{2+} and itself oxidised to SO_4^{2-}.
(4) SO_2 acts as oxidising agent.

17. Down the group bond (H — E) dissociation enthalpy decreases as (H — E) bond length increases and thus thermal stability of hydrides also decreases.

18. Oxygen is soluble in alkaline pyrogallol and ozone dissolves in oil of cinnamon.

19. All three compounds act as bleaching agents ; SO_2 through reduction process whereas H_2O_2 and O_3 through oxidation process.

20. $SO_2 + 2H_2O \longrightarrow H_2SO_4 + 2H$

coloured matter $\underset{\text{Oxidation}}{\overset{\text{Reduction}}{\rightleftharpoons}}$ colourless matter.

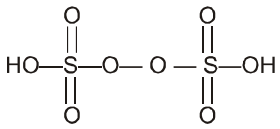
21. It dissolves in water forming H_2SO_3.

22. (1) $SO_2 + Cl_2 \xrightarrow{\text{charcoal}} \xrightarrow{\text{उत्प्रेरक पदार्थ}} SO_2Cl_2$

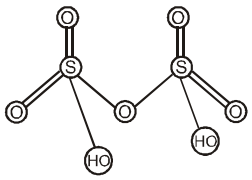
(2) $Cl_2 + SO_2 + 2H_2O \longrightarrow 2HCl + H_2SO_4$

(3) $3Mg + SO_2 \longrightarrow 2MgO + MgS$; $4K + 3SO_2 \longrightarrow K_2SO_3 + K_2S_2O_3$

23.



24.



Pyrosulphuric acid (Oleum)
($H_2S_2O_7$)

EXERCISE # 3
PART - I

1. Acidic nature of oxides decreases down a group. So, N_2O_5 is most acidic.
Another reason of acidic strength of N_2O_5 is that the electronegativity of N is maximum in the given V^{th} group elements. As we know that by increasing the electronegative. character, acidic nature increases.

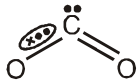
2. CN^- and CO are iso–electronic because they have equal number of electrons.
In CN^- the no. of electrons = 6 + 7 + 1 = 14
In CO the no. of electrons = 6 + 8 = 14

3. In SO_3^{2-} the S is sp^3 hybridised, so
In 'S' the three p–orbitals forms σ bonds with three oxygen atoms and unhybridised d–orbital is involved in π bond formation.
$_{16}O = 1s^2, 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$
In oxygen two unpaired p-orbitals are present, one is involved in σ bond formation while other is used in π bond formation.
Thus in SO_3^{2-}, $p\pi$ and $d\pi$ orbitals are involved for $p\pi - d\pi$ bonding.

5. The correct order of electron gain enthalpy

(electron affinity) is	O	<	S	<	F	< Cl
(electron affinity in eV)	O	<	S	<	F	< Cl
	1.48		2.07		3.45	3.61

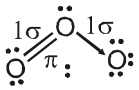
6. ClO_2 shows paramagnetic character due to presence of unpaired electron in its structure.



9. Fluorine has highest electron density among the four species mentioned as options. Hence it will have the greatest tendency to donate the electrons to proton.

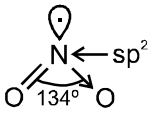
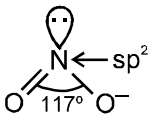
10. (1) SF_4 = irregular tetrahedral (sp^3d, one lone pair)
XeF_4 = square planar, sp^3d^2, two lone pair
(2) SO_3^{2-} = pyramidal (sp^3, one lone pair)
NO_3^- = trigonal planar (sp^2)
(3) BF_3 = trigonal planar (sp^2)
NF_3 = pyramidal (sp^3 one lone pair)
(4) BrO_3^- = pyramidal (sp^3, one lone pair)
XeO_3 = pyramidal (sp^3, one lone pair).

11. In case of single bond, there is only one σ bond, in case of double bond, there is one σ and one π bond while in case of triple bond, there is one σ and two π bonds. Thus, angular shape of ozone (O_3) contains 2σ and 1 π bond as.



12.

	NO_2^+	> NO_2	> NO_2^-	(bond angle)
Bond angle	180º	134º	117º	

O = $\overset{+}{N}\overset{sp}{}$ = O (bond angle = 180º)  

13. The oxidation state can be calculated as :

$H_4P_2O_5$
$+4 + 2x + 5(-2) = 0$
$2x - 6 = 0$
$x = +3$
$H_4P_2O_6$
$+4 + 2x + 6(-2) = 0$
$2x - 8 = 0$
$x = +4$
$H_4P_2O_7$
$+4 + 2x + 7(-2) = 0$
$2x = 10$
$x = +5$

14. $Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + SO_3$

15. If acidic nature is high, Ka is high and PK_a is low

$H_2O < H_2S < H_2Se < H_2Te$	Acidic nature (Order of K_a)
$H_2O > H_2S > H_2Se > H_2Te$	Order of PK_a

16. $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + H_2O$

$Zn(ClO_3)_2 \xrightarrow{\Delta} ZnCl_2 + O_2$

$KClO_3 \xrightarrow{\Delta} KCl + O_2$

$K_2Cr_2O_7 \xrightarrow{\Delta} K_2CrO_4 + Cr_2O_3 + O_2$

17. $H_2O < H_2S < H_2Se < H_2Te$ (acidic strength)

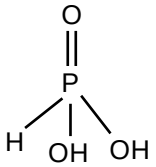
18. O_3 is reduced into O^{-2} ion and
Ag_2O is reduced to Ag so
H_2O_2 is reducing agent in both (a) and (b)

19. SO_2 is used as a food preservatives but NO_2 does not

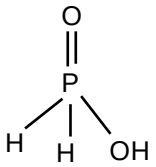
$$Cu + \underset{\text{conc}}{4HNO_3} \longrightarrow Cu(NO_3)_2 + \underset{\text{Brown gas}}{2NO_2} + 2H_2O$$

21.
$$\begin{cases} Cu + \text{conc } HNO3 \longrightarrow NO_2 \\ Cu + \text{dil } HNO3 \longrightarrow NO \end{cases}$$

22. Phosphoric acid (Phosphonic acid) H_3PO_3 (dibasic)



Hypophosphorous acid (Phosphinic acid) H_3PO_2 (monobasic)



23. Reaction of CaC_2 and nitrogen at 1100ºC form nitrolim (calcium cyanamide and carbon mixture).

$$CaC_2 + N_2 \longrightarrow CaCN_2 + C$$

(No answer in matching)

24. $KMnO_4$ is an oxidising so it can oxidise SO_2 readily.

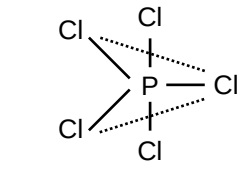
$KMnO_4 + SO_2 \rightarrow Mn^{2+} + SO_3$

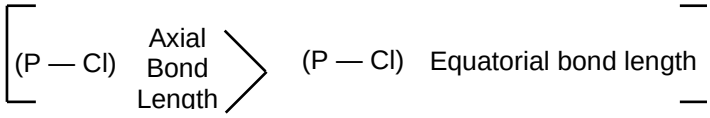
NO_2 is strong oxidising agent, CO_2 is neither oxidising agent nor reducing agent,

25. Decreasing order of oxidation states is : HNO_3, NO, N_2, NH_4Cl

		Oxidation Number of N
HNO_3,	:	+5
NO,	:	+2
N_2,	:	0
NH_4Cl	:	–3

26. It is reactive gas as easily provide Cl_2 gas





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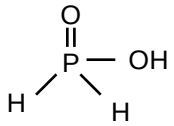
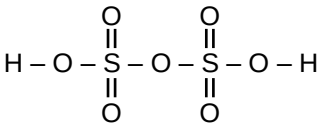
27. In oxygen family down the group thermal stability decreses
order of thermal stability
$H_2O > H_2S > H_2Se > H_2T > H_2Po$]
This is because M–H bond dissociation energy decreases down the group with the increase in the size of central atom

28. H_3PO_2



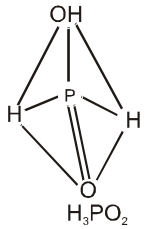
Having two reducing hydrogen atom.

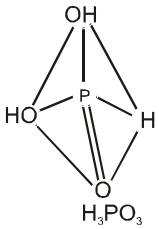
29. Oleum = $H_2S_2O_7$

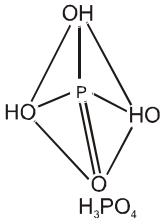


PART - II

1. H_3PO_4, H_3PO_3 and H_3PO_4 are oxyacids of phosphorus. In all these acids, the central atom (P) is sp^3 hybridised and is surrounded by neghbouring atom tetrahedrally.



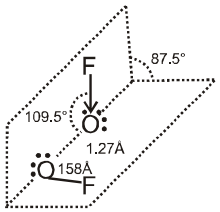




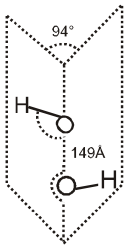
H_3PO_4 — Monobasic
H_3PO_3 — Dibasic
H_3PO_4 — Tribasic

2. The order of heat of vaporisation or boiling point of the following hydrides of VA group elements is
$BiH_3 > SbH_3 > NH_3 > AsH_3 > PH_3$
Boiling point increase with increase in molecular mass hence, boiling point of BiH_3 should be maximum and that of NH_3 should be minimum. But NH_3 highest boiling point because of H-bond present in NH_3.

3. Structure of O_2F_2 is similar to that of H_2O_2 i.e., non-linear and non-planar.



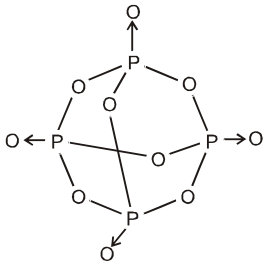
O_2F_2 molecule



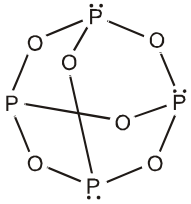
H_2O_2 molecule

4. The common oxidation state of elements of V A group are +3 and +5. In addition nitrogen also exist in +1, +2, and +4 oxidation states in its oxide, viz N_2O, NO, N_2O_3 , NO_2 and N_2O_5 , However due to inert pair effect, bismuth does not exist in +5 oxidation state. Thus nitrogen exist in all oxidation state +1 to +5.

5. The structure of P_4O_{10} and P_4O_6 are as follows :



(P_4O_{10})



(P_4O_6)

Hence, number of P–O–P bridges is 6 in both.

7. $P_2O_5 + 2HNO_3 \rightarrow 2HPO_3 + N_2O_5$

8. $\sigma_b^2\sigma\ {}^{*2}_{a}\ \sigma_a^{*2} = (\pi_b^2 = \pi_b^2)$

σ_b^1 (N_2^+ = 13 electrons) it contains one unpaired electron hence paramagnetic.

9. ON of S in S_8 = 0

ON of S in S_2F_2 = + 1

ON of S in H_2S = – 2

10.

$$\underset{\text{Acidic}}{P_4O_{10} + 2H_2O} \longrightarrow \underset{\text{meta phosphoric acid}}{4HPO_3} \xrightarrow[\text{basic}]{NH_3} \underset{\text{meta ammonium phosphate}}{NH_4PO_3}$$

11. Ozone layer acts as a shield and does not allow ultraviolet radiation from sun to reach earth. It does not prevent infra-read radiation from sun to reach earth, thus option (4) is wrong statement and so it is the correct answer.

12. **(1)** Both assertion and reason are true. reason is the correct explanation of assertion.

$$\underset{\text{(metal (conc.)}}{M + HNO_3} \rightarrow \underset{\text{(metalnitrate)}}{MNO_3} + \underset{\text{(nascenthydrogen)}}{H}$$

$$2HNO_3 + \underset{\text{(nasenthydrogen)}}{2H} \rightarrow 2NO_2 + 2H_2O$$

16. N_2O_5 in solid form exists as NO_3^- & NO_2^-

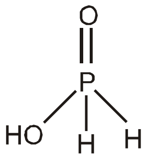
17. In HCOOH $\xrightarrow{H_2SO_4}$ $H_2O + CO$

H_2SO_4 behaves like dehydrating agent.

18. N_2 from azide is also produced by NaN_3. Hence mass of Ba is irrelevant.

19. Black P has graphite like network structure.

PART - III

1. Hypophosphorus acid 

Number of hydrogen atom(s) attached to phosphorus atom is 2 which are called as reducing hydrogen.

2. $\overset{-1}{2HI} + H_2\overset{+6}{S}O_4 \rightarrow \overset{0}{I_2} + \overset{+4}{S}O_2 + 2H_2O$

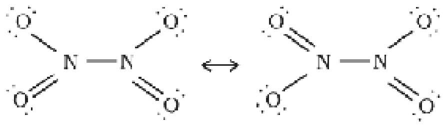
(reduction: $S^{+6} \rightarrow S^{+4}$; oxidation: $I^{-1} \rightarrow I^{0}$)

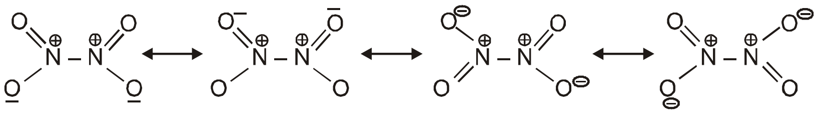
3. $(NH_4)_2SO_4 + 2H_2O \rightarrow (2H^+ + SO_4^{2-}) + 2NH_4OH$
Strong acid Weakbase
$(NH_4)_2$ SO_4 on hydrolysis produces strong acid H_2SO_4, which increases the acidity of the soil.

4.* The stability of hydrides decreases from NH_3 to BiH_3 which can be observed from their bond dissociation enthalpy. The correct order is $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$.

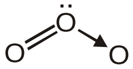
Property	NH_3	PH_3	AsH_3	SbH_3	BiH_3
$\Delta_{diss}H^{\ominus}(E–H)$ / kJ mol^{-1}	389	322	297	255	–

Alternate Solution
N_2O_4 may has four resonating structure but in NCERT only two resonating structure .
Resonating structures of N_2O_4 are





5. Sulphur exhibit + 2, + 4, + 6 oxidation states but + 4 and + 6 are more common.

6. (All statement are correct there is no answer).
(1) ONCl = 8 + 7 + 17 = 32e$^-$
ONO$^-$ = 8 + 7 + 8 + 1 = 24e$^-$ (correct)
(2)  Central atom O is sp^2 hybridised with 1 lone pair, so bent shape (correct)
(3) Ozone is violet-black in solid state. (Ref. NCERT & shriver atkins)
(4) O_3 has no unpaired electrons, so diamagnetic (correct)

7. NO is paramagnetic in gaseous state.

8. H_2O_2 can undergo reduction as well as oxidation because oxidation number of oxygen in H_2O_2 is –1. So, it can act both as reducing agent and oxidising agent.

12. (1) $NH_4NO_2 \xrightarrow{\Delta} N_{2(g)} + 2H_2O_{(\ell)}$

(2) $(NH_4)_2SO_4 \xrightarrow{\Delta} 2NH_{3(g)} + H_2SO_4$

(3) $Ba(N_3)_2 \xrightarrow{\Delta} Ba(s) + 3N_{2(g)}$ (Pure) ¼ग्रा०½

(4) $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_{2(g)} + Cr_2O_{3(s)} + 4H_2O_{(\ell)}$