PHYSICAL / INORGANIC CHEMISTRY

DPP
DAILY PRACTICE PROBLEMS

DPP No. 36

Total Marks : 46

Max. Time : 50 min.

Topic : p-block elements (Nitrogen and Oxygen family)

Type of Questions		M.M., Min.
Single choice Objective ('–1' negative marking) Q.1 to Q.8	(3 marks, 3 min.)	[24, 24]
Subjective Questions ('–1' negative marking) Q.9 to Q.11, Q.14	(4 marks, 5 min.)	[16, 20]
Comprehension ('–1' negative marking) Q.12 to Q.13	(3 marks, 3 min.)	[6, 6]

1. White phosphours has :

(A) six P – P single bonds (B) four lone pairs of electrons

(C) PPP angle of 60ºC (D) all of these

2. Consider the following statements.

(i) β–black phosphorus is a good conductor of electricity

(ii) Metalloids like Sb and As do form their corresponding metal oxy acid with concentrated HNO_3.

(iii) Lead nitrate on heating at a temperature of 673 K liberates only oxygen gas.

(A) (i) and (ii) are correct only (B) (iii) and (iv) are correct only

(C) (i), (iii) and (iv) ae correct only (D) all are correct.

3. **(a)** The decrease stability of higher oxidation state in p–block with increasing atomic number is due to:

(A) decrease in bond energy as going down the group.

(B) energy required to unpair ns^2– electrons is not compensated by the energy released in forming the two additional bonds.

(C) both are correct.

(D) none is correct.

(b) In group 15, the melting points of the elements :

(A) increase regularly on moving down the group.

(B) decrease regularly on moving down the group.

(C) first decrease upto As and then increase to Bi.

(D) first increase form N to As and then decrease to Bi.

4. The thermal stability of the hydrides of group 15 follows the order :

(A) $NH_3 < PH_3 < AsH_3 < SbH_3 < BiH_3$ (B) $NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

(C) $PH_3 > NH_3 > AsH_3 > SbH_3 < BiH_3$ (D) $AsH_3 < PH_3 > SbH_3 > BiH_3 > NH_3$

5 Which of the following order(s) is / are incorrect ?

(A) $H_3PO_4 > H_3PO_3 > H_3PO_2$ (reducing character)

(B) $N_2O < NO < N_2O_3 < N_2O_5$ (oxidation state on nitrogen atom.)

(C) $NH_3 > PH_3 > AsH_3 > SbH_3 \geq$ (basicity.)

(D) $SbH_3 > NH_3 > AsH_3 > PH_3$ (reducing character.)

6. Consider the following statements

S_1 : Ammonia on heating with concentrated solution of sodium hypochlorite gives N_2H_4.

S_2 : The phosphine gas dissolves in water in presence of sunlight and produces phosphonium hydroxide like ammonium hydroxide.

S_3 : Barium azide on heating gives pure nitrogen gas.

S_4 : The oxo-acids of phosphorus in which phosphorus has lower oxidation state less than +5 contain either P–P or P–H bonds but not both in addition to P=O and P–OH bonds.

and arrange in the order of true/false.

(A) T F T T (B) F F T T (C) T T T F (D) T F T F

7. **Statement-1 :** NO_2 and ClO_2 both being odd electron molecules dimerise.
Statement-2 : On dimerisation, NO_2 is converted to stable N_2O_4 molecule with even number of electrons.
(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

8. **Statement-1 :** The order of densities of the various allotropes of phosphorus is as follows; black phosphorus > red phosphorus > white phosphorus because
Statement-2 : As tendency of polymerisation increases, the compactness of substance also increases.
(A) Statement 1 and statement 2 are correct and statement 2 is the correct explanation of statement 1.
(B) Statement 1 and statement 2 are correct but statement 2 is not the correct explanation of statement 1.
(C) Statement 1 is correct while statement 2 is false.
(D) Statement 1 is false while statement 2 is correct.

9. Explain the following.
(a) Single N–N bond is weaker than the single P–P bond.
(b) BiH_3 is the strongest reducing agent amongst all the hydrides.
(c) SbH_3 has higher boiling point than NH_3.

10. **(a)** Give the disproportionation reaction of HNO_2 and H_3PO_3 ?

(b) What happens when ?
(A) White phosphorus reacts with thionyl chloride.
(B) Sulphur dioxide is chlorinated using PCl_5

11. Match the following (one or more than one)

Column - I	**Column - II**
(A) $H_3PO_2 \xrightarrow[\text{(ii) } 435K]{\text{(i) } 415K}$	(p) One of the products acts as reducing agent.
(B) $PCl_3 + H_2O \xrightarrow{435K}$	(q) One of the products is tribasic and non reducing.
(C) $NO_2 + H_2O \longrightarrow$	(r) Dehydration
(D) $HNO_3 + P_4O_{10} \xrightarrow{\Delta}$	(s) In one of the products the central atom is in +5 oxidation state.

Comprehension # (Q.12 to Q.13)

Turning to indicators used in titrations by the oxidation-reduction reaction, we must first work that in some cases it is possible to do without them if the colour of the titration solution undergoes a sharp enough change as the result of the reaction.

Titration without indicator is possible, for example, various reducing agents are oxidised by MnO_4^- in acid solution. We know that the purple-violet colour of MnO_4^- ion disapperas owing to reduction to the almost colourless Mn^{2+} ion. When all the reducing agent has been titrated a single excess drop of MnO_4^- colours the whole solution a distinct pink.

Similarly, reducing agents can be titrated with iodine solution without the use of indicators, because the dark brown colour of iodine disappears as a result of reduction of I_2 to I^-.However, since the colour of I_2 solutions is not very deep, it is convenient in such cases to use an indicator starch solution, which gives an intense blue colour even with very small amount of free iodine. The use of starch is based on its ability to form a blue adsorption compound with iodine, and is unrelated to the oxidising properties of I_2.

Redox indicators are substances which can be reversibly oxidised or reduced with different colours in the oxidised and reduced forms.

The interconversion can be represented as.

$$Ind_{ox} + ne \rightleftharpoons Ind_{red}$$

Applying the nernst equation to it, we have

$$E = E^{\circ} + \frac{0.059}{n} \log \frac{[Ind_{ox}]}{[Ind_{red}]}$$

If we add 1-2 drops of a solution of some redox indicator to a solution of reducing (or oxidising) agent, the $[Ind_{ox}]$ and $[Ind_{red}]$ will be in the ratio of corresponding potential of the solution. The solution acquires colour corresponding to the ratio. However our eye only detect the colour of one form if the concentration of the given form minimum ten times to the concentration of other form.

12. Diphenylamine is an redox indicator having $E^{\circ} = 0.76$ V. For any given reaction n = 2. Within what potential difference diphenylamine changes it colour ?

(A) 0.66 V to 0.86 V (B) 0.7895 V to 0.7306 V

(C) 0.75 V to 0.77 V (D) None of these

13. What is the range of redox indicator ferroin ? The oxidised form of ferroin is $Fe(C_{12}H_8N_2)_3^{3+}$ (pale blue). The reduced form of ferroin is $Fe(C_{12}H_8N_2)_3^{2+}$ (red). For ferroin $E^{\circ} = 1.14$ V

(A) From 1.081 V to 1.199 V (B) From 1.1105 V to 1.199 V

(C) From 0.963 V to 1.317 V (D) From 1 V to 2 V

14. Find the volume of gases evolved by passing 0.965 A current for 1 hr through an aqueous solution of CH_3COONa at $25^{\circ}C$ and 1 atm.

Answer Key

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1. (D) **2.** (A) **3.** **(a)** (C) **(b)** (D) **4.** (B) **5** (A,D)

6. (A) **7.** (D) **8.** (A)

9. (a) High interelectronic repulsion of the non–bonding electrons owing to the small bond length ($\dot{N} \equiv \dot{N}$).

(b) Least $\Delta_{dissociation}H(E - H)$ bond.

(c) SbH_3 higher molecular weight leading to higher vander Waal's force of attraction (by magnitude).

10. **(a)** $3\,HNO_2 \longrightarrow H\,NO_3 + H_2O + 2\,NO$

$4\,H_3PO_3 \longrightarrow 3\,H_3PO_4 + PH_3$

(b) (A) $P_4 + 8SOCl_2 \longrightarrow 4PCl_3 + 4SO_2 + S_2Cl_2$

(B) $SO_2 + PCl_5 \longrightarrow SOCl_2 + POCl_3$

11. (A – p, q, s); (B – p, q, s) ; (C – p, s); (D – r, s) **12.** (B) **13.** (A) **14.** V = 1.763 L

Hints & Solutions

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2. (i) Graphite like layered structure.

(ii) $Sb + 5HNO_3 \longrightarrow H_3SbO_4 + 5NO_2 + H_2O$

(iii) $2Pb(NO_3)_2 \xrightarrow{673K} 2PbO + 4NO_2 + O_2$

4. Down the group $\Delta_{dissociation}H(E-H)$ bond decreases.

6. S_1 - N_2H_4 is formed in aqueous dilute solution in presence of glue or gelatin.

S_2 - PH_3 solution in water explodes forming red phosphrous and H_2.

S_3 - $Ba(N_3)_2 \xrightarrow{\Delta} Ba + 3N_2\uparrow$

S_4 - $H_4P_2O_6$ = P – P bond, H_3PO_2 = P – H bond.

7. ClO_2 does not dimerise because odd electron is present in 'd' orbital and is declocalised not localised as in NO_2.

11. (A) $3H_3PO_2 \xrightarrow{415K} 2H_3PO_3 + PH_3\uparrow$

$4H_3PO_3 \xrightarrow{435K} 3H_3PO_4 + PH_3$

(B) $PCl_3 + 3H_2O \xrightarrow{Hydrolysis} H_3PO_3 + 3HCl$

$4H_3PO_3 \xrightarrow{435K} 3H_3PO_4 + PH_3\uparrow$

(C) $2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$

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

* PH_3 and HNO_2 act as reducing agents.

12. $E = 0.76 + \frac{0.0591}{2}\log\frac{10}{1}$

& $E = 0.76 + \frac{0.0591}{2}\log\frac{1}{10}$

13. $Fe(C_{12}H_8N_2)_3^{3+} + e^- \rightleftharpoons Fe(C_{12}H_8N_2)_3^{2+}$

range $= 1.14 \pm \frac{0.0591}{1}$

14. $2CH_3COONa \xrightarrow{Electrolysis} \underset{\text{at anode}}{C_2H_6 + 2CO_2} + \underset{\text{Cathode}}{H_2}$

Electric supplied $= \frac{0.965 \times 60 \times 60}{96500} = 3.6 \times 10^{-3}$ F

$V_{H_2} = \frac{3.6\times10^{-3}}{2} \times \frac{0.0821\times298}{1} = 0.44$ lit

$V_{total} = V_{C_2H_6} + V_{CO_2} + V_{H_2} = 4 \times 0.44 = 1.76$ lit.