#457729

Topic: Introduction to Nitrogen family - group 15 elements

Discuss the general characteristics of Group 15 elements with reference to their electronic configuration, oxidation state, atomic size, ionisation enthalpy and electronegativity

Solution

(1) Electronic configuration

Group 15 elements have 5 valence electrons with general electronic configuration ns^2np^3.

(2) Oxidation state

They have 5 valence electrons and to complete octet, they need 3 more electrons. This is difficult. Only N can do this as it has small size. Other elements show a formal oxidation state of -3 in covalent compounds. N, P show, -1 and -2 oxidation states apart from -3 oxidation state. All elements shows +3 and +5 oxidation states and the stability c +5 oxidation state decreases down a group and that of +3 oxidation state increases due to inert pair effect.

(3) Atomic size

With increase in the atomic number, the atomic size increases due to increase in the number of shells.

(4) Ionisation enthalpy

On moving down the group, first ionization energy decreases due to increase in size.

(5) Electronegativity

On moving down the group, electronegativity decreases due to increase in size.

#457730

Topic: Phosphorus and phosphine

Why does the reactivity of nitrogen differ from phosphorus?

Solution

Nitrogen forms $p\pi - p\pi$ multiple bonds with itself and with other elements having a small size and high electronegativity (such as C and O). Due to this, nitrogen molecule has $N \equiv N$ triple bond and is non-polar. It has very high dissociation energy (941.4 kJ) and is less reactive under normal conditions. Whereas P is more reactive as it forms P-P sing bonds.

#457731

Topic: Introduction to Nitrogen family - group 15 elements

Discuss the trends in chemical reactivity of group 15 elements.

Solution

The trends in chemical reactivity of group 15 elements are given below:

(i) Reactivity with hydrogen: Group 15 elements form hydrides of the type EH_3 where E is group 15 element. On moving down the group, the stability of hydrides decreases.

(ii) Reactivity with oxygen: Group 15 elements form the oxides E_2O_3 and E_2O_5. In the oxide, when the oxidation state of group 15 element is higher, it is more acidic than the one with lower oxidation state. On moving down the group, the acidic character decreases.

(iii) Reactivity with halogens : Group 15 elements form the salts EX_3 and EX_5. Nitrogen only forms NX_3 but not NX_5 as it lacks the d-orbital. NX_3 is unstable and other trihalides are stable.

(iv) Reactivity towards metals: Group 15 elements form binary compounds with metals. In these compounds, the oxidation state of metal is -3.

#457732

Topic: Introduction to Nitrogen family - group 15 elements

Why does NH_3 form hydrogen bond but PH_3 does not?

Solution

N has small atomic size and high electronegativity. Hence, NH_3 can form hydrogen bonds. P has large size and low electronegativity. Hence, PH_3 cannot form hydrogen bonds.

#457733

Topic: Nitrogen

How is nitrogen prepared in the laboratory? Write the chemical equations of the reactions involved.

Solution

To prepare nitrogen in laboratory, aqueous ammonium chloride is treated with sodium nitrite.

$NH_4Cl(aq) + NaNO_2(aq) \rightarrow N_2(g) + NaCl(aq) + 2H_2O(l)$

Impurites of NO and HNO_3 formed during the reaction can be removed by passing the gas through a mixture of aqueous sulphuric acid and potassium dichromate.

#457734

Topic: Ammonia

How is ammonia manufactured industrially?

Solution

Haber's process is used for manufacturing ammonia.

$N_2(g) + 3_2(g) \rightleftharpoons 2NH_3(g)\ \Delta_f H^o = -46.1\ kJ/mol$

Optimum conditions (to obtain maximum yield of ammonia) are around 200 atm pressure, 700 K temperature and a catalyst containing iron oxide with small amounts of K_2O and Al_2O_3. The reaction is reversible exothermic reaction and optimum conditions mentioned above are in accordance with Le Chatelier's principle.

#457735

Topic: Nitric acid and oxides of nitrogen

Illustrate how copper metal can give different products on reaction with HNO_3.

Solution

Copper reacts with conc. HNO_3 to form copper nitrate and nitrogen dioxide.

$Cu + 4HNO_3(conc.) \rightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

Copper reacts with dilute nitric acid to form copper nitrate and nitric oxide.

$3Cu + 8HNO_3 \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$

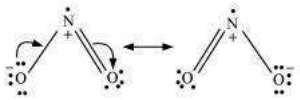
#457736

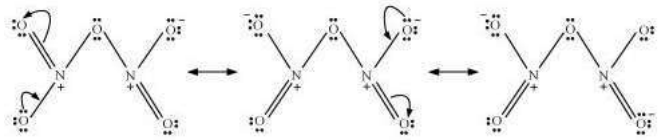
Topic: Nitric acid and oxides of nitrogen

Give the resonating structures of NO_2 and N_2O_5

Solution

The resonating structures are as shown.





#457737

Topic: Introduction to Nitrogen family - group 15 elements

The HNH angle value is higher than $HPH, HAsH$ and $HSbH$ angles. Why?

Solution

The central atom in group 15 hydrides is sp^3 hybridized. One lone pair is present in one of the sp^3 hybrid orbital and the molecule has pyramidal geometry. On moving down tl group 15, atomic size increases and electronegativity decreases. The bond pairs of electrons become more and more away from the central atom. This decreases the repulsio in the bond pairs and decreases the bond angle.

#457738

Topic: Introduction to Nitrogen family - group 15 elements

Why does $R_3P=O$ exist but $R_3N=O$ does not ($R=$ alkyl group)?

Solution

Nitrogen cannot have covalency more than 4. Hence, $R_3N=O$ does not exist. But P can show covalency of 5. Hence, $R_3P=O$ exists.

Note: Nitrogen cannot form $d\pi - p\pi$ bonds but phosphorous can form $d\pi - p\pi$ bonds.

#457739

Topic: Ammonia

Explain why NH_3 is basic while BiH_3 is only feebly basic.

Solution

Both NH_3 and BiH_3 have a lone pair of electron on central atom which can be donated and imparts basic nature. N is small in size and the lone pair is concentrated on smal atom (more electron density) and can be easily donated. Hence, ammonia is basic. Bi has large size and lone pair is diffused over large atom (low electron density). Hence, donation of lone pair is not easy and BiH_3 is partly basic.

#457740

Topic: Phosphorus and phosphine

Nitrogen exists as diatomic molecule and phosphorus as P_4. Why?

Solution

Nitrogen has small atomic size. Two nitrogen atoms can be linked to each other by three covalent bonds to form : $N \equiv N$: The octet of both N atoms is completed. P has larg atomic size and little tendency to form triple bonds. It can complete its octet by sharing valency electrons with three other P atoms to form tetra-atomic P_4 molecule.

#457741

Topic: Phosphorus and phosphine

Write main differences between the properties of white phosphorus and red phosphorus.

Solution

Property	White phosphorous	Red phosphorous
Colour	White (on exposure, becomes yellow)	Dark red
State	Waxy solid	Brittle powder
Density	1.84 g/cm3	2.1 g/cm3
Ignition temperature	307 K	543 K
Chemical reactivity	Highly reactive	Less reactive

The differences are given above:

#457742

Topic: Introduction to Nitrogen family - group 15 elements

Why does nitrogen show catenation properties less than phosphorus?

Solution

$N-N$ single bond is weak as nitrogen has small size and lone pairs on two N atoms repel each other. Phosphorous has larger atomic size and the lone pairs on P repel to smaller extent. Thus, the strength of $P-P$ bond is greater than the strength of $N-N$ bond. High bond enthalpy of $P-P$ bond results in tendency for catenation.

#457743

Topic: Halides, oxides and oxoacids of phosphorus

Give the disproportionation reaction of H_3PO_3.

Solution

Disproportionation of phosphorous acid gives phosphoric acid and phosphine.

$4H_3PO_3 \rightarrow 3H_3PO_4 + PH_3$

#457744

Topic: Halides, oxides and oxoacids of phosphorus

Can PCl_5 act as an oxidising as well as a reducing agent? Justify.

Solution

In PCl_5, P has $+5$ oxidation state.

Phosphorous can show maximum oxidation state of $+5$. It cannot increase its oxidation state beyond 5. Hence, PCl_5 is not a reducing agent. PCl_5 is an oxidizing agent as P can decrease oxidation state from $+5$ to $+3$. Thus, PCl_5 oxidizes Ag to $AgCl$.

It also oxidizes Sn to $SnCl_4$.

#457745

Topic: Introduction to oxygen family - group 16 elements

Justify the placement of O, S, Se, Te and Po in the same group of the periodic table in terms of electronic configuration, oxidation state and hydride formation.

Solution

Group 16 elements (chalcogens) have six valence electrons each. They have general electronic configuration of ns^2np^4, where, n is the number of principal quantum number.

Highly electronegative oxygen shows -2 oxidation state (it gains 2 electrons and completes octet). Other oxidation states of oxygen include -1 (hydrogen peroxide), zero (dioxygen molecule) and +2 (oxygen difluoride). On moving down the group, the stability of -2 oxidation state decreases with decrease in the electronegativity of elements. For remaining elements of the group, d orbitals are available and they show an oxidation state of +2, +4 and +6.

Chalcogens form hydrides of type H_2E. Oxygen and sulphur form hydrides of type H_2E_2.

Group 16 hydrides are covalent in nature.

#457746

Topic: Introduction to oxygen family - group 16 elements

Why is dioxygen a gas but sulphur a solid?

Solution

Oxygen has small atomic size and high electronegativity. It forms $p\pi - p\pi$ double bonds, $O = O$. The inter-molecular forces are weak vander waals forces. Hence, oxygen is a gas. Whereas sulphur does not form stable $p\pi - p\pi$ bonds and does not exist as S_2 molecule. It forms S_8 molecules with puckered ring structure. Thus, each molecule contai $8S$ atoms linked by $S - S$ bonds. Thus, S atoms are strongly held and sulphur is a solid.

#457747

Topic: Introduction to oxygen family - group 16 elements

Knowing the electron gain enthalpy values for $O \rightarrow O^-$ and $O \rightarrow O^{2-}$ as -141 and $702\ kJ\ mol^{-1}$ respectively, how can you account for the formation of a large number of oxides having O^{2-} species and not O^-?

Solution

Oxygen has negative first electron gain enthalpy and positive second ionization enthalpy . Based on this, we should expect the formation of oxides with O^- species and not with O^{2-} species. However, in reality, most oxides have O^{2-} ion due to following reasons:

(i) O^{2-} has stable noble gas electronic configuration.

(ii) The lattice energy of O^{2-} is much higher than the lattice energy of O^-.

This more than compensates the higher energy required for removal of second electron from O^- to form O^{2-} and makes O^{2-} ion stable.

#457748

Topic: Ozone

Which aerosols deplete ozone?

Solution

Ozone depletion is caused by aerosol, freons which are chlorofluorocarbons.

#457749

Topic: Sulphur, sulphur dioxide and sulphuric acid

Describe the manufacture of H_2SO_4 by contact process?

Solution

The steps involved in the manufacture of sulphuric acid by contact process are as shown:

(1) Sulphur (or iron pyrites) are burnt in air to form sulphur dioxide.

$S + O_2 \rightarrow SO_2$

$4FeS_2 + 11O_2 \rightarrow 2Fe_2O_3 + 8SO_2$

(2) Catalytic oxidation of sulphur dioxide to sulphur trioxide.

$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3\ \Delta_r H^o = -196.6$kJ

The reaction is reversible and exothermic.

(3) Sulphur trioxide is dissolved in 98% sulphuric acid to form oleum (fuming sulphuric acid). $SO_3 + H_2SO_4 \rightarrow H_2S_2O_7$

(4) Oleum is diluted with water to form sulphuric acid of desired concentration.

$H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

#457750

Topic: Sulphur, sulphur dioxide and sulphuric acid

How is SO_2 an air pollutant?

Solution

Sulphur dioxide is an air pollutant.

On dissolution in rain water, SO_2 produces acid rain.

$$SO_2 + 0.5O_2 + H_2O \xrightarrow[particles]{soot} H_2SO_4$$

Acid rain contains sulphuric acid and nitric acid.

#457751

Topic: Introduction to Halogen Family - Group 17 elements

Why are halogens strong oxidising agents?

Solution

Halogens are strong oxidizing agents as they have strong tendency to accept electrons. The oxidizing strength decreases from fluorine to iodine.

#457752

Topic: Fluorine and chlorine

Explain why fluorine forms only one oxoacid, HOF.

Solution

Fluorine forms only one oxoacid, HOF due to small atomic size and high electronegativity. Fluorine cannot act as central atom in higher oxoacids.

#457753

Topic: Introduction to Nitrogen family - group 15 elements

Explain why inspite of nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.

Solution

Atomic size of oxygen is smaller than the atomic size of chlorine. Small atomic size favours hydrogen bond formation.

Hence, inspite of nearly the same electronegativity, nitrogen forms hydrogen bonding while chlorine does not.

#457754

Topic: Fluorine and chlorine

Write two uses of ClO_2.

Solution

Uses of chlorine dioxide are as follows:

(1) Bleaching agent for paper pulp and textiles.

(2) In water treatment.

#457755

Topic: Introduction to Halogen Family - Group 17 elements

Why are halogens coloured?

Solution

Halogens absorb radiation in the visible region and excites electrons to higher energy levels. Thus, fluorine being smallest with maximum effective nuclear charge, absorbs hig

energy violet lite and appears pale yellow. Iodine with large size and less effective nuclear charge, absorbs low energy yellow light and appears dark violet.

#457756

Topic: Fluorine and chlorine

Write the reactions of F_2 and Cl_2 with water.

Solution

The reaction of fluorine with water is vigorous.

$2F_2 + 2H_2O \rightarrow 4HF + O_2$
$3F_2 + 3H_2O \rightarrow 6HF + O_3$

The reaction of chlorine with water is slow.

$2Cl_2 + 2H_2O \rightarrow 4HCl + O_2$

#457757

Topic: Hydrogen chloride

How can you prepare Cl_2 from HCl and HCl from Cl_2? Write reactions only.

Solution

(1) HCl is oxidized to chlorine (in Deacon's process) by atmospheric oxygen in presence of cupric chloride catalyst at 723 K.

$4HCl + O_2 \xrightarrow{CuCl_2} 2Cl_2 + 2H_2O$

(2) Hydrogen combines with chlorine to form HCl.

$H_2 + Cl_2 \rightarrow 2HCl$

#457758

Topic: Introduction to Inert gases - group 18 Elements

What inspired N. Bartlett for carrying out reaction between Xe and PtF_6?

Solution

PtF_6, a powerful oxidizing agent combines with oxygen to form $O_2^+[PtF_6]^-$. This shows that PtF_6 has oxidized O_2 to O_2^+.

Following are the similarities between oxygen and xenon:

(i) They have similar first ionization enthalpies, 1170 kJ/mol and 1166 kJ/mol for oxygen and xenon respectively.

(ii) The molecular diameter of oxygen and the atomic radius of Xe are similar (4 Angstroms).

This inspired N. Bartlett to carry out reaction between Xe and PtF_6.

#457759

Topic: Introduction to Nitrogen family - group 15 elements

What are the oxidation states of phosphorus in the following:

(i) H_3PO_3 (ii) PCl_3 (iii) Ca_3P_2 (iv) Na_3PO_4 (v) POF_3?

Solution

The oxidation states of phosphorus in $H_3PO_3, PCl_3, Ca_3P_2, Na_3PO_4$ and POF_3 are $+3,\ +3,\ -3,\ +5$ and $+5$ respectively.

#457760

Topic: Fluorine and chlorine

Write balanced equations for the following:

(i) $NaCl$ is heated with sulphuric acid in the presence of MnO_2.

(ii) Chlorine gas is passed into a solution of NaI in water

Solution

The balanced reaction when NaCl is heated with sulphuric acid in the presence of MnO_2.

(i) $4NaCl + MnO_2 + 4H_2SO_4 \rightarrow MnCl_2 + 4NaHSO_4 + 2H_2O + Cl_2$

The balanced reaction when chlorine gas is passed into the solution of NaI in water.

(ii) $2NaI + Cl_2 \rightarrow 2NaCl + I_2$

#457761

Topic: Introduction to Inert gases - group 18 Elements

How are xenon fluorides $XeF_2,\ XeF_4$ and XeF_6 obtained?

Solution

The preparation of xenon fluorides are given below:

$Xe(g, excess) + F_2(g) \xrightarrow[1\ bar]{673\ K} XeF_2(s)$

$Xe(g, 1mole) + 2F_2(g, 5\ moles) \xrightarrow[7\ bar]{873\ K} XeF_4(s)$

$Xe(g, 1\ mole) + 3F_2(g, 20\ moles) \xrightarrow{60-70\ bar} XeF_6(s)$

#457762

Topic: Introduction to Halogen Family - Group 17 elements

With what neutral molecule is ClO^- isoelectronic? Is that molecule a Lewis base?

Solution

ClO^- is isoelectronic with ClF. It is a Lewis base.

#457763

Topic: Introduction to Inert gases - group 18 Elements

How are XeO_3 and $XeOF_4$ prepared?

Solution

Hudrolysis of XeF_6 can give XeO_3 and $XeOF_4$. The reactions are given below:

$XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$
$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

#457764

Topic: Fluorine and chlorine

Arrange the following in the order of property indicated for each set:

(i) F_2, Cl_2, Br_2, I_2 - increasing bond dissociation enthalpy.

(ii) HF, HCl, HBr, HI - increasing acid strength.

(iii) $NH_3, PH_3, AsH_3, SbH_3, BiH_3$ increasing base strength

Solution

(i) $I_2 < F_2 < Br_2 < Cl_2$

(ii) $HF < HCl < HBr < HI$

(iii) $BiH_3 < SbH_3 < AsH_3 < PH_3 < NH_3$

#457765

Topic: Introduction to Inert gases - group 18 Elements

Which one of the following does not exist?

(i) $XeOF_4$ (ii) NeF_2 (iii) XeF_2 (iv) XeF

Solution

NeF_2 does not exist as it doesn't have d orbitals to accommodate F^- electrons.

#457766

Topic: Introduction to Inert gases - group 18 Elements

Give the formula and describe the structure of a noble gas species which is isostructural with:

(i) ${ICl_4}^-$ (ii) ${IBr_2}^-$ (iii) ${BrO_3}^-$

Solution

(i) XeF_4 is isostructural with ICl_4^-. It is square planar due to sp^3d^2 hybridization which results in octahedral geometry with two lone pairs occupy opposite positions.

(ii) XeF_2 is isostructural with IBr_2^-. It has a linear shape due to sp^3d hybridization which results in trigonal bipyramidal geometry with 3 lone pairs in equatorial plane.

(iii) XeO_3 is isostructural with BrO_3^-. It has a pyramidal shape due to sp^3 hybridisation with terahedral geometry in which one position is occupied by a lone pair.

#457767

Topic: Introduction to Inert gases - group 18 Elements

Why do noble gases have comparatively large atomic sizes?

Solution

The noble gases have comparatively large atomic sizes as the atomic radii corresponds to Van der waals radii which are always large.

#457768

Topic: Introduction to Inert gases - group 18 Elements

List the uses of neon and argon gases.

Solution

Uses of Neon:

(i) To fill discharge tubes for optical decorations and advertisements.

(ii) In neon bulbs, botanical gardens and green houses.

(iii) It can carry extremely high currents even under high voltage. Hence, it is used in safety devices for protecting electrical instruments such as voltmeters, relays, rectifiers etc

(iv) To fill sodium vapor lamps.

(v) in becon light as a safety signal for air navigators as its light has fog penetration power.

Uses of Argon:

(i) Due to inert nature, it is used to fill electric bulb.

(ii) To provide inert atmosphere in high temperature metallurgical processes (arc welding of metals or alloys).

(iii) Pure argon is used in gas chromatography.

(iv) To handle air sensitive substances in laboratory.

(v) To protect metal surfaces from oxidation during steel welding.