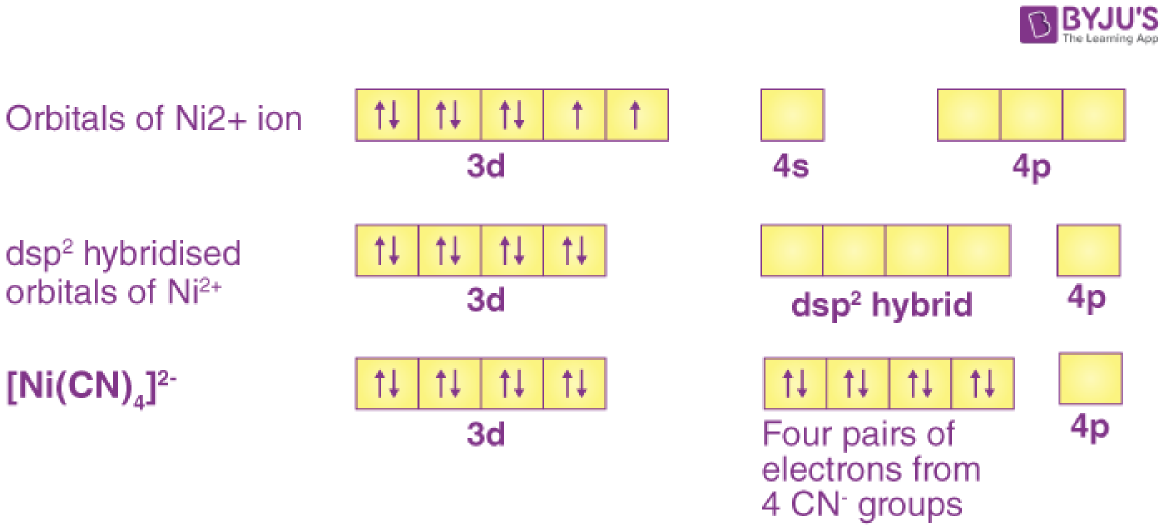
Valence Bond Theory Chemistry Questions with Solutions

Q-1: Explain the nature of bonding in $[Ni(CN)_4]^{2-}$ on the basis of valence bond theory.

Answer: In the complex $[Ni(CN)_4]^{2-}$, nickel is in +2 oxidation state and has the electronic configuration $3d^8$. A cyanide ion delivers a pair of electrons to each of the hybridised orbitals. The ligand cyanide (CN^-) is a strong field ligand. Therefore, it will cause pairing of electrons. The hybridisation scheme is as shown in below diagram:



The absence of unpaired electrons indicates that the compound is diamagnetic.

Q-2: Which of the following is correct for s-orbital?

a) Directional
b) Non directional
c) Has zero angular momentum
d) Electron density is unequal

Answer: b) and c)

Explanation: The probability of finding an electron in all directions at a given distance from the nucleus is the same which makes s-orbital non-directional and spherically symmetrical.

The angular momentum for any orbital can be calculated using the below formula:

$$L = \sqrt{l(l+1)}\frac{h}{2\pi}$$

For s-orbital, l=0

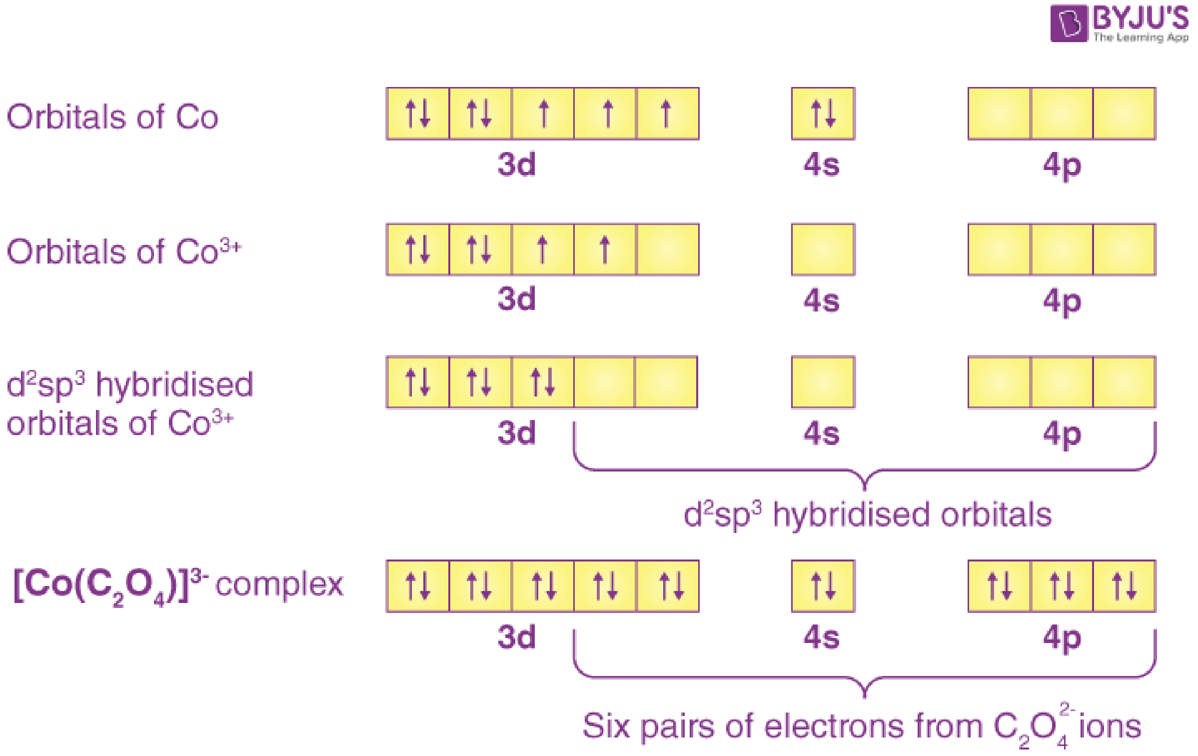
This makes angular momentum L=0.

Q-3: Which of the following is correct for $[Co(C_2O_4)_3]^{3-}$?

a) dsp^2, square planar
b) dsp^2, tetrahedral
c) sp^3d^2, octahedral
d) d^2sp^3, octahedral

Answer: d) d^2sp^3, octahedral

Explanation: In $[Co(C_2O_4)_3]^{3-}$, Co is in +3 oxidation state and has electronic configuration $3d^6$. The ligand oxalate ion is a strong field ligand which causes pairing of electrons. The hybridization scheme is shown below:



Because the hybridisation is d^2sp^3,the complex is octahedral.

Q-4: Calculate the spin only magnetic moment value for $[Mn(Br)_4]^{2-}$. Also predict the geometry of the complex ion.

Answer:
In the complex $[Mn(Br)_4]^{2-}$, Mn has an electronic configuration of $3d^5$ and is in the +2 oxidation state. According to the spectrochemical series, bromide ion (ligand) is a weak field ligand. As a result, all five d-orbital electrons will remain unpaired, giving n = 5.

The spin only magnetic moment of a complex can be calculated using the formula:

$$\mu = \sqrt{n(n+2}$$

Where, n= number of unpaired electrons.

$$\mu = \sqrt{n(n+2} = \sqrt{5(5+2} = 5.9BM$$

Since the coordination number of Mn^{2+} ion in the complex ion is 4, it will be either tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation). However, because the complex ion has a magnetic moment of 5.9 BM, it should be tetrahedral in shape rather than square planar due to the presence of five unpaired electrons in the d orbitals.

Q-5: The orbitals involved in hybridisation in $PtCl_4^{2-}$ is

a) 6s, $6p_x$,$6p_y$,$6p_z$
b) 5s, $5p_x$, $5p_y$,$5p_z$
c) 6s, $6p_x$, $6p_y$, $5d_{x^2-y^2}$
d) 5s, $5p_x$, $5p_y$, $4d_{x^2-y^2}$

Answer: c) 6s, $6p_x$, $6p_y$, $5d_{x^2-y^2}$

<u>Explanation:</u> The coordination number of $PtCl_4^{2-}$ is 4. Coordination number 4 allows for either square planar or tetrahedral shapes. However, when metals from the 4d and 5d series are present, all ligands act as strong field ligands. Strong field strength usually results in a square planar geometry. Because Pt is in the 5d series, $PtCl_4^{2-}$ is square planar.

In square planar geometry, the orbitals involved are 6s, $6p_x$, $6p_y$, $5d_{x^2-y^2}$

Q-6: Which of the following is true for (X) $[Ru(ox)_3]^{3-}$ and (Y) $[Fe(ox)_3]^{3-}$

a) X has low spin and Y has high spin configuration
b) X has high spin and Y has low spin configuration
c) Both X and Y are high spin
d) Both X and Y are low spin

Answer: a) X has low spin and Y has high spin configuration

<u>Explanation:</u> Ru is in the oxidation state +3 and has the d-electronic configuration $4d^5$ in X) $[Ru(ox)_3]^{3-}$.When Ru is in the +3 oxidation state, oxalate acts as a strong field ligand. A low spin complex is produced by a strong field strength.

$[Fe(ox)_3]^{3-}$, on the other hand, has Fe in the oxidation state of +3 and a d-electronic configuration of $4d^5$. When iron is in the +3 oxidation state, oxalate acts as a weak field ligand. A weak field strength produces a high spin complex.

Note: When the metal is in the +3 oxidation state and belongs to the 4d/5d series, oxalate acts as a strong field ligand. Except for cobalt, it acts as a weak field in the 3d series for all metals in the +3 oxidation state.

Q-7: The magnetic moment of $[Ru(H_2O)_6]^{2+}$ corresponds to the presence of

a) Four unpaired electrons
b) Zero unpaired electrons
c) Two unpaired electrons
d) Three unpaired electrons

Answer: b) Zero unpaired electrons

<u>Explanation:</u> Ru is in the +2 oxidation state and has an electronic configuration of $4d^6$ in the given complex. When a metal belongs to the 4d/5d series, all ligands, regardless of oxidation state, act as strong field ligands. As a result of water acting as a strong field ligand, all electrons in $4d^6$ will pair, leaving zero unpaired unpaired electrons. As a result, there is no magnetic moment.

Q-8: In the complex $[Cr(NH_3)_6]Br_3$,chromium has the correct distribution of 3d electrons as

a) $3d^1_{xy}$, $3d^1_{yz}$, $3d^1_{x^2-y^2}$
b) $3d^1_{xy}$, $3d^1_{yz}$, $3d^1_{xz}$
c) $3d^1_{xz}$, $3d^1_{x^2-y^2}$, $3d^1_{yz}$
d) $3d^1_{x^2-y^2}$, $3d^1_{z^2}$,$3d^1_{xz}$

Answer: b) $3d^1_{xy}$, $3d^1_{yz}$, $3d^1_{xz}$

Explanation: In the complex $[Cr(NH_3)_6]Br_3$, chromium has electronic configuration of $3d^3$ with + 3 oxidation state. The distribution of electrons in the d-orbital is shown below:

Q-9: For $[Ni(CO)_4]$ and $K_2[Ni(CN)_4]$, which property is the same for the given pairs.

a) Oxidation state of central atom
b) Magnetic moment
c) Electronic configuration
d) Shape

Answer: b) Magnetic moment

Explanation: Ni has zero and +2 oxidation states in the given complexes, with $3d^{10}$ and $3d^8$ electron configurations, respectively.

The magnetic moment is known to be proportional to the number of unpaired electrons. CO and cyanide ligands are both strong field ligands that cause electrons to pair up in the 3d orbital. As a result, both complexes have zero unpaired electrons and thus have the same magnetic moment value.

Q-10: Consider the following reaction

$$K_2[Ni(CN)_4] \xrightarrow{Na/liq NH_3} K_4[Ni(CN)_4]$$

Will there be any change in magnetic moment?

Answer: No

Explanation: In both the complexes Ni has the same number of unpaired electrons equal to zero. Therefore no change in magnetic moment.

Note: Cyanide is a strong field ligand which causes pairing.

Q-11: State the limitations of Valence Bond theory.

Answer: While the VB theory explains the formation, structures, and magnetic behaviour of coordination compounds to a large extent, it has the following shortcomings:

(i) It is predicated on a number of assumptions.

(ii) No quantitative interpretation of magnetic data is provided.

(iii) It does not account for the colour of coordination compounds.

(iv) It provides no quantitative interpretation of thermodynamics or coordination compound kinetic stabilities.

(v) It cannot tell the difference between weak and strong ligands.

Q-12 Among the following aqua complex, a low spin complex is

a) $[Ti(H_2O)_6]^{3+}$
b) $[Co(H_2O)_6]^{3+}$
c) $[Co(H_2O)_6]^{2+}$
d) None of the above

Answer: b) $[Co(H_2O)_6]^{3+}$

Explanation: Co is in the +3 oxidation state with an electronic configuration of $3d^6$ in $[Co(H_2O)_6]^{3+}$. When cobalt is in a +3 OS state, o-donors (such as H_2O) act as a strong field ligand. As a result, the complex has a low spin value.

When cobalt is in a +2 OS state, o-donors (such as H_2O) act as a weak field ligand.In complex $[Co(H_2O)_6]^{2+}$, water acts as a weak field ligand with Co in +2 oxidation state resulting in high spin complex.

In the complex $[Ti(H_2O)_6]^{3+}$, Ti is in +1 oxidation state with $3d^1$ as electronic configuration. There is no need to check field strength between $3d^1$-$3d^3$. Every complex has a high spin.

Note: $[Co(H_2O)_6]^{3+}$ is the only aqua complex which is low spin.

Q-13: For the complex A: $[Ag(CN)_4]^{-1}$ and B: $[Au(CN)_4]^{2-}$, which statement is true?

a) Both are paramagnetic
b) Bothe are diamagnetic
c) A is paramagnetic and B is diamagnetic
d) A is diamagnetic and B is paramagnetic

Answer: d) A is diamagnetic and B is paramagnetic

Explanation: A diamagnetic complex has zero unpaired electrons and a paramagnetic has unpaired electrons.

$[Ag(CN)_4]^{-1}$ has silver in +3 oxidation state with $4d^8$ as electronic configuration. All electrons get paired up due to the strong field strength of cyanide ion.Hence, a diamagnetic complex.

$[Au(CN)_4]^{2-}$ has gold in an oxidation state of +2 and an electronic configuration of $5d^9$. Despite the fact that cyanide is a strong field ligand, an electron is left unpaired even after pairing. As a result, making it a paramagnetic complex.

Q-14: The structure of the complexes $[Cu(NH_3)_4](ClO_4)_2$ and $[Cu(NH_3)_4](ClO_4)$ in the solution respectively are:

a) Square planar and tetrahedral
b) Octahedral and square pyramidal
c) Octahedral and trigonal pyramidal
d) Tetrahedral and square planar

Answer: a) Square planar and tetrahedral

Explanation: In the complex $[Cu(NH_3)_4](ClO_4)_2$, copper is in +2 oxidation state with electronic configuration of $3d^9$. Upon filing electrons, one electron will remain unpaired and it gets transferred from 3d to 4p. One 3d, one 4s and two 4p orbital gets hybridised to give dsp^2 hybridisation.(square planar)

In the complex $[Cu(NH_3)_4](ClO_4)$, copper is in +1 oxidation state with electronic configuration of $3d^{10}$.One 4s and three 4p orbital gets hybridised to give sp^3 hybridisation.(tetrahedral)

Q-15: Why are inner orbital complexes preferred over outer orbital complexes?

Answer: Inner orbital complexes are made up of metal atoms that use inner shell d orbitals((n-1)d) to hybridise. Outer orbital complexes are made up of metal atoms that use the outermost shell d orbitals(nd) for hybridization.

The energy gap between the ns and (n-1)d is less as compared to ns and nd orbitals of a metal atom.Therefore, inner orbital complexes are preferred over outer orbital complexes.

Practise Questions on Valence Bond Theory

Q-1: The minimum number of monodentate ligand required for the formation of square planar and tetrahedral complex is

a) 2
b) 3
c) 4
d) 6

Answer: c) 4

Explanation: A monodentate ligand is a ligand that donate electrons to the central metal ion from its one site.

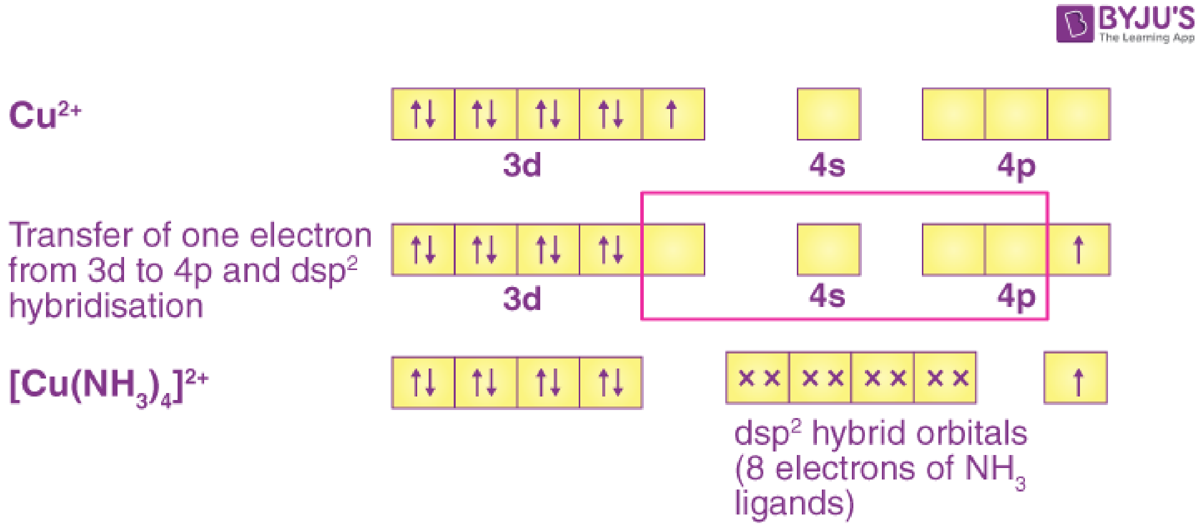
A minimum of 4 such ligands is required for the formation of a tetrahedral (sp^3 hybridisation) or square planar (dsp^2 hybridisation) complex.

Q-2: Cuprammonium ion has ____________ shape.

a) Octahedral
b) Tetrahedral
c) Trigonal
d) Square planar

Answer: d) Square planar

Explanation: The cuprammonium ion is $[Cu(NH_3)_4]^{2+}$.The copper is in +2 oxidation state with the electronic configuration of $3d^9$. The hybridisation takes place in the following manner:



The dsp^2 hybridization corresponds to square planar shape.

Q-3: The square planar geometry is based on

a) Z-exclusion principle
b) Electroneutrality principle
c) None of the above
d) Pauli exclusion principle

Answer: a) Z-exclusion principle

Explanation: The square planar geometry has a hybridisation of either dsp^2 and sp^2d. The orbitals involved here are s, p_x, p_y and $d_{x^2-y^2}$. We can clearly see that there is no involvement of z-direction. Hence it is based on the z-exclusion principle.

Q-4: The zero magnetic moment of octahedral K_2NiF_6 is due to

a) Low spin d^6Ni(IV) complex
b) Low spin d^8Ni(IV) complex
c) High spin d^8Ni(IV) complex
d) High spin d^6Ni(IV) complex

Answer: a) Low spin d^6Ni(IV) complex

Explanation: A low spin complex is formed when the ligands are of strong field strength whereas high spin is characterised by weak field strength.

In K_2NiF_6 , Ni is in +4 oxidation state with d^6 electronic configuration.Here fluoride acts as a strong field ligand resulting in low spin complex.

In a strong field, all of the electrons in d^6 are paired up, leaving zero unpaired electrons, corresponding to a zero magnetic moment.

Note: When metal is in +4 oxidation state all ligands act as strong field ligands.

Q-5: For the central metal atom in a complex, coordination number is

a) The number of ligands bonded by pi-bonds that surround a metal ion.
b) The number of ligands bonded by sigma-bonds that surround a metal ion.
c) The number of ligands bonded by pi-bonds and sigma bonds that surround a metal ion.
d) The number of only neutral ligands bonded to the metal ion

Answer: b) The number of ligands bonded by sigma-bonds that surround a metal ion.

Explanation: Coordination number is the number of ligands that surround the metal ion and are linked to it through sigma bonds.