#### **KEA – VIKASANA PROGRAMME**

#### CHEMISTRY By Ravishankar N





#### d-block elements

- Electronic configuration-3d series
- Periodic properties variation of atomic
- size, ionic size and electronegativity.
- Variable oxidation state.
- •Formation of colored compounds.
- •Magnetic property.







#### Which one of the following is <u>NOT TRUE</u> about transition metals?

ANSWER transitional elements are

predominantly metallic

### (b) In aqueous solution many of their simple ions are coloured

(c) Most of the transitional elements show Show variable oxidation state or valence

(d) Most of the transitional elements show only one oxidation state





## An element in +3 oxidation state has the electronic configuration [*Ar*]3*d*<sup>3</sup>. It's atomic number is

OH

a ANSWER
b) 23
c) 22
d) 21

H<sub>2</sub>C

#### Ar- $1s^2 2s^2 2p^6 3s^2 3p^6 + 3d^3 = 18 + 3 + 3 = 24$





## Which of the following compound is <u>NOT</u> colored ?

a) co ANSWER |phate b) Zinc(II)Chloride c) Chromium (III) sulphate d) Manganese(II) oxalate Hence no d-d transition is possible in Zn(II) ion

ion	EC
Cu(II)	[Ar] 3d <sup>9</sup>
Zn(II)	[Ar] 3d <sup>10</sup>
Cr(III)	[Ar] 3d <sup>3</sup>
Mn(II)	[Ar] 3d <sup>5</sup>





## The configuration of transition element, which shows highest magnetic moment

is		EC	U	np	air	ec		
a) 3d <sup>8</sup> CH		3d <sup>8</sup>	t A					
<b>ANSWER</b>	ОН	3d <sup>5</sup>	1	1	1	1	1	]
c) 3d <sup>7</sup>		3d <sup>7</sup>	$\uparrow\downarrow$	$\uparrow\downarrow$	1	1	Î	]
d) 3d <sup>9</sup>	T ]	3d <sup>9</sup>	$\uparrow\downarrow$	$\uparrow\downarrow$	$\uparrow\downarrow$	↑↓	1	]

ion with higher no. of unpaired electrons exhibits maximum magnetic moment





#### Which of the following is diamagnetic?

C5H11

OH

a) Fe<sup>2+</sup> b) Cr<sup>3+</sup>



d) Cu<sup>2+</sup>

H<sub>3</sub>C



CONTAINS 4 UNPAIRED ELECTRONS.  $\mu = \sqrt{n(n + 2)}$  $\sqrt{24} = 4.89$  BM







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ELEMENT	OS	ELECTRONIC CONFIGURATION	NO. OF UNPAIRED d - e <sup>-</sup>	
Ti Cl <sub>4</sub>	+4	[Ar] 3d <sup>2</sup> 4s <sup>2</sup> [Ar] 3d <sup>0</sup> 4s <sup>0</sup>	0	
VCl <sub>3</sub>	+3	[Ar] 3d <sup>3</sup> 4s <sup>2</sup>	2	
ANSW	/FR	[Ar] 3d <sup>2</sup> 4s <sup>0</sup>		
reci <sub>2</sub>	TZ	[Ar] 3d <sup>6</sup> 4s <sup>2</sup> [Ar] 3d <sup>6</sup> 4s <sup>0</sup>	4	
ZnCl <sub>2</sub>	+2	[Ar] 3d <sup>10</sup> 4s <sup>2</sup> [Ar] 3d <sup>10</sup> 4s <sup>0</sup>	0	





## Which statement about *d*-block elements is true as you move from left to right in the periodic table?









#### **Coordination compounds**

- Molecular compounds-complexes and double salts
- Ligands and its classification
- •Central metal atom , oxidation state, coordination number
- Ionisation and coordination sphere
- •Werner's theory
- Sidgwick theory and EAN
- VBT and structure of complexes
- •lsomerism
- •IUPAC nomenclature.





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### Which of the following pair contains complex salt and double salt respectively?

# a) FeSO<sub>4</sub>, K<sub>4</sub>[Fe(CN)<sub>6</sub>] b) [Cu(NH<sub>3</sub>] ANSWER D<sub>4</sub>.7H<sub>2</sub>O c) [Cu(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub>, K<sub>2</sub> SO<sub>4</sub>Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.24H<sub>2</sub>O d) MgSO<sub>4</sub>7H<sub>2</sub>O, CuSO<sub>4</sub>

C5H11





#### In the following reaction $Cu^{2+} + 4NH_3 \rightarrow [Cu(NH_3)_4]^{2+} (aq),$ Cu<sup>2+</sup> is acting as a(n) a) oxidizing agent b) ANSWER c) solvent d) ligand H<sub>3</sub>C





μ = 2.82 BM means vanadium has two unpaired electrons with an oxidation state of +3 [Ar] 3d<sup>2</sup>

let the charge on the complex ion be X Then X = 1(+3) + (-2) 3 = + 3 - 6 = -3To balan  $K_3 [V(OX)_3]$  put 3 K<sup>+</sup> ions Hence n = 3 $K_3 [V(OX)_3]$ 





#### K<sub>3</sub>[Co(CN)<sub>6</sub>] Oxidation state of cobalt in this complex is +3

#### ANSWER CO IS [AI] 3d<sup>7</sup>4s<sup>2</sup>

Electronic configuration of Co <sup>3+</sup> [Ar] 3d<sup>6</sup>

### $[Cr(en)_2(NH_3)_2] Cl_3$ $[Cr(en)_2(NH_3)_2]^{+3} + 3 Cl^{-1}$ ANSWER X + 0(2) + (0)(2) = +3

X = +3









 $[Cu(en)(NH_3)_2]Cl_2$  $[Cu(en)(NH_3)_2]^{+2} + 2Cl^{-1}$ X + 0(1) + (0)(2) = +2= +2



 $[Cu(en)(NH_3)_2]Cl_2$ 

(ethylene diammine bidentate ligand + two monodentate ligands)

CO = 2+2 = 4



### $\begin{array}{ccc} \text{Co}(\text{H}_2\text{O})_5 \text{ Cl}_3 + 2\text{AgNO}_3 & \rightarrow 2 \text{ AgCl} \\ & & (2 \text{ moles}) \end{array}$

 $\begin{array}{ccc} \text{Co}(\text{H}_2\text{O})_5 \text{ Cl}_3 & \rightarrow & [\text{Co} \text{ Cl}(\text{H}_2\text{O})_5]^{+2} + 2\text{Cl} \\ & & (3 \text{ moles}) \\ & & 2\text{AgNO}_3 \end{array}$ 



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-20



#### The IUPAC name of [CoCl(NO<sub>2</sub>)(en)<sub>2</sub>]Cl is

#### a)Chloronitrobis(ethylenediamine) cobaltic(III) chloride b)chloronitrobis( ANSWER ne)cobalt(II) chloride c)chlorobis(ethylenediamine)nitrocobalt(III) chloride d)bis(ethylenediamine)Chloronitrocobalt (III) chloride





#### The formula of

#### potassium trioxalatoaluminate(III) is

C5H14

a) ANSWER  $)_{3}$ ] b)  $K_{2}[Al(C_{2}O_{4})_{3}]$ c) Al  $[K_{3} (C_{2}O_{4})_{3}]$ d)  $K[Al(C_{2}O_{4})_{3}]$ 

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#### K<sub>4</sub>[Fe(CN)<sub>6</sub>] CENTRAL METAL ION IS Fe OS IS +2 ELECTRONIC CONFIGURATION OF IRON IS [Ar] 3d<sup>6</sup>4s<sup>2</sup> ELECTRONIC CONFIGURATION OF Fe <sup>2+</sup> IS [Ar] 3d<sup>6</sup>



**CONTAINS 4 UNPAIRED ELECTRONS.**  $\mu = \sqrt{n(n + 2)} = \sqrt{24} = 4.89$  BM





#### $PtCl_24NH_3 + AgNO_3 \rightarrow 2AgCl$

#### Hence the formula of the complex is $[Pt(NH_3)_4] Cl_2$

#### Sec. valency = coordination number = 4

#### ANSWER $CoCl_3 4NH_3 + AgNO_3 \rightarrow AgCl$

Hence the formula of the complex is  $[CoCl_2(NH_3)_4]Cl$ 

Sec. valency = coordination number = 6





[Co SO<sub>4</sub> (NH<sub>3</sub>)<sub>5</sub> ]Br (0.02 mole)/2L = 0.01mol/L

1 litre of above  $r_{ANSWER}$  cess  $AginO_3 \rightarrow 0.01$  mol/L of AgBr (Y) [Co Br (NH<sub>3</sub>)<sub>5</sub>] SO<sub>4</sub> (0.02 mole)/2L = 0.01mol/L

1 litre of above mixture +excess  $BaCl_2$  $\rightarrow 0.01 \text{ mol/L of } BaSO_4$ (Z)





In the process of extraction of gold, Roasted gold ore  $+ CN^- + H_2O \xrightarrow{O_2} [X] + OH^ [X] + Zn \rightarrow [Y] + Au$ Identify the complexes [X] and [Y] ANSWER a)  $X = [Au(CN)_2]^{-1}$  and  $Y = [Zn(CN)_4]^{2-1}$ b)  $X = [Au(CN)_4]^{3-1}$  and  $Y = [Zn(CN)_4]^{2-1}$ c)  $X = [Au(CN)_2]^-$  and  $Y = [Zn(CN)_6]^{4-}$ d)  $X = [Au(CN)_4]^-$  and  $Y = [Zn(CN)_4]^2$ 





#### **Chemical bonding-II**

- •Formation of molecular orbital's by the LCAO in homo diatomic molecules  $H_2$ ,  $Li_2$ ,  $O_2$ ,  $He_2$ .
- •BMO and ABMO
- •Bond order
- Energy level diagram
- •Extend the concept to the formation of  $H_2^+$ ,  $Li_2^+$ ,  $O_2^+$ ,  $O_2^-$ ,  $He_2^-$  etc.







#### To overlap, AO's must possess

#### 1. Same symmetry,

2. Similar energy,





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#### Which one of the following combinations is <u>NOT</u> allowed (assume z-axis as inter nuclear axis)

```
a) 2s and 2s
b) 2p<sub>x</sub>and 2p<sub>x</sub>
c) 1s and 1s
ANSWER d 2p<sub>y</sub>
```





## For a homonuclear diatomic molecule, the energy of $\sigma_{25}$ orbital is

Increasing order of energy of molecular orbital is

$$\sigma_{\text{ANSWER}} \sigma_{2S} \sigma_{2S}^* \sigma_{2Pz}^*$$

 $\pi_{2Px} = \pi_{2Py} \quad \pi^*_{2Px} = \pi^*_{2Py}$ 





### Example for super oxide is $KO_2$ and contains $O_2^{-1}$ ion.

#### Electronic configuration of $O_2^-$ ion is $\sigma_{1s}^2 \sigma_{1s}^2 \sigma_{2s}^2 \sigma_{2s}^2 \sigma_{2s}^2 \sigma_{2pz}^2 \pi_{2px}^2 = \pi_{2py}^2 \pi_{2px}^{*2} = \pi_{2py}^{*2} \pi_{2py}^{*2}$ ANSWER

The Bond order = Nb -Na/2 = 10 - 7/2 = 3/2 = 1.5





#### The no. of anti bonding electron pairs in O<sub>2</sub><sup>2-</sup> according to molecular orbital theory is







## How many unpaired electrons are there in $O_2^{2-}$ ion?

#### ANSWER Electronic configuration of $O_2^{2-}$ ion is





## In the molecular orbital diagram for $O_2^+$ ion the highest occupied orbital is







#### Electronic configuration of O<sub>2</sub><sup>+</sup> ion is

$$\sigma_{1S}^{2} \sigma_{1S}^{*} \sigma_{2S}^{2} \sigma_{2S}^{*} \sigma_{2S}^{*} \sigma_{2Pz}^{*} \sigma_{2Pz}^{$$

Bond order = 10-5/2 = 2.5No. of unpaired electrons =1 Paramagnetic Stability more than  $O_2$  due to higher bond order





#### $O_2 + e \rightarrow O_2^-$ Added electron goes to $\pi^*_{2DV}$ molecular orbital Bond order decreases from 2 to 1.5 but bond order is inversely related to bond length. Hence bond length increases.

ANSWER onfiguration of  $O_2^{-1}$   $\sigma_{1s}^2 \sigma_{1s}^{*} \sigma_{2s}^2 \sigma_{2s}^2 \sigma_{2s}^{*} \sigma_{2s}^2 \sigma_{2Pz}^{*} \pi_{2Px}^2 = \pi_{2Py}^{*}^2$   $\pi_{2Px}^{*} \pi_{2Py}^{*} = \pi_{2Py}^{*}^{1}$ Bond order = 10 - 7/2 = 1.5





#### Which of the species is diamagnetic?

a) $O_2^+$ b) $O_2^$ c) $O_2^$ d) $O_2^2^-$ 

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species	No. of unpaired electrons	
0 <sub>2</sub> +	<b>1 (</b> PARAMAGNETIC)	
0 <sub>2</sub>	<b>2</b> (PARAMAGNETIC)	
0 <sub>2</sub> -	<b>1 (</b> PARAMAGNETIC)	
02-	0 (DIAMAGNETIC)	ANSWER



is



## The ascending order of number of unpaired electrons in $O_2$ , $O_2^-$ and $O_2^{2-}$

11110

a)	0 <sup>2-</sup> , 0 <sub>2</sub> , 0 <sub>2</sub> <sup>-</sup>
b)	022-,02-,02
c)	0 <sub>2</sub> <sup>-</sup> , 0 <sub>2</sub> <sup>2-</sup> , 0 <sub>2</sub>
d)	0 <sub>2</sub> , 0 <sub>2</sub> <sup>-</sup> ,0 <sub>2</sub> <sup>2-</sup>

ion	No. of unpaired electrons		
O <sub>2</sub>	2		
O <sub>2</sub> <sup>-</sup>	1		
0 <sub>2</sub> <sup>2-</sup>	0		







## About the species $O_2^+$ , $O_2^{2-}$ , $O_2$ and $O_2^-$ , which one of the following statements is <u>CORRECT</u>?

	N <sub>b</sub>	Na	N <sub>b</sub> - N <sub>a</sub> /2
0 <sub>2</sub> +	10	ANSWER	2.5
02	10	6	2
0 <sub>2</sub> -	10	7	1.5
0 <sub>2</sub> <sup>2-</sup>	10	8	1





# According to MO theory, which of the following statements about the magnetic character and bond order is <u>CORRECT</u> regarding $O_2^+$









#### Which of the following have been arranged in increasing order of bond order as well as bond dissociation energy?

	N <sub>b</sub>	N <sub>a</sub>	$N_b - N_a/2$
	/ER 0	5	2.5
02	10	6	2
0 <sub>2</sub> -	10	7	1.5
O <sub>2</sub> <sup>2-</sup>	10	8	1





## Number of moles of ions present in a solution of 1 molar

#### pottassium ferrocyanide is

ANSWER

a) 2 Potassium Ferrocyanide is  $K_4[Fe(CN)_6]$ 

#### b)3 $K_4[Fe(CN)_6] \rightarrow 4K^+ + 1[Fe(CN)_6]^{4-}$ c)4

C5H11



CH3



### According to IUPAC nomenclature sodium nitroprusside is named as

a)soc b)soc c)sodium pe ANSWER c)sodium pentacyanonitrosylferrate (II)



H<sub>3</sub>C



## Which of the following isTRUE ?a)bond order $\alpha$ 1<br/>bond length $\alpha$ bond energy

b) bond order  $\alpha \frac{1}{bond \, energy} = \alpha$  bond length

c) bond order  $\alpha \frac{1}{bond \, energy} \alpha \frac{1}{bond \, length}$ 

d) bond order  $\alpha$  bond length  $\alpha$  bond energy



H<sub>2</sub>C



#### Werner's theory **DOES NOT** explain

## a)sec. Valency of metal atomb)ionisable and non ionisable valencyc)directional nature of sec. Valency

ANSWER ive atomic number