

# Sri Chaitanya IIT Academy, India

a.p, telangana, karnataka, tamilnadu, maharashtra, delhi, ranchi  $\mbox{\it A}$  right Choice for the Real Aspirant

### ICON CENTRAL OFFICE, MADHAPUR-HYD

 Sec: Sr. IPLCO
 JEE ADVANCED
 DATE : 08-11-15

 TIME : 3:00
 2013\_P1 MODEL
 MAX MARKS : 180

### **KEY & SOLUTIONS**

#### **PHYSICS**

1	С	2	A	3	В	4	В	5	В
6	С	7	В	8	D	9	D	10	С
11	ABC	12	ABC	13	ACD	14	ABC	15	ABCD
16	2	17	6	18	2	19	6	20	6

### **CHEMISTRY**

21	С	22	D	23	D	24	С	25	С
26	С	27	С	28	D	29	В	30	A
31	ABCD	32	ВС	33	ABC	34	ABCD	35	ABCD
36	8	37	4	38	5	39	6	40	3

## **MATHEMATICS**

41	D	42	В	43	A	44	В	45	В
46	A	47	В	48	A	49	D	50	С
51	BCD	52	BCD	53	BD	54	В	55	ABC
56	2	57	3	58	8	59	2	60	4

#### **CHEMISTRY**

The overall formation constant of the  $[co(NH_3)_6]^{2+}$  ion in aqueous solution is  $10^5$ 21. and the standard potentials for the reaction of  $Co^{3+}(aq)$  and  $[Co(NH_3)_6]^{3+}(aq)$  are as follows

$$Co^{3+}(aq)+e^- \rightleftharpoons Co^{2+}(aq)$$
  $E^{\circ}=+1.9V$ 

$$\left[Co\left(NH_3\right)_6\right]^{3+}\left(aq\right) + e^- \Longrightarrow \left[Co\left(NH_3\right)_6\right]^{2+}\left(aq\right) \qquad E^\circ = +0.1V$$

Calculate the overall formation constant of the  $[Co(NH_3)_6]^{3+}$ 

$$Co^{+2} + 6NH_3 \rightleftharpoons \left[Co\left(NH_3\right)_6\right]^{+2}$$
  $k_1 = 10^5$ 

$$Co^{+3} + 6NH_3 \rightleftharpoons \left[Co\left(NH_3\right)_6\right]^{+3}$$
  $k_2 = ?$ 

$$Co^{+3} + e \rightarrow Co^{+2}$$
  $E^{\circ} = 1.9V$ 

$$Co^{+3} + e$$
  $\rightarrow Co^{+2}$   $E^{\circ} = 1.9V$   
 $Co(NH_3)_6^{+2}$   $\rightarrow Co(NH_3)_6^{+3} + e$   $E^{\circ} = -0.1V$ 

$$Co^{+3} + Co(NH_3)_6^{+2} \rightleftharpoons Co^{+2} + Co(NH_3)_6^{+3}$$
  $E^{\circ} = 1.8V$ 

$$E^{\circ} = \frac{0.059}{1} \log \frac{k_2}{k_1}$$
  $1.8 = 0.059 \log \frac{x}{10^5}$   $k_2 = 10^{35}$ 

- Total number of unpaired electrons should be 8 and they should present in 3 iron 22. atoms. So formula must be [Fe(H<sub>2</sub>O)<sub>6</sub>]<sub>2</sub>[Fe(CN)<sub>6</sub>]. Each [Fe(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> contain 4 unpaired electrons while  $[Fe(CN)_6]^{4-}$ contain zero unpaired electrons. So Total unpaired electrons are 8 which give 8/3 or  $2\frac{2}{3}$
- (a)  $Cr^{2+} + Fe^{3+}$ ? As you move from left to right across the d block, stable 23. oxidation states in aqueous solution tend to get lower (for example, form TiO<sup>2+</sup> and  $VO_2^+$  on the left to  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$  and  $Zn^{2+}$  on the right). Based on this trend,

you should expect  $Cr^{2+}$  to be oxidized to  $Cr^{3+}$  at the expense of  $Fe^{3+}$ , which will be reduced to  $Fe^{2+}$ . That is, iron is to the right of chromium, and the trend is left higher, right lower. In fact, the net potential for this redox reaction in aqueous acid is 1.195 V (see Resource Section 3)

$$Cr^{2+}(aq) + Fe^{3+}(aq) \rightarrow Cr^{3+}(aq) + Fe^{2+}(aq)$$
  $E^{o} = 1.195 V$ 

(b)  $CrO_4^{2-} + MoO_2$ ? Recall the trend that higher oxidation numbers become increasingly more stable as you descend a group in the d block. Since you are given two compounds containing Cr(VI) AND Mo(IV), you should expect a redox reaction to occur, with the oxidation of  $MoO_2$   $MoO_2$  and reduction of  $CrO_4^{-2}$ . The products should be  $Cr^{3+}$  and  $H_2MoO_4$  (see Resource Section 3). Note Cr(V) and Cr(VI) are unstable with respect to disproportionation.

$$2 CrO_4^{2-} + 3 MoO_2(s) + 10 H^+ \rightarrow 2 Cr^3 + 3 H_2 MoO_4 + 2 H_2 O E^0 = 0.73 V$$

(c)  $MnO_4^- + Cr^{3+}$ ? This is another case where you should apply the trend left higher, right lower, predicting a reaction between these two species in which  $Cr^{3+}$  is oxidized and  $MnO_4^-$  is reduced. However, since these two elements are immediate neighbours, you should not expect the net  $E^o$  to be very large. In fact, the products are  $Mn^{2+}$  and  $Cr_2O_7^{2-}$  and  $E^o = 0.12 V$ .

$$6MnO_4^- + 10Cr^{3+} + 11H_2O \rightarrow 6Mn^{2+} + 5Cr_2O_7^{2-} + 22H^+ \qquad E^o = 0.12 V$$

24. The metals of the second and third series have greater enthalpies of atomisation than the corresponding elements of first series. This is due to much more

- frequent metat metal bonding Mn belogs to Ist series and Re belongs to IIIrd series in the same group
- 25. More the number of positive charges on cation more the polarising power and thus have more acidic character. So Sc<sup>3+</sup> strongest among the given species among Mn<sup>2+</sup> and Ni<sup>2+</sup>, Ni<sup>2+</sup> is more acidic due to small size.
- In a transition series from left to right the number of oxidation states increases with in increase in the number of ns+(n-1)d electrons up to middle. After d<sup>5</sup> configuration as pairing of electrons starts, number of unpaired electrons decreases. Further as the difference in energy increases between ns and (n-1)d orbitals (n-1)d electrons cannot participate in bonding. So number of oxidation states decrease at the end. Unlike in p-block elements, in d-block elements stability of higher oxidation states are generally stabilized in oxide and fluoride compounds
- 27. Strongly reducing states such as  $Ti^{2+}$ ,  $V^{2+}$ ,  $V^{3+}$  can also form compounds like  $TiF_2$ ,  $VF_3$ ,  $VF_3$ , TiO, VO etc. So statement 3 is wrong other statements are correct.
- 28. Persulphate ion can oxidise  $Mn^{+2}$  to  $MnO_4^-$ . So  $S_2O_8^{2-}$  is stronger oxidising agent than  $MnO_4^-$  Permanganate is stronger oxidising agent than dichromate
- Glycine forms a chelate [Cu(Gly)<sub>2</sub>] which is non electrolyte Acetic acid is produced which is also weak electrolyte. Hence conductivity decreases
- 30. SCN is an ambidentate ligand. If N is donating atom it act as strong ligand but when S is donating atom it act as weak lignad. So Cr(III) –SCN bonded

thiocyanate complexes slowly rearrange to given N-bonded Cr(III) –NCS isothiocyanate complex (Cr<sup>3+</sup> is a hard acid and hence prefers the hard donor N in preference to softer S donor.

31.  $CoCl_4^{2-}$  is tetrahedral while  $\left[Co(H_2O)_6^{\circ}\right]^{2+}$  is octahedral complexes.  $\Delta_i$  is smaller than  $\Delta_0$ . So comparatively  $\left[CoCl_4^{\circ}\right]^{2-}$  absorb a radiation of longer wavelength. While  $\left[Co(H_2O)_6^{\circ}\right]^{2+}$  absorb radiation of shorter wavelength. Tetrahedral complexes are generally intense coloured due to the absence of centre of symmetry both complexes have same magnetic moment as they have same number of unpaired electrons 3  $t_{2g}^5 eg^2$  in  $\left[\overline{C}_0(H_2O)_6^{\circ}\right]^{2+}$  and  $e_g^4 t_{2g}^3$  in  $\left[CoCl_4^{\circ}\right]^{2-}$ 

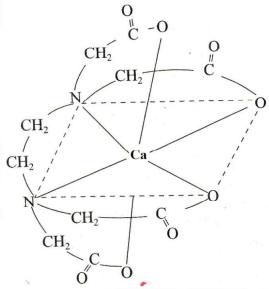
32.

33. A) in both Mn and Cr the electron is to be removed from 4s but in Mn effective nuclear charge is more

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- B)  $_{46}Pd$  has more effective nuclear charge than  $_{45}Rh$ . So  $IE_1$  of Pd > Rh. In Pd the electronic config. Is  $4d^{10}5s^0$  where as in silver it is  $4d^{10}5s^1$  to remove an electron from stable  $d^{10}$  config. In Pd energy required is more than in Ag.
- C) In a transition group generally atomic size increases from first element to second element. So IP decreases. But the atomic sizes of 2<sup>nd</sup> and 3<sup>rd</sup> elements are almost equal due to lanthanide contraction. As the effective nuclear charge is more in 3<sup>rd</sup> element i.e. 5d series IP is more
- D) As explained above N will have more IP than Mo.
- 34. All the statements are correct
- 35. All the statements are correct
- 36. NO, NO<sub>2</sub>, O<sub>2</sub>, K<sub>3</sub>[Fe(CN)<sub>6</sub>], KO<sub>2</sub>, MnSO<sub>4</sub>, NiSO<sub>4</sub>, CuSO<sub>4</sub> are paramagnetic and their weight increases in applied magnetic field
- 37.  $\left[ Co(H_2O)_5 Cl \right] Cl_2 \rightarrow \left[ Co(H_2O)_5 Cl \right]^{2+} + 2Cl^{-}$ 0.01M of complex solution is 0.02N  $\therefore \frac{20 \times 0.02}{0.1} = 4ml$

38.



- 39. Keeping the bidentate ligand constant and changing the monodentate ligands we get 6 geometrical isomers. All of which do not contain plane of symmetry. So six enantiomeric pairs are possible.
- 40.  $\left[Cr(NH_3)_6\right]Cl_3, \left[\overline{V}(H_2O)_6\right]SO_4$  and  $\left[Mn(NH_3)_6\right]SO_4$  are inner orbital complexes and are paramagnetic