

## Section B

(Chemistry of transition elements: 323Ch.)

[40 Marks: 5 marks for each item]

Answer **8 ITEMS ONLY** from the following:

a- Mention **only** the general properties of the transition elements and what is the difference between organometallic and coordination compounds?

**The answer:** General properties of the transition elements are:

- 1- They have variable oxidation states
- 2- They can form coordination and organometallic compounds.
- 3- Most of their compounds are colored.
- 4- Some of them can be used as catalysts.
- 5- Most of them have magnetic properties.
- 6- They conduct heat and electricity.

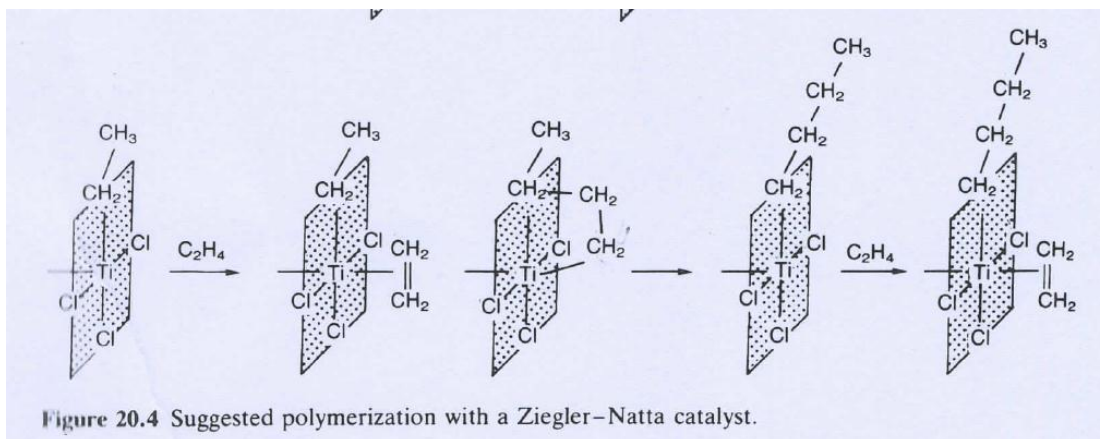
Organometallic compounds have at least one metal-carbon bond among their coordination bonds between the metal and the ligand(s) but the coordination compounds do not that specific bond.

b- What is the role of Ziegler –Natta catalyst?

**The answer:**

### Ziegler–Natta catalysts

Solutions of  $\text{AlEt}_3$  and  $\text{TiCl}_4$  in a hydrocarbon solvent react exothermically to form a brown solid. This is the important Ziegler–Natta catalyst for polymerizing ethene (ethylene) to form polythene. Ziegler and Natta were awarded the Nobel Prize for Chemistry in 1963 for this work. (See also Chapter 12.) (Similar catalytic activity has been found from mixtures of Li, Be or Al alkyls with halides from Groups 4, 5 and 6, the Ti, V and Cr groups.



c- Titanium compounds can be applied for dinitrogen fixation.

Comment.

**The answer:**

Some organometallic  $Ti^{II}$  compounds are able to fix  $N_2$  gas and produce  $NH_3$ . One example is  $(C_{10}H_{10}Ti)_2$ . This cycle could be similar to the dinitrogen fixation process in nature. (Dinitrogen complexes are discussed under ruthenium(II) complexes in Chapter 24.)

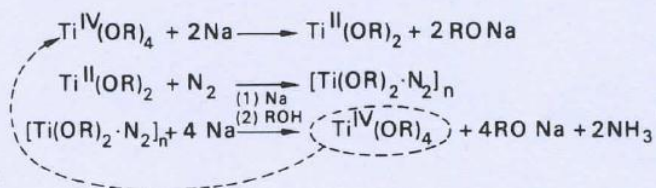


Figure 20.5 Cycle for fixation of dinitrogen.

d- The electronic configuration of Cu is  $[Ar]4s^13d^{10}$ , not  $[Ar]4s^23d^9$ .

Give the reason.

**The answer:**

The Exchange Energy  $[E_{ex}]$  is the energy released when the anti parallel electrons belonging to a degenerate (same energy) subshell are made to have parallel spins. This phenomenon will be explained by taking examples of both the Cu(29) as an example.

$$E_{ex} = K \cdot n(n-1)/2$$

Where, n stands for the the number of electrons having the same spins and occupying the the degerate "d" subshell. K is called Exchange constant and has different values for different metals and are reported in the literature. Cu can have two possible configurations:  $3d^9 4s^2$  [1st case] and  $3d^{10}$

4s<sup>1</sup>[2nd case] and we are to decide as to why the latter should be more stable.

Again calculate E<sub>ex</sub> in both the probable configurations:

Here the systems have two different types of spins

So calculate E<sub>ex</sub> for both types of electrons in the 1st case

1] [1 st case] 3d<sup>9</sup> 4s<sup>2</sup>

Here 3d has 5 electrons with +1/2 [ up] spins while the remaining four electrons are with -1/2 [ down] spins.

a) E<sub>ex</sub> from 5 (up) electrons = K.5.4/2 = 10K/

b) E<sub>ex</sub> from 4 (down) electrons = K.4.3/2 = 6K/

Total E<sub>ex</sub> for this configuration = 16K

2nd case] 3d<sup>10</sup> 4s<sup>1</sup>

i] Here five 3d electrons are with +1/2 [ up] spins and so are the remaining five electrons but with -1/2 [ down] spins.

a) E<sub>ex</sub> from 5 (up) electrons = K.5.4/2 = 10K/

b) E<sub>ex</sub> from 5 (down) electrons = K.5.4/2 = 10K/

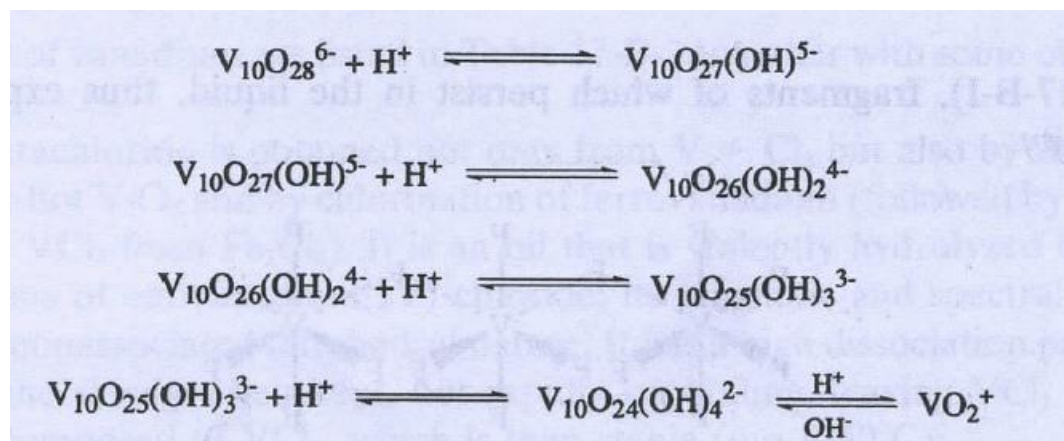
Total E<sub>ex</sub> for this configuration = 20K/

So difference in Exchange energies = 4K/

So that the configuration [3d<sup>10</sup> 4s<sup>1</sup>] of Cu is more stable than the other one.

e- What is the effect of pH values on a vanadate solution?

**The answer:**



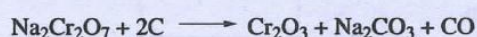
f- How can you produce impure and pure chromium metal?

**The answer:**

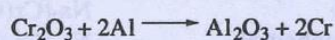
The chief ore<sup>1</sup> is *chromite* ( $\text{FeCr}_2\text{O}_4$ ), which is a spinel with  $\text{Cr}^{\text{III}}$  on octahedral sites and  $\text{Fe}^{\text{II}}$  on the tetrahedral ones. If pure chromium is not required—as for use in ferrous alloys such as the chromium additive used to make stainless steel—the chromite is reduced with carbon in a furnace, affording the carbon-containing alloy ferrochromium:



When pure chromium is required, the chromite is first treated with molten alkali and oxygen to convert the  $\text{Cr}^{\text{III}}$  to chromate(VI), which is dissolved in water and eventually precipitated as sodium dichromate. This is then reduced with carbon to  $\text{Cr}^{\text{III}}$  oxide:

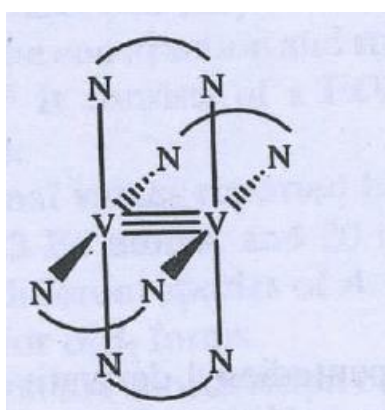
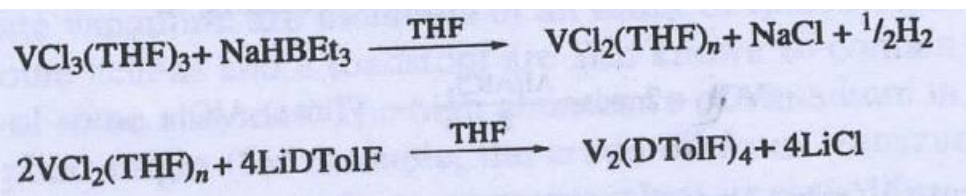


This oxide is then reduced with aluminum:



g- Can vanadium element form dinuclear complexes? Give an example.

**The answer:**



h- Give an example on the electron transfer mechanism.

**The answer:**



Only  $\text{Cr}_2\text{O}_3$ ,  $\text{CrO}_2$ , and  $\text{CrO}_3$  are of importance. The green oxide  $\alpha\text{-Cr}_2\text{O}_3$ , which has the corundum structure, is formed on burning the metal in oxygen, on thermal decomposition of  $\text{Cr}^{\text{VI}}$  oxide or ammonium dichromate, or on roasting the hydrous oxide  $\text{Cr}_2\text{O}_3 \cdot n\text{H}_2\text{O}$ . The latter is normally obtained by adding hydroxide to aqueous  $\text{Cr}^{\text{III}}$  at room temperature and has variable water content. It is often called chromic hydroxide, but there is in fact a true, crystalline hydroxide,  $\text{Cr}(\text{OH})_3(\text{H}_2\text{O})_3$ , that can be prepared by slow addition of base to a cold solution of  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ . The crystalline material quickly becomes amorphous at higher temperatures.

If ignited too strongly,  $\text{Cr}_2\text{O}_3$  becomes inert toward both acid and base, but otherwise it and its hydrous form are amphoteric, dissolving readily in acid to give aqua ions  $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ , and in concentrated alkali to form "chromites."

Chromium oxide and chromium supported on other oxides such as  $\text{Al}_2\text{O}_3$  are important catalysts for a wide variety of reactions.

The black-brown chromium(IV) oxide ( $\text{CrO}_2$ ) is normally synthesized by hydrothermal reduction of  $\text{CrO}_3$ . It has an undistorted rutile structure (i.e., no M—M bonds as in  $\text{MoO}_2$ ). It is ferromagnetic and has metallic conductance, presumably because of delocalization of electrons into energy bands formed by overlap of metal  $d$  and oxygen  $p\pi$  orbitals. Because of its magnetic properties it is used in magnetic recording tape. Above  $250^\circ\text{C}$   $\text{CrO}_2$  decomposes to  $\text{Cr}_2\text{O}_3$ .

Chromium(VI) oxide ( $\text{CrO}_3$ ) can be obtained as an orange-red precipitate on adding sulfuric acid to solutions of Na or K dichromate. The red solid, which consists of infinite chains of  $\text{CrO}_4$  tetrahedra sharing vertices, is unstable above its melting point  $197^\circ\text{C}$ , losing oxygen to give  $\text{Cr}_2\text{O}_3$  after various intermediate stages. It is readily soluble in water and is highly poisonous (see Section 17-C-10).

k-Write **briefly** (i.e. less than one page) on iron element.

**Chemistry of Iron** Fe, Z=26,  $[\text{Ar}]3d^6 4s^2$

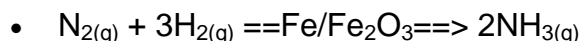
Uses of IRON

- Iron is an extremely useful silvery–white magnetic metal.
- Most iron is converted into steel alloys.
- A steel alloy consists mainly of iron mixed with controlled amounts of carbon C, and other metals like chromium Cr, tungsten W, nickel Ni etc.

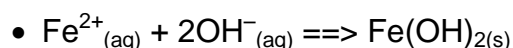
Biological role of iron

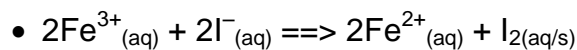
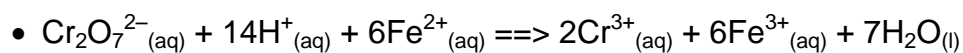
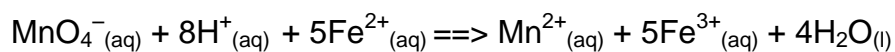
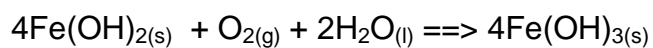
- Iron is an essential element in our diet and is needed for the production of haemoglobin.

**Uses of iron:** An iron/iron(III) oxide mixture is used as a catalyst in the Haber synthesis of ammonia from hydrogen and nitrogen.

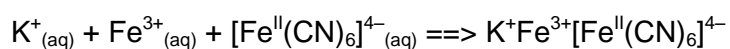
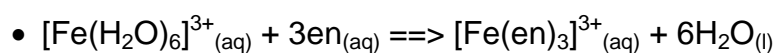
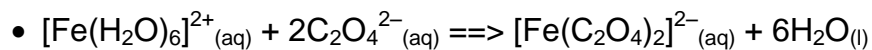


**Some reactions of iron(II) and iron(III) ions:**





Some important complexes of  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$



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**Good Luck**

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