COURSE CODE: *CHM 312*

COURSE TITLE: *Inorganic Chemistry III*

NUMBER OF UNITS: *3 Units*

COURSE DURATION: *Three hours per week*

COURSE DETAILS:

Course Coordinator: **Dr. (Mrs) C.A Akinremi** B.Sc.,M.Sc., Ph.D

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COURSE CONTENT:

Detail chemistry of d- block transition metal series. Introduction to coordination e.g Introduction to organometallic chemistry. Detail treatment of the electronic structure of transition metal. Lanthanide and actinides and the relationship to their physiochemical property.

COURSE REQUIREMENTS:

This is a compulsory course for all 300 LEVEL Chemistry students only. In view of this students are expected to participate in all the course activities and have minimum of 75% attendance to able to write the final examination.

READING LIST:

1. . Basola, F. and Johnson R. Coordination Chemistry , 2nd ed. W. A. Benjamin, Inc. New York. 1964.

2. Lee, J. D. A new Concise Inorganic Chemistry, 3rd Ed., Van Nostrand Reinhold (UK) Co. Ltd, England, 1977.

3. Cotton,F.A.; and Wilkinson,G. Advanced Inorganic Chemistry, a Comprehensive Text , 4th Ed., New York, 1988.

4. Wilkinson,G., Gillard,R.D.,and McCleverty, J.A.Comprehensive Coordination,Vol1,

Pergamon Press, Elmsford, New York, 1987.

5. David. N. Complexes and 1st row Transition elements 1st ed. Macmllian Press Ltd, London, 1974.

LECTURE NOTES

INTRODUCTION

Position in the Periodic Table

The periodic table comprises of the s-block(2 groups), p-block(6 groups), d-block(10 groups) and f-block elements(14 groups). The transition elements are in the central block of the periodic table. There are three rows of elements in the central or d-block of the periodic table. Each contains ten metallic elements and corresponds to the filling of 3d, 4d and 5d orbitals in these atoms.

Table 1.1

3	4	5	6	7	8	9	10	11	12	
Sc^a scandium	Ti^a titanium	V^a vanadium	Cr^a chromium	Mn^a manganese	$Fe^{a/b}$ iron	$Co^{a/b}$ cobalt	$Ni^{a/b}$ nickel	$Cu^{a/b}$ copper	Zn^a zinc	$[Ar]3d^n4s^m$
Y^a Yttrium	Zr^a zirconium	Nb^a niobium	Mo^a molybdenum	$Tc^{a/b}$ technetium	$Ru^{a/b}$ ruthenium	Rh^b rhodium	Pd^b palladium	Ag^b silver	$Cd^{a/b}$ cadmium	$[Kr]4d^n5s^m$
La^a Lantahnum	Hf^a hafnium	Ta^a tantalum	W^a tungsten	$Re^{a/b}$ rhenium	$Os^{a/b}$ osmium	Ir^b iridium	Pt^b platinium	Au^b gold	Hg^b mercury	$[Xe]5d^n6s^m$

[where n and m are the number of electrons which is a maximum of 10 for d-orbital and 2 for s-orbital; For "a" and "b", see section on complex formation].
The general properties are

1. **Metallic properties**: good conductors of heat and electricity, hard, strong, ductile and has metallic lustre. Form alloys with other metals. for example, Ti-Fe, Mn-Fe. They have very high melting and boiling points, higher than 1000ºC[Except La and Ag-920 and 961 ºC respectively] Also Zn-420, Cd-321, Hg melts at -38 ºC[this is because of complete d-shell, so the d-shell donot take part in metallic bonding].

2. **Variable oxidation states:**   The variable oxidation states shown by transition elements are primarily due to the fact that successive ionization energies of a transition metal atom increase gradually. In general, the lower oxidation states are reducing and the higher oxidation states are oxidising. For example, Cr^{+2} is rapidly oxidised to Cr^{+3} in the presence of air [$K_2Cr_2O_7$]. $(K^+)_2(Cr^{+6})_2(O^{-2})_7$ is a powerful oxidising agent and reduced to Cr^{+3}. Also the lower states of these metals gives mainly basic oxides while higher oxidation states gives majorly acidic oxides. Intermediates are usually amphoteric. See Table 1.2.

Table 1.2 Oxides of Manganese

Oxide	Oxidation State	Nature of Oxide	Salts
MnO	+2	Basic	Mn^{+2} salts
Mn_2O_3	+3	Basic	Few Mn^{+3} salts(eg MnF_3)
MnO_2	+4	Amphoteric	$Mn(SO_4)_2$ and K_2MnO_3
MnO_3	+6	Acidic	K_2MnO_4
Mn_2O_7	+7	Acidic	$KMnO_4$

3. **Atomic and ionic size**: Increase of 0.1-0.2A° between 1st and 2nd row transition elements, but hardly any increase between 2nd and 3rd row transition elements. Lanthanide contraction cancels almost exactly the normal size increase on descending a group of transition elements. Therefore, difference in properties greater between 1st and 2nd than 2nd and 3rd.

Table 1.3; Size of Atoms

K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
1.57	1.74	1.44	1.32	1.22	1.17	1.17	1.17	1.16	1.15	1.17	1.25
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
2.16	1.91	1.62	1.45	1.34	1.29	-	1.24	1.25	1.28	1.34	1.41
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
2.35	1.98	1.69	1.44	1.34	1.30	1.28	1.26	1.26	1.29	1.34	1.44

Lanthanide series

Lanthanide Contraction: Each succeeding lanthanides differs from its immediate predecessor in having one or more electron in the 4f (though there are some exceptions) and an extra proton in the nucleus of the atom. The 4f electrons constitute inner shells and are rather ineffective in screening the nucleus. This leads to a gradual increase in the attraction of the nucleus to the electrons in the outermost shell as the nuclear charge increases, and a consequent contraction in the atomic radius.

4. **Density**:In transition elements, there is increased nuclear charge due to poor screening effect of the d-orbitals and so attracts all the electrons added more strongly. In addition, the extra electrons added occupy inner orbitals. Hence, transition elements have higher density compared to Group 1 and 2. Elements with highest density are Osmium-22.57g/cm^3 and iridium-22.61g/cm^3.

5. **Magnetic properties:**

The magnetic properties of complexes give information on the electronic structure and consequently the oxidation state of the central atom and on the character of the bonds. It gives information on the ligand field-weak or strong and electronic structure of the metal-high or low spin.

The magnetic susceptibility is traditionally measured with a Guoy balance, which consists of a sensitive balance from which the sample hangs in the form of a narrow cylinder and lies between the

poles of a magnet. If the sample is paramagnetic, it is drawn to the field and its apparent weight is greater than when the field is off. A diamagnetic sample tends to be repelled by the field and appears to weigh less when the field is turned on. The balance is normally calibrated against a sample of known magnetic susceptibility. This enables predictions to be made regarding the oxidation state, bond type and stereochemistry of the metal complexes.

Magnetic susceptibility is measured by the ratio of the intensity of magnetization produced in a substance to the magnetizing force or intensity of field to which it is subjected. The magnetic moments are not measured directly. Instead, the magnetic susceptibility of a material is measured and then the magnetic moment is then calculated from the magnetic susceptibility

Magnetic moments are expressed in units of Bohr magnetons BM

$$IBM = \frac{eH}{4\pi mc}$$

where e = electronic charge h= Planck's constant m= electron mass

c = speed of light for a single electron, spin only magnetic moment μ_s

∴ μ_s (in BM) = g $[s\ (s+1)]^{\frac{1}{2}}$

where s= absolute value of the spin quantum number

g = gyromagnetic ratio ("g factor").

For a free electron g = 2.00023 ≈ 2.00. s =½

∴ $\mu_s = 2[½(½ +1)]^{\frac{1}{2}} = 1.73BM$.

Therefore any atom ion or molecule with one unpaired electron has a

$\mu_s = 1.73BM$ for example Cu^{2+}, H, ClO_2

If there are several electron spins in each molecule, they combine to a total spin S, and then s(s+1) should be replaced by S(S+1)

:- $\mu_s = g[S(S+1)]^{\frac{1}{2}}$

Where S=sum of the spin quantum number S=½ for the individual electrons.[**See Table 1.4**]

The values attained for experiment sometimes differ from the theoretical values, because of the contribution of orbital motion. Wave mechanics show that

$$\mu_{s+L} = [4S(S+1) +L(L+1)]^{\frac{1}{2}}$$

where L = orbital angular momentum quantum number of ion. The observed μ frequently exceeds μ_s but seldom is as high as μ_{S+L}. This is because the electric field of other atoms, ions and molecules surrounding the metal ion in its compounds restrict the orbital motion of the electrons, so that the orbital angular momentum and hence the orbital moments are wholly or partially "quenched".

Table 1.4: Spin-only magnetic moments

No of unpaired electrons	S	μ_s (BM)
1	½	1.73
2	1	2.83
3	3/2	3.87
4	2	4.90
5	5/2	5.92

Paramagnetism Paramagnetic behaviour results when the applied magnetic field lines up all the existing magnetic moments of the individual atoms or molecules that make up the material. This results in an overall magnetic moment that adds to the magnetic field. Paramagnetic materials usually contain transition metals or rare earth elements that possess unpaired electrons.

Diamagnetism: Here, the substance is repelled by a magnetic field. The diamagnetic behaviour is due to small magnetic moments that are induces by the magnetic field but do not exist in the absence of the field. Therefore, moments so induced are in opposition to the inducing field, thereby causing repulsion.All materials show a diamagnetic response in an applied magnetic field. In fact, diamagnetism is a very general phenomenon, because all paired electrons, including the core electrons of an atom, will always make a weak diamagnetic contribution to the material's response. However, for materials that show some other form of magnetism (such as ferromagnetism or paramagnetism), the diamagnetism is completely overpowered.

Ferromagnetism: A *ferromagnetic* substance is one that, like iron, retains a magnetic moment even when the external magnetic field is reduced to zero. This effect is a result of a strong interaction between the magnetic moments of the individual atoms or electrons in the magnetic substance that causes them to line up parallel to one another. Ferromagnetic materials, when heated, eventually lose their magnetic properties. This loss becomes complete above the Curie temperature, named after the French physicist Pierre Curie, who discovered it in 1895. (The Curie temperature of metallic iron is about 770° C/1420° F.)

6. **Complex ions formation**: The early and lighter transition elements forms stable complex with ligands of donor atoms N, O, F called the "a" class. While the later and heavier transition elements forms more stable complexes with heavier elements from group 15, 16 and 17 called the "b" class. Some display intermediates- **See Table 1.1.** A complex ion is one that contains a central ion linked to other atoms, ions or molecules which are called **LIGANDS**. The most common coordination number is 6.

7. **Formation of coloured compounds**: This formation is caused by

a. Polarization Eg NaCl, NaBr and NaI are ionic and colourless. AgCl is colourless but AgBr is pale yellow and AgI is yellow. This arises because the Ag+ ion polarizes the halide ions, thus distorting

the electron cloud and implying a greater covalent contribution. This polarizability of ions increase with size, thus I is most polarized hence most coloured.

b. Incompletely filled d-shell: this is dependent on how large the splitting is, that is energy difference; the nature of the ligands surrounding the ion; the type of complex formed.

Splitting Diagram for $Ti(H_2O)_6^+$ — Ground State — Excited State
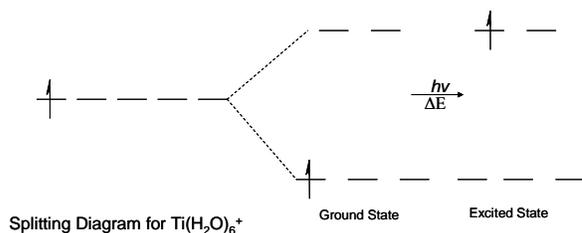
Some are white eg TiO_2, $ZnSO_4$. This is because $Zn=3d^{10}$, $Ti=3d^0$. Also, Sc^{3+}, Ti^{4+}, V^{5+}, Cr^{6+}, Mn^{7+} has d^0, so d-d transition is impossible and hence their compounds should be colourless, but this is not the case. As oxidation state increases, it becomes strongly covalent; instead of charged ionic compounds, it forms oxoions eg TiO^{2-}, VO_2^+-pale yellow, VO_4^{3-}, CrO_4^{2-}-yellow and MnO_4^--intense purple. The colour is due to charge transfer eg for MnO_4^-, an electron is transferred from O to Mn, hence, O^{2-} becomes O^-,, reducing the oxidation state of Mn from +7 to +6. However, charge transfer requires that the energy levels on the two different atoms be fairly close.

8. **Catalytic properties:**

They are good catalysts because they can change their oxidation state easily. The catalytic action of transition metals is probably due to the ability of the atoms on the metal surface to form bonds with the reactant molecules. The large number of 3d and 4S electrons available makes this possible. This has the effect of increasing the concentration of the reactants at the catalyst surface and also of weakening the bonds in the reactant molecules (i.e. the activation energy is lowered).

Examples of industrial processes involving the use of transition metals as catalysts

a. Industrial manufacture of ammonia (Haber process)

$$N_{2(g)} + 3H_{2(g)} \underset{\text{Fe catalyst}}{\overset{\text{Finely divided}}{\rightleftharpoons}} 2NH_{3\,(g)}$$
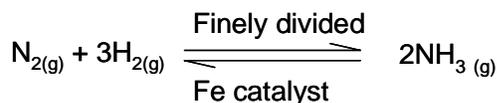
b. Manufacture of sulphur (IV) oxide (Contact Process)

$$2SO_{2(g)} + O_{2(g)} \underset{\text{Catalyst}}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_{3\,(g)}$$
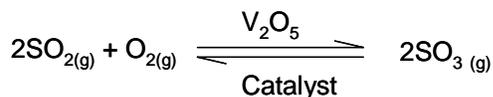
c. Hydrogenation of alkenes

$$CH_2=CH_{2(g)} + H_{2(g)} \underset{\text{Catalyst}}{\overset{\text{Ni}}{\rightleftharpoons}} CH_3—CH_{3\,(g)}$$

Ethene   Ethane
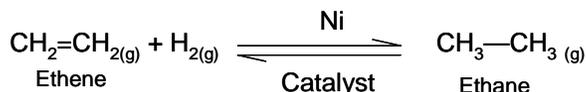
DIFFERENCES BETWEEN 1ST ROW AND OTHER TWO ROWS TRANSITION ELEMENT

1. **M-M bonding and cluster compounds**: M-M bonding is rare in 1st row transition elements but occurs in few carbonyl compounds eg $Mn_2(CO)_{10}$, $Fe_2(CO)_9$ etc. Also in carboxylate complexes such as $Cr_2(CH_3COO)_4(H_2O)_2$. But in 2nd and 3rd row, it is much common eg

   a. carbonyls- $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Ir_4(CO)_{12}$;

   b. Mo, Ru, and Rh form binuclear carboxylate complexes such as $Mo_2(CH_3COO)_4(H_2O)_2$ as for chromium (II) acetate.

   c. halide ions eg $[Re_2Cl_8]^{-2}$ and $[Mo_2Cl_9]^{-3}$.

   d. Lower halides of several elements have a group of 3 or 6 metals bonded together called cluster compounds eg Nb, Mo, Ta, W, Re.- $[Nb_6Cl_{12}]^{+2}$, $[Ta_6Cl_{12}]^{+2}$.

2. **Stability of oxidation state**: +2 and +3 states are more important and stable for 1st row than for 2nd and 3rd row eg $[Cr^{III}Cl_6]^{-3}$, $[Co^{III}(NH_3)_6]^{+3}$. Higher oxidation states are more important and stable for 2nd and 3rd row eg $[CrO_4^{-2}]$, which is a strong oxidizing agent but $[MoO_4]^{-2}$ and $[WO_4]^{-2}$ are stable. Also, manganate$[MnO_4]^-$ is a strong oxidizing agent but , pertechnate$[TcO_4]^-$ and ,perhenate$[ReO_4]^-$ ions are stable. Also at 2nd and 3rd row elements you have high oxidation states like in WCl_6, ReF_7, PtF_6, RuO_4 and OsO_4 which are not present for 1st row.

3 **Complexes:** The coordination number of 6 is most common among the transition elements. 4 is less common but 7 and 8 which are uncommon for 1st row, are common in early members of 2nd and 3rd row.

4. **Size**; The atomic size of 2nd row transition elements are larger than 1st row but due to lanthanide contraction, the radii of 3rd row are almost same as for 2nd row.

5. **Magnetism**: For 1st row octahedral complexes, the d-level splits into t_{2g} and e_g sublevels. If the ligand has a strong field, they cause a large difference in energy between the sublevels, therefore, the electrons on the d-orbital fills the lower t_{2g} before the fill the e_g , even if they have to pair- *low spin*. If the ligand has a weak field, the energy difference will be small due to minimal splitting, hence each of the t_{2g} and e_g are singly filled with electrons before pairing- *high spin*. But for the 2nd and 3rd row elements, only low spin complexes are formed regardless of the ligands. For 1st row transition elements, spin contribution is sufficient but for 2nd and 3rd row, orbital contribution is significant and spin-orbit coupling may occur. Also, 2nd and 3rd row transition elements show extensive temperature dependent paramagnetism due to spin-orbit coupling, removing degeneracy from the lowest energy level in the ground state.

6. **Abundance:** 1st row transition elements are more common-6.79% of the earth's crust. But 2nd and 3rd row transition elements are scarce. Tc does not occur in nature.

2.0 INTRODUCTION TO COORDINATION CHEMISTRY

A **coordination compound**, sometimes called a coordination complex, contains a central metal atom or ion surrounded by a number of oppositely charged ions or neutral molecules (possessing lone pairs of electrons) which are known as **ligands**. If a **ligand** is capable of forming more than one bond with the central metal atom or ion, then ring structures are produced which are known as Metal Chelates, the ring forming groups are described as chelating agents or polydentate ligands. The **coordination number** of the central metal atom or ion is the total number of sites occupied by ligands. Note: a bidentate ligand uses two sites, a tridentate three sites etc.

Although coordination complexes are particularly important in the chemistry of the transition metals, some main group elements also form complexes. Aluminum, tin, and lead, for example, form complexes such as the AlF_6^{3-}, $SnCl_4^{2-}$ and PbI_4^{2-} ions.

Werner's Theory of Coordination Complexes

Alfred Werner developed a model of coordination complexs which explains the following observations. At least three different cobalt(III) complexes can be isolated when $CoCl_2$ is dissolved in aqueous ammonia and then oxidized by air to the +3 oxidation state. A fourth complex can be made by slightly different techniques. These complexes have different colors and different empirical formulas

When excess Ag^+ ion is added to solutions of the $CoCl_3$ 6 NH_3 and $CoCl_3$ 5 NH_3 H_2O complexes, three moles of AgCl are formed for each mole of complex in solution, as might be expected. However, only two of the Cl^- ions in the $CoCl_3$ 5 NH_3 complex and only one of the Cl^- ions in $CoCl_3$ 4 NH_3 can be precipitated with Ag^+ ions.

Measurements of the conductivity of aqueous solutions of these complexes suggest that the $CoCl_3$ 6 NH_3 and $CoCl_3$ 5 NH_3 H_2O complexes dissociate in water to give a total of four ions. $CoCl_3$ 5 NH_3 dissociates to give three ions, and $CoCl_3$ 4 NH_3 dissociates to give only two ions.

Werner explained these observations by suggesting that transition-metal ions such as the Co^{3+} ion have a primary valence and a secondary valence. The *primary valence* is the number of negative ions needed to satisfy the charge on the metal ion. In each of the cobalt(III) complexes previously described, three Cl^- ions are needed to satisfy the primary valence of the Co^{3+} ion.

The *secondary valence* is the number of ions of molecules that are coordinated to the metal ion. Werner assumed that the secondary valence of the transition metal in these cobalt(III) complexes is six. The formulas of these compounds can therefore be written as follows.

$[Co(NH_3)_6^{3+}][Cl^-]_3$	orange-yellow
$[Co(NH_3)_5(H_2O)^{3+}][Cl^-]_3$	red
$[Co(NH_3)_5Cl^{2+}][Cl^-]_2$	purple
$[Co(NH_3)_4Cl_2^+][Cl^-]$	green
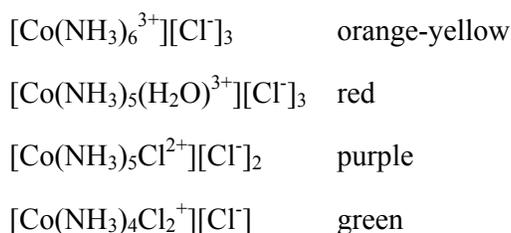
The cobalt ion is coordinated to a total of six ligands in each complex, which satisfies the secondary valence of this ion. Each complex also has a total of three chloride ions that satisfy the primary valence. Some of the Cl⁻ ions are free to dissociate when the complex dissolves in water. Others are bound to the Co^{3+} ion and neither dissociate nor react with Ag^+.

Formation of complexes and Lewis Acid-Lewis base Approach to Bonding in Complexes

In transition metal complexes, non-bonded pairs of electrons on the ligands form coordinate bonds to the central metal. The unshared electron pairs are donated into vacant orbitals of the transition metal ion. The number of coordinate bonds from the ligands to the central ion is known as the coordination number of the central ion.

Coordination compounds, such as the $[FeCl_4]^-$ ion and $CrCl_3$ 6 NH_3, are called such because they contain ions or molecules linked, or coordinated, to a transition metal. They are also known as complex ions or coordination complexes because they are Lewis acid-base complexes. A complex is a combination of a Lewis acid (the central metal atom) with a number of Lewis bases (the ligands). The atom in the Lewis base ligand that forms the bond to the central metal atom is called the **donor atom** because it donates the electrons used in bond formation. The metal atom or ion, the Lewis acid in the complex is the **acceptor atom**.

A Lewis acid is therefore any ion or molecule that can accept a pair of electrons. A Lewis base is an ion or molecule that can donate a pair of electrons.

When Co^{3+} ions react with ammonia, the Co^{3+} ion accepts pairs of nonbonding electrons from six NH_3 ligands to form covalent cobalt-nitrogen bonds. The metal ion is therefore a Lewis acid, and the ligands coordinated to this metal ion are Lewis bases.
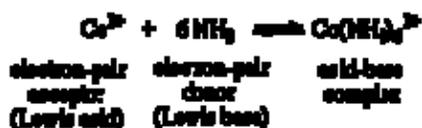
The Co^{3+} ion is an electron-pair acceptor, or Lewis acid, because it has empty valence-shell orbitals that can be used to hold pairs of electrons.

Typical Coordination Numbers

Transition-metal complexes have been characterized with coordination numbers that range from 1 to 12, but the most common coordination numbers are 2, 4, and 6. Examples of complexes with these coordination numbers are given in the table below.

In an Inner-sphere complex, the ligands are attached directly to the central metal atom or ion. These ligands form the primary coordination sphere of the complex and their number is called the coordination number of the central metal atom. For an outer-sphere complex, the complex cations can associate

electrostatically with anionic ligands and by other weak interactions, with solvent molecules, without displacement of the ligands already present. Eg $[Mn(OH_2)_6]^{2+}.SO_4^{2-}$ ions and $[Mn(OH_2)_5SO_4]$ ions.

Three factors govern the coordination number of a complex:

1. The size of the central atom or ion: the large radii of atoms and ions lower the periodic table favour higher coordination number.

2. The steric interactions between the ligands: Bulky ligands often result in low coordination numbers, especially if the ligands are also charged (when unfavorable electrostatic interactions also come into play)

3. Electronic interactions between the central atom or ion and the ligands.

Higher coordination number: This is common with

(a) elements on the left of the period where the ions have a larger radii

(b) metal ions that have only few electrons because a small number of valence electrons means the metal can accept more electrons from Lewis bases eg $[Mo(CN)_8]^{4-}$.

Lower coordination number: This is common with

(a) the right of the d-blocks, if the ions are rich in electrons which will accept less electrons from the Lewis bases eg $[PtCl_4]^{2-}$.

(b) If the ligands can form multiple bonds with the central metal as the electrons provided by each ligand tend to exclude the attachment of more ligands eg MnO_4^-, CrO_4^{2-}.

Typical Ligands

Any ion or molecule with a pair of nonbonding electrons can be a ligand. Many ligands are described as monodentate (literally, "one-toothed") because they "bite" the metal in only one place. Typical monodentate ligands are given in the figure below.
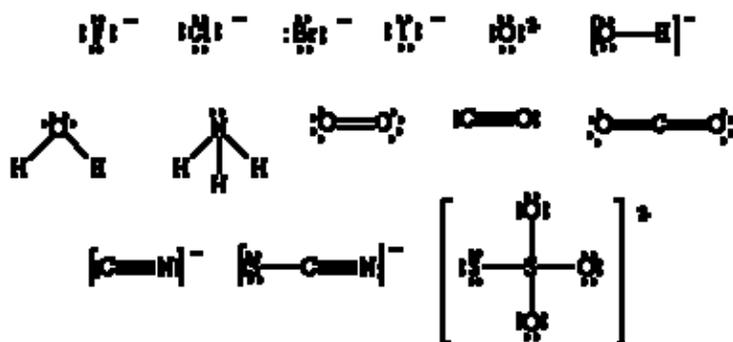
Other ligands can attach to the metal more than once. Ethylenediamine (en) is a typical bidentate ligand.

ethylenediamine (en) Each end of this molecule contains a pair of nonbonding electrons that can form a covalent bond to a metal ion. Ethylenediamine is also an example of a chelating ligand. The term chelate comes from a Greek stem meaning "claw." It is used to describe ligands that can grab the metal in two or more places, the way a claw would. Linking ethylene- diamine fragments gives tridentate ligands and

tetradentate ligands, such as diethylenetriamine (dien) and triethylenetetramine (trien). Adding four -$CH_2CO_2^-$ groups to an ethylenediamine framework gives a hexadentate ligand, which can single-handedly satisfy the secondary valence of a transition-metal ion.

Organometallic Chemistry

Any coordination or complex compound consisting of a heavy metal such as nickel, cobalt, or iron surrounded by carbonyl (CO) groups. Some common metal carbonyls include: tetracarbonylnickel $Ni(CO)_4$, pentacarbonyliron $Fe(CO)_5$, and octacarbonyldicobalt $Co_2(CO)_8$. In general, the metal carbonyls are produced by direct action of carbon monoxide on the finely divided metal. They are used in the preparation of metals of exceptionally high purity and as catalysts in organic syntheses.

The electronic structures of most metal carbonyls containing one metal atom per molecule (mononuclear carbonyls) bear striking resemblances to those of the noble-gas elements. For example, tetracarbonylnickel has 36 electrons (28 from the nickel atom and 8 electrons from the 4 carbonyl groups) surrounding the nickel nucleus. This number, called the effective atomic number (EAN), is also the total number of electrons in the noble-gas element krypton.

Ferocene, also called ***Dicyclopentadienyliron,*** the earliest and best known of the so-called sandwich compounds; these are derivatives of transition metals in which two organic ring systems are bonded symmetrically to the metal atom. Its molecular formula is $(C_5H_5)_2Fe$.

Carborane any member of a class of organometallic compounds having the general formula $C_2B_nH_{n+2}$, in which C, B, and H represent, respectively, carbon, boron, and hydrogen atoms and n an integer; carboranes with n ranging from 3 to 10 have been characterized. The carboranes have polyhedral molecular structures based on networks of boron and carbon atoms, the carbon atoms occupying adjacent positions. They are generally prepared by reaction of acetylene or acetylene derivatives with boron hydrides. The best-studied carborane is o-carborane, $C_2B_{10}H_{12}$, made by reaction of acetylene with decaborane in the presence of diethyl sulfide. Its molecular structure resembles an icosahedron with the 10 boron atoms and 2 adjacent carbon atoms forming the apices.

GROUP 3(IIIB)-SCANDIUM GROUP

Electronic Structure

This comprises of

Scandium Sc   —$[Ar]3d^1 4S^2$

Yttrium Y   —$[Kr]4d^1 5S^2$

Lanthanum La   —$[Xe]5d^1 6S^2$

Actinium Ac   —$[Rn]6d^1 7S^2$

The members of this group and the 14 lanthanides are collectively called the rare earths even though Scandium is a d-block metal and lanthanides are f-block. Also, scandium group is not so rare.

Occurrence and Extraction

Table 2.1: Relative abundance of the Scandium group

Element	Abundance in %(ppm)
Scandium	31%(25)
Yttrium	29%(31)
Lanthanum	28%(35)
Actinium	trace

Scandium: Sc is the 31st most abundant element by weight in the earth's crust. It occurs in a rare mineral thortveitite ($Sc_2[Si_2O_7]$).

Scandium is easily separated from the other rare earths by precipitation of the very insoluble potassium scandium sulfate or by extraction of scandium thiocyanate by diethyl ether. The metal itself was first prepared in 1938 by the electrolysis of potassium, lithium, and scandium chlorides in a eutectic mixture (*i.e.*, a mixture having the lowest melting point possible with those components). Scandium is now produced on a small scale mostly as a by-product of uranium extraction from the mineral davidite, which contains about 0.02 percent scandium oxide.

Yttrium and Lanthanum: These are 29th and 28th (respectively) most abundant elements. The exist together with lanthanide elements in bastnaesite($M^{III}CO_3F$), monazite($M^{III}PO_4$) and other minerals from which it is very difficult to separate due to closeness in size. Stable yttrium-89 is the only naturally occurring isotope. Lanthanum exhibits three allotropic (structural) forms. Two isotopes occur in nature: stable lanthanum-139 (99.911 percent) and very long-lived radioactive lanthanum-138 (0.089 percent). The isotope lanthanum-140 has been detected as a fission product in snow after nuclear-test explosions.

Yttrium occurs especially in the heavy rare-earth ores, of which gadolinite, euxenite, and xenotime are the most important. In the igneous rocks of the Earth's crust, this element is more plentiful than any of the other rare-earth elements except cerium and is twice as abundant as lead. Yttrium also occurs in the products of nuclear fission. Commercially yttrium is separated from the other rare earths by ion exchange, and the metal is produced by reduction of the fluoride with calcium.

Lanthanum is concentrated commercially by crystallization of ammonium lanthanum nitrate. Ion-exchange and solvent extraction methods are used when high purity is desired. The metal itself is prepared by electrolysis of fused anhydrous halides.

Yttrium and Lanthanum can be prepared by reduction of its halides (chlorides or fluorides) with calcium at 1000ºC under an atmosphere of argon.

Actinium:. There is scarcity of the naturally occurring Ac due to the short half lives of its isotopes. A ton of pitchblende ore contains about 0.15 mg of actinium. The most common isotope of actinium is actinium-227[$^{227}_{89}Ac$]; the others, natural and artificial for example actinium-2278[$^{228}_{89}Ac$ with half-life 6hrs] are too short-lived to accumulate in macroscopic quantity. Actinium-227, which is one of the decay products of uranium-235, has a 21.6-year half-life and in turn decays almost entirely to thorium-227, but about 1 percent decays to francium-223.

$$^{232}_{90}Th \xrightarrow{\alpha} {}^{228}_{88}Ra \xrightarrow{\beta} {}^{228}_{89}Ac$$

$$^{235}_{92}U \xrightarrow{\alpha} {}^{231}_{90}Th \xrightarrow{\beta} {}^{231}_{91}Pa \xrightarrow{\alpha} {}^{227}_{89}Ac \xrightarrow{\beta} {}^{227}_{90}Th$$
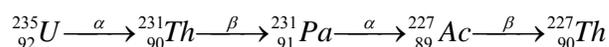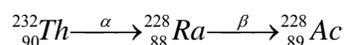
It can also be made by irradiating Ra with neutrons in a nuclear reactor. This whole disintegration chain with its branches is called the actinium decay series.

$$^{226}_{88}Ra + {}^{1}_{0}n \longrightarrow {}^{227}_{88}Ra \xrightarrow{\beta} {}^{228}_{89}Ac$$
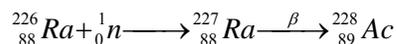
GENERAL PROPERTIES

Table 2.2: Summary of some of the physical properties

	Appearance (in pure state)	Atomic radii	Ionic radii	Ionization energy kJmol^{-1}			M.pºC	B.pºC	Standard Electric Potential Eº(V)
				1st	2nd	3rd			
Sc	Silvery white, rather soft	1.44	0.745	631	1235	2393	1539	3,337	-2.08
Y	Silvery, ductile	1.62	0.900	616	1187	1968	1530	3,337	-2.37
La	Silvery-white ductile and malleable, very soft	1.69	1.0322.	541	1100	1852	920	3,454	-2.52
Ac	Silvery white, glows blue in dark	-	1.12	-	-		817	-	2.6

Oxidation State:

The elements have an oxidation state of $+3 (M^{+3}$ ions). This requires the removal of two **s** electrons and one **d** electron. The ions therefore have d^0 configuration and d-d spectra is not possible. The ions and compounds are colourless and diamagnetic.

Chemical properties:

They have high electrode potential and are reactive. The reactivity increases with increase in size. Lanthanum is the second most reactive of the rare-earth metals.

They tarnish in air and burn in oxygen to give oxides M_2O_3. La ignites in air at 440° C.

$$2La + 3O_2 \rightarrow 2La_2O_3$$
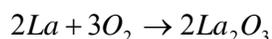
White oxide La_2O_3 is the most alkaline rare-earth oxide. Yttrium however, forms a protective oxide coating in air, which makes it unreactive.

The metals react slowly in cold water but rapidly in hot water, giving off hydrogen to form a basic oxide or hydroxide.

$$2La + 6H_2O \rightarrow 2La(OH)_3 + 3H_2$$

$$La(OH)_3 \rightarrow LaO.OH + H_2O$$
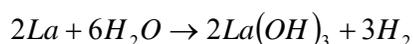
To better understand their chemical properties, we will look at the compounds they form, when the undergo reaction.

Oxides and Hydroxides

Scandium: Scandium hydroxide ($Sc(OH)_3$) doesnot seems to exist as a definite compound but as a basic oxide ScO.OH. The hydrous oxide is amphoteric and hydroxide isostructural with Al_2O_3 (AlO.OH). Because it is amphoteric, it reacts with concentrated NaOH to form a compound, liberating hydrogen in the process.

$$Sc + 3NaOH + 3H_2O \rightarrow Na_3[Sc(OH)_6] + 1\tfrac{1}{2}H_2$$
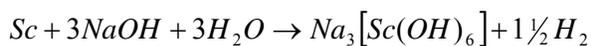
Yttrium and Lanthanum: The yttrium hydroxide ($Y(OH)_3$) and Lanthanum hydroxide ($La(OH)_3$) are more basic than $Sc(OH)_3$,as the basic properties increases on descending the group. The yttrium and Lanthanum oxides and hydroxide reacts with acids to form salts and reacts with carbon (IV) oxide to form salt and water.

$$2Y(OH)_3 + 3CO_2 \rightarrow Y_2(CO_3)_3 + 3H_2O$$
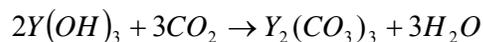
$La(OH)_3$ is a strong enough base as to liberate ammonia from ammonium salts.

Since the oxides and hydroxides are either amphoteric or weak bases, their oxosalts canbe decomposed to oxides on heating as for group 2(IIA) elements(but group 2 elements decomposition occurs more easily at low temperature)

$$2Y(OH)_3 \xrightarrow{\ heat\ } Y_2O_3 + 3H_2O$$

$$Y_2(CO_3)_3 \xrightarrow{\ heat\ } Y_2O_3 + 3CO_2$$

$$2Y(NO_3)_3 \xrightarrow{\ heat\ } Y_2O_3 + 6NO_2 + 1\tfrac{1}{2}O_2$$

$$Y_2(SO_4)_3 \xrightarrow{heat} Y_2O_3 + 3SO_2 + 1\tfrac{1}{2}O_2$$
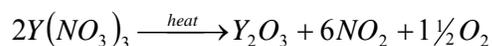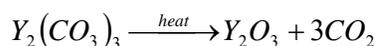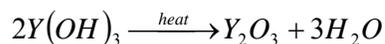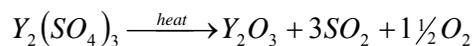
Halides

They generally react with halogens forming trihalides MX_3 which resembles that of calcium. The fluorides are insoluble in water just as CaF and the other halides are soluble and deliquescent just as $CaCl_2$. Scandium fluoride dissolves readily in HF or in NH_4F to give fluoro complexes such as ScF_6^{3-}. The similarity with Al is confirmed by the presence of the cryolite phase Na_3ScF_6 and $NaScF_4$ in the NaF-ScF_3 system.

The chlorides of this group crystallize as hydrated salts, if prepared in solution. Heating the hydrated salts does not give anhydrous halides but gives the oxide (for $ScCl_3.(H_2O)_7$ and oxohalides (for the others).

$$2ScCl_3.(H_2O)_7 \xrightarrow{heat} Sc_2O_3 + 6HCl + 4H_2O$$

$$YCl_3.(H_2O)_7 \xrightarrow{heat} YOCl + 2HCl + 6H_2O$$

$$LaCl_3.(H_2O)_7 \xrightarrow{heat} LaOCl + 2HCl + 6H_2O$$
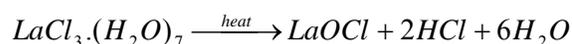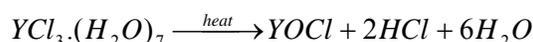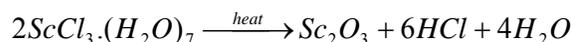
Anhydrous chlorides can be made from the oxides by reaction with NH_4Cl.

$$Sc_2O_3 + 6NH_4Cl \xrightarrow{300°C} 2ScCl_3 + 6NH_3 + 3H_2O$$
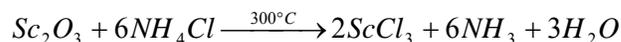
$ScCl_3$ and $ScBr_3$ can also be obtained by P_2O_5 dehydration of the hydrated halides. Unlike $AlCl_3$, it doesnot act as a Friedel craft catalyst.

The salts generally are like those of calcium and the fluorides, carbonates, phosphates and oxalates are insoluble.

Hydrides

The members of this group react with hydrogen on heating at 300ºC to form th highly conducting hydrides, MH_2. These compounds are considered to contain M^{3+} and $2H^-$ and an extra electron in a conduction band. The hydrides [except for scandium hydrides] absorb more hydrogen and lose their conducting power, forming compounds which are not fully stoichiometric but approach a composition of MH_3. The hydrides react with water giving off hydrogen and salt-like (ionic) hydrides with hydride ion H^-.

Carbides

Scandium forms carbides ScC_2 when the oxide is heated with carbon on an electric furnace. The carbide reacts with water to liberate ethyne.

$$Sc_2O_3 + C \xrightarrow{1000°C} 2ScC_2 \xrightarrow{H_2O} C_2H_2 + ScO.OH$$
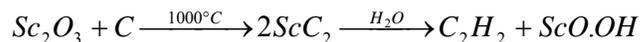
From magnetic studies, scandium carbide contains Sc^{3+} and C_2^{2-} ions and the free ions are delocalized into a conduction band, giving some metallic conduction.

Complexes

The metals of this group do not have a strong tendency to form complexes because of their fairly large size. Sc^{3+} ion forms complexes more readily than the other members because it is the smallest ion.

GROUP 4(IVB)-TITANIUM GROUP

ELECTRONIC STRUCTURE

See table below for the Xenon based electronic structure.

Table 3.1: Electronic structures, oxidation states, relative abundance of the Scandium group

Element	Symbol	Electronic Structure	Oxidation states*	Abundance in %(ppm)
Titanium	Ti	$[Ar]3d^2 4S^2$	(-1),(0),(2), 3, **4**	9%(6320)
Zirconium	Zr	$[Kr]4d^2 5S^2$	(2), (3), **4**	18%(162)
Hafnium	Hf	$[Xe]4f^{14}5d^2 6S^2$	(2), (3), **4**	45%(2.8)

*Most usual oxidation state is in **bold.***

Oxidation state that is unstable or in doubt are in parentheses

OCCURRENCE

Titanium is the 9th most abundant metal in the earth's crust and occurs principally as rutile(titanium(IV) oxide-TiO_2) and ilmenite (FeO. TiO_2).

Zirconium occurs widely over the earth's crust but not in very concentrated deposits. It is found mainly in the minerals baddeleyite, a form of ZrO_2 and zircon, $ZrSiO_4$.

Hafnium is found naturally in all zirconium mineral in the range of 1-2%. It is extremely diffucult to separate the two elements (more difficult than the lanthanides). But can be done satisfactorily by ion exchange, solvent extraction and electrochemical methods.

EXTRACTION

It is not possible to obtain the metal by the common method of reduction with carbon because a very stable carbide is obtained. Also at high temperature, it burns in oxygen and nitrogen and will decompose steam on really strong heating. The metal is obtained by first converting the dioxide into titanium (IV) chloride (a covalent liquid) by mixing it with carbon and heating in a stream of chlorine.

$$TiO_{2(s)} + C_{(s)} + 2Cl_{2(g)} \xrightarrow{900°C} TiCl_{4(l)} + CO_{2(g)}$$

$$2FeTiO_{3(s)} + 6C_{(s)} + 7Cl_{2(g)} \rightarrow 2TiCl_{4(l)} + 6CO + 2FeCl_3$$
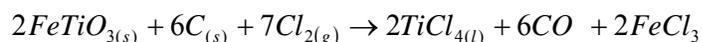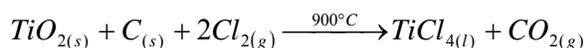
The tetrachloride with boiling point of 137°C is separated from the $FeCl_3$ and other impurities by fractional distillation, then subject to any of the following processes;

a. Kroll process: Here, the $TiCl_4$ is then reduced to metallic Ti by heating with either magnesium or sodium with a blanket of argon(traces of air makes the metal brittle).

$$TiCl_{4(l)} + 2Mg_{(s)} \xrightarrow{1000-1150°C} Ti_{(s)} + 2MgCl_{2(s)}$$
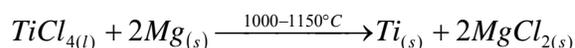
The $MgCl_2$ is removed either by vacuum distillation or by leaching with H_2O or with dilute HCl-as this will dissolve any excess Mg. This gives Ti metal as a spongy mass which may be fused in an electric arc under a high vacuum or an atmosphere of argon. This method is also used to produce zirconium

b. The van Arkel-de Boer method:

This is also used for other metals, (Ti, Zr). Extremely pure but small amount of Ti can be made from this process. Impure Ti or Zr are heated in an evacuated vessel with I_2. TiI_4 or ZrI_4 is formed and

volatilized, therefore separating from other impurities. At atmospheric pressure, TiI_4 melts at 150ºC and boils at 377ºC. ZrI_4 melts at 499ºC and boils at 600ºC. The pure MI_4 vapour is decomposed on a white hot tungsten filament at low pressure. As more metal is deposited on the filament, it conducts electricity better, thus more electric current must be passed to keep it white hot.

$$impure Ti + 2I_2 \xrightarrow{50-250°C} TiI_4 \xrightarrow{1400°C, W filament} Ti + 2I_2$$
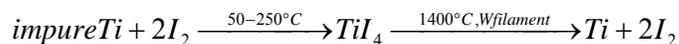
Zirconium is produced in a much smaller scale than Ti.

Zirconium and Hafnium are separated by solvent extraction of their nitrates into tri-n-butyl phosphates or thiocyanates into methylisobutyl ketone. They can also be separated by ion exchange of an alcoholic solution of the tetrachlorides on silica gel columns. On eluting the column with an alcohol/HCl mixture, the Zr comes out first.

GENERAL PROPERTIES

Table 3.2: Some Physical Properties

	Atomic radii	Ionic radii M^{+4}	M.pºC	B.pºC	Density (gcm^{-3})
Ti	1.32	0.605	1667	3285	4.50
Zr	1.45	0.72	1857	4200	6.51
Hf	1.44	0.71	2222	4450	13.28

Titanium:

1. The metal has a hexagonal closed packed lattice and resembles other metals such as Fe and Ni. It is hard, has high melting point and density (about 60% that of steel and about as strong), but much lighter than steel.

2. Ti has better corrosion resistance than stainless steel.

3. It is a better conductor of heat and electricity than scandium group.

4. Although, it is unreactive at ordinary temperature, Ti combines directly with most nonmetals, for example, H_2, the halogens, O_2, N_2, C, B, Si and S at elevated temperature. The nitride TiN and borides (TiB and TiB_2) are interstitial compounds that are very stable, hard and refractory.

5. The metal is not attacked by mineral acids at room temperature or even hot aqueous alkali. It gives Ti^{III} species with hot dilute HCl, whereas hot HNO_3 converts it into a hydrous oxide which is insoluble in acid or base.

6. The best solvents are HF or acids in which fluoride ions has been added. Such media dissolves Ti and hold it in solution as fluoro complexes.

$$Ti + 6HF \rightarrow H_2[TiF_6] + 2H_2$$
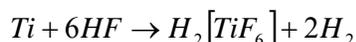
Zirconium and Hafnium:

Zr and Hf have similar properties because of their similar size.

1.   The metals like Ti have high melting points, are hard and corrosion resistance(Zr is more resistant than Ti), resembling stainless steel in appearance.

2.   Zr has low absorption of neutrons, however, Hf absorbs neutrons very strongly

3.   Zr and Hf will burn in air at high temperature(like Ti) reacting more rapidly with nitrogen, than with oxygen to give a mixture of nitride, oxide and oxide nitride (eg Zr_2ON_2).

4.   They are fairly resistant to acids and are best dissolved in HF(like Ti) where the formation of anionic fluoro complexes is important in the stabilization of the solutions.

COMPOUNDS OF TITANIUM GROUP

(+4) States.- d^0

This is the most common and stable oxidation state. It has a d^0 configuration with no unpaired electrons; hence their compounds are typically white or colourless and diamagnetic. The Ti^{4+} ions do not exist in solution, but oxoions are formed instead. The titanyl ion TiO^{2+} is found in solution but it is usually polymerized in crystalline salts.

Polymeric TiO^{2+} chain
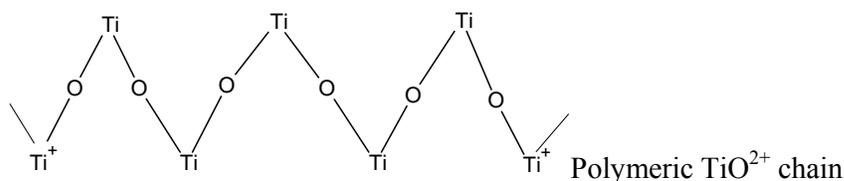
Halides:

They form halides of the form MX_4.

Titanium: Titanium(IV) chloride, $TiCl_4$ is made by passing chlorine over heated titanium or over a heated mixture of TiO_2 and carbon.

$$Ti_{(s)} + 2Cl_{2(g)} \rightarrow TiCl_{4(l)}$$
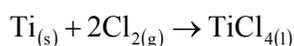
It is a covalent liquid which fumes in moist air and is hydrolysed by water to give TiO_2 and hydrogen chloride.

$$TiCl_{4(l)} + 2H_2O_{(l)} \rightarrow TiO_{2(s)} + 4HCl_{(g)}$$
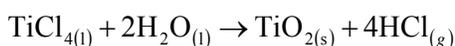
But hydrolysis with HCl, gives the oxochloride.

$$TiCl_{4(l)} + H_2O_{(l)} \xrightarrow{HCl} TiOCl_2 + 2HCl_{(g)}$$
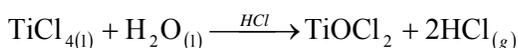
TiBr$_4$ and a metastable form of TiI$_4$ are crystalline at room temperature and isomrphous with SiI$_4$, GeI$_4$ and SnI$_4$ having molecular lattices. The halides are made by heating the halogens and metals. TiF$_4$, a white powder is obtained by reaction of F_2 on titanium at 200ºC. It can also be prepared from TiCl$_4$ by reaction with anhydrous HF. TiF$_4$ sublimes readily and is hygroscopic.

$$TiCl_4 + 4HF \rightarrow TiF_4 + 4HCl$$
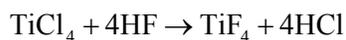
All the halides acts as lewis acids(electron pair acceptor) with a with a variety of donors forming a large number of octahedral complexes. $TiF_4 \xrightarrow{ConcHF} [TiF_6]^{2-}$ very stable

Zirconium and Hafnium

The tetrahalides MCl_4, MBr_4 and MI_4, are tetrahedral monomers in the gas phase, but the solids are polymers with halide bridging.

$ZrCl_4$ is a white solid which sublimes at 331ºC, with zigzag chains of $ZrCl_6$ octahedral. $ZrBr_4$, $HfCl_4$ and $HfBr_4$ are isotypic. In terms of chemical properties, $ZrCl_4$ resembles $TiCl_4$. It also fumes in air and hydrolysed vigorously by water. Partial hydrolysis takes place at room temperature gives a stable oxide chloride. The chemistry of $ZrBr_4$ and ZrI_4 are similar to $ZrCl_4$.

$$Zr + 9H_2O \rightarrow ZrOCl_2.8H_2O + 2HCl$$

ZrF_4 is a white crystalline solid that sublimes at 903ºC and unlike other halides, it is insoluble in dnor solvents. It has 8 coordinate structure with square antiprism joined by sharing fluorides.

$ZrCl_4$, $HfCl_4$ and some other halides also combine with neutral donors to form adducts of different stereochemistry, however, they are mainly octahedral [$transMX_4L_2$, cis $MX_4(LL)$].

Oxides

Titanium: Titanium(IV) oxide, TiO_2, is a white ionic solid which is very stable and non-volatile. It exists in three polymorphic forms. The rutile structure contains $Ti4^{2+}$ ions surrounded octahedrally by six O^{2-} ions(i.e each O^{2-} ion surrounded by 3 Ti^{4+} ions). The anastase and the brookite are distorted octahedral arrangement of oxygen atoms about each Ti, two being relatively close. The oxides are insoluble in water. TiO_2 dissolves in hot conc. H_2SO_4 to give titanyl sulphate($TiOSO_4$

It also forms titanate eg K_2TiO_3, so it is an amphoteric oxide. Barium oxide reacts with TiO_2 to give $BaTiO_3$(barium titanate), Ba_2TiO_4, $Ba_4Ti_{13}O_{30}$, $Ba_6Ti_{17}O_{340}$, This has ferroelectric properties. The $Ba2^+$ ion is so large relative to the small ion Ti^{4+} that the Ti^{4+} rattles round in its octahedral hole. When an electric field is applied to a crystal of this material, it can be highly polarized because each of the titanium ion is drawn over to mone side of its octahedron, thus, causing an enormous electrical polarization of the crystal as a whole. Ba_2TiO_4 has a discrete somewhat distorted TiO_2 tetrahedral.

Zirconium and Hafnium:

Zr(IV)solutions and hydroxides causes precipitation of white gelatinous ZrO_2 nH_2O,. They exist as zirconyl ions ZrO^{2+} in solution and form polymeric species in crystallization. On strong heating, this hydrous oxide gives a hard white insoluble ZrO_2 (B.p 2700ºC) and is resistance to attack by acids and alkalis. It has good mechanical properties which are used for crucibles and furnace cores. The basic properties increase with increase in atomic number, therefore, TiO_2 is amphoteric while ZrO_2 and HfO_2 are increasingly basic.

They also form zirconates and hafnates.

(+3) States.- d^1

They have the d^1 configuration and are coloured and diamagnetic. They are more basic than Ti^{4+} and $TiO_2.(H_2O)n$ is precipitated when alkali is added to Ti^{3+} solution. $TiO_3.(H_2O)_2$ is insoluble in excess alkali and coloured purple.

TiX$_3$ are readily formed by reducing TiX$_4$ compounds.

$$TiCl_4 + H_2 \xrightarrow{600°C, reduction} TiCl_3 - violet powder$$
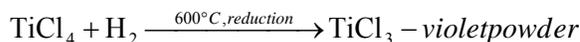
TiCl$_3$ is very important in Ziegler-Natta catalyst.

Also, aqueous solution of $[TiH_2O)_6]^{3+}$ ion can be readily obtained by reducing aqueous Ti^{4+} either electrolytically or with zinc.

$$Ti^{4+} \xrightarrow{Zn, reducing} [Ti(H_2O)_6]^{3+} - violet.aqua.ion$$

This is a powerful reducing agent (more than Sn^{4+}). It is oxidized directly by air and must be kept out of direct sunlight (under N$_2$ or H$_2$). There are two different hydrated forms of TiCl$_3$ with different colours. The two environments gives rise to different degree of crystal field splitting of d levels, hence the energy jump for single d electron is different in the two cases, thus, their different colours.
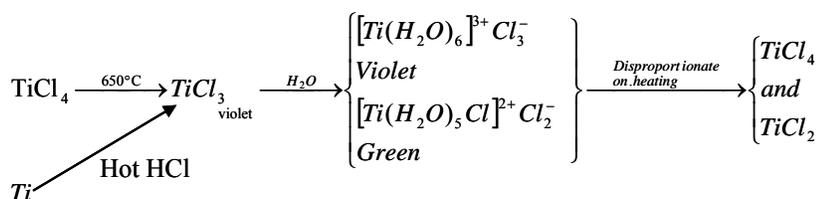
Ti^{3+} is used and for volumetric analysis in the determination of Fe^{3+} and organic nitro compounds. The end point is detected with NH$_4$SCN which remains red while any Fe^{3+} is present or methylene blue which is reduced and discoloured as soon as Ti^{3+} is in excess.

$$FeCl_3 + TiCl_3 + H_2O \rightarrow FeCl_2 + TiO.Cl_2 + 2HCl$$
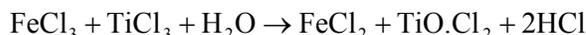
A wide variety of complexes are formed for example, $[Ti^{3+}F_6]^{3-}$, $[TiBr_2.(dipyridyl)_2]^+$, $[TiCl_6]^{3-}$ etc.

Zr(III) and Hf(III) are unstable in water and exist only as solid compounds. ZrCl$_3$, ZrBr$_3$, and ZrI$_3$ exist and canbe synthesized by the reaction of ZnX$_4$ with ZrX in sealed systems at temperature 435 to 600ºC. It is found to hat they have nonstoichiometric phases rather than distinct compounds, ZrX$_x$. Hf$_x$ also exist. Their coordination chemistry is limited.

(+2) States.- d^2

These are less important compounds. Titanium (II) chloride, TiCl$_2$ can be obtained by reduction of the TiCl$_4$, with Ti metal.

$$TiCl_{4(l)} + Ti_{(s)} \rightarrow 2TiCl_{2(s)}$$
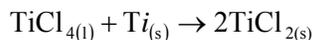
Like other titanium (II) compounds, it is a strong reducing agent. It is rapidly oxidized by air, acids and even water, so the Ti^{2+} ion cannot exist in aqueous solution. There are few complex halides such as $[TiCl_5]^{3-}$ and $[TiCl_4]^{2-}$ and adducts of TiCl$_2$ and MeCN and the complex trans$[TiCl_2dmpe_2]$.

ZrCl$_2$, ZrBr$_2$, and ZrI$_2$ exist and are made by the reaction of ZnX$_4$ with Zr at high temperature in sealed tantalum containers.

GROUP 5(VB)-VANADIUM GROUP

ELECTRONIC STRUCTURE

See table below for the [INERT gas] based electronic structure.

Table 4.1: Electronic structures, oxidation states, relative abundance of the Scandium group

Element	Symbol	Electronic Structure	Oxidation states*	Abundance in %(ppm)
Vanadium	V	$[Ar]3d^3 4S^2$	(-1),(0),(1)(2), **3, 4,** 5	19%(136)
Niobium	Nb	$[Kr]4d^3 5S^2$	(-1),(0),(1),(2), 3, (4), **5**	32%(20)
Tantalum	Ta	$[Xe]4f^{14} 5d^3 6S^2$	(-1),(0),(1),(2), 3, (4), **5**	53%(1.7)

Most usual oxidation state is in **bold.**

Oxidation state that is unstable or in doubt are in parentheses

OCCURRENCE AND EXTRACTION

Vanadium

Vanadium is the 19th most abundant element by weight in the earth's crust and 5th most abundant transition metal. It is widely spread but has few concentrated deposits. Much is obtained as a by-product from other processes. It occurs in the following ores; lead ores as vanadinite $PbCl_2.3Pb_3(VO_4)_2$; Uranium ores as carnotite $K_2(UO)_2(VO_4)_2.3H_2O$ and also traces in crude oil.

The vanadate residues are heated with Na_2CO_3 or NaCl at 800ºC. The sodium vanadate $NaVO_3$ formed is then leached out with water, acidifed with H_2SO_4 to precipitate red coloured sodium polyvanadate and heated to 700ºC to give V_2O_5.This is the converted to ferrovanadium, an alloy with iron by reduction with Al in the presence of steel clippings.

$$3V_2O_{5(s)} + 10Al_{(s)} \rightarrow 6V_{(s)} + 5Al_2O_{3(s)}$$
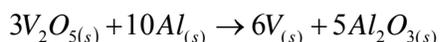
The principal use of the metal is an alloying ingredient in steel, pure vanadium is seldom extracted.

Niobium and Tantalum

Niobium and Tantalum occur together. The main sources of both are columbite-Tantalite series of minerals $[(Fe/Mn)(Nb/Ta)_2O_6]$. Niobium is also obtained from pyrochlorite($CaNaNb_2O_6F$). However, 60% of tantalum is recovered from the slag obtained in the extraction process of Tin.

The ores are dissolved either by fusion with alkali or acids. They are separated by solvent extraction from dilute HF to methyl isobutylketone. The metals are then obtained either by reducing the pentoxides with Na or by electrolysis of molten fluoro complexes such as $K_2[NbF_7]$.

Oxidation State

The maximum oxidation state in this group is (+V). But all show oxidation state from range -1 to +V. In vanadium, the +2 and +3 states are reducing, but +4 is stable and +5 is slightly oxidizing. However, V^{4+} doesnot exist as such in aqueous solution because it is highly charged and has a small ionic radii. Ions like this are able to exert profound polarizing effect on neighboring water molecules and oxo ions(O^{2-}) eg VO^{2-}. For Nb and Ta, +5 is most stable. V(+5) is reduced by Zn and acid to V(2+). Nb(5+) is also reduced to Nb(3+) but Ta(5+) is not reduced. This shows the increasing stability of the 5+ state on descending the group while lower oxidation state becomes less stable.

GENERAL PROPERTIES

: Some Physical Properties of the Vanadium Group

	Atomic radii	Ionic radii		M.p°C	B.p°C	Density (gcm^{-3})
		M^{+2}	M^{+3}			
V	1.22	0.79	0.64	1915	3350	6.11
Nb	1.34		0.72	2468	4758	8.57
Ta	1.34		0.72	2980	5534	16.65

1. They are silvery coloured metals
2. They have high melting point with V having the highest in the 1st row transition metal(this is associated with the maximum participation of d electrons in metallic bonding).
3. The pure metals are soft and ductile, but the presence of impurities(even in trace amounts) makes them hard and brittle.
4. They are resistant to corrosion due to formation of surface film of oxide
5. At room temp., they are unaffected by air, water or acids other than HF with which they form complexes.
6. V dissolves slowly in hot dilute HNO_3 and hot conc. H_2SO_4 and HCl, aqua regia.
7. V is unaffected by alkali but Nb and Ta dissolve in fused alkali.
8. At elevated temp., they combine with nonmetals like N_2 and O_2 to form non stoichiometric compounds
9. The tendency to form ionic compounds decreases as the oxidation states increases.

    V^{2+} and V^{3+} are reducing and exist both in solid and solutions.

    V^{4+} is dominated by VO^{2+} ion. They are stable and exist in solid and solution(as hydrated ion). Also, they form covalent compounds.

    V^{5+} may be covalent or form VO_2^+ or VO_4^{3+}) hydrated ions. Nb and Ta form mainly 5+ compounds.
10. The oxidation states below 5+ are coloured because the have incomplete d shell of electrons(give d-d). The 5+ has a d^o configuration and so colourless compounds are expected. NbF_5, TaF_5 and $TaCl_5$ are white, but V_2O_5 is red, $NbCl_5$ and $NbBr_5$ are yellow and orange respectively. This is attributed to charge transfer.

COMPOUNDS OF VANADIUM GROUP

VANADIUM

Vanadium(5+)

Vanadium (5+) is a powerful oxidant and requires only a mild reducing agent to be reduced to vanadium(4+).

It forms VF_5, a volatile white solid which is readily hydrolysed and is a good fluorinating agent.

Pure V_2O_5 is an orange or red powder depending on its state. It is amphoteric, sparingly soluble in water but dissolves in alkalis to give a wide range of vanadates and in strong acids to form complexes of $[VO_2]^+$. It is prepared by heating $[NH_4][VO_3]$.

$$2[NH_4][VO_3] \xrightarrow{\Delta} V_2O_5 + H_2O + 2NH_3$$
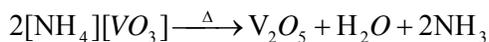
Vanadium(4+)

The highest chloride is VCl4. It is toxic, red-brown liquid.

VO_2 is prepared by heating V_2O_5 with $H_2C_2O_4$.

Vanadium(3+)

The trihalides VF_3, VCl_3, VBr_3 and VI_3 are known.

V trihalides	Properties	Preparation
VF_3	Yellow-green insoluble	From V and HF at 500K
VCl_3	Violet, hygroscopic solid	Anhydrous form prepared by decomposition of VCl_4 at 420K
VBr_3	A green-black water soluble solid	Reaction of VCl_3 with BBr_3 or V with Br_2.
VI_3	Brown, hygroscopic solid	From V with I_2

Vanadium(III) forms a variety of octahedral complexes eg *mer*-$[VCl_3(THF)_3]$

Vanadium(2+)

V trihalides	Properties	Preparation
VF_2	blue	It is converted fromVCl_2 by reaction with HF and H_2
VCl_2	Green	VCl_2 is made from VCl_3 and H_2 at 770K
VBr_2	Brown-red	Same as for VCl_2 from VBr_3
VI_2	Violet	Same as for VCl_2 from VI_3

Vanadium (II) oxide is a grey, metallic solid which is obtained by reduction of the higher oxides at high temperatures. It is non-stoichiometric, varying in composition from 0.8 to 1.3.

Example of a simple complex is $[V(CN)_6]^{4-}$, the K+ salt of which is madeby reducing $K_4[V(CN)_7]$ with K metal in liquid NH_3. $[V(CN)_6]^{4-}$has a magnetic moment of 3.5μ_B but is close to the spin-only value of 3.85μ_B.

Chromium Group / VIB

Element	Electronic structure	Oxidation states
Chromium(Cr)	[Ar] $3d^5 4s^1$	-II,-!, 0,I,II,**III**, IV,V,VI
Molybdenum(Mo)	[Kr] $4d^5 5s^1$	-II,0,I,II,III,IV,**V,VI**
Tungsten (W)	[Xe] $4f^{14} 5d^5 6s^1$	0,I,II,III,IV,**V,VI**

Occurrence and Isolation

The elements have even atomic numbers and are relatively abundant. Cr occurs as the ore chromite ($FeCr_2O_4$) most important Crocoite ($PbCrO_4$) and Chromochre (Cr_2O_3). Mo occurs as molybdenite MoS_2, which is converted to MoO3 and then reduced with H_2. While W, occurs in the form of tungstates the most common being wolframite $FeWO_4$. $MnWO_4$. W is extracted from its ores by fusion with sodium carbonate.

General Properties and Their Trends

- The metals are hard and very high meling points and low volatility. W is the element with the next highest m.pt to C.
- Cr is unreactive or passive at low temperatures because it is protected by a surface of oxide.
- Cr dissolve in HCl and H_2SO_4.
- Mo and W are relatively inert and are only slightly attacked by aqueous acids and alkalis.

Compounds of the Elements

1) Halides

   - Anhydrous Cr(II) halides can be made either by reducing the trihalides with H_2 at 500^oC. The (+II) halides of Mo and W do not have simple formula and do not exist as simple ions.
   - $CrCl_3$ is not very soluble in water unless Cr^{2+} ions are present. Cr^{3+} ions form an enormous number and variety of octahedral complexes including the aquo and halogen complexes.
   - MoF_6 and WF_6 are volatile and easily hydrolysed. They are diamagnetic and colourless as expected for a d^0 configuration.
   - WCl6 is black and WBr_6 is a dark blue.

2) Oxides

   The main oxides are:

+III	+IV	V	+VI
Cr_2O_3	CrO_2	-	CrO_3
-	MoO_2	Mo_2O_5	MoO_3
-	WO_2	-	WO_3

3) Oxyhalides

MO_2Cl_2 may be formed by dissolving the trioxide in strong acids.

Uses

- Cr is used in many ferrous alloys including stainless and for these purposes ferrochromium is produced.
- Mo and W alloyed with steel make very hard alloy which are used to make cutting steel and machine tool.
- W is used as a filament in electric bulbs.

Manganese Group / VIIB

Element	Electronic structure	Oxidation states
Manganese(Mn)	[Ar] $3d^5 4s^2$	-III, ,-I, 0,I,**II**,III, IV,V,VI
Technetium(Tc)	[Kr] $4d^5 5s^2$	0,II,(III),IV,(V), (VI), **VII**
Rhenium (Re)	[Xe] $4f^{14} 5d^5 6s^2$	-1,0,I,II,III,IV,V,VI, **VII**

Occurrence and Isolation

Pure Mn is obtained by reducing MnO2 or Mn_3O_4 with Al(thermite reaction). Technetium is obtained from spent uranium fuel rods from nuclear reactors. Re occurs in small amount in Mo ores and is recovered from flue dust from roasting Mo sulphide ores.

General Properties and Their Trends

- The metals are hard and very high meling points and low volatility.
- Many ionic compounds of Mn are known, but Tc and Re have virtually no aqueous ionic chemistry apart from the oxo ions TcO_4^- and ReO_4^-
- Almost all Mn compounds are coloured, while Re(VII) are colourless.
- Mn is much more reactive than Re, which is in contrast to Group I and II
- Re tends to attain a higher oxidation state than Mn when they both react with the same element.
-

Compounds of the Elements

1) Oxides e.g MnO_2 which is used in the manufacture of dry cell batteries.

2) Oxoanions e.g ReO_4^-

3) Halides and oxyhalides e.g TcF_6, MnF_4 etc

Uses

- Mn is an important additive to steel because it removes both O_2 and S and so improves the strength.
- Used in many alloys

Iron, Cobalt and Nickel Group – Group VIIIB

Iron (Fe)   Cobalt (Co)   Nickel(Ni)

Ruthenium(Ru)   Rhodium(Rh)   Palladium(Pd)

Osmium(Os)   Iridium(Ir)   Platinum(Pt)

The horizontal similarities between these elements are greater than anywhere else in the Periodic Table except among VIIIB of Periodic Table. The elements will be considered in vertical groups.

Iron Group

Element	Electronic structure	Oxidation states
Fe	$[Ar] 3d^6 4s^2$	-II, 0,(I),**II**,III, IV,V,VI
Ru	$[Kr] 4d^6 5s^2$	-III, 0,(I),II,**III**, IV,V, VI, VII, VIII
Os	$[Xe] 4f^{14} 5d^6 6s^2$	0,II,III,**IV**,V,VI, (VII), VIII

Iron is extracted from its oxides (haematite Fe_2O_3, magnetite Fe_3O_4) in blast furnace. Ru and Os are present in trace amount(10^{-3}ppm) in the earth crust.

General Properties

Expectedly, contrast between the first element and the two heavier elements are noticeable.

Iron is white, is not very hard and is quite reactive over other. It dissolves in cold dilute non-oxidizing acids forming Fe^{2+}, but if warm in the presence of air some Fe^{3+} ions are formed whilst oxidizing acids give only Fe^{3+}.

Ru and Os are noble, and are very resistant to attack by acids though Os is oxidized to OsO_4 by aqua regia.

Ru and Os are noble and do not react with water.

Fe also reacts fairly easily with most non-metals while Ru and Os do so only with difficulty at high temperatures except in the case of oxidizing agents such as Cl_2 and F_2.

It is evident that as the size of atom decreases across each period, the tendency to form compounds with high CNs is diminishing, Os has greater tendency than Ru to adopt a CN of 6 in the higher oxidation state.

Oxides

	+VIII	+IV	+III	+II
Fe			Fe_2O_3	FeO
<u>Ru</u>	RuO_4	RuO_2	$Ru_2O_{3.}(H_2O)$	
Os	OsO_4	OsO_2		

Halides and Oxohalides

The halides of this group include : OsF_7, ReF_7, $OsCl_5$

Complexes of the Elements

The (-II) state occurs in the carbonyl ion $[Fe(CO)_4]^{2-}$ and zero valent state occurs in the carbonyl e.g $[Fe(CO)_5]$, $[Fe(CO)_9]$,$[Fe(CO)_{12}]$, $[Os(CO)_5]$ etc.

Copper Group – Group 1B

Element	Electronic structure	Oxidation states
Copper- Cu	[Ar] $3d^{10} 4s^1$	I,**II**,III
Silver- Ag	[Kr] $4d^{10} 5s^1$	I,II,III
Gold- Au	[Xe] $4f^{14} 5d^{10}6s^1$	I,(II),(**III**)

Copper occurs to the extent of 70ppm in the earth's crust. The most common ore is chalcopyrites $CuFeS_2$ but other sulphides Cu_2S and CuS, the basic carbonate malachite $CuCO_3 .Cu(OH)2$ and arsenide ores Cu_3AsS_4 are also found. Ag is widely distributed in sulphide ores of which argentite Ag_2S is most important. Au is also widely distributed and is associated with quartz or pyrite.

Zinc Group – Group IIB

Element	Electronic structure	Oxidation states
Zinc- Zn	[Ar] $3d^{10}\ 4s^2$	**II**
Cadmium-Cd	[Kr] $4d^{10}\ 5s^2$	II
Mercury- Hg	[Xe] $4f^{14}\ 5d^{10}6s^2$	I,II

Zinc occurs in the earth's crust as (ZnFe)S, Zinc blende, ZnS while cadmium and mercury are scarce.

Cd occurs in traces in Zn or