The Chemistry of d-block element (Transition Element)

The d-orbitals are partially filled, they are called transition element

Why are they called d-block? because they've outer orbital in the d-orbital

Introduction:

~~The followin~~ Course Outline

① Position of d-block in periodic table, electronic

Configuration

(ii) Trends in properties of these elements wrt to size of atoms and ions reactivity, catalytic activity, Oxidation state, Colour, complex formation ability, magnetic properties, ~~non stoichiometry~~

(iii) Non stoichiometry, melting and boiling point

Introduction

In the periodic table, the d- block consists of the element of group 3-12.

The d- orbital ~~of~~ the d- block element in 4th periods are filled. The three Series (Triad) of the transition metals are; the 3d series from Scadium to Zinc, 4d Series from (Yttrium) to Cadium, the 5d Series from La - Hg

La ↓ Lanthanum

The 4th 6d series, begins ~~from figures for~~ Actinium and incomplete till now.

Position of d- block in periodic Table

The element ~~pos~~ with incompletely d- orbitals or sub shells in their ground state or most stable oxidaction state are called ~~the~~ d- block element.

They are additionally named as transition element. The Partially filled sub shells incoporate the (n-1)d orbitals

All the d-block element have a similar number of electron in the farthest shell. Consequently, because they have similar number no. of electron in the farthest shell, the display comparable chemical properties

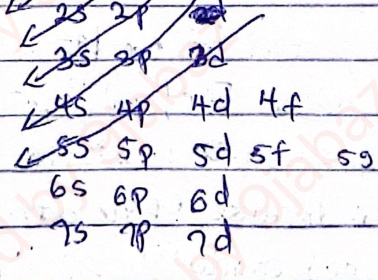
The transition element are set amongst s and p block Shells.

Electronic Configuration

The external electronic configuration remains consistent, so electron is added to the penultimate shell till the d subshell achieves its

There are three series of elements, relying upon the (n-1)d orbitals that is being filled. the orbitals are dispatched altogether of their expanding energy in which case, an orbital of lower energy is filled first (Afbau principle).

Therefore, 4s orbitals with lesser energy is filled first to its full degree, then the 3d orbitals with higher energy is filled.



$4s < 3d$

Triad

$1s < 2s < 2p < 3s < 3p < 4s < 3d$

The precisely half filled and totally filled orbital are extraordinary stable (Cr; $4s^1 3d^5$ and Cu; $4s^1 3d^{10}$)

$[1s^2 2s^2 2p^6 2s^2 3p^6] = Ar$

$_{21}Sc = [Ar] 4s^2 3d^1$

$_{22}Ti = [Ar] 4s^2 3d^2$

$_{23}V = [Ar] 4s^2 3d^3$

$_{24}Cr = [Ar] 4s^1 3d^5$

$_{25}Mn = [Ar] 4s^2 3d^5$ or $[Ar] 3d^5 4s^2$

$_{26}Fe = [Ar] 4s^2 3d^6$

$_{27}Co = [Ar] 4s^2 3d^7$

$_{28}Ni = [Ar] 4s^2 3d^8$

$_{29}Cu = [Ar] 4s^1 3d^{10}$

$_{30}Zn = [Ar] 4s^2 3d^{10}$

The electronic configuration of the 1st series can be represented as $[Ar] 3d^{1-10} 4s^2$ except ~~The electronic configuration of the 1st ser~~ Chromium and Copper because of the extra stability due to half filled and completely filled orbital.

$_{25}Mn = [Ar]\,3d^5\,4s^2$

$Mn^{2+} = [Ar]\,3d^5$, $Mn^{3+} = [Ar]\,3d^4$; $Mn^{4+} = [Ar]\,3d^3$

$Mn^{5+} = [Ar]\,3d^2$; $Mn^{6+} = [Ar]\,3d^1$; $Mn^{7+} = [Ar]\,3d^0$

The electronic configuration of the 2nd series, can be represented; $[Kr]\,4d^{1-10}\,5s^2$

$3d = [Ar]\,3d^{1-10}\,4s^2$

$4d = [Kr]\,4d^{1-10}\,4s^2$

$5d = [Xe]\,5d^{1-10}\,6s^2$

The electronic configuration of the 3rd series can be represented as; $[Xe]\,5d^{1-10}\,6s^2$

Oxidation states

All the elements aside from the first and the last individual from the d-series, display variable oxidation states. Tie indicate Variable valency in their compound. Some fundamental Oxidation conditions the primary, second, and third transition element are listed below

Atomic Number	Elements	Outer Electronic Configuration	Oxidation state
21	Sc	$[Ar]\ 3d^1 4s^2$	+2, +3
22	Ti	$[Ar]\ 3d^2 4s^2$	+2, +3, +4
23	V	$[Ar]\ 3d^3 4s^2$	+2, +3, +4, +5
24	Cr	$[Ar]\ 3d^5 4s^1$	+2, +3, +4, +5, +
25	Mn	$[Ar]\ 3d^5 4s^2$	+2, +3, +4, +5, +6,
26	Fe	$[Ar]\ 3d^6 4s^2$	+2, +3, +4, +5, +6
27	Co	$[Ar]\ 3d^7 4s^2$	+2, +3, +4, +5
28	Ni	$[Ar]\ 3d^8 4s^2$	+2, +3, +4
29	Cu	$[Ar]\ 3d^{10} 4s^1$	+2, +3
30	Zn	$[Ar]\ 3d^{10} 4s^2$	+2

Size of Atoms and Ions

Generally, the sizes of atoms/ions of the element go on decreasing from left to right across the rows in the transition series. Thus, the extra nuclear charge increases as atomic number increases. The extra electrons are added into the Same d-shell/ or orbitals, and the d-orbital electrons are having poor shielding effect.

Therefore, the size of atoms and ions goes on increasing from the first transition series element in the group of transition elements.

The atomic and ionic size goes on increasing from top to bottom due to addition of new shell everytime.

The electrons fill into the anti penultimate shell of Lanthanite which causes steady decrease in size called Lanthanite contraction: It is only applicable to Scadium group

* What exactly leads to variable oxidation state?

Causes of Variable Oxidation State

The valence electron of the transition elements are $(n-1)d$ and ns orbitals which have a little distinction in energies. Both energy levels are utilized as part of bond development.

They demostrate the +2 oxidation state because of the two electrons in ns orbitals, while the electrons in the $(n-1)d$ orbitals remains unaffected

The higher oxidation state from +3 to +7 is because of the utilization of all the ns orbitals and d-electrons in the transition series of the element. In the excited state, the $(n-1)d$

electrons get to be bonding and give the variable state. Subsequently the variable oxidation state is because of the support of both ns and (n-1)d orbitals in bonding

Important Features of Oxidation State of Transition Metals

The most basic oxidation state of transition metals is +2, with the exception of Scadium ~~and Zinc~~ because of the loss of two ns electron

This demonstrates d-orbitals are more stable than s orbital after Scadium. The ionic bonds are bi and large framed as +2 and +3 state while the covalent bond are shaped in higher oxidation state.

Covalent bonds are framed by the sharing of d-electrons for instance, the Permaganate particle (MnO_4^-)

All bonds are shaped among Mn and O

~~The variable oxidation state is because of the support of both ns an (n-1)d orbitals in bond~~

The most not worthy oxidation state increment with expanding nuclear number of elements achieves greatest in the center and after that begins diminishing.

What are complex

For instance, Fe demostrates the normal oxidation state condition of +2 and +3, however, Ruthenium and Osmium in a similar group shape compounds in the +4, +6 and +8 oxidation state

The element at the beginning of the series displaces less oxidation number because of having less number of electron to lose or contribute

The elements in the midst of the series, demostrate the best number of oxidation

For instance, Mn demostrate all the oxidation state from +2 to +7. The most elevated oxidation state appeared by any transition metal is 8, and this demostrated by Ruthenium and Osmium

4d series under Fe

5d series under Ru

Complex Formation Ability

~~Formation of~~ Formation of Complex Compounds

The cations of transition metals have great tendency to form complexes with several molecules or ions called ligands

The bonds involved in the formation of complexes are coordinate/dative and therefore, the complexes are called coordinate complexes, sometimes coordination compounds

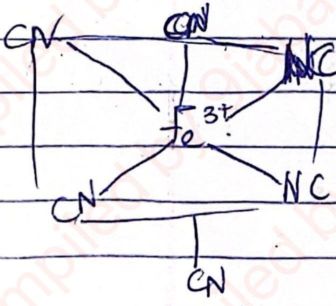
[illegible]

~~$[Fe(H_2O)_6]^{3-}$~~

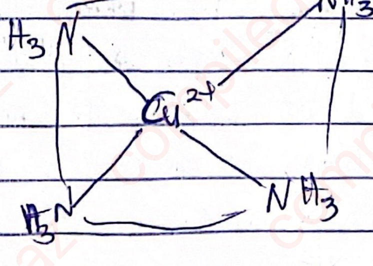
The structure of this complex ion may be linear, square planer, tetrahedral and octahedral depending upon the nature of hybridization of metal ions. The highly electronegative and basic ligand alike fluoride ion, chloride ion can form complexes with transition metals even though there are in higher oxidation state due to the presence of small, highly charged or neutral ligands with lone pairs of electron that can form strong sigma bonds by donating a lone pair of electrons.

In a transition series, the stability of complexes increases with increase in atomic number, hence, the transition metal atom reveals multiple oxidation state. So, the higher valent ion, forms more stable complexes

$[Fe(CN)_6]^{3-}$



octahedral

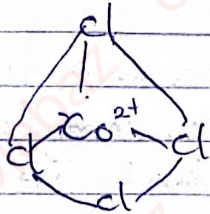


~~tetrahedral~~

d^5 and d^{10} are more willing

* discuss complex formation in transition metals

$[Ag(NH_3)_2]^+$
↓
linear



They are found to form complexes due to the following factors;

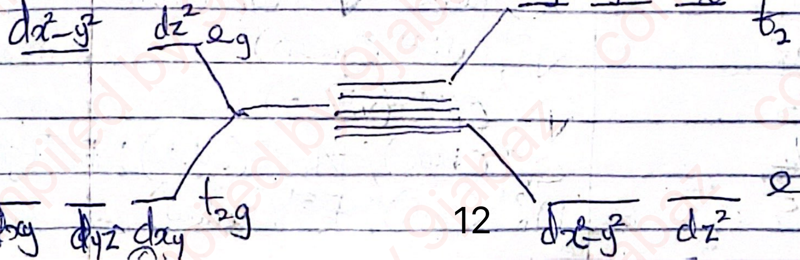
(i) Small size and high charge of metal ions

(ii) Availability of vacant low d-orbitals to accept lone pairs of electrons donated by other group of ligand

(iii) Availability of variable oxidation state and ability to form pi bonds, i.e multiple bond

Colour Formation

Most d-metal compounds are coloured in their solid or liquid states. In the case of transition metal ions under the influence of ligands, the degeneracy of the 5d orbital is lost and they seperate into two distinct energy levels



In the transition metal compounds, the electrons can be advanced from one energy level to another energy level in a similar d-subshe This is referred to as d-d transition. By this property, transition elements display colour

Now, when white light is incident on a transition metal ion the electron in the lower energy d-orbital set absorbs certain radiations and gets promoted to a d-orbital set of higher energy.

The transmitted radiations devoids of the absorbed radiation is the complementary colour of the absorbed light. This complementar colour is the colour of the substance

The Oxidation States of Metals and Their Colour

Number of unpaired electron	Oxidation states/ colour of the compound
0	Sc^{3+}, ~~Cu~~ Ti^{4+}, V^{5+} Cu^{+}, Zn^{2+} (colourless)
1	Ti^{3+}, Purple; V^{4+}, Cu^{2+} (blue)
2	V^{3+}, Ni^{2+} (green)
3	V^{2+}, Cr^{3+} (violet)
4	Cr^{2+} (blue); Mn^{3+} (violet); Fe^{2+} (green)
5	Mn^{2+} (pink); Fe^{3+} (yellow)

Magnetic Properties

The magnetic properties of transition elements, or d-block elements are dictated by the number of unpaired electrons.
There are however some compounds that are diamagnetic, in that they are repelled by the magnetic line of force; when there are no unpaired electron.

When we have unpaired eletrons, It is paramagnetic.

There are two fundamental sources of substances

① Paramagnetic substances: The paramagnetic character imagines in view of the nearness of unpaired electrons. Substances that are paramagnetic are pulled in by the magnetic field

② Diamagnetic Substances: Emerges as a result of the non-appearance of unpaired electron. In other words, electrons are paired. These substances are repelled by the magnetic field either completely filled d-orbitals or d^0 are all diamagnetic

A large portions of the transition elements and their compounds are paramagnetic and are pulled in by the magnetic field. The More prominent, the number of electron in the substances, the more noteworthy is the paramagnetic character and the magnetic character of the substance is expressed as magnetic moment

~~[illegible]~~

Notwithstanding paramagnetic and diamagnetic substances, there are a couple of substance. For example, Fe, Co and Ni is exceedingly magnetic in contrast with other metals. These substances are known as ferro magnetic substances

~~Dens~~ Density

The nuclear volume of transition element is much lower than those of s and p block element. This is a result of the filling of the $(n-1)d$ orbitals that cause an expansion in the atomic charge and pulls the electron internally. This clearly leads to decrease in nuclear volume with the decline in nuclear volume, the nuclear thickness of these elements increases.

Osmium consist of the highest density. In a given transition series, the thickness increment in moving over the period achieve the greatest value at group 18. The thickness increases as we move down the group. The nuclear size of elements of the second and third transition series are approximately the same. Yet, their nuclear weights increment to almost double and the density of elements of third transition series are by and large twice corresponding second transition series.

Other factors that affect variable colour

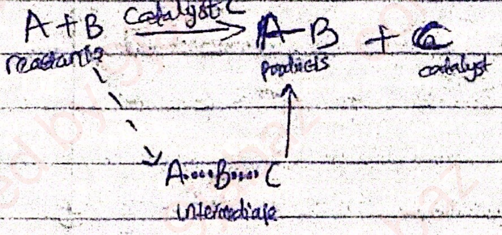
(1) Intraligand charge transfer e.g n – π*, π – π*

(2) Ligand to metal charge transfer (LMCT)

(3) Metal to ligand charge transfer (MLCT).

Catalytic Analysis

The rate of the chemical reaction increases by decrease in energy of activation of the reactant. This decrease is caused by the catalyst by altering the pathway of reaction. For instance;



Intermediate is of lower energy transition state

Bonds are formed between reactant molecules and atoms on the surface of the catalyst (The first row transition metals uses 3d and 4s electron for bonding), 4d and 5s (second row), 5d and 6s (3d row)

The results in the formation of reaction intermediate which provides the activation energy and therefore, increases the rate of the reaction.

The reaction intermediate decompose to form the product and regenerate catalyst. Many transition metals are used as catalyst for a number of reaction. For example, Iron in Haber process, Vanadium in contact process of sulphuric acid and Nickel in hydrogen atom.

The catalytic activity of these transition elements are due to their variable oxidation states. The transition metals can absorb and re-emit quite range of energies. Thus, providing necessary energy of activation

Consider a reaction between Iodide and Thiosulphate

$$I^- + S_2O_8^{2-} \xrightarrow{Fe^{3+}} I_2 + SO_4^{2-}$$

The above reaction occurs in two stages;

$$2I^- + Fe^{3+} \longrightarrow Fe^{2+} + I_2 \quad \ldots\ldots (i)$$

$$2Fe^{2+} + S_2O_8^{2-} \longrightarrow 2Fe^{3+} + 2SO_4^{2} \quad \ldots\ldots (ii)$$

Many transition elements display catalytic activity eg metalloenzymes are biological catalysts that require metal ions of their activity

Nitrogenase enzyme contains Iron and Molybdenum (Mo)

Haemoglobin contains Fe^{2+}

Ribo nucleotide reductase consits of cobalt

Stabilization of Oxidation State

Stability is relative term The Stability of an individual oxidation state for d-block metals depends on the following factors;

① Enthalpy of hydration or Solvation: The higher the hydration energy/enthalpy, the higher the Stability

② electronic Configuration; Half/fully filled electronic configurations leads to higher stability

③ Ligand filled environment and Crystal filled splitting energy: The higher the Crystal field spliting energy, the higher the stability

④ Size of d-orbitals; Larger size d-orbitals leads to higher metal ligand interaction, thereby leading to higher crystal field spliting energy and consequently higher stability

⑤ Metal ligand bond energy and effect of π-back bonding; The higher the bond energy, the higher the stability-

⑥ π-Acid Ligands e.g CO, bipyridine, nitrogen monoxide and Cyanide stabilize lower oxidation states by withdrawing electron density from the metal.

⑦ Highly electromagnetic element (oxygen and fluorine) can stabilize the higher oxidation states between oxygen and fluorine, oxygen can form multiple bonds with metal cations and stabilize the higher oxidation state better than fluorine

Generally, the d-block elements have greater tendency to form coloured complexes. The colour of these complexes may arise due to two reasons;

(i) The d-d transition

(ii) The Charge transfer transition

In the presence of ligand field. The d- orbitals of the metals get splitted according to crystal field theory. The extent of the splitting Δ or [illegible] 10dq depends upon the nature of ligand and the metals, and as well as the coordination number of the metals.

Transition between these two orbitals is called "d-d transi

The following are the transition ...

Coordination number 6 : $t_{2g} \longrightarrow e_g$ Octahedral

" " 4 : $e \longrightarrow t_2$ tetrahedral

" " 4 Square planar : $d_{xz} = d_{yz} \longrightarrow d_{z^2}$

$d_{xz} = d_{yz} \rightarrow d_{xy}$

$d_{xz} = d_{yz} \rightarrow d_{x^2-y^2}$

↓

d-d transi

Charge Transfer Transition

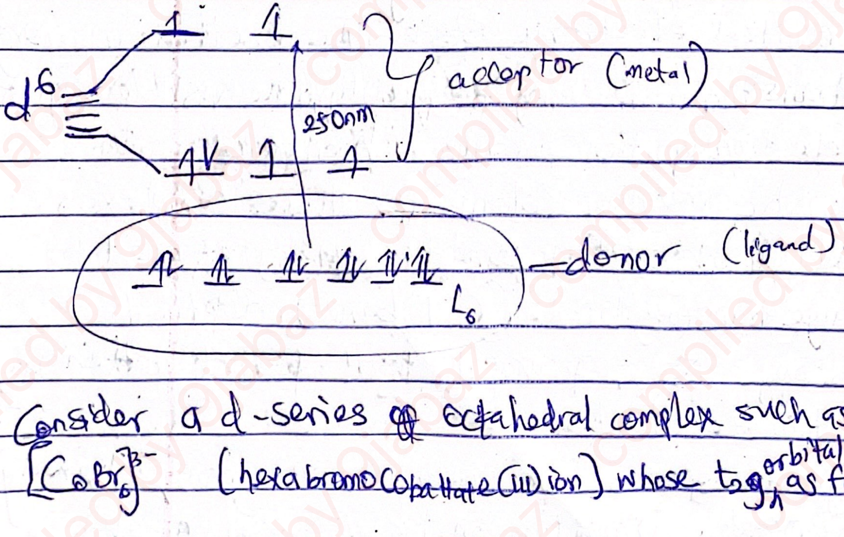
A charge transfer complex (CT complex) or electron donor acceptor complex is an association of two or more molecules, or of different parts of one large molecule in which a fraction of electronic charge is transferred between the molecular entities. The resulting electrostatic attraction provides a stabilizing force for the molecular complex. the source from which the charge is transferred is called the electron donor and the recieving specie is called the electron acceptor.

Many such complexes can undergo an electronic transition into an excited electronic state. The excitation energy of this transition occurs very frequently in the visible region of the electromagnetic spectrum which produces the characteristic intense colour for these complexes. This optical absorption band are often reffered to as charge transfer band (CT band). Optical spectroscopy is a powerful tool for charactarising charge transfer band.

Charge transfer occurs often in inorganic ligand Chemistry involving metals. Depending on the direction of charge transfer, they are classified as either ligand-metal (LMCT) or metal-ligand (MLCT) Charge transfer.

Ligand-Metal Charge Transfer (LMCT)

Ligand-Metal charge complexes (LMCT) arise from transfer of electrons from molecular orbitals with ligand like character to those with metal-like character. This type of transfer is predominant if complexes have ligands with relatively high energy lone pairs (example, sulphur or selenium) or if the metal has low-lying empty orbital, many such complexes have metals in high oxidation state, even D_0. These conditions implies that the acceptor level is available and low in energy



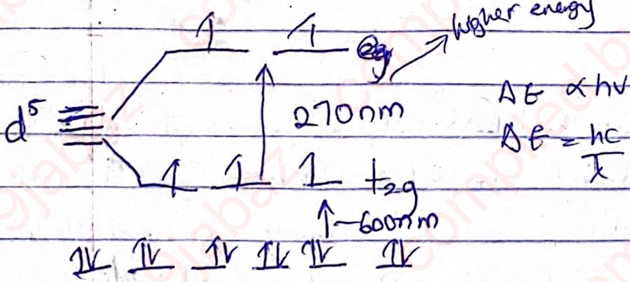
Consider a d-series octahedral complex such as $[CoBr_6]^{3-}$ (hexabromocobaltate (III) ion) whose t_{2g} orbital is fixed.

$_{27}Co = [Ar]\, 3d^7\, 4s^2$

$Co^{3+} = [Ar]\, 3d^6 = d^6$

As a consequence, and intense absorption is observed around 250nm corresponding to a transition from ligand sigma molecular orbital to the empty e_g molecular orbital

However, in hexabromocobaltate(III) ion $[CoBr_6]^{2-}$ that is a d^5 complex, two absorption, one near 600nm and another near 270nm are observed. ~~and another near 27~~ This is because two transitions are possible, one to t_{2g} that can now accomodate 1, 1 electron, and another to e_g. The 600nm band corresponds to transition to the t_{2g} transition band and the 270nm to the e_g molecular orbital of the cobalt.



$$\Delta E \propto h\nu$$

$$\Delta E = \frac{hc}{\lambda}$$

Charge transfer band may also arrive from transfer of electrons from non bonding orbital from the ligand to the e_g molecular orbitals. The energy of transitions correlates with the order of the electrochemical series. The metal ions that are most easily reduced corresponds to the lowest energy transition. For instance,

+7 $MnO_4^- < TcO_4^- < ReO_4^-$

+6 $CrO_4^{2-} < MoO_4^{2-} < WO_4^{2-}$

+5 $VO_4^{3-} < NbO_4^{3-} < TaO_4^{3-}$

The energy

Example includes ① permanganate ion having tetrahadral geometry is intensely purple due to strong absorption involving charge transfer from molecular orbital derived primarily from fill oxyge p orbital to empty molecular orbital derived from Mn (VII)

(ii) Cadium Sulphide (CdS): The colour of active pigment, cadium yellow is due to transition of Cd (II) ion 5s orbital to sulphide ion, π - orbital (p - orbital)

(iii) Mecury Sulphide is red 6s orbital to sulphide ion π - transition.

(iv) Iron (III) oxide red or yellow, due to transition from 3d to oxide π - orbital

Metal-Ligand Charge Transfer Complexes

This arise from transfer of electrons from molecular orbitals with metal-like character with those with ligand like character.

This is most commonly observed in complexes with Ligands having low line π^* orbital especially aromatic ligands. The transitions occur at Low energy if the metal ion has a low oxidation number. For its d-orbitals will be relatively high in energy. Examples of such ligands taking part in metal-ligand charge transfer include; CO, CN^-, bipyridines, phenanthroline.

Question

Comment on the Magnetic Property & Colour

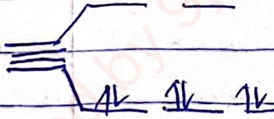
$[Co(CN)_6]^{3-}$ hexa cyanate cobalt (III)

$[Co(Cl)_6]^{3-}$

(find the oxidation number of the metal)

$Co = [Ar]\,3d^7 4s^2$

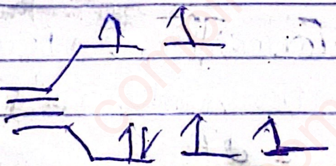
$Co^{3+} = d^6$



$[Co(CN)_6]^{3-}$

Diamagnetic

no magnetic moment



Paramagnetic

$[Co(Cl)_6]^{3-}$

$\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$ $\uparrow\downarrow$

For $[Co(Cl)_6]^{3-}$, magnetic moment is

$\mu = \sqrt{n(n+2)}$ n = number of unpaired electrons

$\mu = \sqrt{4(4+2)}$

$\mu = \sqrt{24} = 4.96BM$

Steps:

① Work out the oxidation number of the metal

② Deduce the number of electron in the d orbital

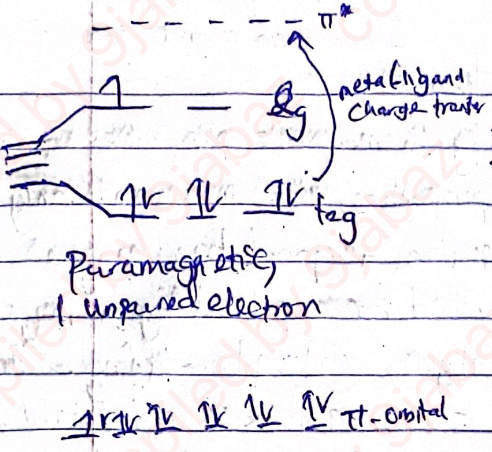
③ Determine whether the ligand is strong or weak. If it is a strong ligand, it forces the the electron to pair, if it is a weak ligand, it simply obey Hund's rule, by singly filling before pairing.

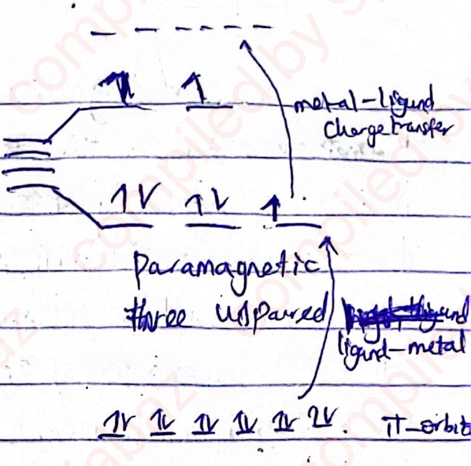
④ Draw the Crystal field splitting diagram, there after fill the diagram with electrons according to the strength

$[Co(CN)_6]^{4-}$ & $[Co(Cl)_6]^{4-}$

oxidation number is +7

$Co^{2+} = d7$





Assignment

$[Fe(CN)_6]^{3-}$ and $[Fe(H_2O)_6]^{3+}$

comment on the magnetic property. colour.

State the similarities and differences of 3d and higher d-block elements

13/11/25

* If it attracted, para
* if it repels, di
* can form magnetic bar, ferro

Magnotochemistry

Magnetochemistry is the study of magnetic properties of materials, by magnetic properties, we mean not only that a material will make a good bar magnet bu whether it will be attracted or repelled by a magnet. This includes synthesis, analysis, and understading. This short description is meant to give a basic understanding before going into more complex treatment.

Magnetism arises from moving charges such as an electric current in a coil of wire. In a material which does not have any current present, there are still magnetic intera Atoms are made of charged particles (proton and electro which are moving constantly. The processes which creates magnetic ~~properties are~~ fields in an atom are;

① Nuclear spin: Some nuclear such as a hydrogen atom have a net spin which creates a magnetic field

② Electron spin: An electron has two intrinsic spin states (similar to a top spining) which we call up and down

③ Electron orbital motion: This is a magnetic field due to the electron moving around the nucleus. Each of this magnetic fields interacts with one another and with external magnetic fields. However, some of these interactions are strong and others are negligible

Measurement of interactions with nuclear spin are used to analyze compounds in nuclear magnetic resonance (NMR) and ~~ele~~ electron spin resonance (ESR) spectrosco

In most other situations, interactions with nuclear spin is a very minor effect. Interactions between the intrinsic spin of one electron and the intrinsic spin of another ~~spin~~ electron are strongest for very heavy elements such as the Actinide this is called spin-spin coupling

For these elements, the coupling can shift the electron orbital energy level.

The interaction between an electron intrinsic spin and its orbital motion is called spin orbit coupling

Spin orbit coupling has a significant effect on the energy levels of the orbital in many inorganic compounds.

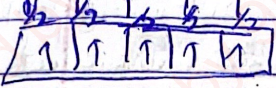
Macroscopic effects such as the attraction of a piece of iron to a bar magnet are primarily due to the numbe of unpaired electron in the compounds and their arrangemen

The various possible cases are called magnetic states of matter

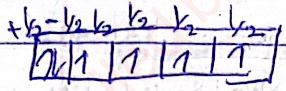
~~Magnetic Sta~~

Magnetic States of Matter

① Diamagnetic: A diamagnetic compound has all of electron spin paired, given a net spin of zero



= net = $5/2$



= net = $4/2$ = 2

Diamagnetic compounds are weakly repelled by a magnet

② Paramagnetic: A paramagnetic compound will have some electrons with unpaired spins. Paramagnetic compound a attracted by a magnet

③ Ferromagnetic: There are unpaired electron spin whi are held in alignment by a process known as ferromagn coupling. Ferromagnetic compounds such as Fe, Co, Ni are strongly attracted to magnets.

④ Ferrimagnet: Have unpaired electron spins which are held in a pattern with some up and some down, this is known as ferrimagnetic coupling

In a ferrimagnetic compounds, there are more spins held in one direction, and so the compound is attracted to a magnet.

⑤ Antiferromagnetic: The unpaired electrons are held in an alignment with an equal number of spins in each direction, the substance in strongly repelled by a magnet. This is referred to as antiferromagnet.

⑥ Superconductor: Superconductors are repelled by a magnetic field because the magnetic field is excluded from passing through them. This property of superconductor called the meissner effect is used to test the presence of a superconducting state.

The underlying theory of how superconductivity arising is still a matter of serious research.

Interaction With External Magnetic Field

A magnetic field H W~~hich~~ is a vector quantity, Since it has both direction and magnitude, it means it is in one direction, that make H and many other quantities will be defined Scalars. This gives a~~ve relance of a~~ us result for a homogenous magnetic field and is a very good approximation for the way that most magnetic measurement are performed. The magnitude of the magnetic field is usually given in unit of Gauss (G) or Tesla (T) where 1 T = 10,000 G.

When a material is placed in a magnetic field, the magnetic field inside the material will be the sum of the external magnetic field and the magnetic field generated by the material itself. The magnitude of the magnetic field in a material is called Magnetic induction and is given the symbol B

$$B = H + 4\pi M \quad ①$$

where B = magnetic induction

H = external magnetic field

$\pi = \frac{22}{7}$ or 3.142

M = magnetization

For mathematical and experimental convenience, this equation is often written as;

$$\frac{B}{H} = 1 + \frac{4\pi M}{H} \quad ——— ⑤$$

$\frac{M}{H} = \chi_v$ χ_v = volume magnetic susceptibility

$$\therefore \frac{B}{H} = 1 + 4\pi\chi_v$$

χ_v is so named because B, H, and M are defined by unit volume. This result in χ_v being unitless
It is convenient to use volume magnetic susceptibility instead of magnetization because the magnetic susceptibility is independent on the magnitude of the external magnetic field H for diamagnetic and paramagnetic materials
Many studies are done using χ_g (magnetic susceptibility per gram), which is $\frac{\chi_v}{\rho}$ (ρ = density)

$$\rho = \frac{m}{v} \Rightarrow \chi_v \times \frac{g}{\cancel{v}} = \chi_{(g)}$$

This gives unit $cm^3 g^{-1}$
Another useful for is χ_m (molar magnetic susceptibility) whi
is χ_g ~~x A~~ multiplied by molecular mass. this gives unit of $cm^3 mol^{-1}$

Another measure of magnetic interaction that is often used is an effective magnetic moment M.

Where $M = 2.828 (X_M T)^{1/2}$

M = effective magnetic moment

X_m = molar magnetic susceptibility

T = temperature (usually in absolute value).

The numeric factor puts M in unit of Bohr magnetons (BM) Where $1BM = 9.274 \times 10^{-24} J T^{-1}$.

The effective magnetic moment is a convenient measure of the materials magnetic property because it is independent of temperature as well as external field strength for diamagnetic and paramagnetic material.

Paramagnetism

The structural feature most prominent in determining paramagnetic ehaviour is the number of unpaired electron in the compound. A spin only formular for the magnetic moment of a aramagnetic compound is given

$$M_{eff} = g(S(S+1))^{1/2}$$

M_{eff} = effective magnetic moment

$g = 2.0023$, gyromagnetic ratio

$S = 1/2$ for one unpaired electron
1 for two " "
$3/2$ for three " "
2 for 4

This equation is sometimes written with $g = 2$ because it does not introduce a significant since this simple spin only treatment is a decent approximation, but is often not accurate even to 2 s.f. An equation that takes into account both spin and orbital motion of the electron is

$$\mu = \{4S(S+1) + L(L+1)\}^{1/2}$$

where μ = effective magnetic momen
$S = 1/2$ for one unpaired electron, 1 for two ... etc.
L = total orbital angular momentum.

This equation is derived for atoms, it is applicable only to molecule with very high symmentry where the energies of the orbitals containing unpaired electrons are degenerate. L is found

In summary, the effective magnetic moment for spin only value is

$$-\mu_{eff} = \sqrt{n(n+2)} = (n(n+2))^{1/2}$$

where n = number of unpaired electron and the unit is BM.

~~Calculate the~~

Calculate the effective magnetic moment for the following compounds

ⓐ $[Fe(H_2O)_6]^{3+}$ ⓑ $[Fe(CN)_6]^{3-}$ ⓒ $[FeCl_6]^{2-}$

ⓐ $Fe = [Ar]\ 3d^6\ 4s^2$

$Fe^{3+} = [Ar]\ 3d^5$

↑	↑	↑	↑	↑

$\mu_{eff} = \sqrt{n(n+2)}$

$= \sqrt{5(5+2)} = \sqrt{5(7)} = \sqrt{35}$

$\mu_{eff} = 5.916\ BM$

ⓑ $Fe^{3+} = [Ar]\ 3d^5$

CN is a strong ligand, therefore it forces the electrons to pair, therefore we have one unpaired electron

$\mu_{eff} = \sqrt{1(1+2)} = \sqrt{1(3)} = \sqrt{3}$

ⓒ ~~Fe~~ $x + (-6) = -2$

$x = +4$

$Fe^{4+} = [Ar]\ 3d^4$

4 unpaired electron since it is a weak ligand field

Ferromagnetism, Antiferromagnetism and Ferrimagnetism

The advantage of using N_{eff} for describing paramagnetic behaviour is that it is a measure of the material's magnetic behavior which is not dependent upon either the temperature or the magnitude of the external field. It is not possible to setal such a convention of ferromagnetic, anti-ferromagnetic and ferrimagnetic.

All the three class of these materials are considered a special of paramagnetic behaviour. The description of Paramagnetic behaviour is based on the assumption that every molecule behaves independently. The materials discussed here results from a situation in which the direction of the magnetic field produced by 1 molecule is accepted by the direction of the magnetic field produced by an adjacent molecule. In other words, their behaviour is coupled. If this occurs in a way in which the magnetic field or tend to align in the same direction, a ferromagnetic material dissolves and the phenomenon is called ferromagnetic coupling.

Antiferromagnetic coupling gives an equal number of magnetic field in opposite direction. Ferrimagnetic coupling gives magnetic fields in two opposite orientation with more in one direction than in the other.

With a few exception, the magnetic moment are not alligned throughout the entire material.

Typically regions called domains will form with different orientation, The existence of domain of coupled molecule gives rise to a number of types of behaviour known as ~~Ferromagneti~~ ferro, antiferro and ferrimagnetism.

Question 19/11/25

Predict the magnetic property of the following and hence calculate the spin only magnetic moment

ⓐ $[Fe(CN)_6]^{4-}$

ⓑ $[Mn(H_2O)_6]^{2+}$

ⓒ $[Fe(F)_6]^{4-}$

(d) $[Ni(CN)_4]^{2-}$

ⓔ $[Ni(NH_3)_6]^{2+}$

Solution

ⓐ $[Fe(CN)_6]^{4-}$

~~Fe~~ $x + (-6) = -4$

$x = +2$

$Fe = [Ar]3d^6 4s^2$

$Fe^{+2} = [Ar]3d^6$

Pless

Similarities of 3d and 4d, 5d-block elements

① * Variable Oxidation state
2 Catalytic activity
3 Formation of Complexes
4 Colour
5 Magnetic properties

Differences

① Oxidation state : ~~Before than~~ The 4d and 5d elements exist in higher oxidation state than the 3d elemts. Because they have low ionization energy. The higher oxidation state in this elements are generally more stable.

② Magnetic properties. The ~~4d and 5d elements~~ According to crystal field theory, the d-oribatal split into t_{2g} and e_g sublevel (octahedral) The magnitude ~~of~~ splitting for any given ligand is greater for 4d and 5d members than 3d elements. These metals form predominantly spin pair complexes. Even in weaker ligands, the complexes are diamagnetic in nature.

The 3d elements form spin free paramagnetic complexes with weak ligands

(CO, CN, bipyradine and phenanthrolene) — Strong ligand

③ Metal – Metal Bonding: The 4d and 5d have a greater tendency ~~have~~ to form metal-metal bonds compared to 3d elements. This results in formation of large number of polynuclear and cluster compounds. Eg $[Re_2Cl_8]^{2+}$, $[Mo_2Cl_9]^{3-}$, $[Rh_4(CO)_{12}]$, $[Ir_4(CO)_{12}]$

④ Coordination number of Complexes: For the 3d series, metal complexes with coordination number 6 and those commonly used. Whereas, the 4d and 5d elements are larger in size and can accomodate a large number of ligands around them. Therefore, 4d and 5d elements form complexes with coordination number greater than 6. [illegible] $[Na_3(ZrF_7)]$ and $[Cu_2(ZsF_6)]$

⑤ Abundance: The 3d series transition metals are more abundant in the earth crust as compared to the other elements. The first series consist about 6.8% of the earth crust while the second and third, ~~fourth and fifth~~ (4d and 5d) constitute only 0.025% of the earth crust

* Colour depends on the one absorbed by EMR. The one that is not absorbed is the one displayed / transmitted.

* Transition metals have partially filled orbitals   28/4/25

* Inert transition element are f-block metals

The f-block metals referred to as inert transition metals. They are Lanthanides and Actinides, 4f and 5f respectively. f has overlying orbitals of 5p and 5s orbitals.

They are also called <u>rare earth elements</u>.

They also also able to form variable oxidation states because of the flexibility of oxidation n

Atomic Number	f-block metals (Lanthanides)	Symbol	
57	Lanthanum	Ln	$[Xe]4f^0 5d^1 6s^2$
58	Cerium	Ce	$[Xe]4f^1 5d^1 6s^2$
59	Praseodymium	Pr	$[Xe]4f^2 5d^1 6s^2$
60	Neodymium	Nd	$[Xe]4f^3 5d^1 6s^2$
61	Promethium	Pm	$[Xe]4f^4 5d^1 6s^2$
62	Samarium	Sn	$[Xe]4f^5 5d^1 6s^2$
63	Europium	Eu	$[Xe]4f^6 5d^1 6s^2$
64	Gadolinium	Gd	$[Xe]4f^7 5d^1 6s^2$
65	Terbium	T	$[Xe]4f^8 5d^1 6s^2$
66	Dysprosium	Dy	$[Xe]4f^9 5d^1 6s^2$
67	Holimium	Ho	$[Xe]4f^{10} 5d^1 6s^2$
68	Erbium	Er	$[Xe]4f^{11} 5d^1 6s^2$
69	Thulium	Tn	$[Xe]4f^{13} 5d^1 6s^2$
70	Ytterbium	Yb	$[Xe]4f^{13} 5d^1 6s^2$
71	Lutetium	Lu	$[Xe]4f^{14} 5d^1 6s^2$

Lanthanides are between the s and p block element at period 6 They are highly electropositive metals and lanthanides they are characterized by the filling of the anti-penultimate 4f energy level which are largely screened from the surrounding by the overlying shell of electrons, i.e 5s and 5p electrons.

short form
→ azimuthal

n+l value ; 4f, n=4, l=3 => 4+3=7

5s, n=5 l=2 => 5+2=7

Principal

energy content

Other factors also come in like kinetics, stability, etc in the determining of the energy are inner obitals of orbital

The 4f orbital is hardly ~~surrounded~~ reachable to bond with. They have similar physical and chemical properties. ~~They chemistry of th~~ This makes their seperation very difficult because the chemistry of these elements are homologous. Though can be seperated by chemical methods ion exchange chromotography is the best ~~done~~ due to different ionic sizes and they ~~have~~ all similar in size because the characterized inner orbital are similar.

* The size of an atom is the distance between the nucleus and the outermost shell. Because electrons go into the inner shell, their stales are almost the same.

Abundance, Sources, and Seperation/ Extraction

Name: Inner transition element, rare earth elements

Abundance

Lanthanites are ~~not~~ very rare except promethium, which is radioactive, i.e not stable

Cerium is as abundant as copper. All the other elements are more abundant than Iodine except promethium which does not occur in nature. ~~They are n~~

They are never found as free metals in the earth crust. They are found in low concentration widely distributed throughout the earth crust. They are found on the moon and in the sun. They naturally occur together because they have similar chemical properties

Odd number elements are less abundance than those with even numbers

~~So~~

Sources

① Monazite sand which contains Lathanites phosphates which are Cerium

It contains 78% of

(ii) Bastnaesite: It is a mixed fluoro carbonates, $M^{III}CO_3F$ where M^{III} is the Lanthanites
It provides 22% of total supply of lanthanites. It only found in USA and Madagascar

(iii) Xenotime: It is the principal source of the heavier elements

(iv) Samarskite: It is the source of Samarium

Extraction

(i) From Monazite: Monazite is hot conc. H_2SO_4, the Lanthanites dissolves as sulphates and they are seperated from ~~in~~soluble material. Thorium is precipitated from the ~~The~~ ~~soluble~~ salt mixture as ~~the~~ thorium(IV) oxide by partial neutralization of NH_4OH (ammonium hydroxide), giving Lanthanite Ln^{3+} suphate solution which can be removed by solvent extraction with n-butyl phosphate. We use ion-exchange chromatography to obtain individual lanthanide element in the mixture.
The metal is finally obtained by electrolysis of the fused Lanthanide chloride ($LnCl_3$) and Calcium chloride or NaCl is added to lower the melting point and then the metal is finally obtained

Cerium and Europium are usually the first to be removed

Cerium by oxidation to cerium (iv) and removal by precipitation of the iodate which is insoluble in 6M HNO_3, or by solvent extraction

Europium is removed by induction to $Europium^{2+}$ and precipitation insoluble $EuSO_4$

* Why are Cerium and Europium the easiest to isolate?

Lanthanide have variable oxidation state. Cerium is $4f^1 5d^1 6s^2$ which is the most stable oxidation state, it can exist as +3 and +4, and Europium as +2 or +3. So, they can exist in other oxidation state apart from the general +3 oxidation state. Therefore when the Lanthanide mixture is oxidized, Cerium is precipitated, while Eu ~~then it~~ is passed through reduction process and Europium is gotten

~~The ion exchange process depends primarily on the hydrated ionic size, therefore, Lanthanum will be high while Lutetium will be the least, i.e La would be tightly bound to the~~

subsequent electron goes in and also reduces the [illegible]

The ion exchange process depends primarily on the hydrated ionic size. Therefore, Lanthanium will be the highest and Lotetium will be the least. Lanthanium will be tightly bound to the while Letetium is least bound because of the size is greater than Lanthanium

Seperation of the Lanthanite Elements

While it is very difficult because of the similarities in the physical and Chemical properties (this is also because of the similar sizes) and they have similar trivalent states.
Due to these reason, only classical methods are used. The classical methods are used to exploit slight difference in their basic properties such as stability, solubility and then Using ion exchange, valency change

Methods: Process of Seperation

(i) precipitation method
(ii) Thermal reaction
(iii) Fractional crystallization
(iv) Complex formation
(v) Valency change
(vi) Ion exchange chromatography
(vii) Solvent extraction

① Preecipitation: The precipitating agent is OH^-. The substance with the lowest solubility is most rapidly precipitated first and it is completely precipitated. The weakest base is Lutetium hydroxide, and it is precipitated first. OH^- is added again, then Ytterbium hydroxide is precipitated, and so on

② Thermal reaction: The mixture is heated and a temp. is reached where a less basic nitrate decomposes to give the oxide. The mixture is now with water. The nitrate is dissolved again and filtered off and will have the insoluble oxide. The process is repeated.

③ Fractional Crystallization

It is used to seperate Lanthanite salt. The solubility decreases from Lanthanum to Lutetium. Lutetium salt crystallize out first and seperated. The nitrate salt, sulphate salt, amides, Oxalates, perchlorate, bromates, Salt of lanthanite have been used because they crystallize out well

Complex formation: The mixture of the lanthanite ion is treated with complex e.g EDTA.

All lanthanite ions forms complexes with EDTA

ions such as Lu^{3+} form the strongest complexes, because of the small size, and it can seperated
The oxalate of the lanthanite ions are insoluble. Therefore, the addition oxalate ions to solutions containing lanthanite and EDTA does not give a precipitate because all the Lanthanide ions have already complexed with EDTA
If acid is added, the least stable EDTA will be seperated/ dissociated, therefore the Lanthanide ion will be available to be complex oxalate.

Valency change

The ability of Cerium and Europium to exist in different state other than the +3 state enables further seperation of the lanthanite. Why? Because the properties of Lanthanum in the +4 state and +2 state are quite different from the properties of Lanthanide in the +3 state and therefore can be easily seperated.
For example, cerium can be easily seperated from lanthanide mixture as it is the only Lanthanide that has Ln^{4+} ions stable in aqueous solution
The seperation is by oxidizing the mixture, the only

that will be oxidized is the Lanthanide ion. The Lanthanid ion and the Ce^{4+} ~~when~~ has a high charge, therefore it is smaller and it is less basic than Ce^{3+} or other Ln^{3+}.
The cerium Ce^{4+} is seperated by carefully controlled precipit of CeO_2 (Cerium(IV) oxide) or $Ce(IO_4)_2$ (cerium iodat
Finally, the CeO_2 can be readily extracted.
Similarly Eu^{2+} has different properties from the Ln^{3+} ions. $EuSO_4$ is insoluble while Ln^{3+} Sulphate is soluble. A mixture of Ln^{3+} ion reduced electrolytically using mercury cathode and zinc amalgam, Eu^{2+} will be produced and w/the presence of H_2SO_4, $EuSO$
will be precipitated and then filtered off.

Samarium has ~~at~~ +2, Sm^{2+} can also be precipitated
The valency change method is still a very useful method for purifying Ce and Eu

(vi) Ion Exchange Chromatography

The ion exchange chromatography method is the most importa the most rapid and the most effective general method of seperation of the Lanthanide. It is also the ~~b~~est

* priciple of column chromatography

The less stable complex will be last to come out

method for the purification of Lanthanides

The basis or the principle is the ability to form complex ion

Procedure

The solution of Lanthanide ion is introduced at the top of a cation exchange column (it is the Dowex-50, which is a sulfonated polysterene). The Ln^{3+} ions adsorbed unto the resin deplacing the H-atoms on the resin

$$Ln^{3+}_{(aq)} + 3H_{(resin)} \rightleftharpoons Ln^{3+}_{(resin)} + 3H^{+}_{(aq)}$$

The Ln^{3+} ions are then <u>eluted</u> in a selective manner using an anionic complexing agent such as citrate, lactate, ~~Slowly~~ which are passed through the column slowly to have interaction between the element and the ions

The anionic chelating ligand form complexes with Ln^{3+} and they are displaced from the ion exchange material onto the solution.

$$Ln^{3+}_{(resin)} + 3H^{+}_{(aq)} + \text{Citrate} \longrightarrow Ln_{(citrate)_3} + 3H_{(resin)}$$

The elusion order follows the order of the hydrated Lanthanide ion such as Lutethium is first eluted and Lanthenum last.

(vi) Solvent Extration: The heavier Lanthanide ions are more soluble tri-n-butyl phosphate because it is an organic solvent, but in water, the solubility is reversed.

Physical and chemical properties

Physical Properties

① They are silvery white metal that tarnish when exposed to air because they are highly electropositive forming the oxides

② They are relative soft metals

③ Highly dense metals

④ They have have melting point and high boiling point

⑤ They form alloys with other metals especially the ions

Chemical properties

① ~~which~~ The element reacts with water slowly in cold and quickly when heated and this due to their electropositive nature

② Order of basicity L
with Lutetium as the least, i.e basicity decreases as the atomi number increases and this basicity differences are indicated in the solubility ~~of the salt~~

and in the formation of the complex species, all this are linked to why the lutetium is eluted first

③ With air and oxygen: They are rapidily oxidized in moist air, reaction with oxygen is slow at room temperature but they can ignite at about 150° - 200°C

③ Reaction with acid: They dissolve rapidly in acid because they are metals

④ They combine with halogens upon heating, they also combine with sulphur, hydrogen, carbon and Nitrogen

⑤ They are highly reducing agent. The reducing properties are similar to that of alkaline earth metals (group 2A) such as Mg.

Oxidation state

(i) When we have half table configuration

(ii) When we have full filled

(iii) While we have thermodynamically or kinetic stable structure (either in aqueous / non aqueous take

Common oxidation state is +3, which is ionic and most stable for all except those

Higher oxidation state can occur for the fluorides

Low " " can occurr for the Iodide

The +2 and +4 state when;

① A noble gas configuration is obtained e.g Ce^{+4}, which is (f^0)

② When there is a half filled orbital e.g Eu^{2+} or Tb^{4+} which is (f^7)

③ When there is a completely filled f-level e.g Yb^{2+}

electronic factors

The Ln^{3+} is the most stable i.e Ln^{2+} and Ln^{4+} are less stable

E.g Ce^{4+} is ~~highly reducing~~ strongly oxidizing, which means it is easily reduced.

Due to electronic factors

Due to kinetic and thermodynamic factors; Sm and Tm

+2 states are well establishing for Tb, Sm and Eu

+4 state; Ce

8/12/25

Q1: If oxalate ions are added to solution containing Ln ions of EDTA. What happens? Why

The ~~EDTA~~ Ln ions would have complexed with EDTA, and because EDTA is a stronger complexing agent, the oxalate cannot displace EDTA and then nothing happens.

Q2: What happens when dil. HCl is added?

When dil HCl is added, dissociation of Ln complex
ronic mixture happens. The first one that will disintegrate
ors is the least stable complex which is the one with the largest size (Lutetium)

Spectral properties of Lanthanide

The Lanthanides are coloured,

* Laporte selection rule says you cannot have transitions unless you have ~~ΔL~~ ($\Delta L \neq 0$)

~~The~~

The colours of the Lanthanide complexes originates almost entirely from charge-transfer interactions between the metal and the ligand.

f→f transitions are symmetric forbidden or Laporte forbidden, just as for transition metals. However

The metals are able to use Vibrony coupling to break this rule. Also most importantly, the buried nature of ~~The valence orbital~~ the f-orbitals coupling with the fact that the molecular vibrations are weak. The Spectral of Ln ions are very weak and the adsorption bands are very narrow.

The f→f transitions are very weak and very narrow than the d-d transitions. Because, the bands are weaker, the colours are very faint. Where the f-f transitions are not possible the ions are colourless in aqueous solution.

Pr^{3+}	$4f^2$	green	14 − n
Tm^{3+}	$4f^{12}$	green	
Nd^{3+}	$4f^3$	pink	14 − n
Er	$4f^{11}$	pink	

Magnetic Properties

The magnetic properties are quite different from the d-block elements, mainly because the 4f electron is possible for the Ln ions are very effectively shielded from the influence of external orbit by the overlying $5s^2$ and $5p^6$ of the shell / orbital. The Ln ions have ~~The Ln ion general~~ grandstate with a single well-defined volume of total angular momentum

Ln^{3+}, Ce^{4+}, La^{3+} $4f^0$ No unpaired electron and therefore diamagnetic

All other f state are paramagnetic due to the presence of f-electrons

compounds

Compounds of Ln exists in +2, +3, +4 oxidation states. Ln(III) compounds are mostly ionic salt, Ln^{2+} compounds the most common divalent of Ln^{2+} is Eu^{2+} which have.

All Ln have divalent halides. The divalent halides are either conventional ~~source~~ salt or they are Ln(III) electride-like salt. Eg YbI_2, EuI_2, SmI_2

Halides

The halides of Ln form tetrahalides, trihalides and dihalides. The only tetrahalides are the tetrafluorides of ~~Cerium, praseodymium~~ Ce, Pr, Tb, Nd, and Dy

Neodymium and Dysprosium tetrafluorides are only known under matrix isolation techniques

For trihalides, ~~all~~ Ln form trihalides with, F, Cl, Br and I and they are high melting compounds and ionic in nature

The fluorides are only slightly soluble in water and not sensitive to air.

The trihalides are very important because the pure metals can be prepared from trihalides

-We have stable dihalides with Eu, Yb and

Oxides of Lanthanides

The ~~Ln~~ reacts with oxygen ~~to~~ to form oxides. The reaction at room temp. can be slow but can be aided by heat. All the Ln form sesquioxides, Ln_2O_3, the lighter or larger Ln adopts a hexagonal seven coordinate structure while the heavier or smaller ones adopt a cubic six cordinate structure.

All the oxides are basic, absorbs water and CO_2 from air to form CO_3^{2-}, OH^- and hydroxl carbonates

The oxides dissolves in acid to form salts

Cerium form stoichiometric dioxide (CeO_2) because

Of the stable oxidation of +4. CeO_2 is also basic and dissolves typically in acids to form Ce^{4+} solution from which Ce^{4+} salt can be isolated

Eu and Yb forms Salt like monoxide EuO and YbO which have a rock salt structure. EuO is ferromagnetic at low temperatures

Hydroxides

All the Ln form hydroxides of the formular $Ln(OH)_3$, since the ionic since decreases from Ln^{3+} to Lu^{3+} the basicity of the OH decrease; i.e $Ln(OH)_3$ is the strongest and $Lu(OH)_3$ is the weakest base The hydroxide can be ppt from the soln of Ln and can be formed by the rxn of Ln oxide with water. Although the reaction btw oxide & water is thermodynamically favourable but kinetically slow for the heavier element

Hydrides

The Ln metals combine endothermically with hydrogen to form Ln dihydrides and with the exception of Eu and Yb which resemble Ba and Ca hydrides, i.e non conducting, transparent salt

like compounds. All the others form black conducting compounds. Conducting because ~~it~~ is a dihydride and in +3 oxidation state, a mobile electron
why conducting

Complexes

The Ln have little tendency to form complexes because of the fact that the available inner orbital is inaccessible. They are f-block orbital, the 4f is deeply buried and covered by 6s. 5p & the
Also, another reason is that they are not small.

They have almost the same size because the inner orbital filled is shielded. The effect of increasing electron leading to strong nuclear attraction is been nullified by the shielding effect.

Small tendency to form complexes because;

(i) They have high charge and this high charge is the reason they form complexes
(ii) Large sizes, large radii
(iii) Vacant orbitals: Unavailability of the 4f orbitals deeply buried inside the atom

They have little tendency to form complex because of the unavailability of 4f orbital which are burried inside the atom

The complexes are not very stable

$$M(H_2O)_n]^{3+} + H_2O \rightarrow M(OH)(H_2O)_{n-1}]^{2+} + H_2O^+$$

The tendency for this hydrolysis increases with increasing atomic number

(2.) Halogeno Complexes

$MF^{2+}_{(aq)}$: they are formed aqueous solution and they are weak complexes

(3) Complexes with Oxygen Ligands

This complexes are the most stable and most common Lanthanide complexes because they form chelates e.g with EDTA complexes are the most stable, also other hydroxo acid such as tartaric acid or citric acid to form water soluble complexes

(4) Complexes with monodentate ligands are less stable than Most of the chelate and tends to dissociate in aqueous solution

(5) Nitrogen Ligands: Addition of amines to form Complexes but complexes with amines are not

formed in aqueous solution, because H_2O is a stronger ligand than ammonia so ammonia cannot displace water. However the amine complexes can be obtained in non aqueous solvent and few nitrogen complexes are know. We can also prepare this amine complexes N-based ligand under anhydrous conditions containing CH_3CN giving rise to polyamine complexes such as trisethylenediamine $(MLen_3Cl_3)$ Ln compound. They form very few stable complexes with CO, CN, and other organometallic compounds.

Lanthanide Contraction

The steady decrease in the size of Lanthanide atoms and ions with increasing atomic number from Lanthanum^{57} to Lutetium^{71}. The addition of electrons into an inner shell 4f leads to screening or shielding effect; i.e the nucleus reduces its attraction on the valence electrons due to the presence of these electrons in the innershell. Therefore there is poor shielding of the 5S and the 5p electrons by the 4f electrons.

Other thing that contributes to the imperfect poor shielding is the shape of the f-orbitals

With the poor shielding the positively charged nucleus has a greater attraction to the electrons therefore decreasing the atomic size as the atomic number increases.

The subsequent electrons goes to the inner 4f orbital leads to poor shielding of 5f and 5p. increase atomic size = greater attraction = decrease size

Consequences of Lanthanide Contraction

① They have similar atomic size
② Identical properties of the Ln elements
③ Difficulty in the seperation of Lanthanides
④ Effect on the basic strength of hydroxides
$Lu(OH)_3$
Lutetium hydroxide less basic than $Ln(OH)_3$ and more covalent
⑤ Ability of complex formation decrease
⑥ Increase in ionization energy
⑦ Increase in electronegativity

Application of Lanthanides

The Ln elements and their compound have many uses but the quantity consumed is very small in comparison to other elements

① They are used as catalytic converters, that consumes about 45% of their uses.

② They are used as petroleum refining catalyst, 25% used

③ 12% are used as Permanent magnet

④ Used as glass polishing and ceramics, CeO_2 is used to polish glass

⑤ Used as Coating for self cleaning ovens

⑥ used for metalleurgical process, i.e formation of alloys

⑦ Used as ~~phosphoros~~ Phosphors in TV screen eg EuO is used as red phosphorusin TV and computer terminal display

⑧ $CeSO_2$ is used as an oxidizing agent in volumetric analysis.

⑨ Lanthanides have been widely used as alloys to impact strength and hardness to metals. The main Ln used for the purpose is Ce is mixed with small amount of La, Nd, Pr. Specifically we have Ln 40% ; Ce 50%, Fe (7% and other metals 3% - This mixture is added to steel for more effective quality to impact strength and workability of steel

⑩ Ln are used in the petroleum industry to refine crude oil into gasoline product

(11) They are used as superconductor, magnets, ceramics

(12) In medicine, current research shows than Ln elements can be used as anticancer agent and the main role of Ln is no inhibit poliferation multiplication of the cell. Ce and Ln has been study as anticancer agent

(13) Ln element used as biological tracer for drugs (because they have sharp absorption spectra) in animals and human beign, because Ln elements are easy be follow spectromically because their peaks are narrow sharp and characterized

(14) They are used for the caliberation of intrument due to their sharp absorption band

(18) They ~~can~~ be used for nuclear purposes e.g the hydrides can be used as hydrogen moderator carriers. The oxide too can be used as diloluent in nuclear fields and the Eu can be used as radiation sources.

ACTINIDES

Actinides are 5f elements and they are also typical metals. They have the properties of both the d-block & f-block element. They are radioactive in nature and release a lot of energy in radioactive decay. Uranium and Thorium are the most abundant naturally occurring actinide

Actinium	Ac	$6d^1 7s^1$	+3
Thorium	Th	$6d^2 7s^2$	+4 (3, 2)
protactinium	pa	$5f^2 6^2$	5 (3, 4)
Uranium	U	$5f^3 6d^1 7s^2$	6 (3, 4 5
Neptunium	Np	$5f^5$ ~~6d~~ $7s^2$	5 (3, 4, 6, 7)
plutonium	Pu	$5f^6 7s^2$	4 (3, 5, 6, 7)
Americium	Am	$5f^7 7s^2$	3 (2, 4, 5, 6)
Curium	Cm	$5f^7 6d^1 7s^2$	3 (4)
Berkelium	Bk	$5f^9 7s^2$	3 (4)
Californium	Cf	$5f^{10} 7s^2$	3, (2)
Einsteinium	Es	$5f^{11} 7s^2$	3, (2)
Fermium		$5f^{12} 7s^2$	3, (2)
Mendelevium		$5f^{13} 7s^2$	3 (2)
Nobelium		$5f^{14} 7s^2$	2 (3)
Lawrencium		$5f^{14} 6d^1 7s^2$	3

General properties

They are also referred to as rare earth metals characterized by the filling antipenultimate 5f orbitals. They are typical metal and have the property of both d and f - block metal. They are also radioactive. They have high diversity in oxidation state, They have similar chemical properties

Actinides are more electropositive than Lanthanides because they have lower ionization energy, they are more reactive and more basic than lanthanides.

They require special handling because some of them are radioactive and unstable. The most common and know element of the Actinide is Uranium which is used as nuclear fuel and can be converted to plutonium through nuclear reaction.

The occure

Occurence

The element of Ac — Th occur in nature but they however undergo radioactive decay.

Th and U are nevertheless rare, they occur in earth crust Th — 8.1 ppm and U — 2.3 ppm. The elements after U have shorter half life hence they undergo decay which takes about few minutes. This makes it impossible to perform anything on them except quick tracer experiment

Th is found in monazite sand which is the combination of

~~Th~~ (Monz ~~and~~ $LnThPO_4$ 10% of Th is gotten from it

Th is found in ~~Thoride~~ ($ThSi(O_4)$) Thoride silicate

U is mined as a ore in pitch blende $-UO_2$, very small quantities actinide ~~can~~ Pa, Np, Pu can also be found in nature but very unstable

Pu is formed in large amount of uranium fuel in nuclear reactors

The elements higher than U are called trace uranium elements

Before 1940, the only actinides known are Th, Pa and U

They were then wrongly thought to be part of the d-series

(i) Because of chemical similarity with group of transition metals, i.e titanium, Zirconium group

(ii) Increase in the number of oxidation state

(iii) Increase in the stability of higher oxidation state

Preparation

The first few members of the actinides are usually formed by neutron-gamma reactions followed by beta emission.

They were first made in 1940 by the bombardment of uranium in a ~~charged proton~~ cyclotron at Berkley

They are now obtained in spent uranium fuel rod

The uranium fuel rod are irradiated with slow neutrons and the main reaction is the fission of ~~U~~ $^{235}_{92}U$ into smaller nuclei

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{236}_{92}U \cancel{+ ^{1}_{0}n} \longrightarrow ^{237}_{92}U \xrightarrow{\beta} ^{237}_{93}Np$$

The half life of is 6.7 days

$$^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{239}_{92}U + \cancel{^{1}_{0}n} \xrightarrow{\beta} | \xrightarrow{\beta} ^{239}_{94}Po$$

$\frac{1}{2}$ life 24 mins t½ 2.3 days

$$^{239}_{94}Po + ^{4}_{2}He \longrightarrow ^{243}_{96}Cm \quad \begin{bmatrix} \alpha - ^{4}_{2}He \\ \beta - ^{0}_{-1}\beta \end{bmatrix}$$

α patch

ratio of neutron to proton becomes so much increased, becomes unstable

Reaction of Actinides

(1) Reactions with air: The tarnish in air because of the electropositivity forming the oxide coating. In case of Th O, the oxide coating is protected

(2) The also react with hot water

(3) ~~They~~ They react readily with acid HCl but slowly in other acids.

Oxidation state

The most stable O.S of the lower element is +3. The most stable O.S is the highes O.S of each element

The +2 state of Am is $5f^7$ which is stable configuration

The +2 state of Am is the most stable

The Am^{2+} only exist in the solid state as the fluoride. In constrast to this, Cf^{2+}, Es^{2+}, Fm^{2+}, Md^{2+} exists as ion in solution and their properties are close to the properties of group 2 especially Ba^{2+}

For the elements, the lower O.S tends to be ionic and the higher O.S tends to be covalent

They all exist in +3 state, however it is not always the most stable state like in the Lanthanide.

$O.S > 3$: Th, Pa, U, Np have O.S greater than 3 by using all the outer electron

Complex Formation

Actinides are better complexing agents than lanthanides from the general properties that favours complex formation

It is often impossible to say which orbitals are utilized in bonding due the similarities of the energy of the 5f, 6d, 7p and 7s levels. Most the complexes are in aqueous solution. The coordination number of the complexes is between 6 and 12

Spectral properties

The colour of the actinides is due to the electronic transition within the 5f levels. Electronic transitions of actinide are about 10 times more intense than those of Lanthanides. The difference is due to the difference in the [illegible]f and 5S electrons.

The f-orbital are deep inside and overlap deeply with ligand metals due to the complexity of the structure

The spectral are very complex and difficult to interpret, U, Np, Pu, Cm have very sharp light in their absorption spectral and this is characteristics of f-f spectra

Magnetic Properties

The magnetic properties of actinide ions arise from the spin and orbital angular momentum of 5f electrons

The 5f electrons are also ~~not~~ not so well localized as the 4f electrons and they have energies comparable to those of the 6d and 7s electrons.

This lead to greater variety in the properties of the actinides. Therefore ligand effect are expected since 5f orbital can participate to some extent in covalent bonding because the 5s electrons are not well localized

	f	Compound	Magnetic moment	Corresponding lanthanid
Th^{4+}	0	$Th(C_5H_5)_4$	Diamagnetic	~~3.59~~
U^{4+}	2	$U(C_5H_5)_4$	2.78	3.59
Np^{4+}	3	$N(C_5H_5)_4$	2.43	3.62
Pu^{3+}	5	$Pu(C_5H_5)_3$	1.12	1.54
Am	6	$Am(C_5H_5)_3$	1.72	3.84

* Lower value of Actinide are due to the ligand effect and spin orbit coupling.

Compounds of Actinides

Halides of Actinides: Majority of the actinide form halides with halogens at specific temperatures.

They combine with halogen with the formular MX_3 and MX_4

The actinides halides are water soluble but the fluorides are insoluble. The halides are very important binary compound.

The trihalides are the most well known halides

$$Ac(OH)_3 + 3HF \xrightarrow{700^\circ C} AcF_3 + 3H_2O$$

$$Th + 2F_2 \longrightarrow ThI_4$$

Uranium usually give colourless hexafluoride which sublimates at a temperature of 56.5°C because of its volatility

The actinides hexafluoride have properties close to anhydride, very sensitive to moisture and they hydrolyze forming the oxyfluorides AnO_2F_2

Oxides of Actinides

All actinides form oxides with different oxidation state and the most common oxides are AC_2O_3

For $M_2O_3 \longrightarrow$ AC, Pu — Es

$MO_2 \longrightarrow$ Th, U

$M_2O_5 \longrightarrow Pa, Np$

$MO_3 \longrightarrow U, (Np)^{query}$

the actinium, An_2O_3 are amphoteric, An_2O_2, AnO_2 and AnO_3 are basic and easily combine with water to form bases

The hydroxides are obtained from action of water on the oxide

$An_2O_3 + 3H_2O \longrightarrow 2An(OH)_3$

The $Pn(OH)_5$ is weak

Important uses of Actinides

The actinides are valuable because they are radioactive. They are mostly used in nuclear weapons are used as a fuel in nuclear reactor. The most useful actinides are U, Th, Pu. The salts of actinides are used in the glass industry for impacting green colour. They are also used in the ceramic industry, textile and medicine

Th is used in the atomic reactors and in the treatment of of cancer

U is used in the nuclear fuel machines

Pu also used in nuclear fuel and also used for making atomic bombs

Americium is used in daily life application such as detecting smoke

Curium is used in gas mantle

Actinium is used in scientific medical reasearch, as neutron source, indicator and gamma source

Chemistry of Thorium and Uranium

Thorium and Uranium are naturally occuring and the most abundant actinide in nature. Uranium mostly occurs in nature/earth crust as a mixture of its oxides and in minerals such as

Uranimide	U_3O_2
Carnotite	$KUO_2NO_3 \cdot 3H_2O$
Autnite	$Ca(UO_2)_2PO_4 \cdot nH_2O$

Naturally occuring Uranium contain three is isotopes of Uranium $^{233}U - 99.3\%$, $^{235}U - 0.7\%$, traces of ^{234}U.

Monazite is the main ~~source~~ one of Thorium $(ThLnPO_4)$

Thorium is also found in Uranothorite which is mixed silicate ~~of~~ Th and U.

Th and U are the easiest to isolate. Th is extracted mainly from monazite. The monazite is treated with NaOH, the soluble hydroxide is filtered of and disolved in HCl. The pH is adjusted to 6 when hydroxide of Th(IV), U(IV) and Ce(IV) are precipitated. This seperates them/from the trivalent lanthanide.

The hydroxide precipitate is dissolved in 6M HCl and extracted with tributyl phosphate and kerosene. This leads to the precipitate of the oxide. The metal can then be obtained by reducing the oxide, ThO_2 with Calcium

Other Properties of Thorium

(i) Th metal is silvery white and bright, because of the absence of ~~f~~ electrons/orbitals.

(ii) Th is soft and melts at 1750°C

(iii) It tarnishes in air to give a dull black colour.

(iv) It exihibits +4 oxidation state, the +4 state is known both in the solid state or aqueous solution

(V) The +2 and +3 oxidation states are only known to iodides ~~of~~ e.g ThI_2

(VI) It form complexes easily due to its high charge.

(Vii) The complexes have high coordination number and uncommon structure especially with oxygen donor ligand.

Chemistry of Uranium

(i) U has a silvery appearance when pure, when attacked by air → yellow colour initially and black coating develops

(ii) Exists in oxidation state of +3 to +6

(iii) Many of the compounds in +4 and +6 are non stoichiometry (variable composition).

(iv) oxide system is very complicated

(v) form hexahalides

Dr. George

11/12/25

H_2O - aquo

They are certain elements that have ~~odd~~ electronic configuration due to stability

* Naming of coordination compounds

$CoCl_2 \rightarrow$ ionic bond

$[CoCl_4]^{2-}$
↓
coordinate covalent bond.

Rules for Naming Coordination Compounds

(i) Name cation before the anion

$\underset{\text{cation}}{K_4}\underset{\text{anion}}{[Fe(CN)_6]}$, $Fe(CN)_6]^{3-}$, $[Co(NH_3)_6]Cl_3$, $[Co(H_2O)_2(en)_2]^{2+}$

(ii) Within the complex, name the ligands first in alphabetical order

H_2O — aquo

en — ethylenediamine

di - bis , ~~tri~~ - tris , ~~tetra~~ - tetrakis

(iii) Calculate oxidation number, written in roman figure and capital letter. If it is an anionic complex, the name of the metal will end with "ate"

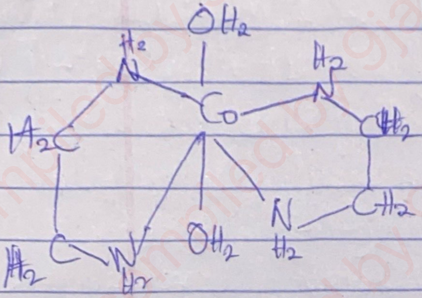
$K_4[Fe(CN)_6]$ - Potassium hexacyanoferate (II)

$[Fe(CN)_6]^{3-}$ - hexacyanoferrate (III) ion

$[Co(NH_3)_6]Cl_3$ - hexaammine cobalt (III) Chloride

Element that donates lone pair in a coordination compound,

N, O, P, S, F^-, Cl^-, Br^-, I



The coordination number gives us idea of the shape ~~dat~~ will adopt

C.n of 6 – octahedra or trigonal prism

C.n of 4 – Square planar or tetrahedral.