MODULE 1

UNIT 1: Applications of lanthanides and actinides

1.0 **Introduction**

2.0 **Objectives**

3.0 **Main content**

  3.1 **Application of lanthanides**

  3.2 **Application of actinides**

4.0 **Summary**

5.0 **Conclusion**

6.0 **Tutor marked assignment**

7.0 **References**

UNIT 2: The chemistry of lanthanide ions

1.0 **Introduction**

2.0 **Objectives**

3.0 **Main content**

  3.1 **The +3 oxidation state**

  3.2 **The +4 oxidation state**

  3.3 **The + 2 oxidation state**

  3.4 **Coordination complexes**

  3.5 **Organometallic compounds**

  3.6 **Optical and spectral properties**

4.0 **Summary**

MODULE 3

UNIT 1: Applications of lanthanides and actinides

MODULE 3

UNIT 2: Comparative chemistry of lanthanides and actinides

INTRODUCTION

Elements in the Periodic Table can be classified in three major ways, namely,

i. Arrangement into groups, which consist of elements with the similar number of valence electrons. For example, Na, K and Cs are in group 1 because they have the same number of valence electron. The alkali earth metals including Mg, Ca and Ba have two valence electrons and they belong to group 2. Group arrangement corresponds to the vertical column. Under an international naming convention, the groups are numbered numerically from 1 to 18 from the leftmost column (the alkali metals) to the rightmost column (the noble gases). Elements in the same group tend to display patterns in variation of atomic radius, ionization energy and electronegativity. From top to bottom in a group, the atomic radii of the elements increase and valence electrons are found farther from the nucleus because the filling of the energy level increases. Ionization energy decreases because it is easier to remove an electron from the less tightly bound atom. Similarly, a group has a top-to-bottom decrease in electronegativity due to an increasing distance between valence electrons and the nucleus. There are exceptions to these trends: for example, in group 11, , electronegativity increases farther down the group

ii. Arrangement into periods which contains elements with similar number of orbitals. For example, K, Ca and Sc belongs to period 4because they have similar number of orbital (i.e 4)

iii. Arrangement into block based on the filled orbital: In the periodic table the vertical columns are called groups. There are eighteen (18) groups in the new IUPAC numbering system. One of the justifications for grouping the elements is the number of electrons in the valence orbitals. Depending on the type of valence orbitals involved, the elements in the periodic table have been classified into s-, p-, d- and f-block elements. Each block is named according to the subshell in which the "last" electron notionally resides.

The s-block comprises the first two groups (alkali metals and alkaline earth metals) as well as hydrogen and helium. The p-block comprises the last six groups, which are groups 13 to

18 in IUPAC group numbering (3A to 8A in American group numbering) and contains, among other elements, all of the metalloids. The d-block comprises groups 3 to 12 and contains all of the transition. The f-block, often offset below the rest of the periodic table, has no group numbers and comprises lanthanides and actinides. The block classification is shown in the figure below,

In view of its unique electronic configuration, the lanthanides and actinides are separated from the rest of the periodic Table and are placed as separate rows at the bottom of the Table (see Fig. 1).

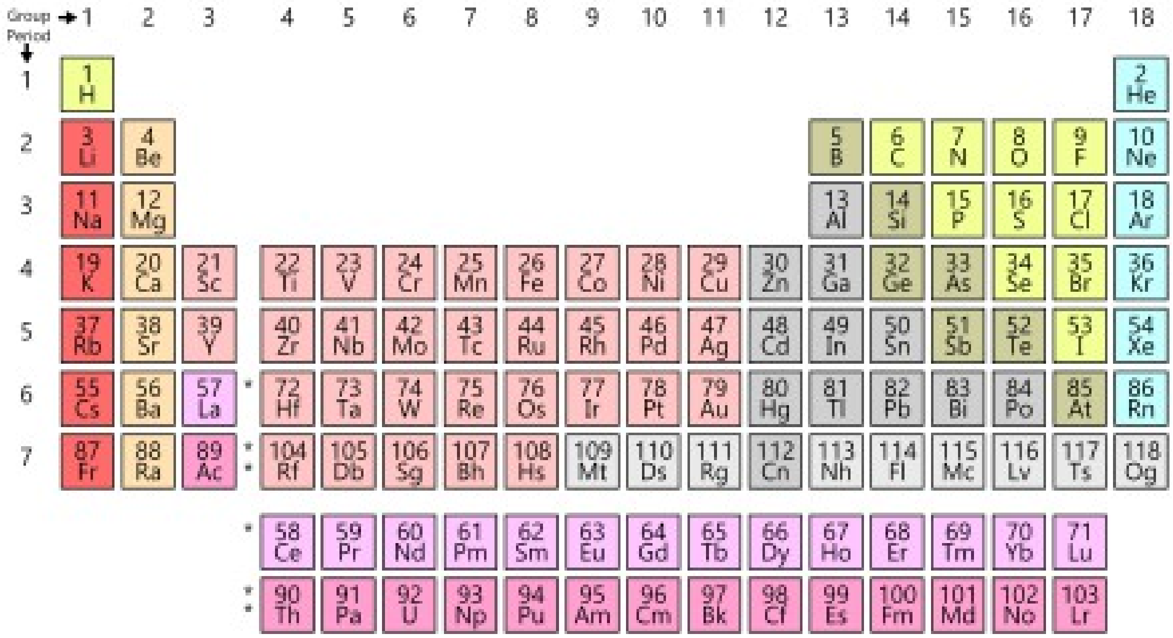

Fig. 1: Periodic Table showing the position of lanthanides and actinides

Abundance, Distribution, Extraction & separation

Lanthanum and actinium are commonly regarded as the remaining group 3 members. This layout originated in the 1940s, with the appearance of periodic tables relying on the electron configurations of the elements and the notion of the differentiating electron. The configurations of caesium, barium and lanthanum are [Xe]$6s^1$, [Xe]$6s^2$ and [Xe]$5d^1 6s^2$. Lanthanum thus has a 5d differentiating electron and this establishes it in group 3 as the first member of the d-block for period 6. A consistent set of electron configurations is seen in group 3: scandium [Ar]$3d^1 4s^2$, yttrium [Kr]$4d^1 5s^2$ and lanthanum [Xe]$5d^1 6s^2$. Still in period 6, ytterbium was assigned an electron configuration of [Xe]$4f^{13} 5d^1 6s^2$ and lutetium [Xe]$4f^{14} 5d^1 6s^2$, "resulting in a 4f differentiating electron for lutetium and firmly establishing it as the last member of the f-block for period 6. However, spectroscopic study work found that the electron configuration of ytterbium was [Xe]$4f^{14} 6s^2$. Thus, ytterbium and lutetium ([Xe]$4f^{14} 5d^1 6s^2$) both had 14 f-electrons indicating the occupancy of a d- rather than an f- differentiating electron" for lutetium and making it an equally valid candidate with [Xe]$5d^1 6s^2$ lanthanum, for the group 3 periodic table position below yttrium. Lanthanum has the advantage of incumbency since the $5d^1$ electron appears for the first time in its structure whereas it appears for the third time in lutetium, having also made a brief second appearance in gadolinium.

MODULE 1

UNIT 1: LANTHANIDES

1.0 **Introduction**

2.0 **Objectives**

3.0 **Main content**

    3.1 **Occurrence, distribution and extraction**

    3.2 **Occurrence and separation of lanthanides**

4.0 **Summary**

5.0 **Conclusion**

6.0 **Tutor marked assignment**

7.0 **References**

1.0 Introduction

The lanthanides refer to the fourteen fifteen metallic elements with atomic number ranging from 58 to 71. Thus it begins with cerium lanthanum and ends with lutetium. The f-orbital of metals are progressively filled while the 4d-orbital is empty. However, lutetium is a d-block element but it is often regarded as lanthanides element because of chemical similarities. All lanthanides forms trivalent cation (i.e Ln^{3+}) and the chemistry of the respective lanthanides depend on its ionic radius. Generally, the ionic radius steadily decreases from cerium lanthanide to lutetium and the effect is called the lanthanide contraction. Consequently, small differences in solubility, complex formation and crystallization may be attributed to lanthanide contraction.

Quantitatively, the effective electron voltage can be expressed according to equation 1,

1

whereZ_{eff} is the effective charge, r is the radius and *l* is angular momentum. The first component of equation 1 represents Coulombic potential while the remaining component represents centrifugal potential. From the above equation, large centrifugal force tends to keep electron away from the nucleus (consequence of Aufbau order). Values of the angular momentum range from 0 to integers value and it takes values of 0, 1, 2 and 3 for s, p, d and *f* orbitals respectively. That means equation 1 becomes,

On the other hand, increase in the effective atomic charge (Z_{eff}) leads to increase in Coulombic attraction (Reasserts hydrogenic order). Hence there is lanthanide contraction across the period. Some general physical properties of the lanthanide elements are,

i. They are metals with silvery white colour appearance.
ii. They generally have high melting and boiling points and are very hard.
iii. They are good conductors of heat and electricity.
iv. Many of the lanthanide ions form coloured ions.
v. The lanthanides exhibit a principal oxidation state of +3.
vi. They exhibit paramagnetic properties because of the presence of unpaired electrons

In chemical reactivity, the lanthanides behaves like calcium. Some of the general chemical properties of lanthanides are

i. They readily tarnish in air and burn to give oxides (all give trioxides except Ce which forms CeO_2).
ii. They also combine with some non-metals including nitrogen, sulphur and hydrogen.
iii. Their hydrides are non-stoichiometric but have a composition of MH_3. These hydrides liberate hydrogen from water.
iv. The lanthanides also liberate hydrogen from water. Their hydrides also behave similarly with vigorous evolution of hydrogen gas from dilute non-oxidizing acids.
v. Lanthanide compounds are predominantly ionic and usually contain lanthanide metal in its +3 oxidation states.

2.0 Objectives

The objectives of this unit include the following,

i. To understand the electronic configuration of the lanthanides and those of its ions

ii. To know stable ions of the lanthanide elements

iii. To understand magnetic and spectral properties of the lanthanide elements

iv. To understand the various coordination numbers that is feasible to the lanthanide elements.

v. To understand stereochemistry of the lanthanide elements

vi. To understand the concept of lanthanide contraction

vii. To understand chemical reactions associated with the lanthanide elements

3.0 Main content

3.1 Occurrence, distribution and extraction

In terms of chemical behaviour and trends going down group 3 for properties such as melting point, electronegativity and ionic radius, scandium, yttrium, lanthanum and actinium are similar to their group 1–2 counterparts. In this variant, the number of *f* electrons in the most common (trivalent) ions of the f-block elements consistently matches their position in the f-block. For example, the f-electron counts for the trivalent ions of the first three f-block elements are Ce 1, Pr 2 and Nd

Lanthanide elements are usually found in mineral form. For example, minerals containing lanthanides in +3 oxidation state often have low content of Eu but trace amount of promethium (Pm) has been found in uranium ore as a consequence of spontaneous fission fragment of ^{238}U. Pm is often isolated from spent fuel of nuclear fission by ion exchange process.

Generally, the lanthanides can be separated from most elements by precipitation of oxalates or fluoride from HNO_2 solution while they can be separated from each other by ion exchange on resin.

In the separation process, Ce and Eu separate first. Ce is oxidized to Ce(IV) and is then precipitated from 6M HNO_3 as ceric iodate or separated by solvent extraction while Eu is reduced to Eu(II) and is removed by precipitation in sulphae. Literature reveals that the ion – exchange behavior depends primarily on the hydrated ionic radius. Therefore, since Lu has the largest hydrated radius, while La has the least hydrated radius, La is the most tightly bound while Lu is the least, and the elution order is Lu → La . Conventional ion exchange resin is a sulphonated polystyrene (represented as HR in the equation below), which corresponds to an insoluble strong acid. Thus when a solution containing the M^{3+} cations is passed down the column, the expected equilibrium reaction is,

The expected trend becomes more noticeable if a complexing agent is used at an appropriate pH. In this case, the ion of smallest radius forms the strongest complexes and enhances the preference for the aqueous phase.

Typical complexing ligands are α-hydroxyisobutyric acid$(CH_3)_2CH$ (OH)COOH, $EDTAH_4$ and some hydroxo or aminocarboxylic acids.

3.1.1 Electronic configuration and stability

Electronic configurations of the lanthanides elements (Table 1) follow the lanthanide configuration by progressive addition of electron to the 4f sub orbital (which can accommodate a maximum of fourteen electrons). The formula for calculating the number of sub orbital is $2l +1= 2(3)+1=7$). Since a maximum of two electrons can be accommodated in any sub orbital, there will be a maximum of fourteen electrons in the f-orbital.

All the lanthanide elements exhibit +3 oxidation state while Ce, Nd, Sm, Gd, Tm, Yb and Lu also exhibit +2 oxidation state. The +4 oxidation is exhibited by Ce, Pr, Gd and Tb. The +4 oxidation state of Ce has the same electronic structure with La^{3+} i.e. an empty 4f level-noble gas configuration). Also, Tb^{4+} has the same electronic structure as Gd^{3+} i.e. a half-filled 4f level. The following examples express some stable lanthanide ions that exhibit zero, half-filled and completely filled 4f sub orbital

i. Zero filled: La^{3+} $4f^05s^25p^6$ $Ce^{4+} = 4f^05s^25p^6$
ii. Half filled: $Tb^{4+} = 4f^75s^25p^6$ $Gd^{3+} = 4f^75s^25p^6$ $Eu^{2+} = 4f^75s^25p^6$
iii. Completely filled :$Yb^{2+} = 4f^{14}5s^25p^6$ $Lu^{3+} = 4f^{14}5s^25p^6$

The most stable oxidation state of lanthanides is +3. Other oxidation states are relatively unstable. For example, the +2 ions are readily oxidized and the + 4 ions are readily reduced to the +3 ion. This agrees with the fact that empty, half- filled or filled shells are especially stable. Thus the removal of 3 electrons leaves stable configurations of $[Ar]3d14s^2$, $[Kr]4d^15s^2$and $[Xe]5d^16s^2$. Gd and Lu forms stable tripositive ions with only with half ($4f^7$) and fully filled ($4f^{14}$) configurations respectively (although other kinetics and thermodynamic factors may also be significant). Generally, the most stable M^{3+} or M^{4+} ions are formed with lanthanides that are able to attain f^0, f^7 and f^{14} configurations upon ionization. Ce, Pr, Gd, and Tb form ions with configuration corresponding to f^1, f^2, f^7 and f^8 respectively. It is worth observing that Ce attain ionic form with f^1 instead of reflecting isoelectronic status of La by losing s-electrons. Table 2 compares the atomic radius and radius of M^{3+} for the lanthanides.

Table 2: Electronic configuration of lanthanides and those of their ions

Element	**Symbol & atomic number**	**Electronic configuration**	**M^{2+}**	**M^{3+}**	**M^{4+}**	**Radii (Angstrom)**	
						M^{2+}	**M^{3+}**
Lanthanide	$_{57}$La	$[Xe]5d^16s^2$		[Xe]		1.87	1.06
Cerium	$_{58}$Ce	$[Xe]54f^26s^2$	$5d^14f^1$	$4f^1$	$4f^1$	1.83	1.03
Praseodymium	$_{59}$Pr	$[Xe]\ 4f^36s^2$		$4f^2$	$4f^2$	1.82	1.01
Neodymium	$_{60}$Nd	$[Xe]\ 4f^46s^2$	$4f^4$	$4f^3$		1.81	0.99
Promethium	$_{61}$Pm	$[Xe]5d^04f^56s^2$		$4f^4$			0.98
Samarium	$_{62}$Sm	$[Xe]5d^04f^66s^2$	$4f^6$	$4f^5$		1.79	0.96
Europium	$_{63}$Eu	$[Xe]5d^04f^76s^2$		$4f^6$		2.04	0.95
Gadolinium	$_{64}$Gd	$[Xe]5d^14f^76s^2$	$4f^7$	$4f^7$	$4f^7$	1.80	0.94
Terbium	$_{65}$Tb	$[Xe]5d^04f^96s^2$		$4f^8$	$4f^8$	1.78	0.92
Dysprosium	$_{66}$Dy	$[Xe]5d^04f^{10}6s^2$		$4f^9$		1.77	0.91
Holmium	$_{67}$Ho	$[Xe]5d^04f^{11}6s^2$		$4f^{10}$		1.76	1.80
Erbium	$_{68}$Er	$[Xe]5d^04f^{12}6s^2$		$4f^{11}$		1.75	1.83
Thulium	$_{69}$Tm	$[Xe]5d^04f^{13}6s^2$	$4f^{13}$	$4f^{12}$		1.74	1.84
Ytterbium	$_{70}$Yb	$[Xe]5d^04f^{14}6s^2$	$4f^{14}$	$4f^{13}$		1.92	1.85
lutetium	$_{71}$Lu	$[Xe]5d^14f^{14}6s^2$		$4f^{14}$		1.74	1.86

Worked example 1

With the aid of electronic configurations, provide at least examples (at least one for each group) of lanthanides that are zero, half and fully filled 4f orbital.

Solution

The following examples express some stable lanthanide ions that exhibit zero, half-filled and completely filled 4f sub orbital

i. Zero filled: $La^{3+}\ \ 4f^05s^25p^6$ $Ce^{4+} = 4f^05s^25p^6$
ii. Half filled: $Tb^{4+} = 4f^75s^25p^6$ $Gd^{3+} = 4f^75s^25p^6$ $Eu^{2+} = 4f^75s^25p^6$
iii. Completely filled :$Yb^{2+} = 4f^{14}5s^25p^6$ $Lu^{3+} = 4f^{14}5s^25p^6$

Table 2: Atomic and M^{3+} ionic radii of the lanthanides

Elements	Symbol	Atomic Radius (pm)	Ionic Radius (3+)
Lanthanide	La	187.7	106.1
Cerium	Ce	182.0	103.4
Praseodymium	Pr	182.8	101.3
Neodymium	Nd	182.1	99.5
Promethium	Pm	181.0	97.9
Samarium	Sm	180.2	96.4
Europium	Eu	204.2	95.0
Gadolinium	Gd	180.2	93.8
Terbium	Tb	178.2	92.3
Dysprosium	Dy	177.3	90.8
Holmium	Ho	176.6	89.4
Erbium	Er	175.7	88.1
Thulium	Tm	174.6	89.4
Ytterbium	Yb	194.0	85.8
Lutetium	Lu	173.4	84.8

Worked example 2

Comment on the stability of the various oxidation states of lanthanides

Solution

The most stable oxidation state of lanthanides is +3. Other oxidation states are relatively unstable. For example, the +2 ions are readily oxidized and the + 4 ions are readily reduced to the +3 ion . This agrees with the fact that empty, half- filled or filled shells are especially stable .

Worked example 3

(a) Write an equation for calculating the effective electron voltage and define all the terms in the equation

(b) What is the implication of the equation to Aufbau order and the filling of f-orbital?

(c) What is the significant of the equation to Reasserts hydrogenic order and lanthanide contraction?

Solution

(a) Quantitatively, the effective electron voltage can be expressed according to the equation,

where Z_{eff} is the effective charge, r is the radius and *l* is angular momentum. The first component of equation represents Coloumbic potential while the remaining component represent centrifugal potential.

(b) From the above equation, large centrifugal force tends to keep electron away from the nucleus (consequence of Aufbau order). Values of the angular momentum for *f*-orbitals is 6 respectively. That means equation 1 becomes,

(c) The effective atomic charge (Z_{eff}) leads to increase in Coloumbic attraction (Reasserts hydrogenic order). Hence there is lanthanide contraction across the period.

3.1.2 Colour

The colour of lanthanides depends on the number of unpaired electron as presented in Table 3. The colourless lanthanides ions are those having zero, one and seven unpaired electrons. This is because absorption of wavelength with the visible region (which is responsible for colour) is not possible. It is evident from the results presented in Table 1 that the colour of the lanthanides depends on the number of unpaired electron. The colour of lanthanide ions is due to the presence of partly filled f orbitals. As a result it is possible to absorb certain wavelength from the visible region of the spectrum. This results in transitions from one 4f orbital to another 4f orbital known as f-f transition.

The 4f electrons are directly responsible for both the magnetic and light absorption properties of the cationic species, and these characteristics are related to the presence of unpaired electrons. Colour depends on the amounts of light of different wavelengths absorbed by each species. The colour that is seen is the result of absorption of light of certain wavelengths and transmission of light of other wavelengths. Consequently, all the tripositive lanthanides ions except Y^{3+}, La^{3+} and La^{3+} and La^{3+} absorb around in the wavelength range 2000-10000 A.' The colored ions absorb in the visible region, and sometimes in the ultraviolet. The colorless species absorb either in the ultraviolet (for example, Ce^{3+}, Gd^{3+}) or the infrared (Yb^{3+}). The dipositive ions absorb strongly in the ultraviolet. The only tetrapositive ion stable in aqueous solution is the Ce^{4+} and it absorbs in the blue and ultraviolet regions.

3.1.3 Magnetic and spectral properties

Magnetic properties are usually associated with the existent of unshared electron(s). When there exists lone pair electron, paramagnetic property manifest. Lanthanide elements that have unpaired electrons are coloured and are paramagnetic. Due to the fact that the 4f orbital is effectively shielded by overlying $5s^2$ and $5p^6$ orbitals, lanthanides element sometimes display magnetic and spectral properties that are not quite different from other elements. The significant shielding of the 4f orbital effectively leads to the various state arising from the f^n configuration to be split by external forces to ($2J + 1$) or ($J + ½$) sub level depending on whether J is integers or half integers. The total angular momentum will be J = (S + L), (S+L-1).../(S-L). Hence f-f electronic transition from one J state of an f^n configuration to another J state gives a very sharp absorption bands that are closely related to that of free atoms but unlike those of d-d transition. All absorption bands found in visible and near infra red spectral of the lanthanide ions have a line like character. However, in some cases, bands may arise as a consequence of f-electron being excited to d, s or p orbital.

Table 3: Number of unpaired electrons and colour of lanthanide elements

Ion	No of unpaired Electrons	Color
La^{3+}	0	Colourless
Ce^{3+}	1	Colourless
Pr^{3+}	2	Green
Nd^{3+}	3	Reddish
Pm^{3+}	4	Pink; yellow
Sm^{3+}	5	Yellow
Eu^{3+}	6	Pale Pink
Gd^{3+}	7	Colorless
Tb^{3+}	6	Pale Pink
Dy^{3+}	5	Yellow
Ho^{3+}	4	Pink; yellow
Er^{3+}	3	Reddish
Tm^{3+}	2	Green
Yb^{3+}	1	Colourless
Lu^{3+}	0	Colourless

La^{3+} and Ce^{4+} have f^0 configuration while Lu^{3+} has an f^{14} configuration hence all their electrons are shared indicating that they do not have unpaired electron and are diamagnetic. However, all other states are paramagnetic because they have unpaired electron. The magnetic moment of transition elements can be calculated through the following equation,

2

is the magnetic moment in Bohr magnetons, S is the spin quantum number while L is the orbital quantum number. In the first row transition metals, orbital contribution is quenched by interaction with the electric field in the ligand environment. Therefore, the spin only formula becomes,

3

Work example 4

Calculate the spin only magnetic moment of (i) La^{3+} (ii) Lu^{3+} (iii) Gd^{3+} ion.

Solution

La^{3+} and Lu^{3+} have no unpaired electron, therefore their spin only magnetic moment is given as,

Gd^{3+} has seven unpaired electrons. Hence,

The spin only moment is effective in explaining the magnetic properties of La^{3+} and Gd^{3+} but not sufficient for the other lanthanide elements because the 4f electron is effectively shielded by the underlying $5s^2$ and $5p^6$ electrons. Consequently, the magnetic effect of electrons in the orbital is not quenched. The resultant magnetic moment is therefore due to contributions from unpaired electrons and the orbital motion. This effect has also been observed in the second and third rows transition metals. However, in the lanthanide elements, the magnetic moment is defined as a consequence of the coupling between the spin and orbital contributions, which gives a new quantum number, designated as J. $J = S + L$ when the shell is more than half filled but $J = L-S$ when the shell is less than half filled. The magnetic moment of these set of lanthanides in Bohr magneton unit can be calculated using the equation,

4

where g is given as

5

Worked example 5

(a) What is responsible for the colour of lanthanides?

(b) What are the features of lanthanides that are colourless?

(c) Give examples of lanthanides colour and compare the colour with the properties that provide for colour

Solution

(a) The colour of lanthanides is due to the number of unpaired electrons.

(b) The colourless lanthanides ions are those having zero, one and seven unpaired electrons.

(c) Example of lanthanide colours are green, red, pink, yellow and pale pink which are associated with 2, 3, 4,5 and 6 unpaired electrons respectively

3.1.4 Coordination number and stereochemistry

Generally, most ions in M^{3+} state have the potential of exhibiting coordination number exceeding 6. Coordination number of 6 is not very common among the lanthanides but coordination numbers of 7, 8 and 9 are significant. However, different structure and coordination number have been reported for lanthanides. For example, coordination number of 9 has been reported for trichlorides of La to Gd while the chlorides of Tb to Lu have $AlCl_3$ structure with the metal being coordinated octahedrally. In solution, different lanthanides exhibit different coordination number.

Worked example 6

(a) Comment on the coordination number of lanthanides and provide evidence for the existent of the coordination number of 9.

Solution

Generally, most ions in M^{3+} state have the potential of exhibiting coordination number exceeding 6. Coordination number of 6 is not very common among the lanthanides but coordination numbers of 7, 8 and 9 are significant. However, different structure and coordination number have been reported for lanthanides. For example, coordination number of 9 has been reported for trichlorides of La to Gd

3.1.5 The 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 means that there will be 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.

Lanthanide contraction explain the steady decrease in the size of the lanthanides atoms and ions with increasing atomic number resulting in greatest size for La and least for Lu. The radius of $La^{3+}$is about0.18Å larger than that of Y^{3+} so that if the 14 lanthanide elements did not intervene we might have expected Hf^{4+} to have a radius 0.2Ågreater than that of Zr^{4+}. However, the lanthanide contraction, amounting to 0.12Åseems to mob off this expected increase. Consequently, the radii of Hf^{4+} and $Zr^{4+}$are almost similar. Lanthanide contraction is attributed to the imperfect shielding of one electron by another in the same sub-shell. A movement across the lanthanide series reveals that the nuclear charge and number of4f electrons increase, but due to the shape of the f orbitals, there is little screening effect of an electron in one f orbital by electrons in other f orbitals by the nucleus. Therefore, each of these electrons will experience an increasing nuclear charge, and the ions state decreases. The most significant decrease occurs with the addition of the first f-electrons and after addition of f^7.

One of the major effects of lanthanide contraction is that the contraction in ionic radii along the lanthanide series increases the ability to form complex ions. This is the basis of their separation on an ion exchange column. Lanthanide contraction also influences the basicity of the metals. Basicity is a measure of the ease at which an atom will lose electrons. This property influences the reactivity of the lanthanides, it would be the lack of attraction that a cation has for electrons or anions. The basicity series of the lanthanides follow the following order:

$La^{3+} > Ce^{3+} > Pr^{3+} > Nd^{3+} > Pm^{3+} > Sm^{3+} > Eu^{3+} > Gd^{3+} > Tb^{3+} > Dy^{3+} > Ho^{3+} > Er^{3+} > Tm^{3+} > Yb^{3+} > Lu^{3+}$

Thus the basicity decreases as the atomic number increases. Basicity differences are shown in the solubility of the salts and the formation of the complex species. The effectsof lanthanide contraction are,

i. Similarity of second and third transition series- Generally the size of atoms increases down a group. So the size of the atoms of an element of second transition series is larger than an atom of the first transition series but the size of the atom of third transition series is nearly same as that of the atom of the second transition series. The similarity in the size of atoms of the elements belonging to the same group of the second and third transition series is due to the effect of lanthanide contraction. For example- Zr^{4+}/ Hf^{4+} and Nb^{5+} /Ta^{5+} possesses similar ionic radii.

ii. Difficulty in the separation of lanthanides- The insignificant differences in the ionic radii of lanthanides account for close similarities in their chemical properties. Consequently, separation of elements in the pure state is relatively difficult. However, properties like solubility, complex formation, hydration etc. shows some differences and it's possible to separate them by ion exchange methods.

iii. Effect on the basic strength of hydroxides- As the size of lanthanides decreases from La to Lu, the covalent character of the hydroxides increases and hence their basic strength decreases. Thus, La $(OH)_3$ is more basic and Lu $(OH)_3$ is least basic.

Worked example 7

(a) Explain why some lanthanides ions are coloured and others are not coloured.

(b) Why are transition metal ions with zero, partially and completely filled orbital colourless.

Solution

(a) Colour depends on the amounts of light of different wavelengths absorbed by each species. The colour that is seen is the result of absorption of light of certain wavelengths and transmission of light of other wavelengths. Consequently, all the tripositive lanthanides ions except Y^{3+}, La^{3+} and La^{3+} and La^{3+} absorb around in the wavelength range 2000-10000 A.' The colored ions absorb in the visible region, and sometimes in the ultraviolet. The colorless species absorb either in the ultraviolet (for example, Ce^{3+}, Gd^{3+}) or the infrared (Yb^{3+}). The dipositive ions absorb strongly in the ultraviolet. The only tetrapositive ion stable in aqueous solution is the Ce^{4+} and it absorbs in the blue and ultraviolet regions.

(b) The 4f electrons are directly responsible for both the magnetic and light absorption properties of the cationic species, and these characteristics are related to the presence of unpaired electrons. The zero, partially completely 4f orbital do not absorbed in the UV region that enehances colour.

3.2 Occurrence and separation of lanthanides

Lanthanide mineral contains all the members of the series. However, each mineral contains different concentrations of the individual lanthanides. The principal ores of lanthanides are,

i. Monazite: contains mostly the lighter lanthanides. The commercial mining of monazite sands in the United States is centered in Florida and the Carolinas

ii. Xenotime: contains mostly the heavier lanthanides

iii. Euxenite: contains a fairly even distribution of the lanthanides

In all the ores, the atoms with an even atomic number are more abundant implying more nuclear stability in accordance with theOddo-Harkins rule, which states that the abundance of elements with an even atomic number is greater than the abundance of elements with an odd atomic number. In addition to these, there are Chinese rare earth reserves which amount to over 70% of the known world total, mainly in the form of the ionic ores from southern provinces. These Chinese ion-absorption ores, weathered granites with lanthanides adsorbed onto the surface of aluminium silicates, are in some cases low in cerium and rich in the heavier lanthanides (Longnan) whilst the Xunwu deposits are rich withthe lighter metals; the small particle size makes them easy to mine. The Chinese ores hav emade them a leading player in lanthanide chemistry.

In order to obtain these elements, adoption of appropriate separating process is necessary. This may include selective reduction or oxidation or by an ion-exchange method.

Good separation process can isolate all the lanthanides content of the mineral with 100 % purity. The lighter metals such as La, Ce, Nd and Gd are obtained by reduction with trichloride with calcium at 1000 °C. The heavier elements, such as Tb, Dy, Ho, Er, Tm and Tb are obtained from reduction with trichloride. Pm is obtained by reduction of PmF_3 with Li.

Eu, Sm, and Tb trichloridesare reduced only to the dihalides by Ca. Reduction of +3 oxides with La at high temperatures gives the metals.

4.0 Summary

This unit discusses in details the electronic configuration of all the lanthanides. Their electronic configuration involves the occupation of the f-orbitals with unpaired electrons, which confers some magnetic properties to the metals. The colour of the metal is also related to their f-electrons. The lanthanide contraction which involves progressive changes in the atomic radii of the lanthanides has significant influence on the behaviour of the lanthanide metals including reactivity, oxidation state, patterns of ionization and other functional properties.

5.0 Conclusion

Lanthanides or lanthanoids refers to the fourteen elements that follows lanthanum. They are closely related in properties. Significant features along the lanthanide series is the lanthanide contraction, number of unpaired electron and electronic configurations. These properties influences major behaviour of the lanthanides elements.

6.0 Tutor marked assignment

1. All of the lanthanide metals react with HCl to form compounds having either the formula MCl_2,MCl_3, or MCl_4 (where M represents the metallic element). Each metal forms a single compound. Write a balance chemical equation for any three named lanthanides that will react to give compounds that correspond to MCl_2,MCl_3, and MCl_4 respectively

2. A chemist has a 0.250 g sample of transition metal, and she wishes to identify the metal. She reacts the metal with excess HCl and obtains 0.357 g of product. Based on this information, identify the metal and write the chemical formula of the product.

3. Highlight three effects of the lanthanide contraction and state three consequences

4. State three principal ores of lanthanides and highlight two extraction or purification methods for lanthanides.

7.0 References

Petrucci, Hardwood, Herring. General Chemistry: Principles & Modern Applications. New Jersey: Macmillan Publishing Company, 2007.

Moeller, Therald. The Chemistry of the Lanthanides. New York: Reinhold Publishing Corporation, 1963.

Cotton, Simon. Lanthanides and Actinides. London: Macmillan Education Ltd, 1991.

Deacon, G. B., Tuong,, T. D., Wilkinson, D. L. and Marks, T. (2007). Lanthanide trichloride by reaction of lanthanide metal with mercury (II) chloride in tetrahydrofuran. Edited by Angelicci, R. A. Wiley, USA.

Theodore, G. (2009). The Elements: A Visual Exploration of Every Known Atom in the Universe. New York: Black Dog & Leventhal Publishers.

Holden, N.E and Coplen, T. (2004). The periodic Table of the elements. Chemistry International.IUPAC.26 (1): 8-18.

MODULE 1

UNIT 2: The chemistry of lanthanide ions

1.0 Introduction

Lanthanide metals are silvery-white in colour and are highly electropositive. They react with H_2O slowly in the cold, rapidly on heating to liberate H_2 according to the following general equations,

They tarnish in air and burn easily to give the oxide M_2O_3 except Ce which gives CeO_2.

For example, samarium and oxygen combine to form the compound samarium oxide. Yttrium has a natural protective oxide coating, making it much more resistant. The lanthanides also form compounds with many nonmetals, such as hydrogen, fluorine, phosphorous, sulphur and chlorine. However, heating may be required to induce these reactions.

Lanthanide metal reacts with all the halogens to form lanthanide(III) halides. So, it reacts with fluorine, F_2, chlorine, Cl_2, bromine, I_2, and iodine, I_2, to form respectively lanthanide(III) fluoride, LnF_3, lanthanide(III) chloride, $LnCl_3$, lanthanide(III) bromide, $LnBr_3$, and lanthanide(III) iodide, LnI_3.

Lanthanides also reacts with oxyflouride. The reaction of lanthanide atoms with OF_2 leads to $LnOF_2$ and LnOF. In $LnOF_2$, except for Ln = Ce, Pr, and Tb which are predominantly in the +IV

oxidation state, the Ln are in the +3 state as they are in LnOF. The Ln−O bonding in $CeOF_2$, LaOF, and LuOF is a highly polarized σ bond and two pseudo π bonds formed by donation from two 2p lone pairs on the O to the Ln. Lanthanum metal dissolves readily in dilute sulphuric acid to form solutions containing the aquated La(III) ion together with hydrogen gas, H_2.

In this case, the existent of $La^{3+}(aq)$ largely in form of the complex ion $[La(OH_2)_9]^{3+}$ has been proposed

Worked example 1

(a) Write suitable equations to show the reaction of lanthanide with cold and hot water

(b) Write equations to show the formation of lanthandes halides of four different types

(c) Write equation to show what happened when lanthanide metal is dissolved in tetraoxosulphate (VI) acid

Solution

(a) Lanhanides react with H_2O slowly in the cold, rapidly on heating to liberate H_2 according to the following general equations, They tarnish in air and burn easily to give the oxide M_2O_3 except Ce which gives CeO_2.

(b) Lanthanum metal reacts with all the halogens to form lanthanum(III) halides. So, it reacts with fluorine, F_2, chlorine, Cl_2, bromine, I_2, and iodine, I_2, to form respectively lanthanum(III) bromide, LaF_3, lanthanum(III) chloride, $LaCl_3$, lanthanum(III) bromide, $LaBr_3$, and lanthanum(III) iodide, LaI_3.

(c) Lanthanides metal dissolves readily in dilute sulphuric acid to form solutions containing the aquated La(III) ion together with hydrogen gas, H_2.

In this case, the existent of La^{3+}(aq) largely in form of the complex ion $[La(OH_2)_9]^{3+}$ has been proposed

2.0 Objectives

The objectives of this unit shall include

i. To understand the chemistry of lanthanide in +3 oxidation state
ii. To understand the chemistry of lanthanide metals in +4 oxidation state
iii. To understand the chemistry of lanthanide metals in +2 oxidation state

3.0 Main content

3.1 The +3 oxidation state

All the Lanthanides exhibit the +3 oxidation state. They form oxides which resembles those of Ca, Ba and Sr groups. They also absorbed oxygen and carbon (IV) oxide from air to form hydroxide and carbonate respectively.

The hydroxides of lanthanides have hexagonal shape and their basicity decreases with increase in atomic number due to decrease in ionic radius. This implies that is most basic while is least. The hydroxides of the lanthanides are amphoteric but can be precipitated from aqueous solution by ammonia or dilute alkali.

Studies have shown that the hydroxides of lanthanoids are strongly basic. They can absorb CO_2 and form carbonates. The basicities of the hydroxides decrease with increasing atomic number. $Ce(OH)_3$ is the most basic while $Lu(OH)_3$is the least basic. Dissolution of the latter member of the series in NaOH produces complex as shown in the following equations,

Worked example 2

(a) With the aid of suitable equations explain what happened when lanthanide absorbed CO_2 and water in the air.

(b) Use suitable equation to explain the dissolution reaction of $Yb(OH)_3$ and $Lu(OH)_3$ in NaOH.

Solution

(a) All the lanthanides exhibit the +3 oxidation state. They form oxides which resembles those of Ca, Ba and Sr groups. They also absorbed oxygen and carbon (IV) oxide from air to form hydroxide and carbonate respectively.

(b) Dissolution of the $Yb(OH)_3$ and $Lu(OH)_3$ in NaOH produces complex as shown in the following equations,

3.1.1 Hydrides

Hydrides of lanthanoids are formed when the metal is heated up to 300 – 400ºC, in the presence of H_2

The products, dihydrides, (LnH_2) are solids: black, metallic and are good conductor of electricity. This is because the Ln ion exists in the +3 and has 2Hionand an electron which occupies a conduction band. The hydrides are thermodynamically stable. They have fluoride structure and their formulation of the hydride is. This formulation has electron delocalized in a metallic conduction band. However, Eu and Yb form the divalent compounds;$EuH_2$and YbH_2. These are salt-like and contain $M^{2+}$and two H ions. Some lanthanoids also form nonstoichiometric hydrides. For example, $YbH_{2.5}$and ,

At high pressure of hydrogen gas, lanthanides form LnH_3, which is formulated as and is characterized by reduced conductivity due to the absence of electron in the conduction band compared to The most stable hydrides of lanthanoids are LnH_2 (except Eu and Yb).

The hydrides generally, liberate hydrogen from water,

They are stable up to 900ºC and react with O_2 to form the oxide. The dehydrates take up hydrogen when heated under pressure and all (except Eu) form salt like hydrides LnH_3(which has $Ln^{3+}$and three H^-.) since there are no delocalized electron, they do not show metallic conduction.

Worked example 3

(a) Under what condition can lanthanides form LnH_2 and LnH_3 types hydrides?
(b) Write the formulation for the different hydrides
(c) Among the two types of hydrides, which of them is more conducting? Give reason for your answer

Solution

(a) Hydrides of lanthanoids are formed when the metal is heated up to 300 – 400 ºC, in the presence of H_2

On the other hand, the LnH_3 is formed under a very high pressure

(b) The formulation for LnH_3 is while that of LnH_2 is
(c) is characterized by reduced conductivity due to the absence of electron in the conduction band compared to . Formulation has electron delocalized in a metallic conduction band which make it to be a good conductor of electricity.

3.1.2 Halides

The fluorides of lanthanides are insoluble and can be precipitated out from the metal solution by addition of hydrofluoric acid or fluoride. However, the fluorides of the heavy lanthanides are soluble in excess of HF because they form complexes with them. The chlorides of lanthanides are soluble in water and can be crystallized out as hydrates. However, the anhydrous chlorides of the metals cannot be obtained from the hydrates because they releases hydrochloric acid on heating and gives the metal oxychloride.

For example, Scand Ce give $Sc_2O_3$and CeO_2 respectively. Anhydrous chlorides of lanthanides can be prepared by heating their respective oxide or oxalate with ammonium chloride at 300 °C according to the following equation,

The behaviour of the bromides and iodides of lanthanides are similar to those of their chlorides.

3.1.3 Oxo and double salts

Lanthanide salts of most oxyacids including sulphate, perchlorate, carbonate, phosphate, oxalates bromate and nitrate do exist. These salts are soluble in water and crystallize as hydrates. However, the carbonate, phosphate and oxalate salts of lanthanides are insoluble in water.

Lanthanide ions also have the ability to form double salts such as $2Ln(NO_3)_3Mg(NO_3)_2.24H_2O$, $Ln(NO_3)_2(NH_4)_2NO_3.4H_2O$ and $Ln_2(SO_4)_3.3Na_2SO_4.12H_2O$. Base on the solubility of the double sulphate salts, lanthanides can be grouped into two classes. The first class is the cerium group which includes La to Eu while the second group is the yttrium group which extends from Gd to Lu and includes Y. Those in the cerium group are sparingly soluble in H_2SO_4 while those in yttrium are significantly soluble.

3.1.4 Carbides

Lanthanides form carbide of the type, LnC_2 and $Ln_4(C_2)_3$. They are formed by the arc melting of the metals with carbon in an inert atmosphere. They can also be formed by reducing the oxides of Ln with carbon in an electric furnace.The lanthanide carbides (LnC_2) are more reactive than CaC_2. They react with water to give ethyne, hydrogen, ethane and ethene. They are best described as acetylides of having extra electron in their conduction band, which makes them to exhibit good electrical conductivity

3.1.5 Other reactions

Lanthanides also reacts directly with non-metals and metalloid to form stable compounds. For example, Ln_2S_3 (except for Eu), Ln_2Se_3, M_2O_2S.Direct reaction of the lanthanides at elevated temperature with some elements such as group V (e.g N, P, As, Sb and Bi). Ln forms sulphide by reactionof $LnCl_3$ with hydrogen sulphide at 1100 °C

Lanthanides also react with boron at elevated temperature to yield borides, LnB_4 and LnB_6. With the group V elements they form LnX, which has NaCl structure. LnN is hydrolysed by water according to the following equation,

3.2 The +4 oxidation state

The +4 oxidation state is most important to cerium and to some extent, praseodymium and terbium. Ce^{4+} is the only Ln^{4+} that exists in solution. Ce^{4+} has a high charge which confers heavily hydrated atmosphere except in strongly acidic solutions. Hydrated Ce^{4+} is easily hydrolysed to give polymeric species and H^+. Ce^{4+} in solution (also called ceric) is obtained by treating Ce^{3+} solutions with strong oxidizing agent such as ammonium peroxodisulphate $(NH_4)_2S_2O_8$ or bismuthate in nitric acid. Ce^{4+} solutions are strong oxidizing agents and are often used in redox titrations in preference to $KMnO_4$ or $K_2Cr_2O_7$. The aqueous Ce(IV) oxidizes concentrated HCl to Cl_2. They are also useful in organic reactions such as oxidation of alcohols, aldehydes and ketones at the alpha carbon atom. Ceric compounds also occurs in solid forms such as CeO_2, $CeO_2.nH_2O$ and CeF.

CeO_2 is a white (when pure) compound that can be obtained by heating Ce or $Ce(OH)_3$ or cerium (III) oxalate in air or oxygen. The compound is inert and cannot be attacked by strong acids or alkalis. However, in the presence of reducing agents (such as H_2O_2 and Sn^{2+}) to give Ce^{3+} in solution, Cerium hydrous oxide ($CeO_2.nH_2O$) is a yellow gelatinous precipitate that can be obtained by reacting Ce^{4+} solution with bases and is soluble in acid. CeF_4 is white in colour having a three dimensional crystal structure. It is easily hydrolysed by water. The compound is obtained by reacting $CeCl_3$ or CeF_3 with fluorine at room temperature. Ce^{4+} also form stable complex such as $[Ce(NO_3)_6]^{2-}$ and $(NH_4)_2$ and $(NH_4)_2[Ce(NO_3)_6]^{2-}$. Due to ligand-to-metal charge transfer, aqueous cerium (*IV*) *ions are* orange-yellow.

Other lanthanoids that form compounds in +4 oxidation state are Pr, Nd, Tb and Dy these compounds are generally unstable in water. They occur only as solids and form only oxides, fluorides and a few fluoro complexes including PrO_2,PrF_4, $Na_2[PrF_6]$,TbO_2, TbF_4, DyF_4, and $Cs_3[DyF_7]$.

3.3 The +2 oxidation state

The only set of lanthanide elements that form compounds in +2 oxidation state are Sm, Eu and Yb[, and]. However is the most stable (which is stable in water) but the solution is strongly reducing. The (aq) ion is readily obtained by reducing with Zn,

Zn/Hg, Mg or electrolysis. Eu(II) compounds have several similarities with calcium compounds including the insolubility of their sulphates and carbonates in water, the insolubility of the dichloride in strong HCl and the solubility in liquid NH_3.However, the dihalides of Eu (II) (EuX_2) have a magnetic moment of 7.9BM with seven unpaired electrons, whereas Ca compounds are diamagnetic.

are often obtained by the electrolytic reduction of their trivalent ions in aqueous solution. They are readily oxidized by air and form sulphates, hydroxide, carbonates, halides and phosphates. They form solid dihalide compounds, $LnCl_2$ and LnI. The dihalides compounds have 8-coordinated Ln^{2+}ions while 7-coordination is found in EuI_2. The LnX_2 compounds react with donor solvents to give solvates e.g. $LnX_2(THF)_x$

3.4 Metallic properties:

The hardness, melting and boiling points of the elements all increase from Ce to Lu because the attraction between the atoms increases with decrease in size. This makes them good conductors of electricity and heat.

3.5 Coordination complexes

forms complexes of high coordination numbers. The coordination numbers for $[Ln(OH_2)_n]^{3+}$in aqueous solution are up to 9 for the early lanthanoids and 8 for the later smaller members. The Ln^{3+}ions readily form complexes with and donor ligands e.g with H_2O,EDTA, β-diketonate, citric acid, oxalic acid ligands. Partially fluorinated β-diketonate ligand $CF_3COCHCOCF_3$(Fod) produces complexes with that are volatile and soluble in organic solvents{because of their volatility, they are used as precursors for the synthesis of lanthanoid-containing superconductors by vapour deposition}Charged ligands have highest affinity for the smallest ion. List of some lanthanoids complex compounds, their coordination number and shape are presented in Table 4.

Table 4: Geometry and coordination number of some lanthanides complexes

Coordination Number	Complex	Shape
4		Tetrahedral
6		Octahedral
6		Octahedral
7	[Y(acetylacetone)$_3$H$_2$O]	Mono-capped trigonal prism
8	[La(acetylacetone)$_3$H$_2$O)$_2$]	Square antiprism
8	$_4$]	Square antiprism
8	[Eu(acetylacetone)$_3$(phenantroline)]	Square antiprism
8	[Ho(tropolonate)4	Docecahedral
9	[NdH$_2$0$_9$	Tri-capped trigonal prism
9	[SmNH$_3$)$_9$	Tri-capped trigonal prism
10	[CO$_3$-O,O')$_5$	
10		(Each nitrate ion is bidentate)
11		
12		Icosahedral(Each nitrate ion is bidendate
12		

3.6 Organometallic compounds

The organometallic compounds of the lanthanoids are dominated by good donor ligands, with complexes of acceptor ligands being rare. This is attributed to

i. The lack of orbitals because the 5d orbitals are empty and the 4f orbitals are buried so this restricts the number of bonding modes that are available to the lanthanoid ions.

ii. The strong electropositive nature of the lanthanoids means they need good donor(e.g alkoxide, amide and halide ligands which are both σ and π donors), not good acceptor ligands(e.g CO and phosphine ligands which are both σ donors and π acceptors)

iii. The bonding form in the organometallic lanthanoid complex is predominantly ionic and governed by electrostatic factors and steric requirements All organometallic complexes are strong Lewis acids and are very sensitive to air and moisture.

Examples of organometallic lanthanoid compounds are $Ln(Cp)_3$(Cp-cyclopentadienyl lignd). These complexes contain ion with a limited number of compounds. σ-bonded alkyl groups are common with compounds containing cyclopentadienyl ligands tending to dominate. Cp groups are electrostatistically bound to a central cation. Other examples arecyclooctatetraene ligands eg$Ce(C_8H_8)_2$.

3.7 Optical properties and spectra

Lanthanide ions are weakly coloured. The spectra of their complexes show much narrower and more distinct absorption bands which is associated with weak f-f transition. The 4f orbital are deeply embedded inside the atom and well shielded by $5s^2$ and $5p^6$ electrons. The f electrons are practically unaffected by complex formation; hence colour remains almost constant for a particular ion regardless of the ligands(see Table 5).The bands due to f-f transition are sharp compared to the broad bands for d-d transition. Absorption bands due to 4f-5d transitions are broad andare affected by ligand environment. All lanthanoid ions (except () and () show luminescence.() and () particularly display strong emissions which may be attributed to the existence of large number of excited states which can decay to the ground state with either emission of energy(fluorecence) or non-radiative pathways. The luminescence of lanthanoid complexes is the reason they are used as phosphors on TV screens and in fluorescent lighting.

The 4f electrons are responsible for the strong magnetism exhibited by the metals and compounds of the lanthanides. In the incomplete 4f subshell the magnetic effects of the different electrons do not cancel out each other as they do in a completely filled subshell. Consequently, the metals display strong magnetic behaviour. At higher temperatures, all the lanthanides except lutetium are paramagnetic (weakly magnetic), and this paramagnetism frequently shows a strong anisotropy.

Table 5: Number of 4f electrons and color of some aqueous Lanthanides

Ions	No of 4f’s	colour	Ions	No of 4f’s	Colour	Ions	No of 4f’s	Colour	Isoelectronic
		Colourless			Colourless			Orange-Red	Colourless
		Colourless			Colourless			Yellow	Pale-pink
		Green			Green			Pale	Colurless
		Lilac			Lilac			Greenishyellow	Colourless
		Pink			Pink			Colurless	
		Yellow			Yellow				
		Pale pink			Pale pink				
		Colourless							

However, at lower temperature, most of the lanthanoids exhibit a point below which they become anti-ferromagnetism (i.e., magnetic moments of the ions are aligned but some are opposed to others), and, as the temperatures are lowered still further, many of them go through a series of spin rearrangements, which may or may not be in conformity with the regular crystal lattice.

4.0 Summary

i. Lanthanides exhibit a very wide range of coordination numbers (generally 6–12, but numbers of 2, 3 or 4are known). Also, all the lanthonoids exhibit +3 oxidation state, few exhibit +4 and +2 oxidation states.

ii. Their coordination geometries are determined by ligand steric factors rather than crystal field effects.

iii. They form labile ‘ionic’ complexes that undergo facile exchange of ligand.

iv. The 4f orbitals in the Ln^{3+} ion do not participate directly in bonding because they are strongly shielded by the $5s^2$ and $5p^6$ orbitals.

v. Spectroscopic and magnetic properties of lanthanoids are largely uninfluenced by the ligand.

vi. They display Small crystal-field splitting and very sharp electronic spectra in comparison with the-block metals.

vii. They prefer anionic ligands with donor atoms of rather high electronegativity (e.g. O, F).

viii. Lanthanoids readily form hydrated complexes (on account of the high hydration energy of the small Ln^{3+} ion) and this can cause uncertainty in assigning coordination numbers.Insoluble hydroxides precipitate at neutral pH unless complexing agents are present.

ix. The chemistry of lanthanoids is largely that of one (3+) oxidation state (certainly in aqueous solution).

x. Lanthanoids do not form Ln=O or Ln≡N multiple bonds of the type known for many transition metals and certain actinides. Also, they do not form stable carbonyls and have (virtually) no chemistry in the 0 oxidation state (unlike the transition elements).

5.0 Conclusion

All *lanthanide* elements form trivalent captions, Ln^{3+}, whose chemistry is largely determined by the *ionic* radius, which decreases steadily from lanthanum to lutetium. This is the most stable oxidation state of lanthanides. +2 and +4 oxidation states also exist but these are unstable. Lanthanides ions react with several compounds including CO_2, H_2O, O_2, and halogen and are capable of forming complexes. Lanthanides do not form Lon=O (double bond) or Lynn (triple bond) multiple bonds of the type common to many transition metals. The chemistry of lanthanide is unique and is greatly influence by lanthanide contraction.

6.0 Tutor marked assignment

1. Use suitable chemical equation to explain why the anhydrous chlorides of lanthanides cannot be obtained from the hydrates.
2. Under what conditions can $LnCl_3$ be prepared from NH_4Cl? Provide chemical equation.
3. Give two examples of ox acids of lanthanides.
4. Write an equation to show the complete reaction that involves lanthanide carbide and water

5. Complete and balance the following chemical reactions

   i.

   ii.

   iv.

   v.

   vi.

6. The organometallic compounds of the lanthanoids are dominated by good donor ligands, with complexes of acceptor ligands being rare. Give three reasons for this observation.

7.0 References

Petrucci, Hardwood, Herring. "General Chemistry: Principles & Modern Applications". New Jersey: Macmillan Publishing Company, 2007.

Moeller, Therald. The Chemistry of the Lanthanides. New York: Reinhold Publishing Corporation, 1963.

Cotton, Simon. Lanthanides and Actinides. London: Macmillan Education Ltd, 1991.

Deacon, G. B., Tuong,, T. D., Wilkinson, D. L. and Marks, T. (2007). Lanthanide trichloride by reaction of lanthanide metal with mercury (II) chloride in tetrahydrofuran. Edited by Angelicci, R. A. Wiley, USA.

Theodore, G. (2009). The Elements: A Visual Exploration of Every Known Atom in the Universe. New York: Black Dog & Leventhal Publishers.

Holden, N.E and Coplen, T. (2004). The periodic Table of the elements..Chemistry International.IUPAC.26 (1): 8-18.

MODULE 2

UNIT 1: The chemistry of actinide elements

8.0 **Introduction**

9.0 **Objectives**

10.0 **Main content**

  10.1 **Properties of actinides**

  10.2 **Actinide contraction**

11.0 **Summary**

12.0 **Conclusion**

13.0 **Tutor marked assignment**

14.0 **References**

1.0 Introduction

The actinides are the elements in which the 5f orbital is filled as the electrons are added. As in lanthanides, the ante-penultimate 5f orbital is filled successively by the addition of one electron at each step. Thus, lanthanides are termed the first inner transition series while actinides constitute the second inner transition series.

Actinide series are named after the element actinium. In this series, the first four elements actinium, thorium, protactinium and uranium occur in nature. The other elements are artificial and are made by the nuclear bombardment. Actinides include the fourteen elements from thorium(Th) to lawrencium (Lr). the Actinides are the second row of the f-block.

Only actinium, thorium, protactinium and uranium occur naturally (i.e. $Z \leq 92$). Others are man-made. They are synthesized by artificial radioactivity i.e. by bombardment with slow moving neutron actinium and protactinium occurs only in trace amounts. Neptunium and plutonium occur in uranium minerals in minute amounts. All isotopes of all the actinides are radioactive. Most of the longer-lived isotopes decay by α-emission. Thorium is widely dispersed and account for about 3 ppm of the earth crust. Natural thorium is essentially 100 % ^{232}Th and occurs in monazite and in uranothorite (which is a mixed Th, U silicate). Thorium can be obtained as

$ThO_2$from mineral extraction process and are effectively used as 99 % ThO_2/1 % CeO_2 in thoria gas mantles.

Uranium is widely distributed in the earth crust and are often found in association with ancient igneous rocks. Natural uranium is about 99.27 % ^{238}U and 0.73 % ^{235}U. Most uranium are obtained from its ore as UO_2. They are used for nuclear fuel, and for colouring glass/ceramic

Plutonium (^{239}Pu) is produced from uranium(^{238}U) by neutron capture in all nuclear reactors. It serves as nuclear fuel in fast-breeder reactors and as a compact energy source. Combination of plutonium with PbTe is used in producing thermoelectric, which is a totally reliable electricity. Plutonium has also been found to be useful in appollo space missions and in human heart pacemakers

2.0 Objectives

The objectives of this unit include

i. Understanding of general physical and chemical properties of actinides

ii. To know the various oxidation states possible to actinides

iii. Understanding of the concept of actinide contraction

iv. To know and understand the electronic configuration of actinide and their significance.

v. To study various compounds of actinides in different oxidation states

vi. To understand the route of formation of actinide halides and their properties

vii. To understand the organometallic chemistry of actinides

3.0 Main document

3.1 Properties of actinides

Actinoids possess the following general properties

i. They are radioactive metals due to instability.

ii. Majority of the actinides are synthetically made by particle accelerators creating nuclear reactions and are short lasting.

iii. Actinides are unstable and reactive because their atomic numbers are above 83 All actinides have a silvery or silvery-white luster appearance in metallic form.

iv. They have the ability to form stable complexes with ligands, such as chloride, sulfate, carbonate and acetate.

v. Most actinides occur in nature in sea water or other minerals.

vi. They are radioactive and hence have the ability to undergo nuclear reactions.

The emission of radioactivity, toxicity, pyrophoricity, and nuclear criticality are properties that make them hazardous to the environment. The types of radiation the actinides possess are alpha, beta and gamma. Radiation also arises when neutrons are produced by spontaneous fissions or when boron, beryllium, and fluorine react with alpha-particles.

The toxicity of actinides arises due to their radioactive and heavy metal characteristics. Pyrophoricity of lanthanides expresses the tendency for the metals and their compounds such as hydrides, carbides, alloys and other compounds to ignite at room temperature in a finely divided state. This will result in spontaneous combustion and spreading of radioactive contaminates.

Nuclear criticality of actinides arises when fissionable materials are combined. This will cause a chain reaction to occur, resulting in lethal doses of radioactivity. However, nuclear criticality depends on the actinides’ chemical form, isotopic composition, geometry, size of surroundings, etc. Also, the interaction of radioactive actinides with different types of phosphors will produce pulses of light.

Worked example 1

What are the factors that make actinides to be exerting negative impact on the environment?

Solution

The emission of radioactivity, toxicity, pyrophoricity, and nuclear criticality are properties that make actinides to be hazardous to the environment. The types of radiation the actinides possess are alpha, beta and gamma. Radiation also arises when neutrons are produced by spontaneous fissions or when boron, beryllium, and fluorine react with alpha-particles.

The toxicity of actinides arises due to their radioactive and heavy metal characteristics.

Worked example 2

(a) What is responsible for nuclear criticality in actinides?

(b) What is the consequence of nuclear criticality?

(c) State three factors that affect nuclear criticality

Solution

(a) Nuclear criticality of actinides arises when fissionable materials are combined.

(b) This will cause a chain reaction to occur, resulting in lethal doses of radioactivity.

(c) Nuclear criticality depends on the actinides' chemical form, isotopic composition, geometry, size of surroundings, etc.

3.1.1 Oxidation states of actinide

Table 6 shows that actinides generally exhibit oxidation states ranging from+2 to +7**.** The oxidation state varies with progressive filling of 5f sub orbital (except for Ac and Th). Only Ac and Lr have one oxidation state (i.e +3). Other actinides have at least two oxidation state. *+2* is unusual oxidation state which is common only for the heavier elements. +2 oxidation state is more stable in No^{2+} and Md^{2+}than in Eu^{2+}. Actinide in+2 oxidation state (i.eAn^{2+}) have properties that are similar to Ln^{2+} and Ba^{2+}.

Table 6: Electronic configuration and oxidation states of actinides

Atomic no	Element	Symbol	Electronic configuration	Oxidation states
89	Actinium	Ac	[Rn] $6d^17s^2$	+3
90	Thorium	Th	[Rn] $6d^27s^2$	+3, +4
91	Protactinium	Pa	[Rn] $5f^26d^17s^2$	+3, +4 +5
92	Uranium	U	[Rn] $5f^36d^17s^2$	+3, +4 +5, +6
93	Neptunium	Np	[Rn] $5f^46d^17s^2$	+3, +4 +5, +6, +7
94	Plutonium	Pu	[Rn] $5f^67s^2$	+3, +4 +5, +6, +7
***95**	Americium	Am	[Rn] $5f^77s^2$	+2, +3, +4, +6
96	Curium	Cm	[Rn] $5f^7 6d^17s^2$	+3, +4
97	Berkelium	Bk	[Rn] $5f^97s^2$	+3, +4
98	Californium	Cf	[Rn] $5f^{10}7s^2$	+2, +3, +4
99	Einsteinium	Es	[Rn] $5f^{11}7s^2$	+2, +3
100	Fermium	Fm	[Rn] $5f^{12}7s^2$	+2, +3
101	Mandelevium	Md	[Rn] $5f^{13}7s^2$	+2, +3
102	Nobelium	No	[Rn] $5f^{14}7s^2$	+2, +3
103	Lawrencium	Lr	[Rn] $f^{14}6d^17s^2$	+3

Worked example 3

Provide answers to the following questions with respect to actinides

i. The range of values for the oxidation states of actinides

ii. How the oxidation state vary

iii. Minimum number of oxidation state for each actinide

iv. Examples of actinides with stable and unstable +2 oxidation state

v. Similarity in properties of actinides compounds in +2 oxidation state to other metallic compound.

vi. The most stable oxidation state for actinides and trans-americium elements

vii. The principal oxidation state for thorium

Solution

i. Actinides generally exhibit oxidation states ranging from+2 to +7

ii. The oxidation state varies with progressive filling of 5f sub orbital (except for Ac and Th).

iii. Only Ac and Lr have one oxidation state (i.e +3). Other actinides have at least two oxidation states.

iv. *+2* is unusual oxidation state which is common only for the heavier elements. +2 oxidation state is more stable in No^{2+} and Md^{2+}than in Eu^{2+}.

v. Actinide in +2 oxidation state (i.eAn^{2+}) has properties that are similar to Ln^{2+} and Ba^{2+}.

vi. The most common oxidation state of actinides is +3 and + 3 oxidation state is also the most stable state for all trans-americium elements.

vii. Oxidation state of +4 is the principal oxidation state for Th

The most common oxidation state of actinides is +3. + 3 oxidation state is also the most stable state for all trans-americium elements (except No). Marginal stability is however observed for Th, Pa and U in +3 oxidation state. General properties of +3 oxidation state resemble that of the lanthanides (Ln^{+3}) and are size dependent. For example, stability constant and isomorphism are closely similar for Ln^{3+} and Au^{3+} of approximately similar sizes. Binary halides, MX_3 of actinides can easily be prepared and are easily hydrolyzed to MOX. Also binary oxides are known for Ac, Th and trans Am elements.

Oxidation state of +4 is the principal oxidation state for Th. The chemistry of Th^{4+} displays strong resemblance to Zr^{4+} and Hf^{4+}. +4 oxidation state is a stable oxidation state for Pa, U and Pu. However, Am, Cm, Bk and Cf are easily reduced. AuO_2 are known for Th to Cf series. Their fluoride structures (AuF_4) are isostructural with lanthanide tetraflourides. However, MCl_4 is only known for Th, Pa, U and Np. Hydrolysis, complexation and disproportionation are important reactions only in aqueous media.

Oxidation state of +5 is the principal state for Pa. Pa^{5+} chemistry resembles that of Nb^{5+} (transition metal). Few compounds of +5 oxidation state are known. For example, fluoride (e.g, PaF_5, NbF_5, UF_5), fluoro anions (e.g,, ,) and oxochloride (e.g $PaOCl_3$, $UOCl_3$) and urinates ($NaUO_3$)

Oxidation state of +6 (mostly) is significant for U, Np, Pu and Am. However, is the most stable. Relatively few other compounds also exist. For example, AnF_6 (An = U, Np, Pu), UCl_6 UOF_4, $U(OR)_6$, etc. Finally, only the marginally stable oxo-anions of Np and Pu, e.g. are known for +7 oxidation state.

3.1.2 Halides

Most actinides form halides with halogens at specific temperatures and trihalides are the most well-known stable halides. For example

The halides are very important binary compounds, sometimes the most important. Although they may have radioactivity that causes problems, they are useful to study to understand the trends in the Actinide series. Table 7 presents some characteristics of halides formed by actinoids

3.1.3 Oxides and oxyhalides

All Actinides form oxides with different oxidation states. The most common oxides are of the form M_2O_3, where M would be one of the elements in the Actinide series. The earliest actinides have a closer relation to the transition metals, where the oxidation state is equal to the number of electrons on the outer shell. The +4 state is more stable in the Actinide series than in the Lanthanides. The following are the different oxides of the Actinide elements:

- M_2O_3:Ac, Pu-Es
- MO_2:Th, U-Cf
- M_2O_5:Pa, Np
- MO_3: U, Np(Not well known)

The oxyhalides of actinides are not binary but some are formed by earlier Actinides, for example, an aqueous Protactinium fluoride reacts with air to form PaO_2F, Thorium can form

$ThOX_2$, Neptunium can form $NpOF_3$, Plutonium forms $PuOF_4$ and UO_2F_2 is made by Uranium (III) oxide and Hydrofluoric acid.

Table 7: Properties actinides halides

Element	
Actinium	Form halide in +3 oxidation state only
Thorium	Forms halides in the 2, 3, and 4 oxidation states, exists in black and gold forms, has high conductivity because it contains free electrons, solids are colourless. Forms many complexes with neutral donors and has an eight coordination number (dodecahedron, sq antiprism).
Protactinium	Forms many different types of halides and several oxyhalides. Chlorides ($PaCl_5$) are yellow-green, bromides ($PaBr_4$) are orange-red, fluorides (PaF_4) are brown, and iodides (PaI_3) are dark brown.
Uranium	Halides exist in oxidation states between +3 to +6. Uranium (VI): UF_6 (colourless, does not require use of elemental fluorine to be made, octahedral, volatile), UCl_6 (dark green, hydroscopic, octahedral, volatile). Uranium (V): rare oxidation states, unstable, six and seven coordination. Uranium (IV): most important uranium halides, U^{+4} does not have reducing tendencies, UI_4 is stable but not to hydrolysis. Uranium (III): ease of oxidation of U^{+3}, all made under reducing conditions, have typical structure of actinide trihalides, UF_3 (green, 11-coordinate structure), UCl_3 and UBr_3 (red, trigonal prism), UI_3 (8-coordinate, black).
Neptunium	Formed halides with different oxidation states but only fluorides are in above +4. It has purple and blue-white fluorides, has green chlorides, has green and red-orange and dark red bromides and has brown iodides. NpF_6 forms a toxic and volatile vapor. Oxyhalides, such as $NpOF_3$ and NpOCl also exist.
Plutonium	Only consists of trihalides and tetrahalides, but PuF_6 exists and it is very volatile, reactive, is best kept in its gas state, does not exist in solid state, and is decomposed by its own radiation. The trihalides have characteristics colours: fluoride (violet-blue), chloride (blue-green), bromide (light-green), iodide (bright-green); +2 state is inaccessible. Its complexes are in the +4 state and are stable except for iodides while its oxyhalides include $PuO_2Cl_2*H_2O$.
Americium	The dihalidesis insoluble. and are black solids.Only the fluorides have higher than +3 oxidation state. Forms important trihalides: fluoride and chloride are pink, bromide is white-pale yellow, and iodide

	is pale yellow.
Californium	The only oxidation states are +3 and +2 and it only forms chloride and iodide halides. For example $CfCl_3$, CfI_3, and CfI_2.
Einsteinium	Form halides with only chlorine and fluoride in +3 oxidation state. For example $EsCl_3$ and EsF_3

Worked example 4

For the reaction of actinium (III) hydroxide with hydrofluoric acid, a) write and balance the equation and b) explain what makes the O.S. of Actinium different from the other Actinides.

Solution

a) $Ac(OH)_3$ +3HF+700°C= AcF_3+$3H_2O$ and b) The difference between Actinium and the other Actinides involving O.S. is Actinium only has one oxidation state which is +3

The Chemistry of Uranium

Halides: Uranium fluoride (UF_6) is the most important fluoride. It prepared via the following reactions

UF_6 has a melting point of 64 °C, vapour pressure of 115 mm/Hg at 25 °C. It is an important compound that is used to separate uranium isotopes. Gas diffusion or centrifugation separates $^{235}UF_6$ from $^{238}UF_6$. Uranium richer in ^{235}U is termed enriched, while those richer in ^{238}U is depleted. UF_6 is a very strong fluorinating agent. UF_6 can react with trimethylsilane chloride to give UF_4 or UF_5 (which are other forms of uranium chloride. The equations for the reactions are

Experiment shows that at high temperature (and in the presence of air or oxygen), ranging from 500 to 600 °C, the above reaction may yield UO_2 and $CFCl_2CFCl_2$ as a product. Mixed valence fluorides of uranium (for example, U_2F_9) have also been reported. UF_4 can be reduced to UF_3 by one half mole of hydrogen gas.

The most important chloride of uranium is UCl_4. It is the starting materials for the preparation of other U(IV) compounds. It is normally prepared by liquid-phase chlorination of UO_3 by refluxing hexachloropropene. UCl_4 is soluble in polar organic solvents and in water. It forms various adducts (2 - 7 molecules) with O and N donors. Actinides trihalides are closely related with the lanthanide trihalides except in redox potentials

3.1.4 Organometallic chemistry

Organometallic chemistry of actinides is relatively recent but is similar to those of lanthanides with respect to cyclopentadienides/cyclo-octatetraenides/alkyls cyclopentadienides, which are pi-bonded to actinides. For example,

is regarded as the most important cyclopentadienide compound of uranium. Uranium also form cyclooctatetraenide and the most important is the uranocene, which posseses the following properties

- i. It is a green crystal, paramagnetic and pyrophoric. It is stable to hydrolysis
- ii. It is stable to hydrolysis
- iii. It is a planar sandwich complex
- iv. Bonding in the complex has 5f and 6d contributions

Worked example 6

(a) Provide the organometallic products of the following reactions,

Solution

(a)

3.2 Actinide contraction

There is a steady decrease in ionic radii with increase in atomic number from actinium to lawrencium. This is called actinide contraction. This contraction is similar to lanthanide contraction. The actinide contraction is due to imperfect shielding of one 5f electron by another in the same shell. Thus, as we move along the actinide series the nuclear charge and the number of 5f electrons increase by one unit.

Work example 7

Write the electronic configuration of the following ions

(a) cerium(III)

(b) Am^{3+}

Hence determine to which series they belong.

Solution

For ions, the *s*-valence electrons are lost prior to the *d* or *f* electrons.

(a) $Ce^{3+}[Xe]4f^1$; Ce^{3+} is an inner transition element in the lanthanide series.

(d) americium(III) $[Rn]5f^6$; actinide.

4.0 Summary

The actinides elements consist of 14 elements that start from thorium to lawrencium. It is not fully establish whether the last electron enters the 5f orbital or the 6d orbital because both have the same energy. Consequently, there are two views regarding the electronic configuration of actinides. According to Seaborg (1951), the 5f orbital is filled from thorium, while in Dawson's view the 5f orbital is filled from uranium and are called uranides. The other approach is the general electronic configuration of actinidesis $[Rn]\ 5f^{0\text{-}14}\ 6d^{0\text{-}2}\ 7s^2$ where Rn is the electronic configuration of the element radon. Unlike lanthanides which show the +3 oxidation states, actinides show a variety of oxidation states from +3 to +6. However, +3 and +4 are the principal oxidation states. The +3 oxidation state is the most stable in Ac and all the other elements of the series. The +4 oxidation state is the most stable in Th and Pu. +5 in Pa and Np and +6 is seen in U. In actinides, the ionic radius decreases as we move across the series. This decrease in ionic radius is termed actinide contraction. This effect is due to poor screening by f electrons. Unlike lanthanides, they have the tendency to form complexes. Complex formation with ligands such as thio-ethers is also seen.

5.0 Conclusion

The study of actinides is as important as the study of lanthanides. However, due to their expanded ability of having higher oxidation states than lanthanides, actinides chemistry displays more reactive features than the corresponding lanthanides. Most significant features of the actinides is their radioactive nature. This singular property has enhanced their industrial and medical applications in numerous ways. However, their chemistry is relatively complicated by their variable oxidation state and the non-natural occurrence (actinium, thorium, protactinium and uranium). Researches are ongoing on more economical viable approaches to the use of actinides.

6.0 Tutor marked assignment

1. State five general properties of actinides
2. Compare and contrast actinide and lanthanide contraction
3. Uranium also form cyclooctatetraenide and the most important is the uranocene. List four properties of this product.
4. Provide the product of the underlisted reactions

What is the type of the reaction expressed in the above reactions.

5. What is the basis of classifying uranium as enriched and depleted
6. UF_6 can react with trimethylsilane chloride to give UF_4 or UF_5 (which are other forms of uranium chloride. Provide equations for the reactions.
7. Write an equation for the reduction of UF_4 by hydrogen gas

7.0 References

Petrucci, Hardwood, Herring. "General Chemistry: Principles & Modern Applications". New Jersey: Macmillan Publishing Company, 2007.

Moeller, Therald. The Chemistry of the lanthanides. New York: Reinhold Publishing Corporation, 1963.

Cotton, Simon. Lanthanides and Actinides. London: Macmillan Education Ltd, 1991.

Deacon, G. B., Tuong,, T. D., Wilkinson, D. L. and Marks, T. (2007). Lanthanide trichloride by reaction of lanthanide metal with mercury (II) chloride in tetrahydrofuran. Edited by Angelicci, R. A. Wiley, USA.

Theodore, G. (2009). The Elements: A Visual Exploration of Every Known Atom in the Universe. New York: Black Dog & Leventhal Publishers.

Holden, N.E and Coplen, T. (2004). The periodic Table of the elements..Chemistry International.IUPAC.26 (1): 8-18.

Seaborg, G. T. (1951). The transuranium elements. – present status: Noble Lecture. UC Berkeley, Radiation Laboratory. OSTI 4406579.

Seaborg, G. T.; Thompson, S.G.; Harvey, B.G.; Choppin, G.R. (July 1954). Chemical properties of elements 99 to 100 (Einsteinium and Fermium. UC Berkeley, Radiation Laboratory. OSTI 44065197.

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MODULE 2

UNIT 1: The chemistry of uranium

8.0 **Introduction**

9.0 **Objectives**

10.0 **Main content**

- 10.1 **Physical properties of depleted uranium**
- 10.2 **Oxides of uranium**
- 10.3 **Uranates**
- 10.4 **Halides**
- 10.5 **Halogen complexes**
- 10.6 **Hydrates of uranium**
- 10.7 **Uranyl salt**
- 10.8 **Aqueous chemistry of uranium**

11.0 **Summary**

12.0 **Conclusion**

13.0 **Tutor marked assignment**

14.0 **References**

1.0 Introduction

Uranium was discovered by Klaproth in 1789 and was used basically for colouring glasses and ceramic while radium extracted from its ore was used for cancer therapy. However, in 1939, Hahan and Strassman discovered nuclear fission which sparked up much research into the chemistry of uranium.

Uranium has 3 isotopes namely ^{238}U (99.2739 %), ^{235}U (0.7204 %) and ^{234}U (0.0057 %). ^{238}U is the parent of the (4n + 2) radioactive decay series and ^{235}U is the parent of the (4n + 3) series while ^{234}U is formed from ^{238}U decay sequence. ^{235}U (0.72 % abundance) is the prime nuclear fuel. However, natural uranium moderated by D_2O, can be used in nuclear reactors. Most reactors and nuclear weapons use enriched uranium while large scale operation of ^{235}U employs gaseous diffusion of UF_6. However a gas centrifuge method is no economical.

Isotope separation is a difficult and energy intensive activity. Enriching U is difficult because the two isotopes have closely related and identical chemical properties and are very similar in weight because ^{235} U is only 1.26 % lighter than ^{238}U. However, gaseous diffusion is among the several methods available for uranium isotope separation technology. It is a technology used to produce enriched uranium by forcing gaseous UF_6, through semi- permeable membrane. This process is based on the principle that in a closed box, all molecules have the same energy. Hence, the lighter molecules on average travel faster than the heavier molecules. As a result, the lighter molecules strike the walls of a container more frequently than their heavier counter parts. Consequently, if a portion of the container consists of a small hole enough to permit the passage of individual gas molecules, but not so large that a mass flow of the gas can occur, then more light molecules than heavy molecules will pass out of the container, since the rate of effusion (diffusion to outside the box) is proportional to the inverse square of the mass. The gas leaving the container is somewhat enriched in the lighter molecule while the residual gas is somewhat depleted. A single container where the enrichment process takes place through gaseous diffusion is called a diffuser. It does not contain one hole, however, but has a porous barrier. Thermal diffusion utilizes the transfer of heat across a thin liquid or gas to accomplish isotope separation. The process exploits the fact that the lighter ^{235}U gas molecules will diffuse toward a hot surface, and the heavier ^{238}U gas molecules will diffuse toward a cold surface.

When uranium is mined, the highly radioactive uranium is removed and used in nuclear weapons and reactors. The waste product is called depleted uranium (DU). DU has a radioactive half-life of 4.5 billion years. DU's extreme density (1.6 times as dense as lead) and its ability to burn easily make it attractive for use in weapons, especially armor-piercing ammunition. For example, in the US arsenal, DU ammunition is fired by Miseries Abrams tanks, , M2 and M3 Bradley Fighting Vehicles,A-10Thunderbolt aircraft, AH-1W Cobra helicopter gunships, Light Amphibious Vehicles (LAV) and AV-8B Harrier jets. US Army test data shows that when a DU penetrator impacts a target, between 2Cf and 70 % of the round burns 7 scattering an extremely fine uranium dust in and around the target.

Depleted uranium is a metal made from uranium hexaflouride which is the byproduct of the uranium enrichment process. Depleted uranium is actually the uranium 238 isotope. Natural uranium contains 99.2% by weight U-238, while DU contains 99.8% by weight of U-238. Recent documents released by the U.S. Department of Energy provide evidence to suggest that a small proportion of other toxic heavy metals such as plutonium also may be present in DU. U-238 emits alpha particles at 4.2MeVand 4.15MeV that cause significant internal ionization with consequent cellular damage. In addition daughter product emits beta and gamma rays that may cause further radiological damage. DU constitutes an internal hazard and with consequent inhalation, ingestion and wound contamination, it poses significant and unacceptable risks. Although DU is 60 % less radioactive than natural uranium because U-235 which emits gamma rays and beta particles have been removed, depleted uranium or uranium 238 is still very dangerous as an internal hazard because the alpha particle emissions are not reduced but proportionally increased. Also spent penetrators or parts of penetrators emit 200 mrem/hour and thus cannot be touch or picked up without protection. .

2.0 Objectives

The objectives of these units shall include the following

i. Introduction to the different grades of uranium
ii. Isolation of uranium
iii. Physical properties of uranium
iv. Explanation of the chemistry behind the formation of uranium oxides, halides, hydrides, oxyacid, uranyl salt, urinates and other compounds
v. Provide suitable chemical equations to explain essential processes
vi. Discuss the aqueous chemistry of uranium

3.0 Main content

3.1 Physical properties of depleted uranium (DU)

Depleted uranium or U-238 has an atomic mass of 238. Its half-life is 4.468billion years. Its natural occurrence is 2.1 parts per million. Uranium is silvery- white, lustrous, malleable, ductile, and pyrophoric. This makes DU an ideal metal for use as kinetic energy penetrators, counterweights and shielding or armor. High density and pyrophoric (catches fire) nature are the two most significant physical properties that guided its selection for use as a kinetic energy penetrator.

3.1.1 Sources of DU

Uranium hexafluoride is the non-fissionable residue or by-product of the uranium enrichment process during which fissionable Uranium 235 and Uranium 234 are separated from natural uranium, Depleted uranium is refined from uranium hexafluoride (UF_6). The United States Department of Energy has so much UF_6 stored at various sites that any use that increases disposal of this waste product is welcome. Consequently economic recovery may supersede health and environmental concerns.

3.1.2 Toxicity of DU

Depleted uranium is a heavy metal that is also slightly radioactive. Heavy metals (uranium , lead , tungsten , etc .) have chemical toxicity properties that , in high doses , can cause adverse health effects . Depleted uranium that remains outside the body is not toxic. DU emits alpha and beta particles as well as gamma rays . Alpha particles , the primary radiation type produced by DU, are blocked by skin, while beta particles are blocked by the boots and battle dress utility uniform (BDUs) typically worn by service members . While gamma rays are a form of highly penetrating energy, the amount of gamma, radiation emitted by depleted uranium is very low. Indicating that DU does not significantly add to the background radiation that we encounter every day.

When fired , or after " cooking off " in fires or explosions , the exposed depleted uranium rod poses an extremely low radiological , threat as long as it remains outside the body. However, if taken into the body via metal fragments or dust-like particles, DU may pose a long-term health hazard to humans if the amount is large. However, the amount which remains in the body depends on a number of factors, including the amount inhaled or ingested, the particle size and the ability of the particles to dissolve in body fluids. U is widely distributed and is more abundant than Ag , Hg , Cd and Bi. It has few economic ores. The main one being uraninite (one form is pitch blend) an oxide of approximate composition UD2 and uranium vanadate.

Uranium is recovered from nitric acid solution by

i. Extraction of uranyl nitrate into diethyl ether or isobutyl ketone. Nitrate salts of NH_4 or Ca^{2+} or Al^{3+} nitrate is added as a salting out agent in order to increase the extraction ratio. However, if tributyl phosphate in kerosene is used, no salting out agent is necessary.

ii. Removal from organic solvent by washing with dilute HNO_3.

iii. Recovery a U_3O_8 or UO_3 by precipitation with ammonia

3.2 Oxides of uranium

The main oxides of uranium are UO_3(which is orange yellow), U_3O_8 (which is black) and UO_2 (the brown oxide). UO_3 is obtained by heating the hydrous oxide ($UO_2(OH)_2$ H_2O). The hydrous oxide is obtained when NH_4OH is added to solutions.

The other oxides are obtained from UO_3 according to the following equations,

All uranium oxides dissolve in HNO_3 to give uranyl nitrate,. Uranium oxide is one of the most complex oxide system known. Their complexities may be due to the multiplicity of oxidation states of comparable stability.

The addition of H_2O_2 to a solution of uranium oxide (at pH 2.5 – 3.5) gives a pale yellow precipitate of formula, $UO_4.2H_2O$. When treated with NaOH and excess of H_2O_2, a stable salt is obtained, $Na_4[UO_2(O_2)_3]_9H_2O$, whose anion consists of linear UO_2 with three peroxo groups in the equatorial plane. All three oxides of uranium are basic and dissolve in HNO_3 to form uranyl nitrate. The uranyl nitrate has an unusual eight coordinate structure consisting of a linear UO_2 group perpendicular to a hexagon of six oxygen atoms (4 of which originate from two bidentate NO_3 groups and two from water molecules).

3.3 Uranates

The fusion of uranium oxides with alkali or alkaline-earthcarbonates , or thermal decomposition of salts of the uranylacetate anion, gives orange or yellow materials generally referred to as uranates, The stoichiometry of the uranates is normally . However, and are known. Addition of aqueous NH_3 to $UO_2(NO_3)_2$ gives ammonium diuranate, which is an hydrate, $UO_2(OH)_2.2H_2O$.

Worked example 1

Provide the product of the under listed reactions and give a general explanation for all of them

Solution

The fusion of uranium oxides with alkali or alkaline-earth carbonates, or thermal decomposition of salts of the uranyl acetate anion, gives orange or yellow materials generally referred to as urinates,

3.3.1 Other Binary compounds of uranium

Direct reaction of uranium with B , C , S , N , P , As , Sb , Se , S , Te and other non-metals and metalloids gives semi metallic compounds. Most of these compounds are non-stoichiometric and resembles the oxides. Others such as silicides are chemically inert. The sulphides are good refractories.

3.4 Halides

The hexafluoride, $UF_6$is obtained as colourless volatile crystals , (m.p.64°C) by fluorination of UF_3 or UF_4 at 4000□C. It is a strong oxidizing and fluorinating agent and is vigorously hydrolysed by water. The green tetrachloride is obtained on refluxing UO_3 with hexachloropropene (C_3Cl_6) , $CCl_3CCl = CCl_2$.

The compound (is soluble in polar organic solvents and in water. Reaction with chlorine gives $U_2Cl_{10}$and under controlled conditions, the unstable UCl_6 is formed:

The triflouride is prepared by reduction of UF_4 by aluminium, The hydrated tetraflouride is obtained from the reaction of UO_3 with as expressed before.

UF_3 resembles the lanthanide fluoride, characterized by high melting point and is non volatile crystalline solid. UCl_6 is moisture sensitive and react to give uranyl chloride and HCl,

In CH_2Cl_2 solution, UCl_6 also decomposes to U_2Cl_{10}.
Oxyhalides of uranium are also common but the stable oxyhalides is UO_2X_2. Oxyhalides of uranium can be prepared through appropriate chemical reactions. For example,

3.5 Halogeno complexes

All Halides can form halogeno complexes, but F^- and Cl^- are most common. For example, uranium in +3 oxidation state (i.eU(III)) gives, and. in +4 oxidation state (U(IV)), andare common. Also common are and. Uranium also form pseudohalide complexes such as . Uranium in +5 oxidation state is usually unstable but deep blue solution of UF_5 in 48 % HF can be slowly oxidised in the air but on cooling a dark blue crystal of $HUF_6.xH_2O$ (x = 2-5) is obtained. This crystal can be hydrolysed to $UF_4$and . However, addition of some metal ions (such as Rb^+, Cs^+) yield a stable product. Uranium in +5 oxidation state is usually unstable in aqueous media.

3.6 Hydrides of uranium

Uranium reacts with hydrogen, even at room temperature to give pyrophoric black powder called uranium hydride,

The hydrides are widely used for the preparation of uranium compounds because it is lighter than the uranium metals. Also, uranium hydride undergoes several reactions including the following,

3.7 Uranyl salt

Uranyl salt that is common is the yellow uranyl nitrate which may have 2 , 3 or 6 molecules of water depending on the source it crystallizes (which maybe from fuming , concentrated or dilute nitric acid). Addition of sodium acetate in excess to solutions in dilute acetic acid will lead to the precipitation of an insoluble salt, . The uranyl ion can be reduced to red-brown U^{3+} by Na/Hg or zinc. The U^{3+}itself can be oxidized in the air to green U^{4+} according to the following equations

Thus the above oxidations depend on potentials as indicated in the above equations.

3.8 Aqueous chemistry of uranium

Uranium exist in four oxidation states and also exhibit extensive possibilities of undergoing complexation and hydrolytic reactions with all ions (except ClO). Therefore, polymeric ion species are often formed.

Aqueous solutions of uranium salts exhibit an acid reaction through hydrolysis. This reaction increases in the order $U^{3+} << U^{4+}$. The main hydrolysed species of at 25^0C are UO_2OH^+, $(UO_2)_2(OH)_2^{2+}$ and $(UO_2)_3OH)^{5+}$. However, the species present depend on the medium. At higher temperature, the monomer UO_2OH^+ is the most stable but the rate at which it undergoes hydrolysis to UO_3 increases. The U^{4+} ion is slightly hydrolyzed in 1 M $HClO_4$ acid solutions.

(1M $HClO_4$ $NaClO_4$)

The equilibrium constant at 25°C for the above reaction is 0.027, which suggest the tendency of the reaction to reverse easily. However, the reaction can lead to the formation of polynuclear species if the acidity is reduced acid solutions. Consequently, U^{4+} ion will produce insoluble precipitate from acid solution in the presence of F^-, PO_4^{3-} and with IO^{3-}

The U^{+5}ion () is extraordinarily unstable towards disproportionation and has a transitory existence under most conditions. However evidence from polarography confirmed it occurrence. It is also an intermediate in photochemical reduction of uranyl ions in the presence of source and similar substances.

U^{+5} can be stabilized in HF solution as UF_6 as well as in concentrated chloride and carbonate solutions. In aqueous solution, and U^{4+} readily form complex ions. For example,

Nitrate complexes also exist, and nitrate solutions of uranium in +5 oxidation state contain $[UNO_3(H_2O)_4]^{3+}$. Complex ions are also formed with citrate and anions of other organic acids including thiocyanate and phosphates. Complexes associated with the phosphates are significant in the aqueous chemistry of uranium because uranium occurs in phosphate minerals, and species such as and have been identified as complexes.

4.0 Summary

Uranium is a chemical element with a silvery-grey appearance. It is one of the most widely studied and investigated actinide elements. Uranium has atomic number of 92 which indicates 92 electrons (of which six are valence electrons) and 92 protons. Uranium is weakly radioactive because all isotopes of uranium are unstable, with half- lives varying between 159,200 years and 4.5 billion years. The most common isotopes of natural uranium are U-238, (which has 146 neutrons and account for more than 99 % t) U-235 (which has 143 neutrons). Uranium is a metal that has the highest atomic weight of the primordially occurring elements. Its density is about 70% higher than that of lead, and slightly lower than that of gold. It occurs naturally in low concentrations of a few ppm in soil, rock and water, and is commercially extracted from uranium-bearing mineral especially uraninite.

Uranium ions undergoes several chemical reactions as discussed in this unit. However, most of its properties are unique when compare to the behaviour of other actinides.

5.0 Conclusion

Uranium is graded into enriched and depleted uranium based on the dominant isotope. The metal form oxides, hydride, halides, uranyl, uranate, and undergoes several aqueous and non aqueous reactions. Uranium stands to be the most widely studied and applied actinide metals.

6.0 Tutor marked assignment

1. Highlight the possibilities of binary salt formation between uranium and other elements
2. Explain how you can obtained UF_6 in the laboratory. Give equation to support your answer.
3. The compound (is soluble in polar organic solvents and in water. It reacts with chlorine under two conditions to give different products respectively. Highlight the various conditions and show the products formed in each. Chemical equations are needed.
4. The triflouride is prepared by reduction of UF_4 by aluminium. Provide an equation for the reaction.
5. Write the equations for the reactions of UCl_6 with water and with CH_2Cl_2.
6. Write two chemical equations to show how oxyhalides of uranium can be prepared.

7.0 References

Petrucci, Hardwood, Herring. "General Chemistry: Principles & Modern Applications". New Jersey: Macmillan Publishing Company, 2007.

Moeller, Therald. The Chemistry of the lanthanides. New York: Reinhold Publishing Corporation, 1963.

Cotton, Simon. Lanthanides and Actinides. London: Macmillan Education Ltd, 1991.

Deacon, G. B., Tuong,, T. D., Wilkinson, D. L. and Marks, T. (2007). Lanthanide trichloride by reaction of lanthanide metal with mercury (II) chloride in tetrahydrofuran. Edited by Angelicci, R. A. Wiley, USA.

Theodore, G. (2009). The Elements: A Visual Exploration of Every Known Atom in the Universe. New York: Black Dog & Leventhal Publishers.

Holden, N.E and Coplen, T. (2004). The periodic Table of the elements..Chemistry International.IUPAC.26 (1): 8-18.

MODULE 3

UNIT 1: Applications of lanthanides and actinides

1.0 Introduction

An Application of lanthanides and actinides is closely related to their unique electronic configuration and other properties. Thus, several applications are unique to the metals and may not have close rival with other metals. Lanthanides and actinides are the only metals that occupy the f-orbitals. This section considers various applications routes for lanthanides and actinides.

2.0 Objectives

The objectives of this section shall include

i. Understanding of optical application of lanthanides

ii. Understand application of lanthanides in ceramic and glass industries

iii. Understand catalytic roles of lanthanides

iv. Understand application of lanthanides in metallurgical industries

v. Understand the application of actinides in nuclear power stations

vi. Understand medical application of actinides

vii. Understand military application of actinides

viii. Understand miscellaneous application of lanthanides and actinides

3.0 Main content

3.1 Applications of lanthanides

3.1.1 Alloys (misch metal)

Some alloys of lanthanoid elements (**misch metals)**containing 50% of Ce together with smaller quantities of other lightlanthanoidsprovide major raw materials for the production of heat resistant , stainless and instrumental steels. These alloys are pyrophoric possessing the property of giving off sparks that are capable of igniting especially when scratched. Therefore, the alloys are also useful as flints in cigarette lighters, miner's safety lamps and in automatic gas lighting devices. Misch metal is also useful in the battery industry because it is a component of nickel metal hydride batteries. These set of batteries replaces nickel cadmium batteries which are not environmentally friendly and are useful in powering portable electronic equipment such as lap tops, computers and mobile phones.

Mg alloys containing up to 3% misch metal and 1% Zr are component of some parts in jet engines because they have significant high strength and creep resistance at 230–316 °C. Misch metal is also an excellent scavenger for oxygen or sulphur in many metal systems .Finally misch metals coupled with yttrium have been found to exhibit a remarkable nodulizing effect upon graphite and thus enhance them malleability of cast iron.

3.1.2 Application in ceramic industries

Cerium (IV) oxide (> 40 %CeO_2)and other oxide mixtures are highly efficient glass with good polishing composition. Neodymium and praseodymium oxides are colouring agents for glass and are useful in the production of standard filters. Lanthanum oxide is used in the preparation of low dispersion, high refraction optical glass. Cerium (IV) oxide is used to improve the stability and discoloration resistance of glass to gamma or electron beam radiations. Cerium (IV) and neodymium oxides are used to counteract the iron (II) compounds that produce green coloration in glasses. 3 % praseodymium oxide in combination with zirconium (IV) oxide is used to give a yellow ceramic glaze and thus opacity enamels. The high melting points of most lanthanides oxides , sulphides(e.g. CeS) , borides , carbides , and nitrides present them for refractories application, although some of these are reactive at high temperatures . Lanthanoids are also used as UVabsorbers and antibrowning agents. They are also use as additives to structural ceramics such as stabilized zirconia and silicon nitride Si_3N_4 , and in optical lenses and glasses . CeO_2(about 47 %) is used in the manufacture of protective transparent glass block. The mixture of CeO_2(47%) ,La_2O_3+Nd_2O_3+ Pr_2O_3(51%) + SiO_2 , Coo , Fe_2O_3 is called **polirite**. Polirite is an abrasive for polishing glasses.

3.1.3 Catalytic applications

Lanthanoid compounds are good catalysts for several reactions including hydrogenation, dehydrogenation, refining of crude oil and oxidation of various organic compounds . Addition of 1 to 5% lanthanoid chloride to a zeolite catalyst increases the catalysts cracking efficiency . They are also included in catalytic converters in automobiles where they stabilise the gamma - alumina support and enhance the oxidation of pollutants. The anhydrous lanthanoid chlorides are used in polyesterification processes while the chlorides and cerium phosphate are useful in petroleum cracking. Heterogeneous catalytic potentials of lanthanoids is linked to unpaired electrons ,paramagnetism , defect structures , or variability in oxidation state.

3.1.4 Magnetic and electronic applications

Lanthanoids are known for their strong para and ferro magnetic properties. The low electrical and eddy current losses of the ferromagnetic garnets, $3Ln_2O_3.5Fe_2O_3$, enhances their usefulness in microwave devices and as magnetic core materials. Certain compounds, e.g. , selenides, tellurides have potential needs as semiconductors or thermoelectrics . The titanates and stannates are useful ceramic capacitors because of their high dielectric constants and low temperature coefficients of capacitance .

3.1.5 Nuclear applications

These include actual and potential uses of high cross-section metals or compounds mainly in control, shielding and flux-suppressing devices. Their oxides are used as diluents in nuclear fuels. Metals are also used for making structural compounds of the reactor. For example, yttrium pipes are used because they are not attacked by molten U even at 1000°C. Tm and Eu are used as radiationsources. Pr is used in the production of atomic batteries. Thorium is a potential atomic fuel source.

3.1.6 Metallurgical applications :Lanthanides are good reducing agents in metallurgical operations . About 30% of lanthanoids are used in metallurgy as an alloying agent to desulphurise steels, as a nodularising agent in ductile iron , as lighter flints and as alloying agents to improve the properties of super alloys and magnesium , aluminium and titanium alloys . CeS is used in the manufacture of special crucibles which can withstand temperatures up to 1800 °C.

3.1.7 Lanthanide complexes in medical analysis and diagnosis

A new emissive lanthanide metal complexes has led to, the development of associated optical equipment and knowledge dissemination based on lanthanide chemistry. Luminescent lanthanide complexes have been commercialised for drug-screening assays in France and in United State of America. The responsive probes have been developed to measure bicarbonate, citrate, lactate and urate in bio-fluids using ratiometric analysis of metal-based emission; and clinical studies are underway assessing the use of citrate as a metabolic marker for prostate cancer.

3.1.8 Miscellaneous applications

Cerium salts are used for increasing hemoglobin content of blood and for the treatment of vomitting and sea-sickness .Lanthanoid compounds are filled into carbon electrodes to give brilliant light .La , Ce , Eu and Sm salts are used in lumino phores as activators and in the coatings of luminescent lamps . Salicylates of Pr, Nd are known as dimals and are useful as germicides . Lanthanoid compounds are used as insecticides, fungicides and as trace elements in fertilizers . Ce $(SO_4)_2$ serves as an oxidizing agent in volumetric titrations. Also, some cerium salts are used indyeing cotton and lead accumulators. Ce$(NO_3)_4$functions as a mordant for alizarin dyes. Radioisotopes of lanthanides such as^{140}La, ^{142}Ce,^{152}Eu and^{160}Tbare used in co-precipitation and chromatographic separation .Major applications (including special properties) of the different lanthanoids and yttrium scandium and thorium are listed in Table 8

Table 8: Applications of lanthanoids

Elements	Remarkable property	Application
Lanthanum	Component of misch metal	Ceramic glazes, high quality optical glass, camera lenses, microwave crystals, ceramic capacitors, glass polishing, petroleum cracking.
Cerium	Most abundant amongst the lanthanides. Major component of misch metal	Glass polishing, petroleum cracking catalysts, alloys – with iron for sparking flints for lighters, with aluminium, magnesium and steel for improving heat and strength properties, radiation shielding, many others.
Praseodymium		Yellow ceramic pigments, tiles, ceramic capacitors. With neodymium in combination for goggles to shield glass makers against sodium glare, Permanent magnets.

		Cryogenic refrigerant
Neodymium	Important in magnetic alloys.	Ceramic capacitors, glazes and coloured glass, lasers, high strength permanent magnets as neodymium iron-boron alloy, petroleum cracking catalysts
Promethium	Not found in nature. Radioactive; produced only in nuclear reactors.	Radioactive promethium in batteries to power watches, guided missile instruments, etc, in harsh environments.
Samarium	Important in magnetic alloys	In highly magnetic alloys for permanent magnet as Samarium Cobalt alloy; probably will be superseded by neodymium. Glass lasers. Reactor control and neutron shielding
Europium	One of rarest, and most rare reactive of rare earths. Absorbs neutrons	Control rods in nuclear reactors. Coloured lamps, cathode ray tubes. Red phosphor in colour television tubes.
Gadolinium		Solid state lasers, constituent of computer memory chips, high temperature refractories, cryogenic refrigerants.
Terbium	Associated with gadolinium	Cathode ray tubes, magnets, optical computer memories; future hard disk components; magnetostrictive alloys
Dysprosium	Absorbs neutrons. Magnetic alloy.	Controls nuclear reactors. Alloyed with neodymium for permanent magnets. Catalysts.
Holmium	Absorbs neutrons.	Controls nuclear reactors; catalysts; refractories.
Erbium	Physical properties almost identical with holmium and Dysprosium	In ceramics to produce a pink glaze; infra-red absorbing glasses.
Thulium	Gives x-rays on irradiation in Nuclear reactor	X-ray source in portable X-ray machines.
Ytterbium	Properties very similar to Lutetium- not well known	Practical values presently unknown. Research.
Lutetium	Chemical and physical propertiesnot well known.	Deoxidiser in stainless steel production, rechargeable batteries, medical uses, red phosphors for colour television, superconductors.
Yttrium	Associated with Holmium, Erbium. Cold or hot forged	Deoxidiser in stainless steel production, rechargeable batteries, medical uses, red phosphors for colour television, superconductors.
Scandium	Close to Aluminium in chemical and physical properties	X-ray tubes, catalysts for polymerization, hardened Ni-Cr super alloys, dental porcelain.
Thorium	Resembles nickel, as soft and as plentiful as lead. Radioactive	Gas mantles. Can be used as nuclear fuel in place of uranium.

3.2 Application of actinides

Even though hazards are associated with radioactivity of actinides, many beneficial applications exist as well. Radioactive nuclides are used in cancer therapy, analytical chemistry, and in basic research in the study of chemical structures and mechanisms. The explosive power of uranium and plutonium are well exploited in making atomic bombs. The uranium enriched atomic bomb that exploded over Japan was the first uranium bomb released. Nuclear reactions of uranium-235 and plutonium-239 are currently utilized in atomic energy power plants to generate electric power. Thorium is economically useful for the reason that fissionable uranium-233 can be produced from thorium-232. Plutonium-238 is used as implants in the human body to power the heart pacemaker, which does not need to be replaced for at least 10 years. Curium-244 and plutonium-238 emit heat at 2.9 watts and 0.57 watts per gram, respectively. Therefore, curium and plutonium are used as power sources on the moon to provide electrical energy for transmitting messages to earth.

Specific applications of actinides are summarized below

i. Uranium-238 is the most abundant isotope of this element and has an unusually long half-life. The half-life of uranium-238 is so long that half of the uranium that exists today has been around since the birth of our planet roughly 4.5 billion years ago. Uranium-235 is fissionable, meaning the atoms can be split apart when bombarded by neutrons. This capability allows it to be used in power plants to generate energy and in the creation of nuclear weaponry.
ii. Thorium is one of the most abundant actinides. Most thorium mined from the earth crust is used in the production of gas mantles. Its high melting and boiling points make thorium an ideal insulator. It melts at 3,100F and boils at 8,100F.
iii. Plutonium is another actinide that is used in the production of nuclear weapons and can be a source of power for nuclear plants. It has also been used to power spacecraft, as the energy source for a radioisotope thermoelectric generator. Interestingly, the rover that is currently exploring Mars, has one of these generators and uses roughly 4.8 kilograms of plutonium-238 as its primary power source. Plutonium was even used in heart pacemakers for decades because it enabled the pacemaker battery to last longer.
iv. Californium is useful for creating neutrons. In a detection device, this can be used to identify gold or silver on the spot without having to send samples to a lab. There are also found in smoke detectors and moisture gauges.
v. Curium, named after Marie Curie and her husband Pierre, is primarily used for scientific research but it has some emerging uses as well. It produces more energy than plutonium, enabling it to be used as a power source for spacecraft and in medicine.

vi. Americium is another element that is under consideration for use as spacecraft fuel. It's also a component in smoke detectors. One isotope, americium-241, is used in brachytherapy, a treatment for cancer.

vii. The majority of the other actinides on this list are used solely for research purposes. Scientists must create them in the laboratories, and many have only been produced a couple of atoms at a time. This allows scientists to observe them but makes them essentially useless for anything other than lab work and research.

Shiokawa *et al*. (2000) found that the electrochemical properties of U, Np and Pu offers unique background for their utilization as active materials of the redox flow battery for electric power storage. A new neptunium redox battery was designed and the galvanic cell was expressed as,

$$(-)Np^{3+},Np^{3+} \square NpO_2^{2+} \square (+).$$

The neptunium battery exhibited more excellent charge and discharge performance than the current vanadium of a uranium redox flow battery.

3.0 Summary

Lanthanides and actinides have numerous applications as discussed in this unit. The metals have unique properties that convey suitability for applications in areas where other metals may not be relevant. Their variable oxidation state, refractory properties and other factors such as radioactive nature of actinides provide strong background for their applications.

4.0 Conclusion

Although several applications of lanthanides and actinides metals have been highlighted. It is significant to state that researches are on-going for future applications these unique elements can provide.

5.0 Tutor marked assignment

1. Highlight one common application that lanthanide and actinide can offer
2. What are the application areas the variable oxidation states of lanthanides and actinides will be of advantage.
3. What advantage can the electrochemical properties of U, Np and Pu offers in industries.
4. State the applications of lanthanides and actinides in the medical industries.

5. Why is actinides elements better than lanthanide elements in nuclear power generation.

7.0 References

Petrucci, Hardwood, Herring. "General Chemistry: Principles & Modern Applications". New Jersey: Macmillan Publishing Company, 2007.

Moeller, Therald. The Chemistry of the lanthanides. New York: Reinhold Publishing Corporation, 1963.

Cotton, Simon. Lanthanides and Actinides. London: Macmillan Education Ltd, 1991.

Deacon, G. B., Tuong,, T. D., Wilkinson, D. L. and Marks, T. (2007). Lanthanide trichloride by reaction of lanthanide metal with mercury (II) chloride in tetrahydrofuran. Edited by Angelicci, R. A. Wiley, USA.

Theodore, G. (2009). The Elements: A Visual Exploration of Every Known Atom in the Universe. New York: Black Dog & Leventhal Publishers.

Holden, N.E and Coplen, T. (2004). The periodic Table of the elements..Chemistry International.IUPAC.26 (1): 8-18.

Actinides - Uses Of Actinides - Uranium, Plutonium, Power, and Thorium - JRank Articleshttp://science.jrank.org/pages/58/Actinides-Uses-actinides.html#ixzz5Jhu5vJtq

Shiokawa, Y., Yamana, H. and Moriyama, H. (2000).An application of actinide elements for a redox flow battery. Journal of Nuclear Science and Technology 37(3): 253-256.

MODULE 3

UNIT 2: Comparative chemistry of lanthanides and actinides

1.0 Introduction

Lanthanides and actinides show some similarities. However, some differences also exist between the two elements due to differences in occupation of 4f and 5f orbitals. Most of the phenomenon observed among lanthanides may not be observed in actinides. If observed, the magnitude of observation may not be exactly similar. This section compares the chemistry and properties of lanthanides with that of actinides. The chemistry of lanthanides is also compared with those of scandium and yttrium

2.0 Objectives

The objectives of this section shall include

i. **Understanding the differences between lanthanides and yttrium**
ii. **Understanding the similarities between lanthanides and scandium**
iii. **Understanding the differences and similarities between lanthanides and actinides**

3.0 Main content

3.1 Lanthanides and yttrium

It is indicative that yttrium and scandium can be considered with lanthanoids because of the similarities in their physical and chemical properties .Yttrium is similar to the lanthanoids in following respects :

i. Y occurs with lanthanoids in rare earth minerals , e.g. Monazite

ii. The radius of trivalent yttrium is comparable to that of $Ho^{3+}$and thus displays some similarity to Ho^{3+}

iii. Y occurs exclusively in + 3 oxidation state. As stated before, the most stable oxidation state of Ln is also +3

iv. YH_2 is better known to exist as $Y^{3+}(H^{-})_2(e^{-})$, similar to $Ln^{3+}(H^{-})_2(e^{-})$.

3.2 Lanthanides and scandium

Also, similarities between scandium and lanthanoids are

i. Sc occurs exclusively in +3 oxidation state in that compounds such as Sc_2O_3 , $ScX_3$are well known ;

ii. Sc forms conducting hydride ScH_2 ,which can also be written as $Sc^{3+}(H^{-})_2(e-)$. This hydride is comparable to $Y^{3+}(H^{-})_2(e^{-})$ and $Ln^{3+}(H^{-})_2(e^{-})$.

iii. Sc forms reduced halides of the type Sc_7Cl_{12} , which is $Sc^{3+}$with Sc_6 clusters .

iv. Sc forms complexes of high coordination number with chelating O – donors e.g. $Na^{+}[Sc(CF_3COCHCOCF_3)]_4$ with coordination number 8 .

v. Most scandium compounds are obtained as hydrated salts e.g. $Sc(NO_3)_3.4H_2O$ and $Sc_2(SO_4)_3.5H_2O$.

vi. Scandium forms organometallic compounds such as $Sc(C_5H_5)_3$.

However , there are sufficient evidence that justify the placement of scandium as a 13 group element , with aluminium . The metal seems to possess properties that are intermediate between the lanthanoids and aluminium . Hence some of the differences between Sc and Ln are

i. Sc^{3+}(r = 74 pm) is appreciably smaller than any of the Ln^{3+}.

ii. $Sc_2O_3$is amphoteric like Al_2O_3unlike Ln_2O_3.

iii. ScF_3dissolves in excess $F^{-}$to give ScF_6^{3-}, unlike Lanthanoids ,which shows scarcity of halogen compounds .

iv. Anhydrous $ScCl_3$is easily obtained by dehydration of respective hydrated halide with P_2O_5.However , $AlCl_3$ is a Friedel-Craft catalyst but $ScCl_3$ is not .

Scandium also shows some similarities with the first row transition metals .For example, both 3d metals and Scandium have the tendency to form complexes with coordination number of 6 and its aqua ion ,$[Sc(H_2O)_6]^{3+}$is susceptible to hydrolysis .

Finally, the lanthanoids show some similarities and dissimilarities with the transition elements and also with actinoides . These are summarized in the Table 9.

3.3 Lanthanides and actinides

Lanthanides and actinides belong to the f block of the modern periodic table. They have both similarities and dissimilarities between them as highlighted below,

Table 9: Comparism of some properties of Ln, pre-transition and transition metals

Property	Pre-Transition Metals	Lanthanoids	Transition Metals
Valence	Essentially Monovalent Show Group(n+) oxidation state	Essentially Monovalent(+3) is characteristic oxidation state +2/+4 for certain configurations	Show Variable Valence (extensive redox chemistry) control by environment ~ ligands, pH etc…
Periodic trends	Dominated by effective nuclear charge	Dominated by Lanthanide Contraction of Ln^{3+}	Size changes are less marked
Occurrence	Widespread on earth	Common mineralogy	Diverse mineralogy
Ligand field effect	No effects	Insignificant effects	Substantial effects
Nature	Always 'hard' (prefer O, Hl, N donors)	Always 'hard' (prefer O, Hal, N donors)	Later(increasingly from Fe)/heavier metals may show a 'soft' side
Nature of organometallics	'Ionic & 'Covalent' Organometallics	'Ionic' organometallics	'Covalent' Organometallics
Coordination number	Poor Coordination Properties (C.N. determined by size)	High Coordination Numbers – 6,7,8,9 (C.N. determined by size)	Extensive Coordination C.N. = 4 and 6 are typical maximum (but many exceptions)
Geometry	Flexibility in Geometry	Flexibility in Geometry	Fixed(by Ligand Field effects)Geometries
Magnetism	No Magnetism from the metal ions due to noble gas configurations of ions	Free Ion ground state magnetism	Orbital Magnetism 'Quenched' by Ligand Fields Excited J-states poulated
Spectra/ Properties	'Ionic' compound formulations large HOMO-LUMO gaps UV spectra	Weak, Narrow Optical Spectra Forbidden, unfacilitated transitions	Stronger, Broader Optical Spectra Forbidden transitions vibronically-assisted

3.4 Similarities between lanthanides and actinides

The lanthanide and actinides elements are characterized by filling of (n-2) f subshell. They possess almost similar outermost electronic configuration hence have some similar properties such as

i. They both have a prominent oxidation state of +3.

ii. They are involved in the filling of (n-2) f orbitals.
iii. They are highly electropositive and very reactive in nature.
iv. With an increase in atomic number, there is a decrease in atomic and ionic size.
v. Both show magnetic properties.

3.5 Differences between lanthanides and actinides

Lanthanoids are involved in the filling of 4f- orbitals whereas actinoids are involved in the filling of 5f-orbitals. The binding energy of 4f electrons is comparatively less than that of 5f-electrons. The shielding effect of 5f-electrons is less effective as compared to that of 4f-electrons. The paramagnetic properties of lanthanoids can be easily explained but this explanation is difficult in case of actinoids. Lanthanides are non-radioactive in nature except promethium whereas all actinide series elements are radioactive. Lanthanides do not have a tendency to form oxocations, but several oxocations of actinide series exist. The compounds formed by lanthanides are less basic on the other hand the compounds of actinides are highly basic. Other basic properties of lanthanides and actinides are presented in Table 10.

Table 10 : Comparison between lanthanoids and actinoids

Property	Lanthanoids	Actinoids
Valence shell configuration	Filling of the 4f subshell	5f subshell
Characteristic oxidation state	+3, +2 and +4 are known but rare	+3oxidation state is not the most stable one for most of them. Oxidation state as high as +7 are also possible in early actinoids
Contraction	Lanthanoid curve consists of two very shallow arcs with a discontinuity at spherically Gd^{+3}	Actinoid contraction initially parallels to that of lanthanides, the elements from curium are smaller than expected
Nature of f orbital	4f orbital are sufficiently low in energy that the electrons are seldom ionized or shared. They are unaffected by the environment to a great extent	5f orbitals have a radial node, which 4forbital lack. 5f electrons are available in the early actinides
Ligand-metal interaction	Less	More
Absorption spectra	Spectra are sharp and line-like	$Am^{3+}$and heavier actinides have spectra resembling Ln^{3+}but Pm^{3+}andlighter actinoids have broader spectra
Magnetic properties	Spin-orbit coupling is large but ligand field effects are small.	Spin-orbit coupling and ligand field effects are of comparable magnitude
Coordination chemistry	Show high coordination	Show high coordination

4.0 Summary

Lanthanides and actinides both show close resemblance because these involve filling of f-subshells. Both have coloured ions, low electronegativity, high re-activity and show magnetic properties. However, these also differ from each other as shown in the following ways.

In lanthanides, the binding energies of 4f electrons are higher than those of actinides. Maximum oxidation state exhibited by lanthanides is +4 whereas in actinides due to lower binding energies they show higher oxidation states such as +4, +5 and +6 in UF_6 and UO_2Cl_2. The 4f electrons in lanthanide has a greater shielding effect than the 5f electrons in actinides. Although both are paramagnetic, the magnetic properties of actinides are completed and difficult to explain. Lanthanides do not form complexes easily while actinides have greater tendency to form complexes. Most lanthanide ions are colourless unlike actinides. Basicity of actinides far surpasses that of the lanthanides. Unlike lanthanides, actinides form oxoacids such as UO_2^{2+}, UO^{+}, NpO_2^{+}, PuO^{2+}.

5.0 Conclusions

The lanthanide and actinide form large families of iso-structural compounds of great interest for significant researches in solid state chemistry and physics. Their compounds allow a systematic and comparative study of the physical properties among the three series of elements. By means of solid solutions material with a continuous and progressive variation of the number of f electrons of chemical pressure and of interatomic distance are obtained. Successful understanding of the chemistry of both group of metals have enabled the discovery of new compounds (with behaviors like complex magnetic structures) and in application of the metals to improve standard of living.

6.0 Tutor marked assignment

1. What is the difference between lanthanide contraction and actinide contraction?
2. Justify the position of lanthanide and scandium in the periodic table.
3. State two similarities and two differences between scandium and lanthanides

4. State two similarities and two differences between lanthanides and actinides

8.0 **References**

Petrucci, Hardwood, Herring. "General Chemistry: Principles & Modern Applications". New Jersey: Macmillan Publishing Company, 2007.

Moeller, Therald. The Chemistry of the lanthanides. New York: Reinhold Publishing Corporation, 1963.

Cotton, Simon. Lanthanides and Actinides. London: Macmillan Education Ltd, 1991.

Deacon, G. B., Tuong,, T. D., Wilkinson, D. L. and Marks, T. (2007). Lanthanide trichloride by reaction of lanthanide metal with mercury (II) chloride in tetrahydrofuran. Edited by Angelicci, R. A. Wiley, USA.

Theodore, G. (2009). The Elements: A Visual Exploration of Every Known Atom in the Universe. New York: Black Dog & Leventhal Publishers.

Holden, N.E and Coplen, T. (2004). The periodic Table of the elements..Chemistry International.IUPAC.26 (1): 8-18.

Actinides - Uses Of Actinides - Uranium, Plutonium, Power, and Thorium - JRank Articleshttp://science.jrank.org/pages/58/Actinides-Uses-actinides.html#ixzz5Jhu5vJtq

Shiokawa, Y., Yamana, H. and Moriyama, H. (2000).An application of actinide elements for a redox flow battery. Journal of Nuclear Science and Technology 37(3): 253-256.