

LECTURE NOTES

ON

CHM 104: Introduction to Inorganic Chemistry

DEPARTMENT OF CHEMISTRY,

UNIVERSITY OF AGRICULTURE, ABEOKUTA(UNAAB)

Topics:

1. **IVA (CARBON GROUP) ELEMENTS**
2. **NUCLEAR CHEMISTRY**
3. **INTRODUCTION TO TRANSITION METALS**

LECTURER

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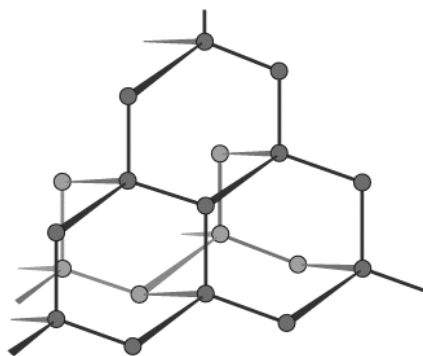
IVA (CARBON GROUP) ELEMENTS

Occurrence and Uses of Group IVA Elements.

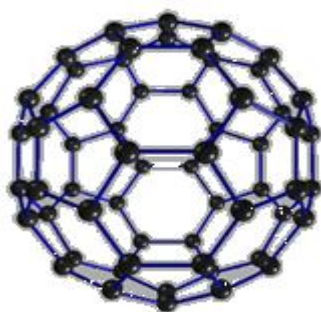
Element	Occurrence	Uses
Carbon	<p>Carbon occurs as crystalline allotropes (diamond and graphite) and molecular allotrope (fullerenes).</p> <p>Diamond occurs naturally in igneous rocks which can be found in South Africa.</p> <p>Graphite occurs naturally in many areas eg. Republic of Korea, Austria, China, Mexico, Madagascar, Germany, Sri Lanka, and Russia.</p> <p>Fullerenes occur naturally in a number of deposits in Australia, New Zealand and North America.</p> <p>Carbon also exists as carbon (IV) oxide (CO_2) at 0.04% of the earth's atmosphere.</p>	<p>Diamond is used as gemstones, cutting tools, abrasives etc</p> <p>Graphite is used as a lubricant. It is exploited commercially for its inertness, high thermal stability, electrical and thermal conductivities.</p> <p>Fullerenes are applied in nanoscience and nanotechnology.</p>
Silicon	Elemental Si does not exist naturally but constitutes 25.7% of the earth's crust in the form of sand, quartz etc	Si is utilized in steel industries, electronic and semiconductor industries. It is also used as the main component of glass in the form of silica(SiO_2)
Germanium	Ge constitutes 1.8ppm of the earth's crust	Used as polymerization catalysts for the production of polyethylene; fibre optics, optical devices (GeO_2), electronic and solar electrical industries.
Tin	Sn occurs naturally as the ore cassiterite (SnO_2)	Used for tin plating for example in steel cans to improve corrosion resistance. Also used as alloys eg bronze.
Lead	Pb occurs naturally as the ore: galena(PbO), anglesite(PbSO_4) and cerussite (PbCO_3)	Lead was used in plumbing industry plant; as Lead acid batteries. Lead oxides are used in the making of lead crystal glass

Allotropes of Carbon

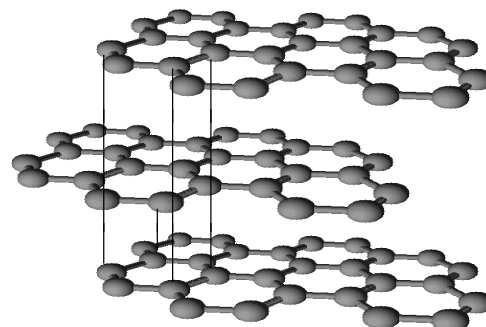
Examples of allotropes of Pure carbon Diamond Graphite and Fullerenes. They occur naturally.



The crystal structure of diamond.



The structure of C_{60} Fullerenes



A view of the planes of atoms in the structure of graphite.

Summary of the Characteristics of Allotropes of Carbon

Characteristics	Diamond	Graphite
Density	3.5gcm ⁻³	2.3gcm ⁻³ -less dense than diamond because its structure is less compact.
Structure	A three dimensional array of carbon atoms, each atom surrounded tetrahedrally by four other carbons. Each diamond crystal is a giant molecule containing very strong bonds.The structure is highly rigid.	A two dimensional array of carbon atoms, each atom surrounded by three other carbons in the same plane and the bonding is covalent. The sheet of carbon atoms are arranged in regular hexagon and are held by weak van der Waal's forces.
Hardness	Hardest naturally occurring substance	Very soft and slippery because the weak forces holding the individual sheets together are easily broken, the sheets are easily moved relative to one another.
Electrical	Does not conduct electricity	Graphite conducts electricity. Since each carbon atoms is surrounded by three other carbons, thus alternate single and double bonds must be present to complete the octet of each carbon atom. The presence of the double bonds means that mobile electrons are present and these can readily be transferred from one hexagon to another by the application of an electric field.

SOME PHYSICAL AND CHEMICAL PARAMETERS OF GROUP IV ELEMENTS

Element	Carbon C	Silicon Si	Germanium Ge	Tin Sn	Lead Pb
Atomic No	6	14	32	50	82
Electronic Configuration	$1s^2 2s^2 2p^2$	$[Ne] 3s^2 3p^2$	$[Ar] 4s^2 4p^2$	$[Kr] 5s^2 5p^2$	$[Xe] 4f^{14} 5d^{10} 6s^2 6p^2$
Atomic radii (nm)	0.077	0.117	0.122	0.140	0.154
Melting point ^o C	3730 ^d	1410	937	232	327
Boiling point ^o C	4830 ^d	2360	2830	2270	1744
Conductivity	Fairly good ^{gr} Non-cond. ^d	Semi-cond	Semi-cond	Good	Good
First ionization energy/kJ mol ⁻¹	1086	787	760	707	715
Type of Structure	Giant molecule	Giant molecule similar to diamond	Giant molecule similar to diamond	Giant metallic	Giant metallic

gr-graphite

d-diamond

Some physical properties of Group IV elements

The similarity between elements in the same family which was obvious in Group I and II are less apparent in Group IV elements. The varying properties are due to their increasing metallic character and decreasing non-metallic properties as atomic number increases.'

Carbon and silicon are non-metallic. Germanium has both metallic and non-metallic properties (metalloid). Tin and lead are definitely metallic.

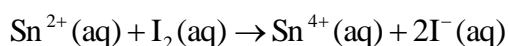
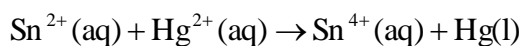
The structure changes from giant molecular lattices in carbon and silicon to giant metallic structure in tin and lead. Si and Ge crystallize in the same structure as diamond. Sn and Pb have distorted close-packed metal structures. As the atomic size increases, the interatomic bonding becomes weaker, as a result, the attraction of neighbouring nuclei for intervening electrons reduces which results in a change in bonding from covalent to metallic down the group.

This results in decrease in melting point, boiling point and ionization energy. At the same time, the increasing metallic character causes a general increase in density and conductivity. Also the first Ionization energy decrease greatly between carbon and silicon but decreases very little for the other elements. The reason for this is that after silicon, there is a larger increase in nuclear charge due to the filling of 'd' and 'f' orbital which counterbalances the increase in atomic radii.

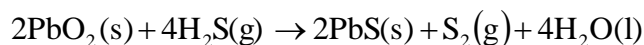
Valency

They exhibit a valency of two and four. Since the energy required to remove four electrons is very high, they form compounds that are predominantly covalent. Also the gain of four electrons is energetically impossible. In carbon and silicon compounds, the 4-valent states are very stable relative to 2-valent state. The 2-valent state is rare and easily oxidised to 4-valent state. Thus, CO reacts very exothermically to form CO₂. SiO₂ is too unstable to exist under normal conditions, although it is obtained at 2000°C. Germanium forms oxides in both 2-valent and 4-valent state. However, GeO₂ is rather more stable than GeO. GeO₂ does not act as an oxidising agent and GeO is readily converted to GeO₂.

The compounds of Sn and Pb are often predominantly ionic. In tin compounds, the 4-valent states are slightly more stable than the 2-valent state, thus their aqueous solutions are mild reducing agents which can convert Hg²⁺ ions to Hg and iodine (I₂) to iodide(I⁻).



For lead compounds, 2-valent state is the most predominant. PbO_2 is a strong oxidising agent, while PbO is relatively stable. PbO_2 can readily oxidise hydrochloric to chlorine and hydrogen sulphide to sulphur.



Ge, Sn and Pb form 2-valent compounds in which the two s electrons are inert (inert pair effect- because, as each of the two electrons is removed from p orbital, the remainder in the s-orbital are held more strongly by the increased positive charge-in the s orbital) and the stability increases from Ge to Pb. The greater stability is well illustrated by the standard electrode potentials of the $\text{M}^{4+}(\text{aq})/\text{M}^{2+}(\text{aq})$ for germanium, tin and lead.(see table 1).

Some Simple compounds of Group IV elements

All members form simple binary compound with hydrogen, oxygen, the halogens and nitrogen. Carbon and silicon also form carbides(binary compounds of carbon with metals and metalloids) and silicides(silicon-metal compounds).

Hydrides

They all form tetravalent hydrides XH_4 . In addition, carbon and silicon form series of catenated molecular hydrides. **CATENATION** is a unique ability of this group in which they form stable compounds containing long chains and rings of atoms.

Hydrocarbons:

Catenation has led to the formation of numerous carbon compounds like the alkanes, alkenes and alkynes. This ability of carbon to catenate results from the fact that the C-C bond is almost as strong as the C-O bond [$\text{C-C}=346\text{kJmol}^{-1}$, $\text{C-O}=360\text{kJmol}^{-1}$]. This makes the oxidation of the carbon compounds to such products as carbon dioxide and water less energetically favorable than silicon.

Silanes:

Silicon hydrides called silanes have been synthesized, some with up to 11 silicon atoms linked together. Si-Si bond is much weaker than Si-O bond [$\text{Si-Si}=226\text{kJmol}^{-1}$, $\text{Si-O}=464\text{kJmol}^{-1}$], therefore catenated compounds of silicon are energetically unstable with respect to SiO_2 and does not occur naturally. The silanes are more reactive than alkanes and their stability decreases with increasing chain length. This increased reactivity compared to hydrocarbons is attributed to the large atomic radius of silicon which leaves it open to attack by nucleophiles.

Silane SiH_4 , is spontaneously flammable in air, reacts violently with halogens and is hydrolysed on contact with water. Silane is also a reducing agent and can reduce Fe^{3+} to Fe^{2+} .

Germane, Stannane And Plumbane:

Also three hydrides of Ge have been synthesized (e.g. GeH_4), but only one hydride each for tin and lead (SnH_4 and PbH_4). They hydrides all have a simple molecular structure and are tetrahedral in shape. They have low melting points and boiling points and are all gases at room temperature

Halides

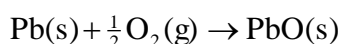
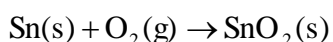
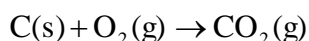
All the elements in this group react directly with halogens to form the tetrahalides, except lead which forms the dihalides. The simplest halocarbons are tetrahalomethanes which vary from the highly stable and volatile CF_4 to the thermally unstable solid Cl_4 .

The tetrahalides have a simple molecular structure and are tetrahedral in shape. They have low melting points and boiling points. All form volatile liquids at room temperature.

NB:The thermal stability of the hydrides and the tetrahalides decreases down the group because the E-H and E-X bonds become weaker and longer.(where E is a group IV element)

Oxide

All members of the group except lead reacts with oxygen on heating to form the dioxide. Lead forms the monoxide, PbO .



Summary of trends as we go down the group from carbon to lead:

1. The elements change from non-metallic to metallic.
2. The 2-valent state becomes more stable relative to 4-valent state.
3. The bonding in compounds changes from covalent to ionic[covalent compounds-eg hydrides and tetrahalide becomes less stable down the group; ionic compounds eg monoxides, become less stable down the group.
4. The nature of the dioxides changes from acidic to amphoteric.
5. The nature of the monoxides changes from neutral to amphoteric.

NUCLEAR CHEMISTRY

Nuclear chemistry investigates the changes that occur in the atomic nucleus.

Nuclear Binding Energy

The mass of a nucleus is slightly less than the sum of the masses of the proton and the neutrons. For example, the helium nucleus contains two protons and two neutrons, therefore the mass of the helium nucleus is 4.0017 atomic mass unit (amu). Whereas the individual masses of the isolated proton and neutron are 1.0073 and 1.0087 amu respectively.

$$\therefore (2 \times 1.0073) + (2 \times 1.0087) = 4.0320 \text{ amu}$$

The difference in mass is 0.0303 amu. This difference in mass is called MASS DEFECT and it is transformed into the BINDING ENERGY. The Binding Energy is defined as the energy required to separate a nucleus into individual nucleons. The Einstein equation corresponds to the release of energy i.e the mass energy relation as shown in the equation, $E = mc^2$.

Where E=energy released (in joules)

m=loss in mass (in Kg)

c=velocity of light ($\approx 3 \times 10^8 \text{ ms}^{-1}$)

NB

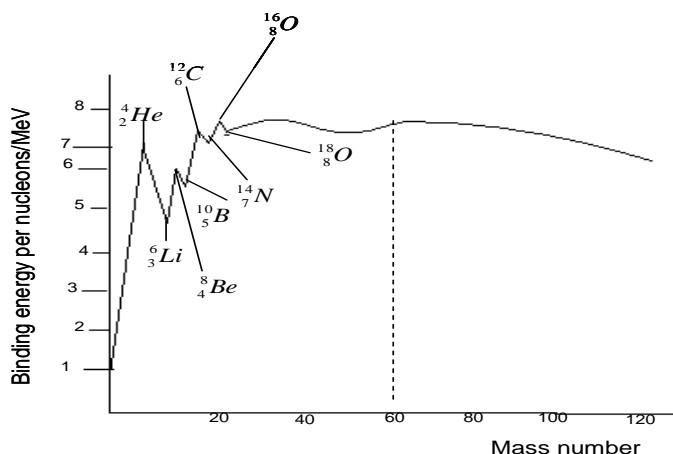
➤ proton + neutron = nucleons

Therefore, mass number = nucleon number

➤ Nuclide= any atomic species where the proton number and nucleon number are specified

Nuclear Stability

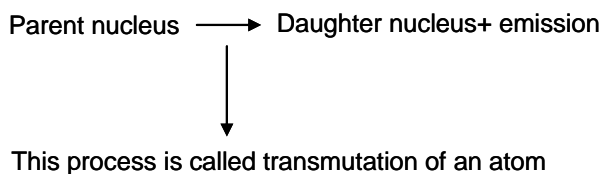
The origin of the forces that are responsible for the nuclear stability is still under study. Nuclear forces acts over incredibly short distances. From the graph, elements with mass number around 60 are most stable. The elements with nuclei heavier than this should be able to split up to form lighter or more stable nuclei with the release of energy (fission). The elements lighter than 60 should be able to combine if the repulsion between nuclear charges can be overcome to form heavier nuclei with the release of energy (fusion).



Radioactivity

Radioactivity is the spontaneous emission of radiation by an element or spontaneous disintegration of nucleus of an atom. Such element is called a Radioactive element. During this disintegration, alpha (α), beta (β) and gamma (γ) rays are emitted.

When an element undergoes radioactivity, it is said to undergo nuclear transformation. Here, the



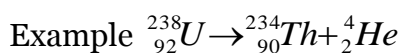
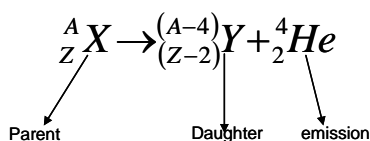
Alpha particles(α)

These are fast moving streams of positively charged nuclei of helium, ${}^4_2\text{He}$.

Properties

1. Has a penetrating power
2. It can be easily absorbed by matter.
3. they exert strong ionizing effect during collision
4. They are positively charged and fairly heavy, hence deflected slightly towards a negative plate in an electrostatic filed.

An element that undergoes α -decay or emits α -radiation has the following equation;



Most of the radioactive elements with atomic number greater than 83 (bismuth) undergoes alpha decay. Examples of the isotopes are radium-226, plutonium-238, polonium-218 and radon-220.

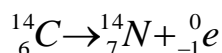
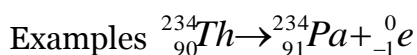
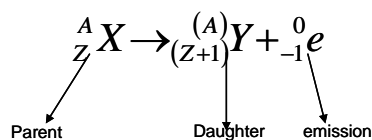
Beta particles (β)

These are very fast moving streams of electrons (${}^0_{-1}e$) which are negatively charged.

Properties

1. It has a relatively small mass.
2. It is markedly deflected towards a positive plate in an electrostatic field.
3. It is more penetrating than α -ray.

When an element undergoes β -decay, it becomes



Elements with atomic number less than 83 do not undergo alpha decay, instead their isotopes emit beta radiation. Examples, carbon-14, strontium-90 and iodine-131.

Gamma particles (γ)

These are electromagnetic waves similar to visible light and x-rays with short wavelength (10^{-12} metres).

Properties

1. It is the most penetrating type of radiation, e.g. it can penetrate several centimeters of lead.
2. It is electrically neutral, therefore not deflected by magnetic or electric field.
3. When an atom emits gamma rays, there is no change in atomic number or mass.
4. It can be diffracted by the lattice of a crystal

Differences between Chemical Reactions and Nuclear Reactions

- During chemical reactions, electrons are redistributed either by transfer from one atom to another or by sharing between atoms. While during a nuclear reaction one element may be converted either by radioactive decay or by atomic fission or fusion.
- Chemical reactions involve only the outer parts of atoms-electrons while nuclear reactions involve the nucleus- the protons and neutrons.
- Energy changes in nuclear reactions are usually greater than those in chemical reactions.

Natural Radioactivity

This is due to uncontrolled and spontaneous disintegration of unstable nuclei which is accompanied by evolution of a large quantity of heat. The decay of a radioactive element is a random process which is not influenced by external factors such as temperature changes.

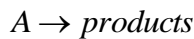
Kinetic Calculation of Half-life

Definition of Half-life:

- ◆ Half-life is a measure of the rate of disintegration of an element.
- ◆ It can be defined as the time taken for half of the total number of atoms in a given sample of the element to decay.

- ◆ It can be defined as the time taken for reaction to undergo half completion.

Following the exponential law, the rate of decay is directly proportional to the number of atoms present. The rate of decay decreases with time. Kinetically, it is a first order reaction;



The equation can be expressed as follows;

$$\text{Rate} = k[N] \quad \text{Hence, } -\frac{dN}{dt} \propto N$$

$$\text{Then, } -\frac{dN}{dt} = kN \text{-----eqn 1}$$

Where N = number of radioactive atoms present, t=time, k= First order rate constant.

$$\text{Eqn 1 can be rearranged as follows; } \quad -\frac{dN}{N} = kdt$$

The integrated form of eqn 1 can be written as

$$\ln N - \ln N_0 = -kt \quad \text{-----eqn 2}$$

$$\ln = \text{Log}_e$$

Where N= number of nuclides at time t

N_0 = number of nuclides present at time $t=0$

$$\text{On rearrangement, this becomes, } \ln\left(\frac{N_0}{N}\right) = kt \text{ or } \frac{N}{N_0} = e^{-kt} \text{ eqn 4}$$

From Napierian log to ordinary log, which is $\ln = 2.303\text{Log}_{10}$. Therefore eqn 4 becomes

$$2.303\text{Log}_{10}\left(\frac{N_0}{N}\right) = kt \text{---eqn 5}$$

Since $t_{1/2}$ represents the time needed for the original substance to reduce to half which is $N_0=2N$ or $1/2N = N_0$. Therefore eqn 5 becomes;

$$2.303\text{Log}_{10}\left(\frac{2N_0}{N_0}\right) = kt_{1/2}$$

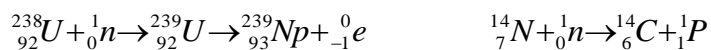
$$0.6932 = kt_{1/2}$$

$$t_{1/2} = \frac{0.6932}{k}$$

K is often represented as λ which is a radioactive decay constant, $t_{1/2} = \frac{0.6932}{\lambda}$.

Artificial Radioactivity

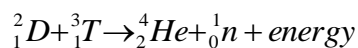
This is carried out by bombarding the various elements with fast moving atomic particles. Examples of fast moving atomic particles are neutrons (very effective, reactive), protons, deuterons and α -particles which yields new elements and energy is released in the process



There are two types of artificial radioactivity;

Nuclear fusion

This is the process whereby two or more light nuclei unite to form a heavier nucleus with the release of energy and radiation. For example is hydrogen fusion bomb;



Thermonuclear reactions are believed to be the source of energy of the sun and stars.

Nuclear fission

This is the process whereby a heavy nucleus is split into 2 or more lighter nuclei with a release of energy and radiation. Eg



Nuclear reactor uses fission reactions to produce energy. The nuclear fission is brought about by bombarding uranium-235 atoms with neutrons traveling at moderate speed. In nuclear reactors, the three neutrons are made to bombard more parent atoms, hence producing more energy and more neutrons establishing a chain reaction.

Nuclear reactors are useful in the synthesis of new elements and in the formation of radioisotopes of common elements.

Applications of Radioactivity/Radioisotopes

- ◆ *Treatment of cancer*; destroys cancerous tissue in preference to healthy tissue
- ◆ *Studying metabolic pathways*: Used to track the path of elements through the body. For example, radioactive iodine-131 given to patient with defective thyroids to enable doctors to follow the iodine path through the body. Its half-life is 8 days.
- ◆ *Sterilization*: Used to sterilize surgical equipments
- ◆ *Thickness gauges and Instruments monitor*: Used to monitor underground leakages in pipes; to measure engine wear; to monitor thickness of metal foil, paper, plastic.
- ◆ *Archeological and geological uses*: used to calculate the age of plants and animal remains. For example carbon -14 radioisotope.
- ◆ *Used in structural analysis*.

INTRODUCTION TO TRANSITION ELEMENT

A transition element is an element with having at least one ion with a partially filled d-subshell. The periodic table is divided into 4 blocks as follows:

s-block-
 p-block-
 d-block-} collectively called the main group elements
 transition elements
 f-block-} lanthanides and actinides

Position in the Periodic Table

The transition elements are in the central block of the periodic table. There are three rows of elements in the central or d-block of the periodic table. Each contains ten metallic elements and corresponds to the filling of d-orbital in these atoms.

Electronic structure of the atoms and ions(1st row only)

Transition Elements	Atomic No.	Electronic Structure of the elements		Electronic Structure of the ions		Electronic Structure of the ions.	
Scandium	21	Sc	[Ar]3d ¹ 4S ²	Sc ³⁺	[Ar]3d ⁰ (NT)	-	-
Titanium	22	Ti	[Ar]3d ² 4S ²	Ti ²⁺	[Ar]3d ²	Ti ³⁺	[Ar]3d ¹
Vanadium	23	V	[Ar]3d ³ 4S ²	V ²⁺	[Ar]3d ³	V ³⁺	[Ar]3d ²
Chromium	24	Cr	[Ar]3d ⁵ 4S ¹	Cr ²⁺	[Ar]3d ⁴	Cr ³⁺	[Ar]3d ³
Manganese	25	Mn	[Ar]3d ⁵ 4S ²	Mn ²⁺	[Ar]3d ⁵	Mn ³⁺	[Ar]3d ⁴
Iron	26	Fe	[Ar]3d ⁶ 4S ²	Fe ²⁺	[Ar]3d ⁶	Fe ³⁺	[Ar]3d ⁵
Cobalt	27	Co	[Ar]3d ⁷ 4S ²	Co ²⁺	[Ar]3d ⁷	Co ³⁺	[Ar]3d ⁶
Nickel	28	Ni	[Ar]3d ⁸ 4S ²	Ni ²⁺	[Ar]3d ⁸	-	-
Copper	29	Cu	[Ar]3d ¹⁰ 4S ¹	Cu ²⁺	[Ar]3d ⁹	Cu ⁺	[Ar]3d ¹⁰ (NT)
Zinc	30	Zn	[Ar]3d ¹⁰ 4S ² (NT)	Zn ²⁺	[Ar]3d ¹⁰ (NT)	-	-

Note: NT means non-transitional

Copper and Chromium have special electronic structure because, when all the five 3d levels are singly filled, a degree of stability is conferred on the atom or ion.

Physical Properties of Transition Metals

1. Hardness: transition metals are harder and stronger than s-block elements. The strength and hardness of the transition metals increases when they form alloys for example, Ti-Fe, Mn-Fe.
2. They have high melting and boiling points.

Explanation: The melting points and hardness depends on the number of electrons per atoms holding the lattice together. The s-blocks are softer and have lower melting and boiling points than that of transition metals or d-blocks because s-block provide only one electron in the outer shell while transition metals contributes both s and d electrons to the electron cloud and form lattices with strong metallic bonding.

3. They also have high densities.
4. They have high electrical conductivity.

Chemical properties of Transition Metals

Across the period, s-blocks and d-blocks have different properties. But for d-blocks, that is the transition series, the extra electron are added to the same inner electron shell (3d). The elements therefore have similar chemical properties across the series.

The main features that differentiates them from the s-block are

1. They have variable oxidation states.
2. They form complex ions.
3. They form coloured compounds.
4. They can act as catalysts.