كيمياء العناصر الانتقالية

لطلاب

الفرقة الثالثة كلية التربية عام

برنامج اللغة

شعبة الكيمياء

٢٠٢٤

القائم بالتدريس:

د. هبه نصار

Inorganic Chemistry

WHAT IS INORGANIC CHEMISTRY?

If organic chemistry is defined as the chemistry of hydrocarbon compounds and their derivatives, inorganic chemistry can be described broadly as the chemistry of "every-thing else." This includes all the remaining elements in the periodic table, as well as carbon, which plays a major role in many inorganic compounds. Organometallic chemistry, a very large and rapidly growing field, bridges both areas by considering compounds containing direct metal-carbon bonds, and includes catalysis of many organic reactions. Bioinorganic chemistry bridges biochemistry and inorganic chemistry, and environmental chemistry includes the study of both inorganic and organic compounds. As can be imagined, the inorganic realm is extremely broad, providing essentially limitless areas for investigation.

A generally-accepted definition of Inorganic Chemistry is the study of non-carbon molecules, or all the elements on the periodic table except carbon. But, this definition is not completely correct because the field of Inorganic Chemistry also includes organometallic compounds and the study of some carbon-based molecules that have properties that are familiar to metals (like conduction of electricity).

This makes the field of inorganic chemistry very broad, and practically limitless.

Inorganic chemistry deals with synthesis and behavior of inorganic and organometallic compounds. This field covers chemical compounds that are not carbon-based, which are the subjects of organic chemistry. The distinction between the two disciplines is far from absolute, as there is much overlap in the sub discipline of organometallic chemistry. It has applications in every aspect of the chemical industry, including catalysis, materials science, pigments, surfactants, coatings, medications, fuels, and agriculture.

Many inorganic compounds are ionic compounds, consisting of cations and anions joined by ionic bonding. Examples of salts (which are ionic compounds) are magnesium chloride $MgCl_2$, which consists of magnesium cations Mg^{2+} and chloride anions Cl^-; or sodium oxide Na_2O, which consists of sodium cations Na^+ and oxide anions O^{2-}. In any salt, the proportions of the ions are such that the electric charges cancel out, so that the bulk compound is electrically neutral. The ions are described by their oxidation state and their ease of formation can be inferred from the ionization potential (for cations) or from the electron affinity (anions) of the parent elements.

Important classes of inorganic compounds are the oxides, the carbonates, the sulfates, and the halides. Many inorganic compounds are characterized by high melting points. Inorganic salts typically are poor conductors in the solid state. Other important features include their high melting point and ease of crystallization. Where some salts (e.g., NaCl) are very soluble in water, others (e.g., FeS) are not.

The simplest inorganic reaction is double displacement when in mixing of two salts the ions are swapped without a change in oxidation state. In redox reactions one reactant, the oxidant, lowers its oxidation state and another reactant, the reductant, has its oxidation state increased. The net result is an exchange of electrons. Electron exchange can occur indirectly as well, e.g., in batteries, a key concept in electrochemistry.

When one reactant contains hydrogen atoms, a reaction can take place by exchanging protons in acid-base chemistry. In a more general definition, any chemical species capable of binding to electron pairs is called a Lewis acid; conversely any molecule that tends to donate an electron pair is referred to as a Lewis base. As a refinement of acid-base interactions, the HSAB theory takes into account polarizability and size of ions.

Industrial inorganic chemistry

Inorganic chemistry is a highly practical area of science. Traditionally, the scale of a nation's economy could be evaluated by their productivity of sulfuric acid. The manufacturing of fertilizers, which often begins with the Haber-Bosch process, is another practical application of industrial inorganic chemistry.

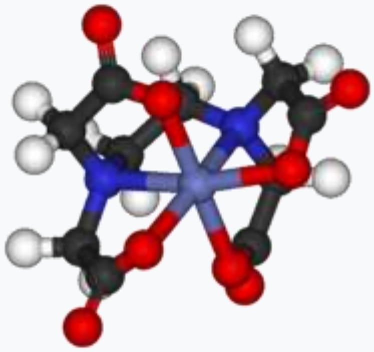
Coordination compounds

Classical coordination compounds feature metals bound to "lone pairs" of electrons residing on the main group atoms of ligands such as H_2O, NH_3, Cl^-, and CN^-. In modern coordination compounds almost all organic and inorganic compounds can be used as ligands. The "metal" usually is a metal from the groups 3-13, as well as the trans-lanthanides and trans-actinides, but from a certain perspective, all chemical compounds can be described as coordination complexes.

The stereochemistry of coordination complexes can be quite rich, as hinted at by Werner's separation of
two enantiomers of $[Co((OH)_2Co(NH_3)_4)_3]^{6+}$, an early
demonstration that

chirality is not inherent to organic compounds. A topical theme within this specialization is supramolecular coordination chemistry.

Examples: $[Co(EDTA)]^-$, $[Co(NH_3)_6]^{3+}$, $TiCl_4(THF)_2$.



EDTA chelates an octahedrally coordinated Co^{3+} ion in $[Co(EDTA)]^-$

Transition metal compounds

Compounds containing metals from group 4 to 11 are considered transition metal compounds. Compounds with a metal from group 3 or 12 are sometimes also incorporated into this group, but also often classified as main group compounds.

Transition metal compounds show a rich coordination chemistry, varying from tetrahedral for titanium (e.g., $TiCl_4$) to square planar for some nickel complexes to octahedral for coordination complexes of cobalt. A range of transition metals can be found in biologically important compounds, such as iron in hemoglobin.

- Examples: iron pentacarbonyl, titanium tetrachloride, cisplatin

Periodicity

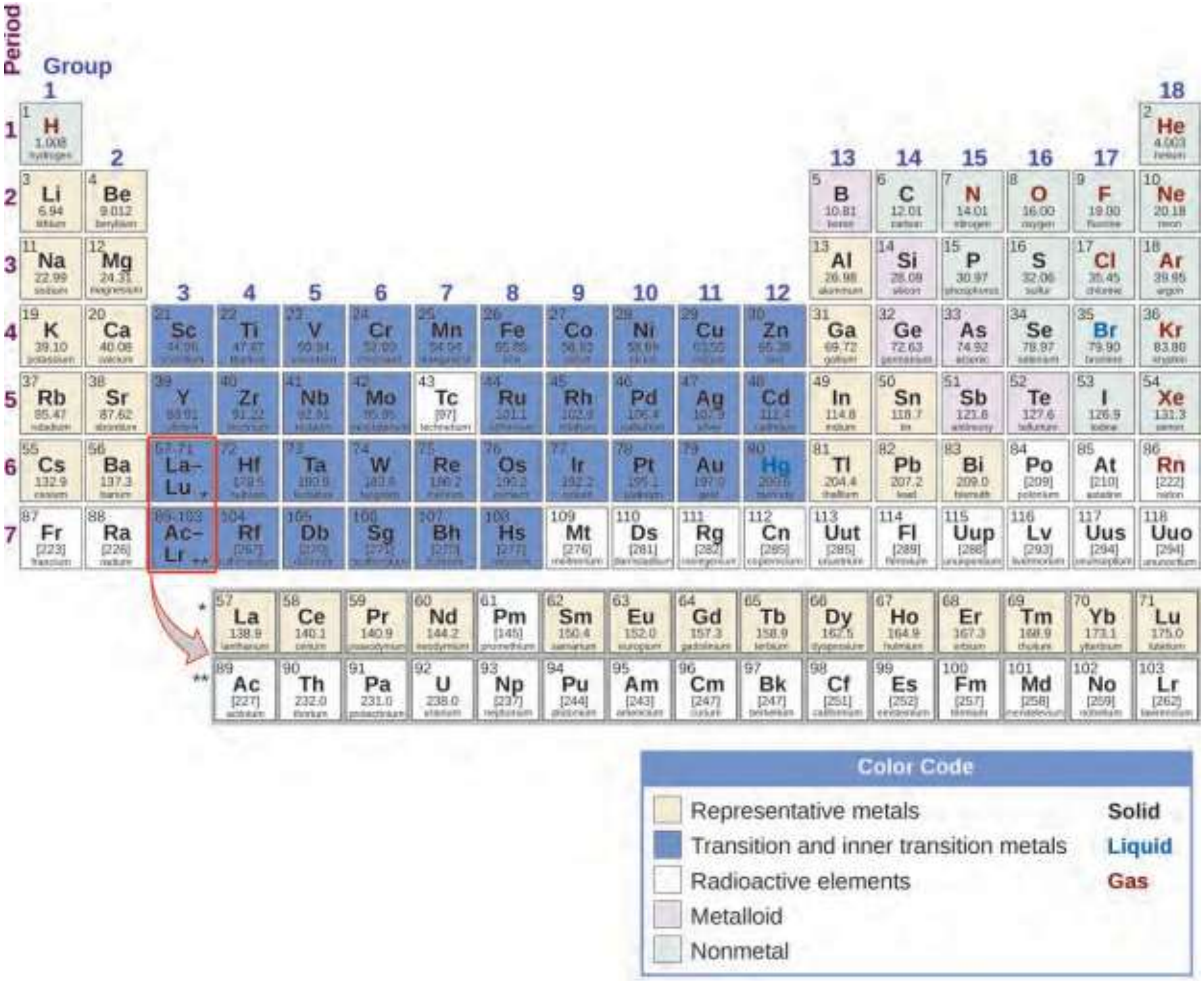
We begin this section by examining the behaviors of representative metals in relation to their positions in the periodic table. The primary focus of this section will be the application of periodicity to the representative metals.

It is possible to divide elements into groups according to their electron configurations. The representative elements are elements where the s and p orbitals are filling. The transition elements are elements where the d orbitals (groups 3–11 on the periodic table) are filling, and the inner transition metals are the elements where the f orbitals are filling. The d orbitals fill with the elements in group 11; therefore, the elements in group 12 qualify as representative elements because the last electron enters an s orbital. Metals among the representative elements are the representative metals. Metallic character results from an element’s ability to lose its outer valence electrons and results in high thermal and electrical conductivity, among other physical and chemical properties. There are 20 nonradioactive representative metals in groups 1, 2, 3, 12, 13, 14, and 15 of the periodic table (in Figure 1). The radioactive elements copernicium, flerovium, polonium,

and livermorium are also metals but are beyond the scope of this chapter.

In addition to the representative metals, some of the representative elements are metalloids. A metalloid is an element that has properties that are between those of metals and nonmetals; these elements are typically semiconductors.

The remaining representative elements are nonmetals. Unlike metals, which typically form cations and ionic compounds (containing ionic bonds), nonmetals tend to form anions or molecular compounds. In general, the combination of a metal and a nonmetal produces a salt. A salt is an ionic compound consisting of cations and anions.



Period	Group 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [97]	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57-71 La–Lu *	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po [209]	85 At [210]	86 Rn [222]
7	87 Fr [223]	88 Ra [226]	89-103 Ac–Lr **	104 Rf [267]	105 Db [270]	106 Sg [271]	107 Bh [272]	108 Hs [277]	109 Mt [276]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Uut [285]	114 Fl [289]	115 Uup [288]	116 Lv [293]	117 Uus [294]	118 Uuo [294]

*	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm [145]	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.1	71 Lu 175.0
**	89 Ac [227]	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]

Color Code	
Representative metals	Solid
Transition and inner transition metals	Liquid
Radioactive elements	Gas
Metalloid	
Nonmetal	

The alkali metals lithium, sodium, potassium, rubidium, cesium, and francium constitute group 1 of the periodic table. Although hydrogen is in group 1 (and also in group 17), it is a nonmetal and deserves separate consideration later in this chapter. The name alkali metal is in reference to the fact that these metals and their oxides react with water to form very basic (alkaline) solutions.

Group 2: The Alkaline Earth Metals

The alkaline earth metals (beryllium, magnesium, calcium, strontium, barium, and radium) constitute group 2 of the periodic table. The name alkaline metal comes from the fact that the oxides of the heavier members of the group react with water to form alkaline solutions. The nuclear charge increases when going from group 1 to group 2. Because of this charge increase, the atoms of the alkaline earth metals are smaller and have higher first ionization energies than the alkali metals within the same period. The higher ionization energy makes the alkaline earth metals less reactive than the alkali metals; however, they are still very reactive elements. Their reactivity increases, as expected, with increasing size and decreasing ionization energy. In chemical reactions, these metals readily lose both valence electrons to form compounds in which they exhibit an oxidation state of 2+. Due to their high reactivity, it is common to produce the alkaline earth metals, like the alkali metals, by electrolysis. Even though the ionization energies are low, the two metals with the highest ionization energies (beryllium and magnesium) do form compounds that exhibit some covalent characters. Like the alkali metals, the heavier alkaline earth metals impart color to a flame. As in the case of the alkali metals, this is part of the emission spectrum of these elements.

Calcium and strontium produce shades of red, whereas barium produces a green color.

Transition Metals

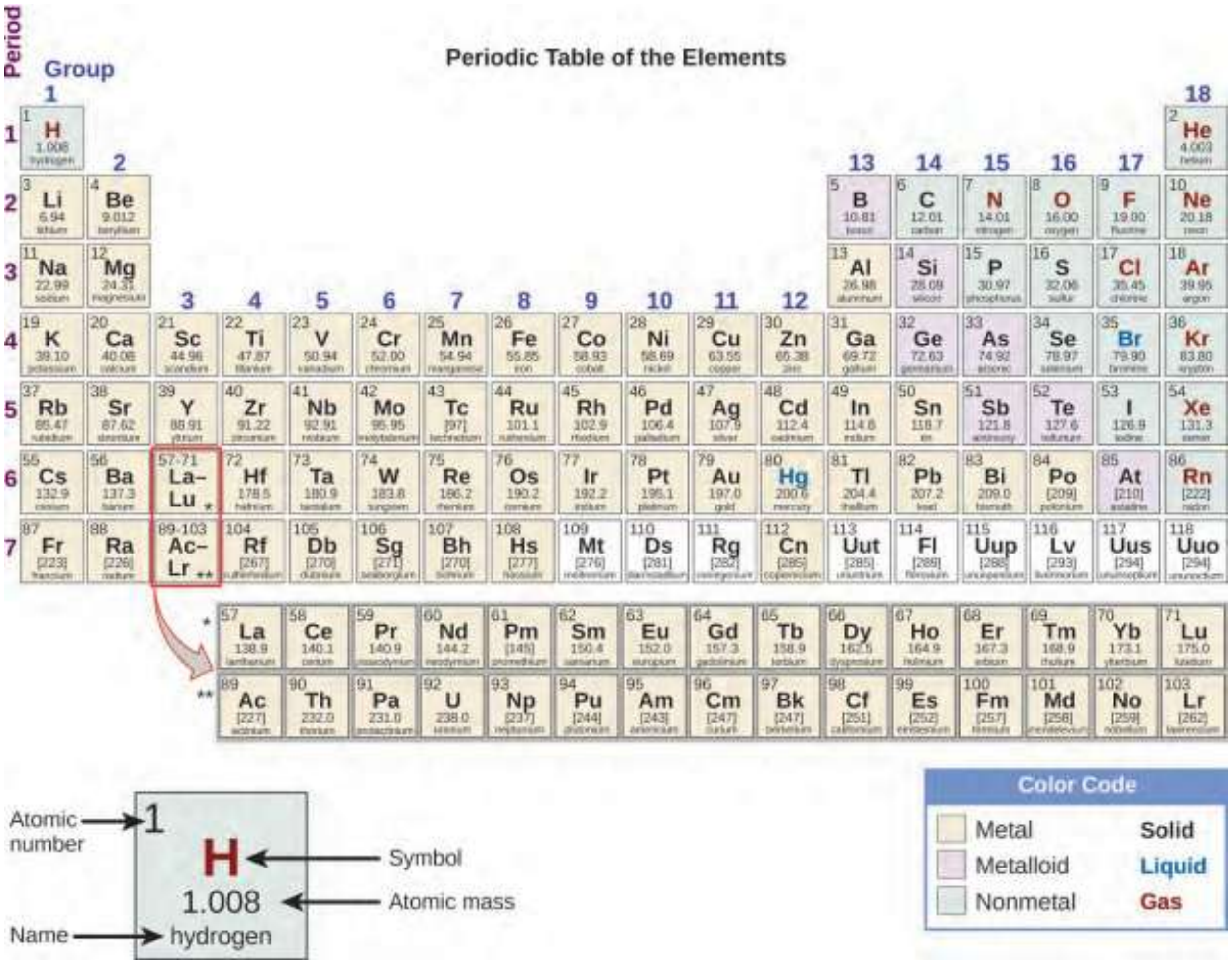
Introduction

We have daily contact with many transition metals. Iron occurs everywhere—from the rings in your spiral notebook and the cutlery in your kitchen to automobiles, ships, buildings, and in the hemoglobin in your blood. Titanium is useful in the manufacture of lightweight, durable products such as bicycle frames, artificial hips, and jewelry. Chromium is useful as a protective plating on plumbing fixtures and automotive detailing.

In addition to being used in their pure elemental forms, many compounds containing transition metals have numerous other applications. Silver nitrate is used to create mirrors, zirconium silicate provides friction in automotive brakes, and many important cancer-fighting agents, like the drug cisplatin and related species, are platinum compounds.

The variety of properties exhibited by transition metals is due to their complex valence shells. Unlike most main group metals where one oxidation state is normally observed, the valence shell structure of transition metals means that they usually occur in several different stable oxidation states. In addition, electron transitions in these elements can correspond with absorption of photons in the visible electromagnetic spectrum, leading to colored compounds. Because of these behaviors, transition metals exhibit a rich and fascinating chemistry.

Transition metals are defined as those elements that have (or readily form) partially filled d orbitals. As shown in Figure 2, the d-block elements in groups 3–11 are transition elements. The f-block elements, also called inner transition metals (the lanthanides and actinides), also meet this criterion because the d orbital is partially occupied before the f orbitals. The d orbitals fill with the copper family (group 11); for this reason, the next family (group 12) are technically not transition elements. However, the group 12 elements do display some of the same chemical properties and are commonly included in discussions of transition metals. Some chemists do treat the group 12 elements as transition metals.



Periodic Table of the Elements

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H 1.008																	2 He 4.003
2	3 Li 6.94	4 Be 9.012											5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18
3	11 Na 22.99	12 Mg 24.31											13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.06	17 Cl 35.45	18 Ar 39.95
4	19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.94	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.63	33 As 74.92	34 Se 78.97	35 Br 79.90	36 Kr 83.80
5	37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.95	43 Tc [97]	44 Ru 101.1	45 Rh 102.9	46 Pd 106.4	47 Ag 107.9	48 Cd 112.4	49 In 114.8	50 Sn 118.7	51 Sb 121.8	52 Te 127.6	53 I 126.9	54 Xe 131.3
6	55 Cs 132.9	56 Ba 137.3	57-71 La–Lu *	72 Hf 178.5	73 Ta 180.9	74 W 183.8	75 Re 186.2	76 Os 190.2	77 Ir 192.2	78 Pt 195.1	79 Au 197.0	80 Hg 200.6	81 Tl 204.4	82 Pb 207.2	83 Bi 209.0	84 Po [209]	85 At [210]	86 Rn [222]
7	87 Fr [223]	88 Ra [226]	89-103 Ac–Lr **	104 Rf [267]	105 Db [270]	106 Sg [271]	107 Bh [270]	108 Hs [277]	109 Mt [276]	110 Ds [281]	111 Rg [282]	112 Cn [285]	113 Uut [285]	114 Fl [289]	115 Uup [288]	116 Lv [293]	117 Uus [294]	118 Uuo [294]

*	57 La 138.9	58 Ce 140.1	59 Pr 140.9	60 Nd 144.2	61 Pm [145]	62 Sm 150.4	63 Eu 152.0	64 Gd 157.3	65 Tb 158.9	66 Dy 162.5	67 Ho 164.9	68 Er 167.3	69 Tm 168.9	70 Yb 173.1	71 Lu 175.0
**	89 Ac [227]	90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np [237]	94 Pu [244]	95 Am [243]	96 Cm [247]	97 Bk [247]	98 Cf [251]	99 Es [252]	100 Fm [257]	101 Md [258]	102 No [259]	103 Lr [262]

Color Code	
Metal	Solid
Metalloid	Liquid
Nonmetal	Gas

Figure 2: The transition metals are located in groups 3–11 of the periodic table. The inner transition metals are in the two rows below the body of the table.

The **f-block elements** are the elements Ce through Lu, which constitute the lanthanide series (or lanthanoid series), and the elements Th through Lr, which constitute the actinide series (or actinoid series). Because lanthanum behaves very much like the lanthanide elements, it is considered a lanthanide element, even though its electron configuration makes it the first member of the third transition series. Similarly, the behavior of actinium means it is part of the actinide series, although its electron configuration makes it the first member of the fourth transition series.

The **d-block elements** have been defined as “the elements whose atoms receive the last electron in the d-subshell belonging to the penultimate or (n-1)th shell”. The d-block elements are also called the transition elements or metals. This is because they exhibit gradual transitional behaviour between highly reactive s-block (electropositive) and p-block (electronegative) elements, i.e. their properties have been found to be intermediate between those of the s-block and p-block elements. Thus these elements are located in the middle of the periodic table and are the members of the Groups 3 to 12 (IIIB to VIII to II B) in the modern periodic table.

According to IUPAC definiton, “a transition element is an element which has an incomplete d-subshell in either neutral atom or in ions in chemically significant (or common) oxidation state”. According to this definition zinc (Zn), cadmium (Cd) and mercury (Hg) are excluded from the list of transition elements as they neither have partly filled d-subshell in their atoms or ions nor they show the usual properties of transition elements to an appreciable extent. Still in order to rationalize the classification of elements, they are studied along with other d-block elements.

Now according to IUPAC, transition metals are defined as metals which have incomplete d subshell either in neutral atom or in their ions. Zinc, cadmium and mercury of group 12 have full d10 configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals.

However, being the end members of the 3d, 4d and 5d transition series, respectively, their chemistry is studied along with the chemistry of the transition metals.

The presence of partly filled d or f orbitals in their atoms makes transition elements different from that of the non-transition elements. Hence, transition elements and their compounds are studied separately. However, the usual theory of valence as applicable to the non- transition elements can be applied successfully to the transition elements also.

Various precious metals such as silver, gold and platinum and industrially important metals like iron, copper and titanium belong to the transition metals series.

We shall first deal with the electronic configuration, occurrence and general characteristics of transition elements with special emphasis on the trends in the properties of the first row (3d) transition metals along with the preparation and properties of some important compounds. This will be followed by consideration of certain general aspects such as electronic configurations, oxidation states and chemical reactivity of the inner transition metals.

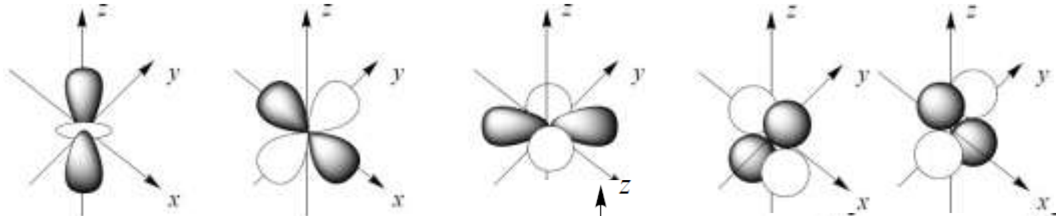
The d-block elements are divided into the **first transition series** (the elements Sc through Cu), **the second transition series** (the elements Y through Ag), and the **third transition series** (the element La and the elements Hf through Au). Actinium, Ac, is the first member of the **fourth transition series**, which also includes Rf through Rg.

There are four series of elements which constitute the d-block elements. Each series comprises ten elements as given below:

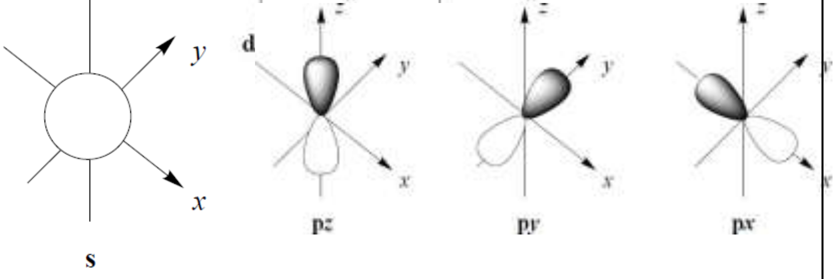
1. **Elements of the First Transition series or 3d-Transition series**: The elements from scandium (Sc, Z = 21) to Zinc (Zn, Z = 30) form the 3d-series.
2. **Elements of the Second Transition series or 4d-Transition series**: This series consists of the elements from yttrium (Y, Z = 39) to cadmium (Cd, Z = 48).
3. **Elements of the Third Transition series or 5d-Transition series**: The elements lanthanum (La, Z= 57) and hafnium (Hf, Z= 72) to mercury (Hg, Z = 80) constitute the 5d-Transition series.
4. **Elements of the Fourth Transition series or 6d-Transition series**: The elements actinium (Ac, Z = 89) and rutherfordium (Rf, Z = 104) to copernicum (Cn, Z = 112) are the members of this series. All these elements are radioactive and do not occur in nature. These have been artificially made in the laboratory.

Transition Metal Valence Orbitals

- *n*d orbitals



- (*n*



- dx^2-dy^2 and dz^2 (e$_g$) lobes located on the axes
- dxy, dxz, dyz lobes (t$_{2g}$) located between axes

CHARACTERISTIC PROPERTIES OF D-BLOCK ELEMENTS

The transition elements have several characteristic properties.

- All are metals with high tensile strength and good conductor of heat and electricity.
- All, except mercury (which is liquid at room temperature), appear as high melting point and boiling point lustrous solids. The high melting points are attributed to the involvement of greater number of electrons from (n-1) d orbitals in addition to the ns electrons in the interatomic metallic bonding. In a particular row, in general, the melting points rise to a maximum at d5, except for anomalous values of Mn and Tc, and fall regularly as the atomic number increases .
- All have high enthalpy of atomization. The higher enthalpy values of atomization for the second and third series account for the occurrence of much more frequent metal – metal bonding in compounds of the heavy transition series.
- All form alloys with one another, and with metallic main group elements.

- Many of them are sufficiently electropositive to react with mineral acids to form salts, though some of them are rather inert in this respect.
- Most of them show more than one oxidation state (variable valence).
- Because of partly filled d orbitals some transition metal ions containing odd number of electrons form paramagnetic compounds.
- They have unparallel tendency to form coordination compounds with Lewis bases because of their small size, high charge and availability of low energy orbitals.
- Many form coloured compounds in one if not in all oxidation states; the absorption of visible light being associated with the presence of partly filled d orbitals.
- The redox behavior, magnetic and optical properties of the transition elements are important features underlying their use in innumerable applications.

Atomic Structures and Properties

- **Electronic Configuration and Variable Oxidation States**

- **Electronic configurations**
- The electronic configurations of the valence shells of the d-block elements can be given as
- $(n-1)d^{1-10}\, ns^{1-2}$, where (n-1) stands for the inner d orbitals (Table 1). It is observed that the electron first enters in higher principal quantum number orbital (n) rather than in unoccupied (n-1)d orbital. The reason for the preferential filling up of 4s in comparison to 3d can be understood in terms of the shielding effect and the effective nuclear charge. In fact, the relative energies of the atomic orbitals varies with increase in atomic number as shown in figure 2. In building up the elements from hydrogen (Z=1) to calcium (Z=20), the unoccupied 3d orbitals are effectively shielded from the increasing nuclear charge by the electrons of (Ar) core. As a consequence, the energy of 3d orbitals remains fairly constant.

- In contrast, the energies of the 4s and 4p orbitals are declining as they penetrate the (Ar) core more. However, the 3d orbitals penetrate the 4s and 4p orbitals so that after Ca a 3d electron is not fully shielded from the increasing nuclear charge by the 4s electrons. Thus, by the time Sc (Z=21) is reached the energy of 3d orbitals fall below the level of 4p orbitals and close to that of 4s orbital. The next electron therefore enters the 3d orbital. Since the d electrons shield one another rather poorly from the nuclear charge, the energy of 3d orbitals continues to fall as Zeff increases. Thus, by the time Ga (Z=31) is reached, the new filled d orbitals have fallen well below the
- 4s and 4p orbitals in energy and are no longer part of the valence shell, but become a core. The same sequence of events follow in the case of the heavier transition metal series.

Table 1: Electronic Configurations of outer orbitals of the Transition Elements(ground state)

1st Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Z	21	22	23	24	25	26	27	28	29	30
4*s*	2	2	2	1	2	2	2	2	1	2
3*d*	1	2	3	5	5	6	7	8	10	10

2nd Series

	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Z	39	40	41	42	43	44	45	46	47	48
5*s*	2	2	1	1	1	1	1	0	1	2
4*d*	1	2	4	5	6	7	8	10	10	10

3rd Series

	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Z	57	72	73	74	75	76	77	78	79	80
6*s*	2	2	2	2	2	2	2	1	1	2
5*d*	1	2	3	4	5	6	7	9	10	10

4th Series

	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn
Z	89	104	105	106	107	108	109	110	111	112
7*s*	2	2	2	2	2	2	2	2	1	2
6*d*	1	2	3	4	5	6	7	8	10	10

Transition Elements	**Atomic Number**	**Electronic Configuration**
Sc	21	[Ar] $3d^1$ $4s^2$
Ti	22	[Ar] $3d^2$ $4s^2$
V	23	[Ar] $3d^3$ $4s^2$
Cr	24	[Ar] $3d^5$ $4s^1$
Mn	25	[Ar] $3d^5$ $4s^2$
Fe	26	[Ar] $3d^6$ $4s^2$
Co	27	[Ar] $3d^7$ $4s^2$
Ni	28	[Ar] $3d^8$ $4s^2$
Cu	29	[Ar] $3d^{10}$ $4s^1$
Zn	30	[Ar] $3d^{10}$ $4s^2$
Y	39	[Kr] $4d^1$ $5s^2$
Zr	40	[Kr] $4d^2$ $5s^2$
Nb	41	[Kr] $4d^4$ $5s^1$
Mo	42	[Kr] $4d^5$ $5s^1$
Tc	43	[Kr] $4d^5$ $5s^2$
Ru	44	[Kr] $4d^7$ $5s^1$
Rh	45	[Kr] $4d^8$ $5s^1$
Pd	46	[Kr] $4d^{10}$
Ag	47	[Kr] $4d^{10}$ $5s^1$
Cd	48	[Kr] $4d^{10}$ $5s^2$

- **Radii of atoms and ions**

In general, atomic radii (Table 1) of the elements show progressive decrease with increasing atomic number across a row in the transition series. This is because as the new electron enters a d orbital, each time the nuclear charge increases by unity. Since the shielding effect of a d electron is not that effective, the net electrostatic attraction between the nuclear charge and the outermost electron increases and hence a contraction in size. The same trend is observed in the ionic radii of a given series. However, the variation within a series is quite small. It may be attributed to the two opposing factors : one the increasing nuclear charge tending to decrease the size and the other electron-electron repulsion, because of addition of electrons in the same penultimate d shell, tending to increase the size.

An interesting feature emerges when atomic sizes of one series are compared with those of the corresponding elements in the other series. The data in Figure 3 show an increase from the first (3d) to the second (4d) series of the elements but the radii of the third (5d) series are virtually the same as those of the corresponding members of the second series. This phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called Lanthanoid contraction which essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g. Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

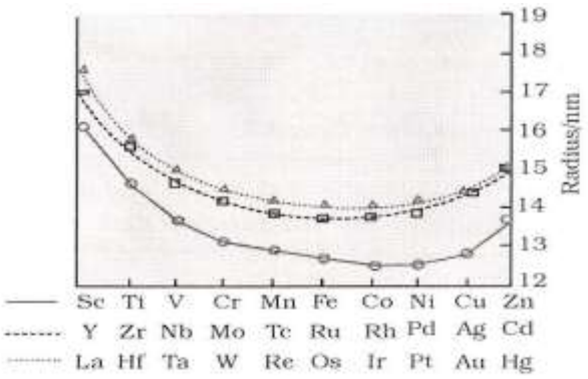


Figure3 : The variation in atomic radii of transition metals across the series

The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of these elements. Thus from titanium (Z=22) to copper (Z=29) the increase in the density is significant.

- **Ionization enthalpies**

With increasing nuclear charge, which accompanies the filling of the inner d orbitals, there is an increase in magnitude of ionization enthalpy along each series of the transition elements from left to right. However, many small variations occur. Table 1 gives the values for the first three ionization enthalpies corresponding to successive removal of electrons from outermost s orbital and d orbital of the first row elements.

These values show that the successive enthalpies of these elements do not increase as steeply as in the main group elements. Although the first ionization enthalpy (removal of electron from s orbital), in general, increase, the increase in the second and third ionization enthalpies for the successive elements are not of the same magnitude. However, the trend is similar for the second ionization enthalpies, which for the most part increase smoothly as the atomic number increases; the exceptions are
chromium and copper for which these values are notably larger than those of their neighbors.

The irregular trend in the first ionization enthalpy of the 3d metals, though of little chemical significance, can be accounted for by considering that the removal of one electron alters the relative energies of 4s and 3d orbitals. There is thus a reorganization energy accompanying ionization with some gain in exchange energy as the number of electrons increases.

In general, there is an expected increasing trend in the values as the effective nuclear charge increases with the value of Cr being lower because of the absence of any change in the d configuration and the value of Zn being relatively high because of ionization from the filled 4s level. The lowest common oxidation state of these metals is +2. To form the M^{2+} ions from the gaseous atoms, the sum of the first and second ionization energies is required in addition to the enthalpy of atomization for each element. The dominant term is the second ionization enthalpy which shows unusually high values for Cr and Cu where the d5 and d10 configurations of the M^{+} ions are disrupted, with considerable loss of exchange energy. The value for Zn is correspondingly low as the ionization leads to the production of the stable d^{10} configuration. The trend in the third ionization enthalpies is not complicated by the 4s orbital factor and shows the greater difficulty of removing an electron from the $d^{5}(Mn^{2+})$ and $d^{10}(Zn^{2+})$ ions superimposed upon the general increasing trend. In general, the third ionization enthalpies are quite high and there is a marked break between the values for Mn^{2+} and Fe^{2+}.

Also the high values for copper, nickel and zinc indicate difficulty in obtaining oxidation state greater than two for these elements.

Although ionization enthalpies give some guidance concerning the relative stabilities of oxidation states, this problem is complicated by differing salvation (hydration) energies of different ions and, therefore not easily amenable for broad generalization .

- **Oxidation states**

The oxidation states (or number) exhibited by the transition elements . The most common and important ones are shown in bold type. It is obvious that the transition metals exhibit a great variety of oxidation states. The elements which give the greatest number of oxidation states occur in or near the middle of the series. Manganese, for example, exhibits all the oxidation states from +2 to +7. Ruthenium and Osmium commonly form compounds in +8 oxidation state, which is among the highest for isolable compounds. The lesser number of oxidation states at the extreme ends stems from either too few electrons to lose or share (Sc, Ti) or too many d electrons (hence fewer orbitals available for sharing electrons with others) for higher valence (Cu, Zn.). Thus, early in the series scandium(II) is virtually unknown and titanium(IV) is more stable than Ti(III) or Ti(II). At the other end, the only oxidation state of zinc is +2 (no d electrons are involved).

The maximum oxidation states of reasonable stability correspond to the sum of the s and d electrons upto manganese (TiO_2, VO^{2+}, CrO_4^{2-}, MnO_4^-) followed by a rather abrupt decrease in stability of higher oxidation states, so that the typical species to follow are Fe II, III, Co II,III, Ni II, Cu I,II, Zn II. It is mainly because the latter transition metals require more energy to remove the electrons.

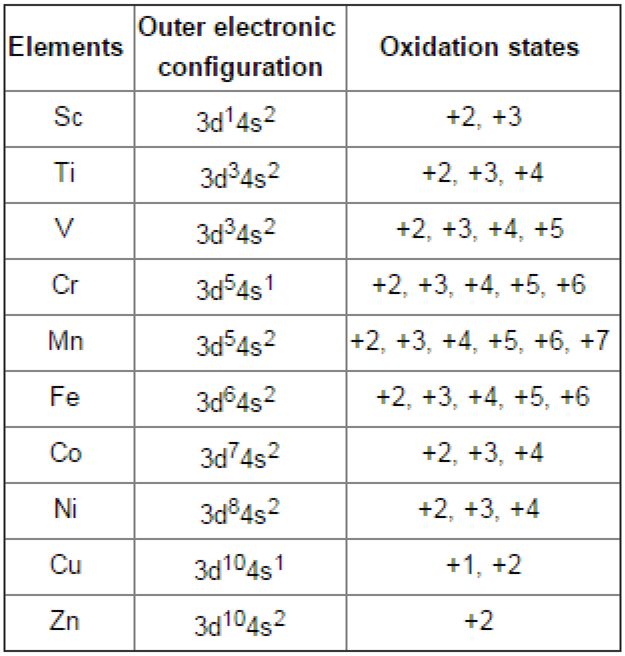
Most of the d-block elements show several oxidation states (variable) in their compounds due to the availability of d-electrons in the valence shell which comprises of the two subshells, viz., (n-1)d and ns whose orbitals are quite close together in energy and hence the electrons can be used from both the subshells for bonding and under different conditions different number of electrons can be used by them. The variability in the oxidation states increases towards the middle of the series from both ends, i.e. left → middle ← right. It has been observed that the d-block elements can form ionic bonds in their lower oxidation states and the ionic character of the bond decreases as well as the covalent character increases with increasing oxidation state.

As a result, with decreasing ionic character the acidic character of the oxides and chlorides increases.

The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of d orbitals in such a way that their oxidation states differ from each other by unity, e.g. VII, VIII, VIV, Vv. This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by units of two.

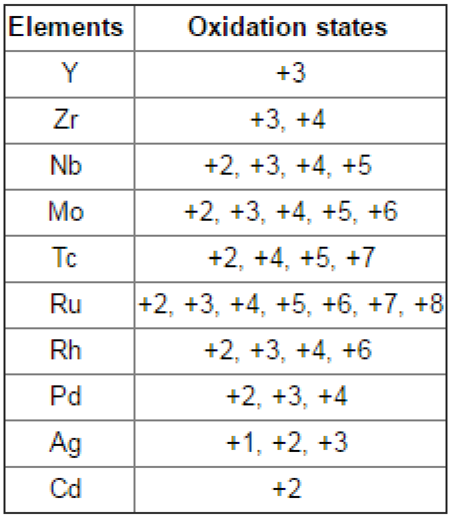
Low oxidation states are found when a complex compound has ligands capable of π–acceptor character in addition to the σ- bonding. For example in $Ni(CO)_4$ and $Fe(CO)_5$ the oxidation state of nickel and iron is zero.

Oxidation States of 3d Series



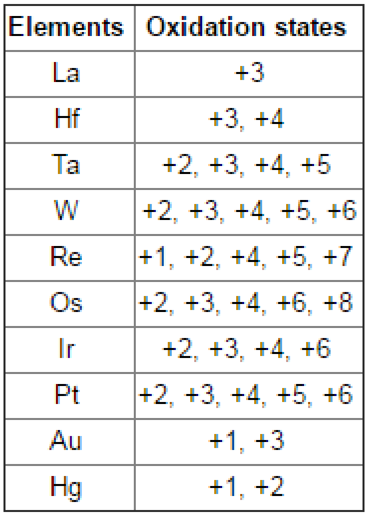
Elements	Outer electronic configuration	Oxidation states
Sc	$3d^1 4s^2$	+2, +3
Ti	$3d^3 4s^2$	+2, +3, +4
V	$3d^3 4s^2$	+2, +3, +4, +5
Cr	$3d^5 4s^1$	+2, +3, +4, +5, +6
Mn	$3d^5 4s^2$	+2, +3, +4, +5, +6, +7
Fe	$3d^6 4s^2$	+2, +3, +4, +5, +6
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4
Cu	$3d^{10} 4s^1$	+1, +2
Zn	$3d^{10} 4s^2$	+2

Oxidation state of 4d series



Elements	Oxidation states
Y	+3
Zr	+3, +4
Nb	+2, +3, +4, +5
Mo	+2, +3, +4, +5, +6
Tc	+2, +4, +5, +7
Ru	+2, +3, +4, +5, +6, +7, +8
Rh	+2, +3, +4, +6
Pd	+2, +3, +4
Ag	+1, +2, +3
Cd	+2

Oxidation State of 5d Series



Elements	Oxidation states
La	+3
Hf	+3, +4
Ta	+2, +3, +4, +5
W	+2, +3, +4, +5, +6
Re	+1, +2, +4, +5, +7
Os	+2, +3, +4, +6, +8
Ir	+2, +3, +4, +6
Pt	+2, +3, +4, +5, +6
Au	+1, +3
Hg	+1, +2

Cause for Variable Oxidation States

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

They demonstrate the +2 oxidation state because of the 2 electrons in ns

orbitals when the electrons of (n-1) d stay unaffected.

The higher oxidation state from +3 to +7 is because of the utilization of all 4s and 3d electrons in the transition series of elements. In the excited state, the (n-1) d electrons get to be bonding and give the variable states to the iota. Subsequently, the variable

oxidation state is because of the support of both ns and (n-1) d orbitals in bonding.

- **Magnetic Properties:**

The magnetic properties of D-Block Elements are dictated by the number of unpaired electrons in it.

There are two fundamental sorts of substances.

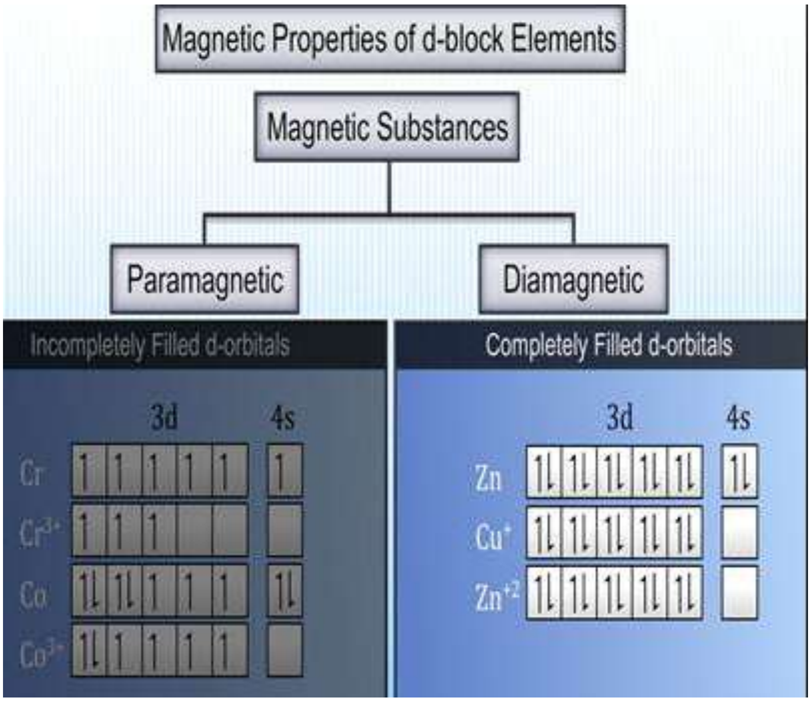
(i) Paramagnetic substances

The paramagnetic character emerges in view of the nearness of unpaired electrons. Paramagnetic substances are the substances which are pulled in by the magnetic field.

(ii) Diamagnetic Substances

Diamagnetic character emerges as a result of the nonappearance of unpaired electrons. Diamagnetic substances are the substances which are repulsed by the magnetic field.

A large portion of the transition elements and their compounds are paramagnetic and are pulled in by the magnetic field. More prominent the number of unpaired electrons in the substance more noteworthy is the paramagnetic character


Magnetic Properties of d-block Elements
Magnetic Substances
Paramagnetic
Diamagnetic
Incompletely Filled d-orbitals
Completely Filled d-orbitals
3d
4s
Cr
Cr3+
Co
Co3+
3d
4s
Zn
Cu+
Zn+2

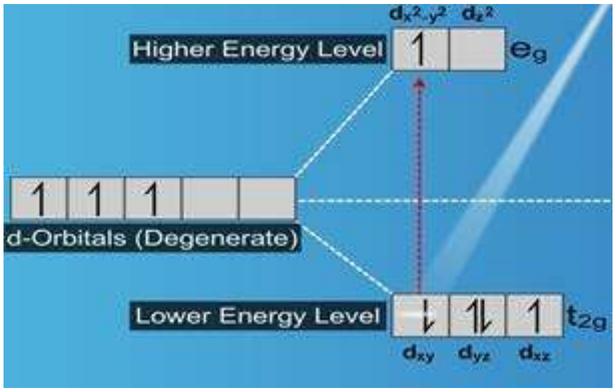
- **Formation of colored compounds:**

Most d-block metal compounds are coloured in their solid or liquid states.

In the case of transition metal ions, under the influence of ligands, the degeneracy of the 5 d-orbitals is lost and they separate into two distinct energy levels.

eg set: d x^2- y^2 and dz^2 orbitals

t_2g set: dxy, dxz and dyz orbitals



When white light is incident on a transition metal ion, the electron in the lower energy d-orbital set absorbs certain radiations and gets promoted to a d-orbital set of higher energy. The transmitted radiation devoid of the absorbed radiations is the complementary colour of the absorbed light. This complementary colour is the colour of the substance.

Colour in transition-series metal compounds is generally due to electronic transitions of two principal types.

- charge transfer transitions. An electron may jump from a predominantly ligand orbital to a predominantly metal orbital, giving rise to a ligand-to-metal charge-transfer (LMCT) transition. These can most easily occur when the metal is in a high oxidation state. For example, the colour of chromate, dichromate and permanganate ions is due to LMCT transitions. Another example is that mercuric iodide, HgI_2, is red because of a LMCT transition.

A metal-to-ligand charge transfer (MLCT) transition will be most likely when the metal is in a low oxidation state and the ligand is easily reduced.

In general charge transfer transitions result in more intense colours than d-d transitions.

- d-d transitions. An electron jumps from one d-orbital to another. In complexes of the transition metals the d orbitals do not all have the same energy. The pattern of splitting of the d orbitals can be calculated using crystal field theory. The extent of the splitting depends on the particular metal, its oxidation state and the nature of the ligands. The actual energy levels are shown on Tanabe–Sugano diagrams.

- **Catalytic Activity**

Transition metals and their compounds are often good catalysts. A few of the more obvious cases are mentioned below, but you will find catalysis explored in detail elsewhere on the site (follow the link after the examples). Transition metals and their compounds function as catalysts either because of their ability to change oxidation state or, in the case of the metals, to adsorb other substances on to their surface and activate them in the process. All this is explored in the main catalysis section.

Iron in the Haber Process

The Haber Process combines hydrogen and nitrogen to make ammonia using an iron catalyst.

Nickel in the hydrogenation of C=C bonds

This reaction is at the heart of the manufacture of margarine from vegetable oils. However, the simplest example is the reaction between ethene and hydrogen in the presence of a nickel catalyst.

Vanadium(V) oxide in the Contact Process

At the heart of the Contact Process is a reaction which converts Sulfur dioxide into Sulfur trioxide. Sulfur dioxide gas is passed together with air (as a source of oxygen) over a solid vanadium(V) oxide catalyst.

Iron ions in the reaction between persulfate ions and iodide ions

Persulphate ions (peroxodisulphate ions), $S_2O_8^{2-}$, are very powerful oxidizing agents. Iodide ions are very easily oxidized to iodine. And yet the reaction between them in solution in water is very slow. The reaction is catalyzed by the presence of either iron(II) or iron(III) ions.

$S_2O_8^{2-}+2I^{-}\rightarrow 2SO_4^{2-}+I_2$ (1)

- **Alloy formation**

The transition metals readily form alloys with each other because of similar radii. The alloys so formed are hard and have often high melting points. The best known are ferrous alloys; vanadium, chromium, molybdenum, tungsten and manganese are used for the production of variety of steels and stainless steel.

Industrially important alloys of transition metals with non-transition metals are brass (copper-zinc), bronze (copper-tin) etc.

- **Coordination Compounds**

The transition metals and their ions have much higher tendency to from coordination compounds as compared to the s- and p- block elements. It is because of their relatively smaller sizes, higher ionic charges and the availability of d orbitals for bond formation. Coordination compounds, unlike normal compounds, retain their identity even when dissolved in water or any other suitable solvent. The properties of these compounds are totally different from those of their constituents.

Alfred Werner can be considered to be the pioneer in the field of coordination chemistry and he received Nobel Prize in 1913 in recognition of his efforts. He showed that neutral molecules were bound directly to the metal so that complex salt such as $CoCl_3.6NH_3$ is correctly formulated as $[Co(NH_3)_6]^{3+}(Cl^-)_3$.

G.N. Lewis and N.V. Sidgwick proposed that a chemical bond required the sharing of an electron pair. This led to the idea that a neutral molecule with an electron pair can donate these electrons to a metal ion or other electron acceptor.

Thus, in a coordination compound, the metal species acts as electron acceptor (Lewis acid) and neutral molecule with lone pair of electrons or anion as electron donor (Lewis bases). A metal atom or ion when bonded directly to a fixed number of anions or molecules constitutes a coordination entity. For example, $[Pt(NH_3)_2Cl_2]$ is a coordination entity in which platinum(II) is surrounded by two ammonia molecules and two chloride ions. Other examples are $[Fe(CN)_6]^{4-}$, $[Co(NH_3)_5Cl]^{2+}$, $[Ni(CO)_4]$ etc. In a coordination entity, the atom/ion to which a fixed number of ions/ groups are bound in a definite geometrical arrangement around it, is called the central atom or ion. For example, the central atom in $[Ni(NH_3)_6]^{2+}$ is Ni(II), in $[Mo(CN)_8]^{3-}$, Mo(V), and in $[Co(PR_3)_3Cl]$, Co(I). The charged ions or neutral molecules bound to the central atom in the coordination entitiy are called ligands. For example, PR_3 and Cl- are ligands in $[CoCl(PR_3)_3]$.

The number of ligand donor atoms directly bonded to the central atom is defined as the coordination number. For example, in the complex species $[Mo(CN)_8]^{3-}$ and $[CoCl(PR_3)_3]$, the coordination number of Mo and Co are 8 and 4, respectively. The central atom and the ligands bonded to it are enclosed in square bracket and is collectively termed as the coordination sphere. For example in the complex $[Ni(NH_3)_6]Cl_2$, the coordination sphere is $[Ni(NH_3)_6]^{2+}$. The spatial arrangement of the ligands around the central atom is termed as coordination polyhedron. The most common coordination polyhedra are octahedral, tetrahedral and square planar.

- **Melting and Boiling Points**

The melting and boiling points of these elements are generally very high showing that they are held by strong forces. The melting and boiling points have the highest values in the middle of the series because, perhaps these elements have the maximum number of unpaired d-electrons available for bonding, detailed account of which will be given ahead for every series.

Scandium

Definition

Scandium is a transition element in Group 3 (IIIB) and Period 4 with an atomic number of 21.

Chemical Properties of Scandium

Scandium is the lightest Group 3 (IIIB) element and is the lightest of the transition metals. Its atomic number (proton number) is 21, has only one long-lived isotope, and has an atomic mass of 44.95591 a.m.u. Scandium’s electronic configuration is $[Ar]4s^2 3d^1$, and only occurs in the trivalent state (Sc^{3+}) in nature. Thus, unlike most other period 4 transition metals, the geochemical behavior of scandium is not affected by redox conditions, and shows lithophile behaviour. The effective ionic radii in six- and eight-fold coordination are 74.5 and 87 pm, respectively (Shannon 1976) and its Pauling electronegativity is 1.36. Pure scandium metal has a melting point of 1541 ℃ at 1 atm. The International Union of Pure and Applied Chemistry consider Sc to be a rare earth element (REE) (Damhus et al. 2005), however, the ionic radius and electronic configuration of Sc are sufficiently different from yttrium and the lanthanides that it is generally excluded from discussions of the REE.

Scandium was “discovered” by Lars Fredrik Nilson in 1879 by separation from rare earth mixtures from euxenite and gadolinite, and is named for Scandinavia.

Sources and Uses

Global production of Sc is small (~10 tonnes per year) as a by-product from mining of ores of titanium, rare earths, apatite, and uranium. Bauxites are another potential source of Sc, as it gets concentrated, along with other elements, in the “red mud” residue that results from Al processing (Deady et al. 2014). The principal uses of Sc are in Sc-Al alloys and in solid oxide fuel cells. Minor amounts of Sc are also used in variety of other applications including electronics, lasers, and lighting.

Titanium

Chemistry of Titanium

Discovered independently by William Gregor and Martin Klaproth in 1795, titanium (named for the mythological Greek Titans) was first isolated in 1910. Gregor, a Cornish vicar and amateur chemist isolated an impure oxide from ilmenite ($FeTiO_3$) by treatment with HCl and H_2SO_4 .Titanium is the second most abundant transition metal on Earth (6320 ppm) and plays a vital role as a material of construction .

For example, when it's alloyed with 6% aluminum and 4% vanadium, titanium has half the weight of steel and up to four times the strength.

Uses of titanium

Titanium is a highly corrosion-resistant metal with great tensile strength. It is ninth in abundance for elements in the earth's crust. It has a relatively low density (about 60% that of iron). It is also the tenth most commonly occurring element in the Earth's crust. That all means that titanium should be a really important metal for all sorts of engineering applications. In fact, it is very expensive and only used for rather specialized purposes.

Titanium is very expensive because it is awkward to extract from its ores - for example, from rutile, T iO_2. Whilst a biological function in man is not known, it has excellent biocompatibility--that is the ability to be ignored by the human body's immune system--and an extreme resistance to corrosion. Titanium is now the metal of choice for hip and knee replacements

Titanium Extraction

Titanium cannot be extracted by reducing the ore using carbon as a cheap reducing agent, like with iron. The problem is that titanium forms a carbide, TiC, if it is heated with carbon, so you don't get the pure metal that you need. The presence of the carbide makes the metal very brittle. That means that you have to use an alternative reducing agent. In the case of titanium, the reducing agent is either sodium or magnesium. Both of these would, of course, first have to be extracted from their ores by expensive processes.

The titanium is produced by reacting titanium(IV) chloride, $TiCl_4$ - NOT the oxide - with either sodium or magnesium. That means that you first have to convert the oxide into the chloride. That in turn means that you have the expense of the chlorine as well as the energy costs of the conversion. High temperatures are needed in both stages of the reaction.

Titanium is made by a batch process. In the production of iron, for example, there is a continuous flow through the Blast Furnace. Iron ore and coke and limestone are added to the top, and iron and slag removed from the bottom. This is a very efficient way of making something. With titanium, however, you make it one batch at a time. Titanium(IV) chloride is heated with sodium or magnesium to produce titanium. The titanium is then separated from the waste products, and an entirely new reaction is set up in the same reactor. This is a slow and inefficient way of doing things. Traces of oxygen or nitrogen in the titanium tend to make the metal brittle. The reduction has to be carried out in an inert argon atmosphere rather than in air; that also adds to costs.

Wilhelm J. Kroll developed the process in Luxemburg around the mid 1930's and then after moving to the USA extended it to enable the extraction of Zirconium as well. Titanium ores, mainly rutile (TiO_2) and ilmentite ($FeTiO_3$), are treated with carbon and chlorine gas to produce titanium tetrachloride.

$$TiO_2 + Cl_2 \rightarrow TiCl_4 + CO_2$$

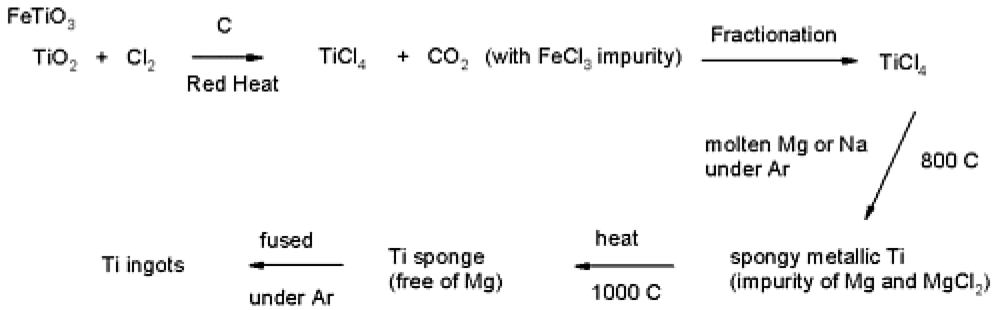
Fractionation

Titanium tetrachloride is purified by distillation (Boiling point of 136.4) to remove iron chloride.

Reduction

Purified titanium tetrachloride is reacted with molten magnesium under argon to produce a porous “titanium sponge”.

$$TiCl_4 + 2\ Mg \rightarrow Ti + 2\ MgCl_2$$



Kroll process

Titanium Halides

- Titanium(Halides IV) TiX_4

Preparations

They can all be prepared by direct reaction of Ti with halogen gas (X_2). All are readily hydrolyzed. They are all expected to be diamagnetic.

- Titanium(III) halides TiX_3

Preparations

They can be prepared by reduction of TiX4 with H2. Titanium Oxides and Aqueous Chemistry

Titanium oxides

Preparations

obtained from hydrolysis of TiX_4 or Ti(III) salts. TiO_2 reacts with acids and bases.

In Acid: $TiOSO_4$ formed in H_2SO_4 (Titanyl sulfate)

In Base: $MTiO_3$ metatitanates (eg Perovskite, $CaTiO_3$ and ilmenite, $FeTiO_3$) M_2TiO_4 ortho titanates. Peroxides are highly colored and can be used for Colorimetric analysis.

$TiCl_4$ is a good Lewis acid and forms adducts on reaction with Lewis bases

$TiCl_3$ has less Lewis acid strength but can form adducts

Conversion of titanium oxide into titanium chloride

The ore rutile (impure titanium(IV) oxide) is heated with chlorine and coke at a temperature of about 900°C.

$TiO_2 + 2Cl_2 + 2C \rightarrow TiCl_4 + 2CO$

Other metal chlorides are formed as well because of other metal compounds in the ore. Very pure liquid titanium(IV) chloride can be separated from the other chlorides by fractional distillation under an argon or nitrogen atmosphere. Titanium(IV) chloride reacts violently with water. Handling it therefore needs care and is stored in totally dry tanks.

Reduction of the titanium chloride

Reduction by sodium: The titanium(IV) chloride is added to a reactor in which very pure sodium has been heated to about 550°C - everything being under an inert argon atmosphere. During the reaction, the temperature increases to about 1000°C.

$TiCl_4 + 4\,Na \rightarrow Ti + 4\,NaCl \qquad (4)$

After the reaction is complete, and everything has cooled (several days in total - an obvious inefficiency of the batch process), the mixture is crushed and washed with dilute hydrochloric acid to remove the sodium chloride.

Reduction by magnesium

This is the method used in the rest of the world. The method is similar to using sodium, but this time the reaction is:

$$\mathrm{TiCl_4 + 4\ Mg \rightarrow Ti + 2\ MgCl_2} \quad (5)$$

The magnesium chloride is removed from the titanium by distillation under very low pressure at a high temperature.

Vanadium

Chemistry of Vanadium

Vanadium takes its name from the Scandinavian goddess Vanadis and was discovered in 1801 by Andrés Manuel del Rio. It was isolated in 1867 by Henry Roscoe as a silvery-white metal that is somewhat heavier than aluminum but lighter than iron. It has excellent corrosion resistance at room temperature.

The history of its discovery is an interesting tale. del Rio sent his brown ore samples, containing what he thought was a new element to Paris for analysis and confirmation, along with a brief explanation that was ambiguous. The complete analysis and description of his work were lost in a shipwreck so the Paris lab saw nothing but brown powder and a brief confusing note. A second sample sent to Berlin was mislabeled lead chromate when it arrived. del Rio gave up, losing confidence in his discovery. The element was rediscovered in 1867 by Nils Sefstrôm.

Vanadium has an unusually large number of stable oxidation states (+2, +3, +4, +5)each of which is characterized by a unique color in solution. The metal is used as an alloying agent for steel. It combines with nearly all non-metals in compounds.

Vanadium(V) oxide as a Catalyst

During the Contact Process for manufacturing sulfuric acid, sulfur dioxide has to be converted into sulfur trioxide, which is done by passing sulfur dioxide and oxygen over a solid vanadium(V) oxide catalyst.

This is a good example of the ability of transition metals and their compounds to act as catalysts because of their ability to change their oxidation state (oxidation number). The sulfur dioxide is oxidized to sulfur trioxide by the vanadium(V) oxide. In the process, the vanadium(V) oxide is reduced to vanadium(IV) oxide.

$$SO_2 + V_2O_5 \rightarrow SO_3 + V_2O_4$$

The vanadium(IV) oxide is then re-oxidized by the oxygen.

$$V_2O_4 + 1/2\ O_2 \rightarrow V_2O_5$$

Although the catalyst has been temporarily changed during the reaction, at the end it is chemically the same as it started.

Vanadium's oxidation states

Vanadium has oxidation states in its compounds of +5, +4, +3 and +2. This section looks at ways of changing between them. It starts with a bit of description, and then goes on to look at the reactions in terms of standard redox potentials (standard electrode potentials).

Chromium

Chromium Chemistry

History

Discovered in 1797 by the French chemist Louis Nicolas Vauquelin, it was named chromium (Greek chroma, "colour") because of the many different colours characteristic of its compounds.

Occurrence

Chromium is the earth's 21st most abundant element (about 122 ppm) and the 6th most abundant transition metal.

The principal and commercially viable ore is chromite, $FeCr_2O_4$, which is found mainly in southern Africa (with 96% of the worlds reserves), the former U.S.S.R and the Philippines. Less common sources include crocoite, $PbCrO_4$, and chrome ochre, Cr_2O_3, while the gemstones emerald and ruby owe their colours to traces of chromium.

See the International Chromium Development Association web site for more details.

Extraction

Chromite, $FeCr_2O_4$, is the most commercially useful ore, and is extensively used for extraction of chromium. Chromium is produced in two forms

Ferrochrome by the reduction of chromite with coke in an electric arc furnace. A low-carbon ferrochrome can be produced by using ferrosilicon instead of coke as the reductant. This iron/chromium alloy is used directly as an additive to produce chromium-steels which are "stainless" and hard.

Chromium metal by the reduction of Cr_2O_3. This is obtained by aerial oxidation of chromite in molten alkali to give sodium chromate, Na_2CrO_4, which is leached out with water, precipitated and then reduced to the Cr(III) oxide by carbon. The oxide can be reduced by aluminium (aluminothermic process) or silicon:

$Cr_2O_3 + 2Al \rightarrow 2Cr + Al_2O_3$ $2Cr_2O_3 + 3Si \rightarrow 4Cr + 3SiO_2$

The main use of the chromium metal so produced is in the production of nonferrous alloys, the use of pure chromium being limited because of its low ductility at ordinary temperatures. Alternatively, the Cr_2O_3 can be dissolved in sulphuric acid to give the electrolyte used to produce the ubiquitous chromium-plating which is at once both protective and decorative. The sodium chromate produced in the isolation of chromium is itself the basis for the manufacture of all industrially important chromium chemicals. World production of chromite ores approached 12 million tonnes in 1995.

Chromium Compounds

Most compounds of chromium are coloured , the most important are the chromates and dichromates of sodium and potassium and the potassium and ammonium

Preparations:

Reduction of CrX_3 with H_2/HX gives CrX_2.

$$Cr + Cl_2 \rightarrow CrCl_3$$

$$Cr_2O_3 + C + Cl_2 \rightarrow CrCl_3$$

List of References:

1- Fundamental Concepts of Inorganic Chemistry

E.S. Gilreath

2- Coordination Compounds

S. F. A. Kettle

3- Advanced Inorganic Chemistry: A Comprehensive Text

Cotton and Wilkinson