

CHAPTER 5.
PERIODIC CLASSIFICATION OF ELEMENTS

Chapter contents

- **Periodic classification of D. Mendeleev,**
- **Modern periodic classification,**
- **Evolution and periodicity of the physico-chemical properties of the elements,**
- **Calculation of radii (atomic and ionic),**
- **The successive ionization energies,**
- **Electron affinity and electronegativity (Mulliken scale) by Slater's rules**

I- Periodic classification of D. Mendeleev

In 1869, the Russian chemist **Dmitri Ivanovich Mendeleev** (1834–1907) and the German chemist **J. Lothar Meyer** (1830–1895), working independently, made similar discoveries. They found that when they arranged the elements in order of atomic mass, they could place them in horizontal rows, one row under the other, so that the elements in each vertical column have similar properties. A tabular arrangement of elements in rows and columns, highlighting the regular repetition of properties of the elements, is called a **periodic table**.

REIHEN	GRUPPE I R ² O	GRUPPE II RO	GRUPPE III R ² O ³	GRUPPE IV RH ⁴ RO ²	GRUPPE V RH ³ R ² O ³	GRUPPE VI RH ² RO ²	GRUPPE VII RH R ² O ³	GRUPPE VIII RO ⁴
1	H = 1							
2	Li = 7	Be = 9,4	B = 11	C = 12	N = 14	O = 16	F = 19	
3	Na = 23	Mg = 24	Al = 27,3	Si = 28	P = 31	S = 32	Cl = 35,5	
4	K = 39	Ca = 40	-- 44	Ti = 48	V = 51	Cr = 52	Mn = 55	Fe = 56, Co = 59, Ni = 59, Cu = 63.
5	(Cu = 63)	Zn = 65	-- 68	-- 72	As = 75	Se = 78	Br = 80	
6	Rb = 85	Sr = 87	?Yt = 88	Zr = 90	Nb = 94	Mo = 96	-- 100	Ru = 104, Rh = 104, Pd = 106, Ag = 108.
7	(Ag = 108)	Cd = 112	In = 113	Sn = 118	Sb = 122	Te = 125	J = 127	
8	Cs = 133	Ba = 137	?Di = 138	?Ce = 140	--	--	--	----
9	(-)	--	--	--	--	--	--	
10	--	--	?Er = 178	?La = 180	Ta = 182	W = 184	--	Os = 195, Ir = 197, Pt = 198, Au = 199.
11	(Au = 199)	Hg = 200	Tl = 204	Pb = 207	Bi = 208	--	--	
12	--	--	--	Th = 231	--	U = 240	--	----

Figure 4-1 Mendeleev's early periodic table (1872). "J" is the German symbol for iodine.

II- Modern periodic classification

In the early part of this century, it was demonstrated that elements are characterized by their atomic numbers, rather than their atomic masses. Each entry lists the atomic number, atomic symbol, and atomic mass of an element.

- This classification is called the **periodic table** due to the repetition of similar outer shell electronic configurations at a certain regular interval.
- It consists of 18 vertical columns called **groups** and 7 horizontal rows called **periods**.
- Currently, 118 elements are known to us. Each of these has different properties. Of those, only 98 are naturally occurring.

1. Structural features of the periodic table

The basic structure of the periodic table is its division into rows (**periods**) and columns (**groups**). The elements in any one group have **similar properties, such as radii, ionic radii, inert gas radii, Ionization enthalpy, electron gain enthalpy, electronegativity, and** valency.

For simplicity, chemists refer to specific elements using one- or two-letter symbols. The first letter of an element's symbol is always capitalized, and the second letter, if any, is lowercase. Many of the symbols are just the first one or two letters of the element's English name. Other

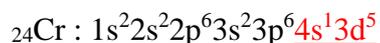
1st period	$n = 1$: contains only two elements. electronic configuration $1s$
2nd period	$n = 2$: contains 8 elements. electronic configuration $2s2p$
3rd period	$n = 3$: contains 8 elements. electronic configuration $3s3p$
4th period	$n = 4$: contains 18 elements. electronic configuration $4s3d4p$
5th period	$n = 5$: contains 18 elements. electronic configuration $5s4d5p$
6th period	$n = 6$: contains 32 elements. electronic configuration $6s4f5d6p$
7th period	$n = 7$: contains 32 elements. electronic configuration $7s5f6d7p$

- ✓ The periodic table is complete in its neatest form – all seven periods of elements currently known are filled.
 - ✓ The 14 elements with atomic numbers (Z) = 58 – 71 (occurring after lanthanum La in the periodic table) are called **lanthanides** or **rare earth elements** and are placed at the bottom of the periodic table. The valence electrons of these elements lie in the **4f** orbital.
 - ✓ The 14 elements with atomic numbers (Z) = 90 – 103 (Occurring after actinium Ac in the periodic table) are called **Actinides** and are placed at the bottom of the periodic table. The valence electrons of these elements lie in the **5f** orbital.
- **A group** consists of the elements in any one column of the periodic table.
- ✓ Groups 1, 2, and 13–18 are **the main group elements**, listed as **A** in older tables. Groups 3–12 are in the middle of the periodic table and are **the transition elements**, listed as **B** in older tables.
 - ✓ **Group IA** are the **alkali metals**: These are (except for hydrogen) soft, shiny, low-melting, highly reactive metals, which tarnish when exposed to air. The valence electron is easily lost, forming an ion with a 1+ charge
 - ✓ **Group IIA** are the **alkaline earth metals**: In most cases, the alkaline earth metals are ionized to form a 2+ charge.
 - ✓ There are exceptions of Aufbau Principle in transition elements where, one electron has passed from the s-orbital to a d-orbital to generate a half-filled or filled subshell. In this case, the usual explanation is that "half-filled or completely filled subshells are particularly stable arrangements of electrons". However this is not supported by the facts, as tungsten (W) has a Madelung-following $d^4 s^2$ configuration and not $d^5 s^1$, and niobium (Nb) has an anomalous $d^4 s^1$ configuration that does not give it a half-filled or completely filled subshell.

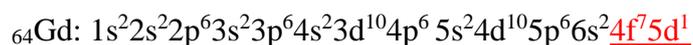
I _A																	O	
ns ¹ The Alkali Metals	II _A											III _A	IV _A	V _A	VI _A	VII _A		
	ns ² The Alkaline Earth	III _B	IV _B	V _B	VI _B	VII _B		VIII _B	I _B	II _B		Lewis Acids	Group of carbone	Lewis Basis	The Chalcogens	The Halogens	The Noble Gases	
		The transition elements $ns^2(n-1)d^x$ $1 \leq x \leq 10$																
Block S	La	Ac	Block d								Block p (ns^2np^x) $1 \leq x \leq 6$							
			Lanthanides (4f) Actinides (5f)										Block f					

Exemples :

Rather than ${}_{24}\text{Cr} : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$, Cr's electronic configuration is :



Rather than ${}_{64}\text{Gd} : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^8$, Gd's E.C is



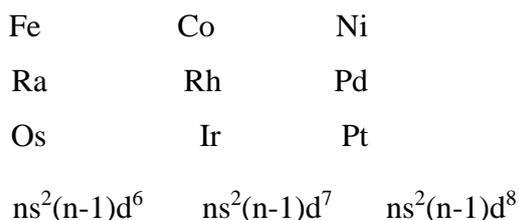
Exception of Aufbau Principle in Transition Elements

Element	Symbol	Atomic number	Aufbau's prediction	Experimental observed
Chromium	Cr	24	[Ar] 4s ² 3d ⁴	[Ar] 4s ¹ 3d ⁵
Copper	Cu	29	[Ar] 4s ² 3d ⁹	[Ar] 4s ¹ 3d ¹⁰
Niobium	Nb	41	[Kr] 5s ² 4d ³	[Kr] 5s ¹ 4d ⁴
Molybdenum	Mo	42	[Kr] 5s ² 4d ⁴	[Kr] 5s ¹ 4d ⁵
Ruthenium	Ru	44	[Kr] 5s ² 4d ⁶	[Kr] 5s ¹ 4d ⁷
Rhodium	Rh	45	[Kr] 5s ² 4d ⁷	[Kr] 5s ¹ 4d ⁸
Palladium	Pd	46	[Kr] 5s ² 4d ⁸	[Kr] 4d ¹⁰
Silver	Ag	47	[Kr] 5s ² 4d ⁹	[Kr] 5s ¹ 4d ¹⁰
Platinum	Pt	78	[Xe] 6s ² 4f ¹⁴ 5d ⁸	[Xe] 6s ¹ 4f ¹⁴ 5d ⁹
Gold	Au	79	[Xe] 6s ² 4f ¹⁴ 5d ⁹	[Xe] 6s ¹ 4f ¹⁴ 5d ¹⁰

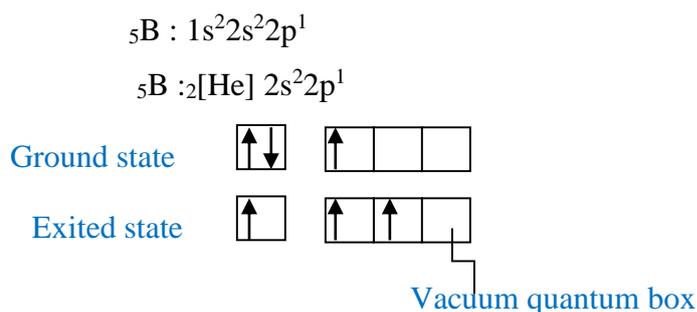
Exception of Aufbau Principle in Lanthanide and Actinide

Element	Symbol	Atomic number	Aufbau's prediction	Experimentally observed
Lanthanum	La	57	[Xe] 6s ² 4f ¹	[Xe] 6s ² 5d ¹
Cerium	Ce	58	[Xe] 6s ² 4f ²	[Xe] 6s ² 4f ¹ 5d ¹
Gadolinium	Gd	64	[Xe] 6s ² 4f ⁸	[Xe] 6s ² 4f ⁷ 5d ¹
Actinium	Ac	89	[Rn] 7s ² 5f ¹	[Rn] 7s ² 6d ¹
Thorium	Th	90	[Rn] 7s ² 5f ²	[Rn] 7s ² 6d ²
Protactinium	Pa	91	[Rn] 7s ² 5f ³	[Rn] 7s ² 5f ² 6d ¹
Uranium	U	92	[Rn] 7s ² 5f ⁴	[Rn] 7s ² 5f ³ 6d ¹
Neptunium	Np	93	[Rn] 7s ² 5f ⁵	[Rn] 7s ² 5f ⁴ 6d ¹
Curium	Cm	96	[Rn] 7s ² 5f ⁸	[Rn] 7s ² 5f ⁷ 6d ¹
Lawrencium	Lr	103	[Rn] 7s ² 5f ¹⁴ 6d ¹	[Rn] 7s ² 5f ¹⁴ 7p ¹

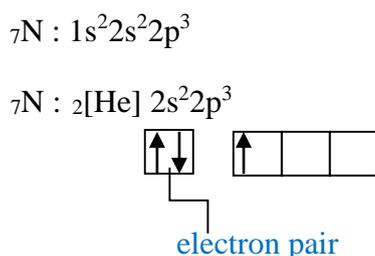
- ✓ **Group VIII_B** is called Triad. It is composed of elements which share similar chemical and physical characteristics. They are found adjacent to each other in period 4 of the periodic table.



- ✓ **Group III_A** is called **Lewis Acids**, which are electron pair *acceptors*.

Example:

- ✓ **Group V_A** is called **Bases Acids**, which are electron pair *donors*.

Example :

- ✓ **Group VII_A** is called **The Halogens**: include fluorine, chlorine, bromine, and iodine. Astatine is also in the group, but is radioactive and will not be considered here. They are strong oxidizing agents and are readily reduced to the X^- ions, and so the halogens form numerous ionic compounds.
- ✓ **Group O is the Noble Gases** : are the naturally occurring members of column 18 of the periodic table: helium (He), neon (Ne), argon (Ar), krypton (Kr), xenon (Xe), and radon (Rn). All the orbitals in the valence shell of the noble gases are completely filled by electrons and it is very difficult to alter this stable arrangement by the addition or removal of electrons.

1.2. Classification in Blocks

In yet another classification, the long form of the periodic table has been divided into four blocks (i.e. s, p, d and f), depending upon the subshell to which the last electron enters.

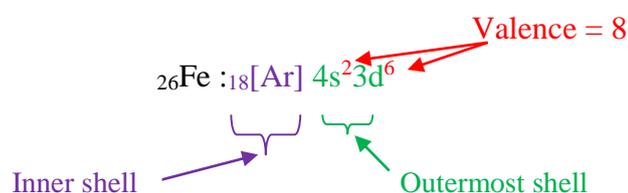
- **s-block elements**: The elements of Group 1 (alkali metals) and Group 2 (alkaline earth metals) which have ns^1 and ns^2 outermost electronic configuration belong to the *s*-Block Elements.
- **p-block elements**: The ***p*-Block Elements** comprise those belonging to Group 13 to 18 and these together with the *s*-Block Elements are called the Representative Elements or Main Group Elements. The outermost electronic configuration varies from ns^2np^1 to ns^2np^6 in each period. At the end of each period is a noble gas element.
- **d-block elements**: These are the elements of Group 3 to 12 in the center of the Periodic Table. These are characterised by the filling of inner *d* orbitals by electrons and are therefore referred to as *d*-Block Elements. These elements have the general outer electronic configuration $(n-1)d^{1-10}ns^{0-2}$.
- **f-block elements**: The two rows of elements at the bottom of the Periodic Table, called the Lanthanoids, Ce ($Z = 58$) – Lu ($Z = 71$) and Actinoids, Th ($Z = 90$) – Lr ($Z = 103$) are characterised by the outer electronic configuration $(n-2)f^{1-14} (n-1)d^{0-1}ns^2$. The last electron added to each element is filled in *f*- orbital.

2. Position of Elements in the Periodic Table

2.1. Outermost shells: The outermost shell is known as the valence shell, and the electrons found in it are called valence electrons. If the outer shell of an atom has less than its maximum number of electrons, then it will not be stable. It will react with other atoms to get a full outer shell.

2.2. Inner shell electrons are any electrons not in the outermost shell and they are **the core electrons**.

2.3. Valency : The valency of an element is determined by the number of valence electrons present in the outermost shell of its atom. It determines the kind and number of bonds formed by an element.

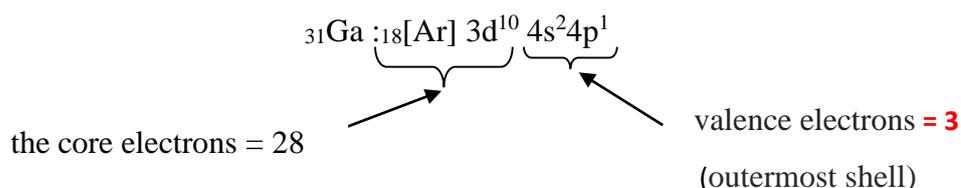
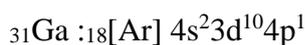


Valence is the number of electrons an atom must lose or gain to attain the nearest noble gas or inert gas electronic configuration. **“Electrons in the outer shells that are not filled”**.

Since **filled *d* or *f*** subshells are seldom disturbed in a chemical reaction, we can define valence electrons as follows: **The electrons on an atom that are not present in the previous rare gas, ignoring filled *d* or *f* subshells.**

Exemple

Gallium therefore has three valence electrons.



Exercise 1

- What neutral elements have each electron configuration below?
 - $1s^2 2s^2 2p^3$
 - $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
 - $[\text{Ne}] 3s^2 3p^3$
 - $[\text{Kr}] 5s^2 4d^5$
- How many core and valence electrons are in each atom above?

❖ Electron Configurations and the Periodic Table

- The subshell, to which the last electron enters in the electronic distribution, defines the block of the element.
- An element belongs to **A list** if the subshell that receives the last electron in the electron configuration is **p or s**.
- An element belongs to **B list** if the subshell that receives the last electron in the electron configuration is **d or f**.

Example : oxygen electronic configuration is : ${}_8\text{O} : 1s^2 2s^2 2p^4$

The last electron enters in the subshell p, so oxygen belongs to p-block and group **A**.

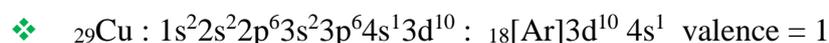
- The group of an element is determined by the number of valence electrons.
- The period corresponds to the largest principal quantum number n in the electron configuration.
- The column represents the total number of electrons that come after the noble gas.

Example :

The largest principal quantum number $n = 3$

The last electron enters the subshell s (liste A)

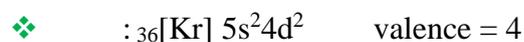
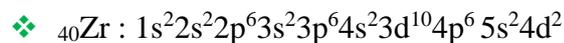
So, Mg belongs to the s-block, group IIA, and the 3rd period, column 2.



The largest principal quantum number $n = 4$

The last electron enters the subshell d (liste B)

So, Cu belongs to the d-block, group IB, and the 4th period, column 11.



The largest principal quantum number $n = 5$

The last electron enters in the subshell d (liste B)

So Zr belongs to the d-block and group IVB and the 5th period and column 4.

Exercise 2

- What is the position of the element in the periodic table satisfying the electronic configuration $(n-1)d^1 ns^2$ for $n=4$?
- Germanium Ge belongs to the column of ${}_6\text{C}$ and the period of ${}_{19}\text{K}$. Determine :
 1. Its position in the periodic table.
 2. Its atomic number.
 3. Describe the valence shell (number of electron pairs, single electrons and empty quantum box).
 4. Determine the four quantum numbers of the valence electrons.

Exercise 3

An element has fewer than 18 electrons and has two free electrons.

- What are the possible electronic distributions?
- What is the formula of this element, knowing that it belongs to the ${}_{50}\text{Sn}$'s group and the ${}_3\text{Li}$'s period?

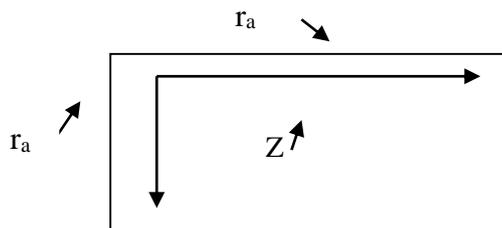
III- Evolution and periodicity of the physico-chemical properties of the elements

The position of an element in the Periodic Table reveals its chemical reactivity.

IV- Calculation of radii (atomic and ionic)

- Atomic radius decreases from left to right across a period due to increasing Z because of the nucleus charge increases as Z increases.

- Atomic radius increases down a column of the periodic table because the distance of the electron from the nucleus increases as n increases.

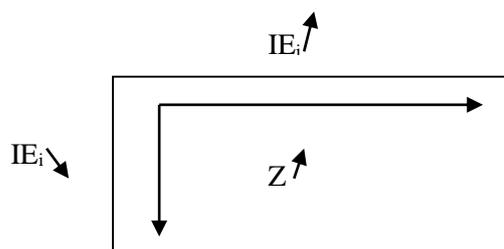


V- The successive ionization energie

Ionization energy (IE): minimum energy needed to remove an electron from an atom in the gas phase. In general, ionization energy increases as Z increases.



- IE_i increases from left to right across a period due to increasing Z .
- IE_i decreases down a column of the periodic table because the distance of the electron from the nucleus increases as n increases.

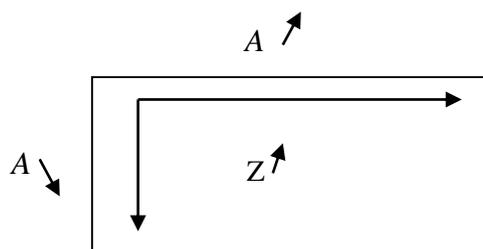


VI- Electron affinity and electronegativity (Mulliken scale) by Slater's rules

Electron Affinity (A): energy released when an atom in the gas phase accepts an electron.



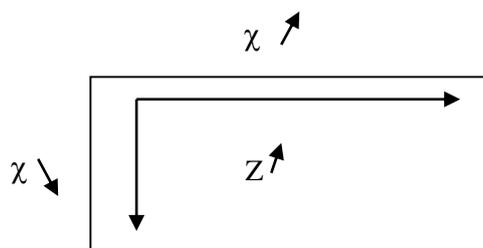
- A increases from left to right across a period due to increasing Z .
- A decreases down a column of the periodic table because the distance of the electron from the nucleus increases as n increases.



Electronegativity (χ)

A chemical property that describes the tendency of an atom or a functional group to attract electrons toward itself.

- χ increases from left to right across a period due to increasing Z .
- χ decreases down a column of the periodic table.

**VII- Metals and Nonmetals**

The metal elements are found on the left-hand side of the periodic table, and the non-metal elements are found on the right.

The following table presents some physical properties of metals and nonmetals.

Metals	Nonmetals
High electrical conductivity that decreases with increasing temperature	Poor electrical conductivity (except carbon in the form of graphite)
High thermal conductivity	Good heat insulators (except carbon in the form of diamond)
Metallic gray or silver luster*	No metallic luster
Almost all are solids‡	Solids, liquid, or gases
Malleable (can be hammered into sheets)	Brittle in solid state
Ductile (can be drawn into wires)	Nonductile

* Except copper and gold.

‡ Except mercury, cesium and gallium melt in a protected hand.

The table below present some chemical properties of metals and nonmetals.

Metals	Nonmetals
Outer shells contain few electrons, usually three or fewer.	Outer shells contain four or more electrons.*
Form cations (positive ions) by losing electrons.	Form anions (negative ions) by gaining electrons.
Form ionic compounds with nonmetals.	Form ionic compounds with metals† and molecular (covalent) compounds with other nonmetals.
In the solid state, metals are characterized by metallic bonding.	Exist as covalently bonded molecules; noble gases are monatomic.

* Except hydrogen and helium.

† Except the noble gases.

The majority of elements on the periodic table are metals. The metallic properties change as follows on the periodic table:

- Me decreases from left to right across a period due to increasing Z.
- Me increases down a column of the periodic table.