

Chapter IV - Periodic classification of elements

I-Introduction

The periodic table remains the primary tool for comparing chemical elements, as it helps explain the grouping of elements, their chemical properties, and their structural characteristics. The study of the electronic structure of atoms provides a deeper insight into the periodic classification of elements, commonly known as Mendeleev's periodic classification, which was established in 1869.

II-Mendeleïev's Periodic Classification

As the number of known chemical elements increased, 19th century chemists felt the need to order them. In 1869, D. Mendeleev classified the periodicity of the properties of 63 chemical elements known at that time in a table based on the ascending order of their atomic masses. This periodic table not only facilitates the comparison between elements but also has allowed for a better understanding of the relationship between chemical properties and their atomic structures

1 H 1.0079	2											13 B 10.811	14 C 12.011	15 N 14.007	16 O 15.999	17 F 18.998
3 Li 6.941	4 Be 9.0122											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453
11 Na 22.990	12 Mg 24.305	3	4	5	6	7	8	9	10	11	12	13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.065	17 Cl 35.453
19 K 39.098	20 Ca 40.078	?	22 Ti 47.867	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.845	27 Co 58.933	28 Ni 58.693	29 Cu 63.546	30 Zn 65.39	?	?	33 As 74.922	34 Se 78.96	35 Br 79.904
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	?	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.76	52 Te 127.60	53 I 126.90
55 Cs 132.91	56 Ba 137.33	?	?	73 Ta 180.95	74 W 183.84	75 Re 186.21	76 Os 190.23	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	?	?

Figure I: Periodic Table of D. Mendeleev in 1869

III-Modern periodic classification

At present, the modern classification is based on the ascending order of the atomic number Z . Periodic classification is based on Pauli's exclusion principle, Hund and Klechkowski's rules.

MODERN PERIODIC TABLE

Legend:

- Alkali Metals
- Alkaline Earth Metals
- Transition Metals
- Post-transition Metals
- Reactive Nonmetals
- Noble Gases
- Alkali Metals
- Actinides
- Lanthanides
- Unknown Properties

Atomic Number, Atomic Mass, Name, Average Atomic Mass

57 138.906 La LANTHANUM

Figure III-1: Modern Periodic Table

The periodic table is described as follows:

1-Blocks: Elements are placed in three blocks:

Block (S): Corresponds to the filling of the subshell (ns). The s-block consists of elements found in columns 1 (alkali metals) and 2 (alkaline earth metals) of the periodic table, as well as hydrogen and helium. They are called so because their highest (in energy) occupied orbital is of type s.

Block (P): Corresponds to the filling of the subshell (np). The p-block consists of elements found in columns 13 to 18 of the periodic table. They are called so because their highest (in energy) occupied orbital is of type p. This block includes the icosagens (column 13), the crystallogens (column 14), the pnictogens (column 15), the chalcogens (column 16), the halogens (column 17), and the noble gases (column 18), excluding helium.

Block (d): Corresponds to the filling of the subshell ((n-1) d). The d-block consists of elements found in columns 3 to 12 of the periodic table. They are called so because the highest (in energy) occupied orbital is of type d.

Block (f): Corresponds to the filling of the subshell ((n-2) f). The f-block consists of internal transition elements of the periodic table: the lanthanides and actinides. They are called so because the highest (in energy) occupied orbital of these atoms is of type f.

Figure III-2: Different Blocks of the Periodic Table

Periods (Rows): A period corresponds to an electron shell identified by its principal quantum number denoted as (n). There are seven electron shells known in the ground state, hence seven periods.

Groups (Columns): There are eighteen columns, including Eight in subgroup A ten in subgroup B Elements of the same family have the same number of valence electrons; the family number corresponds to the number of valence electrons. Each subgroup consists of 8 groups, as shown in Figure. The group is symbolized by Roman numerals (I-VIII). By definition, the group represents the valence electrons

All elements in the same period have the same core electron configuration.

All the elements in the same column have the same valence electron configuration.

These two classifications, which are not very different from each other, are presented in the form of a table containing 7 rows (period) and, depending on their external structure, these elements are classified in 18 columns.

1A	2A		3	4	5	6	7	8	9	10	11	12		13	14	15	16	17	18
			3B	4B	5B	6B	7B	8B	9B	10B	11B	12B		3A	4A	5A	6A	7A	8A
1s ²																			
2s ²														2p ¹	2p ²	2p ³	2p ⁴	2p ⁵	2p ⁶
3s ²														3p ¹	3p ²	3p ³	3p ⁴	3p ⁵	3p ⁶
4s ¹	4s ²		3d ¹	3d ²	3d ³	3d ⁴	3d ⁵	3d ⁶	3d ⁷	3d ⁸	3d ⁹	3d ¹⁰		4p ¹	4p ²	4p ³	4p ⁴	4p ⁵	4p ⁶
5s ¹	5s ²		4d ¹	4d ²	4d ³	4d ⁴	4d ⁵	4d ⁶	4d ⁷	4d ⁸	4d ⁹	4d ¹⁰		5p ¹	5p ²	5p ³	5p ⁴	5p ⁵	5p ⁶
6s ¹	6s ²		5d ¹	5d ²	5d ³	5d ⁴	5d ⁵	5d ⁶	5d ⁷	5d ⁸	5d ⁹	5d ¹⁰		6p ¹	6p ²	6p ³	6p ⁴	6p ⁵	6p ⁶
7s ¹			6d ¹	6d ²	6d ³	6d ⁴	6d ⁵	6d ⁶	6d ⁷	6d ⁸	6d ⁹	6d ¹⁰		7p ¹	7p ²	7p ³	7p ⁴	7p ⁵	7p ⁶
			4f ¹	4f ²	4f ³	4f ⁴	4f ⁵	4f ⁶	4f ⁷	4f ⁸	4f ⁹	4f ¹⁰	4f ¹¹	4f ¹²	4f ¹³	4f ¹⁴			
			5f ¹	5f ²	5f ³	5f ⁴	5f ⁵	5f ⁶	5f ⁷	5f ⁸	5f ⁹	5f ¹⁰	5f ¹¹	5f ¹²	5f ¹³	5f ¹⁴			

Figure III-2: Periodic Table Groups and Periods

The 18 columns of the periodic table are divided into groups. The group contain 2 subgroups:

An element belongs to subgroup A if the valence electrons are distributed in the subshell (ns^x), ($ns^x np^y$), or $ns^x (n-1)d^{10} np^y$, with x and y different from 0.

An element belongs to subgroup B if its valence electrons are distributed in the shell $ns^2(n-1)d^x np^0$, with x ranging from 1 to 10, or $ns (n-2) f (n-1) d np^0$. (the f subshell appears from $n=6$ onwards).

Subgroup A

Group I: ns^1

Group II: ns^2

Group III: $ns^2 np^1$

Group IV: $ns^2 np^2$

Group V: $ns^2 np^3$

Group VI: $ns^2 np^4$

Group VII: $ns^2 np^5$

Group VIII: (noble gas): $ns^2 np^6$

Subgroup B

Group I: $(n-1)d^{10} ns^1$

Group II: $(n-1)d^{10} ns^2$

Group III: $(n-1)d^1 ns^2$

Group VI: $(n-1)d^2 ns^2$

Group V: $(n-1)d^3 ns^2$

Group VI: $(n-1)d^4 ns^2$

Group VII: $(n-1)d^5 ns^2$

Group VIII(Triade): $(n-1)d^x ns^2$

Example for Elements of Subgroup A(Main Group Elements):

column	group	Electron Configuration
1	IA	ns^1
2	IIA	ns^2
13	IIIA	$ns^2 np^1$
14	IVA	$ns^2 np^2$
15	VA	$ns^2 np^3$
16	VIA	$ns^2 np^4$
17	VIIA	$ns^2 np^5$
18	VIIIA	$ns^2 np^6$

Example for Elements of Subgroup B (Transition Elements):

column	group	Electron Configuration
3	IIIB	[Ar]4s ² 3d ¹
4	IVB	[Ar]4s ² 3d ²
5	VB	[Ar]4s ² 3d ³
6	VIB	[Ar]4s ¹ 3d ⁵ (Cr exception)
7	VIIB	[Ar]4s ² 3d ⁵
8	VIIIB	[Ar]4s ² 3d ⁶
9	IXB	[Ar]4s ² 3d ⁷
10	XB	[Ar]4s ² 3d ⁸
11	IB	[Ar]4s ¹ 3d ¹⁰ (Cu exception)
12	IIB	[Ar]4s ² 3d ¹⁰

Example: determine the group, subgroup for the following elements

Element	Electronic configuration	Valence Electrons	Period	Group/subgroup
¹¹ Na	1S ² 2S ² 2p ⁶ <u>3S¹</u>	1	3	I _A
¹⁸ Ar	1S ² 2S ² 2p ⁶ <u>3S²3p⁶</u>	8	3	VIII _A
²² Ti	1S ² 2S ² 2p ⁶ 3S ² 3p ⁶ <u>4S²3d²</u>	4	4	IV _B
²⁵ Mn	1S ² 2S ² 2p ⁶ 3S ² 3p ⁶ <u>4S²3d⁵</u>	7	4	VII _B
²⁶ Fe	1S ² 2S ² 2p ⁶ 3S ² 3p ⁶ <u>4S²3d⁶</u>	8	4	VIII _B Triades
³⁰ Zn	1S ² 2S ² 2p ⁶ 3S ² 3p ⁶ <u>4S²3d¹⁰</u>	2	4	II _B
³⁵ Br	1S ² 2S ² 2p ⁶ 3S ² 3p ⁶ 4S ² 3d ¹⁰ 4p ⁵	7	4	VII _A
⁴² Mo	1S ² 2S ² 2p ⁶ 3S ² 3p ⁶ 3d ¹⁰ 4S ² 3d ¹⁰ <u>5s¹4d⁵</u>	6	5	VI _B
⁴⁷ Ag	1S ² 2S ² 2p ⁶ 3S ² 3p ⁶ 4S ² 3d ¹⁰ 4p ⁶ <u>5s¹4d¹⁰</u>	1	5	I _B

2-Element Families

The periodic table is divided into several families, each consisting of elements whose atoms share the same valence shell configuration. The principal families of the periodic table include:

Alkali Metals Family (Column 1): Group IA, with an electron configuration of the type ns^1 .

Alkaline Earth Metals Family (Column 2): Group IIA, with an electron configuration of ns^2 .

Halogens Family (Column 17): Group VIIA, with an electron configuration of ns^2np^5 .

Noble Gases Family (Column 18): Group VIIIA, with an electron configuration of ns^2np^6 .

Metalloids (Semiconductors) Family: These elements form a boundary that separates metals and non-metals. It includes all elements from the 13th column to the 18th column. These elements share properties with non-metals but conduct electric current to varying degrees. Examples include Si, Ge, As, and Sb.

Transition Elements Family (Columns 3 to 12): These elements have incompletely filled (d) orbitals.

Rare Earth Elements Family: Involves f-orbital elements, with two types in this family: Lanthanides, corresponding to elements in the 6th period with $57 \leq Z \leq 71$, and Actinides, concerning atoms in the 7th period with $89 \leq Z \leq 103$.

Alkali metals	Alkaline earth metals	Transition metals										Boron family	Carbon family	Nitrogen family	Oxygen family	Halogens	Noble gases
		Inner transition metals															

Figur III-2: Families of the periodic table

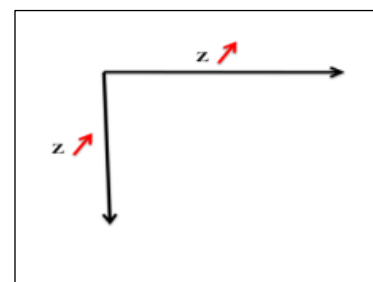
IV- Evolution And Periodicity of Physico-Chemical Properties

IV-1-Variation in protons number Z

On a row of the classification, number of proton

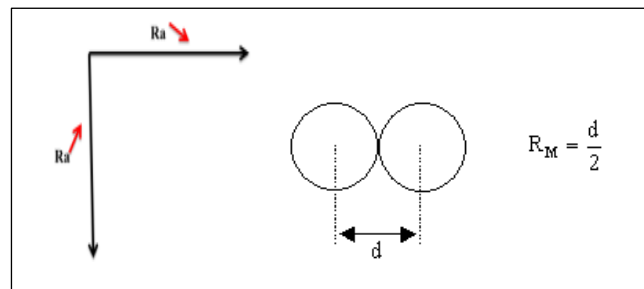
Z increases regularly from left to right.

In the same column, Z increases from top to bottom.



IV-2-Atomic radius

The atomic radius is the covalent radius,
It is defined as the half-distance between
the nuclei of two adjacent atoms.



When the atomic number Z increases over a period, the atomic radius decreases.

In a group: when the atomic number Z increases, the atomic radius increases.

And as the quantum number n main orbitals valence increases, the size of the orbitals increases

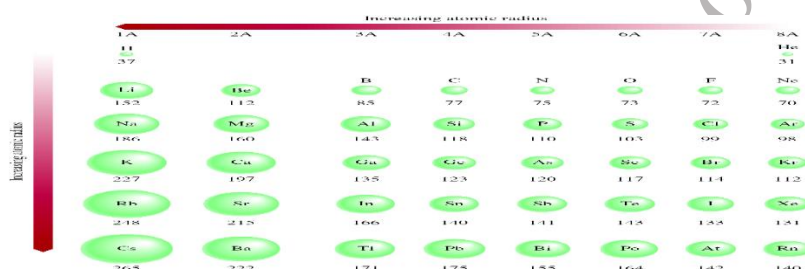


Figure IV-2: evolution of atomic radius

IV-3-Ionic radius

The ionic radius characterises the volume occupied by the electrons in the electron cloud, except that for ions, the number of electrons differs from the neutral form, which explains two opposite phenomena: for cations, this radius is always smaller than the positive charge and will be smaller than the atomic radius of the atom.

Conversely, for anions, which are negatively charged and have more electrons, the ionic radius will be greater than the atomic radius, and the greater the charge, the greater the ionic radius.

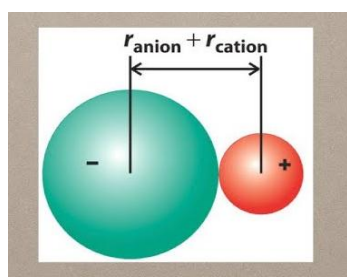
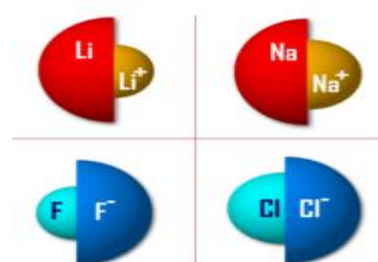


Figure IV-3: Ionic radius for cations and anions

IV-4-Ionisation energy I

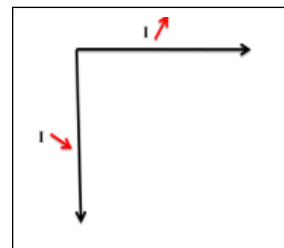
This is the energy required to remove an electron from an atom or ion in the gaseous state:

 **In one period:**

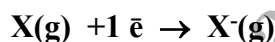
the peripheral electrons are harder to pull off
as Z increases, because the attractive force
of the nucleus increases, so if Z increases, EI increases.

 **In a group:**

Ionisation energy EI decreases as Z increases, as we move from the n layer to the $(n+1)$ layer, so the peripheral electrons are further away from the nucleus.

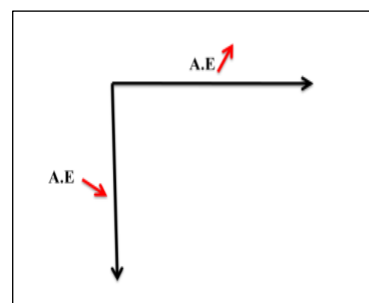
**IV-5-Electron affinity AE**

The electron affinity **AE** is the amount of energy associated when an atom in the gas phase captures an electron



In a period, when Z increases, A increases (in absolute value). There are several exceptions to this rule. The variation in A as a function of Z can be explained by a variation in inter-electron repulsion depending on the electronic configuration.

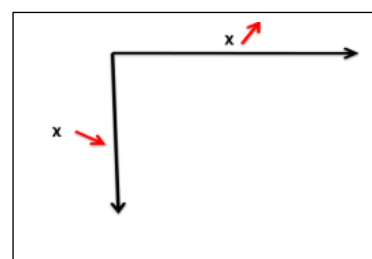
In a group, AE generally decreases (in absolute value)
as Z increases because the added electron has to occupy
an orbital further and further away from the nucleus.

**IV-6-Electronegativity (χ)**

Electronegativity is the ability of an element to attract an electron.

In a period: χ increases as you move to the right,

In a group: χ decreases as you move downwards.



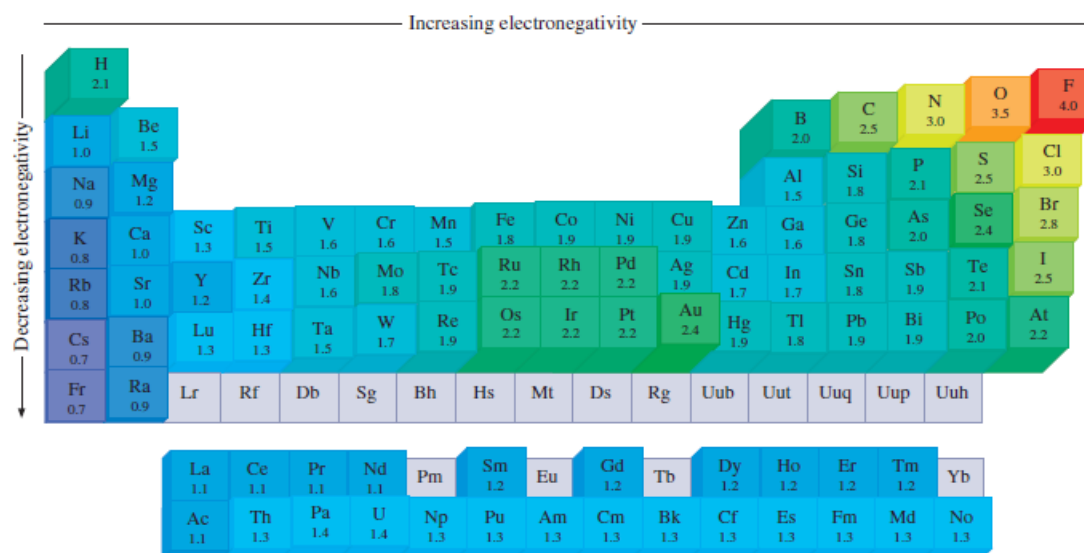


Figure IV-6: Electronegativities of elements

IV-6-1-Mulliken scale

Mulliken originally defined electronegativity as the average of an element's first ionization energy and its electron affinity. A highly electronegative element tends to attract electrons strongly, meaning it requires a large amount of energy to remove an electron (high ionization energy) but readily gains one.

The electronegativity of an atom of a chemical element involved in a chemical bond is given by the relationship:

IV-6-2-Slater model

Slater's model is a simple model which allows us to calculate average charges, actually perceived by the electrons (taking into account the charge of the nucleus and those of the other electrons, the latter eclipsing the nucleus).

From these effective charges, we can calculate the energy levels of the atomic orbitals and the electronic energies of atoms in their ground state.

Consider an atom whose nucleus has a charge Z . Consider the attraction between the Z protons in the nucleus and any electron E in the atom.

The attraction is disturbed by the electrons located between the nucleus and electron E .

These electrons form a **screen**. We then define a screen constant that depends on the position of the atom's electrons relative to electron E

- ✚ The charge Z of the nucleus of the atom then becomes an effective charge $Z^* < Z$ relative to the electron E :

$$Z^* = Z - \sigma = Z - \sum \sigma_i$$

where σ is called the screen constant.

Note!

The effective charge Z^* depends on the electron for which the calculations are being made.

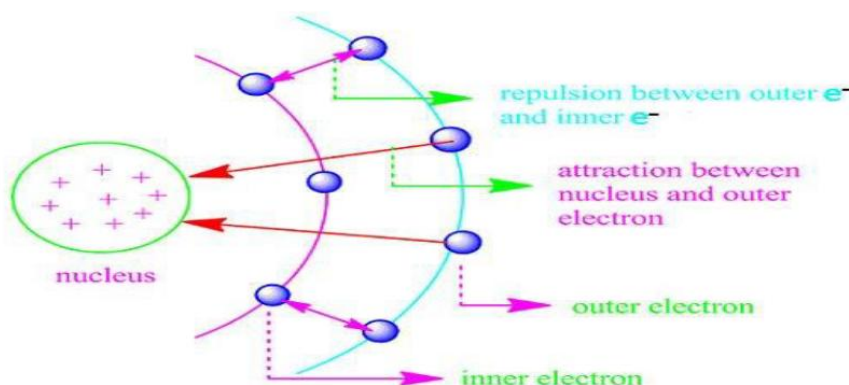


Figure IV-6-2: Representation of Slater's Rule

IV-6-3-Calculation of the effective charge Z^*

1- Write down the electronic configuration of the element and order it according to: (1s) (2s,2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p)...

2- Choose the electron for which we are looking for the effective charge. All the other electrons will make a partial contribution σ_i to the total screen constant σ .

This contribution depends on:

- the type of orbital (s, p), (d) or (f) of the electron,
- the electron's electronic layer n .

3- The value of σ_i is summarised in the following table:

		e_j							
		1s	2s,2p	3s,3p	3d	4s4p	4d	4f	5s,5p
e_i	1s	0.31	0	0	0	0	0	0	0
	2s,2p	0.85	0.35	0	0	0	0	0	0
	3s,3p	1	0.85	0.35	0	0	0	0	0
	3d	1	1	1	0.35	0	0	0	0
	4s4p	1	1	0.85	0.85	0.35	0	0	0
	4d	1	1	1	1	1	0.35	0	0
	4f	1	1	1	1	1	1	0.35	0
	5s,5p	1	1	1	1	0.85	0.85	0.85	0.35

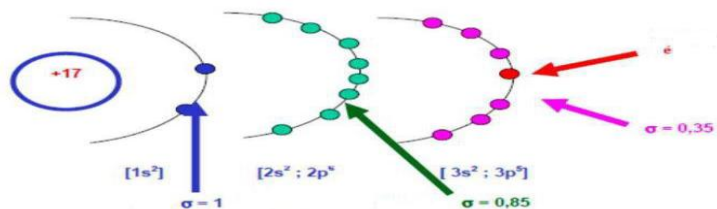
Examples: Calculate the effective atomic number of: ${}_6\text{C}$ and ${}_{17}\text{Cl}$

${}_6\text{C}$: $1s^2 2s^2 2p^2$

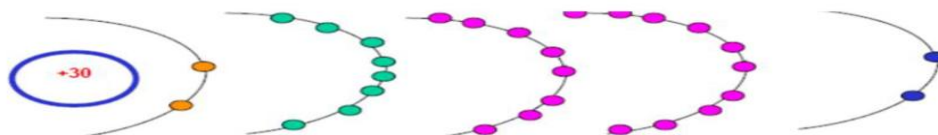
$$Z_{\text{eff}} = 6 - (3 \times 0,35 + 2 \times 0,85) \Rightarrow z_{\text{eff}} = 3,25$$

${}_{17}\text{Cl}$: $[1s^2] ; [2s^2 ; 2p^6] ; [3s^2 ; 3p^5]$

$$Z_{\text{eff}} = 17 - (6 \times 0,35) - (8 \times 0,85) - (2 \times 1) = 6,1$$



$\text{Zn} : Z = 30 : [1s^2] ; [2s^2 ; 2p^6] ; [3s^2 ; 3p^6] ; [3d^{10}] ; [4s^2]$



$$Z^* 4s = 30 - (1 \times 0,35) - (18 \times 0,85) - (8 \times 1) - (2 \times 1) = 4,35$$

$$Z^* 3d = 30 - (9 \times 0,35) - (8 \times 1) - (8 \times 1) - (2 \times 1) = 8,85$$

$$Z^* 3s 3p = 30 - (7 \times 0,35) - (8 \times 0,85) - (2 \times 1) = 18,75$$