ATOMIC STRUCTURE

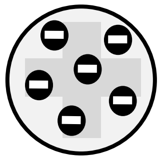
Democritus, ancient Greece: “All matter is made of tiny invisible particles, atoms.”

Dalton’s atomic theory, 1807

- All elements are made of very small particles called atoms. (atomos (gr.) = indivisible)
- Atoms cannot be created, destroyed or divided.
- Atoms of the same element are identical but differ in mass from those of other elements.
- Atoms form compounds by combining chemically in simple whole number ratios

1. *Which of the Dalton`s statements is not correct?*

Thomson’s model of the atom, 1899



The discovery of the .... by Thomson, 1897 led to the introduction of Thomson’s model.

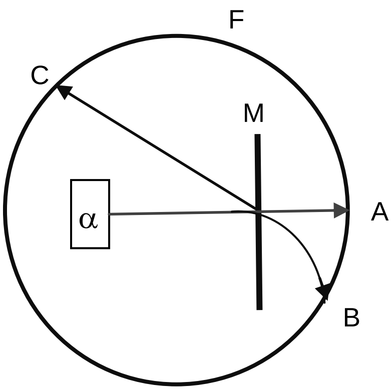
Atoms consist of negative electrons placed in a sphere of positive charge. The negative and positive charges balance → atoms are ....

The discovery of the nucleus, 1909

Geiger and Marsden bombarded a thin metal foil with α particles (He^{2+} ions).

Most of the α- particles passed straight through the foil or were very slightly deflected.

Some of the α particles were reflected $\Rightarrow$ they collided with a particle of a .... mass and a .... charge, it means with the ....



α =

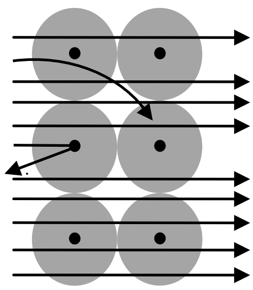
M = a thin metal foil (10^4 atoms thick)

F = fluorescent screen

A =

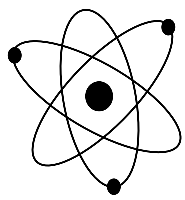
B =

C =



http://www.mhhe.com/physsci/chemistry/essentialchemistry/flash/ruther14.swf

Rutherford’s model, 1911



The mass of the atom concentrated in the .... charged ....

Negative electrons move around the nucleus in .... trajectories.

The attractive force is balanced by the .... force.

Electrons behave according to .... principles → planetary model.

TENTO PROJEKT JE SPOLUFINANCOVÁN EVROPSKÝM SOCIÁLNÍM FONDEM A STÁTNÍM ROZPOČTEM ČESKÉ REPUBLIKY

The discovery of the .... by Chadwick, 1932

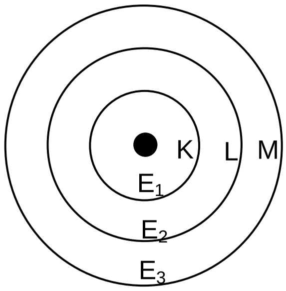
Bohr's model, 1913

Rutherford's model did not conform to physical laws. When circulating the electron emits electromagnetic radiation, its energy would decrease; the electron would get closer and closer to the nucleus.

2. *What would finally happen?*

Bohr suggested that:

- The electron moves around the nucleus along fixed paths, or orbits.
- The electron can emit or absorb energy only when it falls or when it is raised to another energy level.



$E_1 < E_2 < E_3 < \dots$

Bohr's equation: $E = - b/n^2$,

for hydrogen: $b = 2.18 \times 10^{-18}$ J

n = the number of the orbit

The electron can exist only in states with certain energy and it can change it only by certain amounts. However, Bohr's model and equation is correct for atoms with one electron only (H, He^+, Li^{2+}).

ELECTRONIC STRUCTURE

Quantum mechanics, 1925 – 1927

Electrons have both :

- **particle properties**, e.g. rest mass
- **wave properties**, e.g. diffraction of a beam of electrons

⇒ **wave - particle duality** of an electron

- It is impossible to fix both the position of an electron in an atom and its energy (Heisenberg's uncertainty principle)
- It is possible to calculate the probability of finding an electron with a given E within a given space (Schrödinger's equation).
- The energy of an electron is quantizied - can reach certain values only.
- The region in an atom with the greatest probability to find an electron with a certain (allowed) value of energy is called **ORBITAL** (region with a high electron density).

Quantum numbers

For the wave description of the electron in an atom we need three numbers: ***n, l, m***. They are all integers, but their values cannot be selected randomly.

TENTO PROJEKT JE SPOLUFINANCOVÁN EVROPSKÝM SOCIÁLNÍM FONDEM A STÁTNÍM ROZPOČTEM ČESKÉ REPUBLIKY

1. The principal quantum number, *n* = 1, 2, 3,…

It determines the **energy** of an electron, it is also the measure of the size of an orbital. Two electrons with the same value of *n* are said to be in the same **electron shell**.

n	1	2	3	4	5	6	7
name of the shell							

2. The subsidiary quantum number, l = 0, 1, 2,…, n-1

The electrons of a given shell can be grouped into subshells; each characterized by a different value of **l** corresponding to a different **orbital shape**. The value of ***n*** limits the values of ***l***.

n = 1 ⇒ ***l*** = ... ⇒ ..... subshell(s) in the ***n*** = 1 shell

n = 2 ⇒ ***l*** = ... ⇒ ..... subshell(s) in the ***n*** = 2 shell

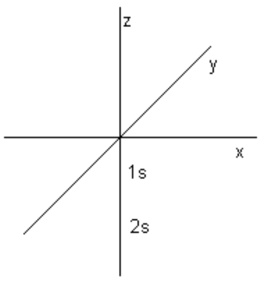
n = 3 ⇒ ***l*** = ... ⇒ ..... subshell(s) in the ***n*** = 3 shell

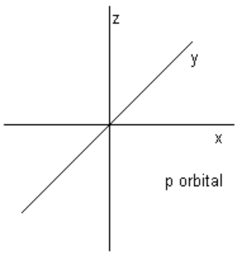
l	0	1	2	3
label of the subshell				

s orbitals … spherical shape

p orbitals … dumb-bell shaped

d orbitals … more complex shape



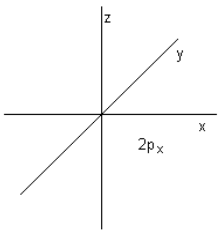


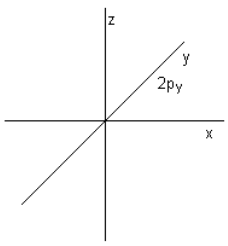
3. The magnetic quantum number, m = {-l,…,0,…,l}

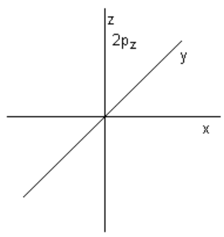
Orbitals in a given subshell differ only in their **orientation** in space. The number of values of *m* for a given subshell (= 2*l* + 1) specifies the number of orientations that exist for the orbitals of that subshell and thus the number of orbitals in the subshell.

s orbital: *l* = 0 ⇒ *m* = {….}, ... value ⇒ only .... *s* orbital in each shell

p orbitals: *l* = 1 ⇒ *m* = {............}, ... values ⇒ .... *p* orbitals: p_x, p_y, p_z







d orbitals: l = 2 ⇒ m = {..................}, …. values ⇒ .... *d* orbitals

f orbitals: l = 3 ⇒ m = {...........................}, …. values ⇒ .... *f* orbitals

The orbitals with the same values of **n** and **l** = **degenerated orbitals**. They have the same energy.

HW: Try to make out models of orbitals using such materials as paper, balloons, plasticine, cork,...

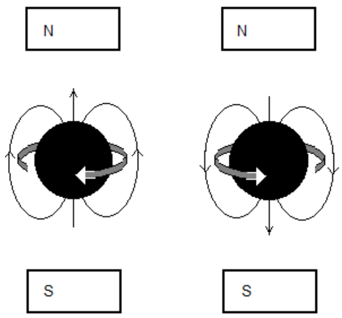
3. *Complete the following statements:*
   a. *When n = 2, the values of l can be ___ and ___.*
   b. *When l = 1, the values of m can be ___, ___, and ___, and the subshell has the letter label ___.*
   c. *When l = 2, the subshell is called a ___ subshell.*
   d. *When a subshell is labelled s, the value of l is ___ and m has the value ___.*
   e. *When a subshell is labelled p, ___ orbitals occur within the subshell.*
   f. *When a subshell is labelled f, there are ___ values of m, and ___ orbitals occur within the subshell.*
4. *What are the n and l values for each of the following orbitals: 6s, 4p, 5d, and 4f?*
5. *Which of the following sets of quantum numbers can belong to one electron?*
   a. *n=5, l=2, m=0*
   b. *n=4, l=-3, m=-3*
   c. *n=0, l= 0, m=0*
   d. *n=1, l=1, m=-1*
   e. *n=2, l=1, m=1*
   f. *n=1, l=2, m=2*
   g. *n=1, l=1, m=0*
   h. *n=0, l=-1, m=-1*
   i. *n=2, l=1, m=2*

<u>4. The **spin** number (spin), **s =** -1/2 or +1/2</u>

n, ***l***, ***m*** define an orbital for an electron.

s – spin number expresses the behaviour of an electron in a magnetic field. It is spinning either clockwise (*s* = ½) or counterclockwise (*s* = -½)

⇒ electrons are expressed as arrows pointing up (↑) or down (↓)



Pauli exclusion principle:

No two electrons in the same atom can have identical values for all four of their quantum numbers. The maximum number of electrons in any orbital is two and when there are two electrons in one orbital they have opposite spins.

The notation for two electrons in one orbital is: $\boxed{\uparrow\downarrow}$

6. *What is the maximum number of electrons in a completely filled set of:*
   a. *s-orbitals*
   b. *p-orbitals*
   c. *d-orbitals*
   d. *f-orbitals*

7. *What is the maximum number of electrons in the orbitals:*
   - *a. 3d*
   - *b. 4s*
   - *c. 4f*
   - *d. 5d*
   - *e. 5f*
   - *f. 1s*
8. *What is the maximum number of electrons for:*
   - *a. l = 0*
   - *b. l = 1*
   - *c. l = 2*
   - *d. n = 2*
   - *e. n = 4*

Filling the orbitals by electrons

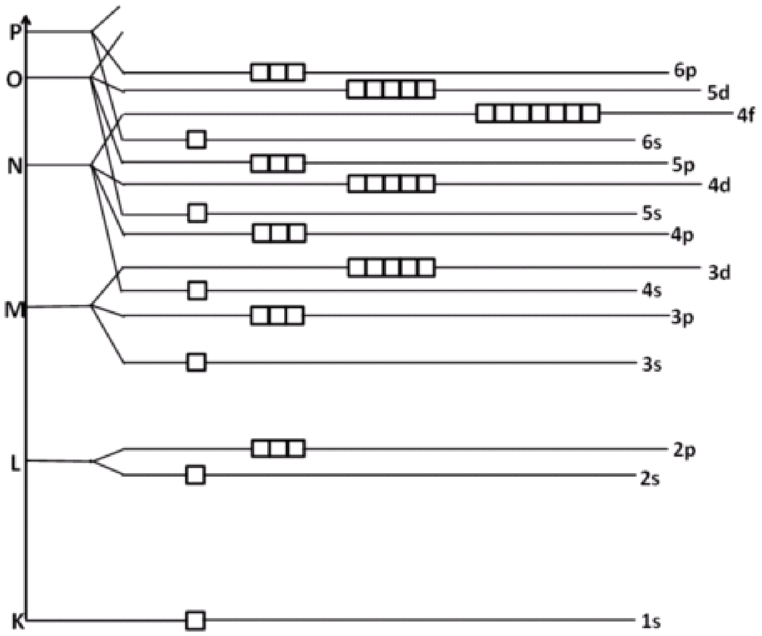
Aufbau (building up) principle

Electrons are assigned in such a way that the total energy of the atom is as low as possible.

- The energy increases with increasing principal quantum number.
- Energy within a shell increases with the increasing *l*.
- All the orbitals of a given subshell have the same energy = **degenerated orbitals**.

Energy level diagram for orbitals:

Orbitals are expressed as boxes, degenerated orbitals have the boxes connected.



7s …

6s 6p …

5s 5p 5d 5f …

4s 4p 4d 4f …

3s 3p 3d

2s 2p

1s

9. *Choose the orbital which is filled by electrons as the first one from the following triplets:*
   - *a. 3s , 3p, 4s*
   - *b. 4p, 3d, 5s*
   - *c. 4s, 3d, 3p*
   - *d. 6p, 7s, 5d*
   - *e. 2s, 2p, 3s*
   - *f. 7d, 8s, 7p*
   - *g. 4f, 6p, 5d*
   - *h. 6f, 7d, 8p*
   - *i. 6p, 7s, 4f*
10. *What is the maximum of electrons in the fourth shell if the last orbital which is filled is:*
    - *a. s-orbital in the shell with the principal quantum number 6?*
    - *b. s-orbital in the shell with the principal quantum number 5?*

Hund's rule

When electrons are placed in a set of orbitals of equal energy, they are spread out as much as possible to give as few paired electrons as possible. The unpaired electrons have the same spin.

11. *Decide which from the notations below is correct:*

a. | ↓↑ | ↓↑ | ↑ | ↑ | ↑ |

b. | ↓↑ | ↓ | |

c. | ↓ | ↓ | ↓ | ↓ | | | |

d. | ↑ | ↓ | ↓ | ↓ | ↓ | ↓ | ↓ |

12. *Fill the arrows (electrons) to the orbital diagram for the following elements and write down their electronic configurations.*

	1s	2s	2p	
H				The one electron of H is in the 1*s* orbital because it has the .... E.
He				The two electrons of He have .... spin according to .... principle.
Li				The third e$^-$ of Li cannot be in the 1*s* orbital. Because of the Pauli exclusion principle in each orbital there is maximum of .... electrons. The third e$^-$ is in the orbital of the second lowest E: in ....
Be				
B				The fifth e$^-$ of B is in the ..... subshell. It may be in any of its orbitals because they have the same ....
C				The sixth e$^-$ of carbon cannot be in the same orbital as the fifth one due to .... rule. The fifth and the sixth electrons have .... spin.
N				
O				
F				
Ne				

The notation of the electron configuration includes not only the symbols of subshells but also the number of electrons in each subshell.

13. *Draw the orbital diagram of silicon $_{14}$Si and write down its electron configuration.*
14. *Write down the electron configuration of a vanadium atom (Z = 23) and represent this configuration diagrammatically, showing how electron spins are paired.*
15. *Write down the electron configuration of a polonium atom (Z = 84).*
16. *Write down the electron configurations for: $_{28}$Ni, $_{51}$Sb, $_{32}$Ge and $_{11}$Na.*

17. *What are the electron configurations for magnesium and sulphur? Use the box diagrams. Describe the relation of the atom's electron configuration to its position in the periodic table. ($_{12}Mg$, $_{16}S$)*

Electron configuration of an element and the Periodic Table

The Periodic Table was introduced in 1869 by .... It consists of:

- vertical **.............**; the number of the group corresponds to the number of .... in the last shell
- horizontal **.................**; the number of the period corresponds to the number of ...., i.e. .... quantum number (n) of the last shell.

Valence electrons = electrons from the last shell + *d* or *f* electrons from the previous shells in the case that their orbitals *are/are not* completely filled. They are responsible for the .... properties of an element.

18. *The electronic configurations of elements A – H (the letters are not symbols of elements) are below:*

A: $1s^2\ 2s^2\ 2p^1$

B: $1s^2\ 2s^2\ 2p^6$

C: $1s^2\ 2s^1$

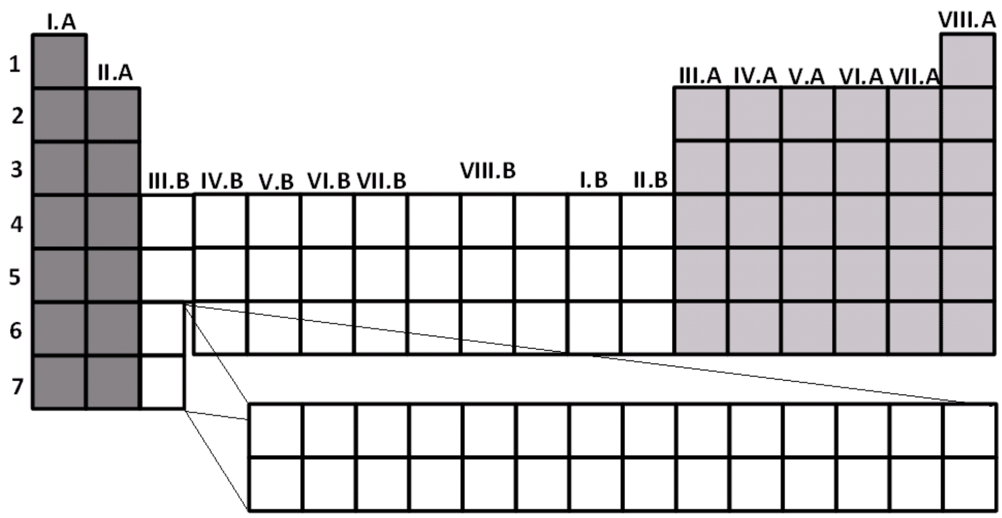
D: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6$

E: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^1$

F: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

G: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^5$

H: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^5$



a. *Underline their valence electrons and draw their box diagrams.*

b. *Estimate what elements are in the same group of the periodic table.*

c. *Place the elements into the periodic table.*

The Periodic Table is divided to .... blocks of elements of similar properties. They have similar electron configurations.

***s*-block elements: I.A and II.A Group**

Valence electrons have the configuration ....

***p*-block elements: III.A – VIII.A Group**

Valence electrons have the configuration ....

***d*-block elements: transition metals**

The elements have partially filled ....orbitals, the general electron configuration of the valence electrons is: ns^2 $(n-1)d^{.........}$.

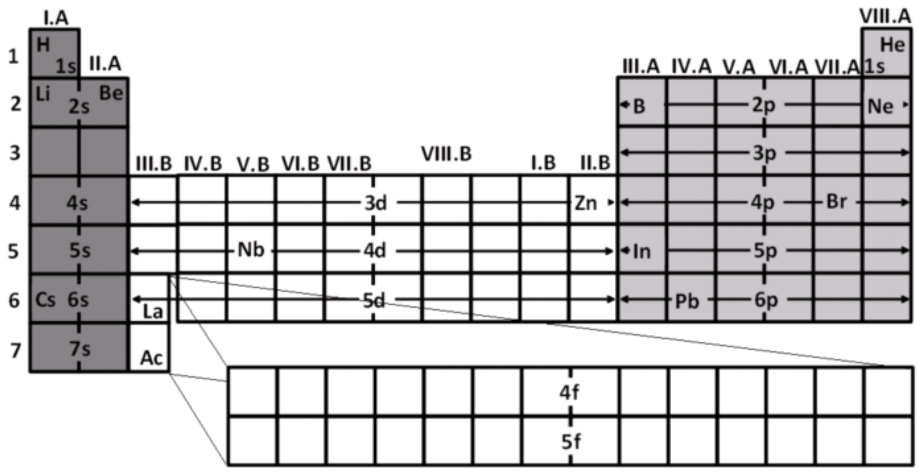
***f*-block elements: lanthanides and actinides**

The elements have partially filled ....orbitals, the general electron configuration of the valence electrons is: ns^2 $(n-2)f^{.........}$.

19. Label the four blocks s, p, d, f in the periodic table above.

__Making the electron configuration of an atom using the PT__

20. Derive the electron configuration of bromine using the periodic table.



Br:

21. *Use the periodic table to find out the electron configuration of:*

a. zinc

b. indium

c. lead

d. caesium

e. niobium.

Noble gas notation

The electron configuration of an element may be abbreviated with the help of a noble gas notation. E.g. $_{19}$K: $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ $4s^1$ may be abbreviated to: $_{19}$K:.................. because $1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$ is the completely filled configuration of ....

22. Use the periodic table to write the noble gas notation for:

a. tungsten
b. calcium
c. bismuth
d. tin

Excited state

An atom with its electrons in the lowest possible energy levels is said to be in its **............. state**.

23. What happens to an electron when energy is supplied?

The atom that has more energy than in its ground state is said to be in an **.................. state**. There are many possible excited states for an atom; the most important are **.................. excited states** – the jump occurs within the valence shell, an electron from an energetically .... orbital jumps to an empty energetically .... orbital. The number of unpaired electrons is *increased/decreased*.

The valence excited states are important for making bonds.
E.g.: carbon atom in its ground and excited state:

$_6$C: [$_2$He] $2s^2$ $\boxed{}$ $2p^2$ $\boxed{}\boxed{}\boxed{}$

$_6$C*: [$_2$He] $2s^1$ $\boxed{}$ $2p^3$ $\boxed{}\boxed{}\boxed{}$

Some atoms have more valence excited states:

$_{16}$S: [$_{10}$Ne] $3s^2$ $\boxed{}$ $3p^4$ $\boxed{}\boxed{}\boxed{}$

$_{16}$S*: [$_{10}$Ne] $3s^2$ $\boxed{}$ $3p^3$ $\boxed{}\boxed{}\boxed{}$ $3d^1$ $\boxed{}\boxed{}\boxed{}\boxed{}\boxed{}$

$_{16}$S**: [$_{10}$Ne] $3s^1$ $\boxed{}$ $3p^3$ $\boxed{}\boxed{}\boxed{}$ $3d^2$ $\boxed{}\boxed{}\boxed{}\boxed{}\boxed{}$

Some atoms have no valence excited state, e.g. fluorine has no other orbitals in the valence shell.

$_9$F: [$_2$He] $2s^2$ $\boxed{\uparrow\downarrow}$ $2p^5$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}$

24. Write the electron configuration and the box diagram for:

*a. P**
*b. Si**
*c. B**
d. Al.*

25. *Are there possible excited states of nitrogen, germanium and oxygen?*

26. *How many possible valence excited states are there for the chlorine atom? Draw their box diagrams.*

Ion formation

27. *What will happen when an atom gains more and more energy?*
28. *Give ways how an atom may gain this energy.*

Energy required to remove an electron from an atom in the gas phase = **...................... ....**

The first ionization energy I_1: $M(g) \rightarrow e^- +$ ....

The second ionization energy I_2: $M^+(g) \rightarrow e^- +$ ....

The second ionization energy is always *higher/lower* than the I_1 because..
.... The *lower/higher* the ionization energy, the easier is a cation formed.

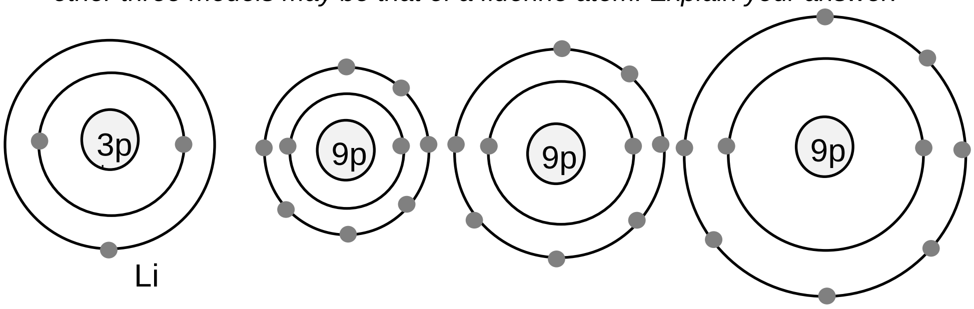
Trends in the PT:

29. *Draw Bohrs models of atoms of Li and of K.*

30. *Is it easier to remove the valence electron from lithium or from potassium? Why?*

<u>Conclusion:</u> Ionization energy *increases/decreases* when going down the group.

31. *The model of an atom of lithium is drawn below. Compare the sizes and predict which of the other three models may be that of a fluorine atom. Explain your answer.*



32. *Is it easier to remove the valence electron from lithium or fluorine? Why?*

<u>Conclusion:</u> Ionization energy *increases/decreases* when going across the period.

When an atom accepts an electron energy is liberated. Its amount is described by **.......................** **.........................(*EA*)**

A(g) + e → .... (g)

The higher *EA* the easier is an .... formed.

33. *Use the pictures above to predict the following:*

When going down the group it is *easier/more difficult* for an atom to accept an electron because of *increasing/decreasing* atomic size and so the electron affinity is *increasing/decreasing* going down the group.

When going across the period it is *easier/more difficult* for an atom to accept an electron because of *increasing/decreasing* atomic size and so the electron affinity is *increasing/decreasing* going across the period.

Electron configuration of ions

34. *Make the electron configuration of $_{9}F^{-}$ and $_{20}Ca^{2+}$.*

$_{9}F^{-}$ has together ...... electrons ⇒ $_{9}F^{-}$: $1s^2\ 2s^2\ 2p^{....}$

$_{20}Ca^{2+}$ has together .... electrons ⇒ $_{20}Ca^{2+}$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^{....}4p^{.....}$

35. *The first ionization energy of Li is 520 kJ/mol, that of Na is 500, K 420, Rb 400 and that of Cs is 380 kJ/mol. Explain the variation in the first ionization energies with atomic number.*

36. *The table shows the ionization energies (in kJ/mol) of five elements A,B,C,D, E,F.*

Element	I_1	I_2	I_3	I_4	*Number of the group*
A	*500*	*4600*	*6900*	*9500*	
B	*420*	*3100*	*4400*	*5900*	
C	*740*	*1500*	*7700*	*10500*	
D	*900*	*1800*	*14800*	*21000*	
E	*580*	*1800*	*2700*	*11600*	
F	*710*	*1450*	*3100*	*4100*	

a. *Estimate the positions (numbers of the groups) of the elements in the periodic table.*
b. *Which of these elements is most likely to form an ion with a charge 3+?*
c. *Which element would require the least energy to convert one mole of gaseous atoms into ions carrying two positive charges?*

37. *Write the electron configuration of the following particles: Al^{3+}, Li^{+}, I^{-}, Mg^{2+}, O^{2-}, S^{2-} and Cl^{-}.*

Questions:

1. *Fill in the missing words*

The region in an atom with the greatest probability finding an electron with a certain (allowed) value of energy is called ....

An electron in an atom is described by four ....

The first three ones describe an .... The fourth one describes the behaviour of an electron in a .... field.

The principal quantum number is labelled ......and it determines the .... of an electron, it is also the measure of the size of an orbital. Two electrons with the same value of *n* are said to be in the same ....

The electrons of a given shell can be grouped into subshells; each characterized by a different value of .... quantum number labelled .... It determines the .... of an orbital.

When *l* = 0, the orbital has ....shape and it is labelled by a letter .... When *l* = 1, the orbital has ....shape and it is labelled by a letter .... When *n* = 3, the values of *l* can be ...., ..., and ....which means that in the third shell may be orbitals ...., ... and ....

The 3D orientation of an orbital is described by .... quantum number. The number of the values of this quantum number for certain *l* may be calculated as follows: ....

When a subshell is labelled *d*, the value of *l* is .... , *m* may have the values ....and (how many) .... orbitals occur within the subshell.

The orbitals with the same values of *n* and *l* are called................... orbitals. They have the same ......

The behaviour of an electron in a magnetic field is described by .... number. It may have the value .... or .... In the *l* = 1 subshell there is a maximum number of .... electrons, in the third shell there is a maximum number of .... electrons.

2. *Which of the following symbols of orbitals are wrong? 5s, 4d, 3f, 2p*
3. *Use the PT to write down the noble gas electronic configuration of:*
   a. *oxygen*
   b. *iodine*
   c. *magnesium*
   d. *potassium*
   e. *carbon*
   f. *hydrogen*
   g. *bismuth*
   h. *iron*
   i. *technecium*

   Underline their valence electrons and draw their box diagrams.

TENTO PROJEKT JE SPOLUFINANCOVÁN EVROPSKÝM SOCIÁLNÍM FONDEM A STÁTNÍM ROZPOČTEM ČESKÉ REPUBLIKY

4. *Which electronic structure is that of an element in Group VI of the periodic table?*
   - a. $1s^2 2s^2 2p^2$
   - b. $1s^2 2s^2 2p^4$
   - c. $[Ar]\ 4s^2 3d^6$
   - d. $[Ar]\ 4s^2 3d^{10} 4p^6$
   - e. $[Kr]\ 5s^2$
   - f. $[Xe] 6s^2 4f^{14} 5d^{10} 6p^4$
5. *What is the particle made of 13 protons, 10 electrons and 14 neutrons?*
6. *Write down the electronic configurations of:*
   - a. Sb^{3+}
   - b. Se^{2-}
   - c. Br^{-}
   - d. C^{*}
   - e. Al^{*}
7. *What is meant by the first ionization energy of sodium?*
8. *Write equations representing the following:*
   - a. *the first ionization energy of potassium*
   - b. *the electron affinity of chlorine*
   - c. *the third ionization energy of aluminium*
9. *Compare the first ionization energy of Be and Sr.*
10. *Compare EA(Cl) and EA(I)*