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65

2 Atomic structure

2.3 Electrons: energy levels, atomic orbitals, ionisation energy



ELECTRONIC CONFIGURATION

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2 Atomic structure

This topic describes the type, number and distribution of the fundamental particles which make up an atom and the impact of this on some atomic properties.

		Learning outcomes Candidates should be able to:
2.3 Electrons: energy levels, atomic	a)	describe the number and relative energies of the s, p and d orbitals for the principal quantum numbers 1, 2 and 3 and also the 4s and 4p orbitals
orbitals, ionisation	b)	describe and sketch the shapes of s and p orbitals
energy, electron affinity	C)	state the electronic configuration of atoms and ions given the proton number and charge, using the convention 1s ² 2s ² 2p ⁶ , etc.
	d)	(i) explain and use the term <i>ionisation energy</i>
		(ii) explain the factors influencing the ionisation energies of elements
		(iii) explain the trends in ionisation energies across a Period and down a Group of the Periodic Table (see also Section 9.1)
	e)	deduce the electronic configurations of elements from successive ionisation energy data
	f)	interpret successive ionisation energy data of an element in terms of the position of that element within the Periodic Table
	g)	explain and use the term <i>electron affinity</i>

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DISCLAIMER

A complete discussion of the experimental evidence for the modern theory of atomic structure is beyond the scope of the CIE A Level Syllabus.

In this chapter only the results of the theoretical treatment will be described. These results will have to be memorized as "rules of the game," but they will be used so extensively throughout the general chemistry course that the notation used will soon become familiar.

ELECTRON ARRANGEMENT

The electronic configuration describes the arrangement of electrons in atoms.

An atom's electrons are arranged outside the nucleus in energy levels (or shells).

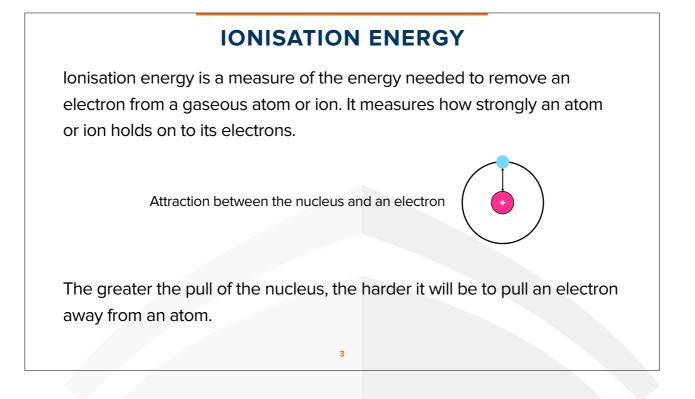
Each shell or energy level holds a certain maximum number of electrons.

The energy of levels becomes greater as they go further from the nucleus and electrons fill energy levels in order.

2

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FIRST IONISATION ENERGY

lonisation energies give evidence for the arrangement of electrons in atoms in shells and sub-shells.

The first ionisation energy for an element is the energy needed to remove **one mole** of electrons from **one mole** of **gaseous atoms**.

Na (g) \rightarrow Na ⁺ (g) + e ⁻	$\Delta H_{i1} = 496 \text{ kJ mol}^{-1}$
Ca (g) \rightarrow Ca ⁺ (g) + e ⁻	ΔH _{i1} = 590 kJ mol ⁻¹
F (g) → F⁺(g) + e-	ΔH _{i1} = 1680 kJ mol ⁻¹

4

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SUCCESSIVE IONISATION ENERGIES

Successive ionisation energies for the same element measure the energy to remove a second, third, fourth electron and so on.

Na⁺(g) → Na²⁺(g) + e⁻ Δ H_{i2} = 4563 kJ mol⁻¹ Na²⁺(g) → Na³⁺(g) + e⁻ Δ H_{i3} = 6913 kJ mol⁻¹

It is possible to measure energy changes involving ions which do not normally appear in chemical reactions.

5

SKILL CHECK 1

Which equation represents the second ionisation energy of an element X?

6

$$\mathbf{A} X_{(g)} \longrightarrow X^{2+}(g) + 2e^{-1}$$

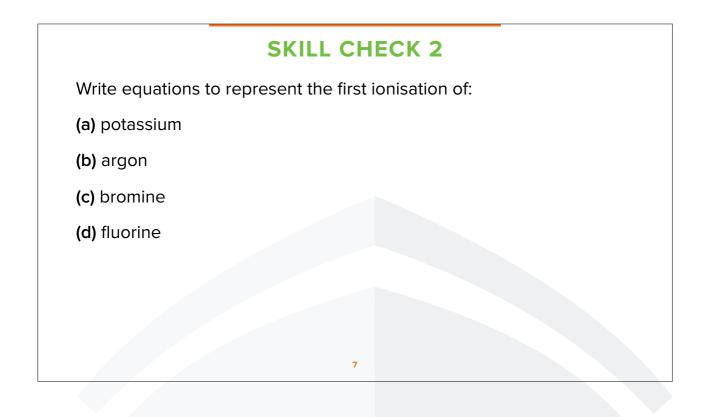
$$\mathbf{B} X^{+}_{(g)} \longrightarrow X^{2+}_{(g)} + e^{-}$$

$$c X_{(g)} + 2e^{-} \longrightarrow X^{2}_{(g)}$$

$$D X^{-}_{(g)} + e^{-} \longrightarrow X^{2-}_{(g)}$$

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	energies (01 7.				
1st	2nd	3rd	4th	5th	6th	7th
950	1800	2700	4800	6000	12300	15000

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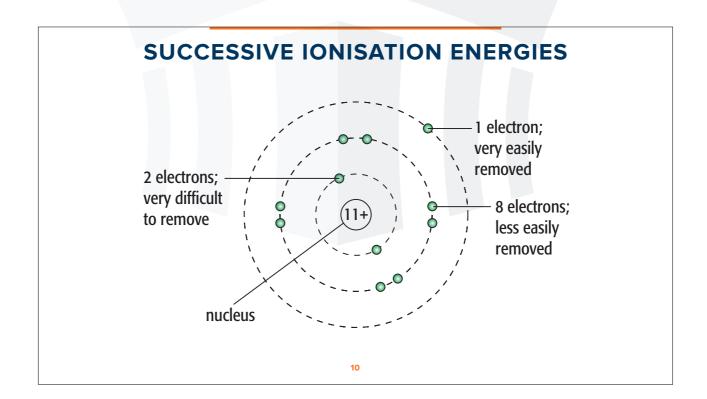
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SUCCESSIVE IONISATION ENERGIES

After an electron has been removed the rest of them will be more strongly attracted by the nucleus.

Hence more energy is required to pull the 2^{nd} electron and thus the 2^{nd} I.E. is greater than the 1^{st} I.E.

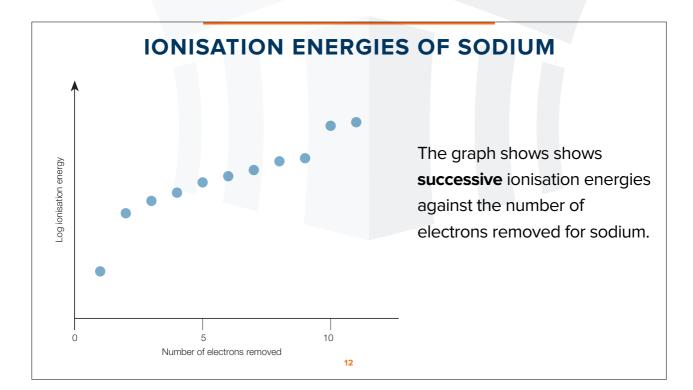
Successive ionisation energies are always greater than the previous one.



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	E١	/IDI	ENC	CE C	OF E	NER	GY	LEVE	ELS		
The arrang from the va							2		t can b	be dec	luced
The succes	ssive	I.E of	sodiı	um illi	ustrat	e the c	hange	e clearl	y.		
										1	1
electron		2	3	4	5	6	7	8	9	10	11
removed	1	2	5		U	0	/	°	9	10	
	1 500	4600	6900	9500	13400	16600	20100	25500	28900	141000	
removed ionisation				9500							
removed ionisation				9500		16600					158000



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IONISATION ENERGIES OF SODIUM

There is a big difference between **some** successive ionisation energies. For sodium the first big difference occurs between the 1st and 2nd ionisation energies.

These **large changes** indicate that for the **second** of these two ionisation energies, the electron being removed is from a shell **closer** to the nucleus.

13

IONISATION ENERGIES OF SODIUM

electron removed	1	2	3	4	5	6	7	8	9	10	11
ionisation energy	500	4600	6900	9500	13400	16600	20100	25500	28900	141000	158000

There is a **big jump** in the value of the **second** ionisation energy. This suggests that the second electron is in a shell closer to the nucleus than the first electron.

Taken together, the 1st and 2nd ionisation energies suggest that sodium has **one electron** in its **outer shell**.

14

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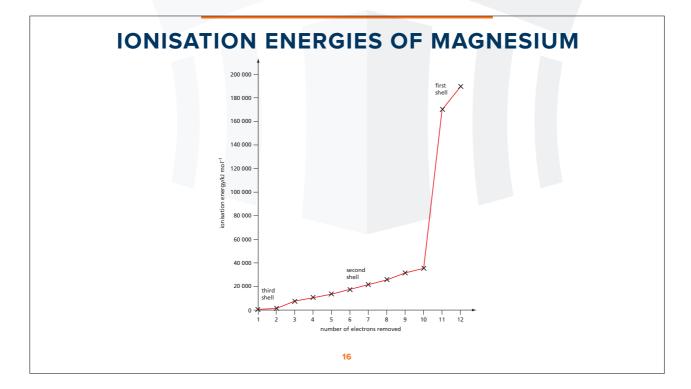
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electron removed	1	2	3	4	5	6	7	8	9	10	11
ionisation energy	500	4600	6900	9500	13400	16600	20100	25500	28900	141000	15800

From the second to the ninth electrons removed there is only a **gradual** change in successive ionisation energies. This suggests that all these eight electrons are in the **same** shell.

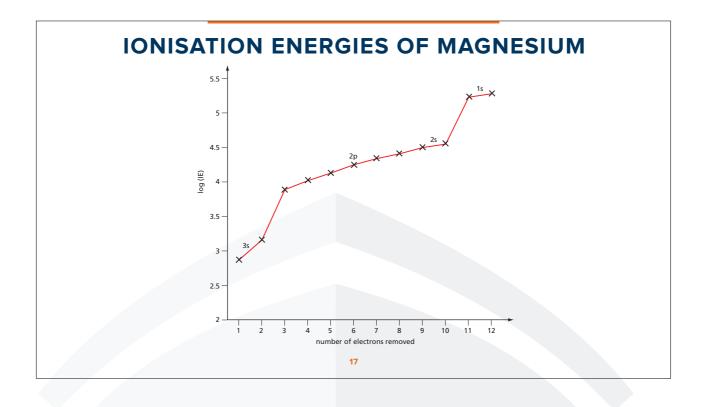
There is a **big jump** in the value of the 10th ionisation energy. This suggests that the 10th electron is in a shell **closer** to the nucleus than the 9th electron.

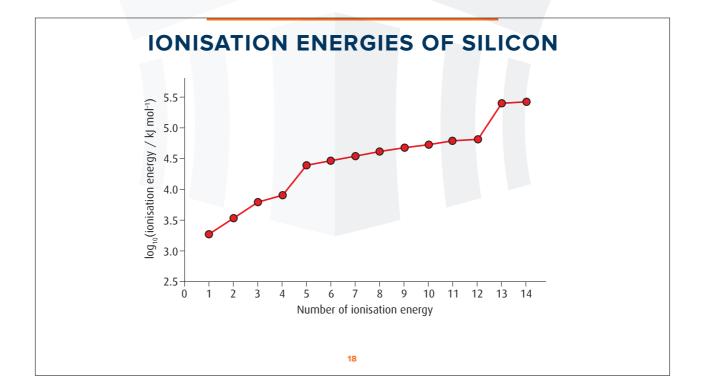
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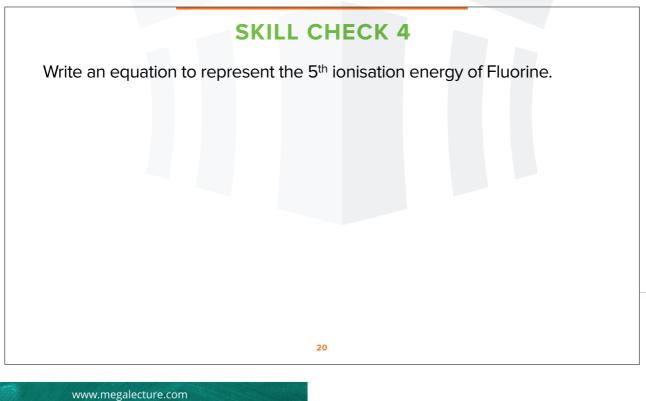


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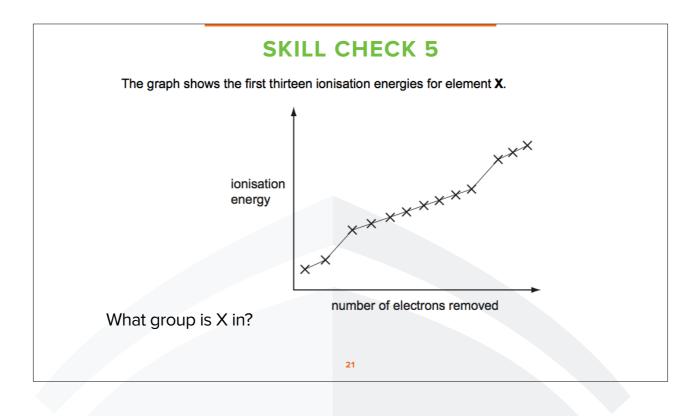


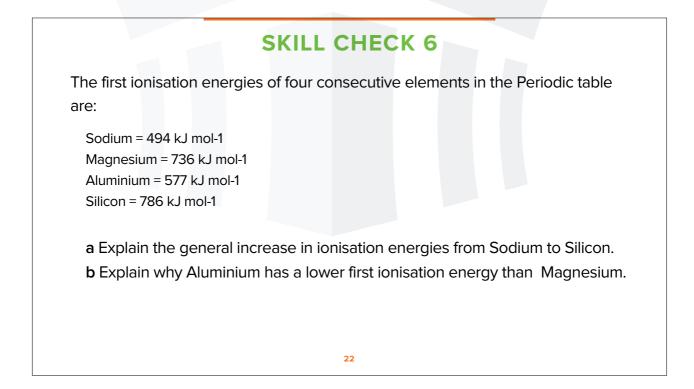
ss repulsion between ectrons - electrons pulled **IONISATION ENERGIES OF POTASSIUM** closer to nucleus 6.0 5.5 8 electrons 5.0- $\log_{10}(1E / k) \text{ mol}^{-1})$ 4.5 8 electrons 4.0 3.5 3.0 2.5 2.0 7 8 9 10 11 12 13 14 15 16 17 18 19 5 2 3 4 6 1 Number of ionisation energy 19



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SKILL CHECK 7

The first six ionisation energies of an element are, or 1090, 2250, 4610, 6220, 37,800, and 47,300kJ mol⁻¹. Which group in the Periodic Table does this element belong to? Explain your decision.

23

<section-header><section-header>brancessive ionisation energies dH, of an element X are shown in the
table below. Which group in the Periodic Table does X belong to:Number of electrons removed12345678910Dt/r b mol-11002603904507008500270031670358043140

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SUCCESSIVE IONISATION ENERGIES

We can use successive ionisation energies in this way to confirm:

- The simple electronic configuration of elements.
- The number of electrons in the outer shell of an element and hence the group to which the element belongs.

The successive ionisation energies for an element rise and there are big jumps in value each time electrons start to be removed from the next shell in towards the nucleus.

25

IONISATION ENERGIES OF OXYGEN

electron removed	1	2	3	4	5	6	7	8
ionisation energy	1310	3390	5320	7450	11000	13300	71300	84100

Large increases can be used to predict the group of any element. The electron configuration of oxygen is 2,6.

Since the large change is after the removal of 6 electrons, it signifies that there are 6 electrons in the shell farthest from the nucleus.

Therefore, Oxygen is in Group VI.

26

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						ELECT	RONS RE	MOVED				
Elei	ment	1	2	3	4	5	6	7	8	9	10	11
1	н	1310										
2	He	2370	5250									
3	Li	519	7300	11800								
4	Be	900	1760	14850	21000							
5	в	799	2420	3660	25000	32800						
6	с	1090	2350	4620	6220	37800	47300					
7	N	1400	2860	4580	7480	9450	53300	64400				
8	ο	1310	3390	5320	7450	11000	13300	71300	84100			
9	F	1680	3370	6040	8410	11000	15200	17900	92000	106000		
10	Ne	2080	3950	6150	9290	12200	15200	20000	23000	117000	131400	
11	Na	494	4560	6940	9540	13400	16600	20100	25500	28900	141000	158700

SKILL CHECK 9

The successive ionisation energies, in kJ mol⁻¹, of different elements are given below. Which groups are the following elements in?

	1	2	3	4	5	6	7	8
Α	799	2420	3660	25000				
в	736	1450	7740	10500				
с	418	3070	4600	5860				
D	870	1800	3000	3600	5800	7000	13200	
E	950	1800	2700	4800	6000	12300		

28

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SKILL CHECK 10

The successive ionisation energies of beryllium are 900, 1757, 14,849 and 21,007 kJ mol⁻¹.

- a What is the atomic number of beryllium?
- **b** Why do successive ionisation energies of beryllium always get more endothermic?
- c To which group of the Periodic Table does this element belong?

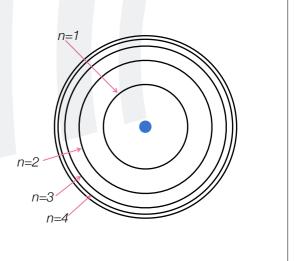
29

SHELLS (ENERGY LEVELS)

The principal energy levels are designated n = 1, 2, 3, and so forth.

The energy levels are **not** equally spaced.

The energy gap between successive levels gets increasingly smaller as the levels move further from the nucleus.



30

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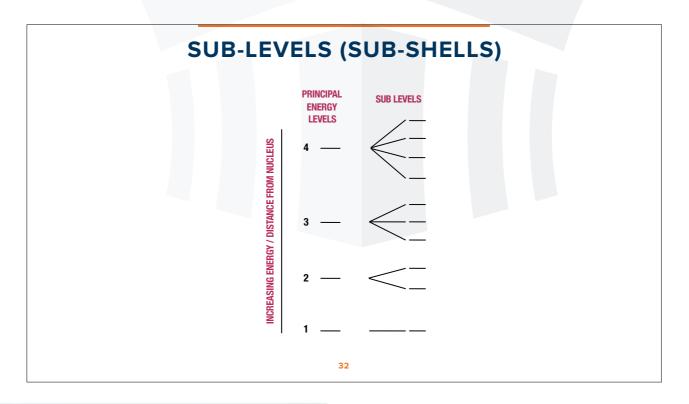
SUB-LEVELS (SUB-SHELLS)

Electron shells are numbered 1,2,3 etc. These numbers are known as the **principle quantum numbers**.

Each energy level (shell) consists of a number of sub-levels (sub-shells), labeled **s**, **p**, **d**, or **f**.

Energy Level	Number of sub-levels	Name of sub-levels
1	1	S
2	2	s, p
3	3	s, p, d
4	4	s, p, d, f

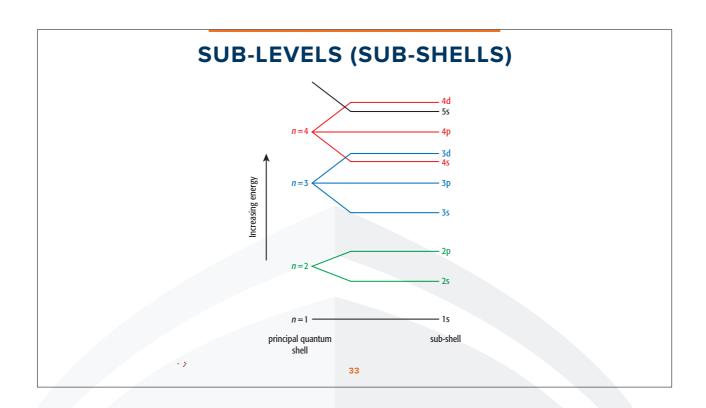
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	SUB-LEVELS									
Each sub-level c	an hold a certain	maximum number of el	ectrons.							
	Type of sub-level	Maximum # of electrons]							
	S	2								
	р	6								
	d	10								
	f	14								
			-							

34

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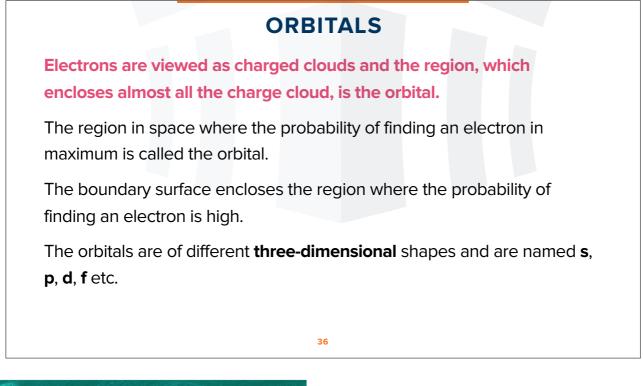
ORBITALS

An **atomic orbital** is a region of space around the nucleus of an atom which can be occupied by one or two electrons **only**.

Each sub-level contains a **fixed number** of orbitals that contain electrons.

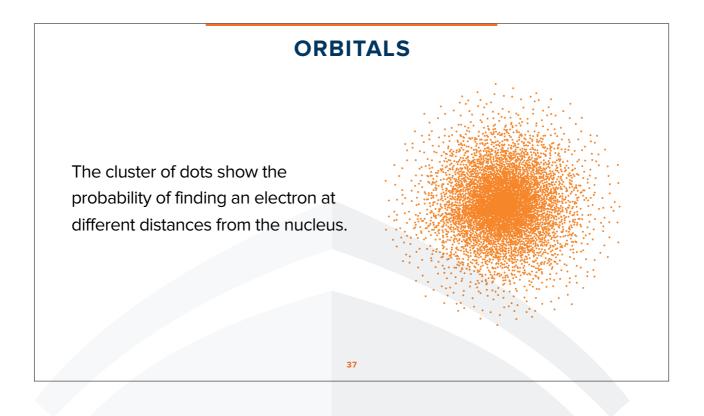
Type of sub-level	Maximum # of electrons	Number of orbitals
S	2	1
р	6	3
d	10	5
f	14	7

35



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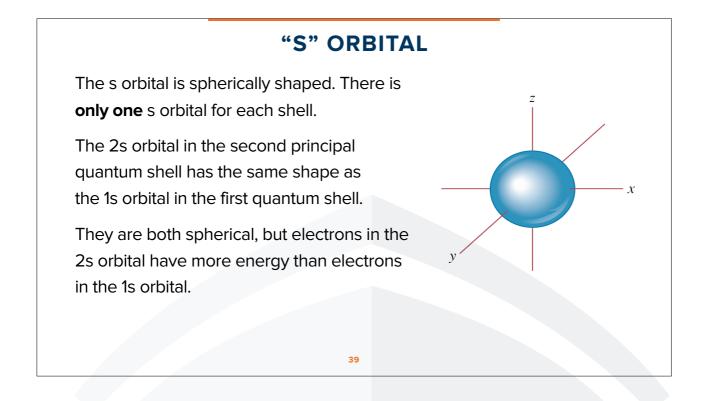
SHELLS, SUB SHELLS AND ORBITALS

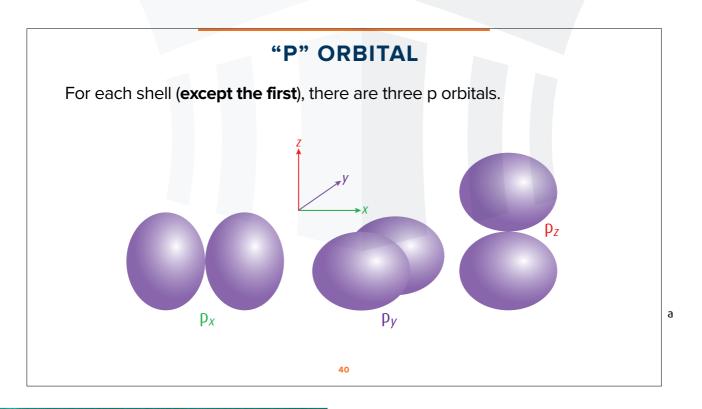
Energy Level	Type of sub-level	Number of orbitals	Maximum # of electrons
1	S	1	2
2	S	1	2
	р	3	6
3	S	1	2
	р	3	6
	d	5	10
4	S	1	2
	р	3	6
	d	5	10

38

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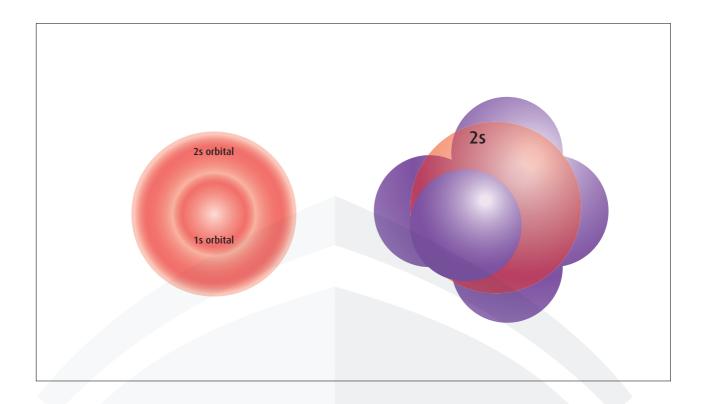
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2s

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 \mathbf{P}_{V}



ELECTRONIC CONFIGURATION

Electrons are distributed in different energy levels in the atom of the element.

The order in which they fill up the sub-levels is governed by **stability**.

When electrons fill up the orbitals having the **least energy** they attain **maximum stability**.

There are three principles that describe how electrons fill up in orbitals.

Aufbau Principle: Electrons enter the orbital that is available with the **lowest** energy. The orbitals are arranged in the order of increasing energy and the electrons are added until the proper number of electrons for the element have been accommodated

42

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ELECTRONIC CONFIGURATION

Pauli's Exclusion Principle: No orbital can accommodate more than two electrons. If there are two electrons in an orbital, they must have opposite spin.

Hund's Rule of Maximum Multiplicity: When there are a number of orbitals of equal energy, electrons first fill them up individually and then get paired. By filling up individually, **mutual repulsion** between electrons is avoided and thereby maximum stability is achieved.

43

ELECTRON SPIN

Electrons are all identical. The only way of distinguishing them is by describing how their **energies** and **spatial distributions** differ.

Thus an electron in a 1s orbital is different from an electron in a 2s orbital because it occupies a different region of space **closer to the nucleus**, causing it to have **less** potential energy.

An electron in a $2p_x$ orbital differs from an electron in a $2p_y$ orbital because although they have exactly the same potential energy, they occupy different regions of space.

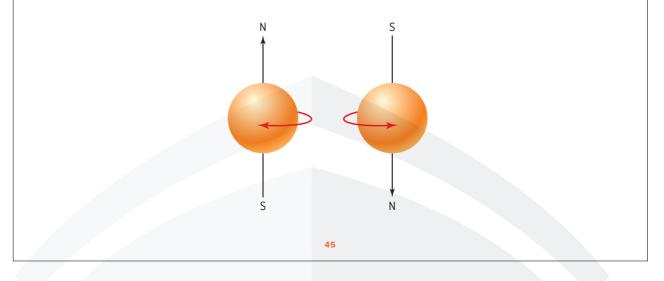
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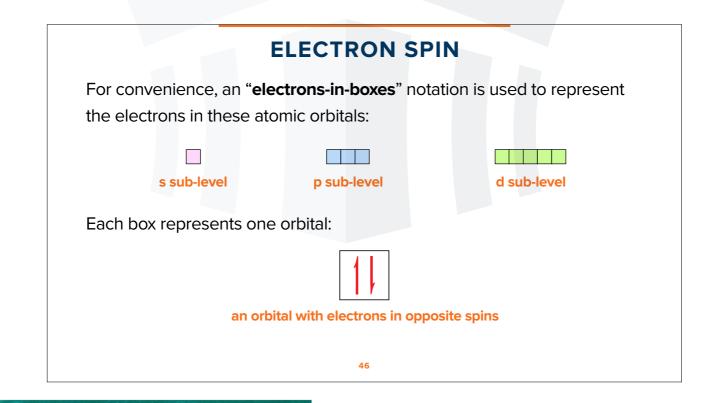
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ELECTRON SPIN

There can only be two electrons in each orbital, and they must have opposite directions of spin.

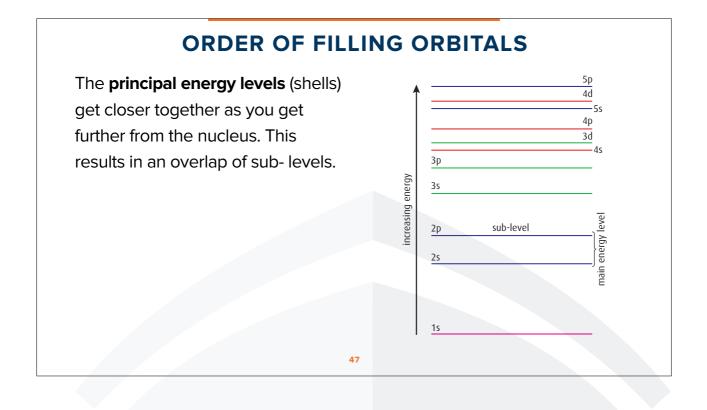


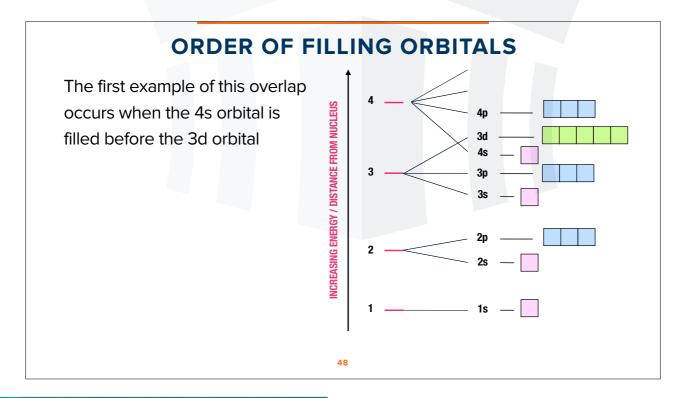


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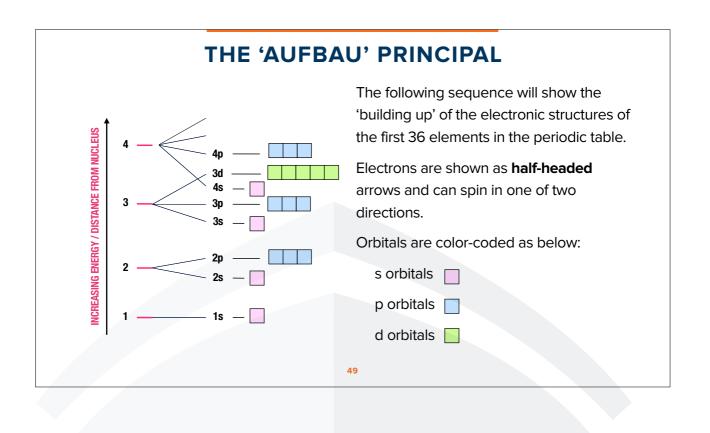


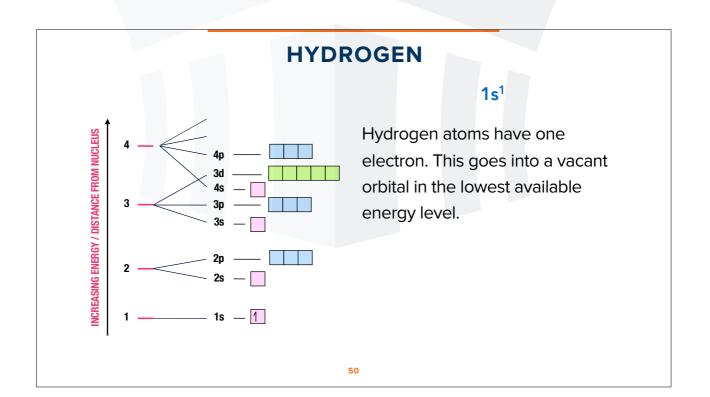


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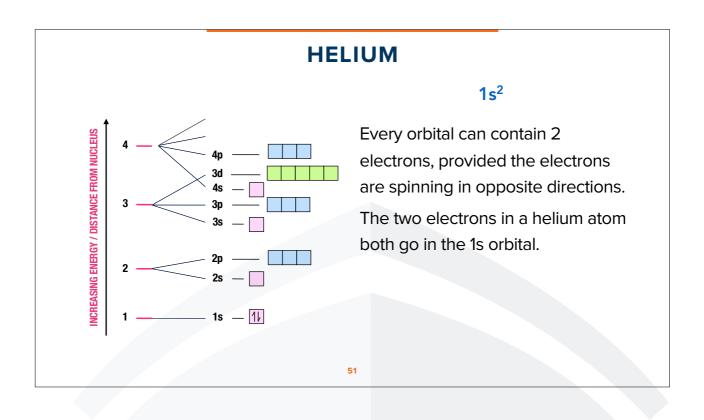


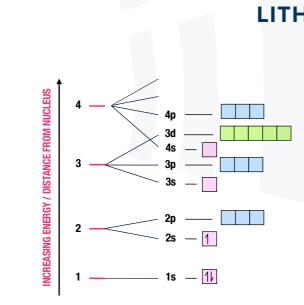
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LITHIUM

1s² 2s¹

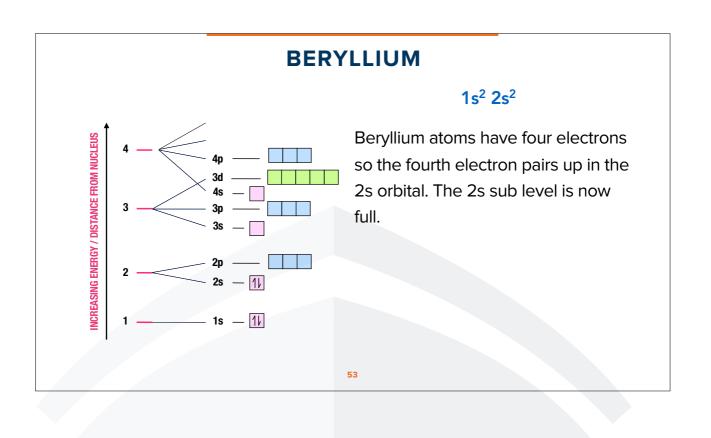
1s orbitals can hold a maximum of two electrons so the third electron in a lithium atom must go into the next available orbital of higher energy. This will be further from the nucleus in the second principal energy level.

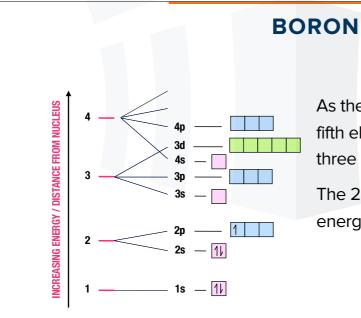
The second principal level has two types of orbital (s and p). An s orbital is lower in energy than a p.

52

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1s² 2s² 2p¹

As the 2s sub level is now full, the fifth electron goes into one of the three p orbitals in the 2p sub level.

The 2p orbitals are slightly higher in energy than the 2s orbital.

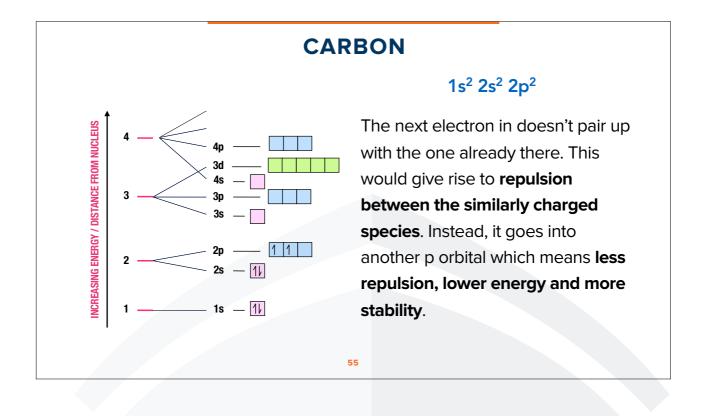
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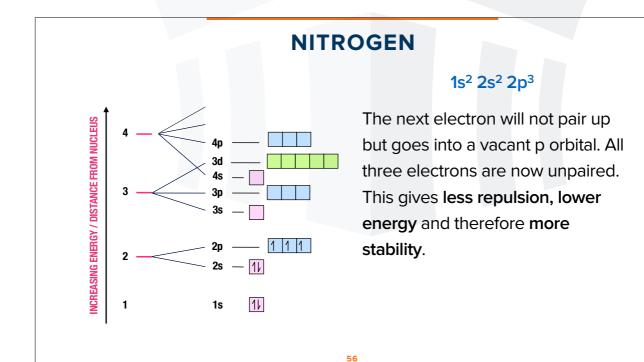
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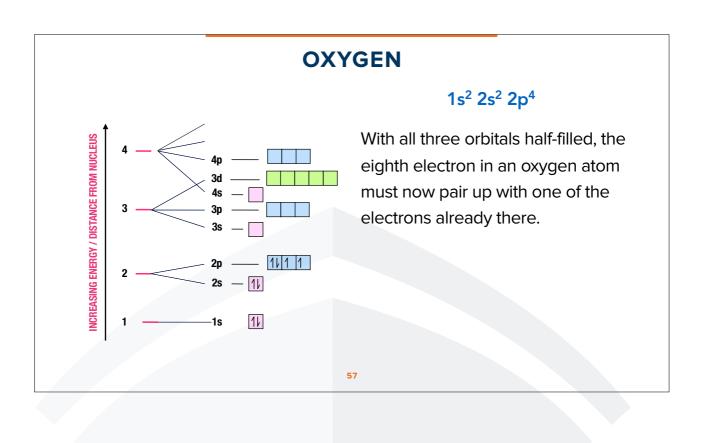
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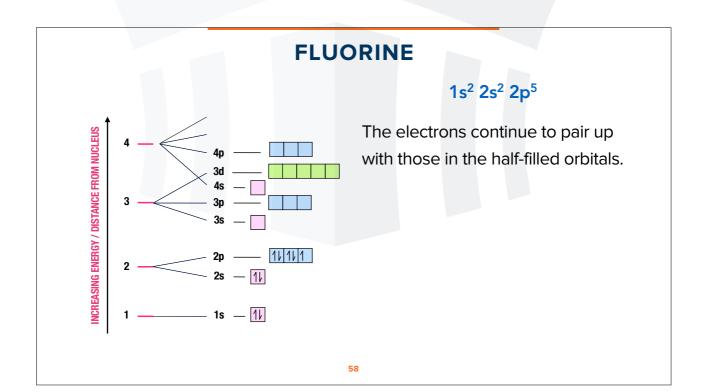




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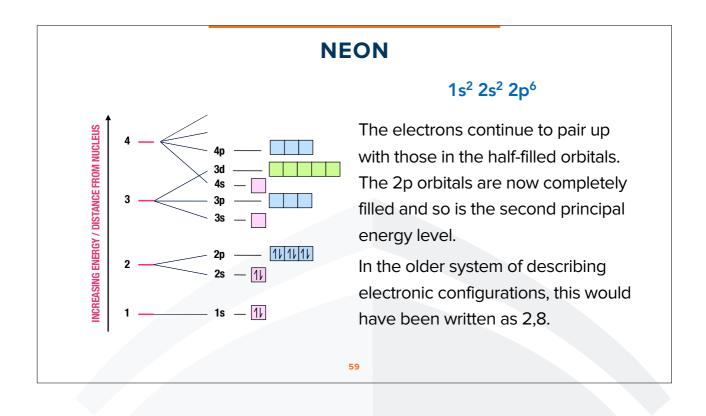


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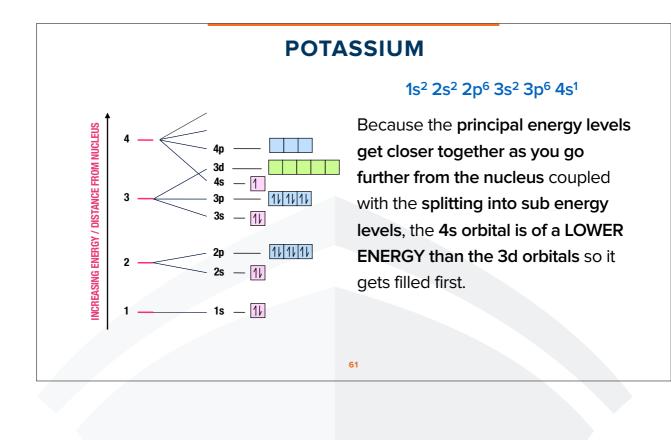


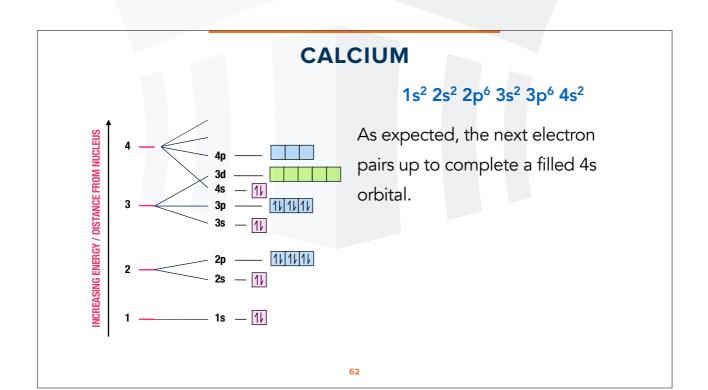
SO	DIUM TO ARGON
Na	1s ² 2s ² 2p ⁶ 3s ¹
Mg	1s ² 2s ² 2p ⁶ 3s ²
AI	1s ² 2s ² 2p ⁶ 3s ² 3p ¹
Si	1s ² 2s ² 2p ⁶ 3s ² 3p ²
Р	1s ² 2s ² 2p ⁶ 3s ² 3p ³
S	1s ² 2s ² 2p ⁶ 3s ² 3p ⁴
CI	1s ² 2s ² 2p ⁶ 3s ² 3p ⁵
Ar	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶
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Period 1			Н					He
Atomic no.			1					2
Electron shell structure			1					2
Electron sub-shell structure			1s ¹					1s ²
Period 2	Li	Be	В	С	Ν	0	F	Ne
Atomic no.	3	4	5	6	7	8	9	10
Electron shell structure	2, 1	2, 2	2, 3	2, 4	2, 5	2, 6	2, 7	2, 8
Electron sub-shell structure	1s ² 2s ¹	1s ² 2s ²	1s ² 2s ² 2p ¹	1s ² 2s ² 2p ²	1s ² 2s ² 2p ³	1s ² 2s ² 2p ⁴	1s ² 2s ² 2p ⁵	1s ² 2s ² 2p ⁶

ELEMENTS WITH PROTON NUMBERS 11 TO 20

Period 3	Na	Mg	AI	Si	Р	S	CI	Ar
Atomic no.	11	12	13	14	15	16	17	18
Electron shell structure	2, 8, 1	2, 8, 2	2, 8, 3	2, 8, 4	2, 8, 5	2, 8, 6	2, 8, 7	2, 8, 8
Electron sub-shell structure	1s ² 2s ² 2p ⁶ 3s ¹	1s ² 2s ² 2p ⁶ 3s ²	1s ² 2s ² 2p ⁶ 3s ² 3p ¹	1s ² 2s ² 2p ⁶ 3s ² 3p ²	1s ² 2s ² 2p ⁶ 3s ² 3p ³	1s ² 2s ² 2p ⁶ 3s ² 3p ⁴	1s ² 2s ² 2p ⁶ 3s ² 3p ⁵	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶
Period 4	К	Ca						
Atomic no.	19	20						
Electron shell structure	2, 8, 8, 1	2, 8, 8, 2						
Electron sub-shell structure	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ¹	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 4s ²						

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SKILL CHECK 11

65

Copy and complete the following information for the quantum shell with **principal quantum number 3**.

- (a) total number of sub-shells
- (b) total number of orbitals
- (c) number of different types of orbital
- (d) maximum number of electrons in the shell

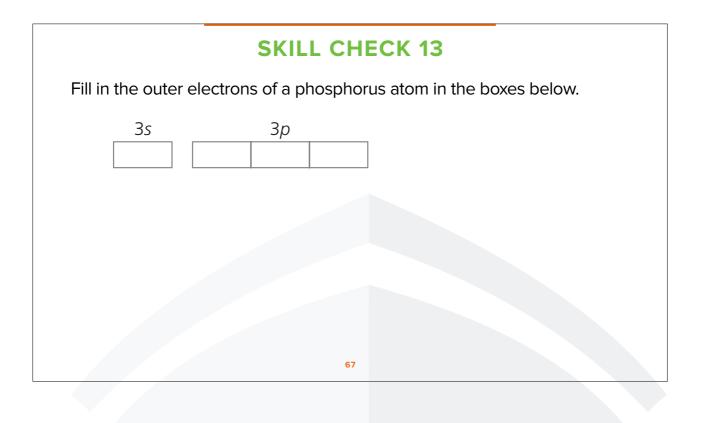
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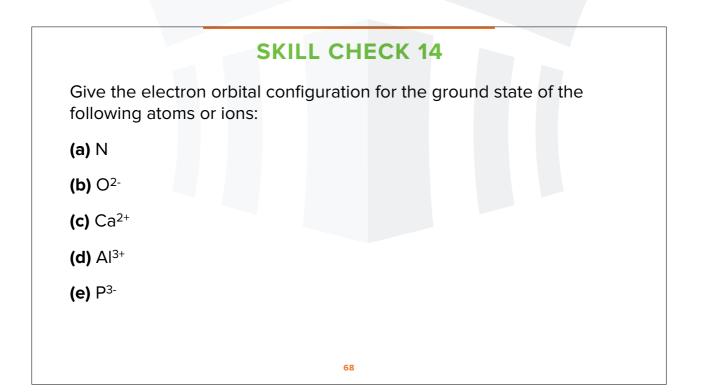
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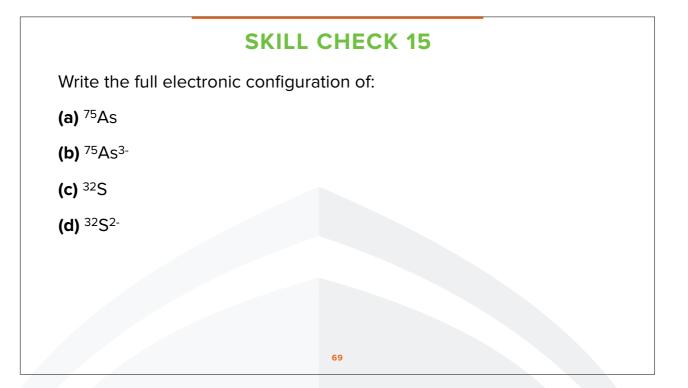
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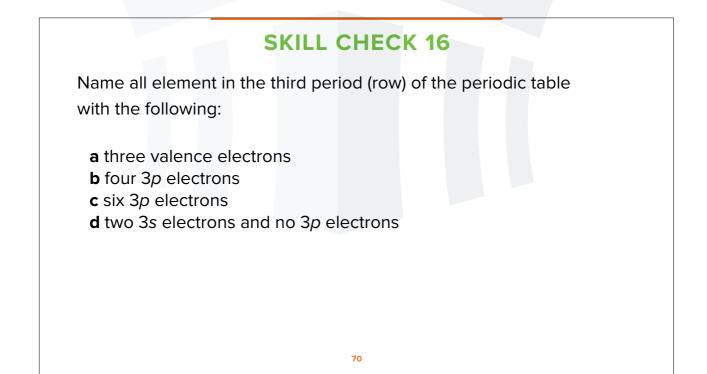




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EXCEPTIONS IN TRANSITION ELEMENTS

Though the s orbital is at lower energy level than the d of the penultimate shell, after the filling of the d sub-level, the order changes.

The d electrons, because of the shape of the d orbital, penetrate into the region of space between the nucleus and the s orbital and repel the s electrons and push them to higher energy level.

71

Before filling: 1s 2s 2p 3s 3p 4s 3d

After filling: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^x 4s^2$

EXCEPTIONS IN TRANSITION ELEMENTS

Thus the electronic configuration of iron is

 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

and not

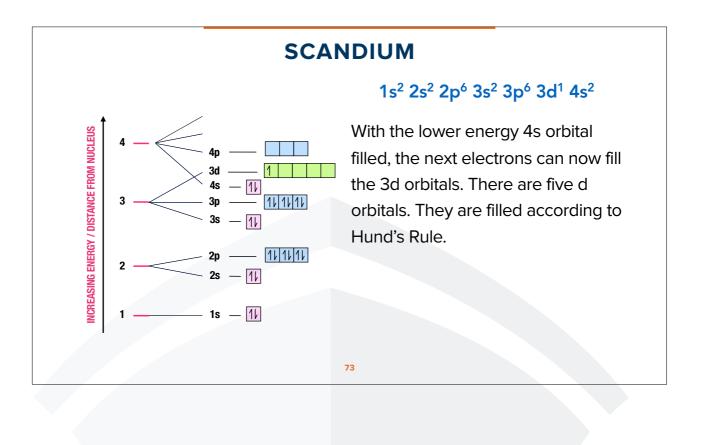
 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^6$

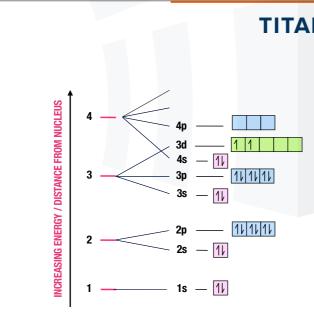
Remember: 3d is higher than 4s in terms of energy levels!

72

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TITANIUM

1s² 2s² 2p⁶ 3s² 3p⁶ 3d² 4s²

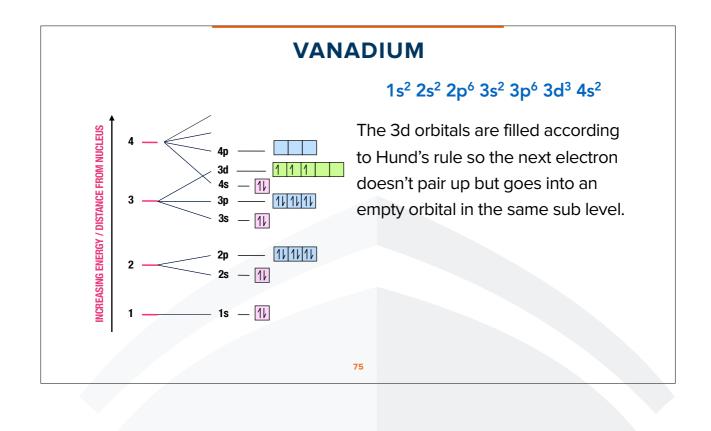
The 3d orbitals are filled according to Hund's rule so the next electron doesn't pair up but goes into an empty orbital in the same sub level.

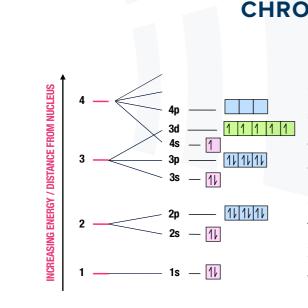
74

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CHROMIUM

1s² 2s² 2p⁶ 3s² 3p⁶ 3d⁵ 4s¹

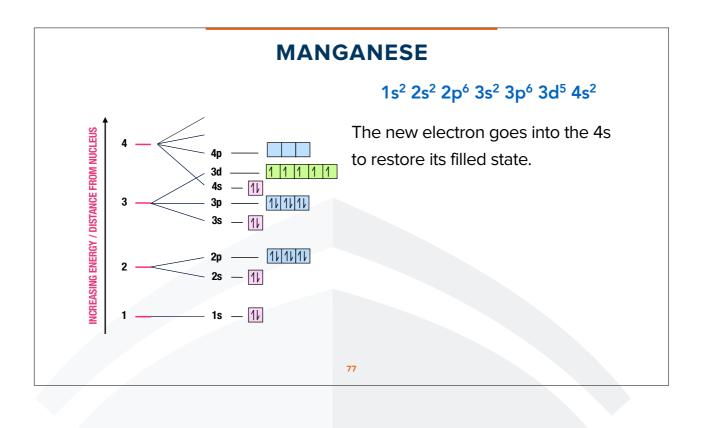
One would expect the configuration of chromium atoms to end in 3d⁴ 4s².

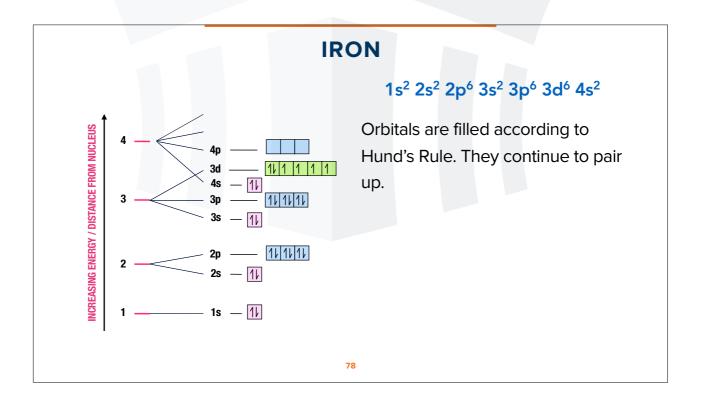
To achieve a more stable arrangement of lower energy, one of the 4s electrons is promoted into the 3d to give six unpaired electrons with lower repulsion.

76

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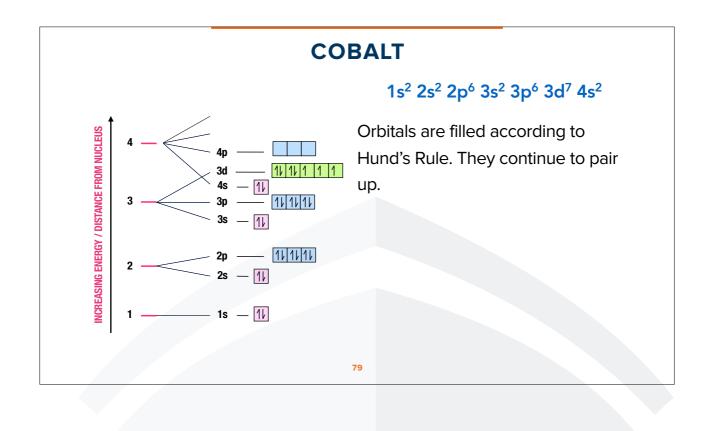


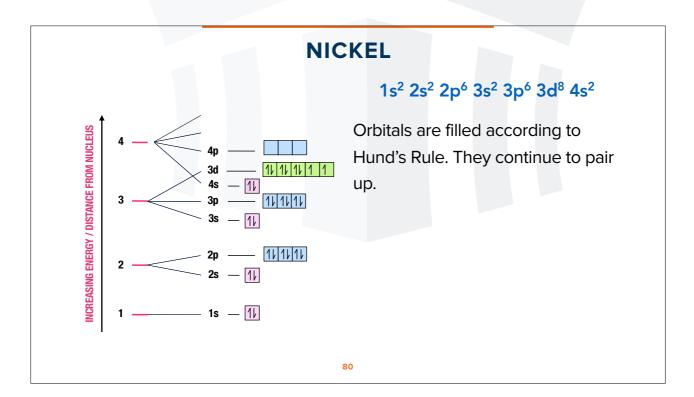
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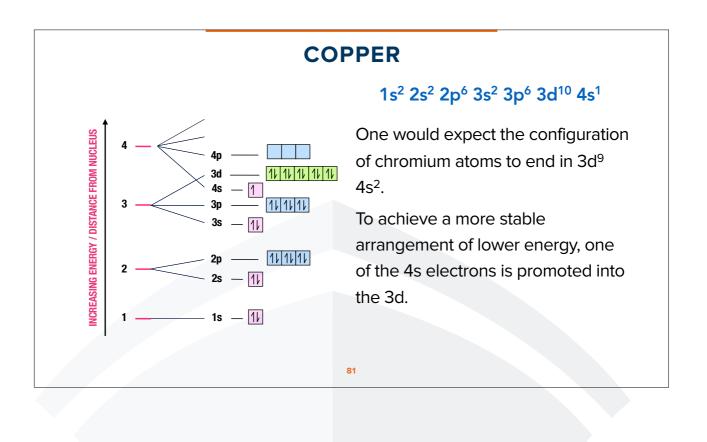


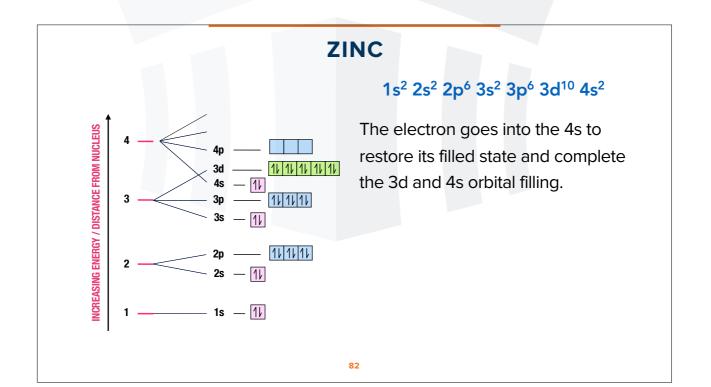


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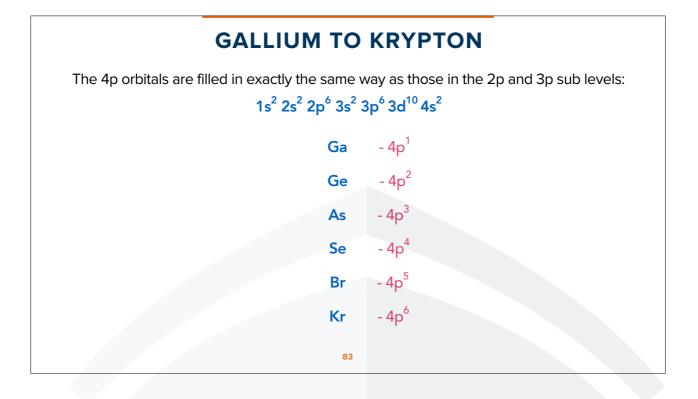




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ELECTRONIC CONFIGURATION OF IONS

Metallic elements, belonging to Group I, II and III form positively charged ions by losing electrons in their outermost shell, so that the ions may be iso-electronic with the preceding noble gas.

84

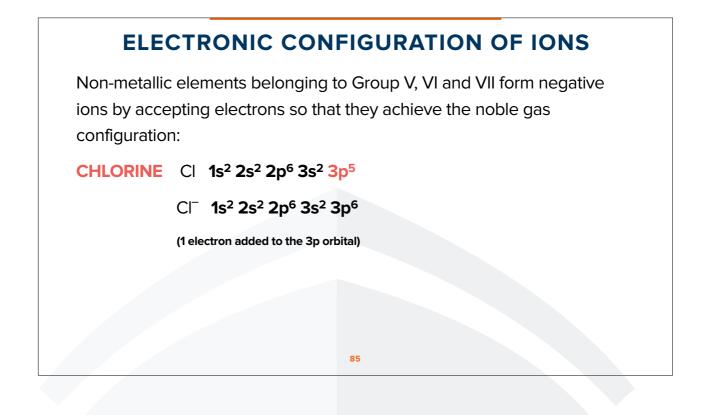
SODIUM Na **1s² 2s² 2p⁶ 3s¹**

Na⁺ 1s² 2s² 2p⁶

(1 electron removed from the 3s orbital)

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TRANSITION METAL IONS

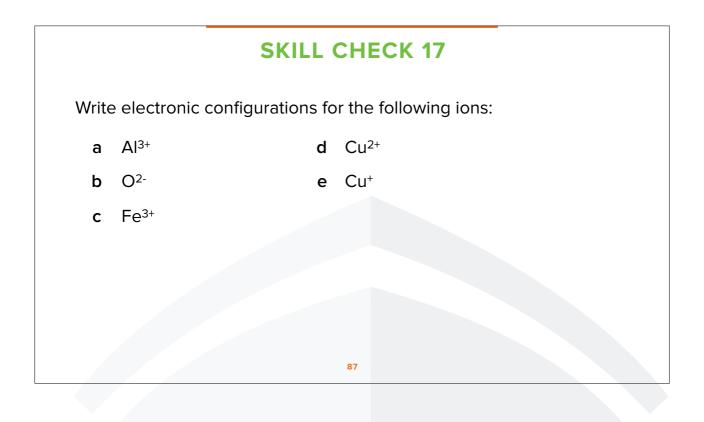
When transition metals form ions, electrons are lost first from the outermost s orbital and then from the penultimate d sub-level.

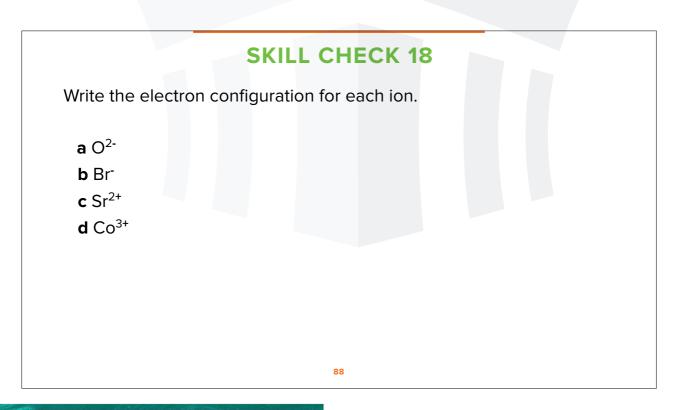
Electrons in the 4s orbital are removed before any electrons in the 3d orbitals.

TITANIUM	Ti	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ² 4s ²
	Ti+	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ² 4s ¹
	Ti2+	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ²
	Ti3+	1s ² 2s ² 2p ⁶ 3s ² 3p ⁶ 3d ¹
	Ti4+	1s² 2s² 2p ⁶ 3s² 3p ⁶ `
		86

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SKILL CHECK 19

Q. What is the order of increasing energy of the listed orbitals in the atom of titanium?

- A 3s 3p 3d 4s
- **B** 3s 3p 4s 3d
- C 3s 4s 3p 3d
- D 4s 3s 3p 3d

SKILL CHECK 20

89

A simple ion X⁺ contains eight protons.

What is the electronic configuration of X⁺?

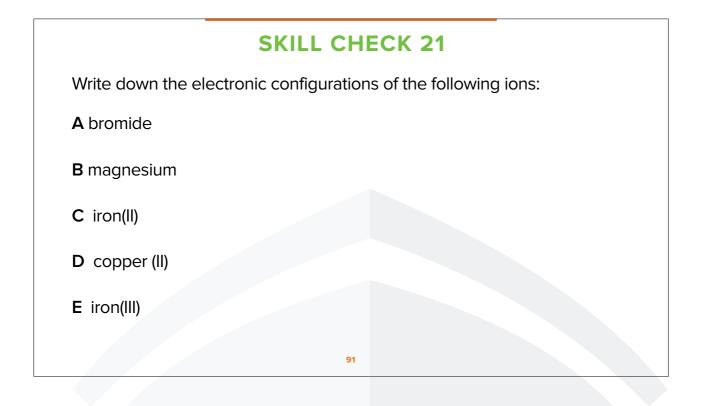
A 1s² 2s¹ 2p⁶

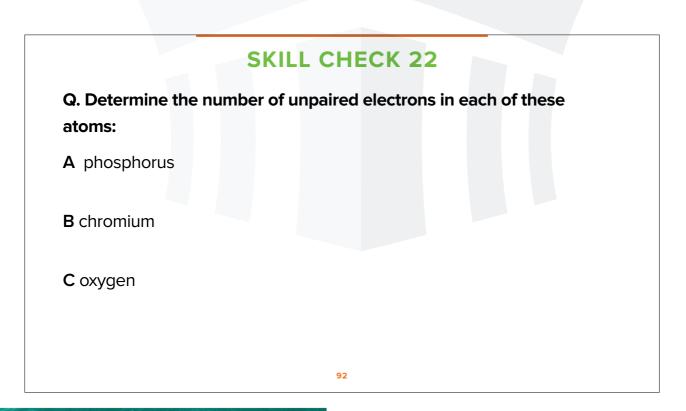
- **B** 1s² 2s² 2p³
- $C 1s^2 2s^2 2p^5$
- **D** 1s² 2s² 2p⁷

90

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SKILL CHECK 23

Use the periodic table to determine the element corresponding to each electron configuration.

A [Ar] $4s^2 3d_{10} 4p^6$ **B** [Ar] $4s^2 3d^2$ **C** [Kr] $5s^2 4d^{10} 5p^2$ **D** [Kr] $5s^2$

PERIODIC TABLE

93

The modern Periodic Table is arranged such that elements with similar electronic configuration lie in vertical groups.

Thus elements with electronic configuration ending up as ns^1 are put in one group while those that end up as ns^2 are put in another group.

The elements that fill up the s orbital of the highest energy level are said to belong to the s block, comprising of Groups 1 and 2.

94

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PERIODIC TABLE

The elements that similarly fill up the p orbitals of the highest energy are said to belong to the p block, which comprises of Groups 13 to 0.

So there are two columns in the s block and six columns in the p block.

95

The elements that fill up the d sub-level of the penultimate shell are called the d block elements or the Transition Metal series.

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