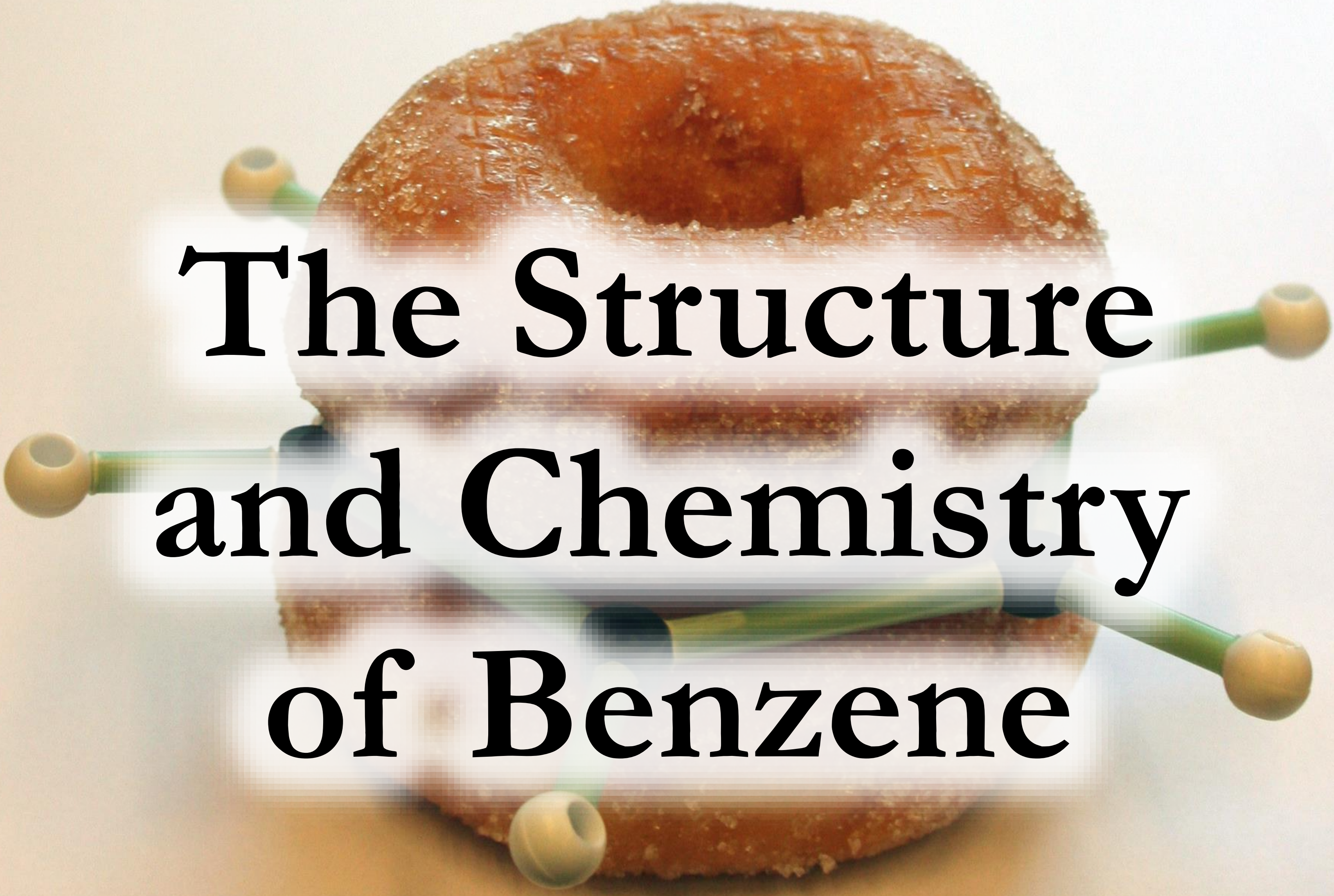

The Structure and Chemistry of Benzene

The Properties of Benzene

The general properties of benzene are outlined below:

- Molecular formula = C_6H_6
- Molar mass = 78.11 g mol^{-1}
- Density = 0.88 g cm^{-3}
- Solubility in water = 1.79 g dm^{-3} at 25 °C
- Melting point = 5.5 °C
- Boiling point = 80.1 °C

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Question:

- What is the concentration of a saturated solution of benzene in water at 25 °C?

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- Boiling point = 80.1 °C

Answer:

moles in 1 dm^3 = mass in grams ÷ molar mass

moles in 1 dm^3 = 1.79 g ÷ 78.11 g mol^{-1}

moles in 1 dm^3 = 0.023 mol dm^{-3}

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Question:

- Comment on the relatively low solubility of benzene in water.

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Answer:

Water is polar (electronegativity values of oxygen and hydrogen are 3.5 and 2.1 respectively) while benzene is non-polar (electronegativity values of carbon an hydrogen are 2.5 and 2.1 respectively).

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Question:

- What is the physical state of benzene at 21.0 °C?

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Answer:

Solid ← 5.5 °C → Liquid ← 80.1 °C → Gas

Hence benzene will be a liquid at room temperature and pressure.

The Properties of Benzene

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- Boiling point = 80.1 °C

Question:

- Write a balanced chemical equation for the complete combustion of benzene.

The Properties of Benzene

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- Melting point = 5.5 °C
- Boiling point = 80.1 °C

Answer:

$$C_6H_6 + 7\tfrac{1}{2}O_2 \rightarrow 6CO_2 + 3H_2O$$

$$2C_6H_6 + 15O_2 \rightarrow 12CO_2 + 6H_2O$$

The Properties of Benzene

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Question:

- Comment on the appearance of the flame that is produced when benzene burns in air.

The Properties of Benzene

The general properties of benzene are outlined below:

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- Density = 0.88 g cm^{-3}
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- Melting point = 5.5 °C
- Boiling point = 80.1 °C

Answer:

Benzene will burn with a luminous and sooty flame due to the high ratio of carbon to hydrogen within the compound.

Hexane C:H = 3:7

Benzene C:H = 1:1

The Properties of Benzene

The hazards associated with using benzene:

The Discovery of Benzene

Michael Faraday
(1791 – 1867).

Benzene was discovered in 1825 by the English scientist *Michael Faraday*, who isolated it from oil gas.

In 1833, the German chemist *Eilhard Mitscherlich* produced benzene by distilling benzoic acid (from gum benzoin) in the presence of lime.

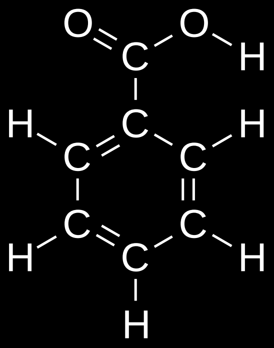
Eilhard Mitscherlich
(1794 – 1863).

The Discovery of Benzene

Question:

- Complete the two chemical equations below to show the synthesis of benzene from a) benzoic acid and calcium oxide and b) benzoic acid and calcium hydroxide:

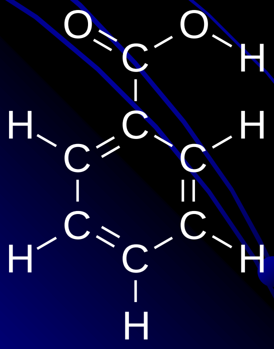
a)



$+ \ CaO \longrightarrow$

Benzoic Acid

b)



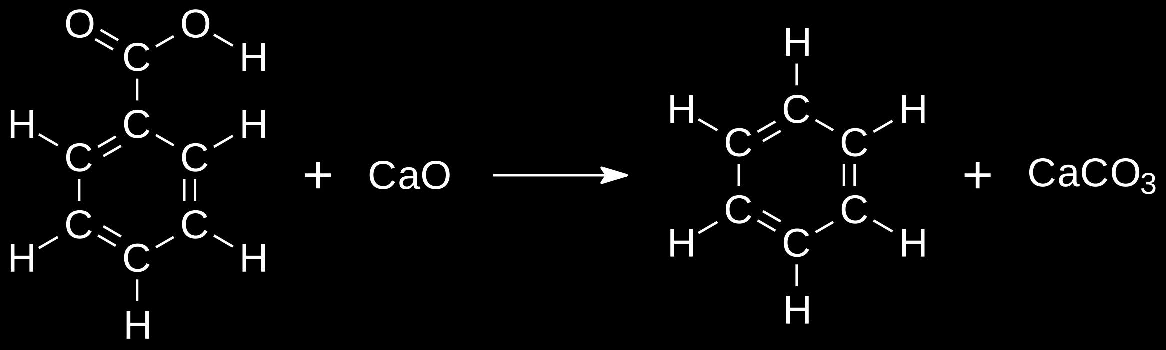
$+ \ Ca(OH)_2 \longrightarrow$

The Discovery of Benzene

Answer:

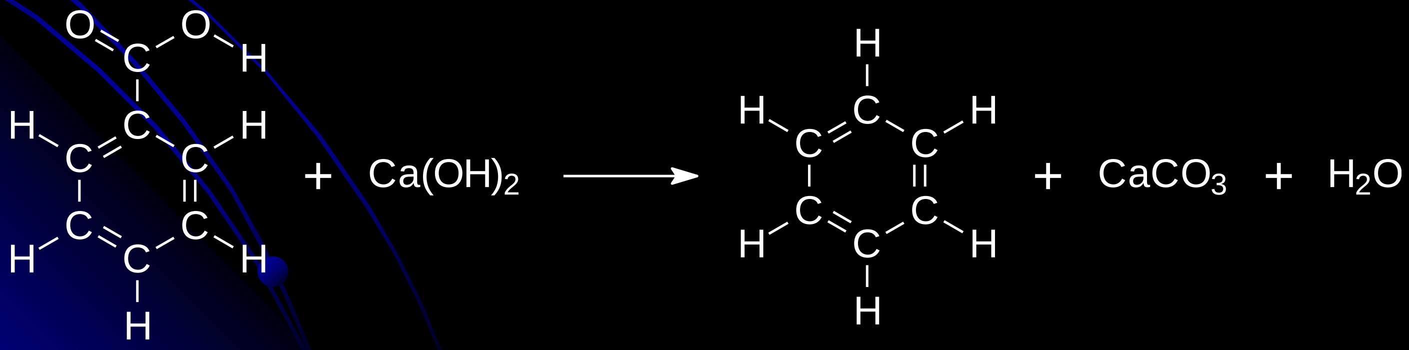
- Carbon dioxide is removed from the benzoic acid molecule (a process known as *decarboxylation*) to yield benzene, calcium carbonate and water.

a)



Benzoic Acid

b)



The Discovery of Benzene

August Wilhelm
von Hofmann
(1818 – 1892).

In 1845, the English chemist *Charles Mansfield*, working under *August Wilhelm von Hofmann*, isolated benzene from coal tar. Four years later, Mansfield began the first industrial scale production of benzene based on the coal tar method.

Isomers of C_6H_6

For many years there was speculation over the structure of benzene. After 1834, when the molecular formula was established as C_6H_6, chemists started to propose structural formulae for benzene.

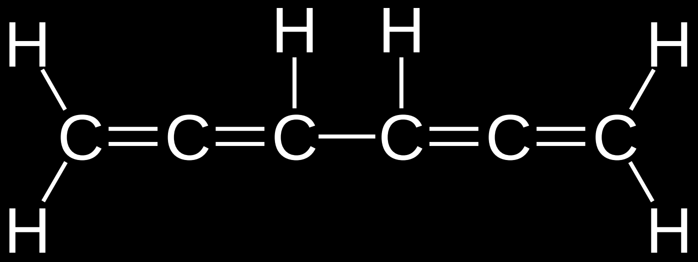
Question:

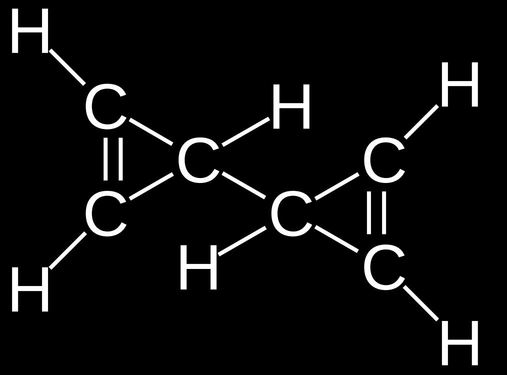
Imagine that you were a chemist living and working in 1834. Propose at least *four* structural formulae for benzene.

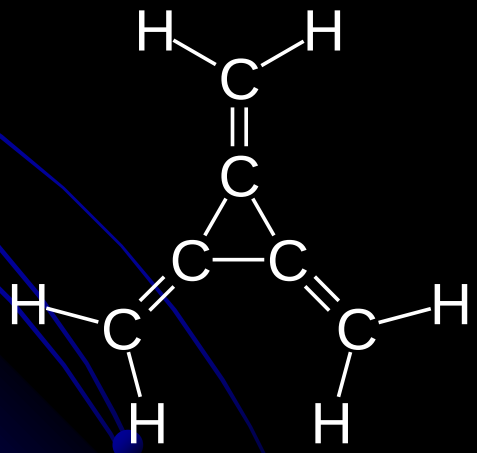
Isomers of C_6H_6

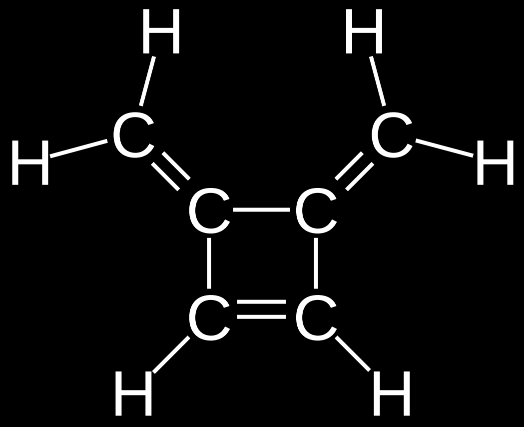
Answer:

The structural formulae of some compounds with the formula C_6H_6:





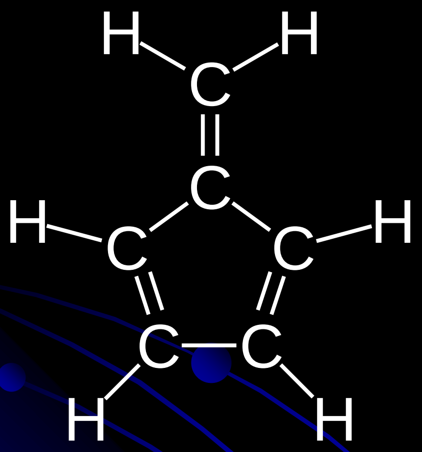


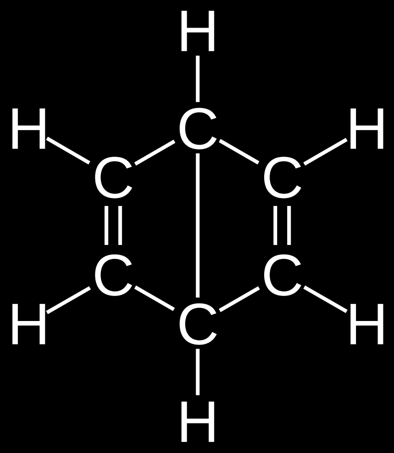


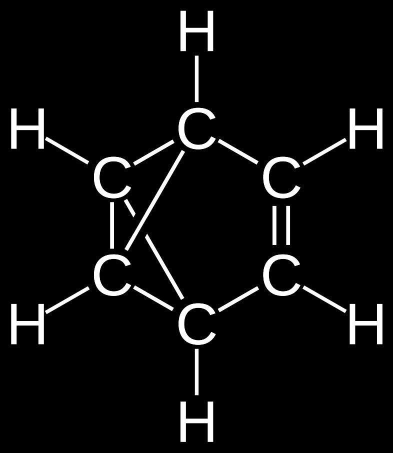
Isomers of C_6H_6

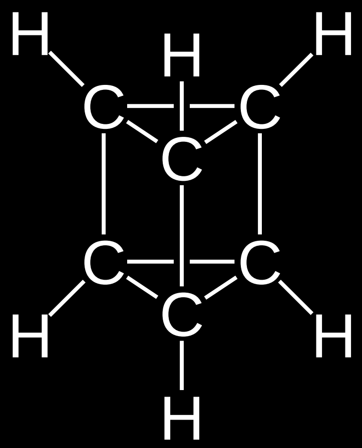
Answer:

The structural formulae of some compounds with the formula C_6H_6:

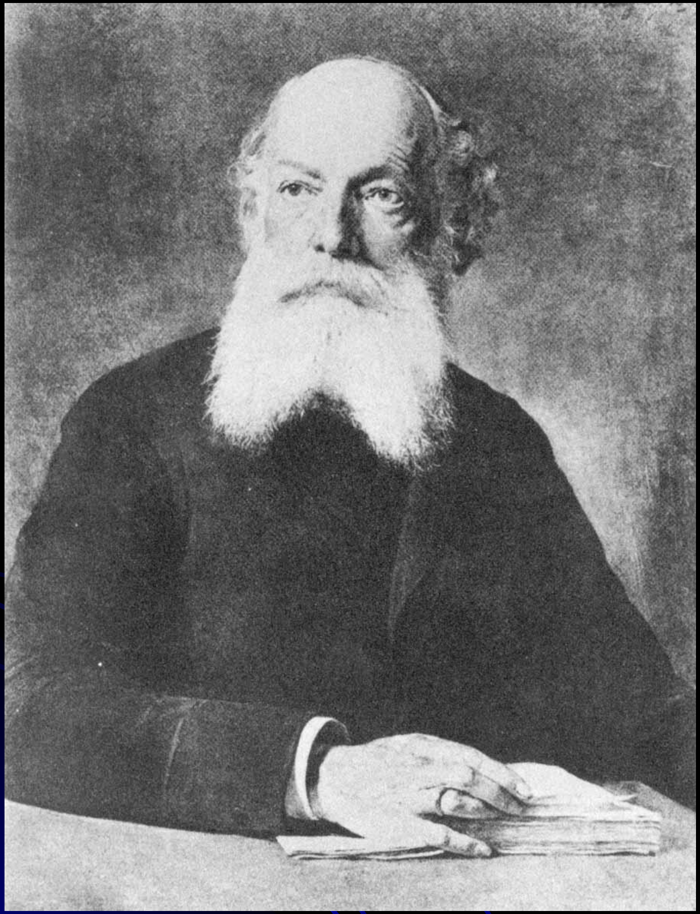






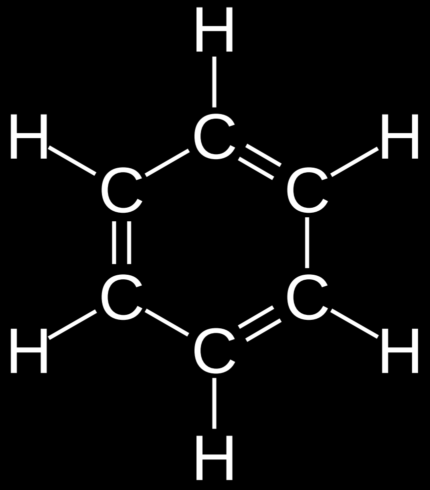


The Kekulé Structure of Benzene



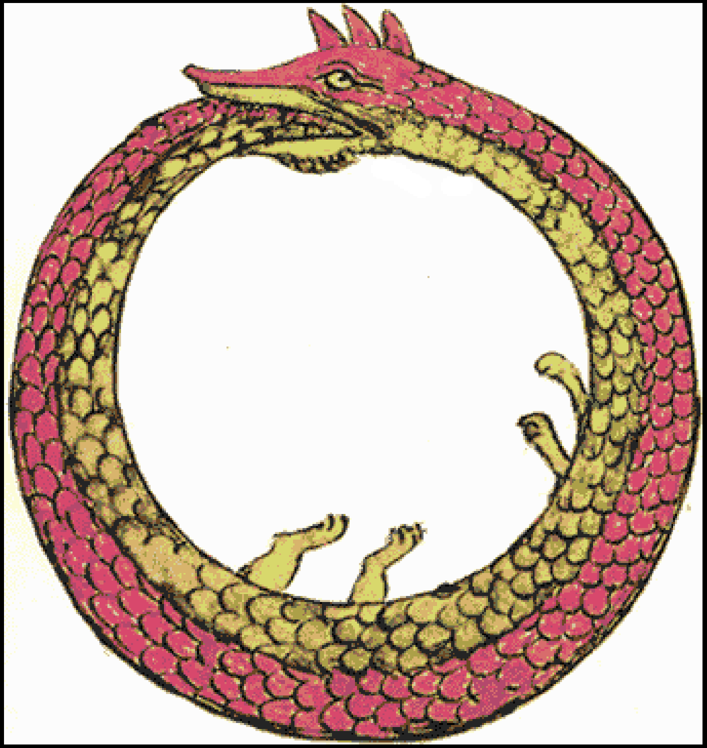
August Kekulé
(1829 – 1896).

In 1865, August Kekulé suggested the structure of benzene shown below:



The Kekulé Structure of Benzene

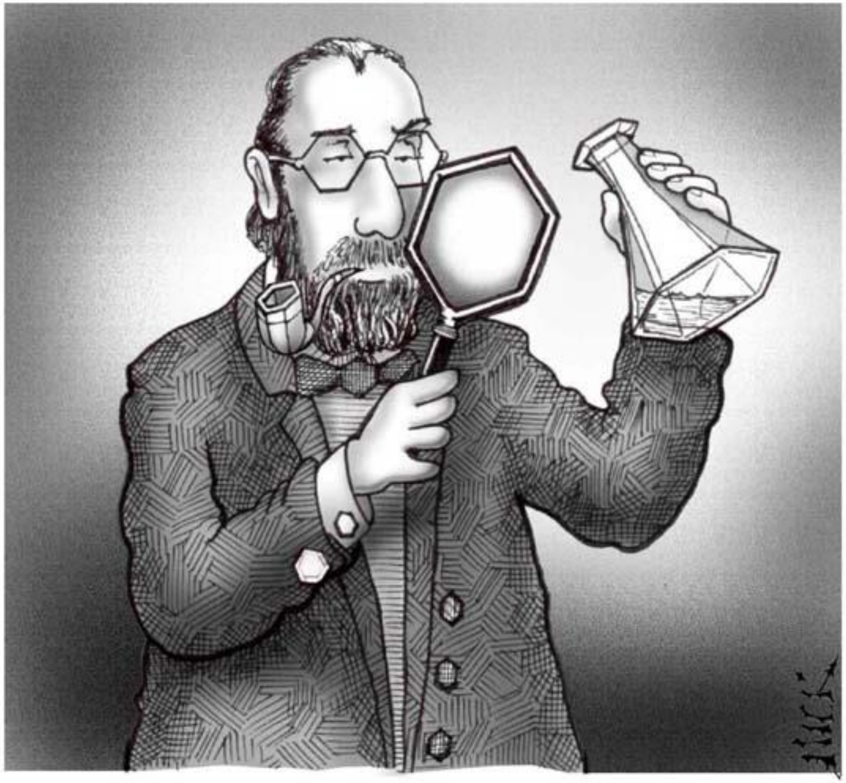
There are many stories of how Kekulé deduced the structure of benzene. Some say that he dreamt one night of a snake swallowing its own tale (a symbol known as the *Ouroboros*) while other stories say that he fell asleep on top of a London trolley bus and dreamt of six monkeys holding hands and then entwining their tails!



Ouroboros.

The Kekulé Structure of Benzene

Great events in Chemistry...



1865: Kekulé, moments before his brilliant insight into the structure of benzene.

Fig. 1.

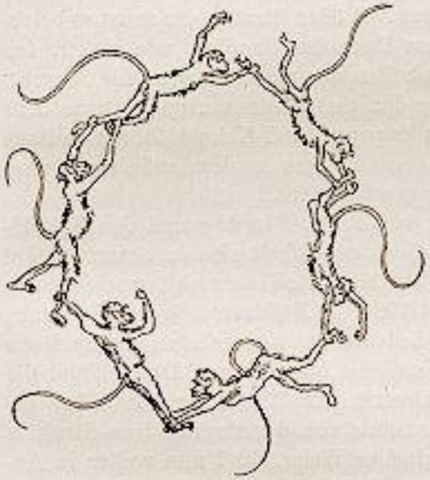


Fig. 2.

The Kekulé Structure of Benzene

However, the Kekulé structure of benzene is *incorrect* because it fails to explain three important properties of benzene.

The Kekulé Structure of Benzene

Question One:

How would you expect Kekulé’s benzene to react with bromine?

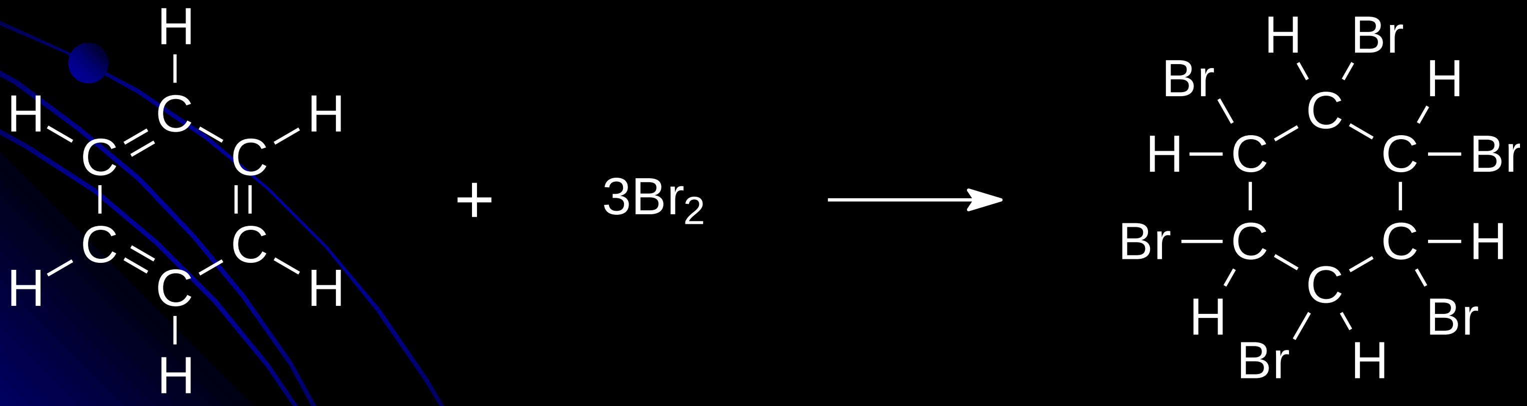
State what you would expect to observe and write a balanced chemical equation to explain your observation.

The Kekulé Structure of Benzene

Answer:

Kekulé's benzene contains three carbon-to-carbon double covalent bonds. Such a highly unsaturated compound would be expected to undergo an *addition reaction* with bromine resulting in an orange to colourless colour change.

$$C_6H_6 + 3Br_2 \rightarrow C_6H_6Br_6$$



The Kekulé Structure of Benzene

Reality:

If bromine is added to benzene at room temperature and pressure, the mixture *remains orange* and no colour change is observed. This indicates that there is no chemical reaction taking place between the bromine and the benzene.

Inference:

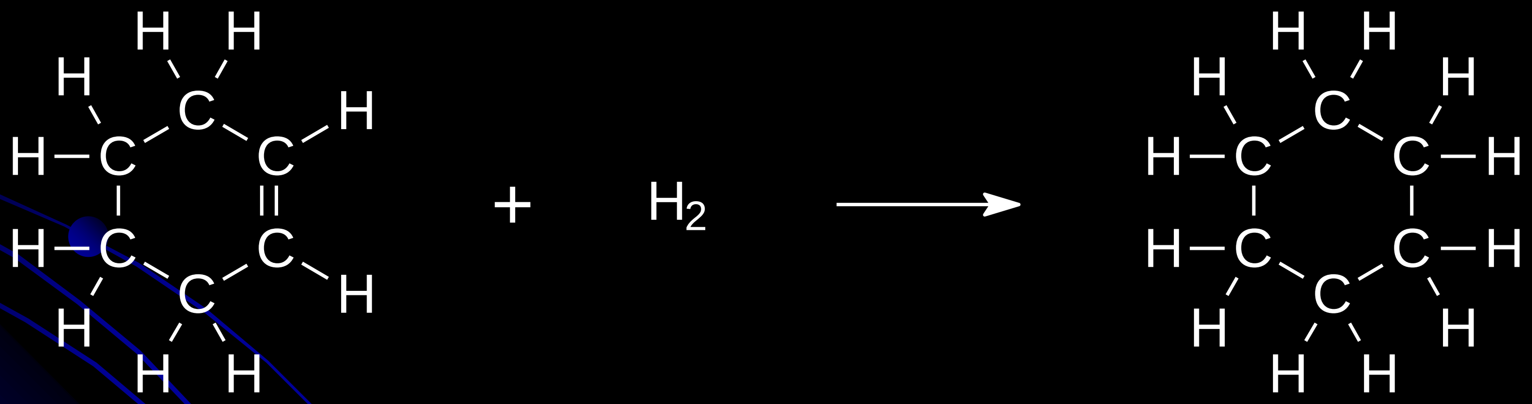
The *actual* structure of benzene results in the compound being more stable and hence less reactive than the structure of benzene proposed by Kekulé.

The Kekulé Structure of Benzene

Question Two:

The molar enthalpy change for the catalytic hydrogenation of cyclohexene is *-120 kJ mol^{-1}*:

$$C_6H_{10} + H_2 \rightarrow C_6H_{12} \qquad \Delta H = -120 \text{ kJ mol}^{-1}$$

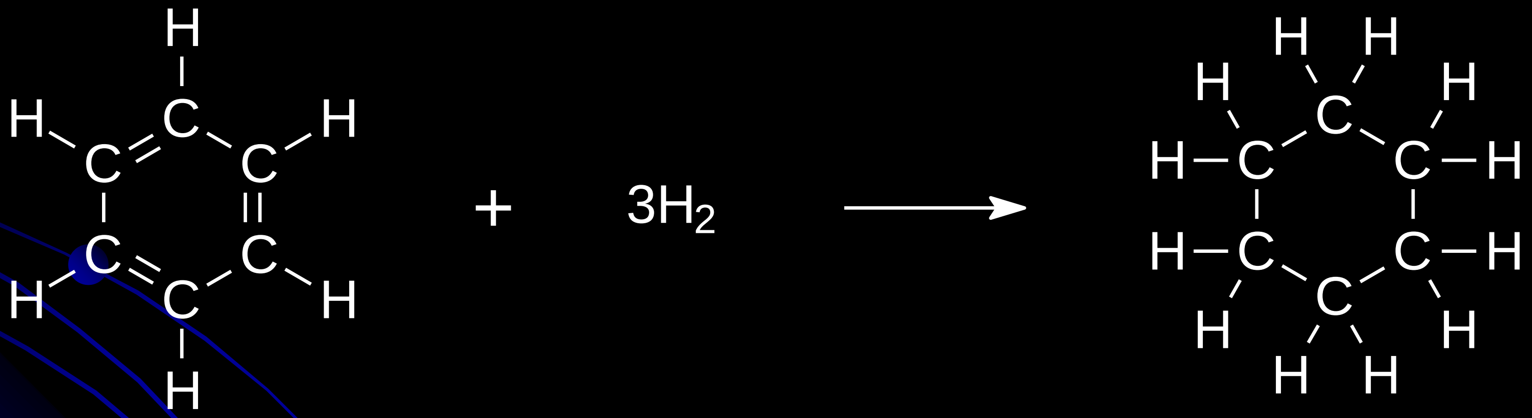


Write a balanced chemical equation for the catalytic hydrogenation of Kekulé's benzene and hence calculate the molar enthalpy change for its catalytic hydrogenation.

The Kekulé Structure of Benzene

Answer:

$$C_6H_6 + 3H_3 \rightarrow C_6H_{12}$$



$(-120\ \text{kJ mol}^{-1}) \times 3 = -360\ \text{kJ mol}^{-1}$

The Kekulé Structure of Benzene

Reality:

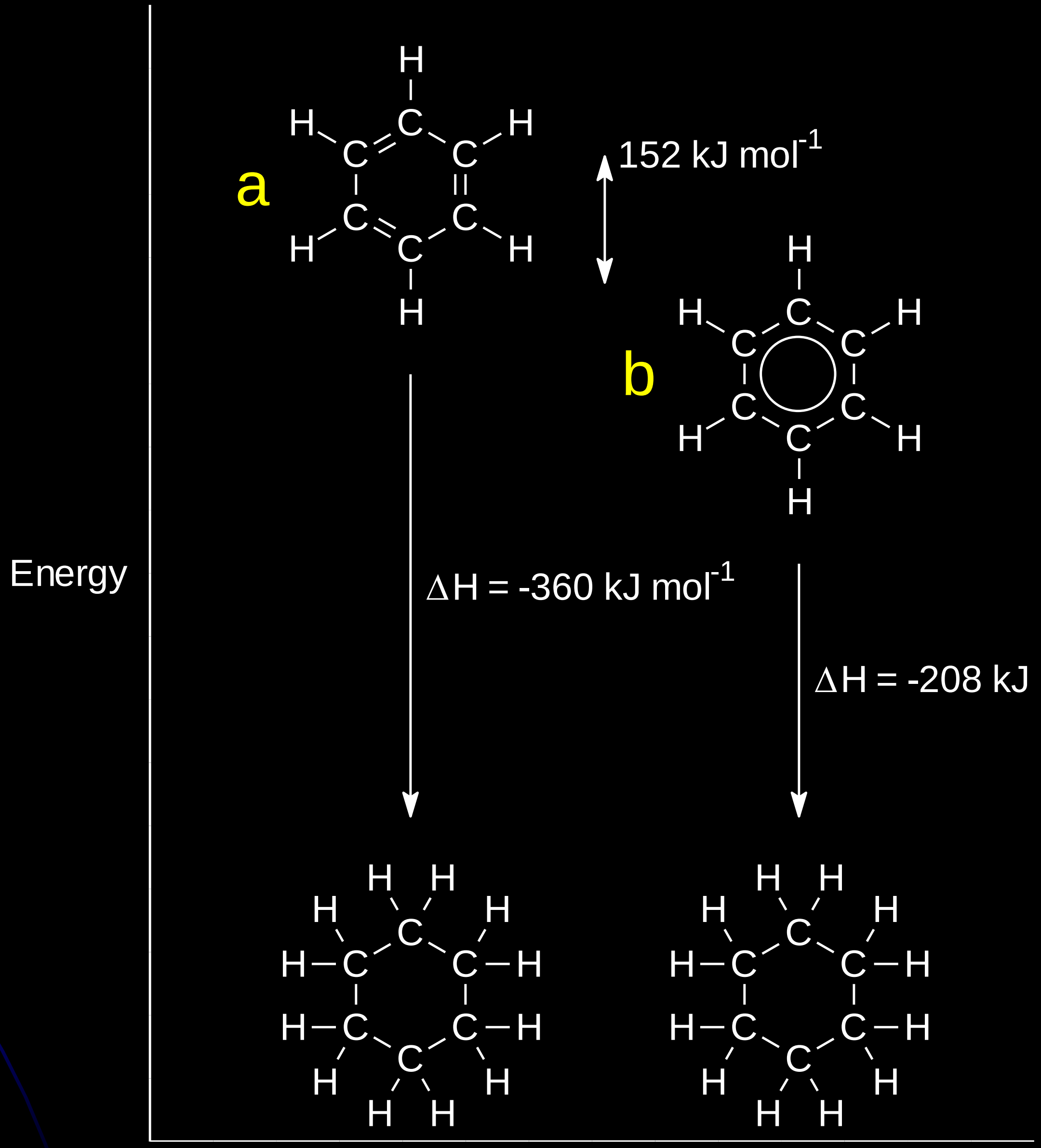
The actual molar enthalpy change for the catalytic hydrogenation benzene measured by experiment is *-208 kJ mol^{-1}*.

Inference:

The catalytic hydrogenation of real benzene releases less energy (*-208 kJ mol^{-1}*) than the value calculated for Kekulé’s benzene (*-360 kJ mol^{-1}*). This demonstrates that real benzene is more stable than Kekulé’s benzene by *152 kJ mol^{-1}*.

The Kekulé Structure of Benzene

The actual structure of benzene (b) is 152 kJ mol^{-1} more stable than the Kekulé structure of benzene (a).



The Kekulé Structure of Benzene

Question Three:

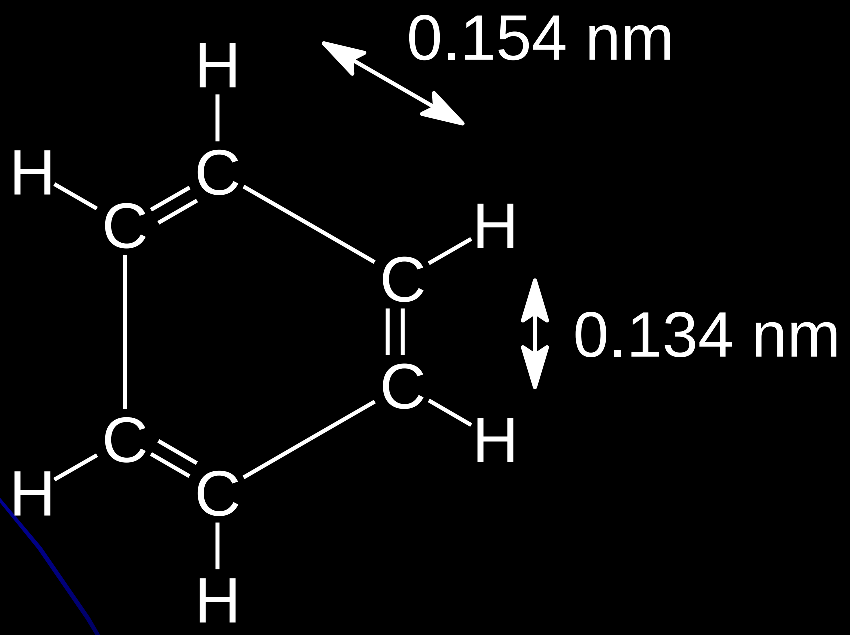
The length of a carbon-to-carbon *single* covalent bond is *0.154 nm* while the length of a carbon-to-carbon *double* covalent bond is *0.134 nm*.

Use this information to draw the structure of Kekulé's benzene, clearly indicating the shape of the molecule.

The Kekulé Structure of Benzene

Answer:

The resulting structure contains three carbon-to-carbon bonds which are 0.154 nm long alternating with three carbon-to-carbon bonds which are 0.134 nm long.



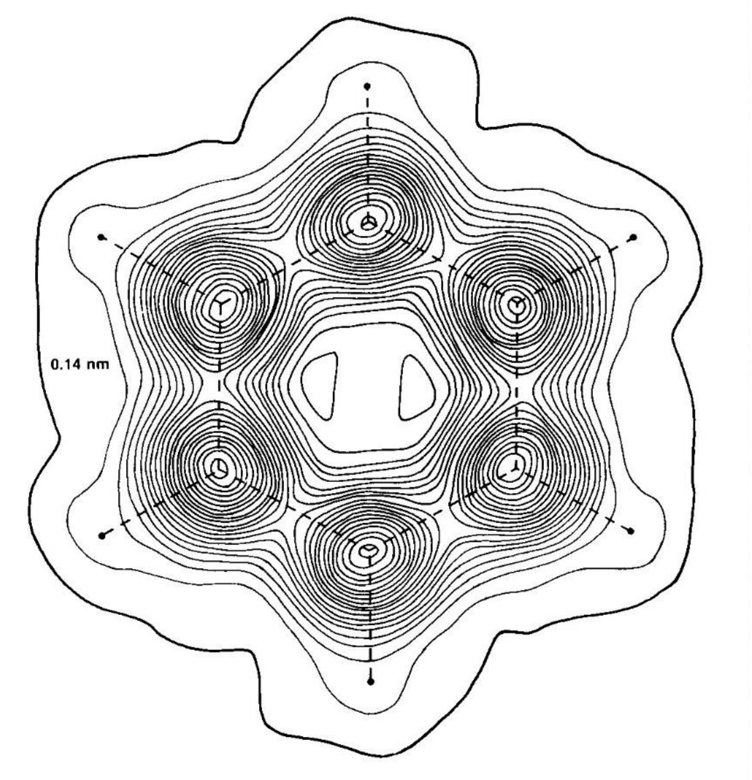
The Kekulé Structure of Benzene

Kathleen Lonsdale
(1903-1971).

Reality:

Kathleen Lonsdale analysed the structure of benzene by a technique known as *x-ray crystallography*. Her results showed that benzene is a cyclic, planar molecule in which all of the carbon-to-carbon covalent bonds have the *same length* of *0.139 nm*, which is longer than a C = C bond (0.134 nm) but shorter than a C — C (0.154 nm).

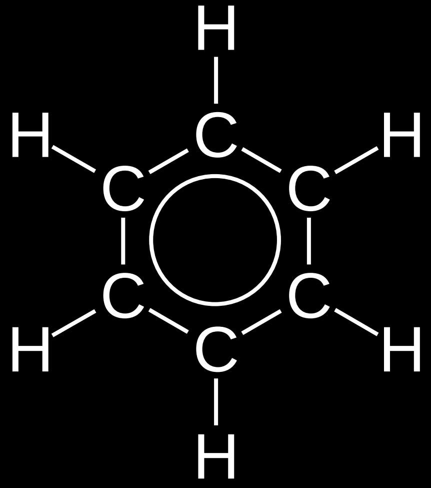
The Kekulé Structure of Benzene



The x-ray diffraction pattern of benzene.

Inference:

Real benzene contains carbon-to-carbon covalent bonds which are a hybrid of the individual C — C or C = C bonds originally proposed by Kekulé.

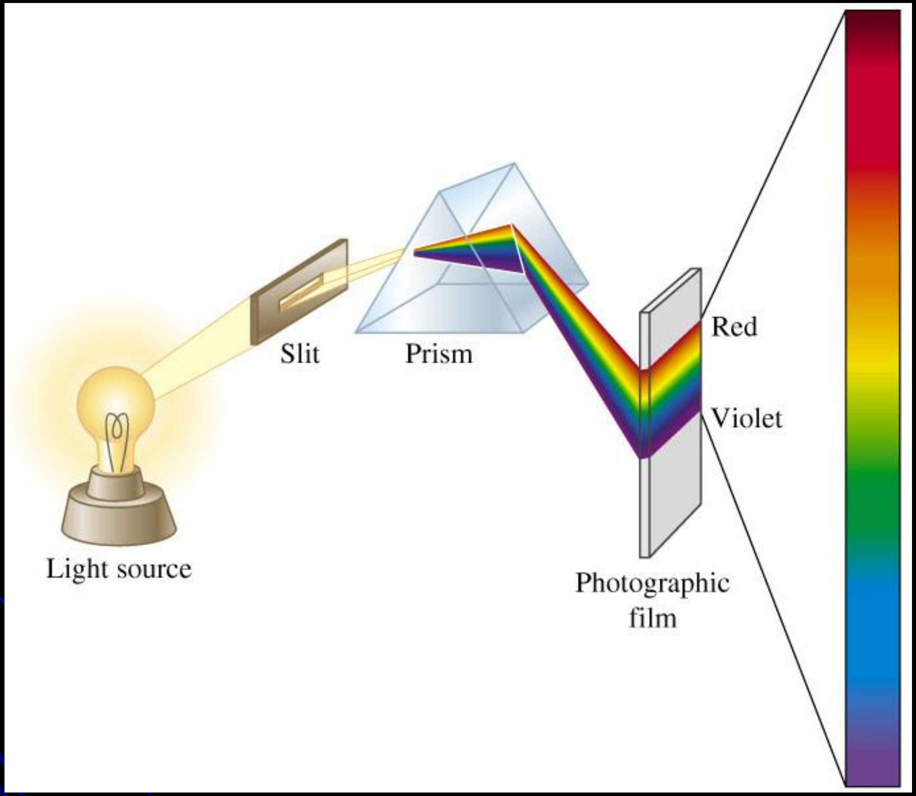


STUDENT ADVISORY

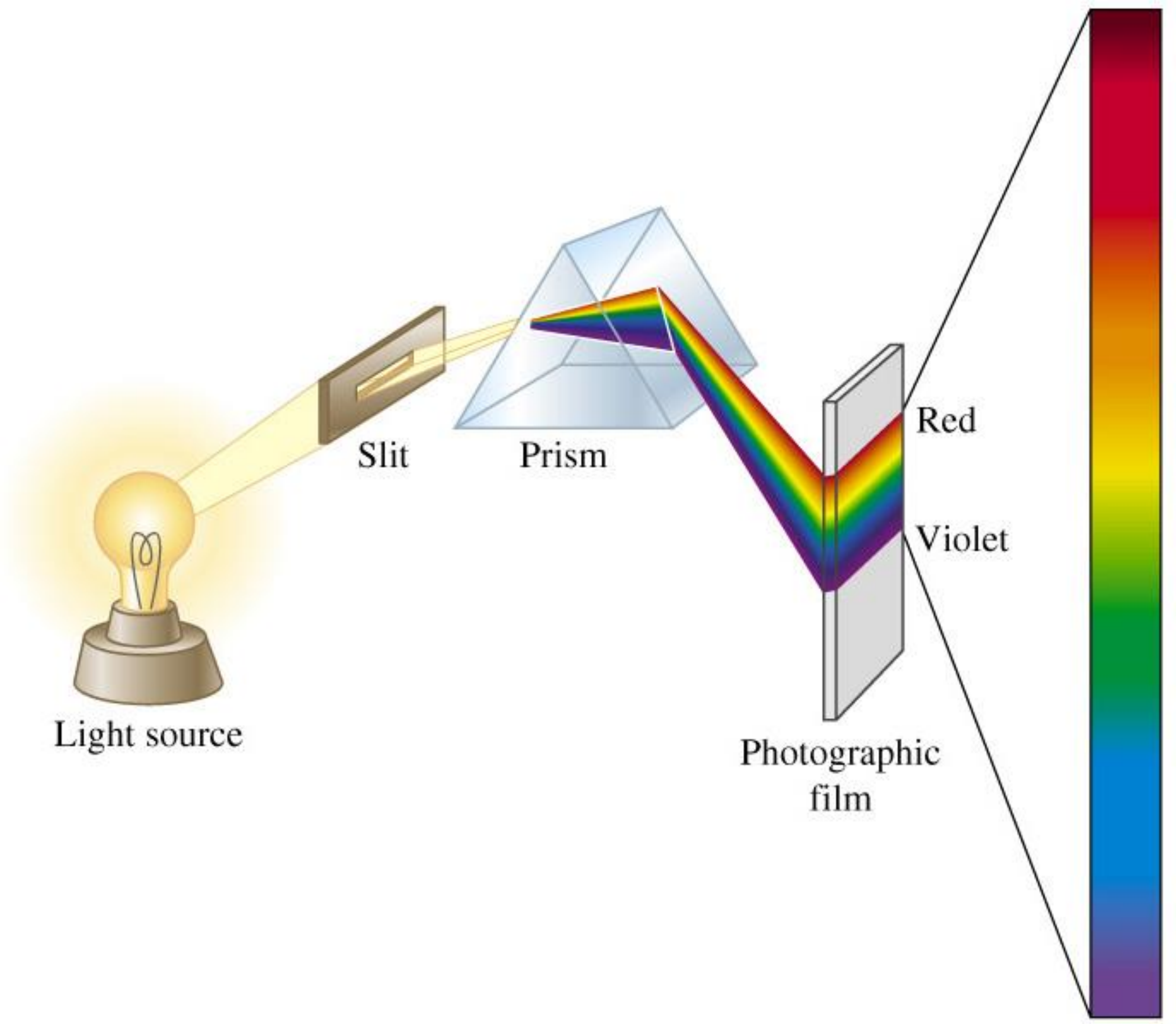
ADVANCED CONCEPTS

Quantum Mechanics

If white light is shone through a prism, it is *diffracted* to produce a *continuous spectrum* of colours; red, orange, yellow, green, blue, indigo and violet.

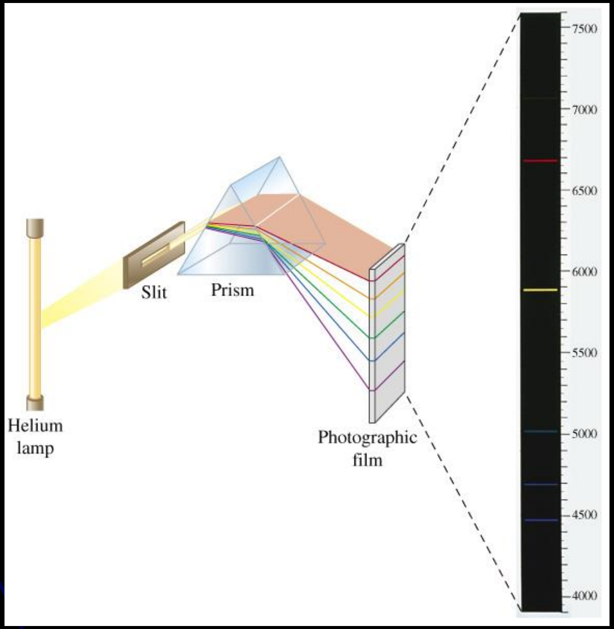


Quantum Mechanics

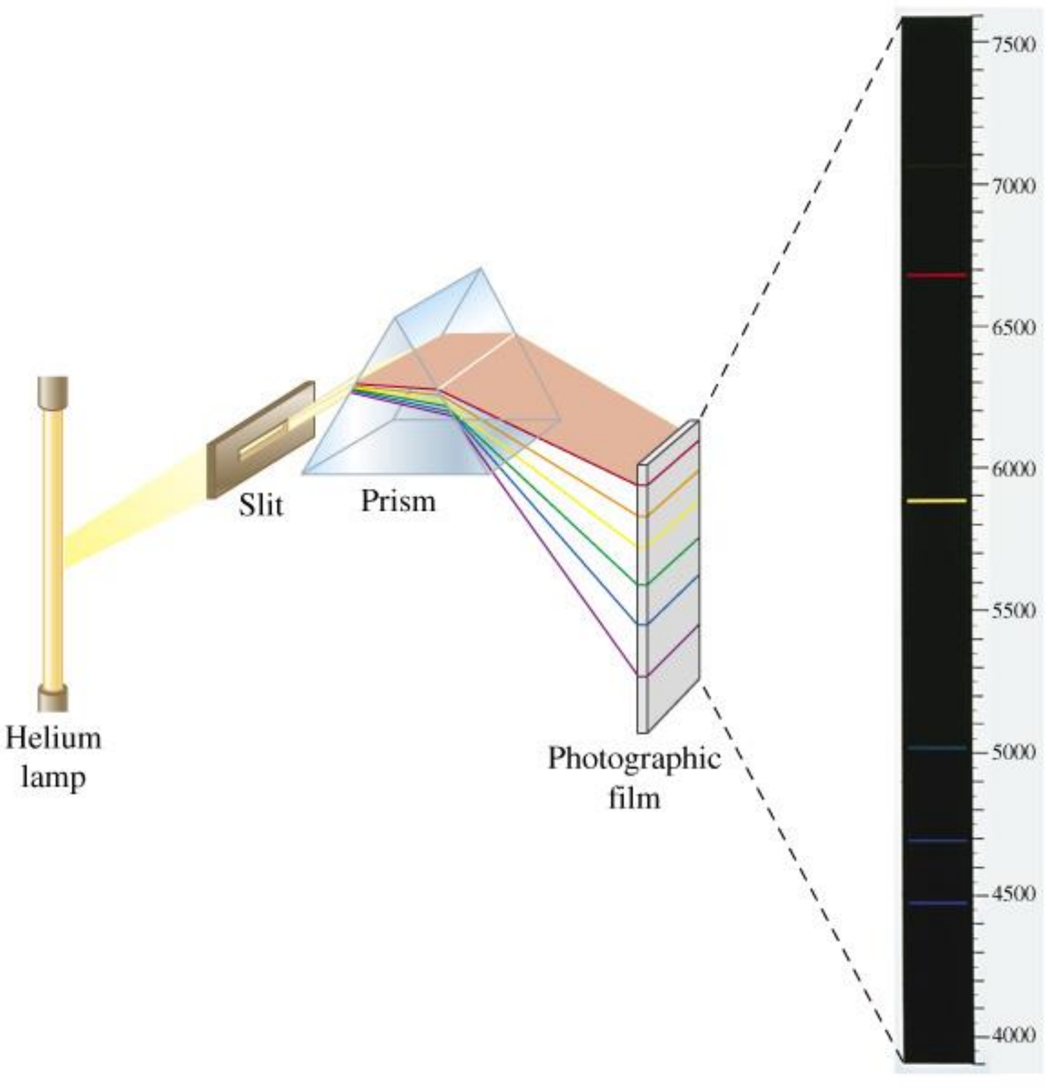


Quantum Mechanics

If atoms and molecules are heated to sufficiently high temperatures, they emit light of certain wavelengths. The diagram below shows a discharge tube containing a gaseous element. The observed spectrum consists of a number of coloured lines on a black background. The spectrum is called an *atomic emission spectrum* or *line spectrum*.

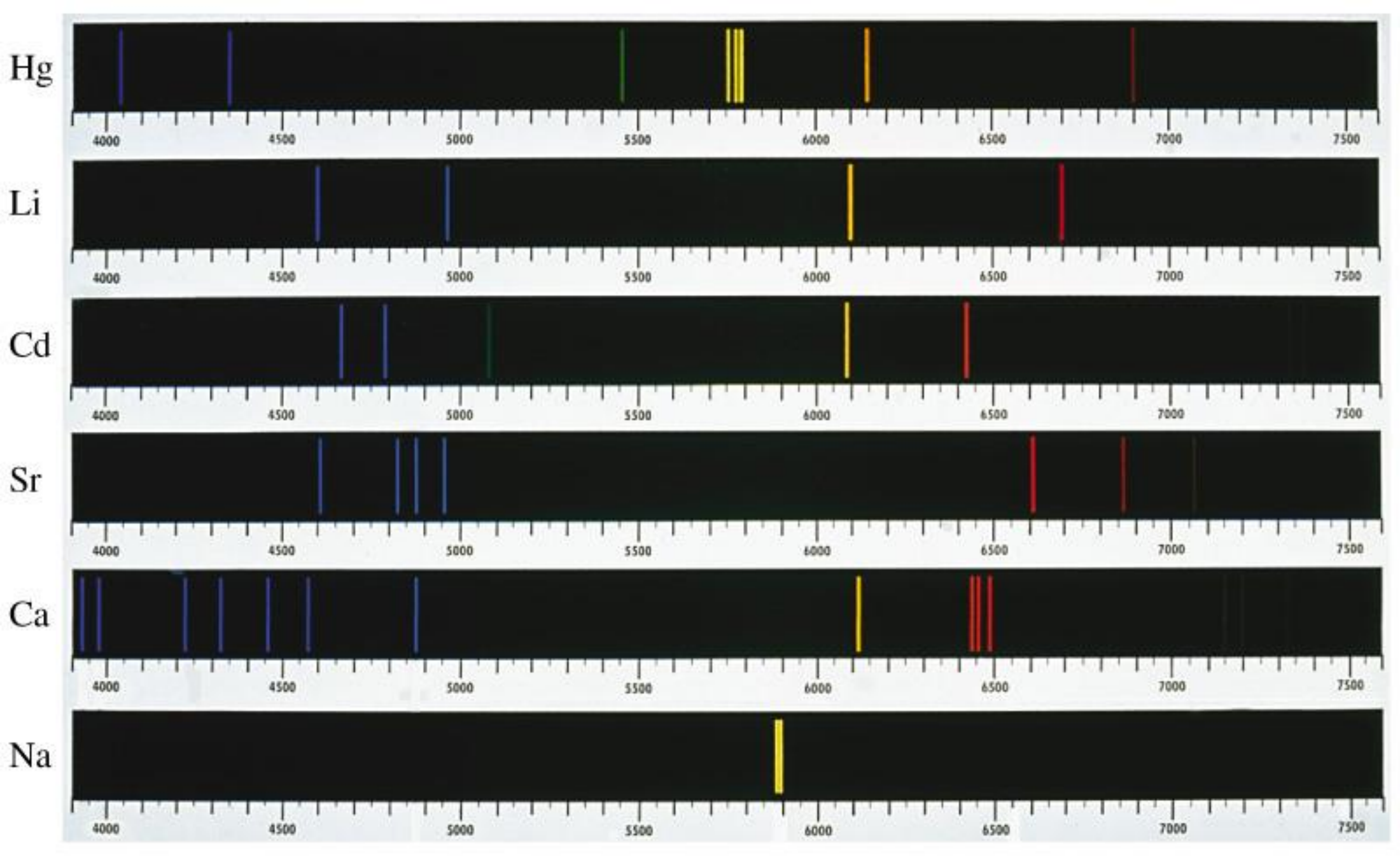


Quantum Mechanics



Quantum Mechanics

The atomic emission spectra of *mercury*, *lithium*, *cadmium*, *strontium*, *calcium* and *sodium*:

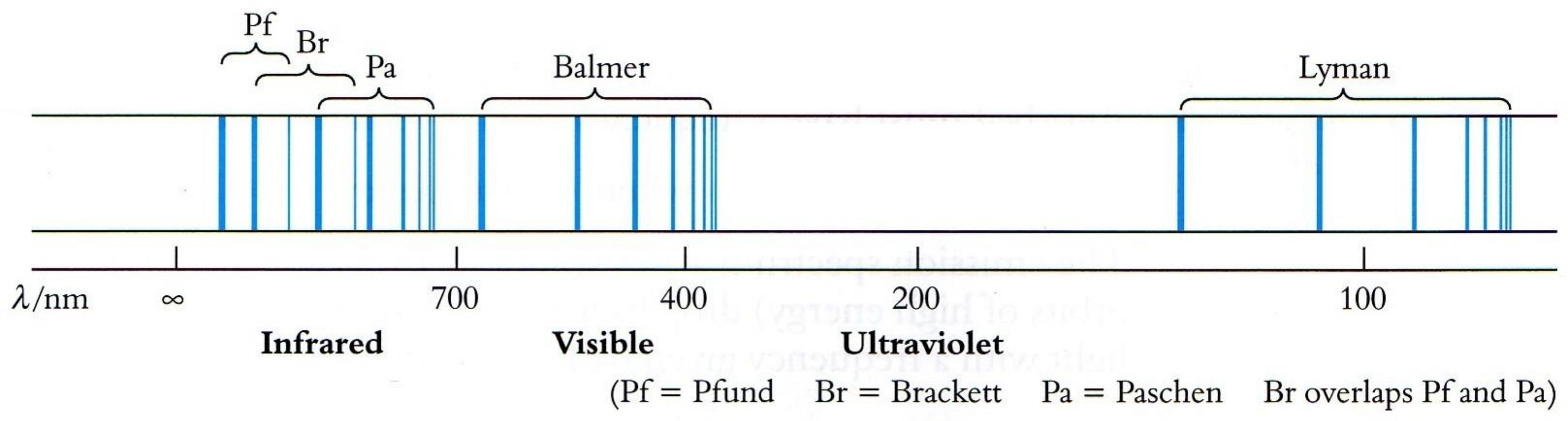


Quantum Mechanics

The visible spectrum of *hydrogen* consists of 4 bands of light of specific wavelengths. This spectrum is generated when gaseous hydrogen is excited by an electrical current and the light given off by the gas is split by a prism.

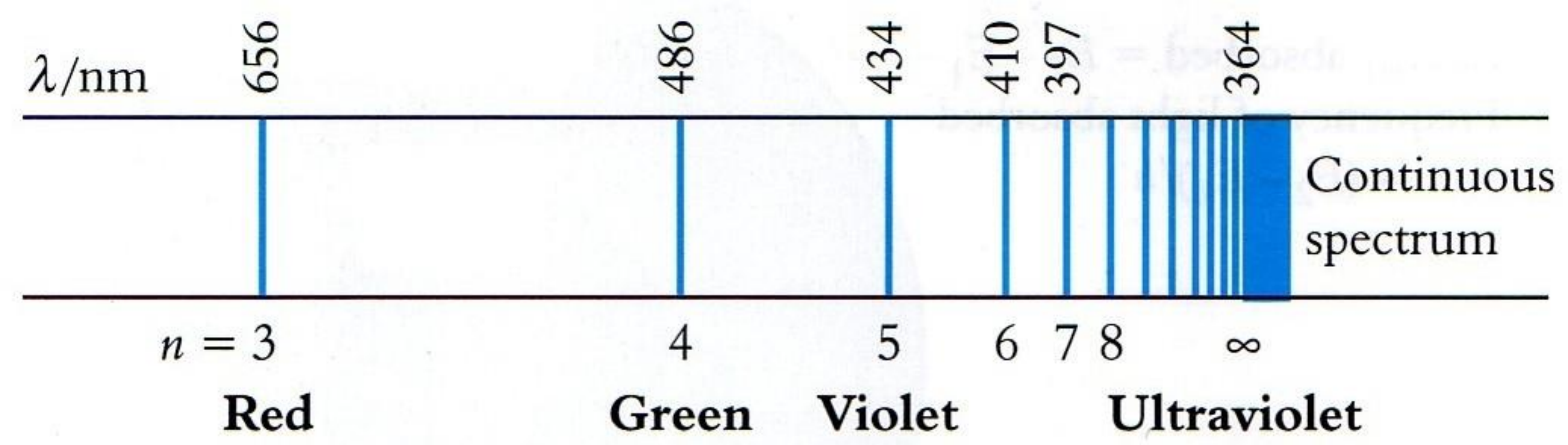
Quantum Mechanics

Viewed through a *spectrometer*, the emission spectrum of hydrogen is seen to be a number of separate sets of lines, or a *series* of lines. Each series of lines is named after the scientist who discovered them as shown in the diagram below:



Quantum Mechanics

A more detailed view of the *Balmer* series of hydrogen is shown in the diagram below:



Note how the intervals between the frequencies of the lines becomes smaller and smaller towards the higher frequency end of the spectrum until the lines *converge together* to form a *continuous spectrum* of light.

Quantum Mechanics

- Why do atoms absorb or emit light of certain frequencies?
- Why do atomic spectra consist of discrete (separate) lines?
- Why do the spectral lines converge at higher frequencies to form a continuous spectrum?

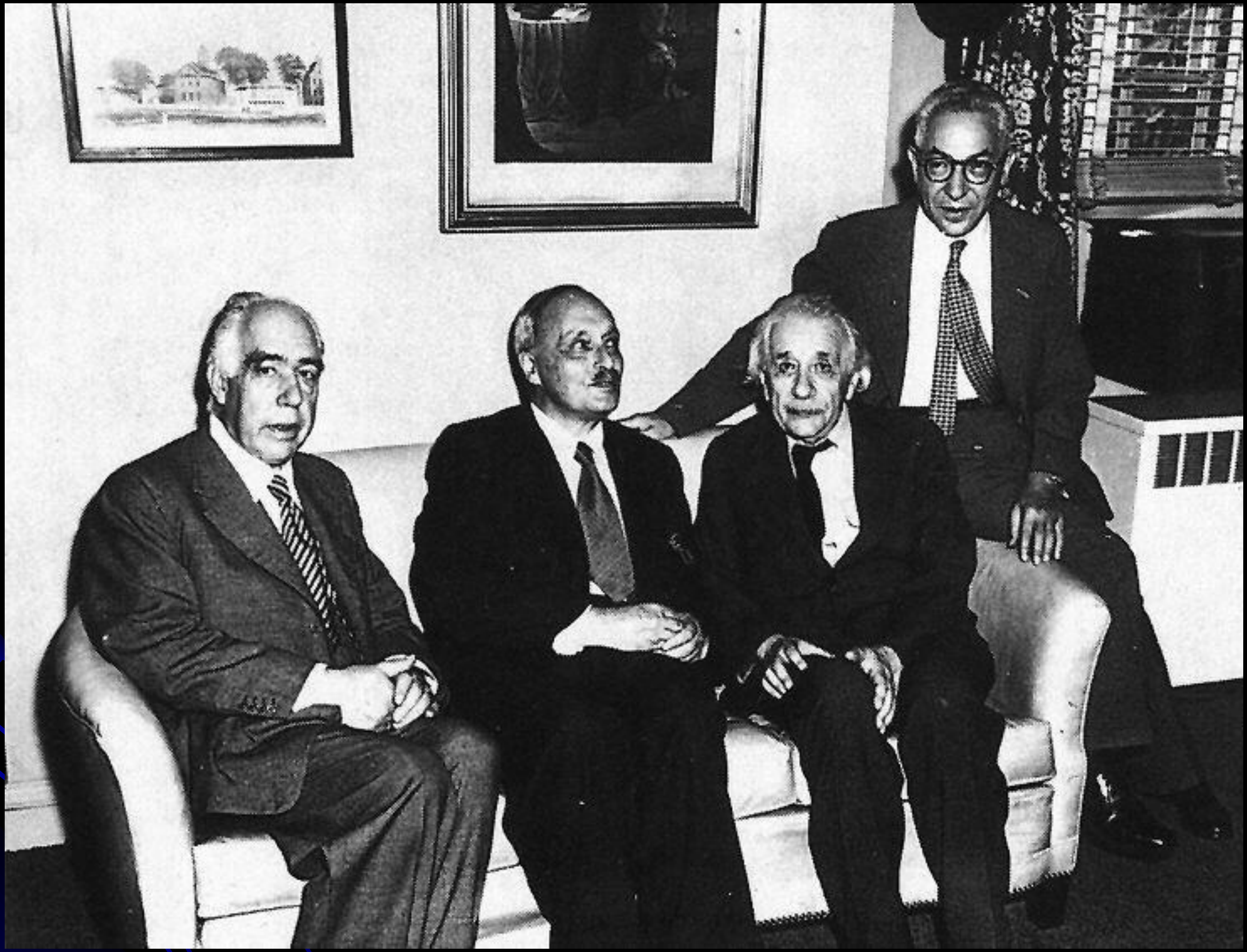
Quantum Mechanics

Niels Bohr
(1885 – 1962)
Nobel Prize
for Physics
1922.

In 1913, *Niels Bohr* put forward his structure of the atom to answer these questions. Bohr referred to *Max Planck's* recently discovered *quantum theory*, according to which energy can be absorbed or emitted in certain amounts, like separate packets of energy, called *quanta*.

Max Planck
(1858 – 1947)
Nobel Prize
for Physics
1918.

Quantum Mechanics



Niels Bohr and Albert Einstein.

Quantum Mechanics

Niels Bohr suggested the following:

1) An electron moving in an orbit can only have certain amounts of energy, not an infinite number of values, *i.e.* the electron's energy is *quantised*.

2) The energy that an electron needs to move in a particular orbit depends upon the radius of the orbit. An electron that is moving in an orbit *distant* from the nucleus has a *higher* energy compared to an electron that is moving in an orbit near to the nucleus of the atom.

Quantum Mechanics

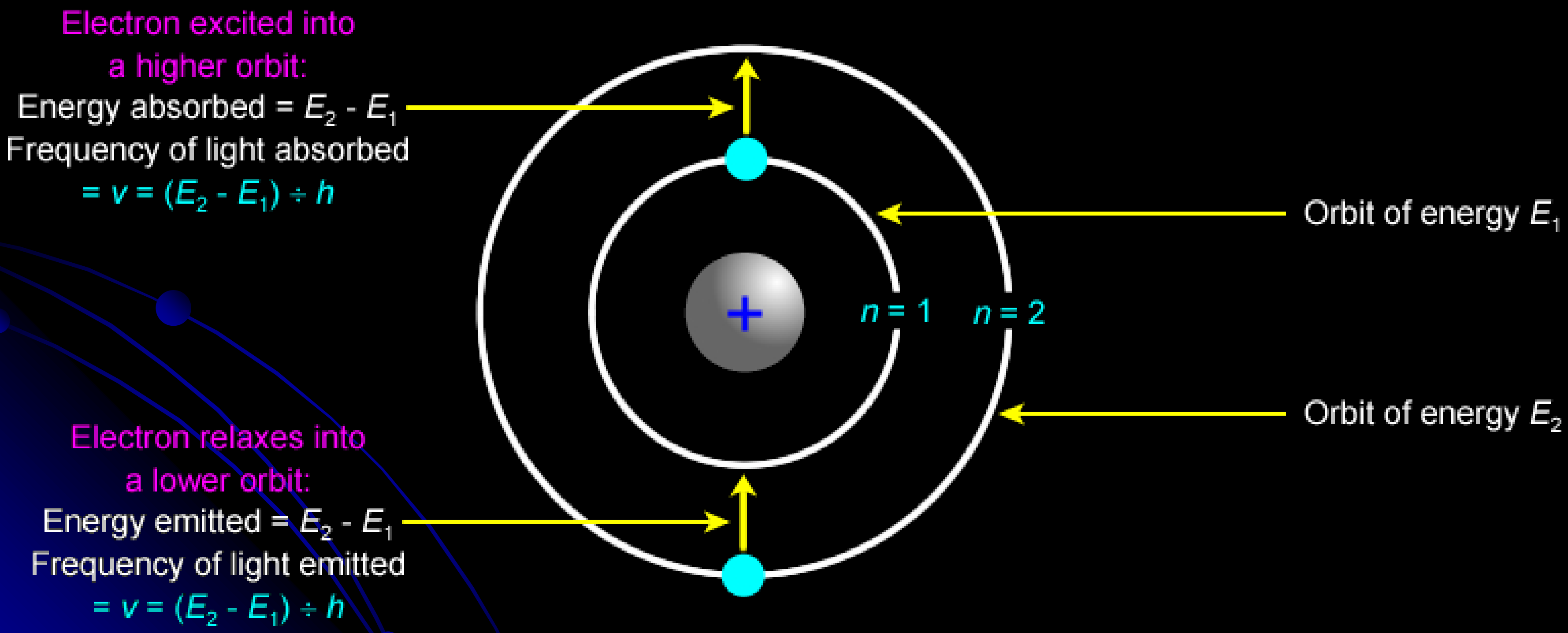
3) If the energy of the electron is quantised, then the radius of the orbit must also be quantised. An atom therefore contains a restricted number of orbits, not an infinite number of orbits.

4) An electron moving in one of these orbits does not emit energy. In order to move to an orbit further away from the nucleus, the electron must *absorb* energy to do work against the attraction of the nucleus. If an atom absorbs a *photon* of light, then the absorbed energy can promote (*excite*) an electron from an inner orbit to an outer orbit. When an electron falls (*relax*) from a higher orbit to a lower orbit, then energy is *released* as a photon of light.

Quantum Mechanics

For an electron to move from an orbit of energy E_1 to E_2, the light absorbed must have a frequency given by *Planck's equation:*

$h\nu = E_2 - E_1$ where ν = frequency and h = Planck's constant.

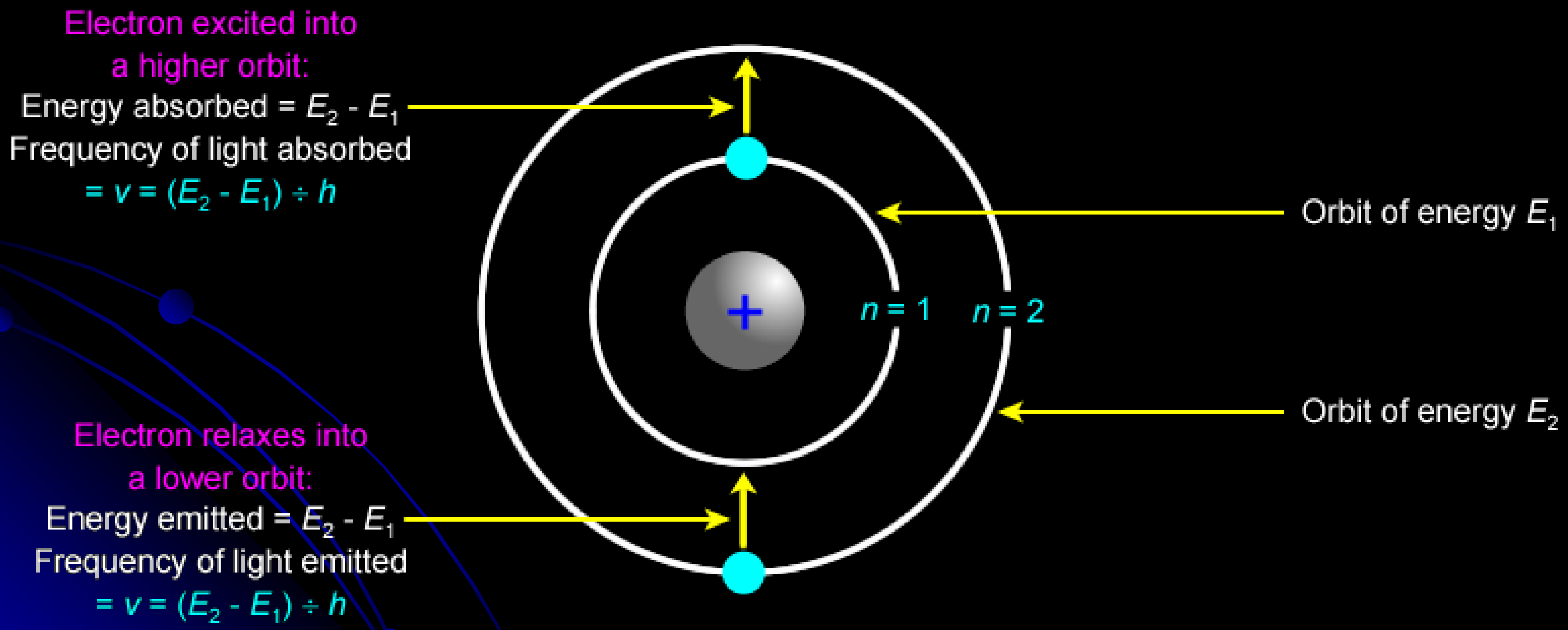


Electron excited into a higher orbit:
Energy absorbed = $E_2 - E_1$
Frequency of light absorbed
$= \nu = (E_2 - E_1) \div h$

Electron relaxes into a lower orbit:
Energy emitted = $E_2 - E_1$
Frequency of light emitted
$= \nu = (E_2 - E_1) \div h$

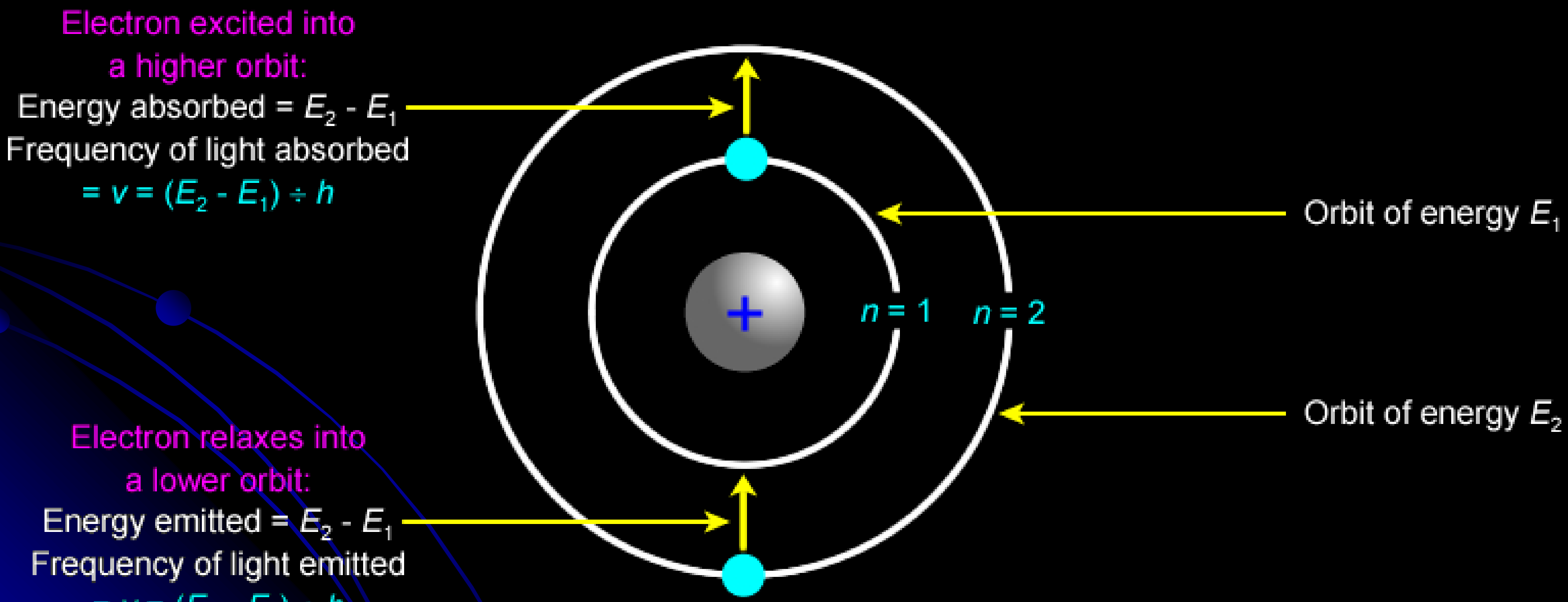
Quantum Mechanics

The emission spectrum arises when electrons which have been excited (raised into orbits of higher energy) fall back to orbits of lower energy. As these electrons relax, they emit energy as light with a frequency given by Planck’s equation.

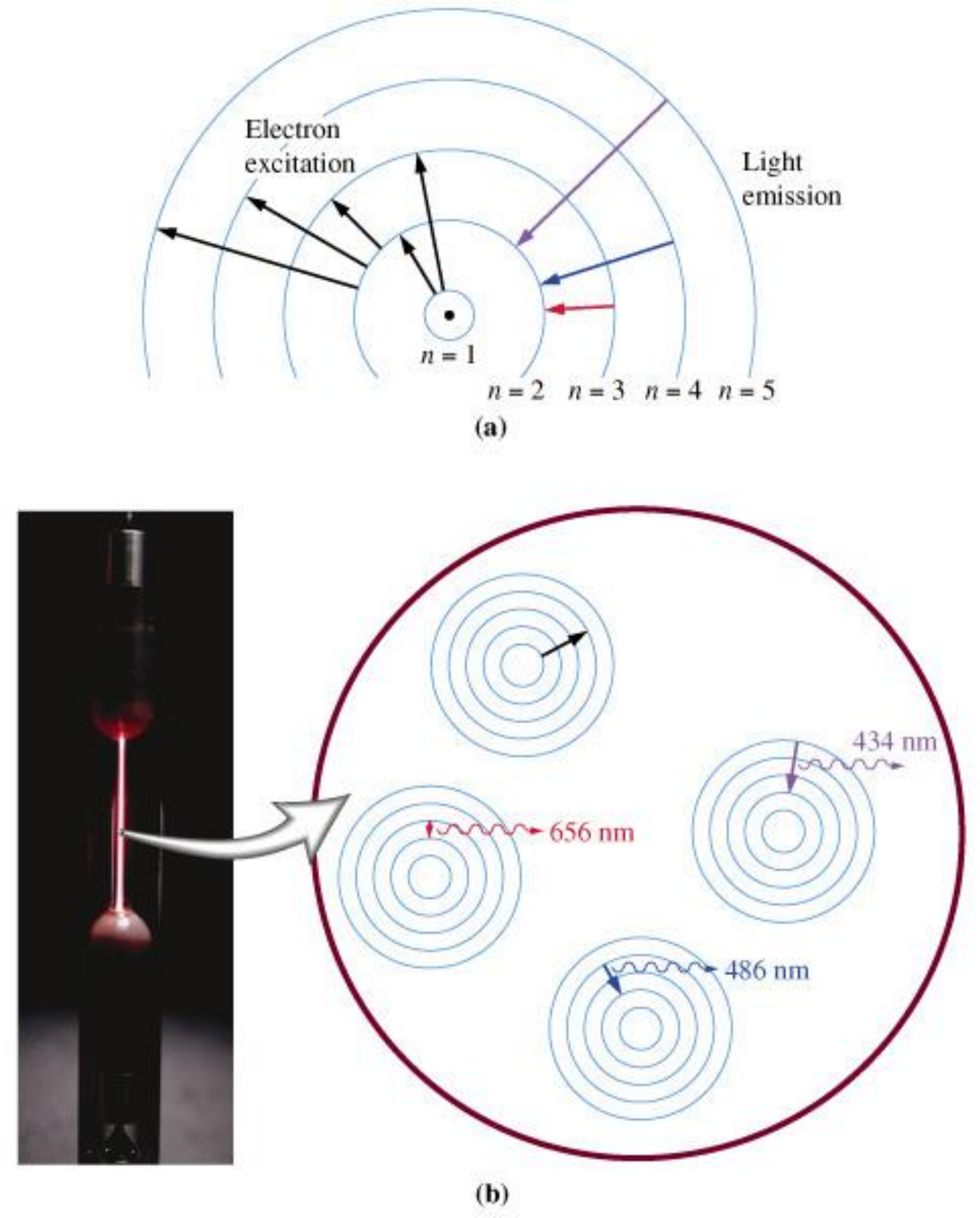


Quantum Mechanics

Bohr assigned *quantum numbers* to the orbits. He gave the orbit of lowest energy (closest to the nucleus) the quantum number *1*. An electron in this orbit is said to be in its *ground state*. The next energy level has a quantum number of *2*.



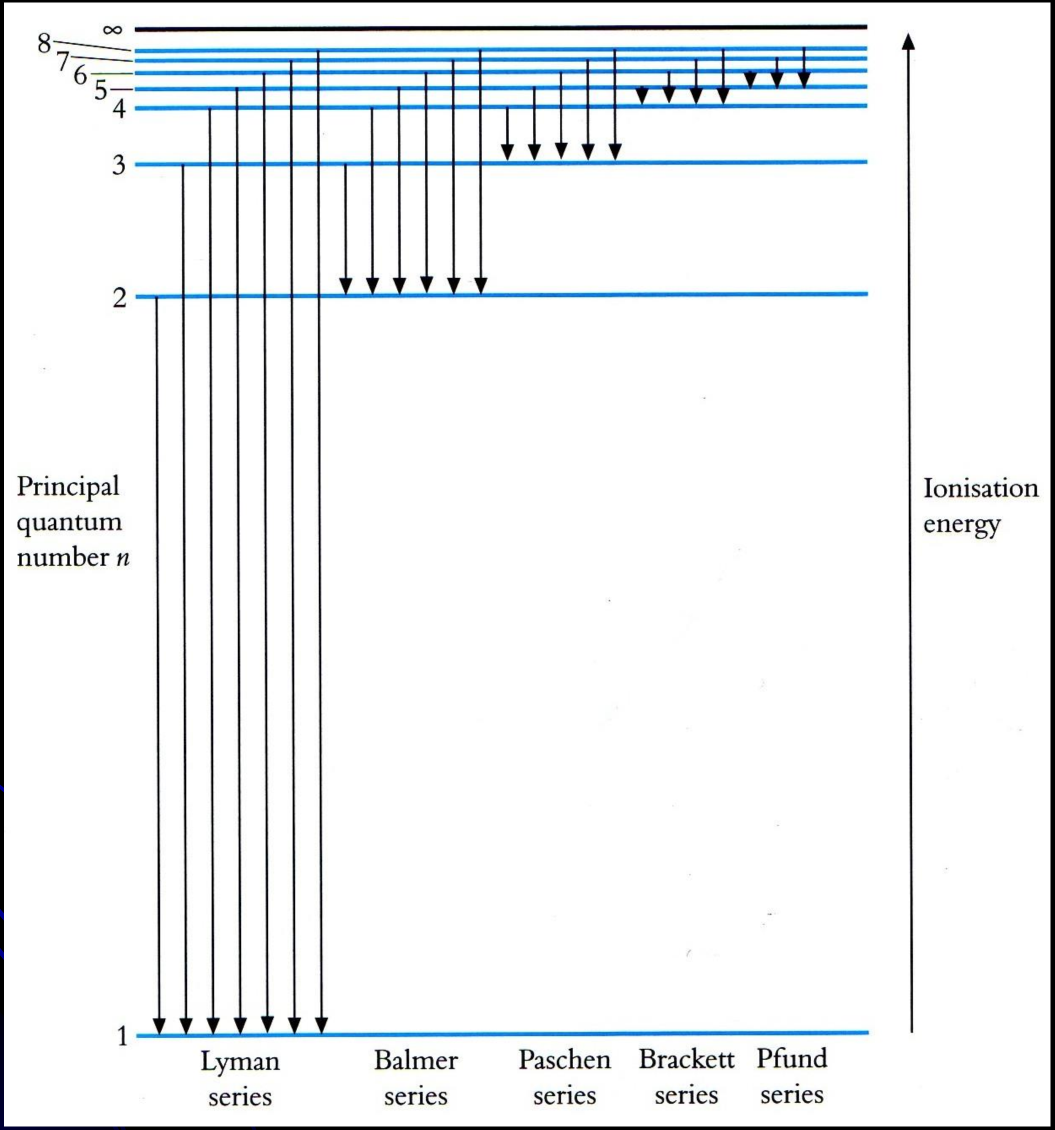
Quantum Mechanics



The emission spectrum of hydrogen arises when the electron in its ground state absorbs energy and is excited into a higher energy orbit. When the electron relaxes into a lower energy orbit, it releases energy as light with a frequency given by Planck's equation:

$hv = E2 - E1$

Quantum Mechanics



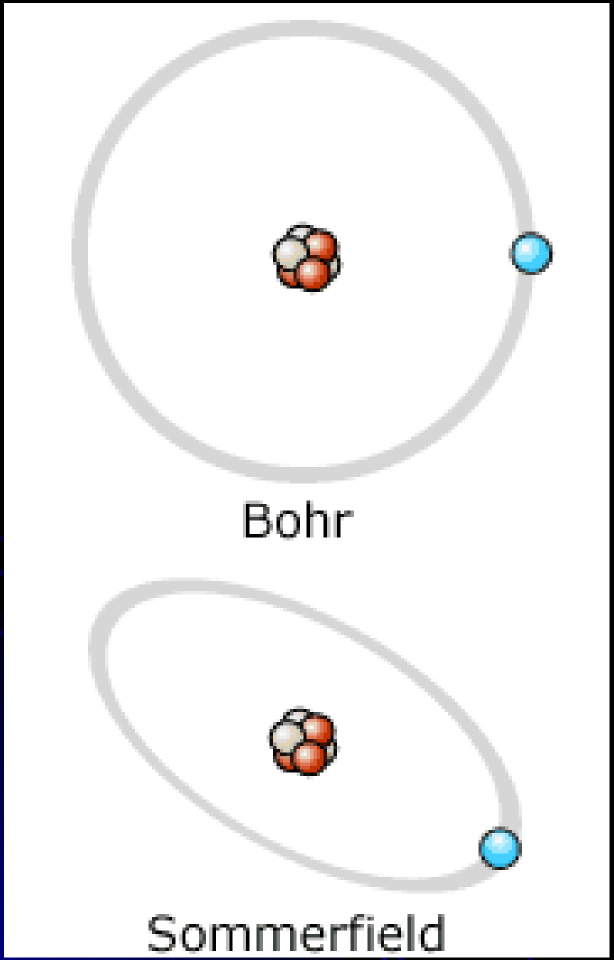
View Animation

Quantum Mechanics

Arnold Sommerfeld (1868 – 1951)
and Niels Bohr

Arnold Sommerfeld elaborated on Bohr's theory in1916. He proposed that each quantum number governed the energy of a circular orbit and also a set of *elliptical orbits* of similar energy.

Quantum Mechanics



Sommerfeld also called *n* the *principle quantum number* and introduced a second quantum number to describe the shapes of the elliptical orbits.

The second quantum number, *l*, can have values from (*n – 1*) down to *0*. For example, if $n = 4$, then the values of *l* would be *3*,*2*,*1* and *0*.

Quantum Mechanics

Louis de Broglie
(1892 – 1987)
Awarded the Nobel Prize
for Physics in 1929.

According to the wave theory of light, refraction and diffraction can be explained by the properties of waves. Other properties of light, such as the origin of line spectra and the photoelectric effect need a particle or photon theory for their explanation. The success of the duel theory of light led *Louis de Broglie* to speculate in 1924 on whether particles might have wave properties. He made the bold suggestion that *electrons have wave properties* as well as the *properties of particles*.

Schrödinger’s Wave Equation


Scan ©American Institute of Physics

Erwin Schrödinger
(1887 – 1961)
Awarded the Nobel Prize
for Physics in 1933.

Paul Dirac
(1902 – 1984)
Awarded the Nobel Prize
for Physics in 1933.

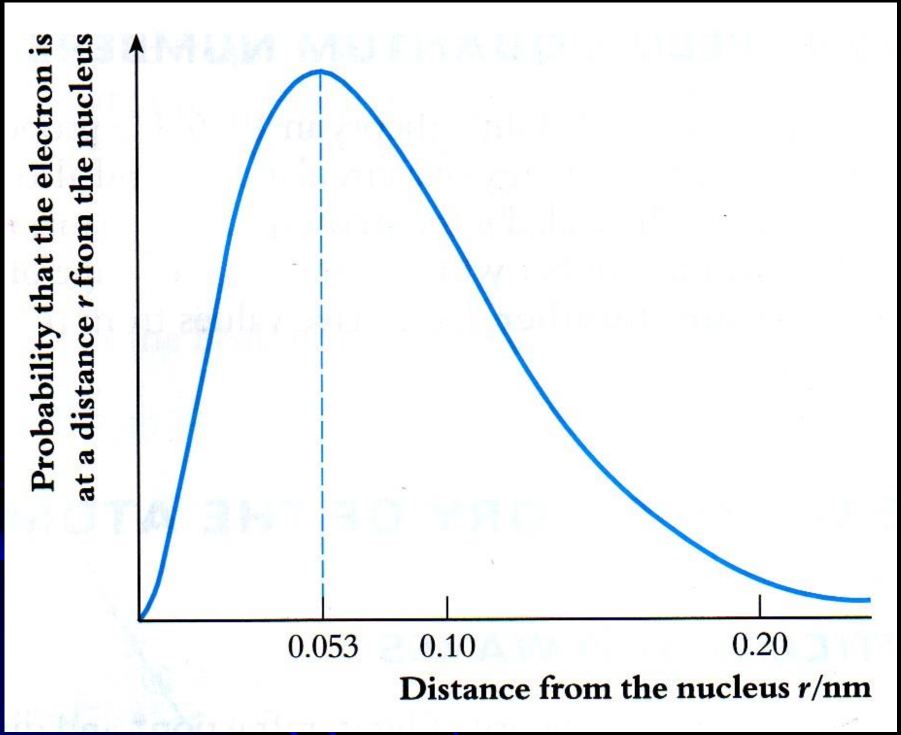
Schrödinger's Wave Equation

Erwin Schrödinger used this theory to work out a wave theory for the atom. One version of Schrödinger's famous wave equation is given below:

$$\frac{\delta^2\Psi}{\delta x^2} + \frac{\delta^2\Psi}{\delta y^2} + \frac{\delta^2\Psi}{\delta z^2} + \frac{8m\pi^2}{h^2}(E - V)\Psi = 0$$

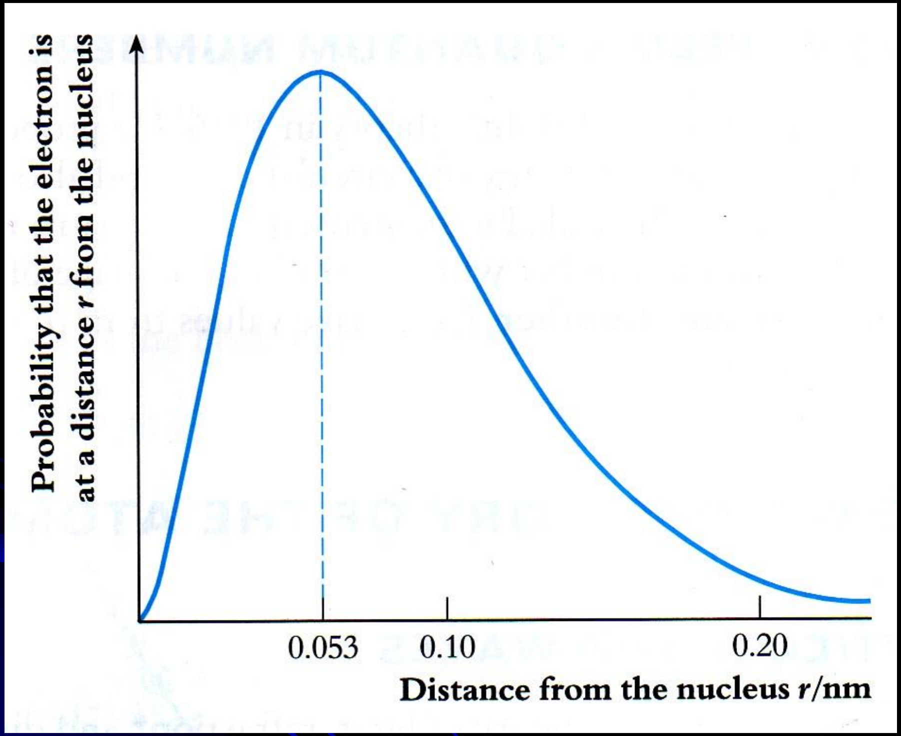
The solution to the wave equation gives the *probability density* of the electron. This is the probability that the electron is present in a small given region of space.

Schrödinger's Wave Equation



The graph on the left shows a probability density diagram for a hydrogen atom in its ground state. The maximum probability of finding an electron is *0.053 nm* from the nucleus.

Schrödinger's Wave Equation



There is a possibility that the electron will be either closer to the nucleus or outside the radius of 0.053 nm. The probability of finding the electron decreases sharply as the distance from the nucleus increases beyond *3r*. The volume of space in which there is a *95%* chance of finding the electron is called the *atomic orbital*.

Schrödinger's Wave Equation

Solutions of the wave equation can be obtained if the orbitals are described by *four quantum numbers*.

The first is Bohr's principle quantum number, *n*.

The second quantum number, *l*, corresponds to Sommerfeld's quantum number describing the shape of the elliptical orbits. The values of *l* are assigned letters:

l = 0 = s
l = 1 = p
l = 2 = d
l = 3 = f

Schrödinger’s Wave Equation

If an electron has a principle quantum number $n = 2$ and a second quantum number $l = 0$, it is said to be a *2s* electron. For various values of n, the different combinations of the two quantum numbers are:

1s
2s   2p
3s   3p   3d
4s   4d   4d   4f

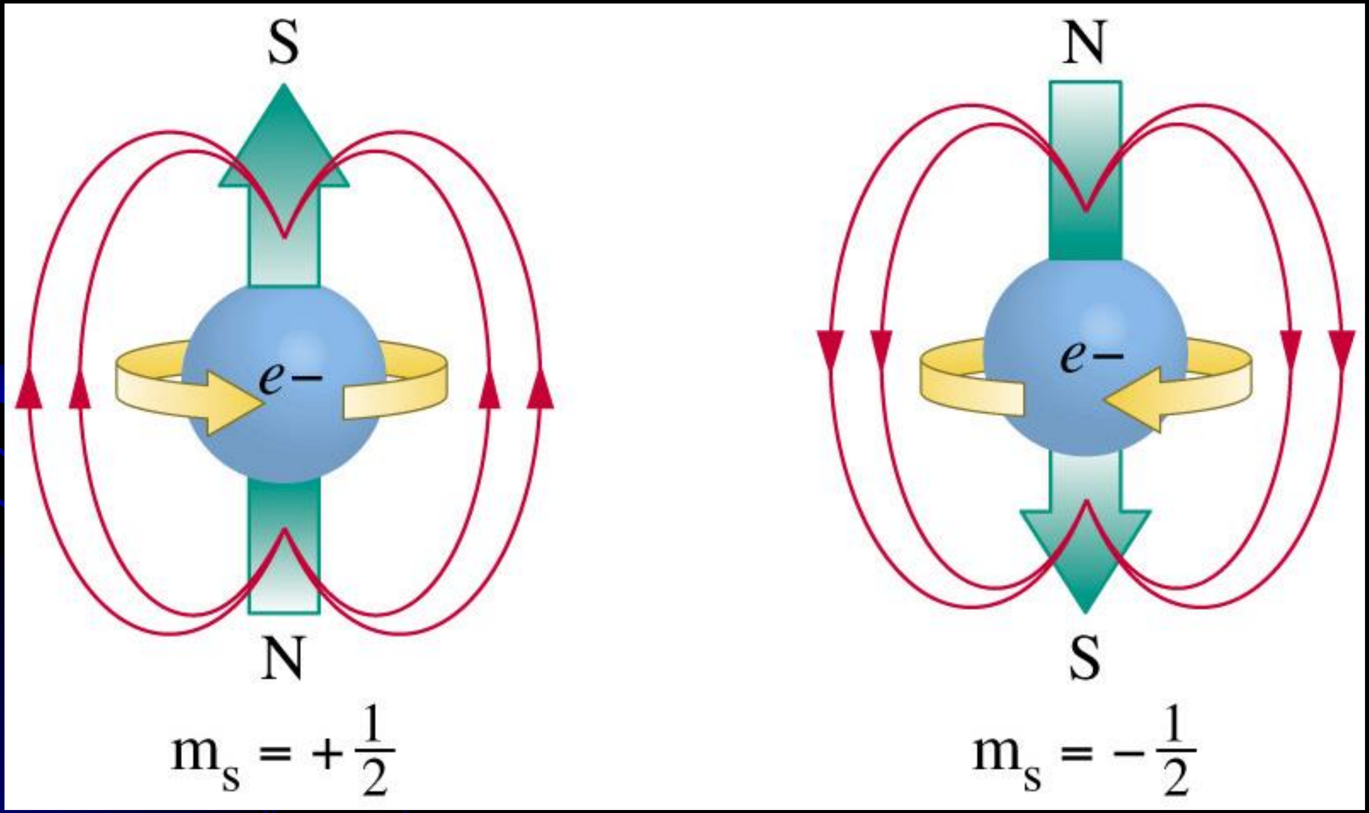
Schrödinger’s Wave Equation

Schrödinger’s wave equation leads to a third quantum number, m_l. This gives the maximum number of orbitals for the different values of l:

one	*s*	*orbital*
three	*p*	*orbitals*
five	*d*	*orbitals*
seven	*f*	*orbitals*

Schrödinger's Wave Equation

The fourth quantum number is called the *spin quantum number*, m_s. It has values of +½ and -½ and represents the spin of the electron on its own axis.



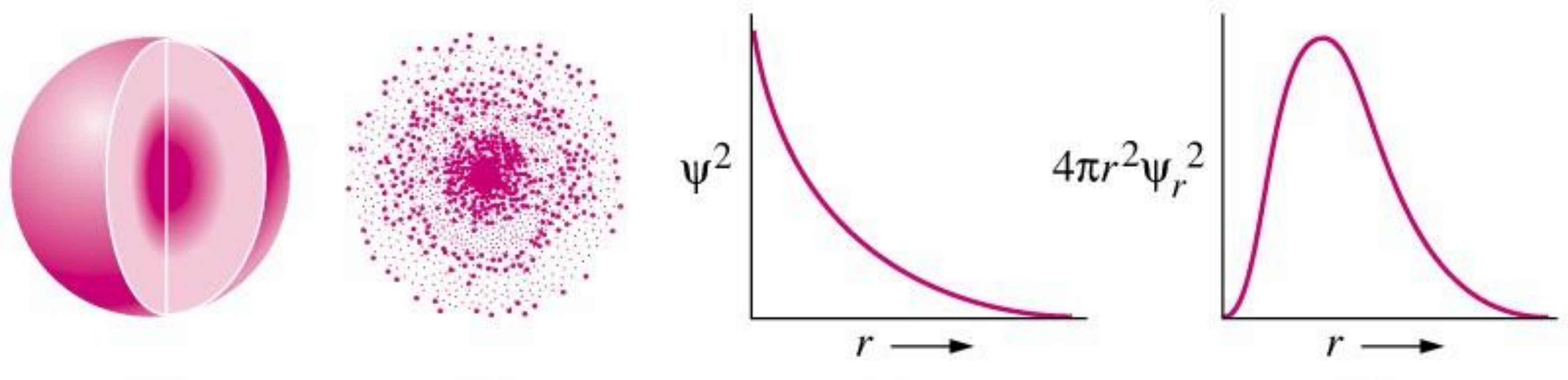
Schrödinger's Wave Equation

Wolfgang Pauli
(1900 – 1958)
Awarded the Nobel Prize
for Physics in 1945.

Pauli's exclusion principle states that *no two electrons in an atom can have the same four quantum numbers*. It therefore follows that if two electrons in an atom have the same values of n, l, and m_l, they must have different values of m_s, *i.e. their spins must be opposed*. The consequence of this is that an orbital can hold a maximum number of *two* electrons with *opposite spins*.

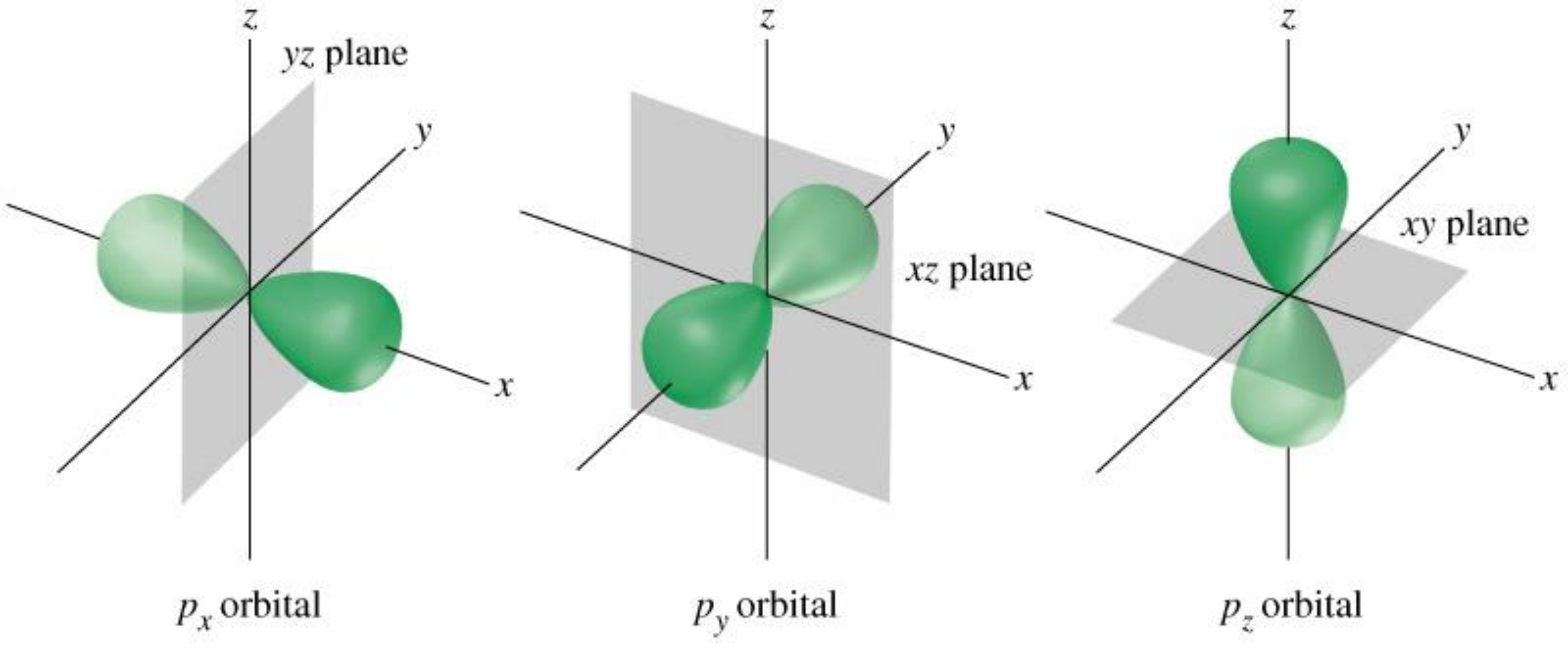
Schrödinger’s Wave Equation

The shape of an *s-orbital* is spherically symmetrical about the nucleus. The orbital has no preferred direction. The probability of finding an electron at a distance *r* from the nucleus is the same in all directions.



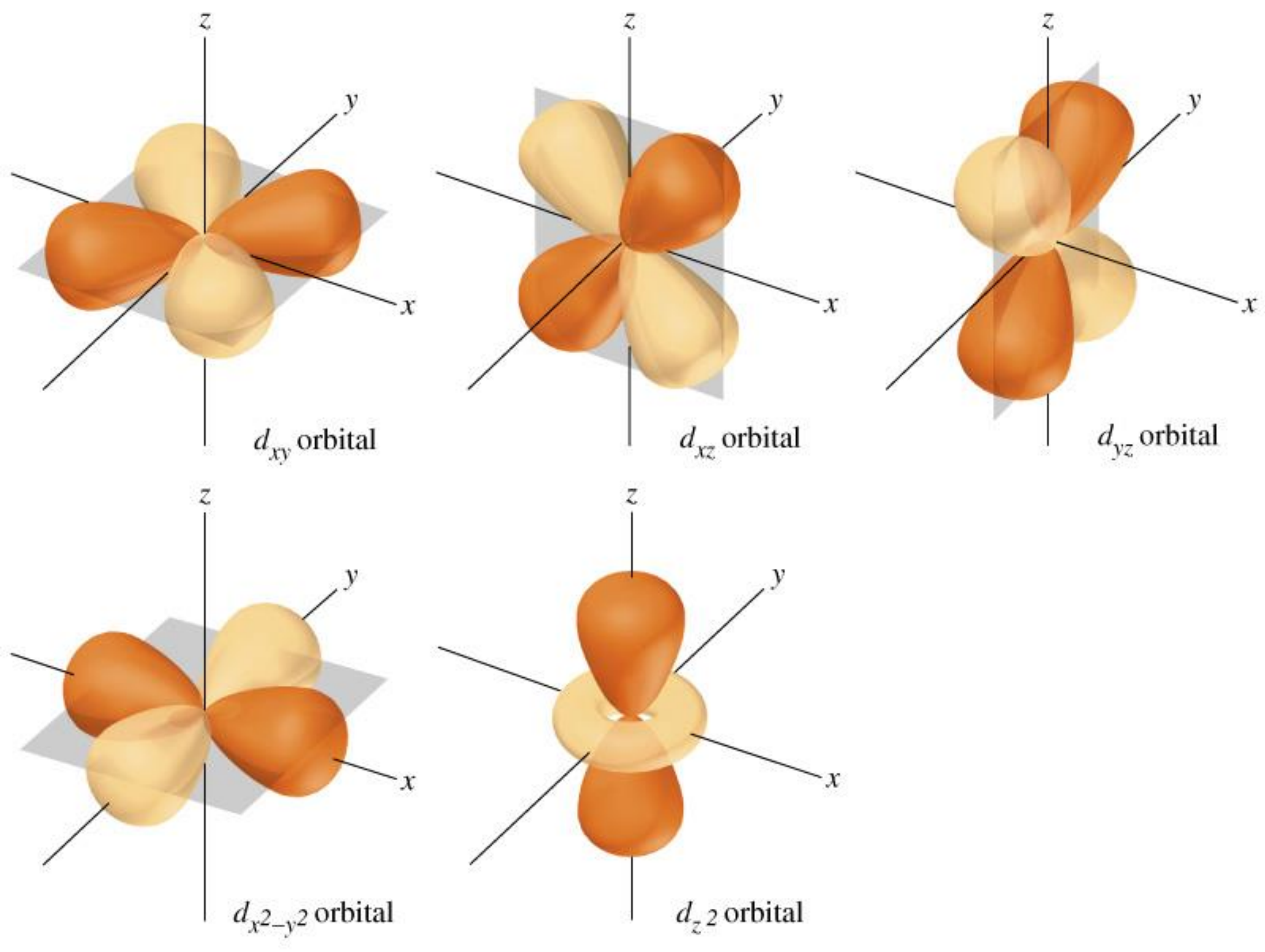
Schrödinger’s Wave Equation

A *p-orbital* is concentrated in certain directions. *p-orbitals* exits in groups of *three* arranged at 90° to each other.



Schrödinger’s Wave Equation

d-orbitals are arranged in groups of *five*.



Electron Configurations

The term *shell* is used for a group of orbitals with the same principle quantum number (*n*). A *sub-shell* is a group of orbitals with the same principle and second quantum numbers (*n* and *l*), *e.g.* the *3p subshell*.

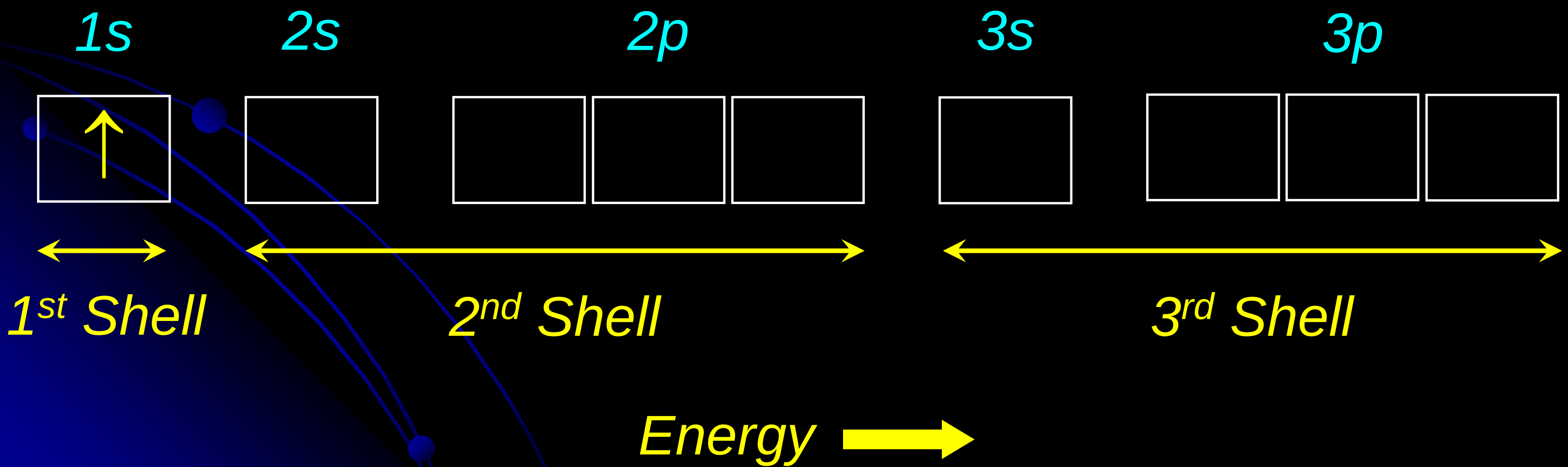
When writing out the electron configurations of atom, it is convenient to remember the following:

- Electrons should be arranged so that they have the minimum possible energy.
- The Pauli Exclusion Principle – no two electrons in the same atom can have the same four quantum numbers.
- Orbitals fill-up in the order *1s*, *2s*, *2p*, *3s*, *3p*, *4s*, *3d*, *4p*.

Electron Configurations

It is convenient to draw “*electrons in boxes*” diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Hydrogen



1s *2s* *2p* *3s* *3p*

1st Shell

2nd Shell

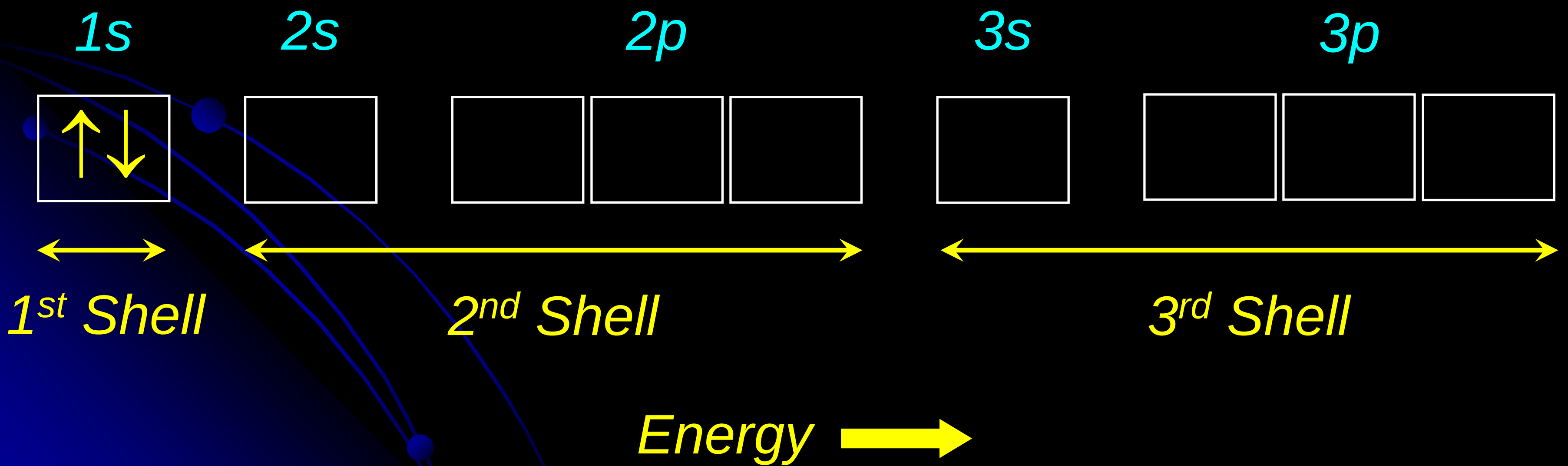
3rd Shell

Energy

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Helium



1s *2s* *2p* *3s* *3p*

↑↓

1st Shell

2nd Shell

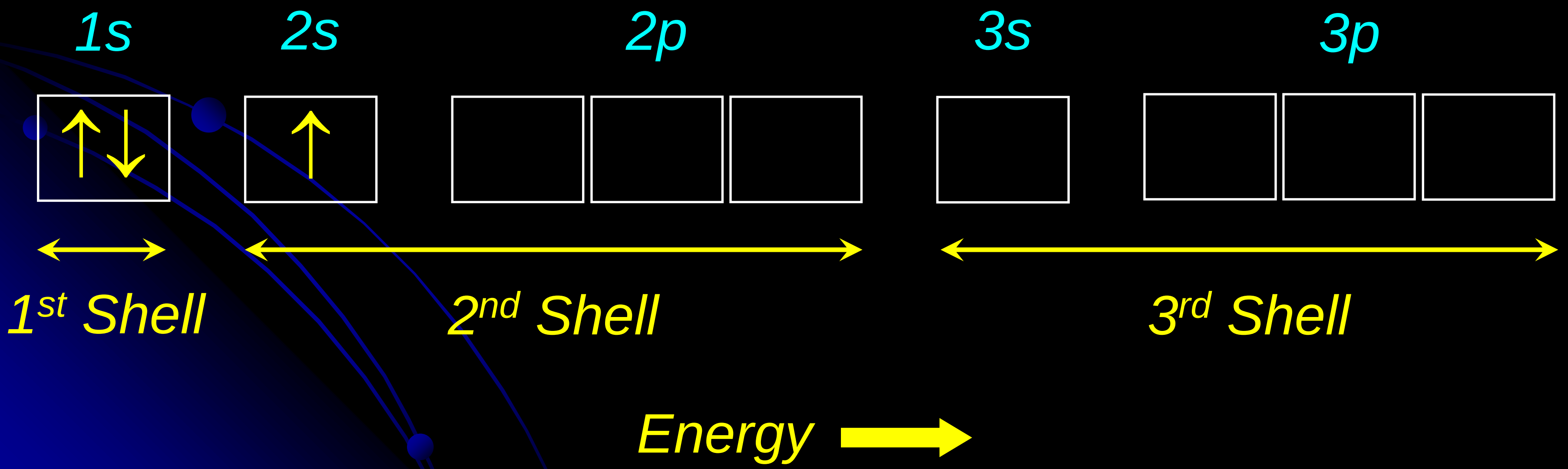
3rd Shell

Energy →

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Lithium



1s *2s* *2p* *3s* *3p*

↑↓ ↑

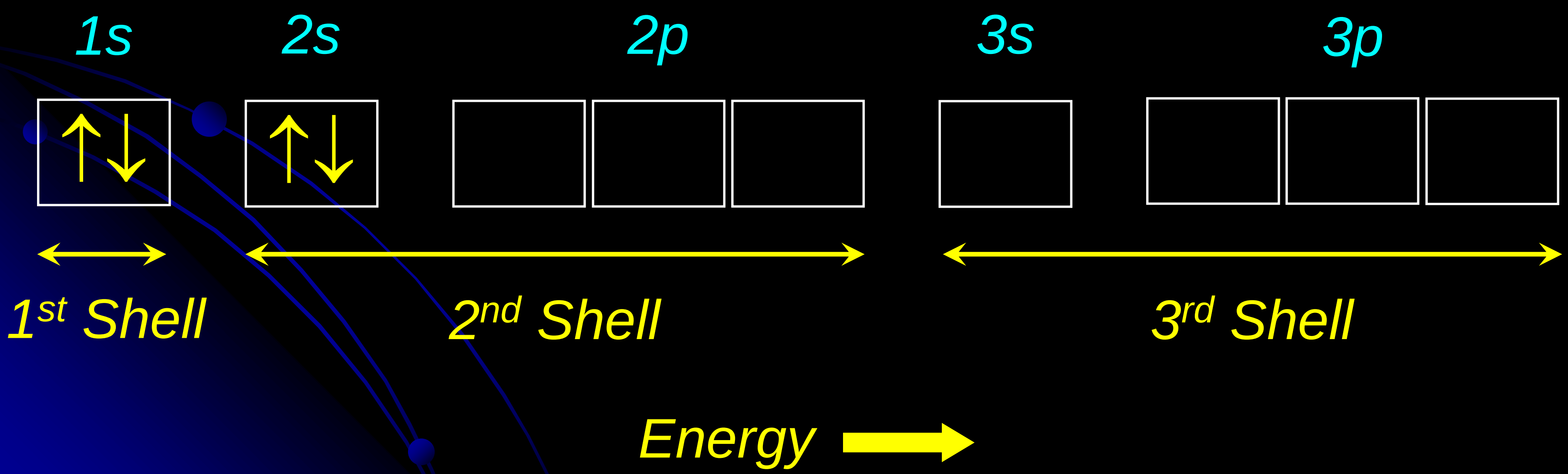
1st Shell *2nd Shell* *3rd Shell*

Energy →

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Beryllium



1s *2s* *2p* *3s* *3p*

1st Shell

2nd Shell

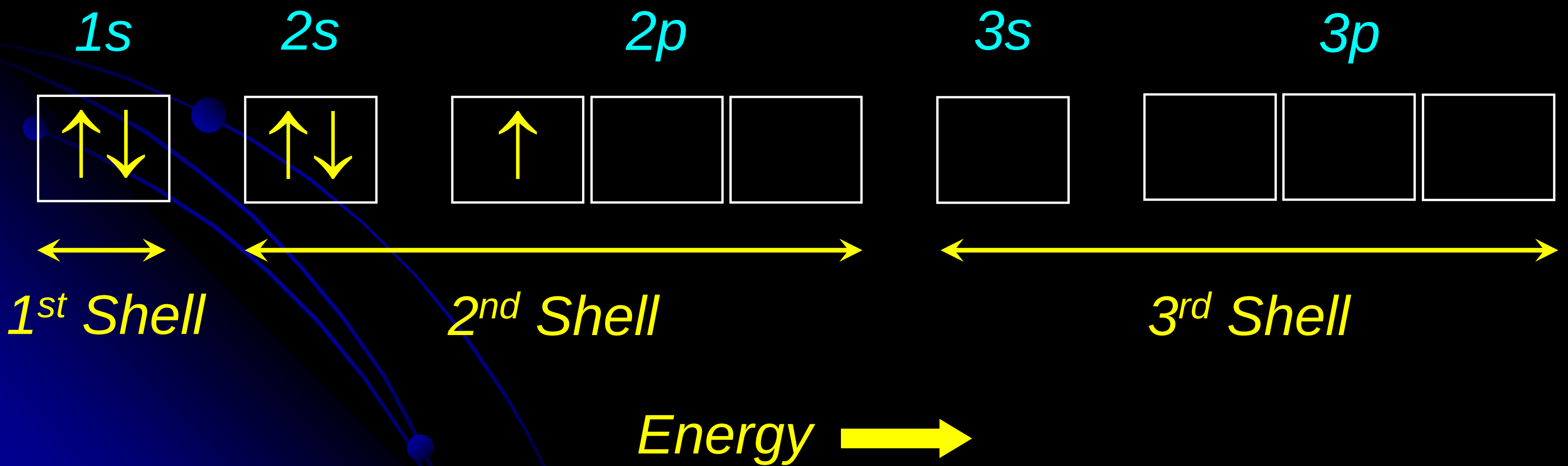
3rd Shell

Energy

Electron Configurations

It is convenient to draw “*electrons in boxes*” diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Boron



1s *2s* *2p* *3s* *3p*

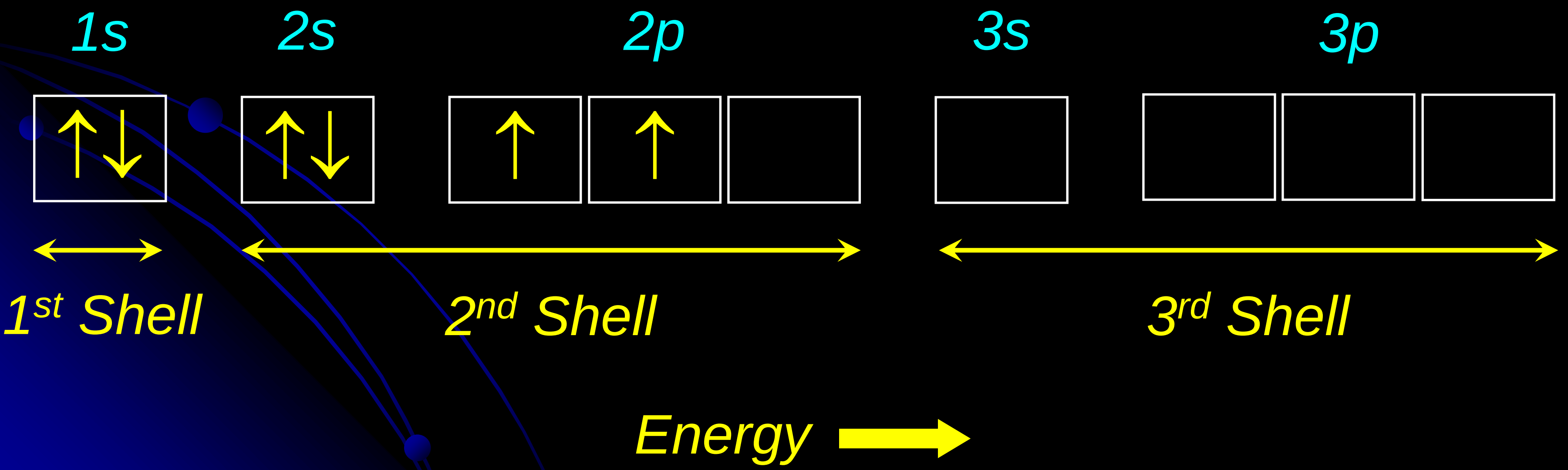
1st Shell *2nd Shell* *3rd Shell*

Energy

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Carbon



1s *2s* *2p* *3s* *3p*

↑↓ ↑↓ ↑ ↑

1st Shell

2nd Shell

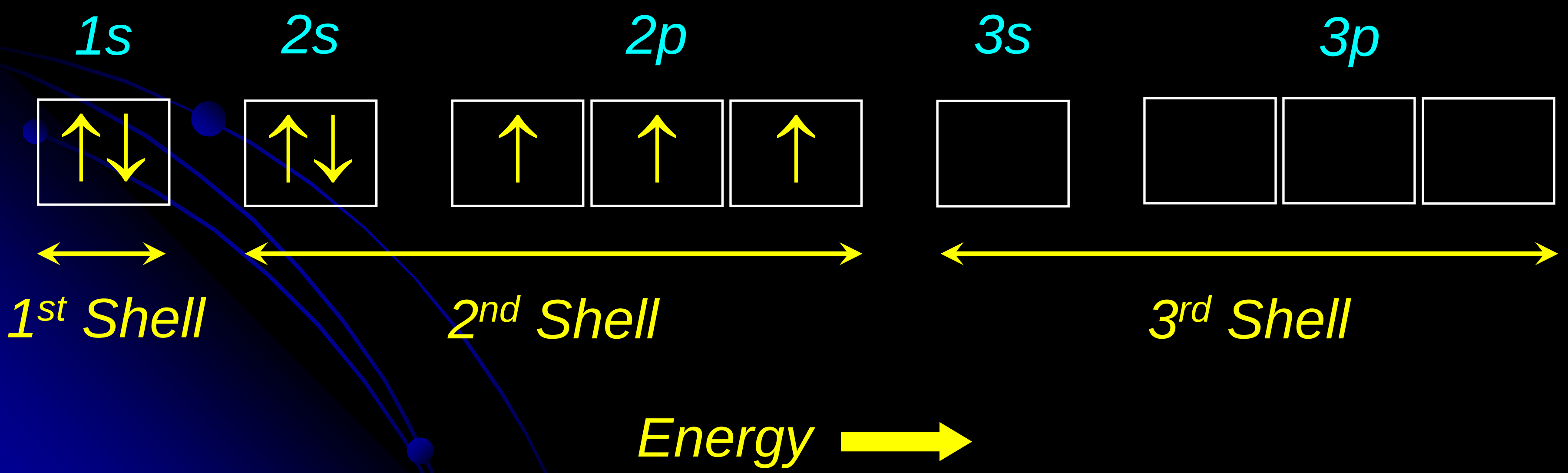
3rd Shell

Energy

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Nitrogen



1s

2s

2p

3s

3p

1st Shell

2nd Shell

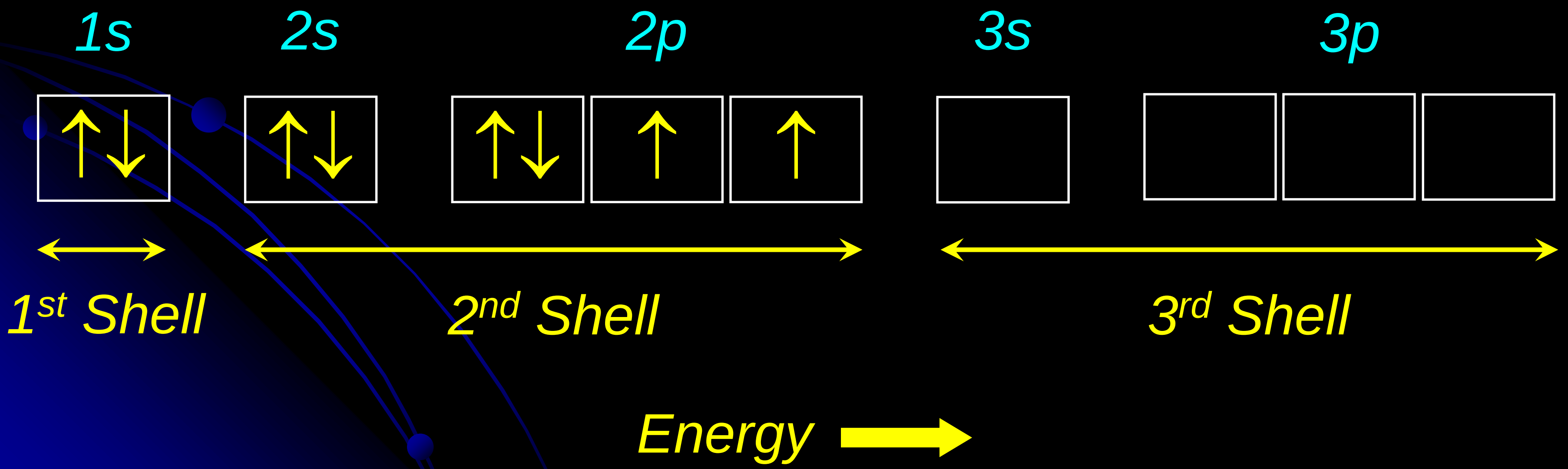
3rd Shell

Energy

Electron Configurations

It is convenient to draw “*electrons in boxes*” diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Oxygen



1s ↑↓

2s ↑↓

2p ↑↓ ↑ ↑

3s

3p

1st Shell

2nd Shell

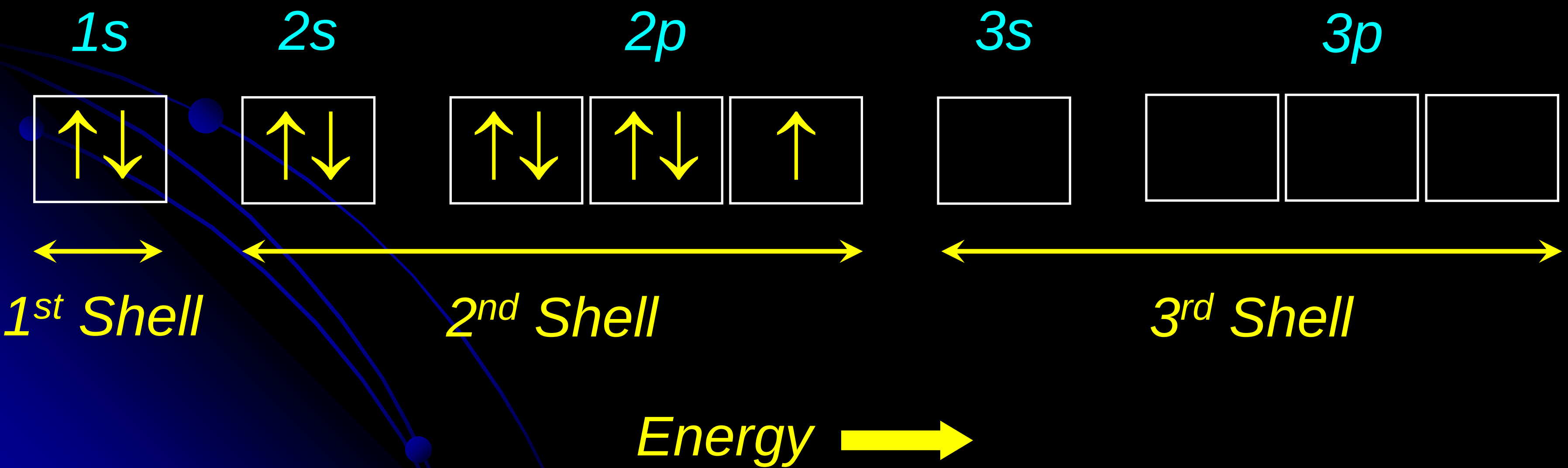
3rd Shell

Energy →

Electron Configurations

It is convenient to draw “*electrons in boxes*” diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Fluorine



1s *2s* *2p* *3s* *3p*

↑↓ ↑↓ ↑↓ ↑↓ ↑

1st Shell

2nd Shell

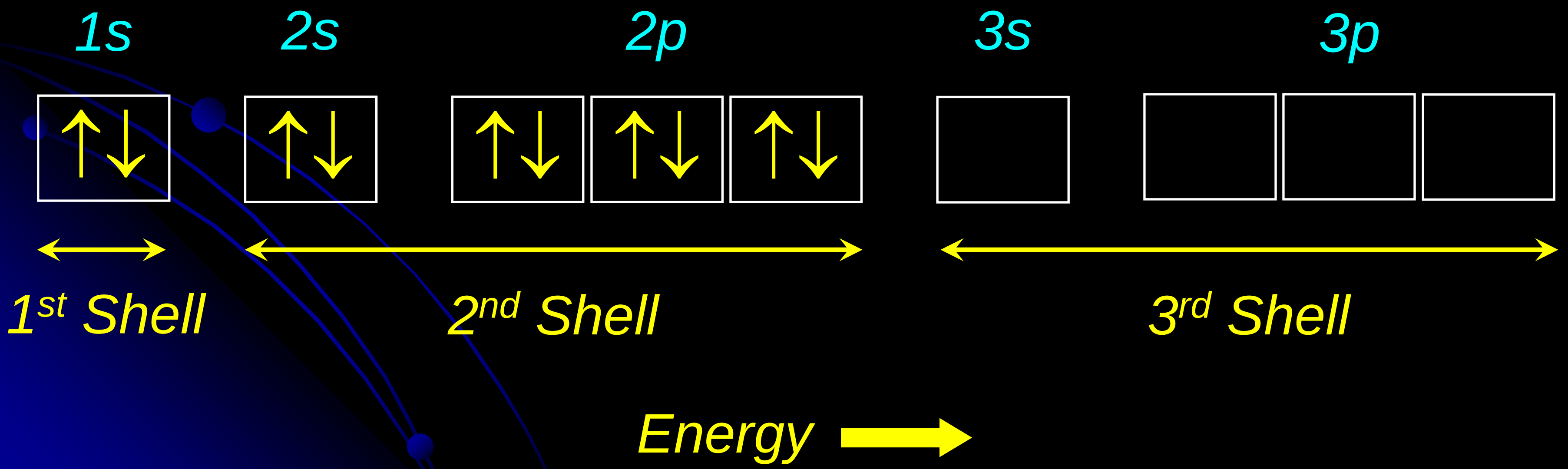
3rd Shell

Energy

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Neon



1s	*2s*	*2p*	*2p*	*2p*	*3s*	*3p*	*3p*	*3p*
↑↓	↑↓	↑↓	↑↓	↑↓				

1st Shell

2nd Shell

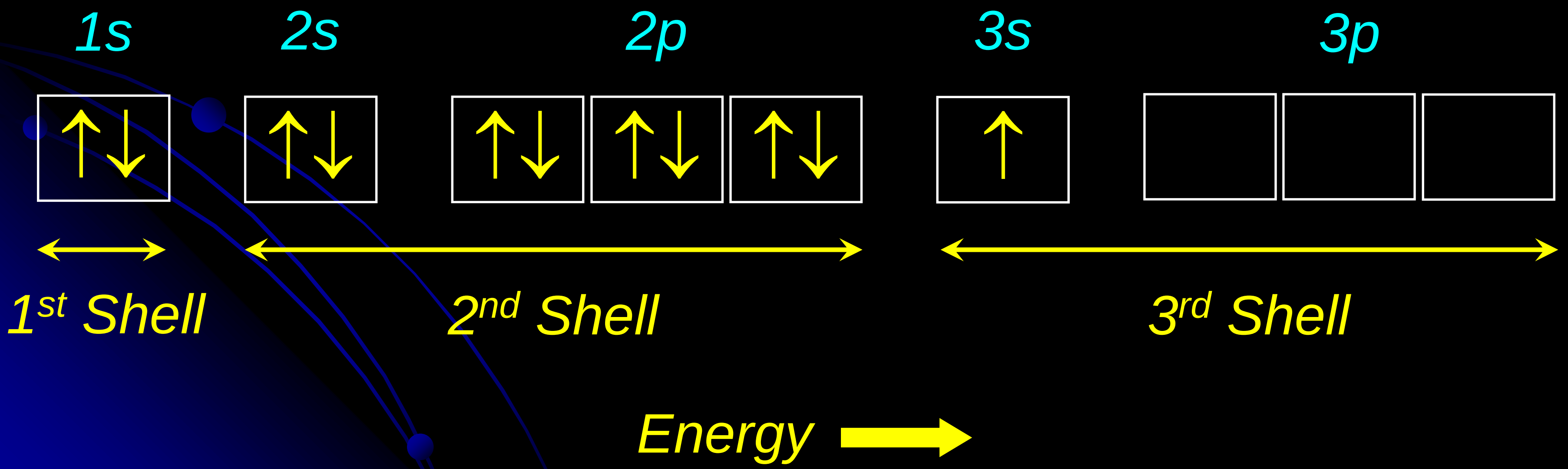
3rd Shell

Energy →

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Sodium



1s ↑↓

2s ↑↓

2p ↑↓ ↑↓ ↑↓

3s ↑

3p ☐ ☐ ☐

1st Shell

2nd Shell

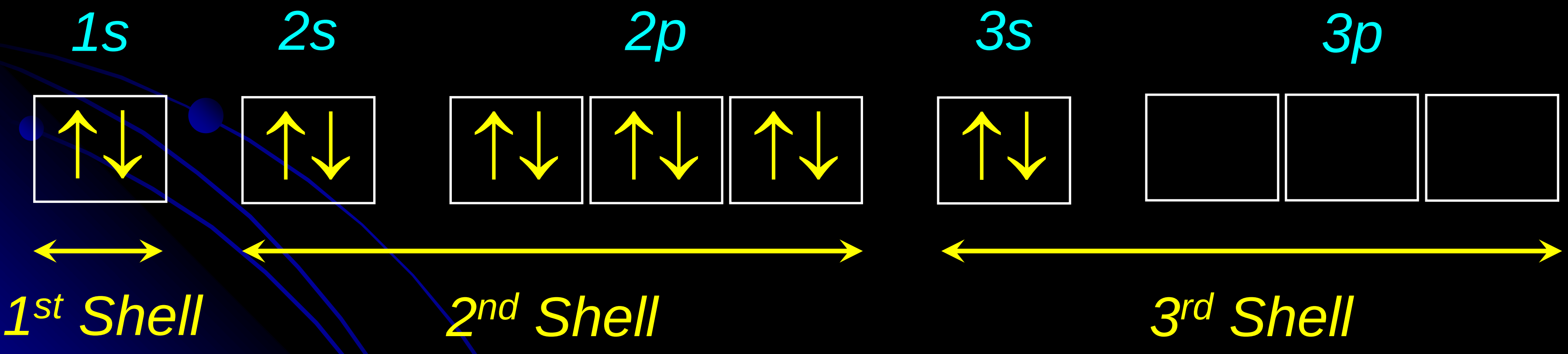
3rd Shell

Energy →

Electron Configurations

It is convenient to draw “*electrons in boxes*” diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Magnesium



1s *2s* *2p* *3s* *3p*

↑↓ | ↑↓ | ↑↓ ↑↓ ↑↓ | ↑↓ | ☐ ☐ ☐

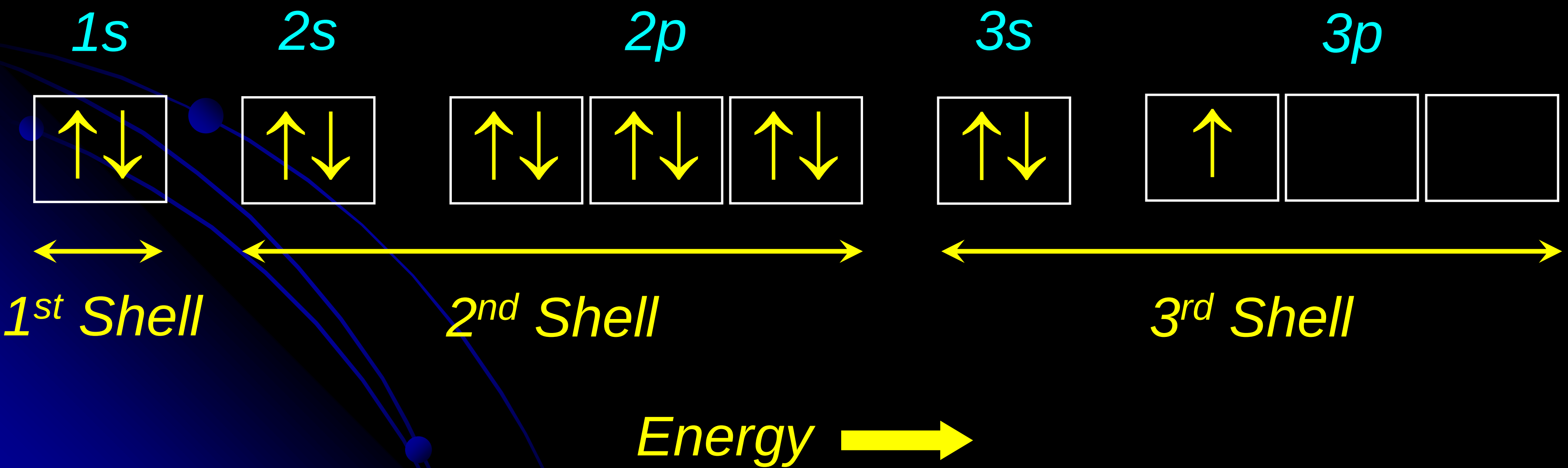
1st Shell *2nd Shell* *3rd Shell*

Energy →

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

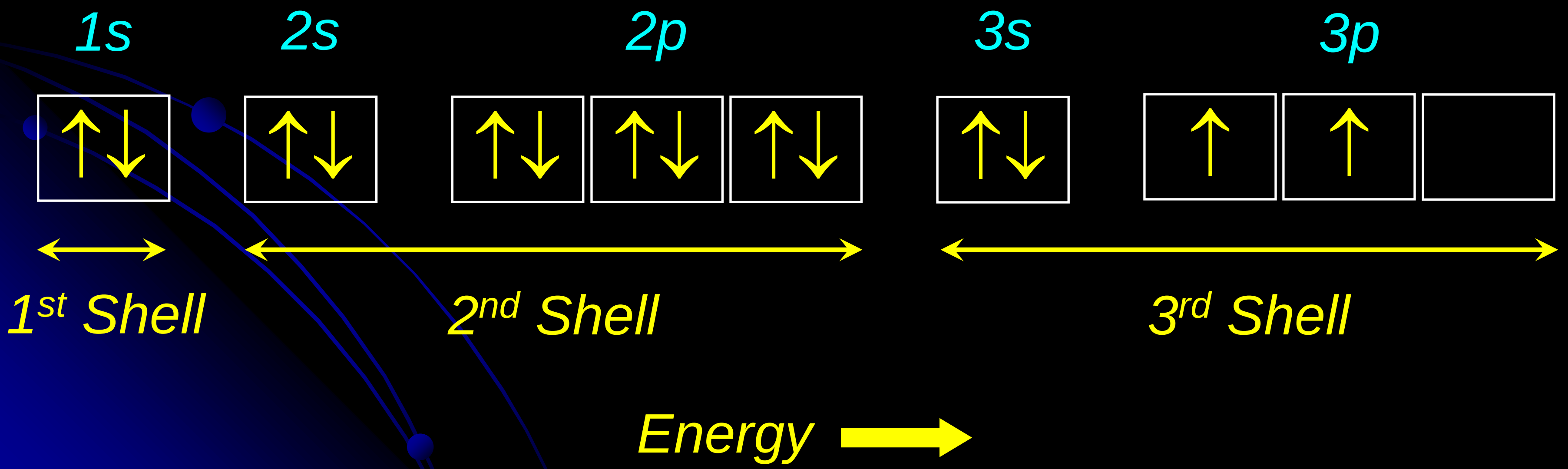
Aluminium



Electron Configurations

It is convenient to draw “*electrons in boxes*” diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Silicon



1s	*2s*	*2p*	*3s*	*3p*
↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑ ↑

1st Shell

2nd Shell

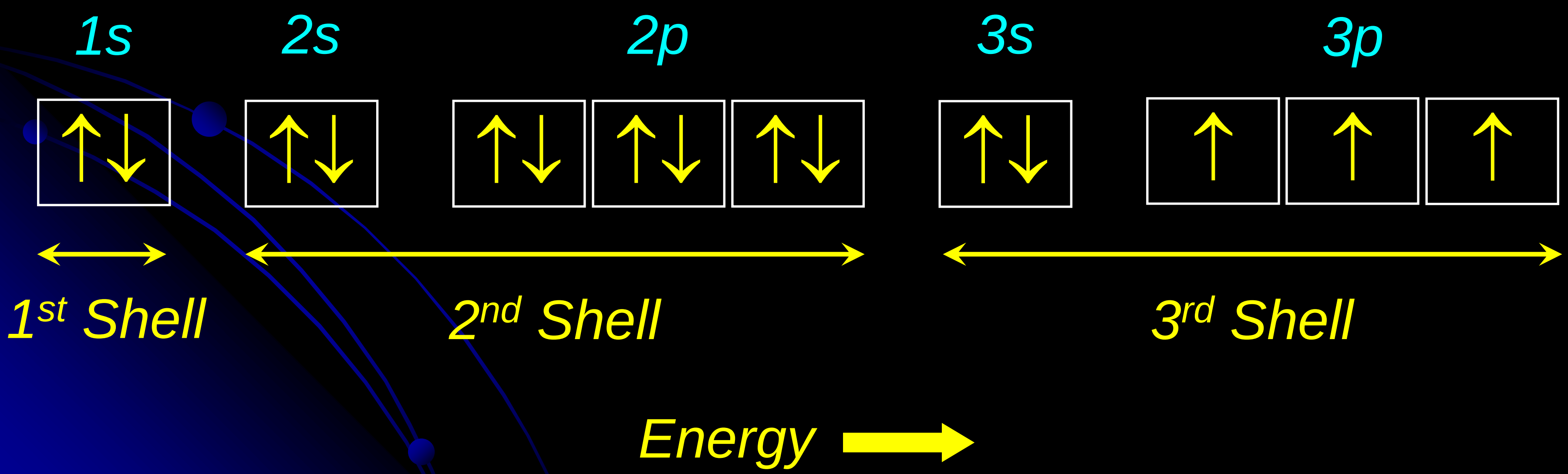
3rd Shell

Energy

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Phosphorus



1s | *2s* | *2p* | *3s* | *3p*

↑↓ | ↑↓ | ↑↓ ↑↓ ↑↓ | ↑↓ | ↑ ↑ ↑

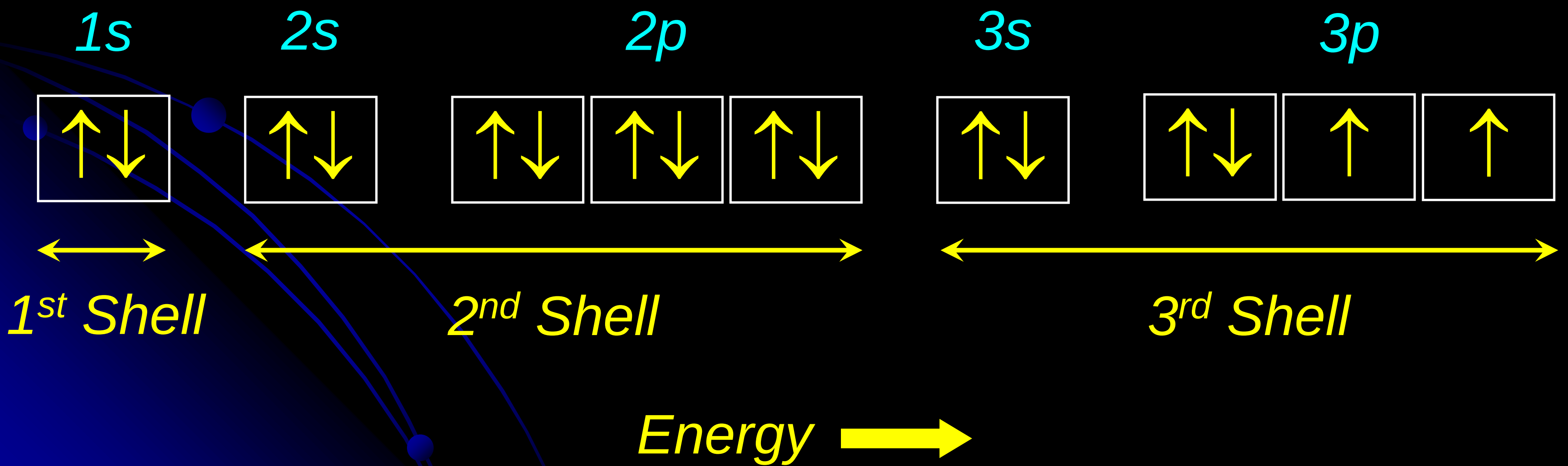
1st Shell | *2nd Shell* | *3rd Shell*

Energy →

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Sulphur



1s	*2s*	*2p*	*3s*	*3p*
↑↓	↑↓	↑↓ ↑↓ ↑↓	↑↓	↑↓ ↑ ↑

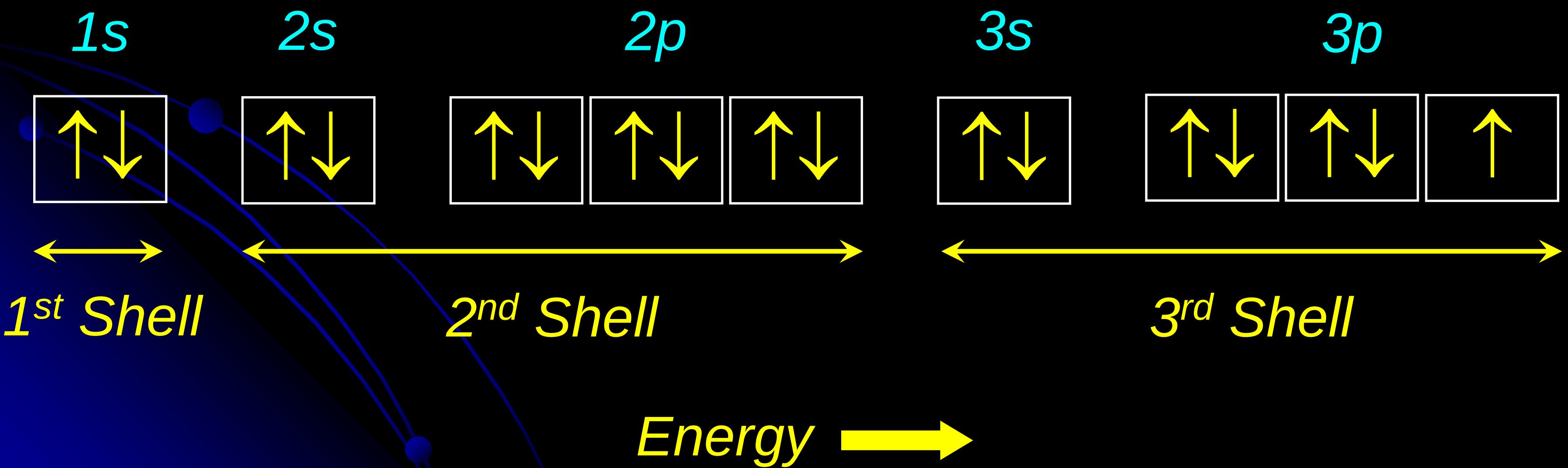
1st Shell ↔ *2nd Shell* ↔ *3rd Shell*

Energy ➡

Electron Configurations

It is convenient to draw “*electrons in boxes*” diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Chlorine



1s ↑↓

2s ↑↓

2p ↑↓ ↑↓ ↑↓

3s ↑↓

3p ↑↓ ↑↓ ↑

1st Shell

2nd Shell

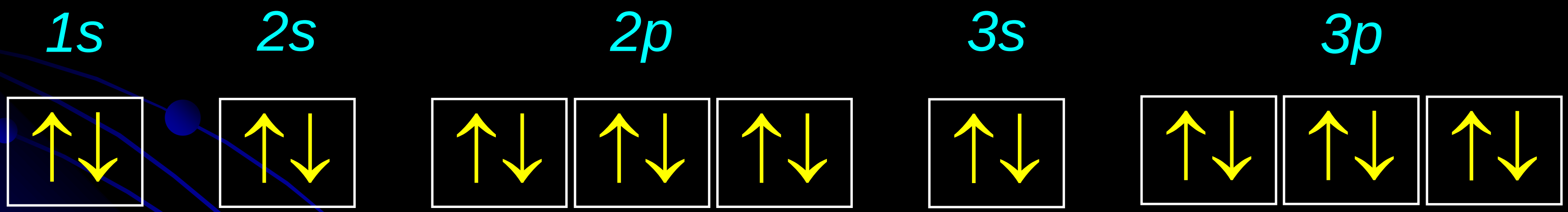
3rd Shell

Energy →

Electron Configurations

It is convenient to draw "*electrons in boxes*" diagrams to show the arrangement of electrons in orbitals. Arrows are used to represent the electrons. Arrows pointing in opposite directions represent electrons with opposite spin.

Argon

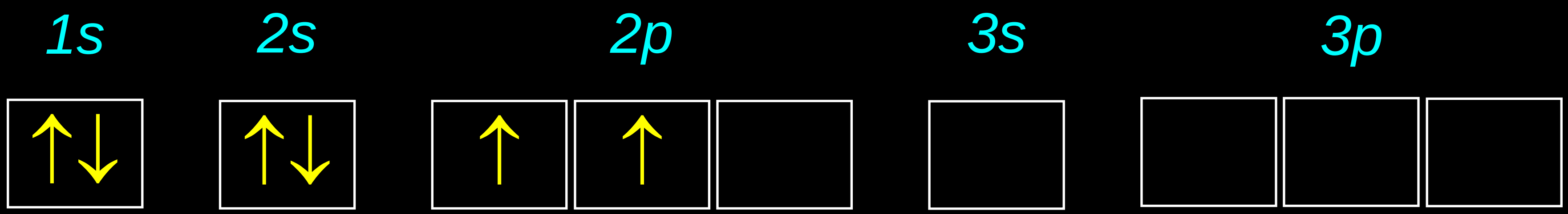


1s	*2s*	*2p*			*3s*	*3p*		
↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Electron Configurations

The electron configuration of carbon is given below:

Carbon



Questions:

- From the electron configuration shown above, how many covalent bonds would you expect a carbon atom to make?
- How is it possible for a carbon atom to make *four* covalent bonds?

Sp^3 Hybridisation

	1s	*2s*	*2p*		
Carbon (*ground state*):	↑↓	↑↓	↑	↑	

	1s	*2s*	*2p*		
Carbon (*excited*):	↑↓	↑	↑	↑	↑

	1s	*sp^3 hybridised*			
Carbon (*sp^3 hybridised*)	↑↓	↑	↑	↑	↑

Sp^3 Hybridisation

Carbon (*ground state*):

1s	*2s*	*2p*		
↑↓	↑↓	↑	↑	

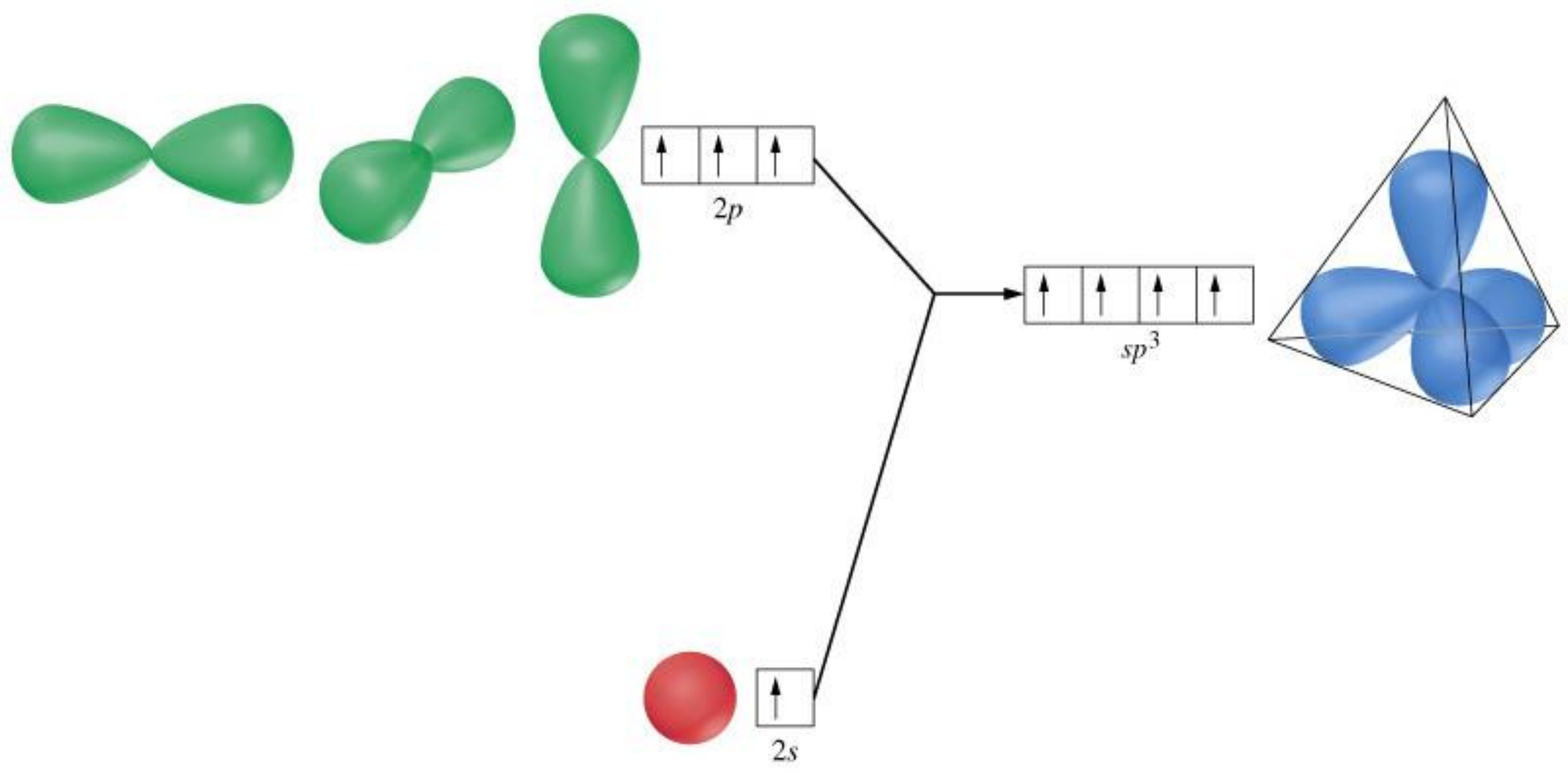
Carbon (*excited*):

1s	*2s*	*2p*		
↑↓	↑	↑	↑	↑

Carbon (*sp^3 hybridised*)

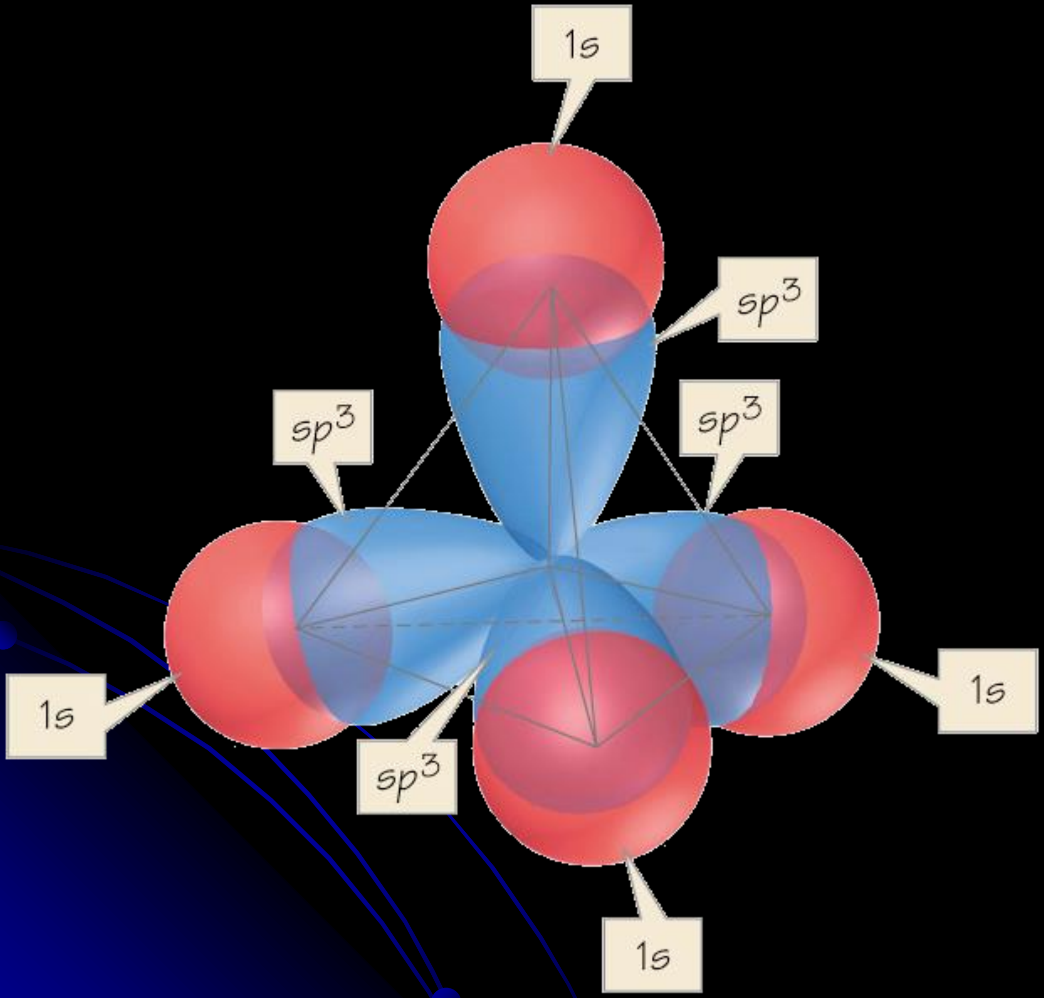
1s	*sp^3 hybridised*			
↑↓	↑↓	↑↓	↑↓	↑↓

Sp^3 Hybridisation



The *sp*^{3} hybridisation of carbon.

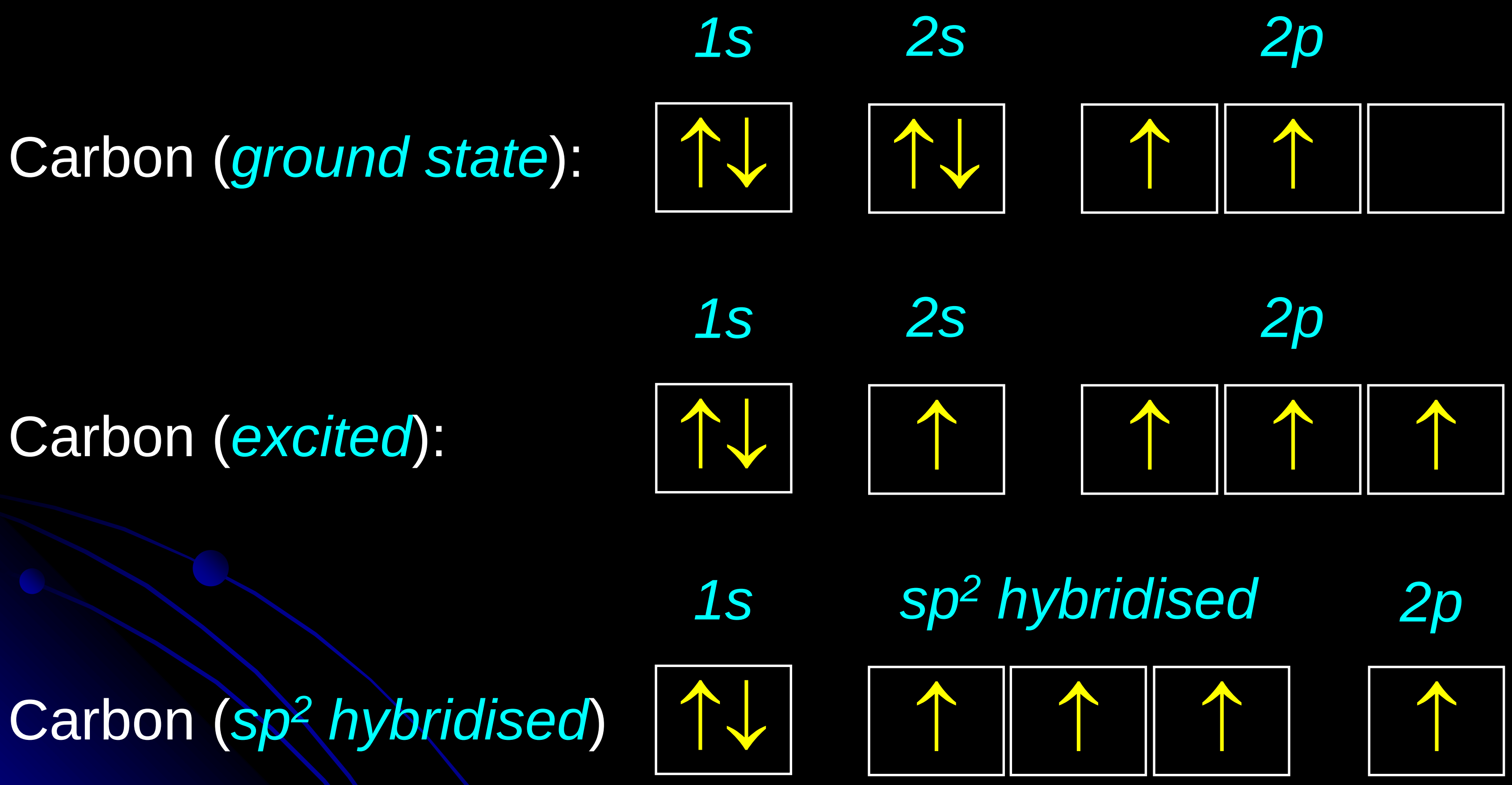
Sp^3 Hybridisation



The bonding in methane (CH_4):

The four *sp^3 hybridised orbitals* of the carbon atom (blue) overlap with the *s-orbitals* of four hydrogen atoms (red) to form four *σ-bonds*.

Sp^2 Hybridisation

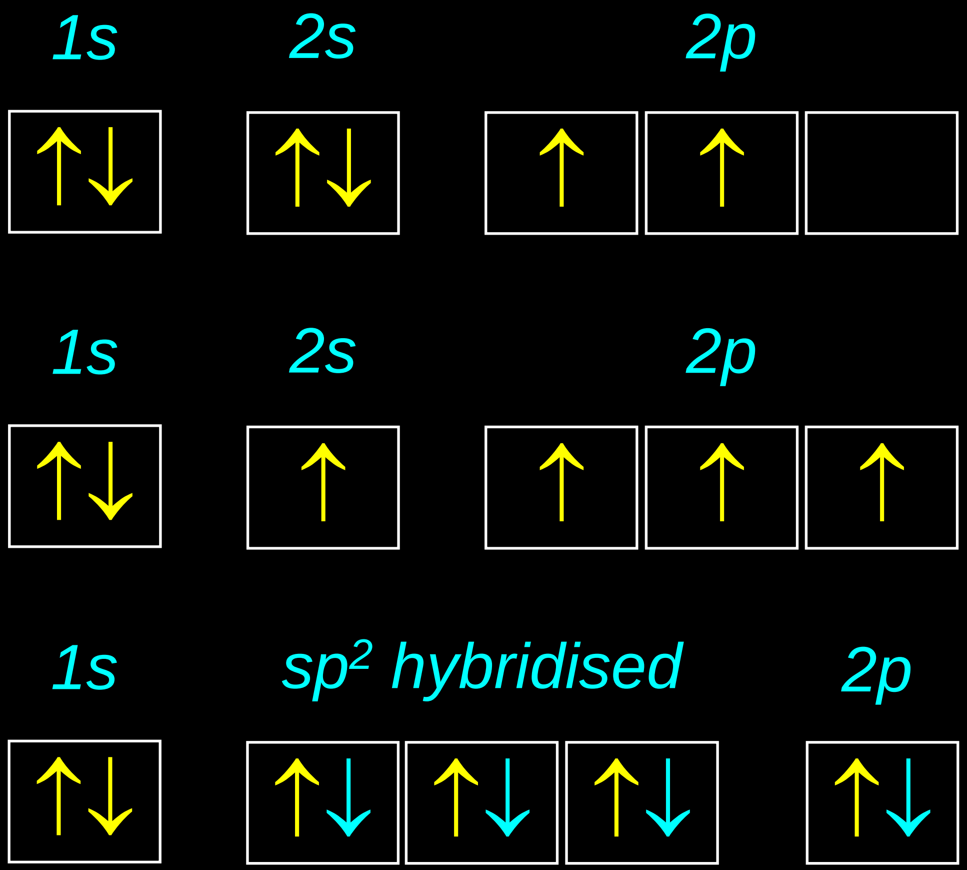


Carbon (*ground state*): *1s* ↑↓ *2s* ↑↓ *2p* ↑ ↑ ☐

Carbon (*excited*): *1s* ↑↓ *2s* ↑ *2p* ↑ ↑ ↑

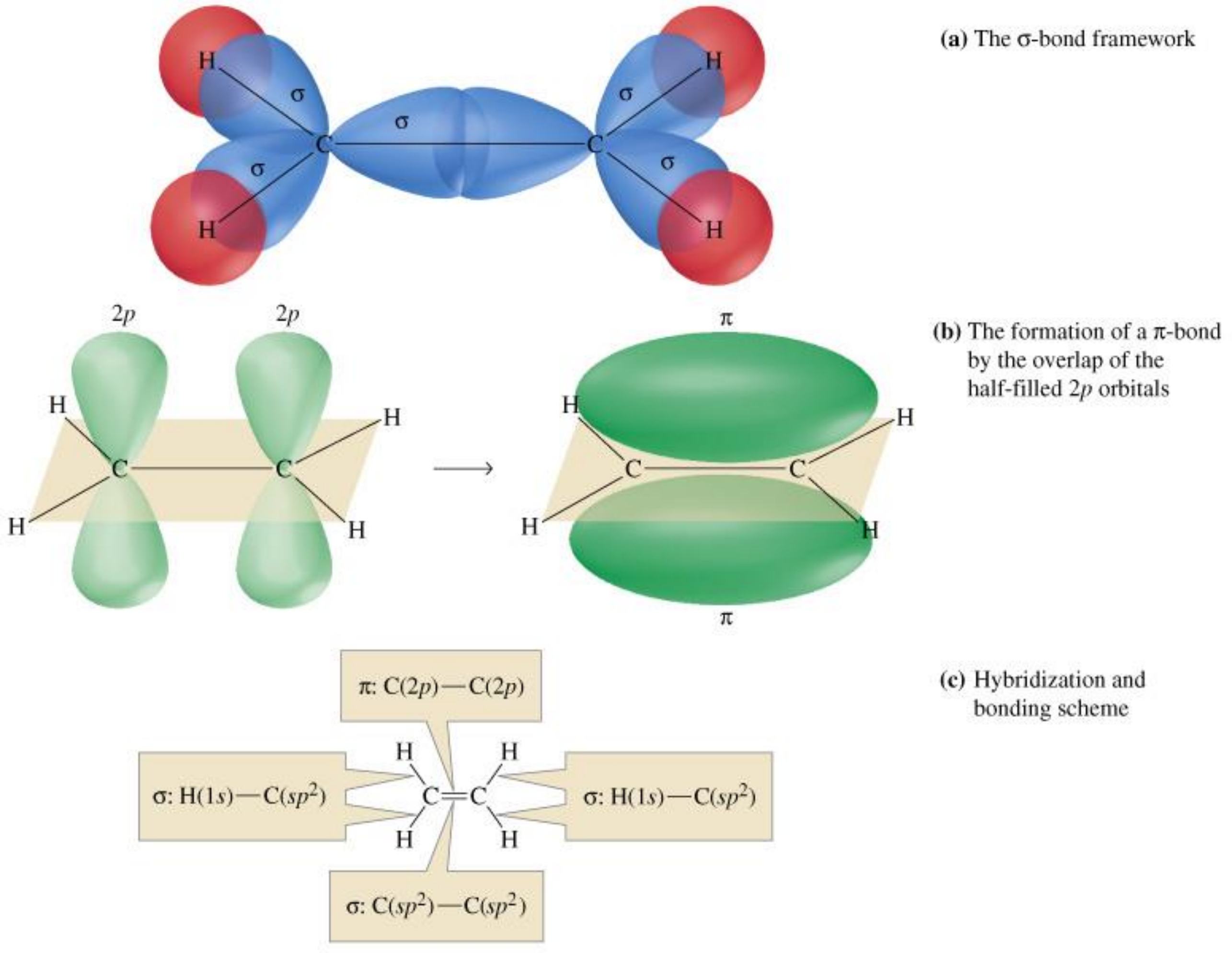
Carbon (*sp^2 hybridised*) *1s* ↑↓ *sp^2 hybridised* ↑ ↑ ↑ *2p* ↑

Sp^2 Hybridisation



	1s	2s	2p		
Carbon (*ground state*):	↑↓	↑↓	↑	↑	
	1s	2s	2p		
Carbon (*excited*):	↑↓	↑	↑	↑	↑
	1s	sp^2 hybridised			2p
Carbon (sp^2 *hybridised*)	↑↓	↑↓	↑↓	↑↓	↑↓

Sp^2 Hybridisation



(a) The σ-bond framework

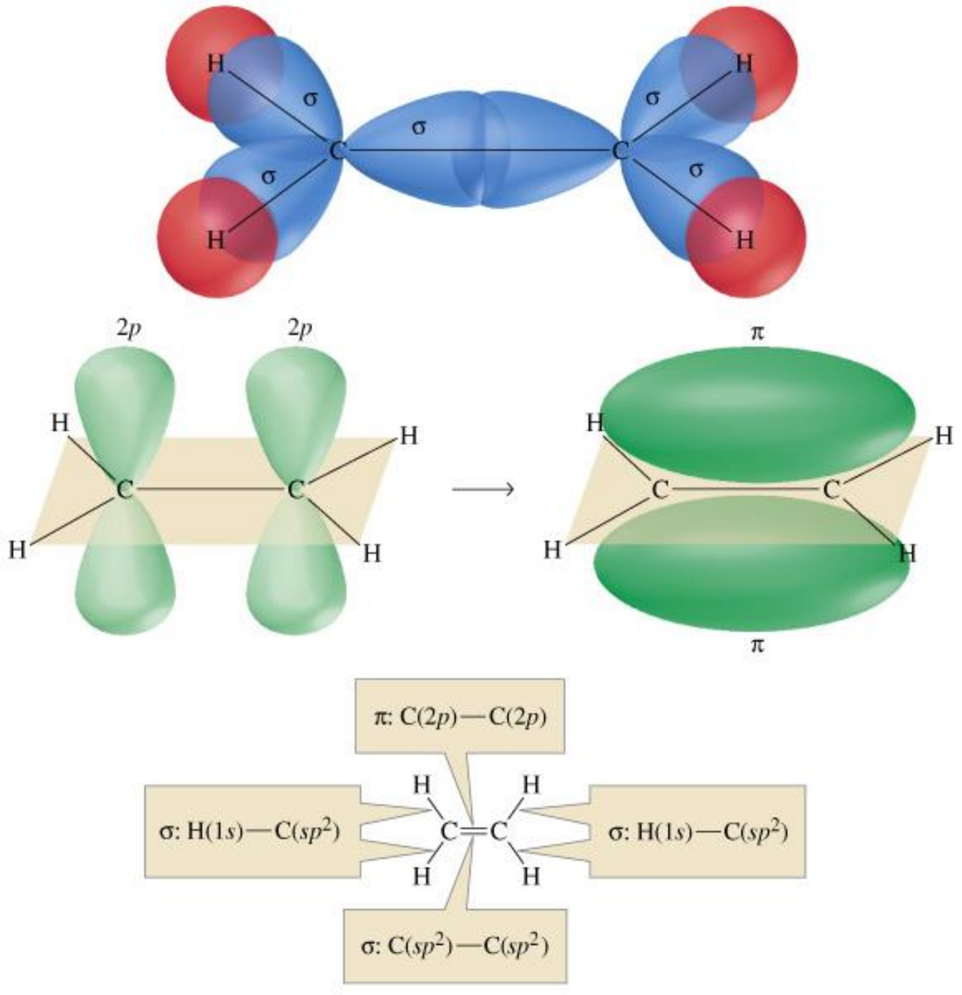
(b) The formation of a π-bond by the overlap of the half-filled 2p orbitals

(c) Hybridization and bonding scheme

The bonding in ethene (C_2H_4) *#1*:

The three *sp^2 hybridised orbitals* of each carbon atom (blue) overlap with each other and also with the *s-orbitals* of four hydrogen atoms (red) to form a total of five *σ-bonds*.

Sp^2 Hybridisation



(a) The σ-bond framework

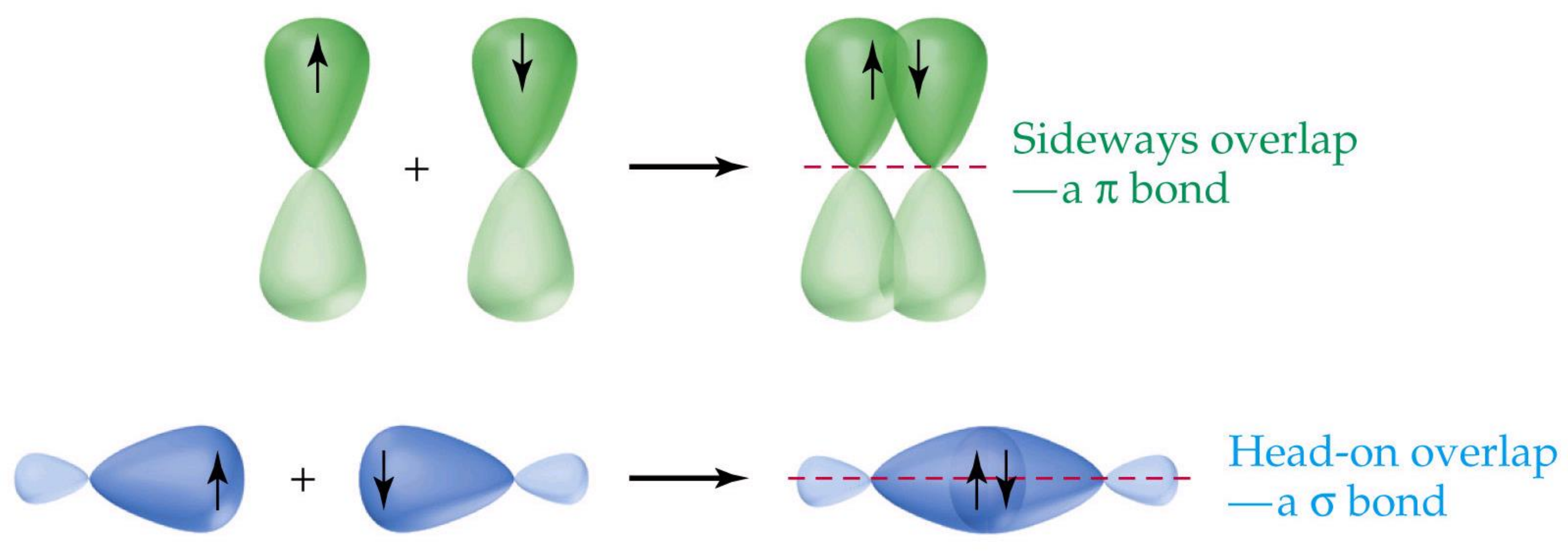
(b) The formation of a π-bond by the overlap of the half-filled 2*p* orbitals

(c) Hybridization and bonding scheme

The bonding in ethene (C_2H_4) *#2*:

The *p-orbitals* of each carbon atom which are not hybridised (green) are arranged parallel to each other. They overlap above and below the plane of the molecule forming a *π-bond*.

σ-Bonds and π-Bonds



A comparison of *σ-bonds* and *π-bonds*:

σ-bonds are formed when the region of orbital overlap lies directly between the nuclei of the two bonding atoms.

π-bonds are formed when the region of orbital overlap does not lie directly between the nuclei of the two bonding atoms, but instead lies above and below the plane of the molecule.

The Existence of C ≡ C Bonds

Question:

Elaborate on this information to propose a model for the bonding in *ethyne*:

H—C≡C—H

Your answer should take into account:

- The existence of *s-orbitals* and *p-orbitals*.
- The ability for carbon’s *2s* and *2p* orbitals to *hybridise*.
- The *linear* shape of the ethyne molecule.

Sp Hybridisation

	1s	*2s*	*2p*		
Carbon (*ground state*):	↑↓	↑↓	↑	↑	

	1s	*2s*	*2p*		
Carbon (*excited*):	↑↓	↑	↑	↑	↑

	1s	*sp hybridised*		*2p*	
Carbon (*sp hybridised*)	↑↓	↑	↑	↑	↑

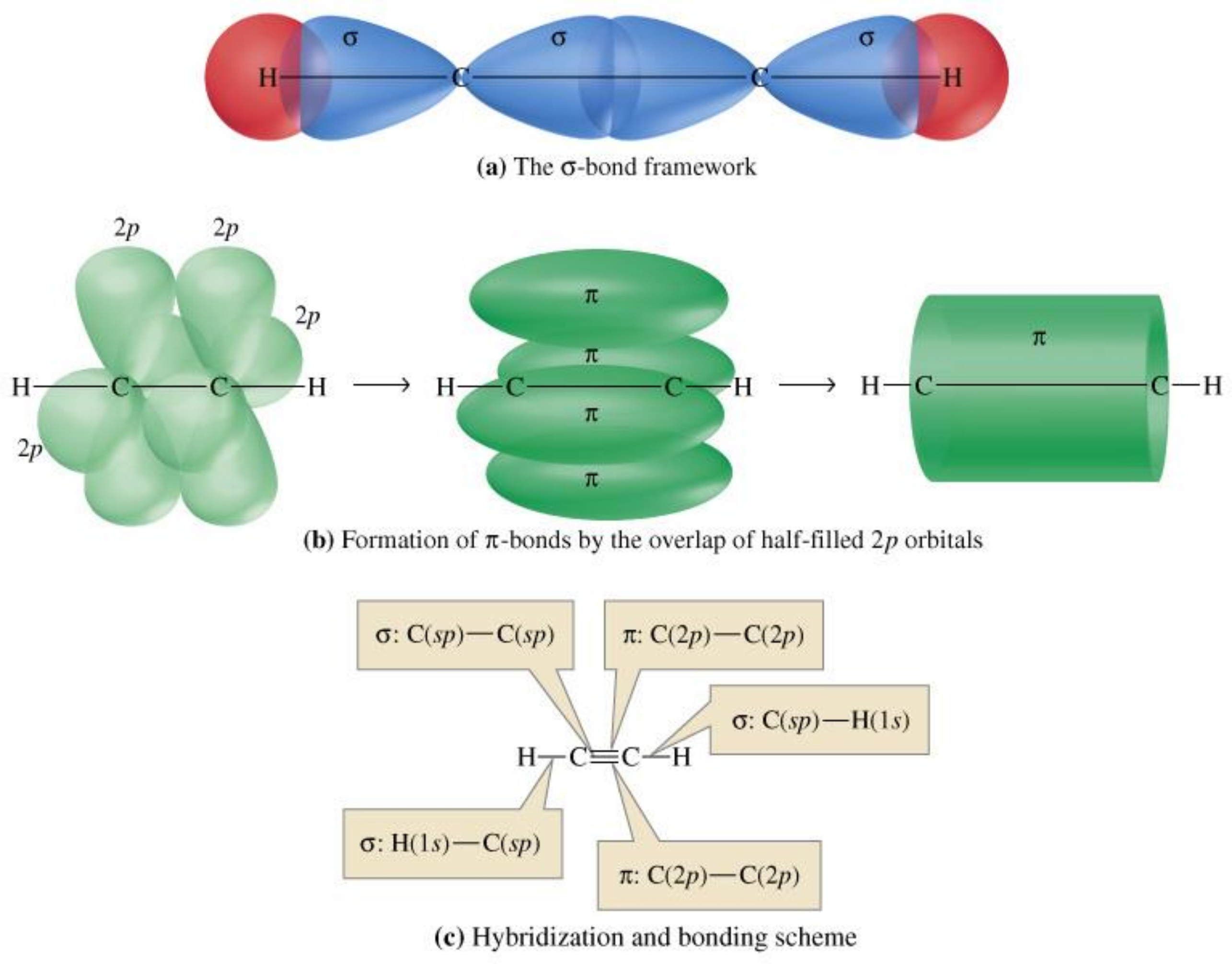
Sp Hybridisation

	1s	*2s*	*2p*		
Carbon (*ground state*):	↑↓	↑↓	↑	↑	

	1s	*2s*	*2p*		
Carbon (*excited*):	↑↓	↑	↑	↑	↑

	1s	*sp hybridised*		*2p*	
Carbon (*sp hybridised*)	↑↓	↑↓	↑↓	↑↓	↑↓

Sp Hybridisation



(a) The σ-bond framework

(b) Formation of π-bonds by the overlap of half-filled 2*p* orbitals

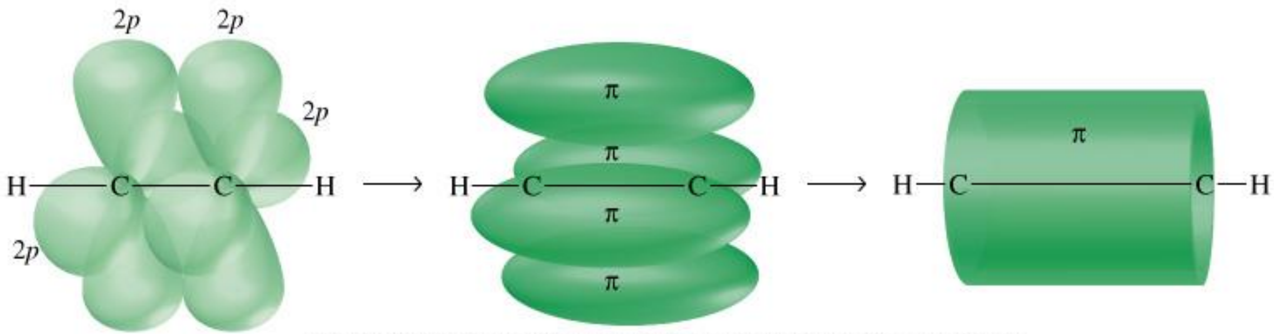
(c) Hybridization and bonding scheme

The bonding in ethyne (C_2H_2) *#1*:

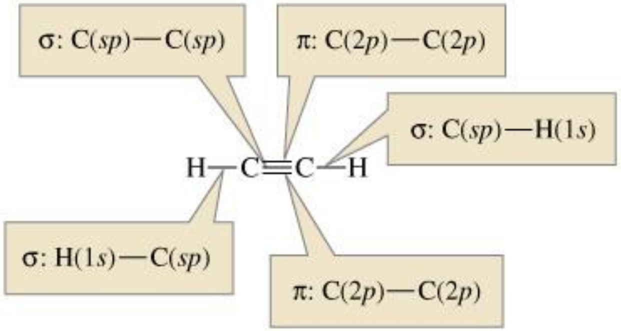
The *sp hybridised orbitals* of each carbon atom (blue) overlap with each other and also with the *s-orbitals* of two hydrogen atoms (red) to form a total of three *σ-bonds* arranged in a *linear* formation.

Sp Hybridisation

(a) The σ-bond framework



(b) Formation of π-bonds by the overlap of half-filled 2p orbitals

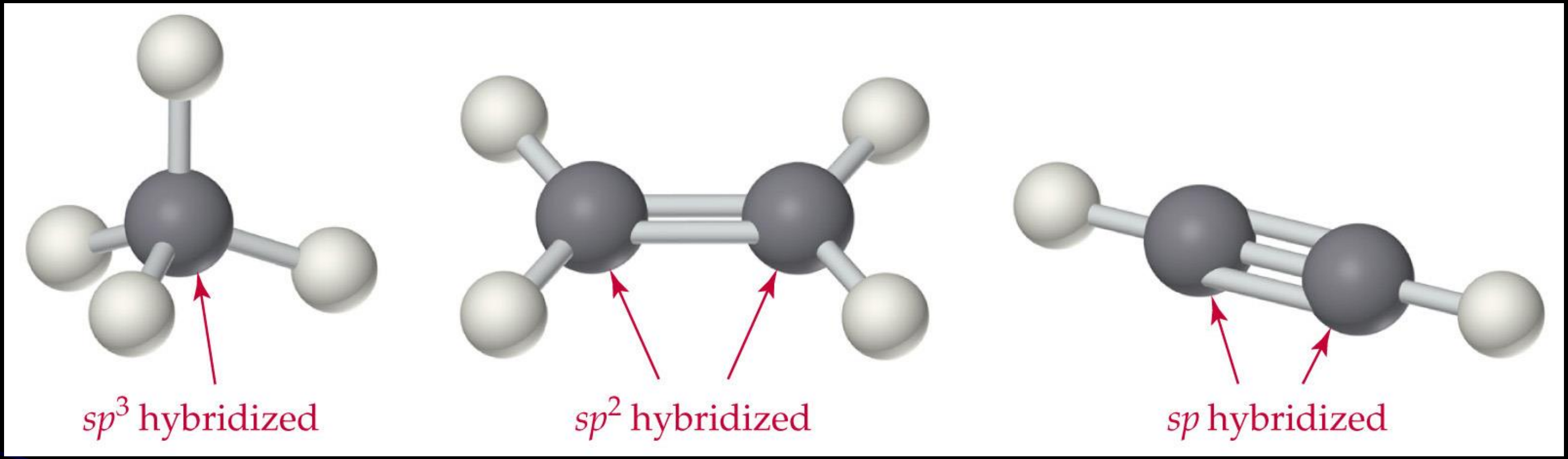


(c) Hybridization and bonding scheme

The bonding in ethyne (C_2H_2) #2:

Each carbon atom has *two p-orbitals* (green) which are not hybridised. They arranged at 90° to each other within the same carbon atom and parallel to each other between the individual carbon atoms. Overlap of the four p-orbitals results in the formation of *two π-bonds* between the two carbon atoms.

A Summary of sp^3, sp^2 and sp Hybridisatio



- The carbon atoms forming a *C – C* bond are *sp^3 hybridised*.
- The carbon atoms forming a *C = C* bond are *sp^2 hybridised*.
- The carbon atoms forming a *C ≡ C* bond are *sp hybridised*.

The Modern Structure of Benzene

Question:

With this information, propose a structure for benzene which takes into account:

- The existence of *s-orbitals* and *p-orbitals*.
- The ability for carbon’s *2s* and *2p* orbitals to *hybridise*.
- The shape of the benzene molecule as determined by *x-ray crystallography*.
- The relative *stability* of benzene.

The Modern Structure of Benzene

	1s	*2s*	*2p*		
Carbon (*ground state*):	↑↓	↑↓	↑	↑	

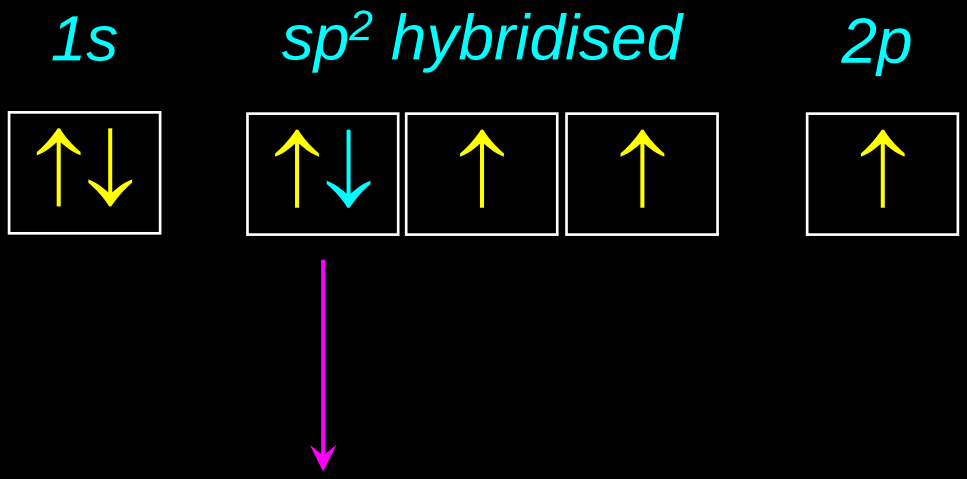
	1s	*2s*	*2p*		
Carbon (*excited*):	↑↓	↑	↑	↑	↑

	1s	*sp^2 hybridised*			*2p*
Carbon (*sp^2 hybridised*)	↑↓	↑	↑	↑	↑

The Modern Structure of Benzene

	1s	*sp^2 hybridised*			*2p*
Carbon (*sp^2 hybridised*)	↑↓	↑	↑	↑	↑

The Modern Structure of Benzene

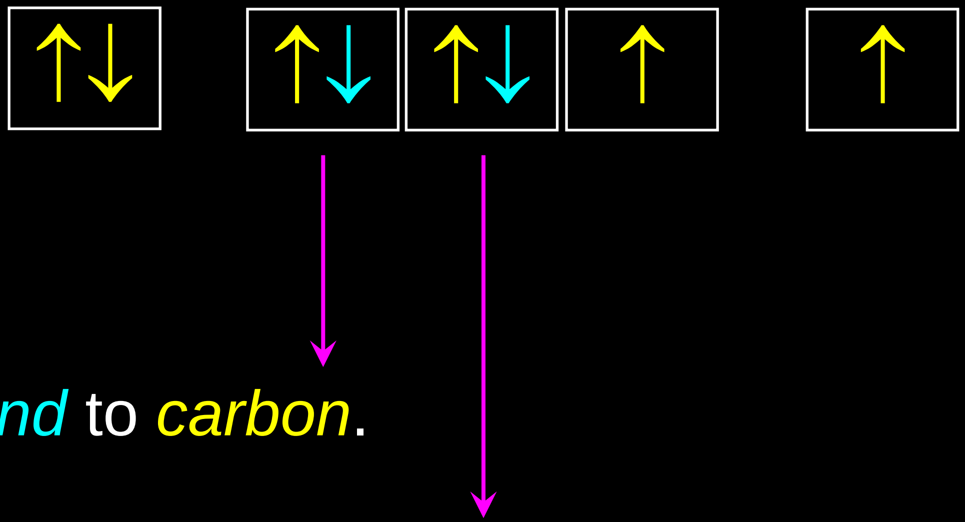


1s *sp^2 hybridised* *2p*

Carbon (*sp^2 hybridised*) ↑↓ ↑↓ ↑ ↑ ↑

σ-bond to *carbon*.

The Modern Structure of Benzene

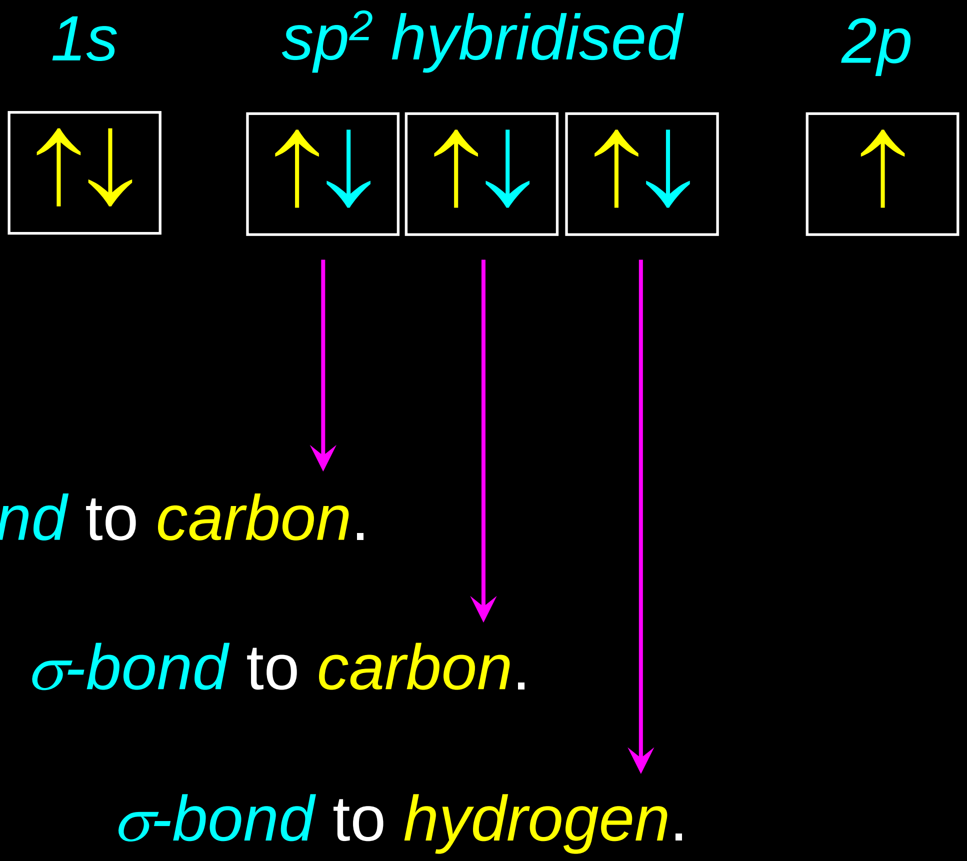


Carbon (*sp^2 hybridised*)

σ-bond to *carbon*.

σ-bond to *carbon*.

The Modern Structure of Benzene



1s *sp*^{2} *hybridised* *2p*

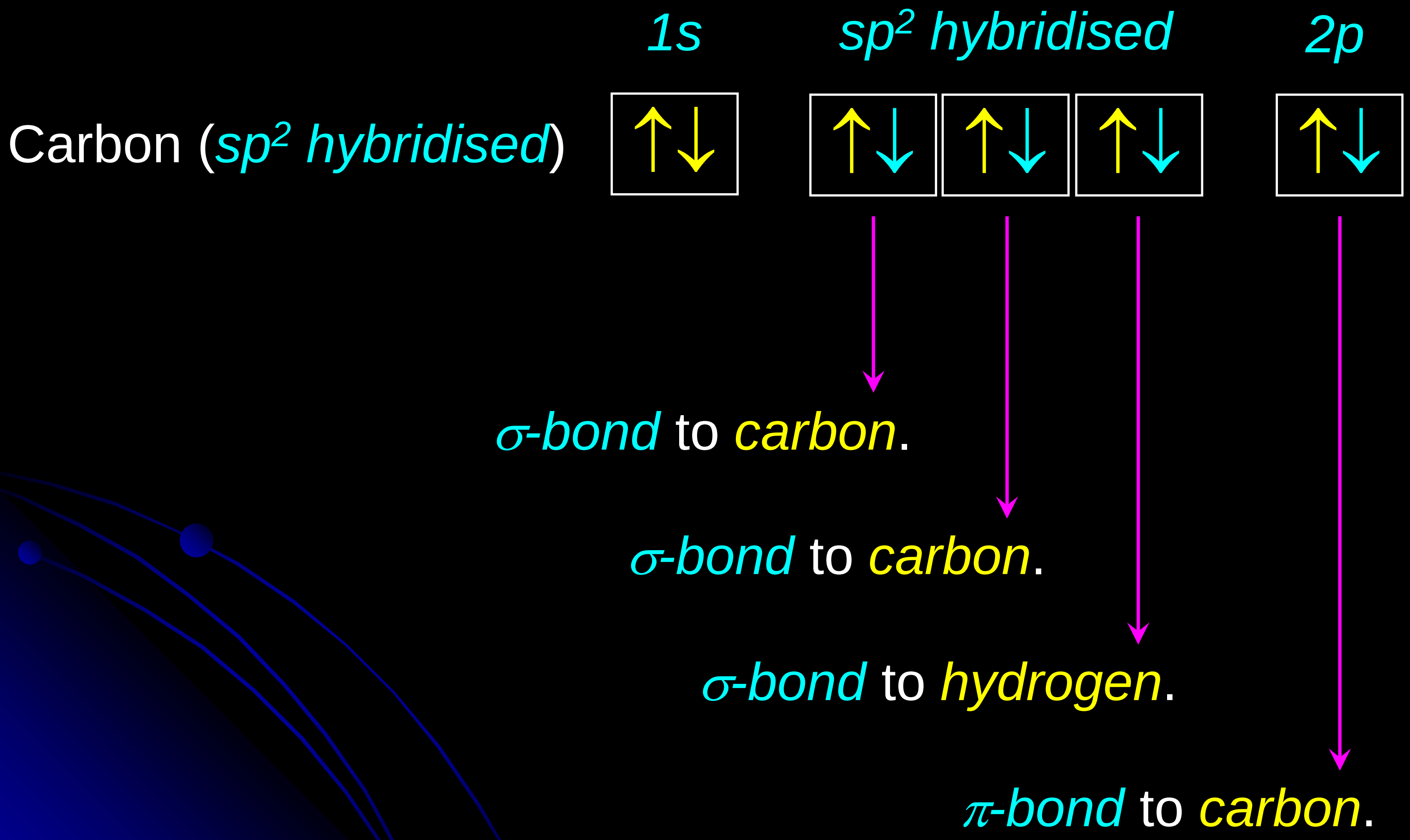
Carbon (*sp*^{2} *hybridised*) ↑↓ ↑↓ ↑↓ ↑↓ ↑

σ-bond to *carbon*.

σ-bond to *carbon*.

σ-bond to *hydrogen*.

The Modern Structure of Benzene



Carbon (*sp*^{2} *hybridised*)

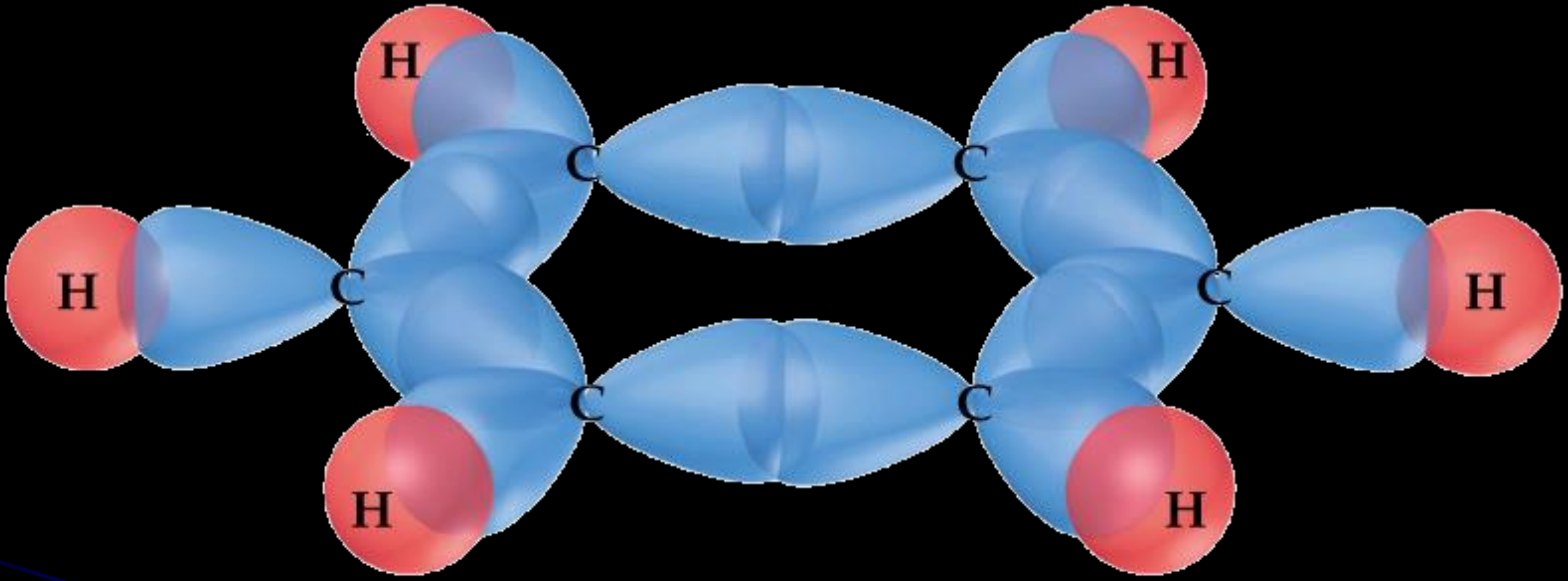
σ-bond to *carbon*.

σ-bond to *carbon*.

σ-bond to *hydrogen*.

π-bond to *carbon*.

The Modern Structure of Benzene



The structure of benzene *#1*.

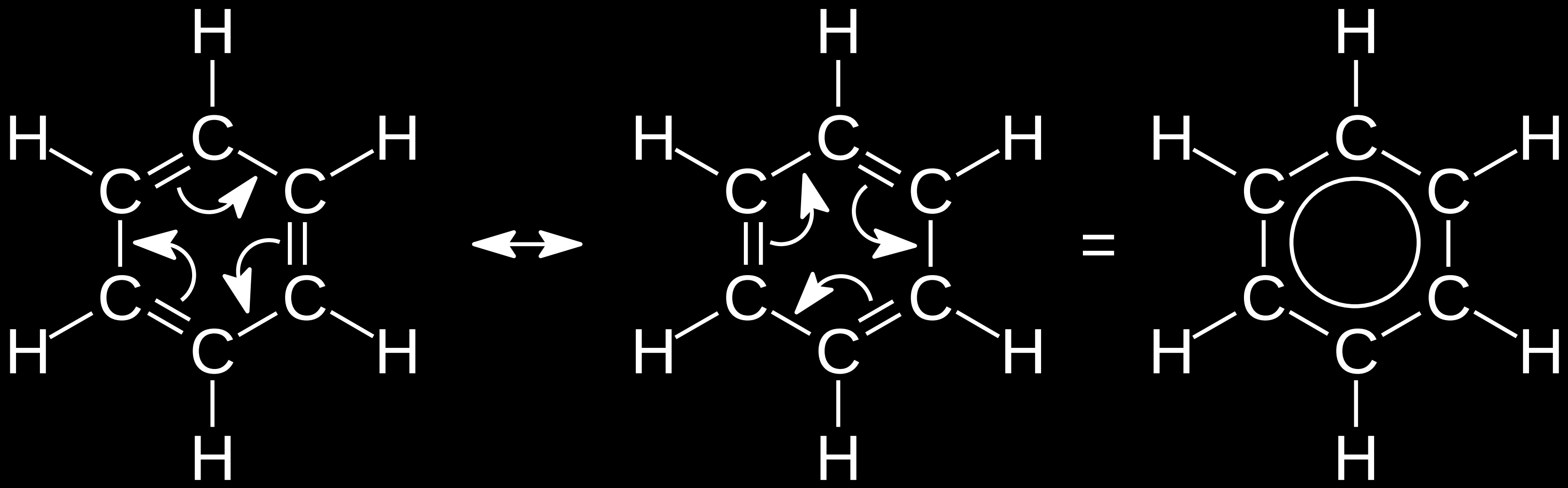
All six of the carbon atoms in benzene are *sp^2 hybridised*. This results in *σ-bonding* between the *sp^2* hybridised orbitals of carbon (blue) and the *s-orbitals* of hydrogen (red).

The Modern Structure of Benzene

The structure of benzene #2.

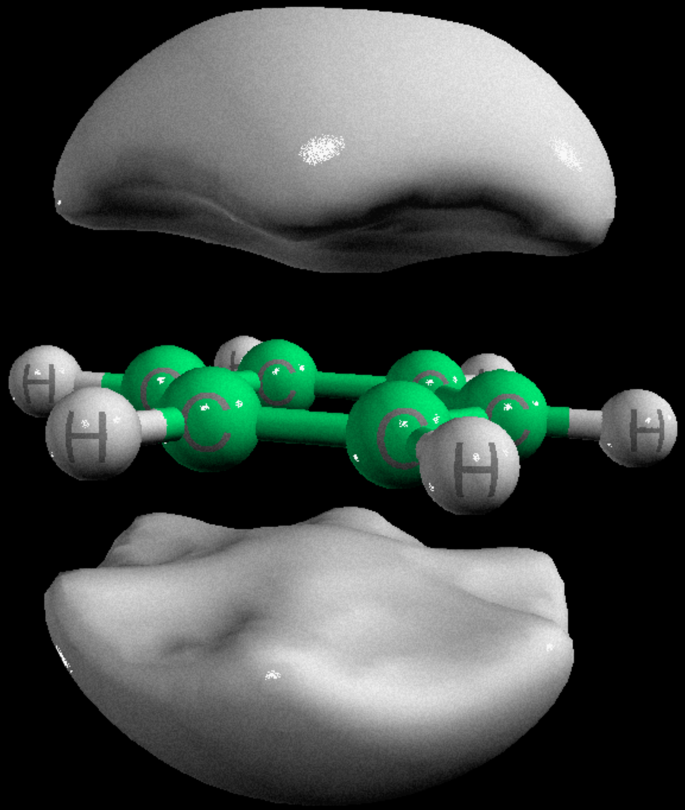
The *p-orbitals* of carbon which are not hybridised (purple) are arranged parallel to each other and overlap both above and below the plane of the benzene ring forming a cloud of *delocalised of* π*-bonding electrons*.

The Modern Structure of Benzene



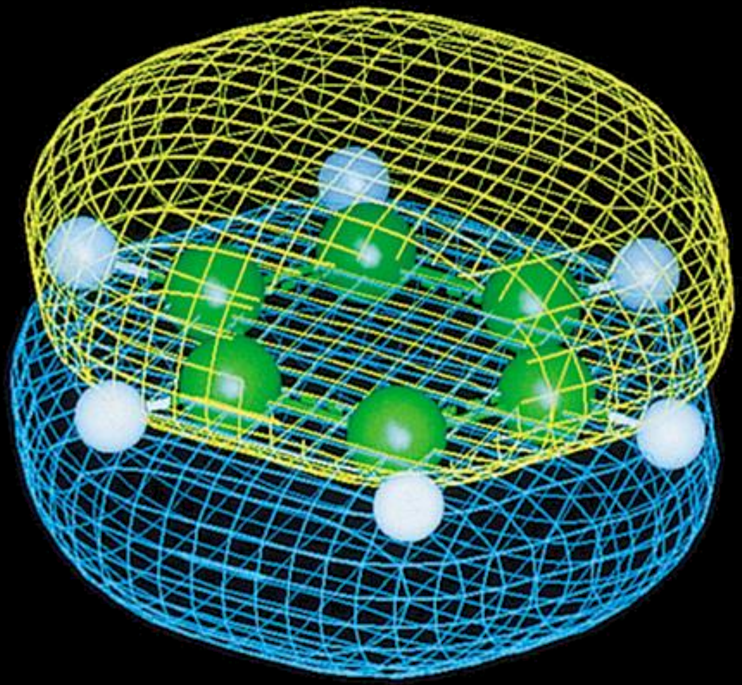
Delocalisation of the *π-bonding electrons* around the benzene ring lowers the energy of the structure by approximately *150 kJ mol^{-1}*, a value often referred to as the *delocalisation enthalpy*.

The Modern Structure of Benzene



A cloud of *delocalised π-bonding electrons* exists above and below the plane of the benzene ring.

The Modern Structure of Benzene



Benzene is a regular, planar hexagon in which all of the bond angles are *120°* and all of the carbon-to-carbon covalent bond lengths are *0.139 nm*.

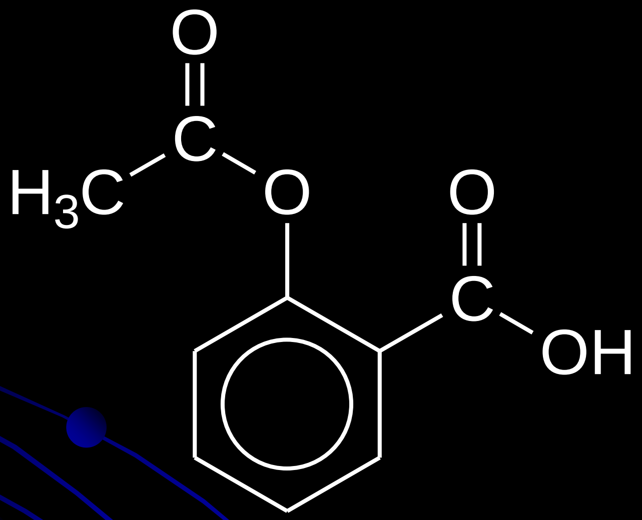
Try to make your own model of benzene!

STUDENT

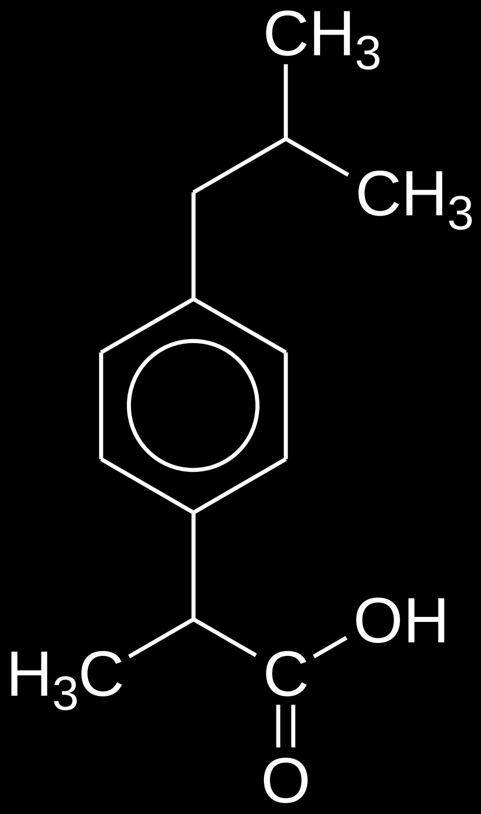
ADVISORY

ADVANCED CHEMISTRY

The Chemistry of Benzene

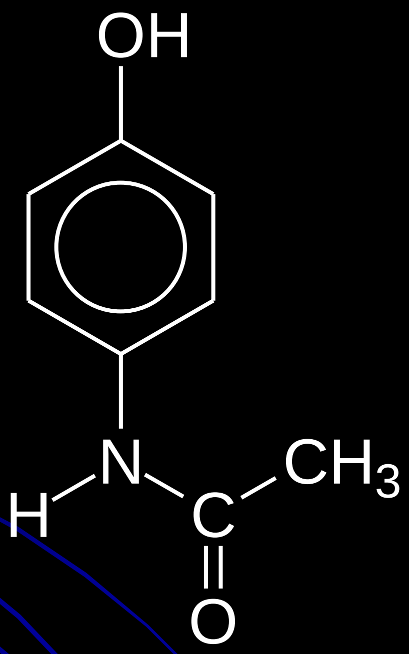


Aspirin

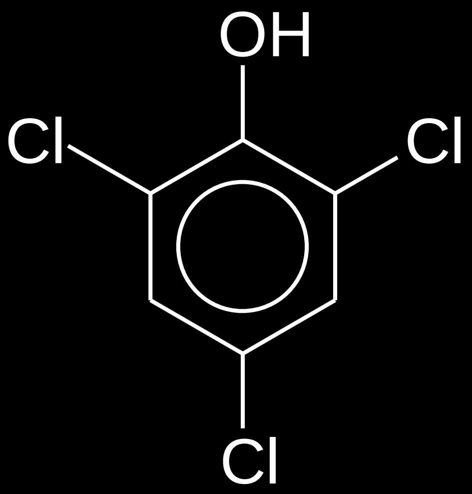


Ibuprofen

The Chemistry of Benzene



Paracetamol

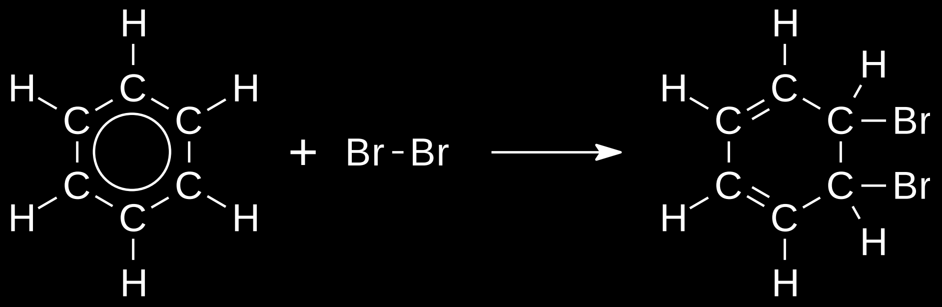


TCP

The Chemistry of Benzene

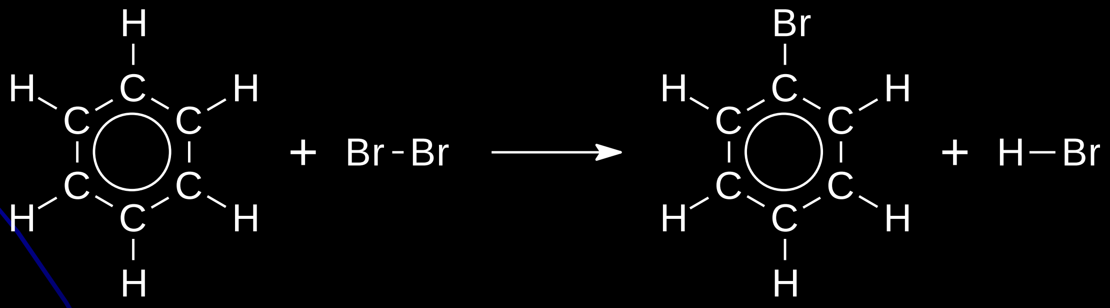
Benzene usually undergoes *electrophilic substitution* reactions in which the delocalised π-bonding electron system is preserved, therefore retaining the molecule’s stability.

Addition results in the loss of the delocalised π-bonding electron system and is therefore unfavourable.



☹

Substitution retains the delocalised π-bonding electron system and is therefore favourable.



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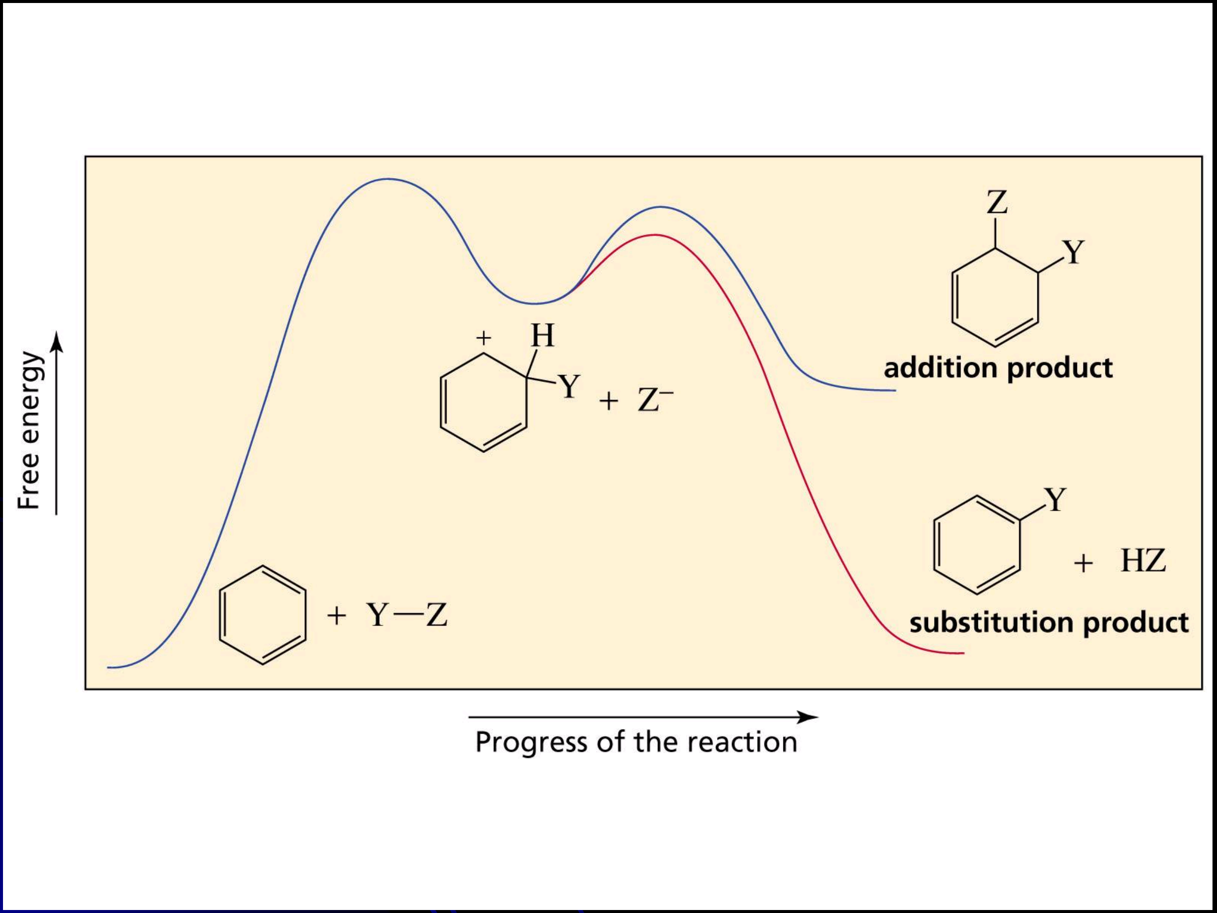
The Chemistry of Benzene



When benzene reacts, the energy of the *substituted* product is much less than that of the corresponding *addition* product, *i.e.* the substituted product is *more stable* than the addition product. As a consequence, the chemistry of benzene favours *substitution reactions*.

The Chemistry of Benzene

Question:

- What is an *electrophile*?

Answer:

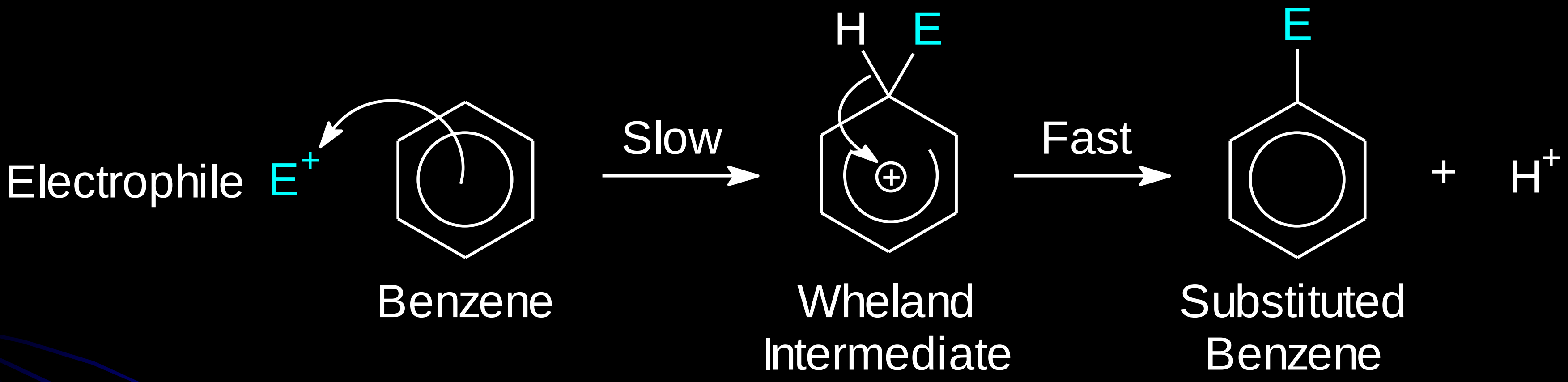
An *electrophile* is chemical species that is attracted towards a region of negative charge, such as an *anion*, *δ– atom* in a polar covalent bond or a cloud of *π-bonding electrons*.

An electrophile is also described as an *electron pair acceptor*.

Electrophiles are either *cations* or *δ+ atoms* in a polar covalent bond.

The Chemistry of Benzene

The general mechanism for electrophilic substitution into benzene:



The *electrophile* is attracted towards the delocalised cloud of *π-bonding* electrons that exists above and below the plane of the benzene ring.

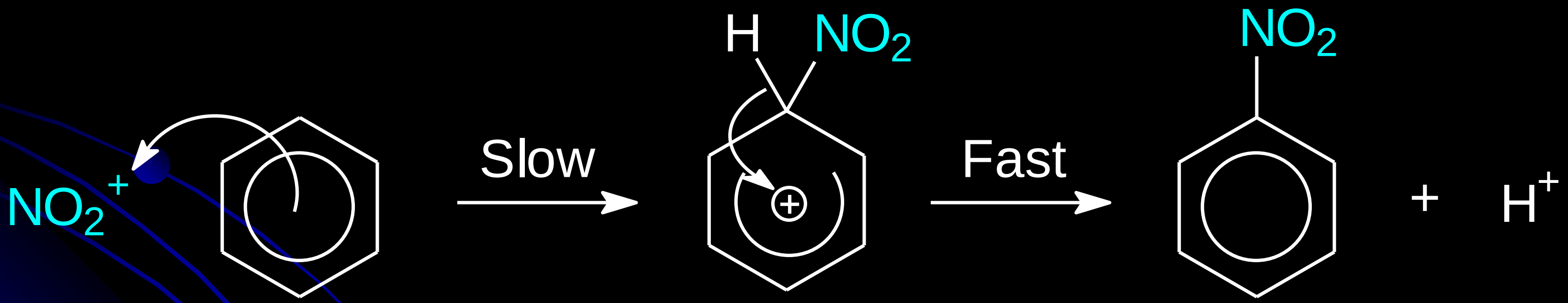
Formation of the electrophile requires a *Friedel-Crafts catalyst* which is usually $AlCl_3$ or $FeBr_3$.

The Chemistry of Benzene

Nitration of benzene:

$$H_2SO_4 + HNO_3 \rightarrow HSO_4^- + H_2NO_3^+$$

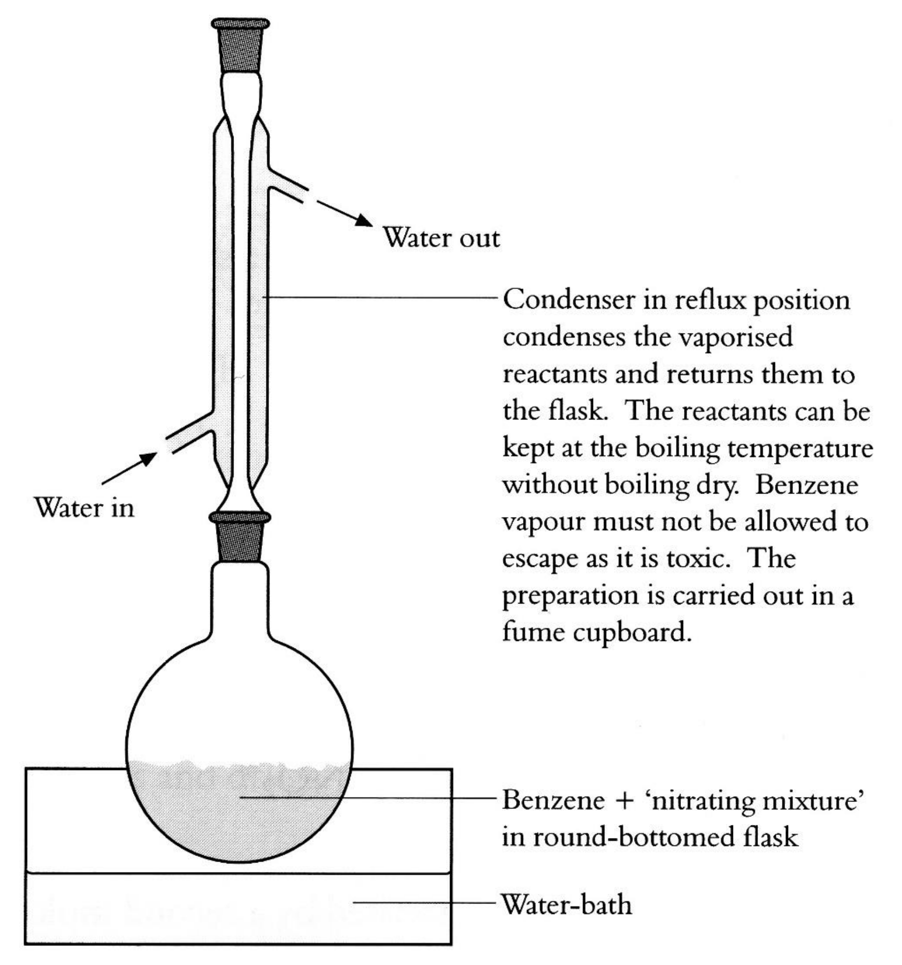
$$H_2NO_3^+ \rightarrow NO_2^+ + H_2O$$



NO_2^+ + Benzene $\xrightarrow{\text{Slow}}$ Wheland Intermediate $\xrightarrow{\text{Fast}}$ Nitrobenzene + H^+

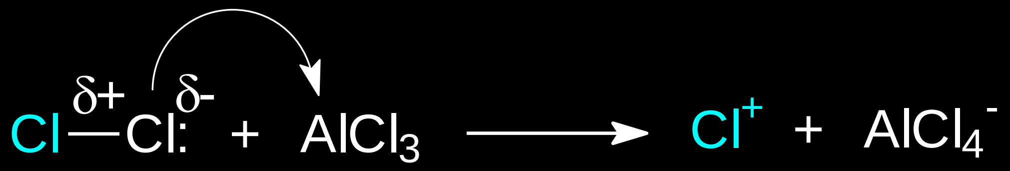
The Chemistry of Benzene

Nitration of benzene:

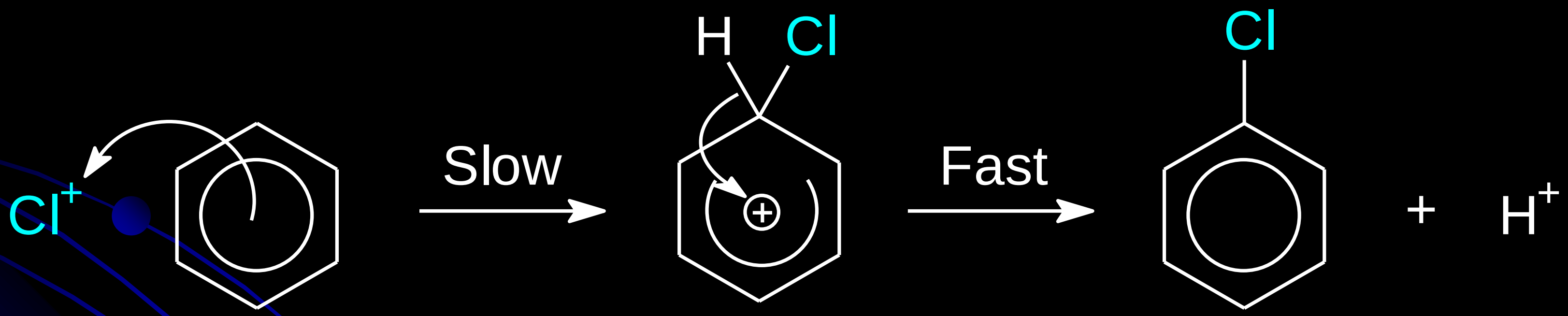


The Chemistry of Benzene

Friedel-Crafts chlorination of benzene:



$$\overset{\delta+}{Cl}-\overset{\delta-}{Cl}: + AlCl_3 \longrightarrow Cl^+ + AlCl_4^-$$



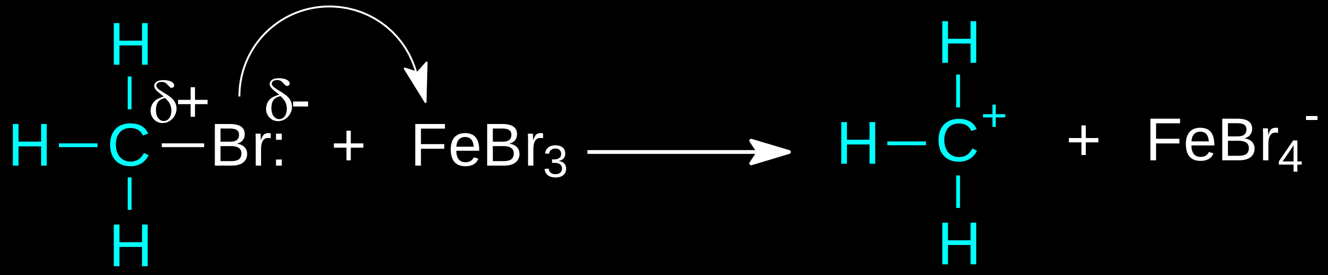
Benzene

Wheland Intermediate

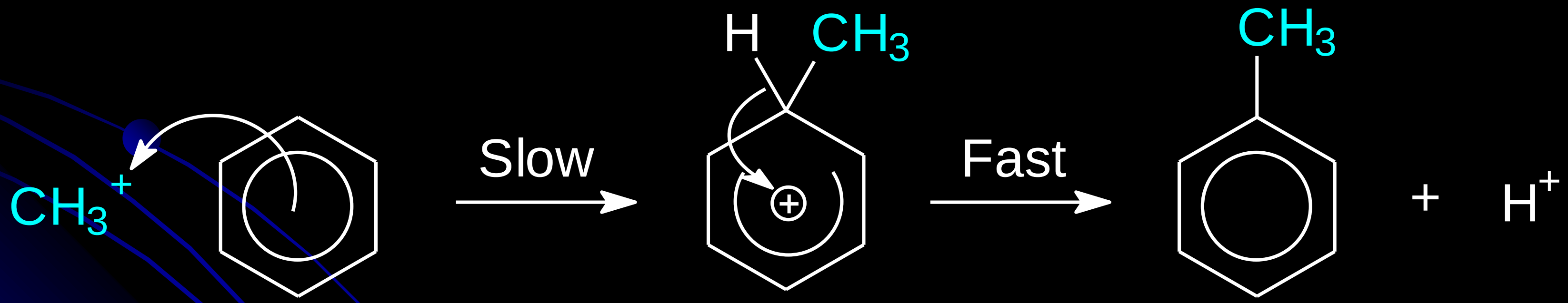
Chlorobenzene

The Chemistry of Benzene

Friedel-Crafts alkylation of benzene:



$$\mathrm{H{-}\overset{H}{\underset{H}{|}}\!\!\overset{\delta+}{C}{-}\overset{\delta-}{Br}{:}} + \mathrm{FeBr_3} \longrightarrow \mathrm{H{-}\overset{H}{\underset{H}{|}}\!\!C^{+}} + \mathrm{FeBr_4^{-}}$$



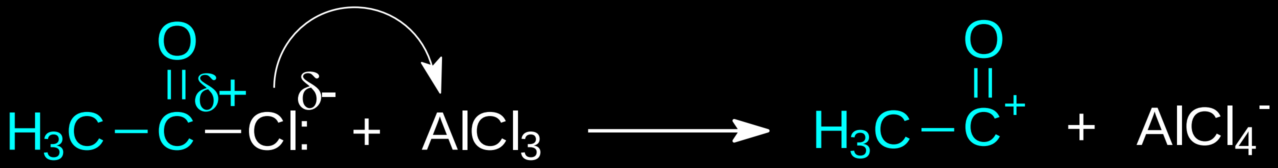
Benzene

Wheland
Intermediate

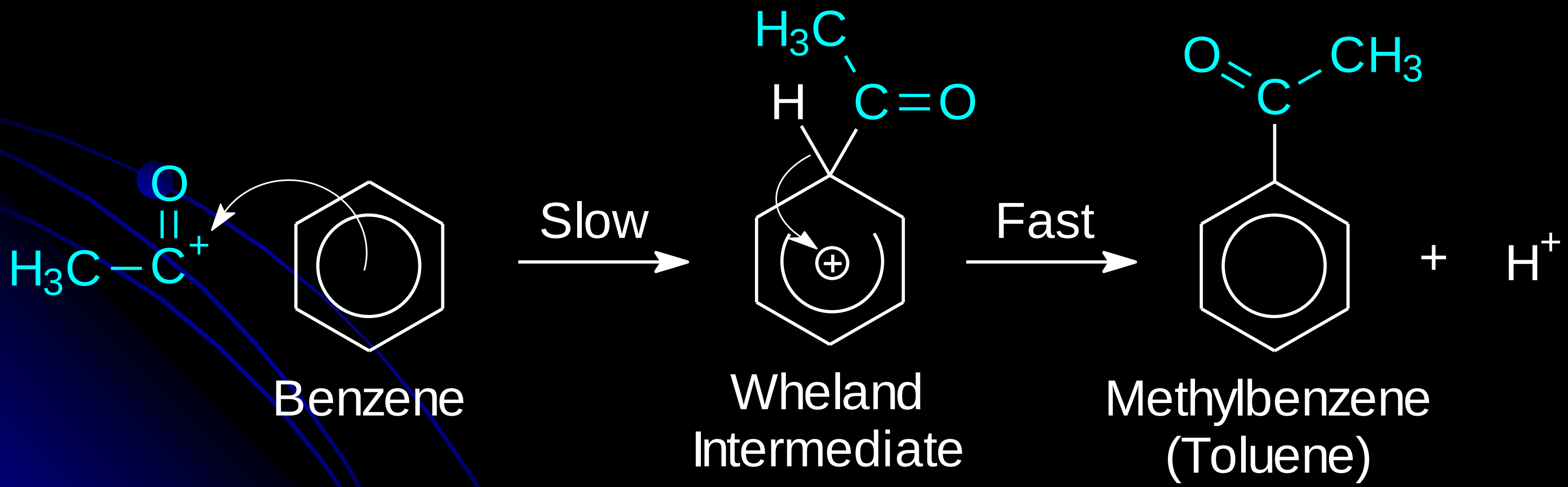
Methylbenzene
(Toluene)

The Chemistry of Benzene

Friedel-Crafts acylation of benzene:

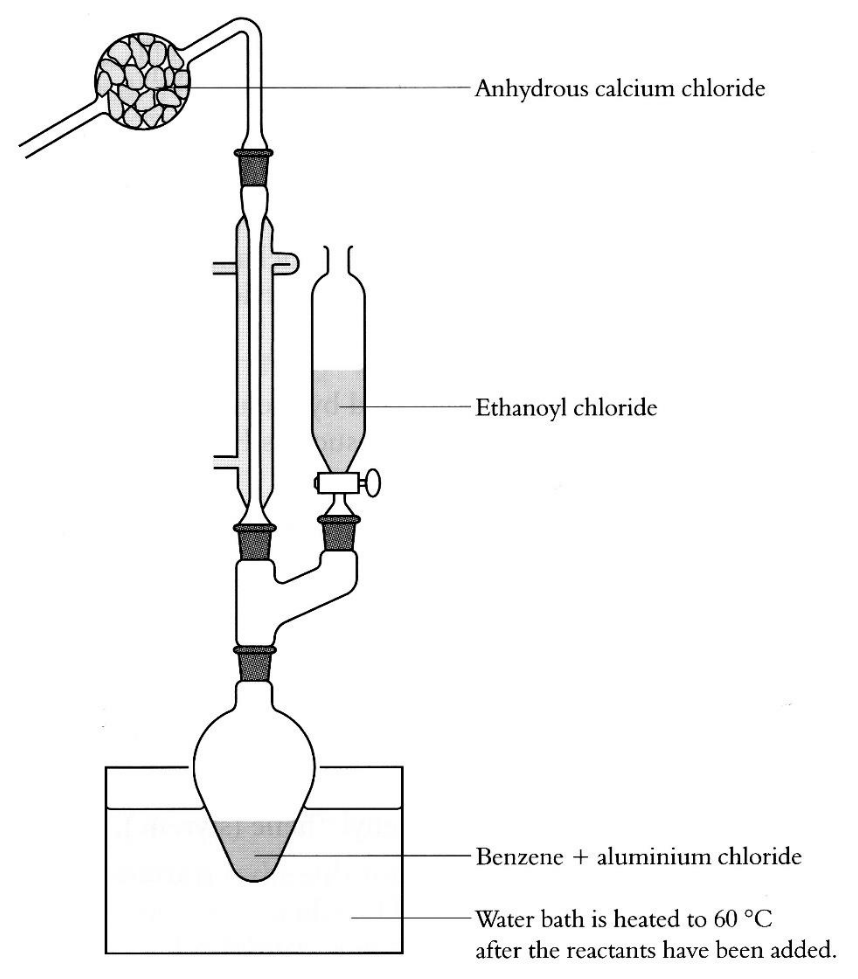


$$\mathrm{H_3C-\overset{\overset{O}{\|}}{C}{}^{\delta+}-\overset{\delta-}{Cl}: + AlCl_3 \longrightarrow H_3C-\overset{\overset{O}{\|}}{C}{}^{+} + AlCl_4^{-}}$$

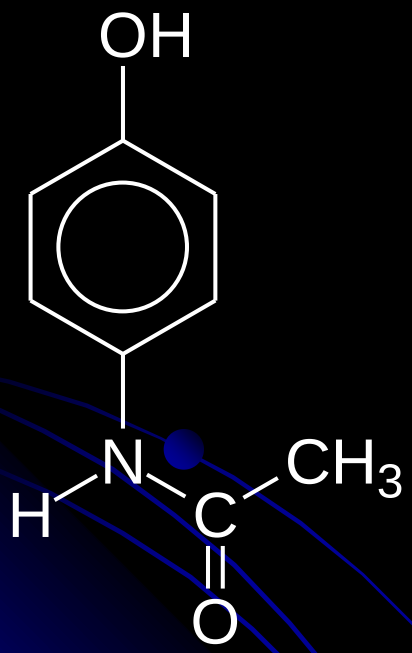


The Chemistry of Benzene

Friedel-Crafts acylation of benzene:



The Synthesis of Paracetamol from Benzene (Macroconcept – Change)



Paracetamol

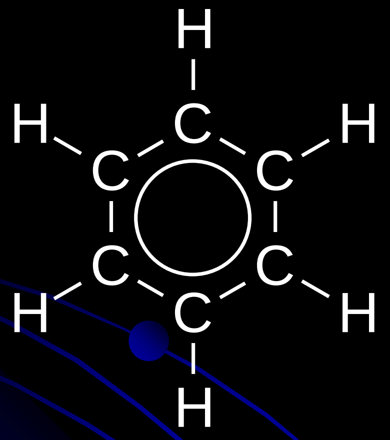
Paracetamol is both an *analgesic* and an *antipyretic*. Unlike aspirin and ibuprofen, paracetamol has no *anti-inflammatory* properties. Paracetamol is toxic to the liver and consequently high doses can be fatal:

Acute poisoning – 10g in a single dose.

Chronic poisoning – 5g every 24 hours for a prolonged period of time.

The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

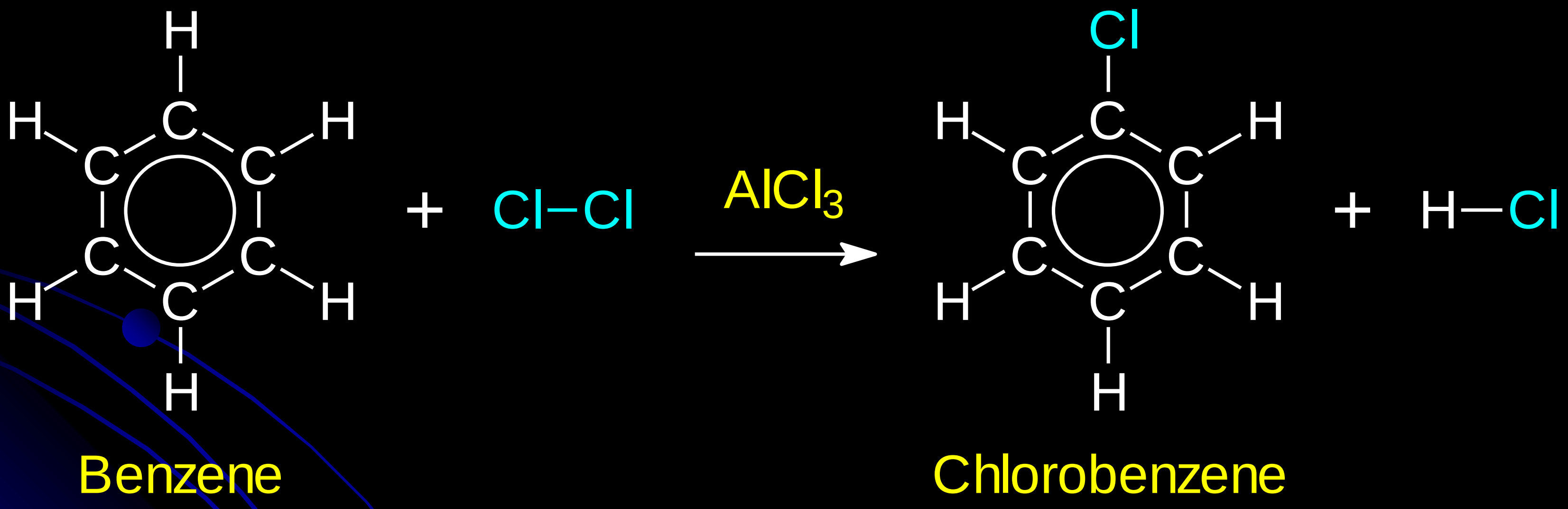
Step #1: Synthesis of Chlorobenzene from Benzene:



Benzene

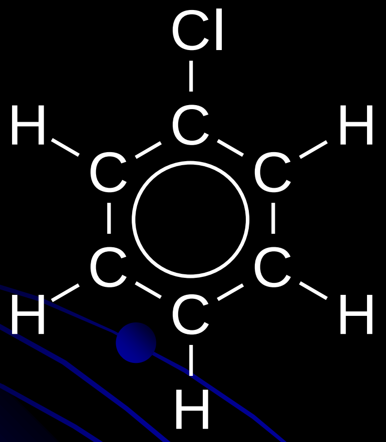
The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

Step #1: Synthesis of Chlorobenzene from Benzene:



The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

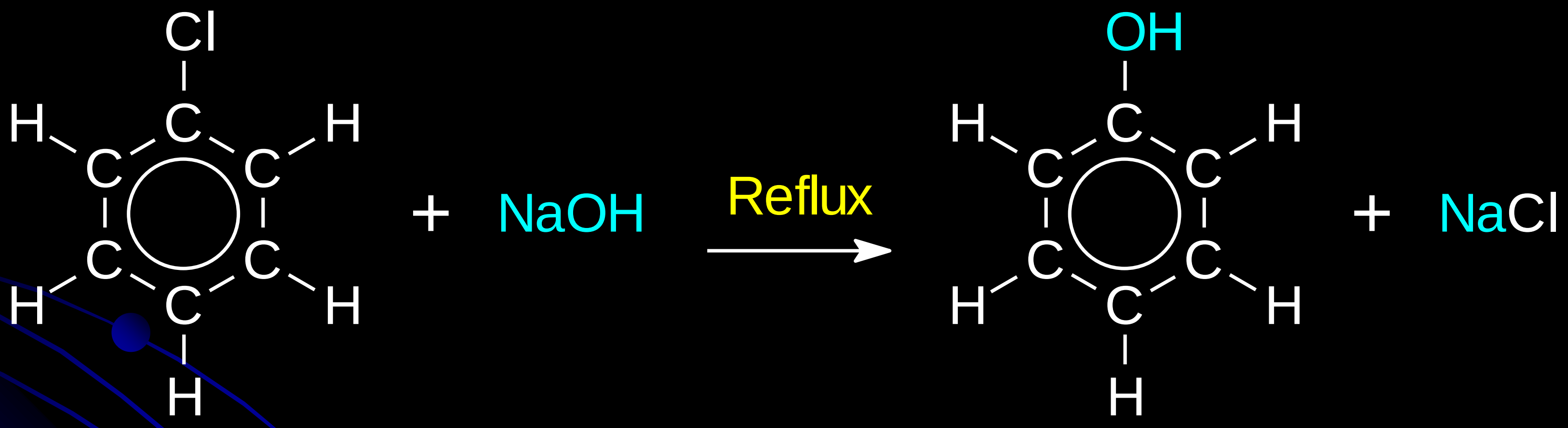
Step #2: Synthesis of Phenol from Chlorobenzene:



Chlorobenzene

The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

Step #2: Synthesis of Phenol from Chlorobenzene:

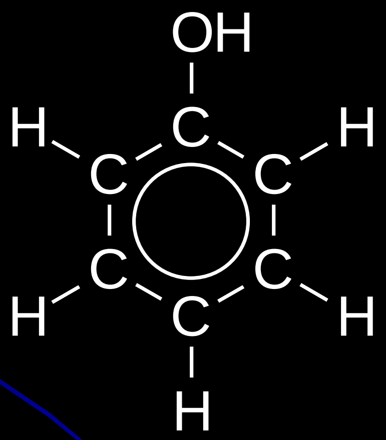


Chlorobenzene

Phenol

The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

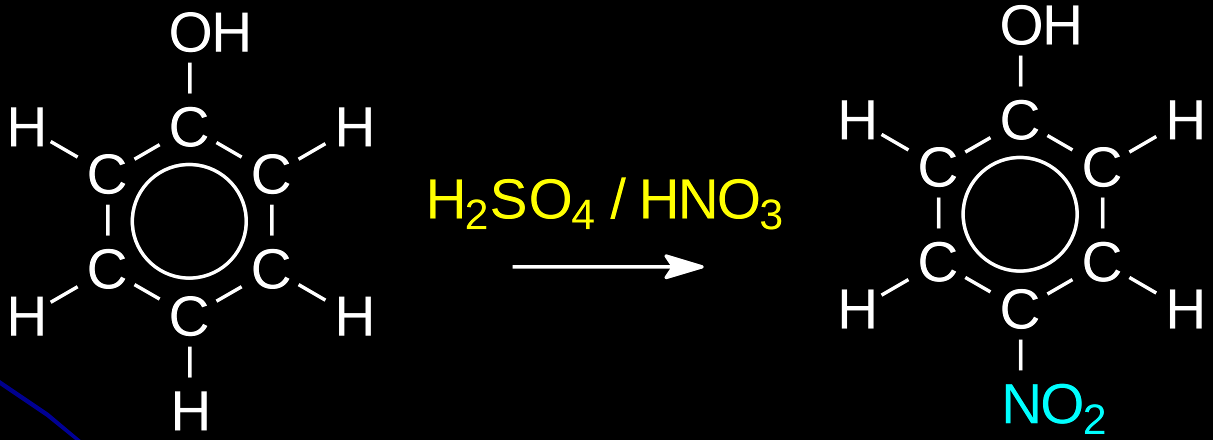
Step #3: Nitration of Phenol:



Phenol

The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

Step #3: Nitration of Phenol:

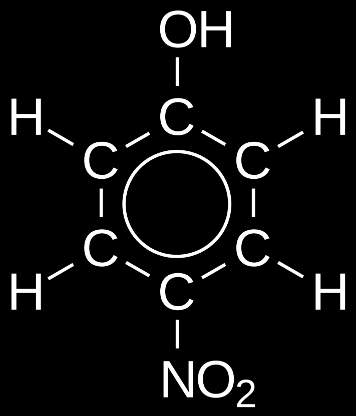


Phenol

4-Nitrophenol

The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

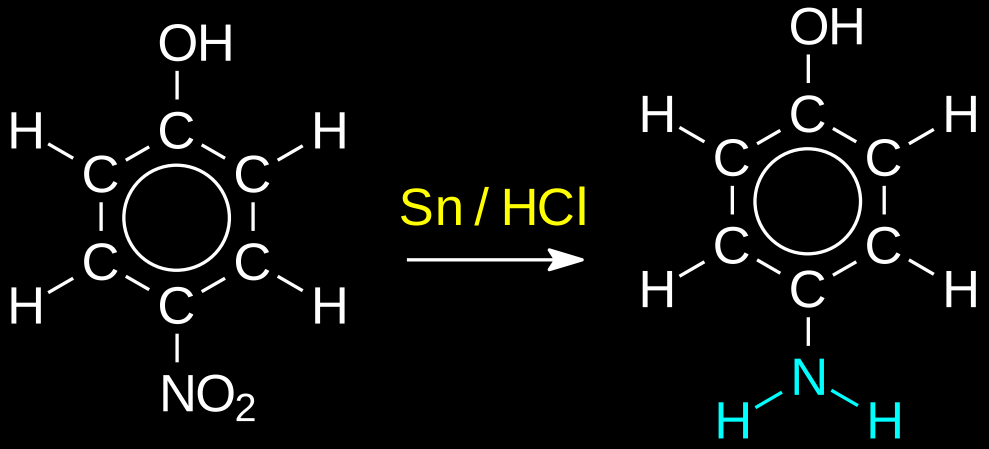
Step #4: Reduction of the Nitro Group to an Amine:



4-Nitrophenol

The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

Step #4: Reduction of the Nitro Group to an Amine:

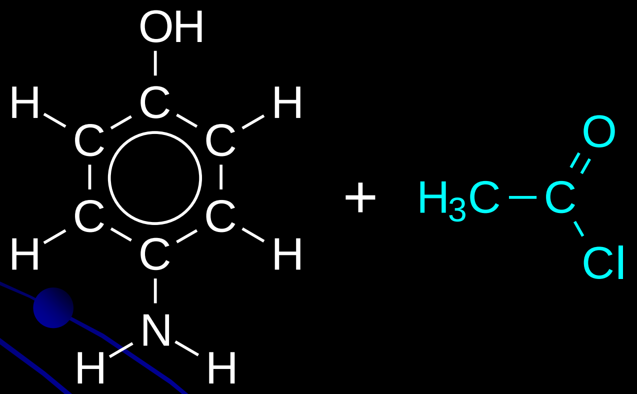


4-Nitrophenol

4-Aminophenol

The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

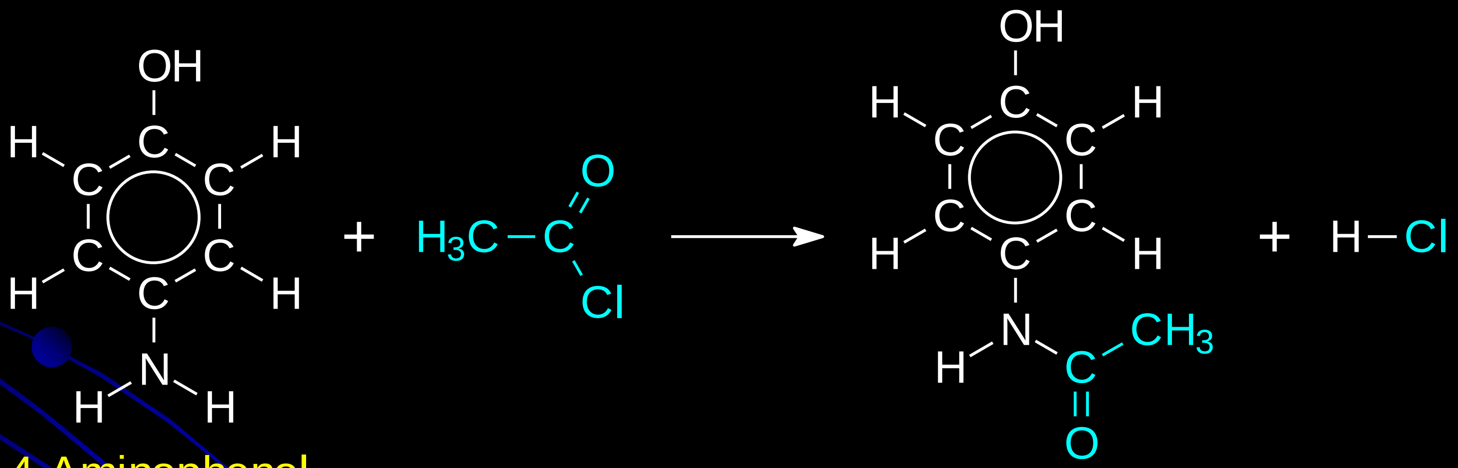
Step #5: Synthesis of the Amide:



4-Aminophenol

The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

Step #5: Synthesis of the Amide:



4-Aminophenol

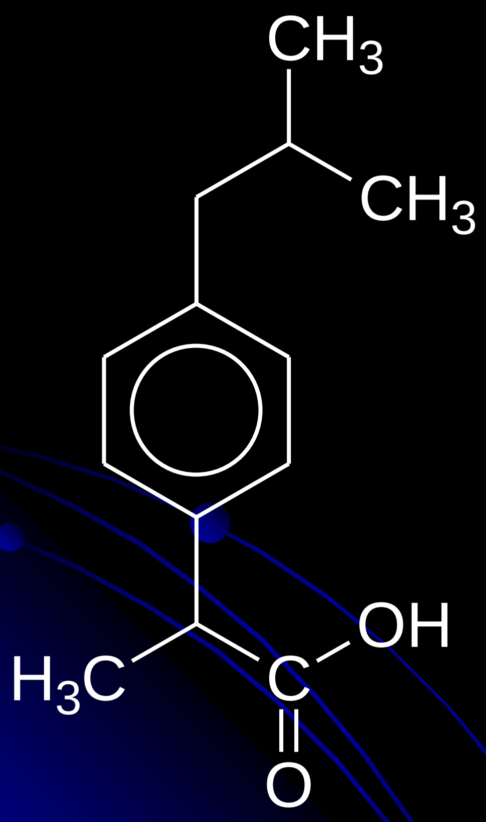
Paracetamol

The Synthesis of Paracetamol from Benzene (Macroconcept – Change)

Question:

- If each step in the synthesis of paracetamol gives a yield of *80%*, what mass of paracetamol will be synthesised from *1.0 kg* of benzene?

The Synthesis of Ibuprofen from Benzene (Macroconcept – Change)

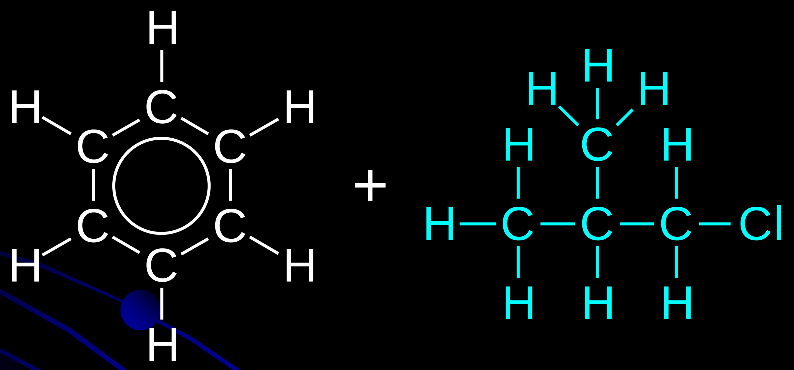


Ibuprofen

Ibuprofen is classified as a *non-steroidal anti-inflammatory* drug (abbreviated to NSAID). Ibuprofen is mostly used to treat pain resulting from inflammation, *e.g.* rheumatism. The side-effects of ibuprofen are far less significant than those of other NSAID compounds such as aspirin.

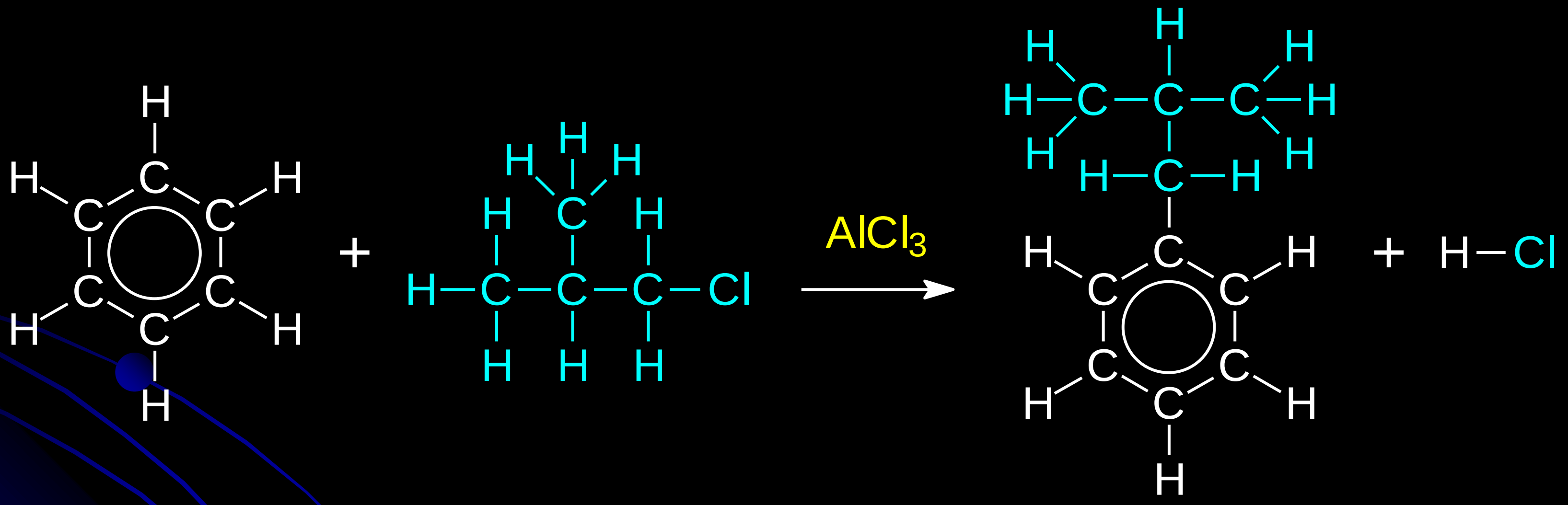
The Synthesis of Ibuprofen from Benzene

Step #1: Friedel-Crafts alkylation:



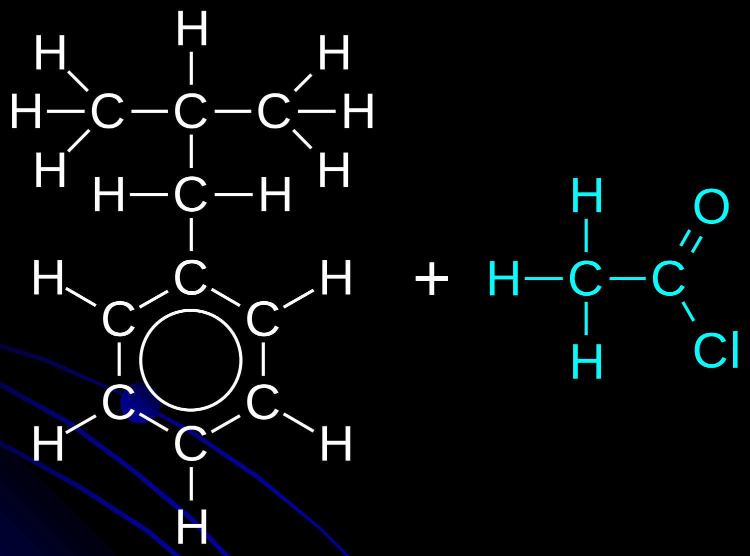
The Synthesis of Ibuprofen from Benzene

Step #1: Friedel-Crafts alkylation:



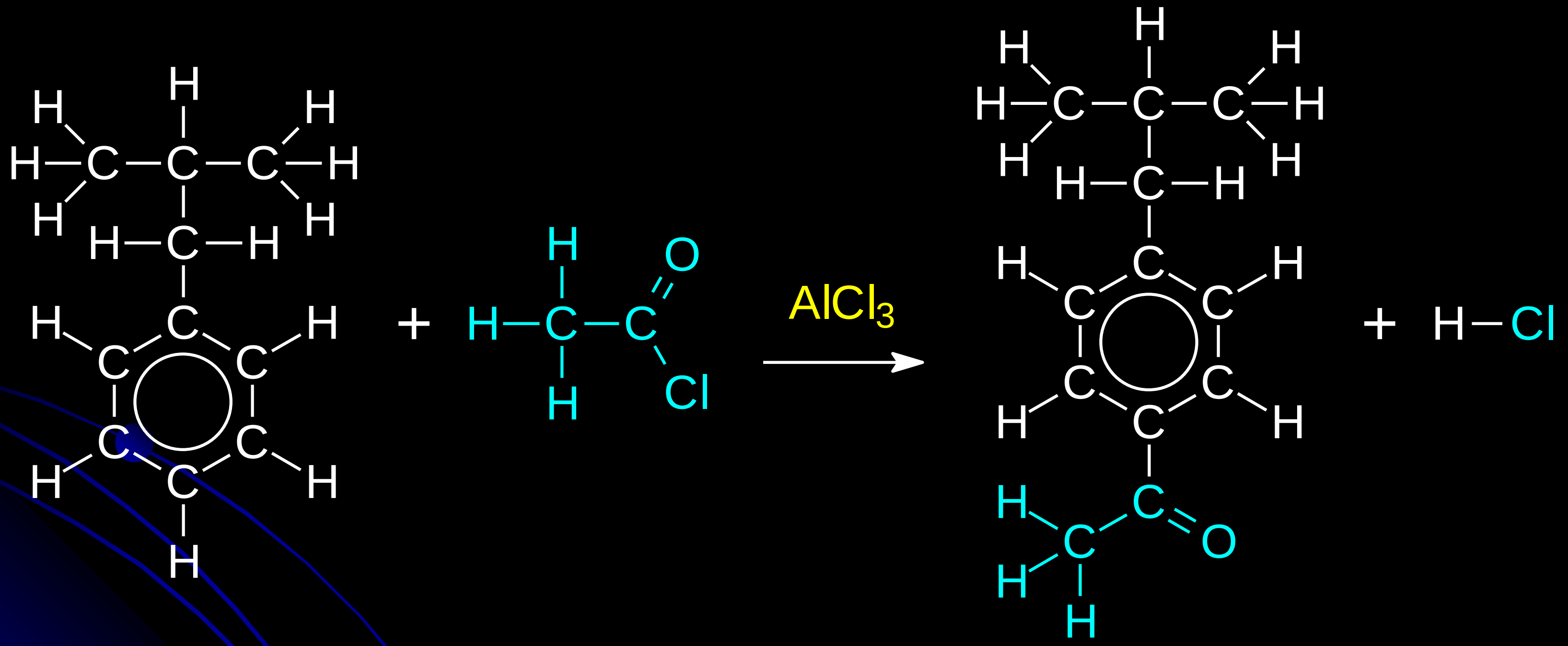
The Synthesis of Ibuprofen from Benzene

Step #2: Friedel-Crafts acylation:



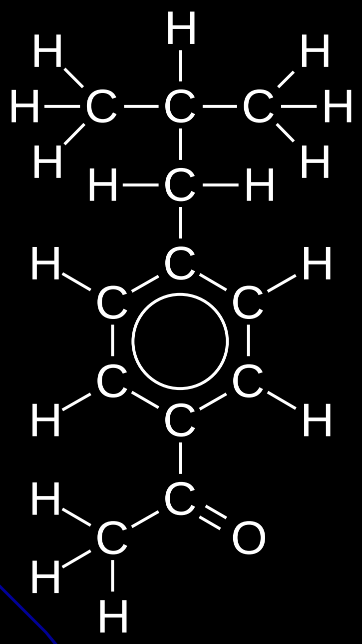
The Synthesis of Ibuprofen from Benzene

Step #2: Friedel-Crafts acylation:



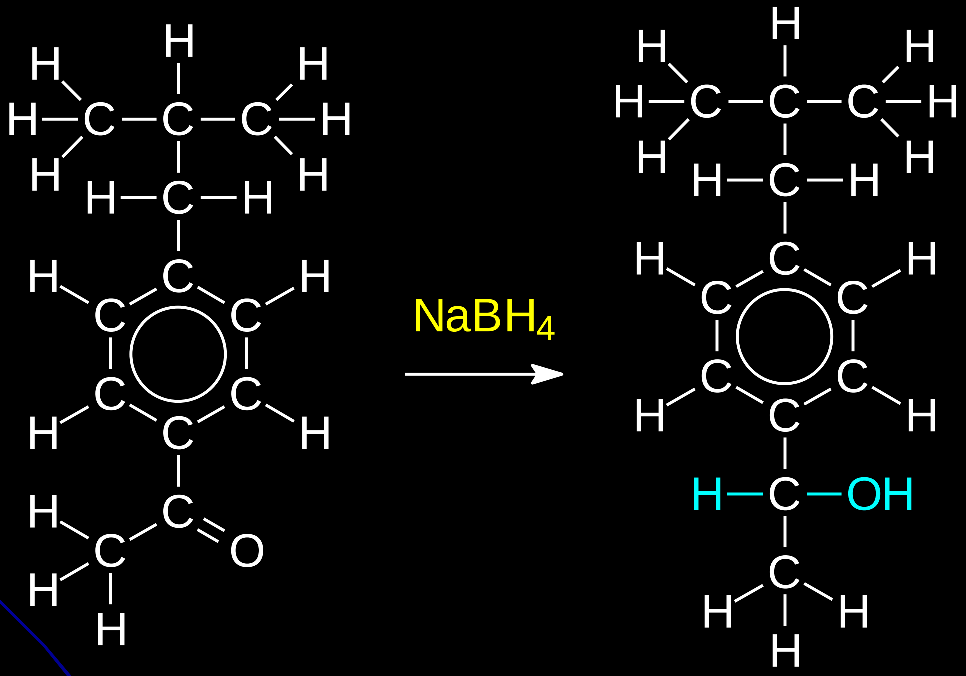
The Synthesis of Ibuprofen from Benzene

Step #3: Reduction of the ketone to an alcohol:



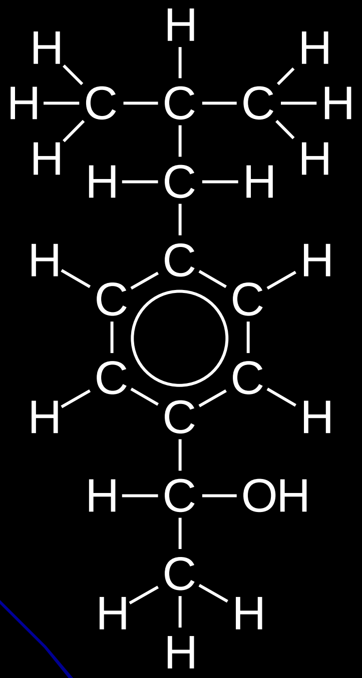
The Synthesis of Ibuprofen from Benzene

Step #3: Reduction of the ketone to an alcohol:



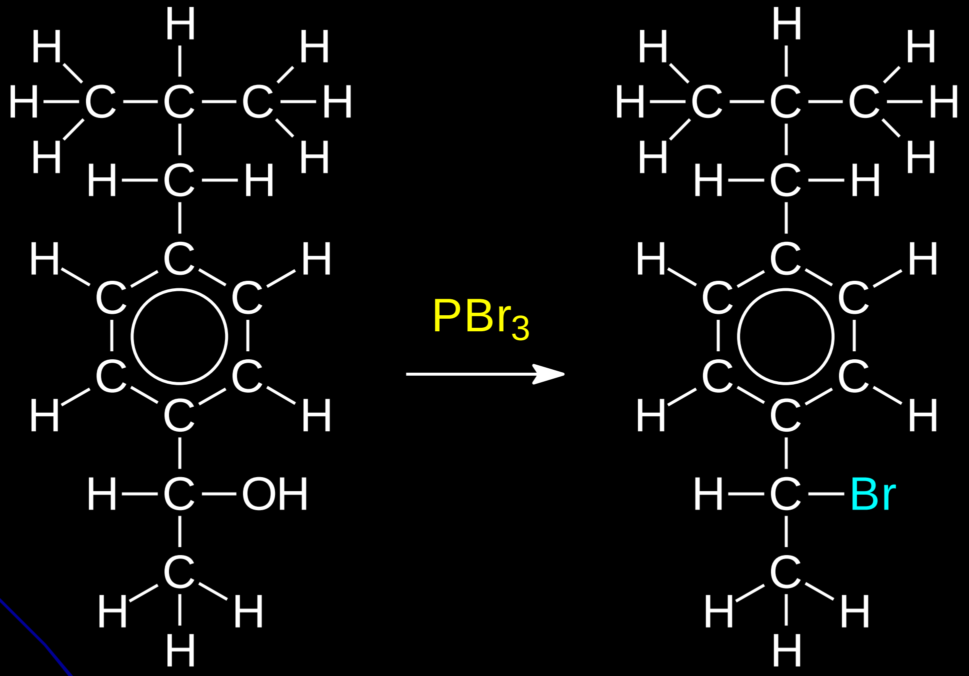
The Synthesis of Ibuprofen from Benzene

Step #4: Substitution of –OH by –Br:



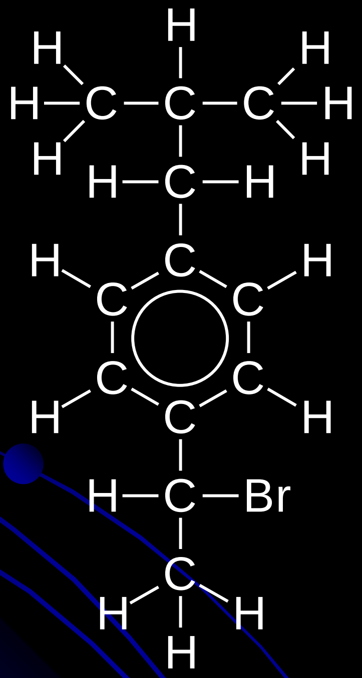
The Synthesis of Ibuprofen from Benzene

Step #4: Substitution of –OH by –Br:



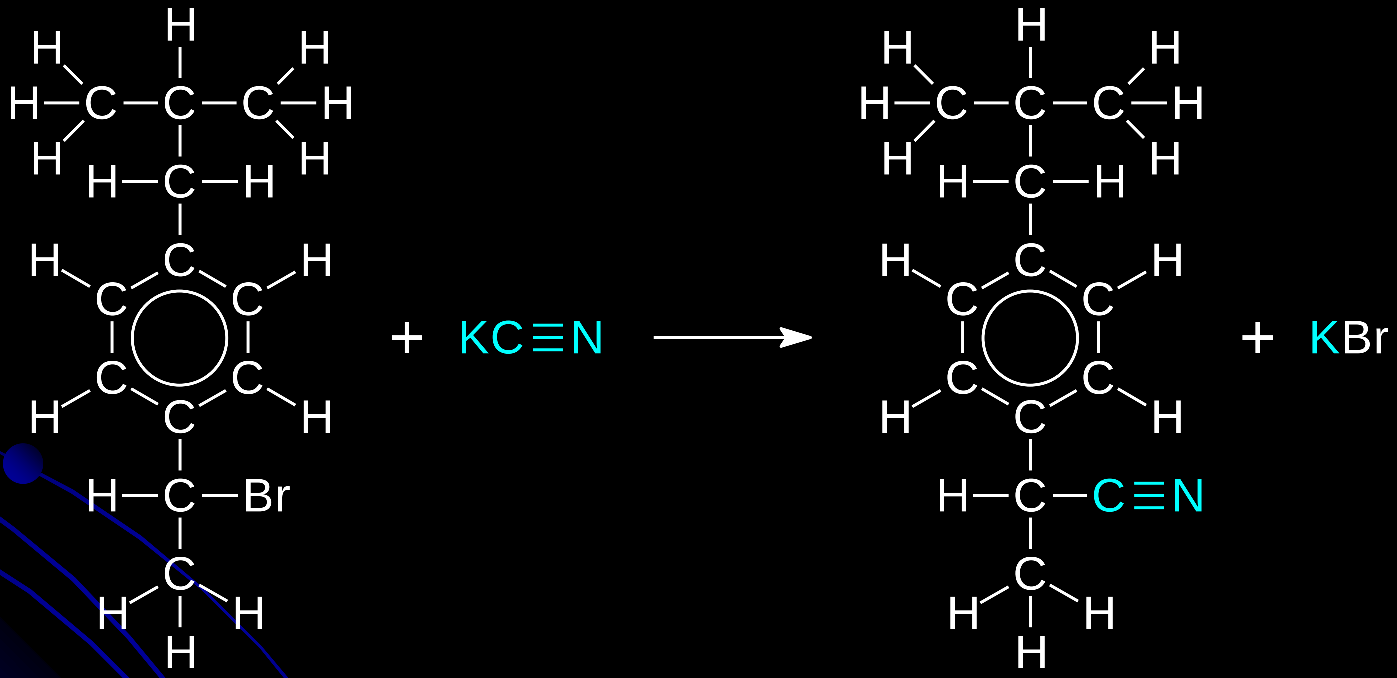
The Synthesis of Ibuprofen from Benzene

Step #5: Substitution of –Br by –C≡N:



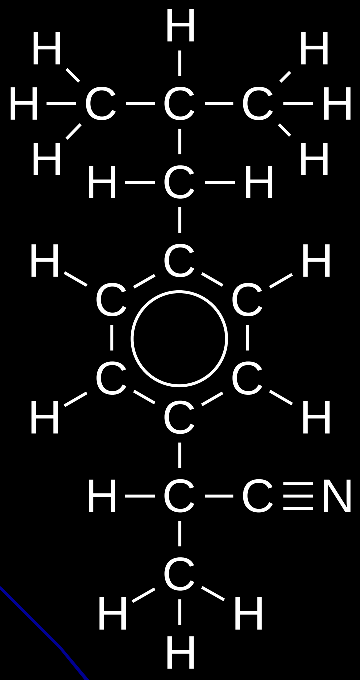
The Synthesis of Ibuprofen from Benzene

Step #5: Substitution of –Br by –C≡N:



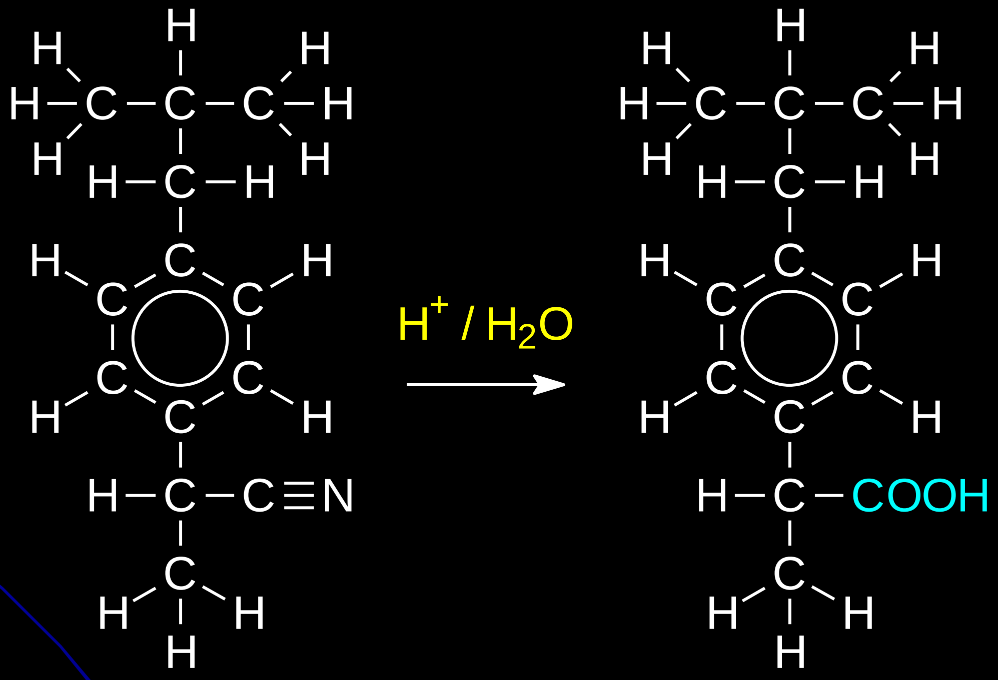
The Synthesis of Ibuprofen from Benzene

Step #6: Hydrolysis of –C≡N to form –COOH:



The Synthesis of Ibuprofen from Benzene

Step #6: Hydrolysis of –C≡N to form –COOH:



Ibuprofen

The Synthesis of Ibuprofen from Benzene

Question:

- The United Kingdom market for ibuprofen is *3 000 000 kg per year*.

a) If a typical ibuprofen tablet contains *0.2g* of the drug, how many ibuprofen tablets are produced each year in the United Kingdom?

b) The population of the United Kingdom is *60 000 000*.
i) How many ibuprofen tablets does a single person consume in the United Kingdom each year?
ii) Evaluate how reasonable your answer is.

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