Inorganic, Physical and Organic Chemistry

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Teaching timetable

Monday 10:00 – 13:00 (Green)
Thursday 15:00 – 18:00 (Yelow)

Course Evaluation

PRACTICALS (15 marks)
CAT (15 MARKS)
Final Exam (70 MARKS)

Recommended text books

1. General Chemistry, Raymond Chang
2. Organic Chemistry, John McMurry

Course Outline

Inorganic Chemistry

- Definition of Chemistry
- Matter
- Atoms
- Electronic Configuration
- Periodic Table
- Bonding in carbon compounds Covalent bond and Hybridization
- Polar Covalent Bonds
- Intermolecular Forces

Physical Chemistry

Chemical equilibrium

What is equilibrium?

Expressions for equilibrium constants, K_c;

Calculating K_c using equilibrium concentrations;

Calculating equilibrium concentrations using initial concentration and K_c value;

Relationship between K_c and K_p;

Factors that affect equilibrium;

Le Chatelier’s Principle

Organic Chemistry

What is Organic Chemistry?

Carbon in the Periodic table.

Introduction to Functional Groups

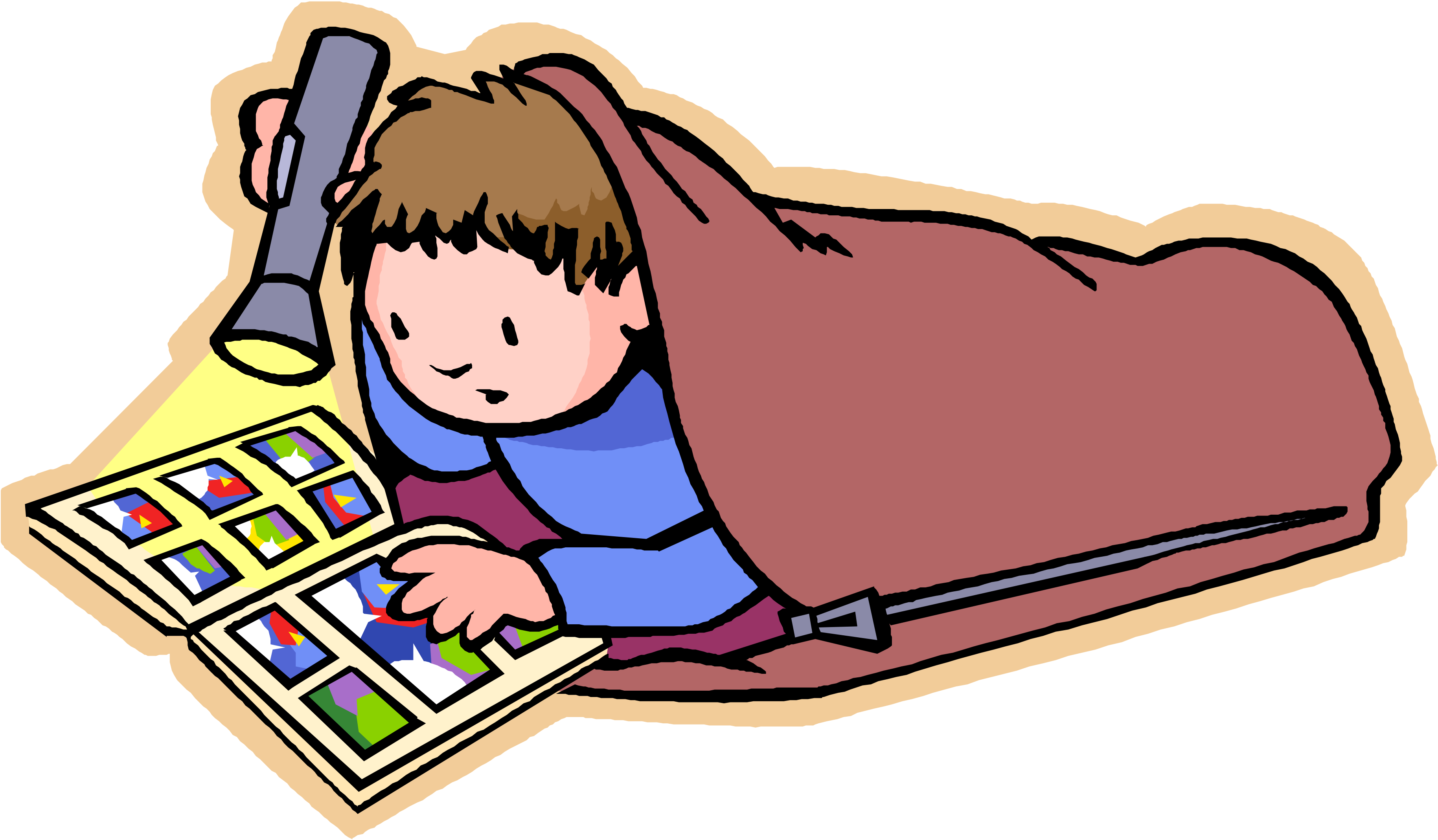
Bonding In Carbon Compounds - Covalent Bond and Hybridization.

Polar Covalent Bonds: Electronegativity, Dipole Moment.

Intermolecular Forces and physical properties.

Nomenclature of organic compounds.

Inter-conversion of functional groups.



READ MORE

Knowledge is power.

DO IT WELL

Whatever you do, do your best.

WORK HARD

Success is 1% inspiration, 99% perspiration.

Success Depends on the Second Letter

Definition of Chemistry

Chemistry is the study of the composition, structure, properties and reactions of matter.

Chemistry is the study of matter and the changes it undergoes.

Definition of matter

Matter is anything that occupies space and has mass.

- It includes things we can see and touch (such as water, earth, and trees), as well as things we cannot (such as air).
- Thus, everything in the universe has a “chemical’’ connection.

The different types of matter can be **distinguished** through two components: Composition and Properties.

Matter

Composition

different components of matter along with their relative proportions

H_2O: Components: Hydrogen and Oxygen (2 parts hydrogen, 1 part Oxygen)

Properties

qualities/attributes that distinguish one sample of matter from another

Color: Yellow/green
Texture: Squishy/soft
Changes: Browning

The properties of matter

Physical Properties

Physical properties are those that can be determined **without changing** the composition or identity of the substance being studied.

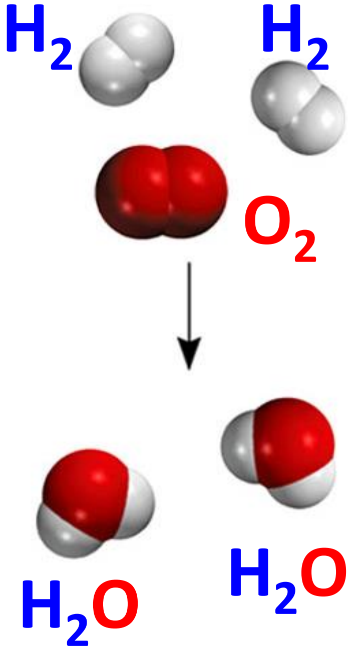
Melting of ice

Chemical Properties

Chemical properties are properties that are determined using a process that **changes** the identity of the substance of interest. It describe the way a substance can change or react to form other substances.

Burning of hydrogen in air to give water

When liquid water (H_2O) freezes into a solid state (ice), it appears changed; however, this change is only physical as the composition of the constituent molecules is the same: 11.19% hydrogen and 88.81% oxygen by mass.



The burning of hydrogen gas in oxygen gas to form liquid water is a chemical property. After burning, the original chemical substance, the hydrogen gas, will have vanished, and all that will be left is a different chemical substance—water. We cannot recover the hydrogen from the water by means of a physical change, such as boiling or freezing.

Measurable properties of matter fall into two categories: extensive and Intensive properties.

An **extensive property** of a mater depends upon how much matter is being considered.

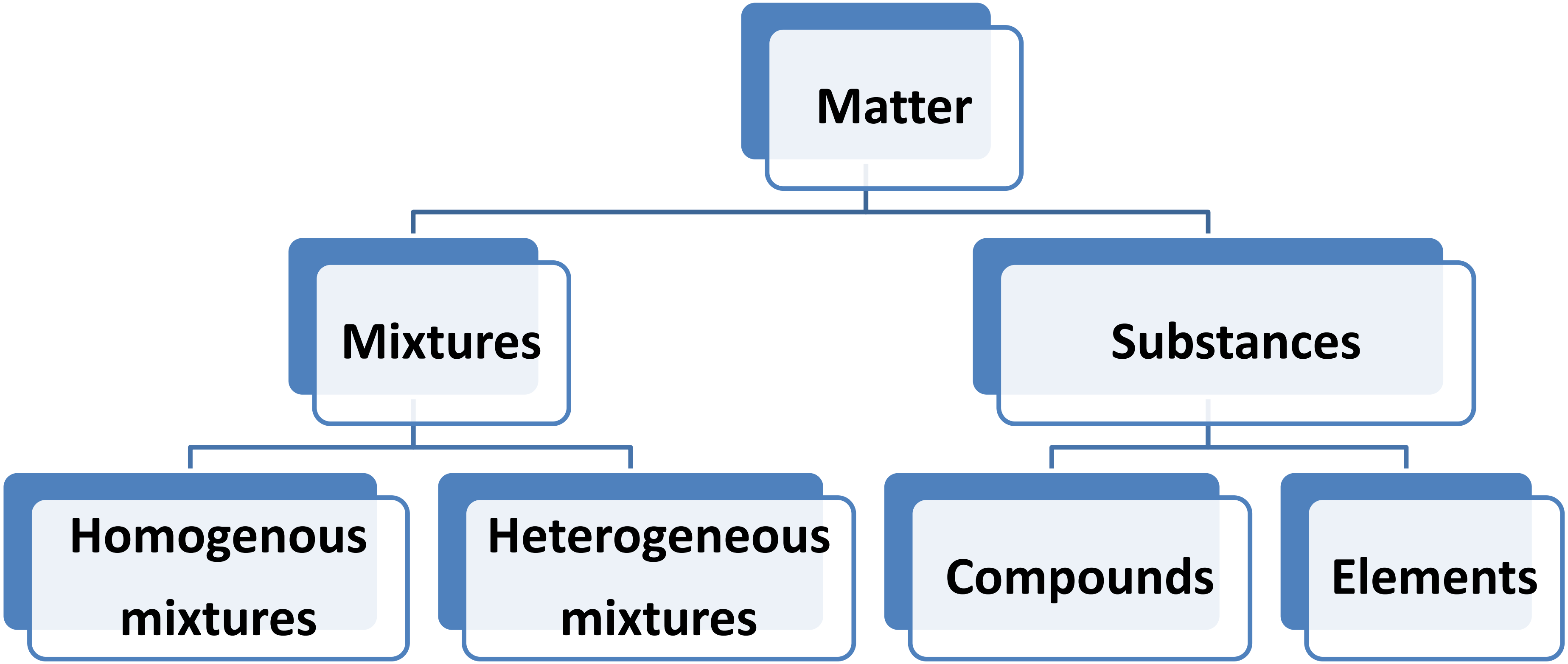
- **Mass**
- **Length**
- **Volume**

An **intensive property** of a mater does not depend upon how much matter is being considered.

- **Density**
- **Temperature**
- **Color**

Classification of Matter

Matter is classified into two: **Mixtures** (Homogenous and Heterogeneous) and **Substances** (Elements and Compounds).



Matter

Mixtures

Substances

Homogenous mixtures

Heterogeneous mixtures

Compounds

Elements

Mixture

A mixture is a **combination of two or more substances** in which the substances retain their distinct identities. It is formed by physically mixing substances and but not by chemical combination.

Some familiar examples are air, soft drinks, milk and cement.

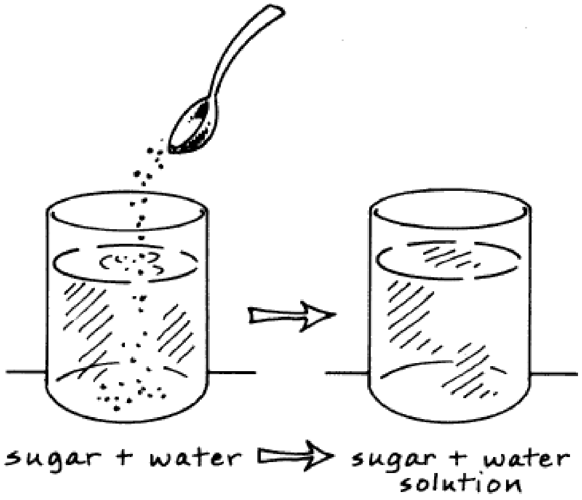
Mixtures do not have constant composition. Therefore, samples of air collected in different cities would probably differ in composition because of differences in altitude, pollution, and so on.

Mixtures

Homogenous

the composition is the same throughout

Sugar dissolved in water



Heterogeneous

the composition is not uniform.

Sand mixed with iron filings

Any mixture, whether homogeneous or heterogeneous, can be created and then separated by physical means into pure components without changing the identities of the components.

Separation of homogenous mixtures

Magnet

Separation of heterogeneous mixtures

Substance

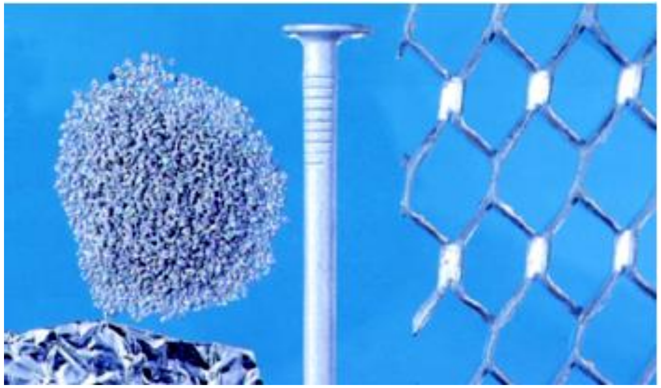
A substance is a form of matter that has a definite (constant) composition and distinct properties. Substances are divided into elements and compounds.

An element is a substance that cannot be separated into simpler substances by chemical means.

A compound is a substance composed of atoms of two or more elements chemically united in fixed proportions. Unlike mixtures, compounds can be separated only by chemical means into their pure components.

Elements

An element is a substance that cannot be separated into simpler substances by chemical means. To date, 118 elements have been positively identified. Eighty-three of them occur naturally on Earth. The others have been created by scientists via nuclear processes.



Aluminum

Sulfur

For convenience, chemists use symbols of one, two, or three letters to represent the elements. The first letter of a symbol is always capitalized, but any following letters are not.

For example, Co is the symbol for the element cobalt, whereas CO is the formula for the carbon monoxide molecule. The symbols of some elements are derived from their Latin names—for example, Au from *aurum (gold), Fe from ferrum* (iron), and Na from *natrium (sodium)—while most of them come from their English* names.

Some Common Elements and Their Symbols

Aluminum	Al	Fluorine	F	Oxygen	O
Arsenic	As	Gold	Au	Phosphorus	P
Barium	Ba	Hydrogen	H	Platinum	Pt
Bismuth	Bi	Iodine	I	Potassium	K
Bromine	Br	Iron	Fe	Silicon	Si
Calcium	Ca	Lead	Pb	Silver	Ag
Carbon	C	Magnesium	Mg	Sodium	Na
Chlorine	Cl	Manganese	Mn	Sulfur	S
Chromium	Cr	Mercury	Hg	Tin	Sn
Cobalt	Co	Nickel	Ni	Tungsten	W
Copper	Cu	Nitrogen	N	Zinc	Zn

Problem 1

1. Give an example of a homogeneous mixture and an example of a heterogeneous mixture.
2. Using examples, explain the difference between a physical property and a chemical property?
3. How does an intensive property differ from an extensive property? Which of the following properties are intensive and which are extensive? (a) length, (b) volume, (c) temperature, (d) mass.
4. Give an example of an element and a compound. How do elements and compounds differ?
5. Classify each of the following substances as an element or a compound: (a) hydrogen, (b) water, (c) gold, (d) sugar.
6. Classify each of the following as an element, a compound, a homogeneous mixture, or a heterogeneous mixture: (a) seawater, (b) helium gas, (c) sodium chloride (table salt), (d) a bottle of soft drink, (e) a milkshake, (f) air, (g) concrete.

Atoms

The basic building block of all matter is called an atom. Atoms are a collection of various subatomic particles containing negatively charged electrons, positively charged protons and neutral particles called neutrons.

Each element has its own unique number of protons, neutrons and electrons. Both protons and neutrons have mass, whereas the mass of electrons is negligible.

The three fundamental subatomic particles of an atom are electrons, protons and neutrons.

Particle	Actual mass (kg)	Relative mass (amu)	Charge (Coulomb)	charge
Proton, p	1.6726×10^{-27}	1.007	1.6022×10^{-19}	+1
Neutron, n	1.6749×10^{-27}	1.008	0	0
Electron, e^-	9.1094×10^{-31}	5.489×10^{-4}	-1.6022×10^{-19}	-1

mass p ≈ mass n ≈ 1840 × mass e^-

Protons and neutrons exist at the centre of the atom in the nucleus.

Atomic Number, Mass Number, and Isotopes

Elements differ from one another according to the number of protons in their atoms, a value called the element’s atomic number (Z). All atoms of the same element contain the same number of protons.

In a neutral atom the number of protons is equal to the number of electrons, so the atomic number also indicates the number of electrons present in the atom. The chemical identity of an atom can be determined solely from its atomic number.

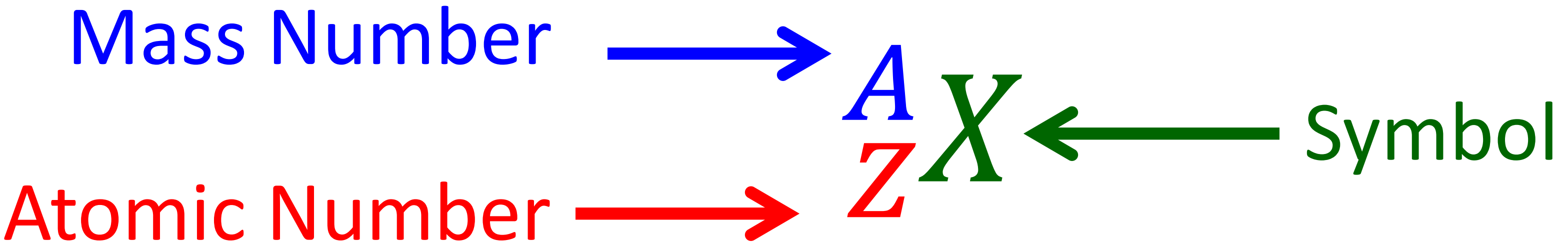
The mass number (A) is the total number of neutrons and protons present in the nucleus of an atom of an element.

Atomic number (Z) = number of protons in nucleus

Mass number (A) = # of protons + # of neutrons

= Z + # of neutrons

The accepted way to denote the atomic number and mass number of an atom of an element (X) is as follows:



Mass Number

$$^{A}_{Z}X$$

Symbol

Atomic Number

Atoms of a given element do not all have the same mass. Most elements have two or more isotopes, atoms that have the same atomic number but different mass numbers. Atoms with identical atomic numbers but different mass numbers are called **isotopes.** This is because atoms of the same element can have different number of neutrons.

For example, there are three isotopes of hydrogen. One, simply known as hydrogen, has one proton and no neutrons. The *deuterium isotope contains one proton and one* neutron, and *tritium has one proton and two neutrons.*

$^{1}_{1}\mathrm{H}$ $^{2}_{1}\mathrm{H}$ (D) $^{3}_{1}\mathrm{H}$ (T)

The chemical properties of an element are determined primarily by the protons and electrons in its atoms; neutrons do not take part in chemical changes under normal conditions. Therefore, isotopes of the same element have similar chemistries, forming the same types of compounds and displaying similar reactivities.

How many protons, neutrons, and electrons are in $^{14}_{6}C$?

6 protons, 8 (14 - 6) neutrons, 6 electrons

How many protons, neutrons, and electrons are in $^{11}_{6}C$?

6 protons, 5 (11 - 6) neutrons, 6 electrons

Problem 2

1. What is the difference between an atom’s atomic number and its mass number?
2. What is the difference between an element’s atomic number and its atomic mass?
3. What is an isotope?
4. Carbon-14 and nitrogen-14 both have the same mass number, yet they are different elements. Explain.
5. How many protons, neutrons, and electrons are in each of the following atoms?

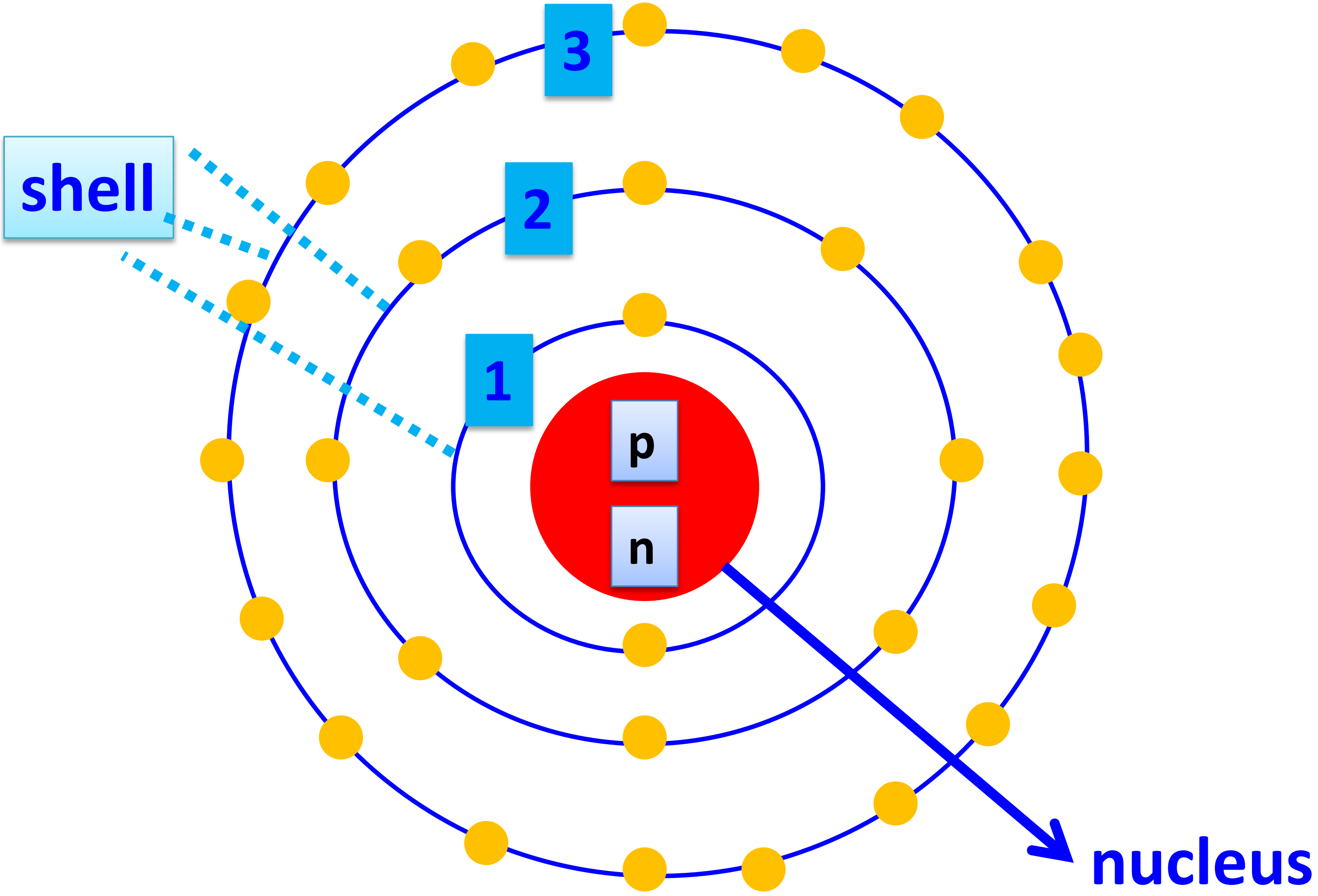
a) $^{15}_{7}N$ **b)** $^{60}_{27}Co$ **c)** $^{135}_{53}I$ **d)** $^{142}_{58}Ce$

It is important to understand the location of electrons, as it is the arrangement of the electrons that creates the bonds between the atoms. Electrons are involved in the chemical bonding and reactions of an atom.

Electrons move around the nucleus, and are arranged in shells at increasing distances from the nucleus. These shells represent different energy levels, the outermost shell being the highest energy level.

Electrons do not move freely in the space around the nucleus but are confined to regions of space called shells.

Model of an atom



p = protons **n** = neutrons ● = electrons

Each shell can contain up to a maximum of $2n^2$ electrons, where n is the number of the shell. For the first shell n = 1, for the second shell n = 2, for the third shell n = 3 and so on.

Low energy

High energy

Shell	Maximum number of electrons
1	2
2	8
3	18
4	32

Each shell contains subshells known as atomic orbitals.

Electrons are said to occupy orbitals in an atom. An orbital can hold two electrons.

The different orbitals are *s, p, d and f.*

Subshell	**# of orbitals of equal energy**	**Maximum # of electrons**
s	**1**	**2**
p	**3**	**8**
d	**5**	**18**
f	**7**	**32**

Each shell contains subshells known as atomic orbitals.

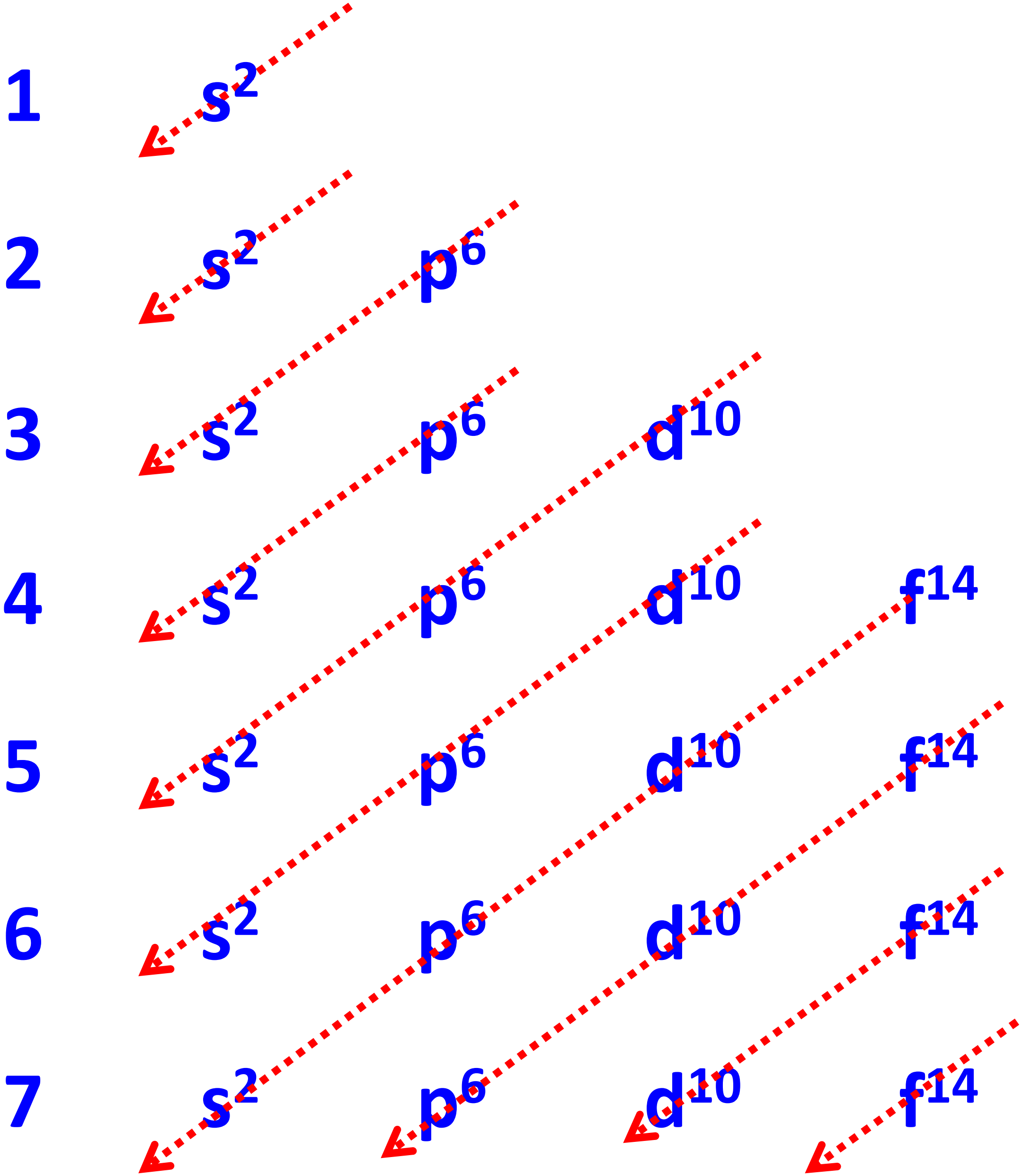
Shell	Subshells and Orbitals
1	1s
2	2s and 2P (p_x, p_y and p_z)
3	3s and 3P (p_x, p_y and p_z) and five 3 d

Electronic Configuration

The electronic configuration of an atom describes the number of electrons that an atom possesses, and the orbitals in which these electrons are placed

The arrangements of electrons in orbitals, subshells and shells are called electronic configurations.

Building up of electronic configurations



1 s^2

2 s^2 p^6

3 s^2 p^6 d^{10}

4 s^2 p^6 d^{10} f^{14}

5 s^2 p^6 d^{10} f^{14}

6 s^2 p^6 d^{10} f^{14}

7 s^2 p^6 d^{10} f^{14}

Rules of Filling Electron Orbitals

Aufbau Principle:

Electrons are added one at a time to the lowest energy orbitals available until all the electrons of the atom have been accounted for.

Pauli Exclusion Principle:

An orbital can hold a maximum of two electrons. To occupy the same orbital, two electrons must spin in opposite directions.

Hund's Rule:

Electrons occupy equal-energy orbitals so that a maximum number of unpaired electrons results.

Element	Electron Configuration	Orbital Filling					
		1s	2s	$2p_x$	$2p_y$	$2p_z$	3s
$_{1}$H	$1s^1$	↑					
$_{2}$He	$1s^2$	↑↓					
$_{3}$Li	$1s^2 2s^1$	↑↓	↑				
$_{6}$C	$1s^2 2s^2 2p^2$	↑↓	↑↓	↑	↑		
$_{7}$N	$1s^2 2s^2 2p^3$	↑↓	↑↓	↑	↑	↑	
$_{8}$O	$1s^2 2s^2 2p^4$	↑↓	↑↓	↑↓	↑	↑	
$_{9}$F	$1s^2 2s^2 2p^5$	↑↓	↑↓	↑↓	↑↓	↑	
$_{10}$Ne	$1s^2 2s^2 2p^6$	↑↓	↑↓	↑↓	↑↓	↑↓	
$_{11}$Na	$1s^2 2s^2 2p^6 3s^1$	↑↓	↑↓	↑↓	↑↓	↑↓	↑

Valence Electrons

- Valence electrons are electrons in all the subshells with the highest principal energy shell (outermost shell)
- Core electrons are in lower energy shells
- Valence electrons are responsible for both chemical and physical properties of atoms.
- Valence electrons are responsible for chemical reactions

Rb = 37 electrons = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$

- The highest principal energy shell of Rb that contains electrons is the 5th, therefore Rb has *1 valence electron* and *36 core electrons*

Kr = 36 electrons = $1s^2 2s^2 2p^6 3s^2 3p^6 \underline{4s^2} 3d^{10} \underline{4p^6}$

- The highest principal energy shell of Kr that contains electrons is the 4th, therefore Kr has *8 valence electrons* and *28 core electrons*

How many valence electrons does each atom have?

Carbon: $1s^2\underline{2s^22p^2}$

Four valence electrons

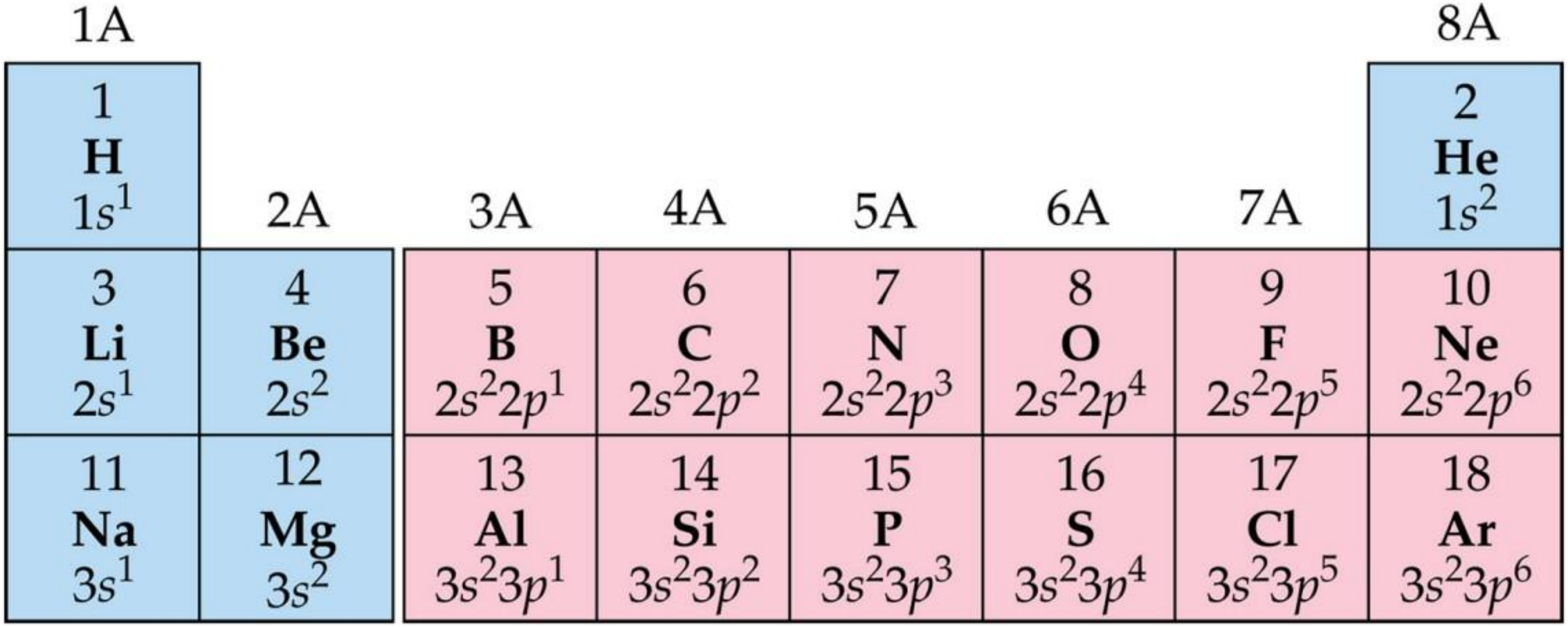
Chlorine: $1s^22s^22p^6\underline{3s^23p^5}$

Seven valence electrons

Electron Configurations from the Periodic Table

- Elements in the same period (row) have valence electrons in the same principal energy shell.
- The number of valence electrons increases by one as you progress across the period.
- Elements in the same group (column) have the same number of valence electrons and they are in the same kind of subshell.

Electron Configurations and the Periodic Table



1A	2A	3A	4A	5A	6A	7A	8A
1 **H** $1s^1$							2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$	5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$	13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$

Electron Configuration & the Periodic Table

- Elements in the same column have similar chemical and physical properties because their valence shell electron configuration is the same

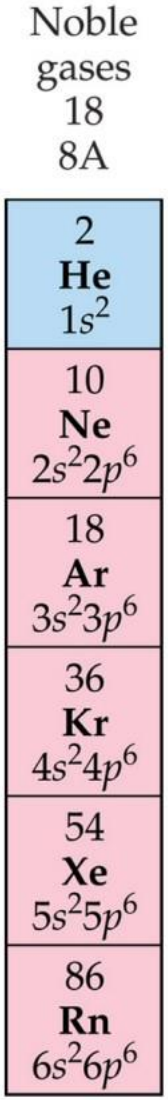
- The number of valence electrons for the main group elements is the same as the group number

- The properties of the elements are largely determined by the number of valence electrons they contain

- Since elements in the same column have the same number of valence electrons, they show similar properties

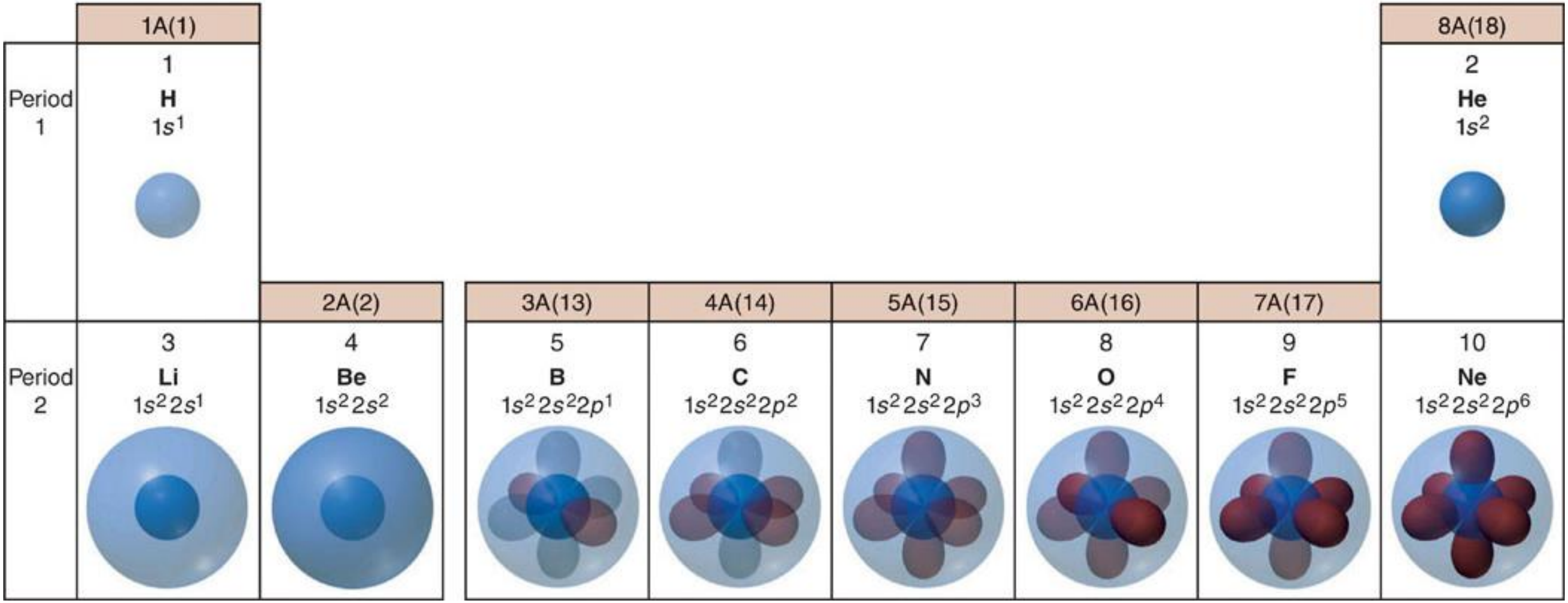
The Noble Gas: Electron Configuration

- The noble gases have 8 valence electrons
  - except for He, which has only 2 electrons
- Noble gases are especially unreactive
  - He and Ne are practically inert
- Reason noble gases are unreactive is that the electron configuration of the noble gases is especially stable, because they have octet of electrons in the outer shell.

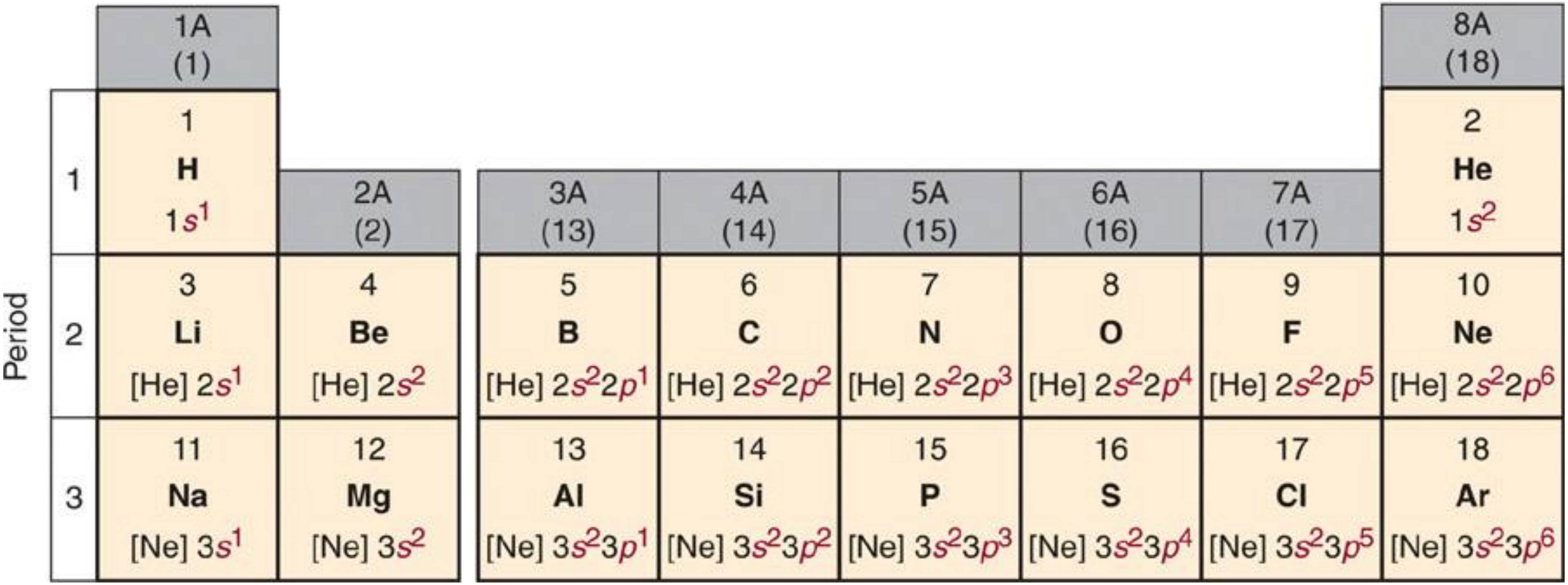


Noble gases 18 8A
2 **He** $1s^2$
10 **Ne** $2s^22p^6$
18 **Ar** $3s^23p^6$
36 **Kr** $4s^24p^6$
54 **Xe** $5s^25p^6$
86 **Rn** $6s^26p^6$

Orbital occupancy for the first 10 elements, H through Ne.



Condensed ground-state electron configurations in the first three periods.



Period	1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
1	1 **H** $1s^1$							2 **He** $1s^2$
2	3 **Li** [He] $2s^1$	4 **Be** [He] $2s^2$	5 **B** [He] $2s^2 2p^1$	6 **C** [He] $2s^2 2p^2$	7 **N** [He] $2s^2 2p^3$	8 **O** [He] $2s^2 2p^4$	9 **F** [He] $2s^2 2p^5$	10 **Ne** [He] $2s^2 2p^6$
3	11 **Na** [Ne] $3s^1$	12 **Mg** [Ne] $3s^2$	13 **Al** [Ne] $3s^2 3p^1$	14 **Si** [Ne] $3s^2 3p^2$	15 **P** [Ne] $3s^2 3p^3$	16 **S** [Ne] $3s^2 3p^4$	17 **Cl** [Ne] $3s^2 3p^5$	18 **Ar** [Ne] $3s^2 3p^6$

Write the electronic configuration of the following elements by abbreviating their configuration with the nearest noble gas and draw an orbital filling diagram, indicating the electrons as up or down arrows

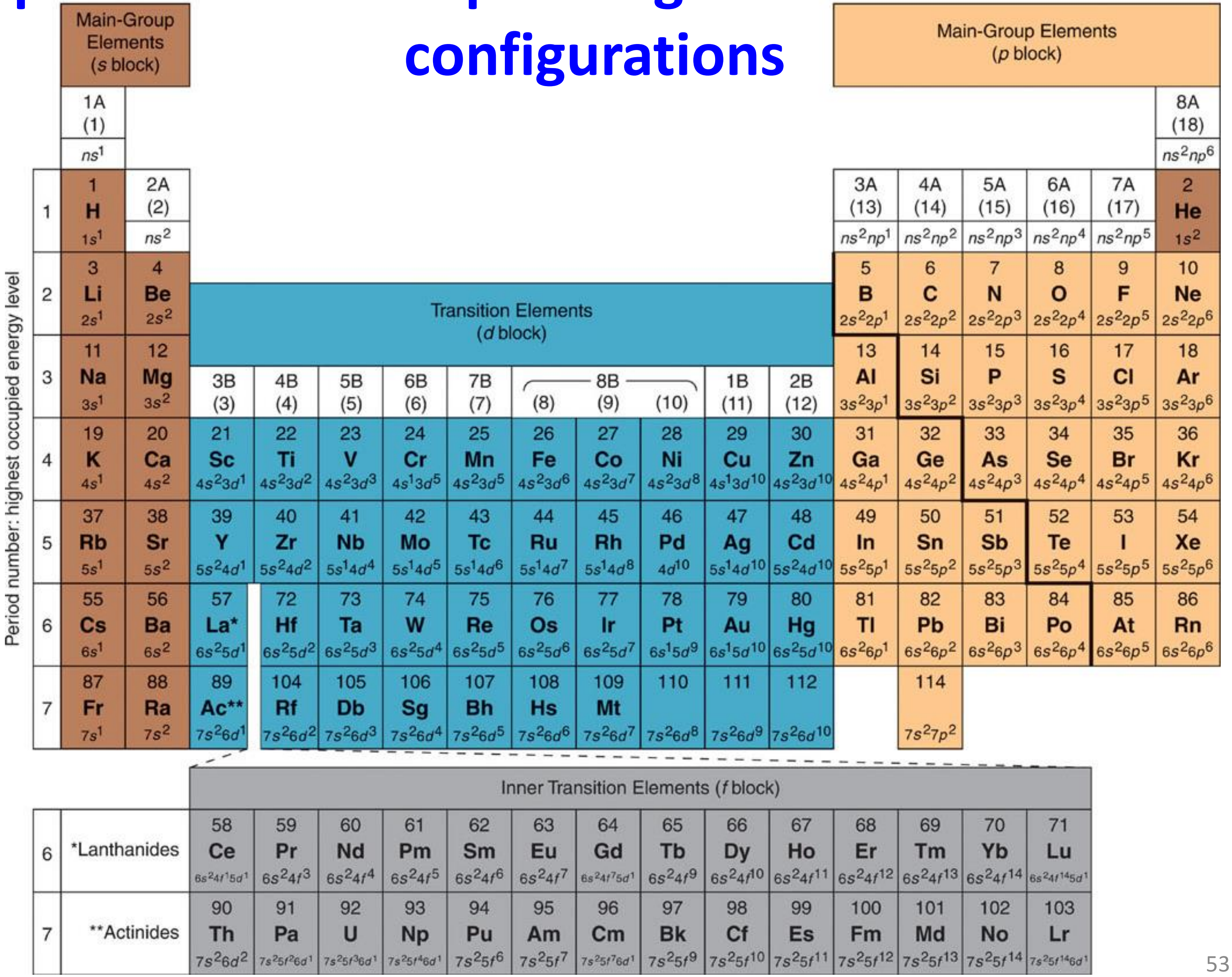
Z = 24

Z = 33

Z = 29

Z = 47

A periodic table of partial ground-state electron configurations



Main-Group Elements (s block)

Transition Elements (d block)

Main-Group Elements (p block)

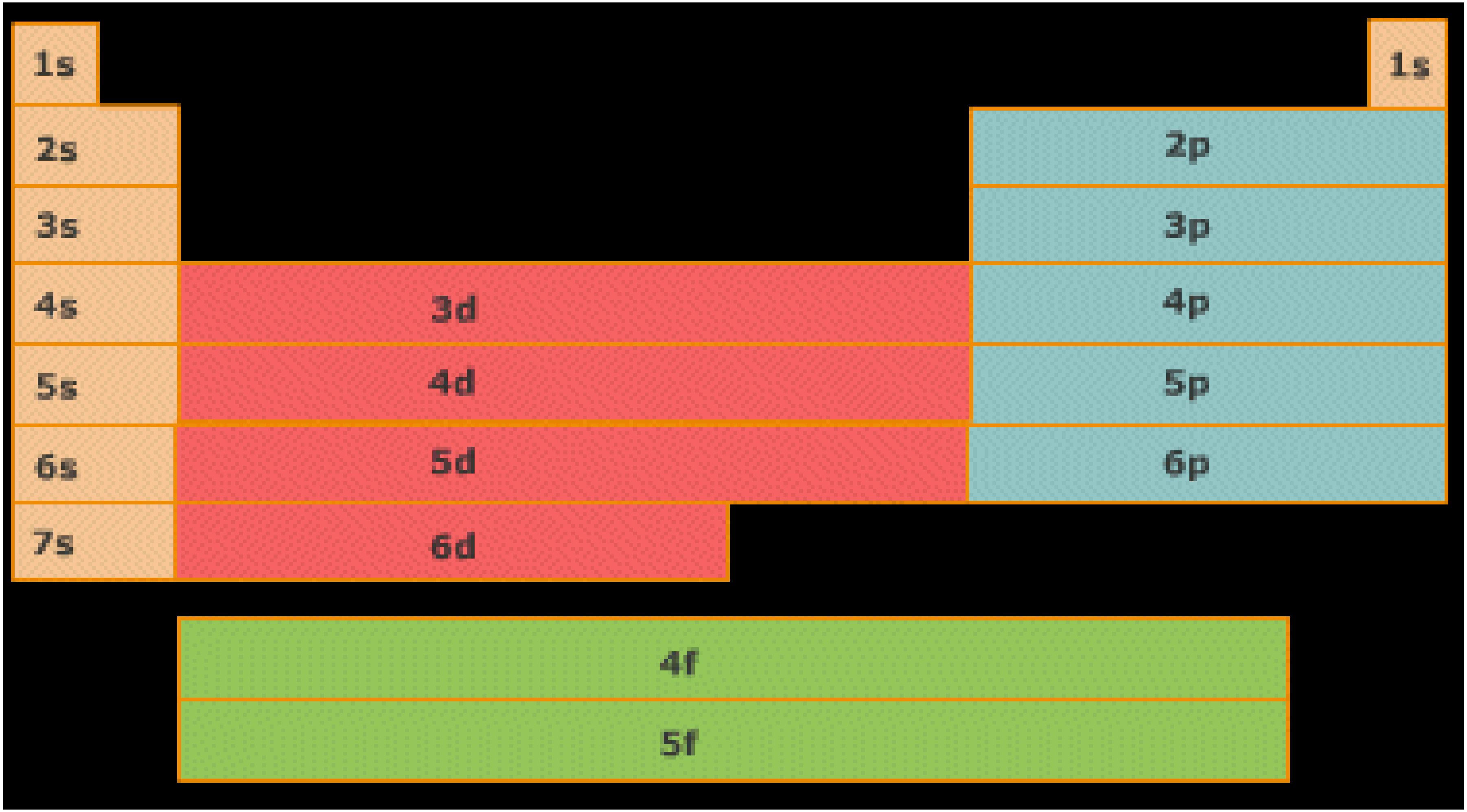
Period number: highest occupied energy level

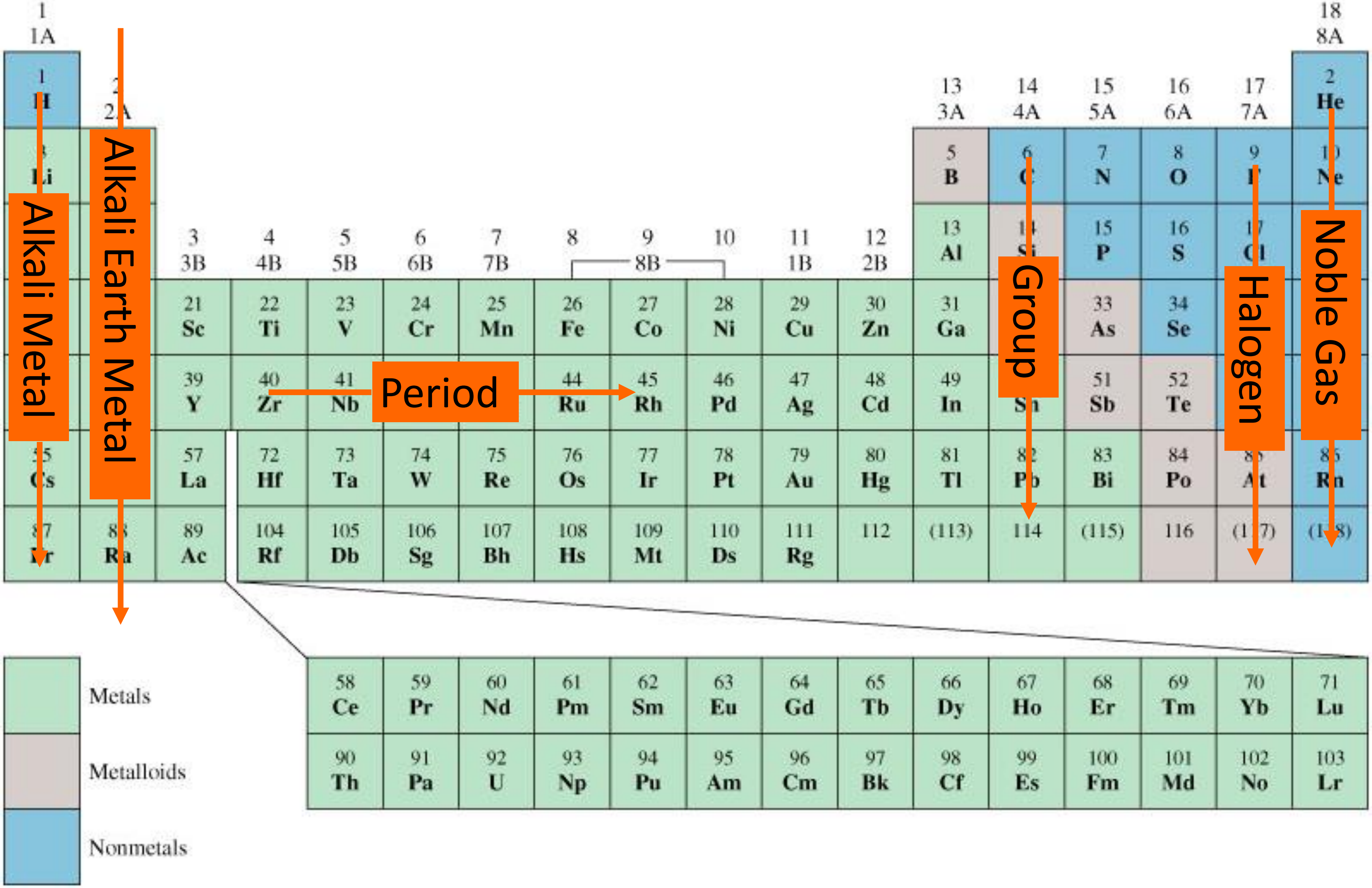
Period	1A (1)	2A (2)	3B (3)	4B (4)	5B (5)	6B (6)	7B (7)	8B (8)	8B (9)	8B (10)	1B (11)	2B (12)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
	ns^1	ns^2											ns^2np^1	ns^2np^2	ns^2np^3	ns^2np^4	ns^2np^5	ns^2np^6
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^23d^1$	22 **Ti** $4s^23d^2$	23 **V** $4s^23d^3$	24 **Cr** $4s^13d^5$	25 **Mn** $4s^23d^5$	26 **Fe** $4s^23d^6$	27 **Co** $4s^23d^7$	28 **Ni** $4s^23d^8$	29 **Cu** $4s^13d^{10}$	30 **Zn** $4s^23d^{10}$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^24d^1$	40 **Zr** $5s^24d^2$	41 **Nb** $5s^14d^4$	42 **Mo** $5s^14d^5$	43 **Tc** $5s^14d^6$	44 **Ru** $5s^14d^7$	45 **Rh** $5s^14d^8$	46 **Pd** $4d^{10}$	47 **Ag** $5s^14d^{10}$	48 **Cd** $5s^24d^{10}$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La*** $6s^25d^1$	72 **Hf** $6s^25d^2$	73 **Ta** $6s^25d^3$	74 **W** $6s^25d^4$	75 **Re** $6s^25d^5$	76 **Os** $6s^25d^6$	77 **Ir** $6s^25d^7$	78 **Pt** $6s^15d^9$	79 **Au** $6s^15d^{10}$	80 **Hg** $6s^25d^{10}$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac**** $7s^26d^1$	104 **Rf** $7s^26d^2$	105 **Db** $7s^26d^3$	106 **Sg** $7s^26d^4$	107 **Bh** $7s^26d^5$	108 **Hs** $7s^26d^6$	109 **Mt** $7s^26d^7$	110 $7s^26d^8$	111 $7s^26d^9$	112 $7s^26d^{10}$		114 $7s^27p^2$				

Inner Transition Elements (f block)

6	*Lanthanides	58 **Ce** $6s^24f^15d^1$	59 **Pr** $6s^24f^3$	60 **Nd** $6s^24f^4$	61 **Pm** $6s^24f^5$	62 **Sm** $6s^24f^6$	63 **Eu** $6s^24f^7$	64 **Gd** $6s^24f^75d^1$	65 **Tb** $6s^24f^9$	66 **Dy** $6s^24f^{10}$	67 **Ho** $6s^24f^{11}$	68 **Er** $6s^24f^{12}$	69 **Tm** $6s^24f^{13}$	70 **Yb** $6s^24f^{14}$	71 **Lu** $6s^24f^{14}5d^1$
7	**Actinides	90 **Th** $7s^26d^2$	91 **Pa** $7s^25f^26d^1$	92 **U** $7s^25f^36d^1$	93 **Np** $7s^25f^46d^1$	94 **Pu** $7s^25f^6$	95 **Am** $7s^25f^7$	96 **Cm** $7s^25f^76d^1$	97 **Bk** $7s^25f^9$	98 **Cf** $7s^25f^{10}$	99 **Es** $7s^25f^{11}$	100 **Fm** $7s^25f^{12}$	101 **Md** $7s^25f^{13}$	102 **No** $7s^25f^{14}$	103 **Lr** $7s^25f^{14}6d^1$

The elements are grouped into s, p d an f blocks to reflect their electronic configuration.





Alkali Metal

Alkali Earth Metal

Period

Group

Halogen

Noble Gas

1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 8B	10	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H**																	2 **He**
3 **Li**												5 **B**	6 **C**	7 **N**	8 **O**	9 **F**	10 **Ne**
												13 **Al**	14 **Si**	15 **P**	16 **S**	17 **Cl**	
		21 **Sc**	22 **Ti**	23 **V**	24 **Cr**	25 **Mn**	26 **Fe**	27 **Co**	28 **Ni**	29 **Cu**	30 **Zn**	31 **Ga**		33 **As**	34 **Se**		
		39 **Y**	40 **Zr**	41 **Nb**			44 **Ru**	45 **Rh**	46 **Pd**	47 **Ag**	48 **Cd**	49 **In**	**Sn**	51 **Sb**	52 **Te**		
55 **Cs**		57 **La**	72 **Hf**	73 **Ta**	74 **W**	75 **Re**	76 **Os**	77 **Ir**	78 **Pt**	79 **Au**	80 **Hg**	81 **Tl**	82 **Pb**	83 **Bi**	84 **Po**	85 **At**	86 **Rn**
87 **Fr**	88 **Ra**	89 **Ac**	104 **Rf**	105 **Db**	106 **Sg**	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112	(113)	114	(115)	116	(117)	(118)

58 **Ce**	59 **Pr**	60 **Nd**	61 **Pm**	62 **Sm**	63 **Eu**	64 **Gd**	65 **Tb**	66 **Dy**	67 **Ho**	68 **Er**	69 **Tm**	70 **Yb**	71 **Lu**
90 **Th**	91 **Pa**	92 **U**	93 **Np**	94 **Pu**	95 **Am**	96 **Cm**	97 **Bk**	98 **Cf**	99 **Es**	100 **Fm**	101 **Md**	102 **No**	103 **Lr**

🟩 Metals

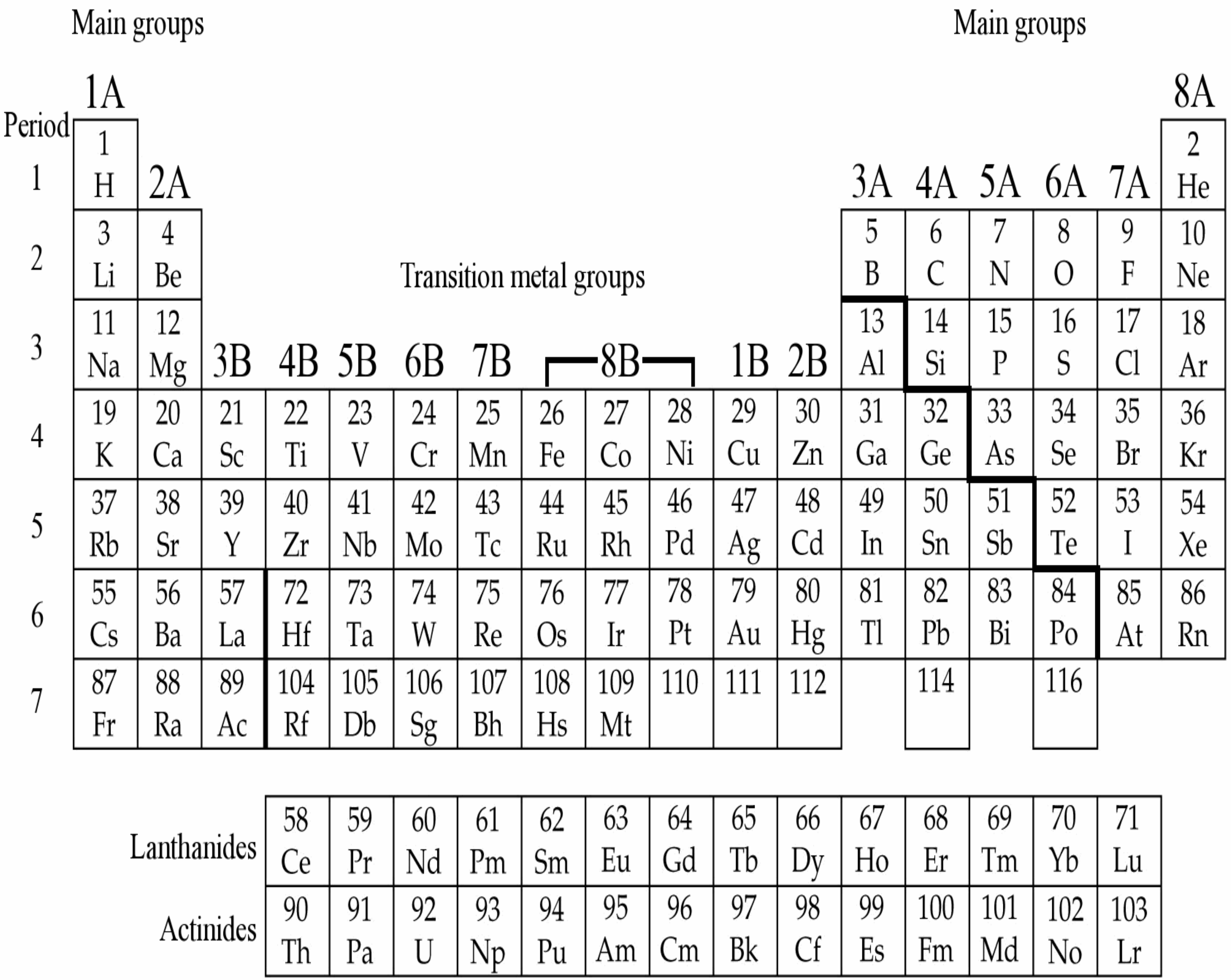
⬜ Metalloids

🟦 Nonmetals

Periodic Table

- Is a chart/ tabular display of the 118 known chemical elements, in which the elements having similar chemical and physical properties are grouped together
- Elements are arranged in atomic numbers (shown above the element) in *horizontal rows* called ***periods*** and in *vertical columns* known as ***groups/ families***
- Elements with similar physical and chemical properties at repeated regular intervals appear in same column

- ❑It has eight principle vertical columns (groups) and seven horizontal rows, (periods)
- ❑The periods are numbered from 1-7, while groups are numbered in two different ways;
- ❑The main groups are numbered the roman numerals 1A to 8A are used.
- ❑Groups 1B and 3B through 8B are transition elements
- ❑Group 2B elements are neither representative elements no transition elements

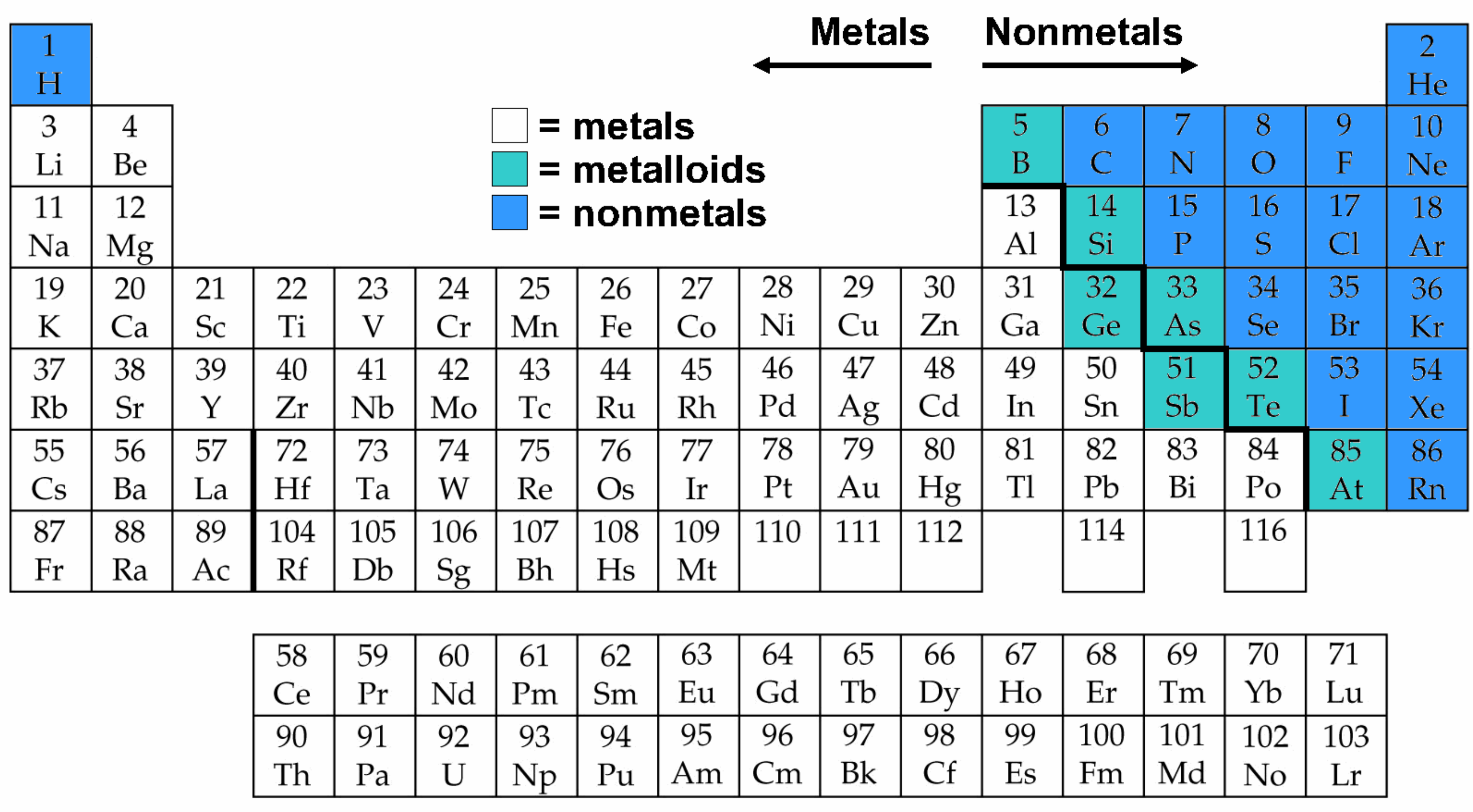


Period	Main groups		Transition metal groups										Main groups					
	1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	3A	4A	5A	6A	7A	8A
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		

Lanthanides	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
Actinides	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

- Elements can be divided into 3 categories: metals, non metals and metalloids
- A jagged line on the periodic table separates the nonmetals (right) from the metals (left, except H):
- Metals are shiny solids (except for Hg)
  - good conductors of electricity and heat.
  - malleable (can be hammered into thin sheets).
  - ductile (can be drawn into wire).
- Nonmetals are usually found in compounds,
  - no metallic luster; not malleable or ductile.
  - poor conductors of electricity and heat.

- Along the dividing line are the semimetals (or metalloids), which have properties intermediate between metals and nonmetals.

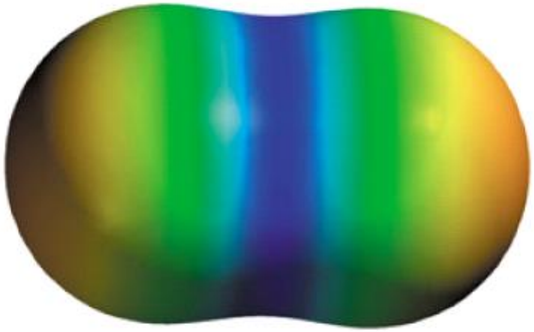


1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110	111	112		114		116		
			58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
			90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Polar Covalent Bonds

- **Atoms with equal or nearly equal electronegativities form covalent bonds in which both atoms exert equal attractions for the bonding electrons.**

$H-H$ $\qquad$ $N\equiv N$ $\qquad$ $Cl-Cl$



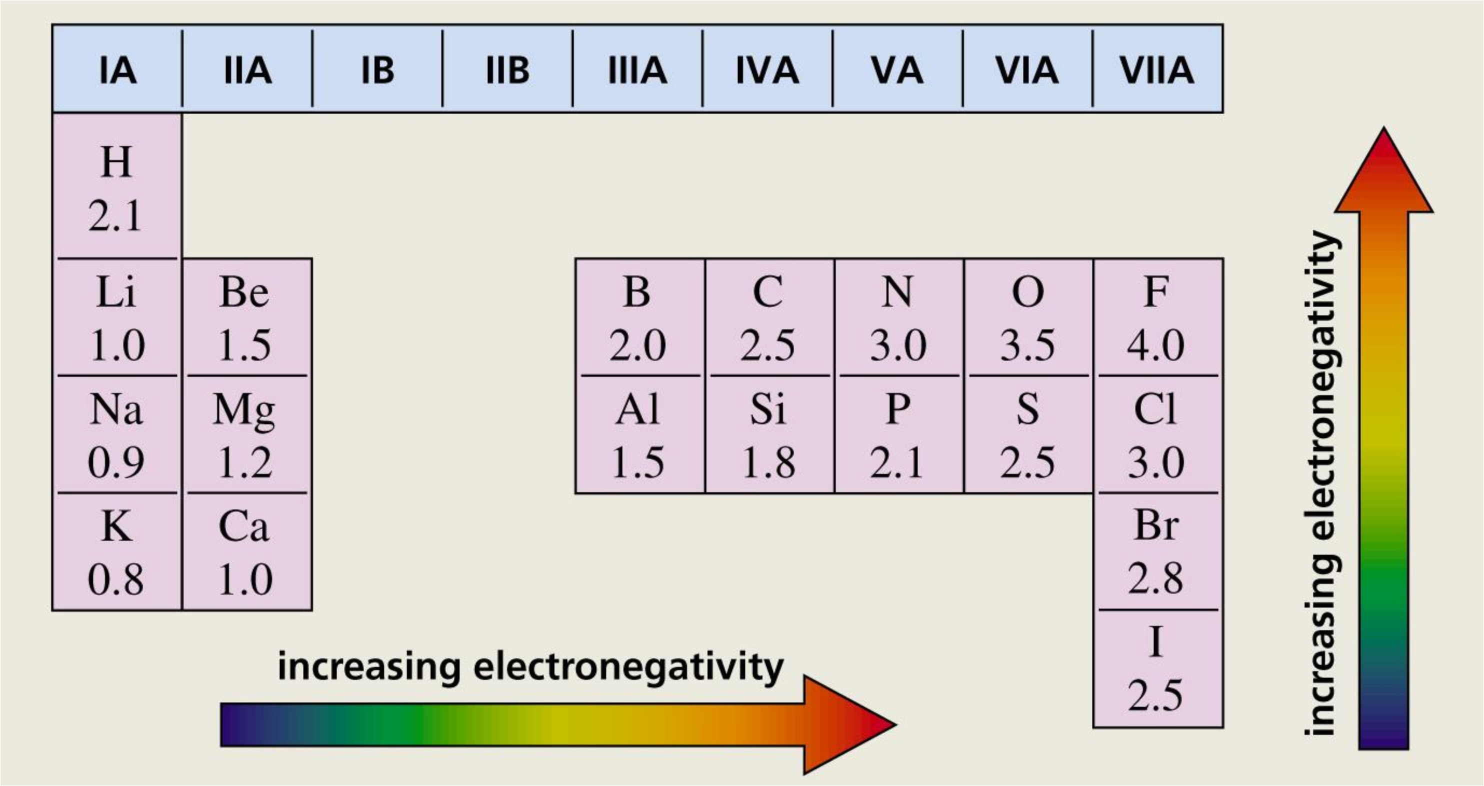
- **This type of covalent bond is nonpolar bond.**

But, if the two atoms that are combined via covalent bond are different, then there is unequal sharing of electrons.

This is due to differences in the electronegativities of the two atoms involved in bonding.

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons.

The Pauling scale is the most commonly used. Fluorine (the most electronegative element) is given a value of 4.0, and values range down to caesium and francium which are the least electronegative at 0.7.



IA	IIA	IB	IIB	IIIA	IVA	VA	VIA	VIIA
H 2.1								
Li 1.0	Be 1.5			B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9	Mg 1.2			Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
K 0.8	Ca 1.0							Br 2.8
								I 2.5

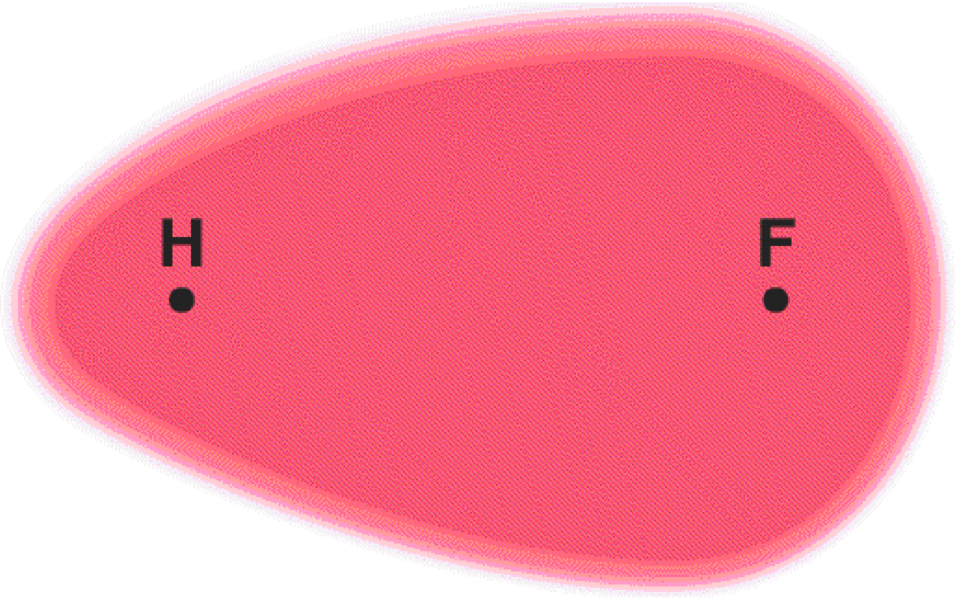
- **In covalent bonds with substantial difference in electronegativity, the electrons involved in bonding are not shared equally.**

- **The more electronegative atom has a greater attraction for the bonding electrons-not enough of an attraction for the atom to break of as an ion, but enough so that this atom takes the largest share of the electron density.**

2.1

4.0

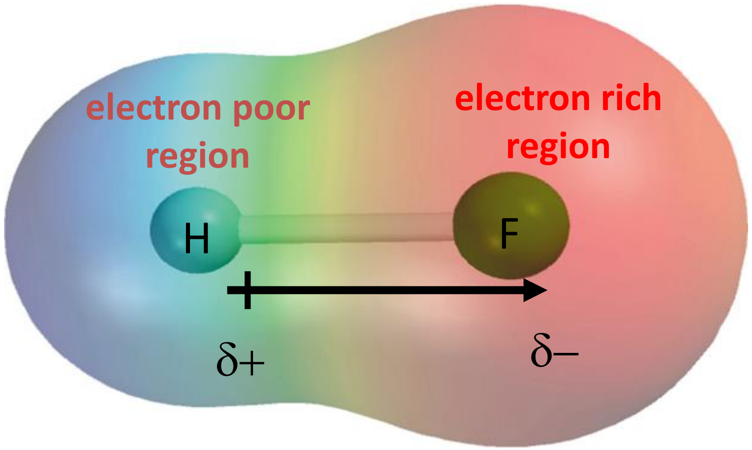
H–F



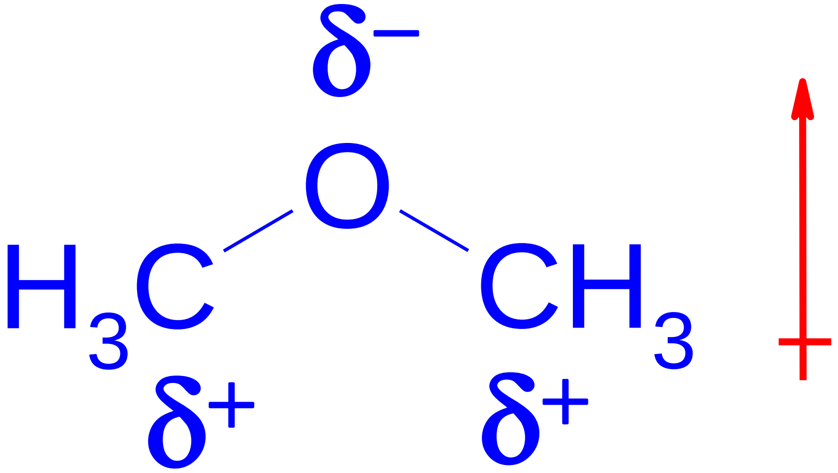
- **The result is a polar covalent bond, a bond with uneven distribution of electron density.**
- **The degree of polarity of a bond particularly depends on the difference in electronegativities of the two atoms bonded together and partly on other factors such as the size of the atoms.**

Such types of covalent bonds are Polar Covalent bonds.

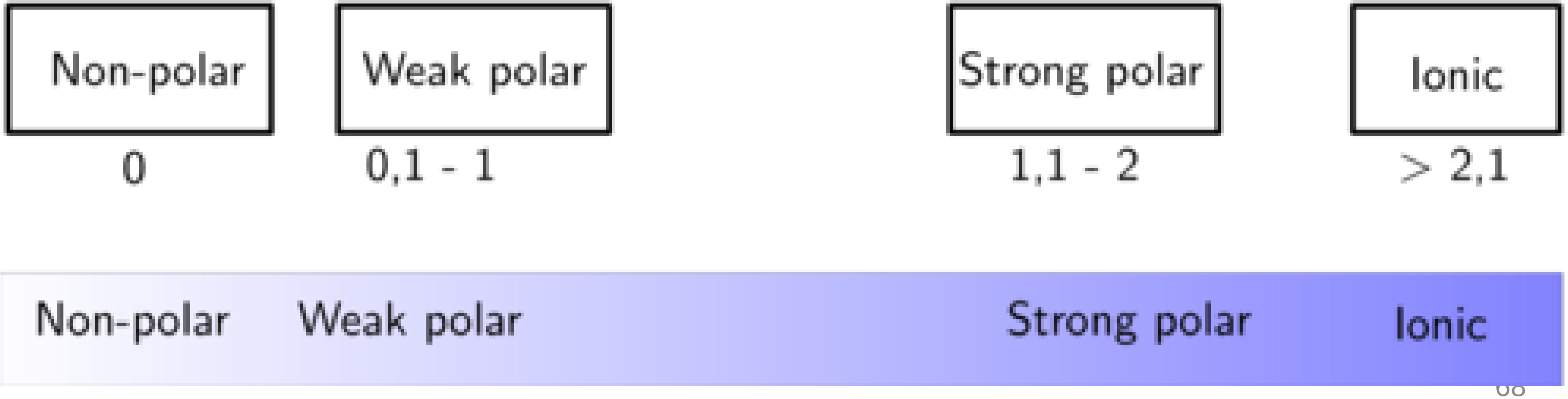
- **The distribution of electrons in a polar molecule are symbolized by partial (δ) charges.**



- **Another way of representing the different electron densities within a molecule is by a crossed arrow, that points from the partially positive end of a molecule to the partially negative end.**



Dipole Moment


Non-polar
0

Weak polar
0,1 - 1

Strong polar
1,1 - 2

Ionic
> 2,1

Non-polar Weak polar Strong polar Ionic

Problem

Use the (δ^+/δ^-) convention to show the direction of expected polarity for each of the bonds indicated.

(a) CH_3-Cl **(b) CH_3-NH_2** **(c) H_2N-H**

(d) H_3C-SH **(e) H_3C- MgBr** **(f) H_3C- F**

- A dipole moment is reported in a unit called a debye (D) (pronounced de-bye).
- The dipole moment is a measure of the polarity of a molecule. The more polar the bond the higher the dipole moment.

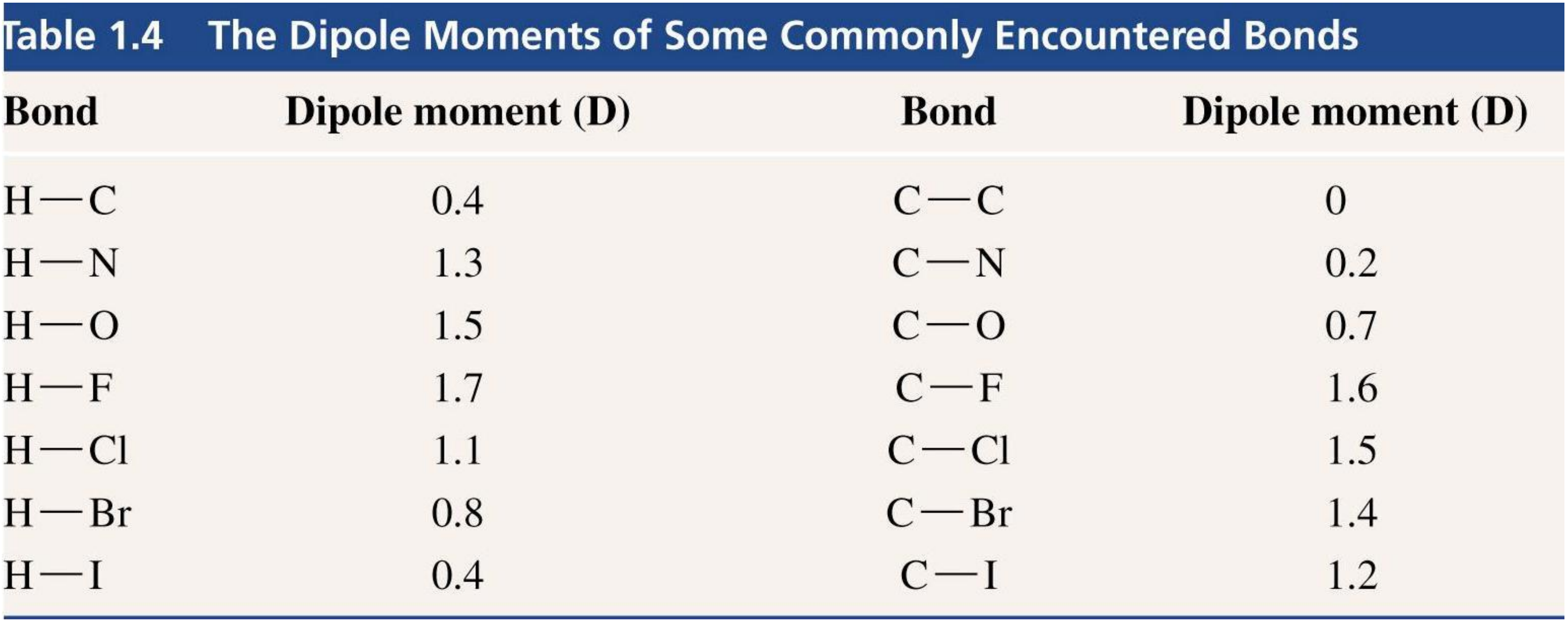


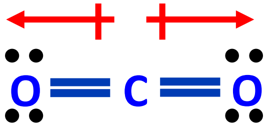
Table 1.4 The Dipole Moments of Some Commonly Encountered Bonds

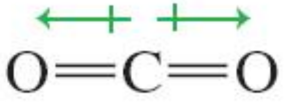
Bond	Dipole moment (D)	Bond	Dipole moment (D)
H—C	0.4	C—C	0
H—N	1.3	C—N	0.2
H—O	1.5	C—O	0.7
H—F	1.7	C—F	1.6
H—Cl	1.1	C—Cl	1.5
H—Br	0.8	C—Br	1.4
H—I	0.4	C—I	1.2

In a molecule with only one covalent bond, the dipole moment of the molecule is identical to the dipole moment of the bond. For example, the dipole moment of hydrogen chloride (HCl) is 1.1 D, because the dipole moment of the single bond is 1.1 D.

The dipole moment of a molecule with more than one covalent bond depends on the dipole moments of all the bonds in the molecule and the geometry of the molecule.

For example, let’s look at the dipole moment of carbon dioxide. The individual carbon–oxygen bond dipole moments cancel each other—because the bond angle in CO_2 is 180°—giving carbon dioxide a dipole moment of zero D.

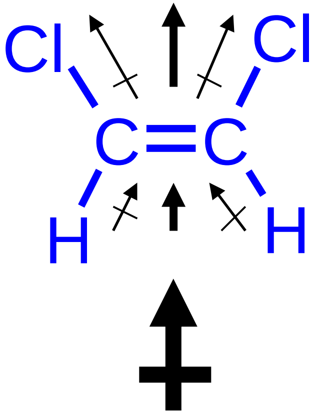




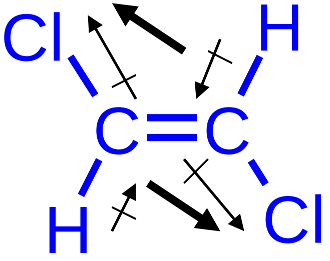
carbon dioxide
$\mu = 0$ D

Therefore, for molecules that have more than one covalent bond, the geometry of the molecule must be taken into account because both the *magnitude* and the *direction* of the individual bond dipole moments (the vector sum) determine the overall dipole moment of the molecule. Symmetrical molecules, therefore, have no dipole moment.

Bond vs. Molecular dipole moment

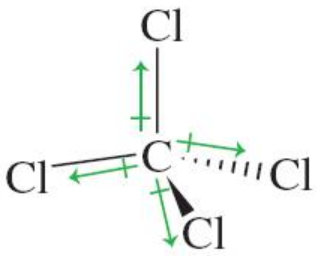


$\mu > 0$



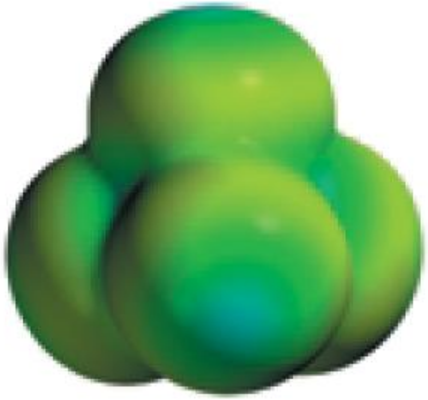
$\mu = 0$

Another symmetrical molecule is carbon tetrachloride. The four atoms bonded to the carbon atom are identical and project symmetrically out from the carbon atom. Thus, the symmetry of the molecule causes the bond dipole moments to cancel.

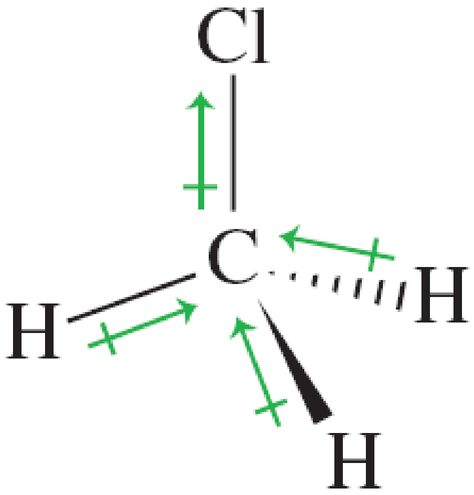


carbon tetrachloride

$\mu = 0$ D



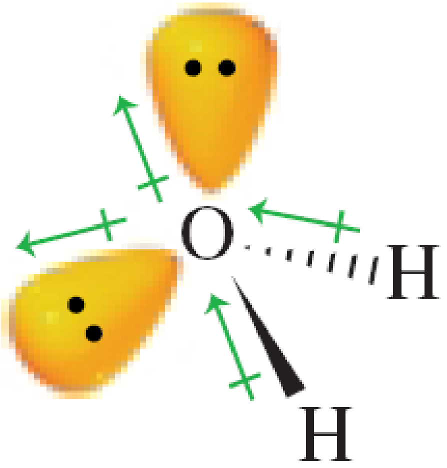
The dipole moment of chloromethane is greater (1.87 D) than the dipole moment of the bond (1.3 D) because the dipoles are oriented so that they reinforce the dipole of the bond—they are all in the same relative direction.



chloromethane

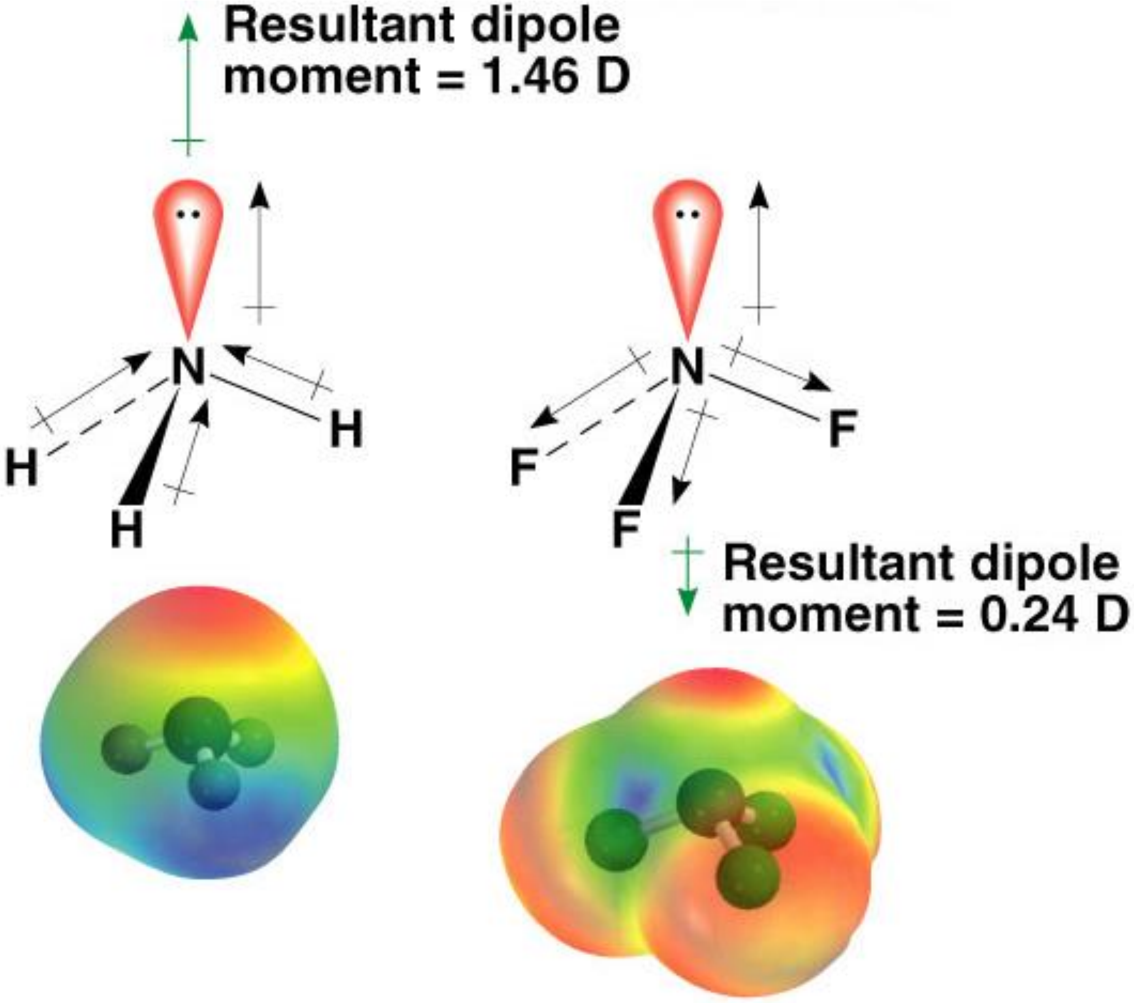
$\mu = 1.87$ D

The dipole moment of water (1.85 D) is greater than the dipole moment of a single bond (1.5 D) because the dipoles of the two bonds reinforce each other. The lone-pair electrons also contribute to the dipole moment.



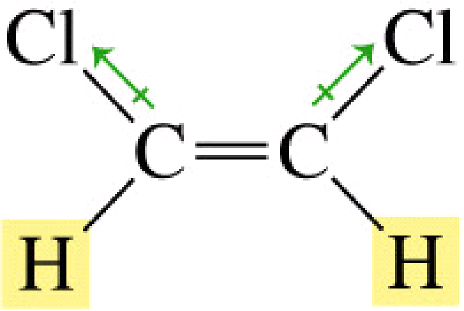
water

$\mu = 1.85$ D



Resultant dipole moment = 1.46 D

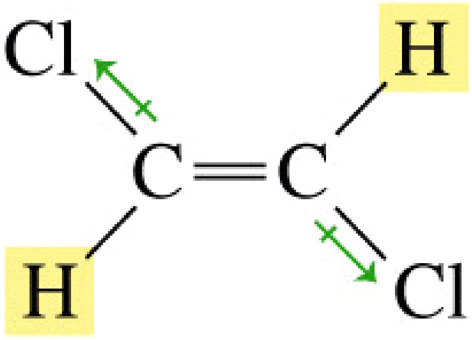
Resultant dipole moment = 0.24 D



cis-1,2-dichloroethene

bp = 60.3 °C

μ = 2.95 D



trans-1,2-dichloroethene

bp = 47.5 °C

μ = 0 D

Problem

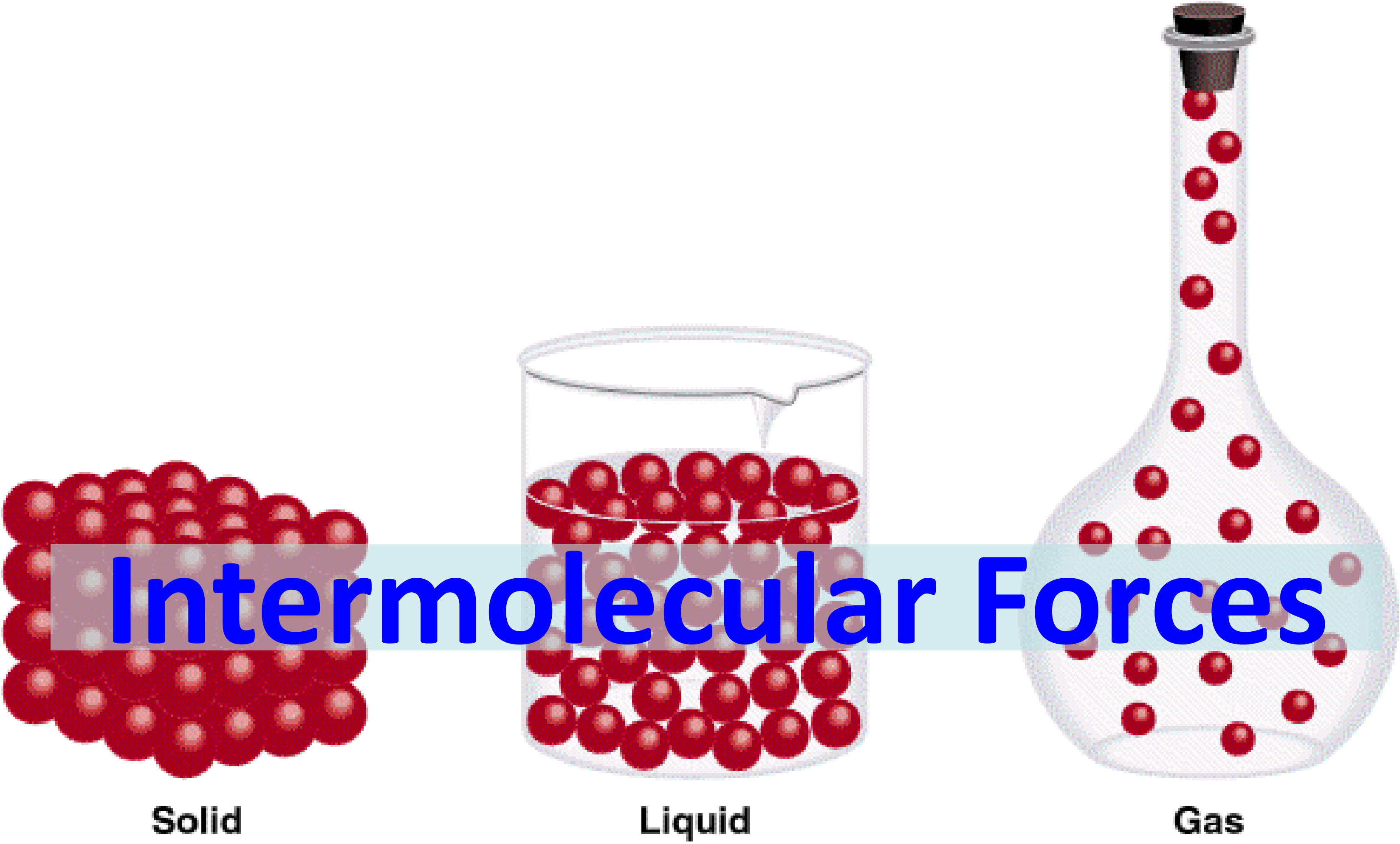
Give explanation for the following observations:

I. The dipole moment (μ) for ammonia (μ = 1.64) is substantially higher than that of ammonia trifluoride (μ = 0.24) although the latter contains the highly electronegative fluorine.

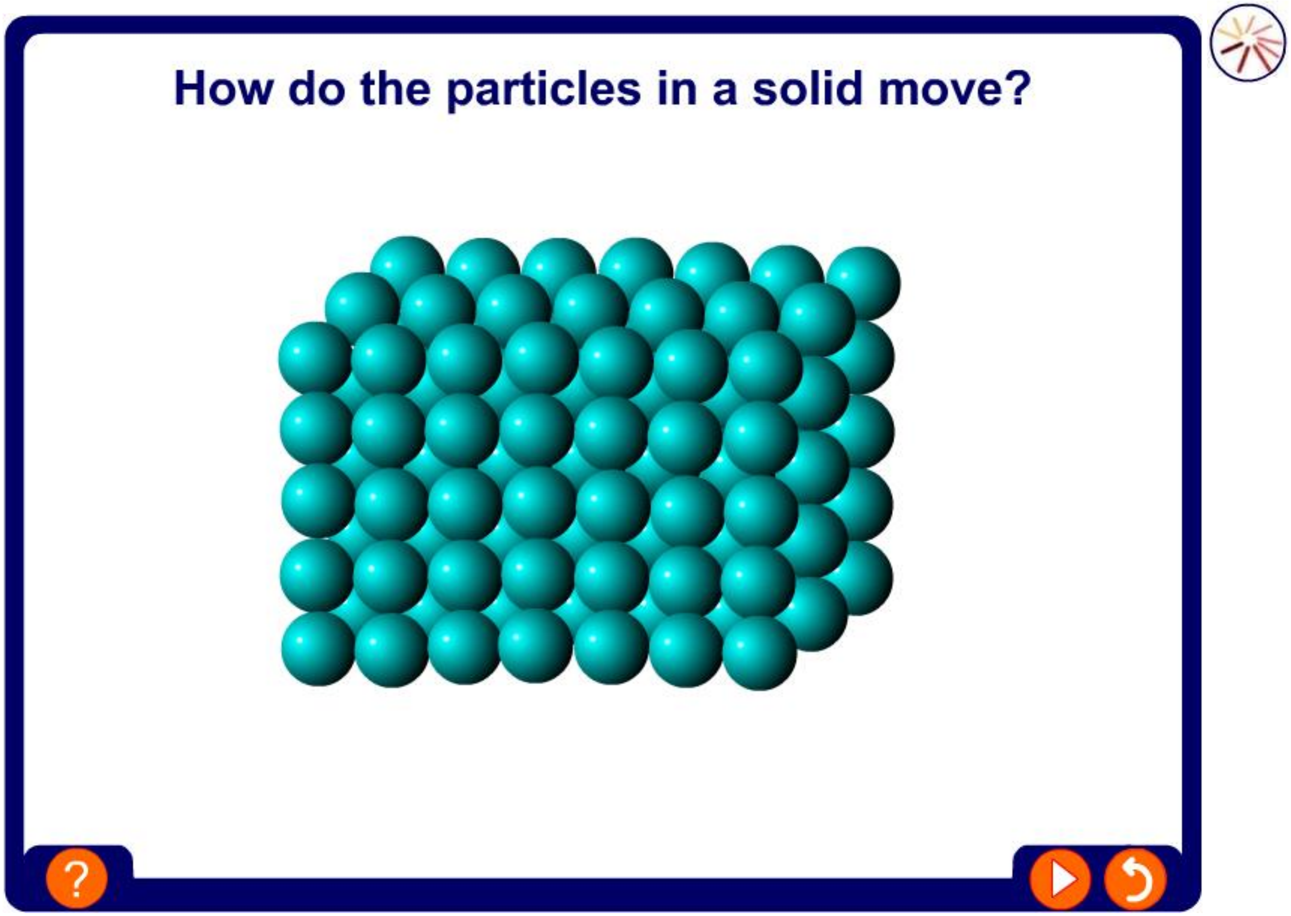
II. Phosgene, $Cl_2C{=}O$, has a smaller dipole moment than formaldehyde, $H_2C{=}O$. Even though, it contains electronegative chlorine atoms in place of hydrogen. Explain.

III. Fluoromethane (CH_3F, μ = 1.8 D) has a smaller dipole moment than chloromethane (CH_3Cl, μ = 1.87 D) even though fluorine is more electronegative than chlorine.

Intermolecular Forces

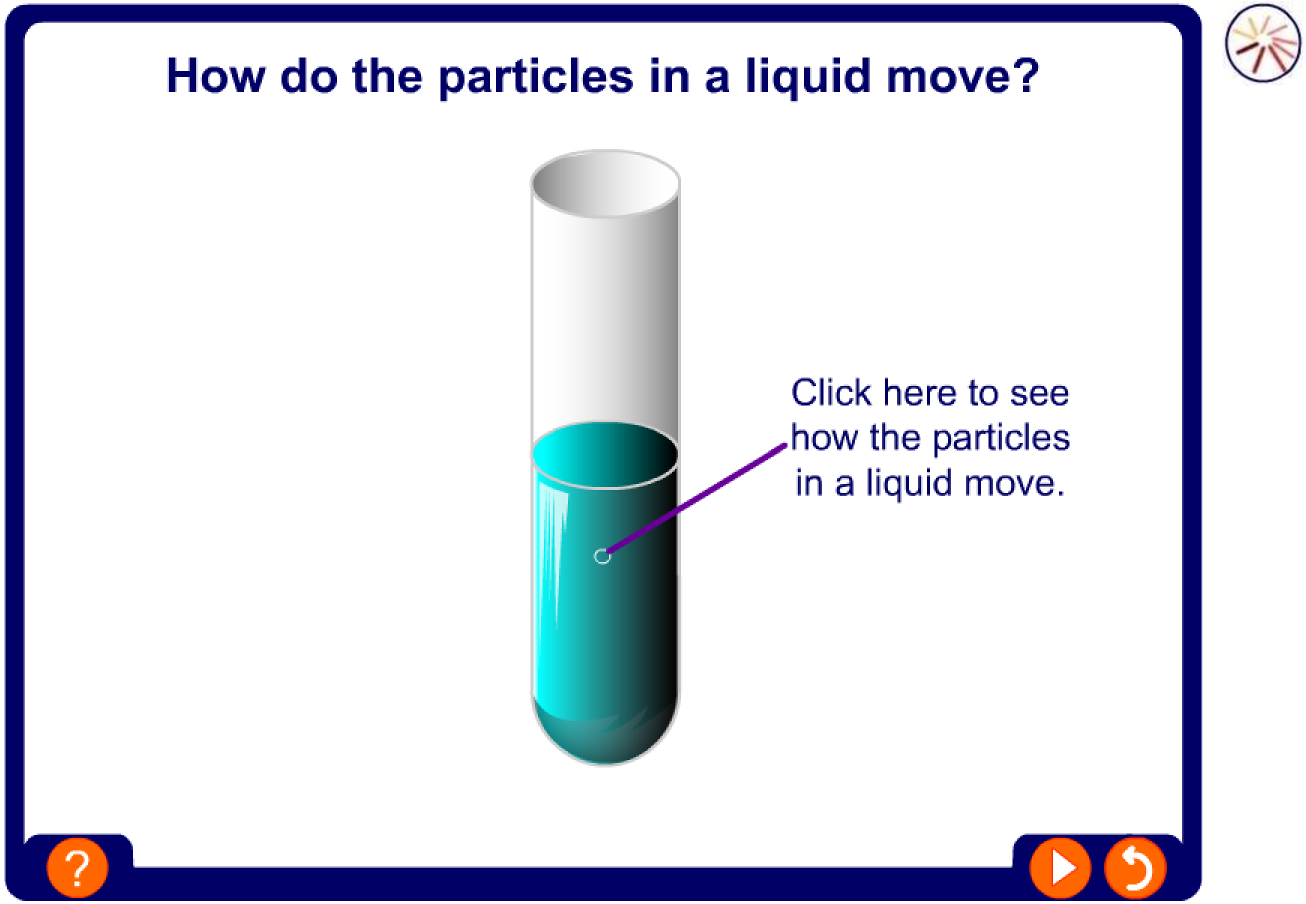


Particles in a solid – animation



How do the particles in a solid move?

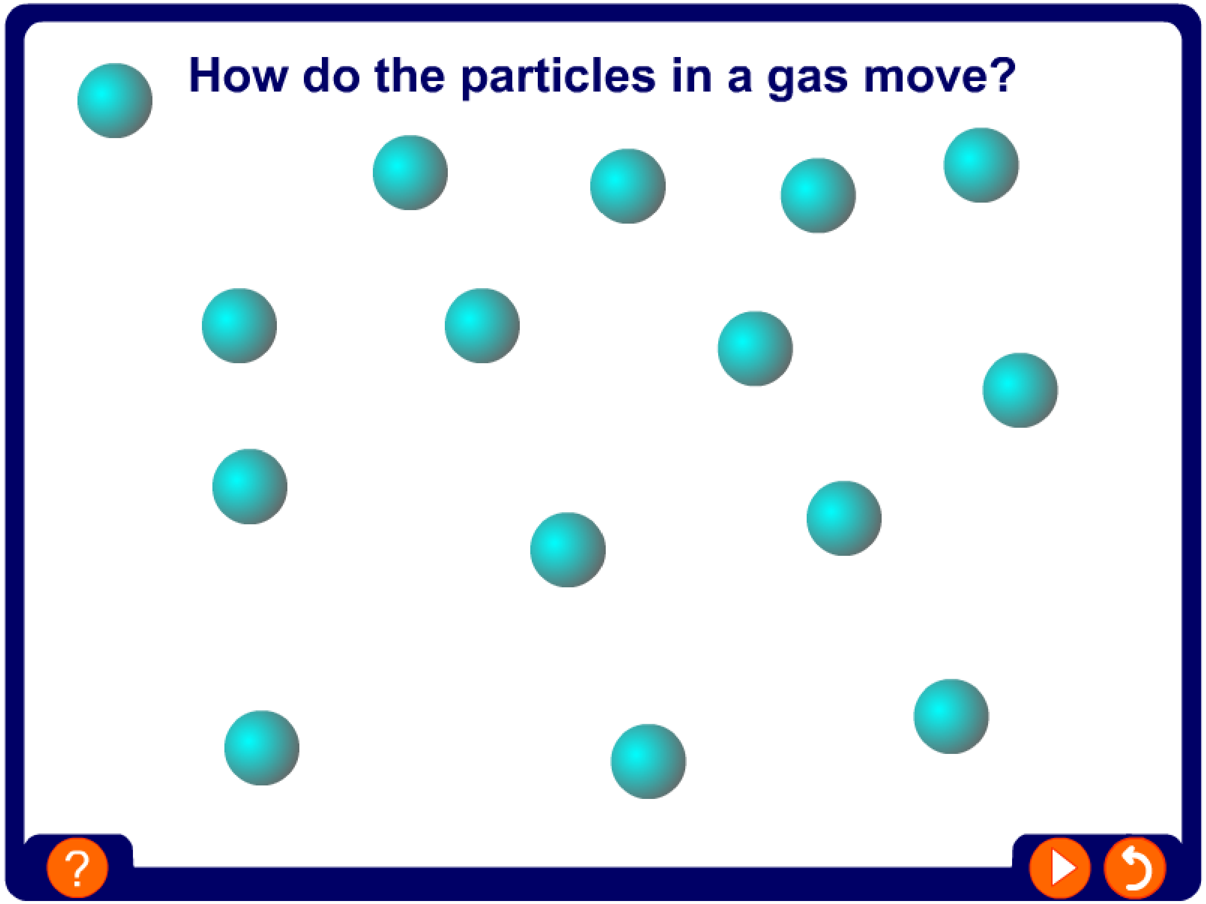
Particles in a liquid – animation



How do the particles in a liquid move?

Click here to see how the particles in a liquid move.

Particles in a gas – animation



How do the particles in a gas move?

- Covalent compounds may be gases, liquids or solids.

- Compounds that have low molecular weight and no dipole moments, such as methane (CH_4) and carbon dioxide (CO_2), are gases. The forces that act between such molecules are very weak.

- The forces that act between molecules are called intermolecular forces.

- **These interactions increases significantly as the molecular weight and the size of the molecule increases.**
- **They also increase with increasing polarity of the molecule.**
- **The greater the attractive forces between molecules, the higher is the boiling point of the compound.**

Three types of intermolecular forces are important:

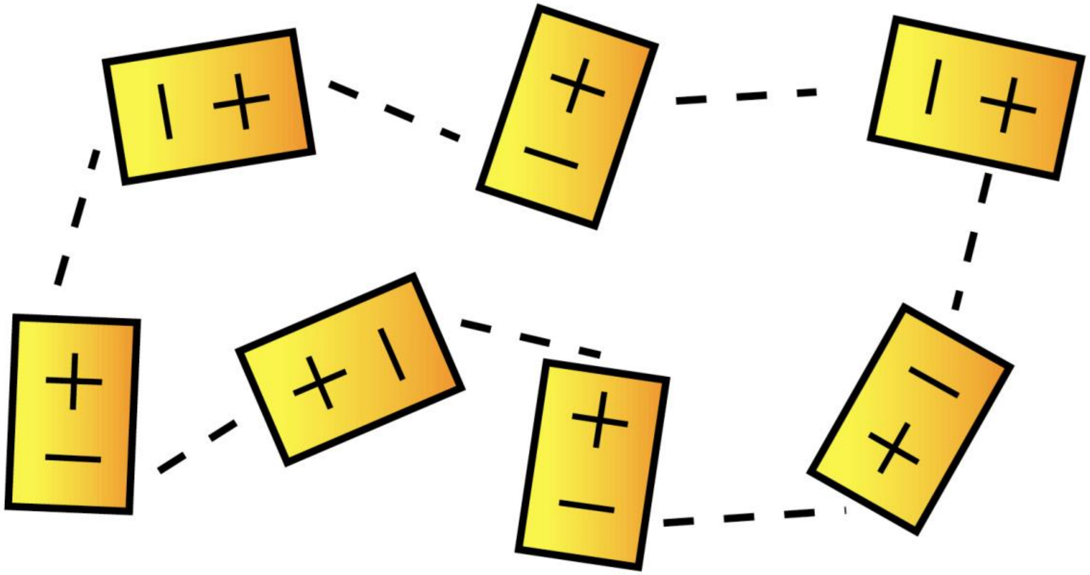
Dipole–Dipole interaction

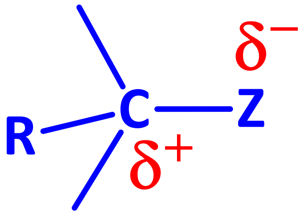
van der Waals force

Hydrogen bonding

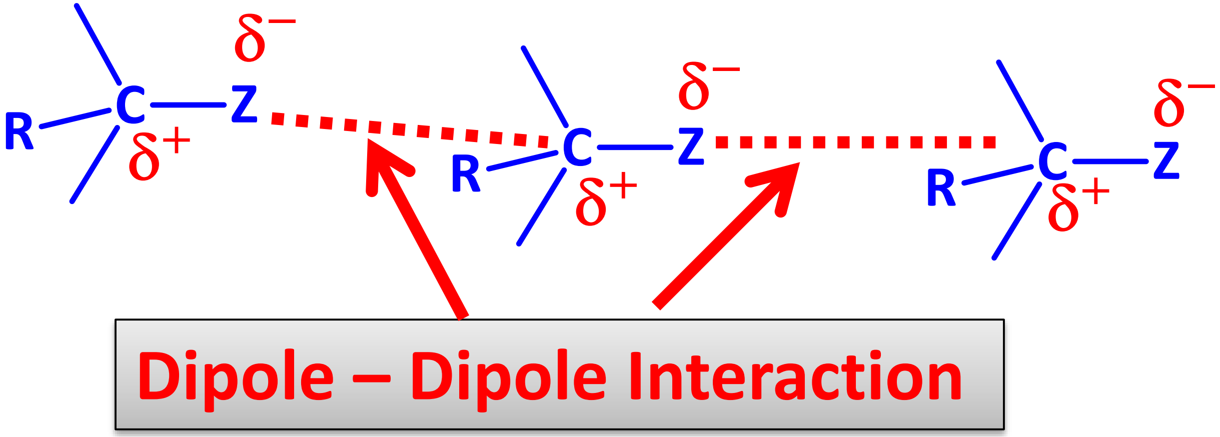
Dipole–Dipole Interaction

Molecules with dipole moments tend to orient themselves in the liquid and solid phases so that the negative end of the molecule is facing the positive end of another molecule.





Z = N, O, F, Cl or Br



Dipole – Dipole Interaction

As a result of such dipole-dipole interactions CH_3I is liquid at room temperature while CH_4 is gas at room temperature.

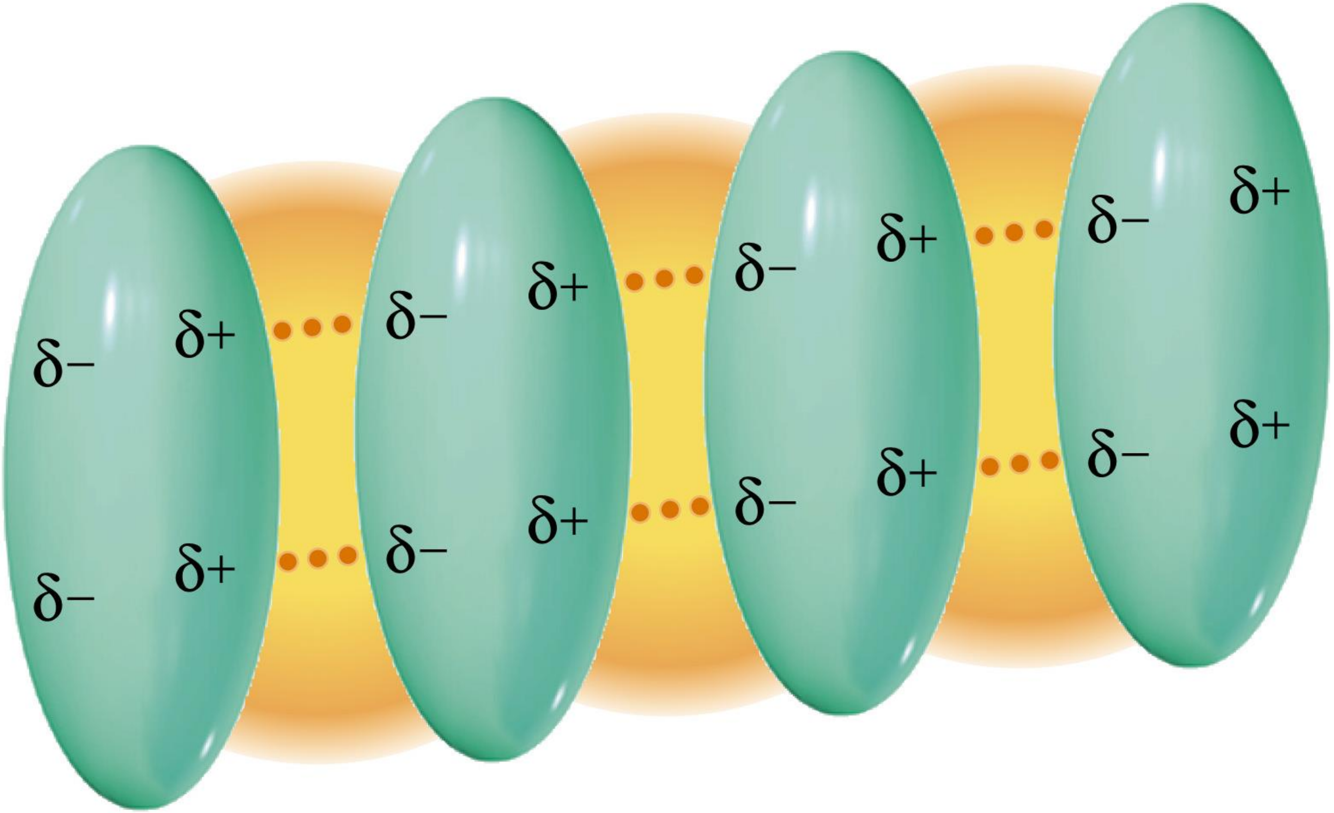
van der Waals force

Intermolecular forces act to attract even non-polar molecules.

CH_4 (methane)	Gas (b.p. -162°C)
$CH_3(CH_2)_4CH_3$ (hexane)	Liquid (b.p. 69°C)
$CH_3(CH_2)_{18}CH_3$ (icosane)	Solid (m.p. 36°C)

- **The weak forces of attraction that exist between nonpolar molecules are called van der Waals.**
- **These forces are the result of a constant motion of electrons which create a small distortions in the distribution of charges in nonpolar molecules leading to a small temporary dipole moment.**
- **This small dipole in one molecule can then create a dipole with the opposite orientation, an induced dipole, in second molecule.**

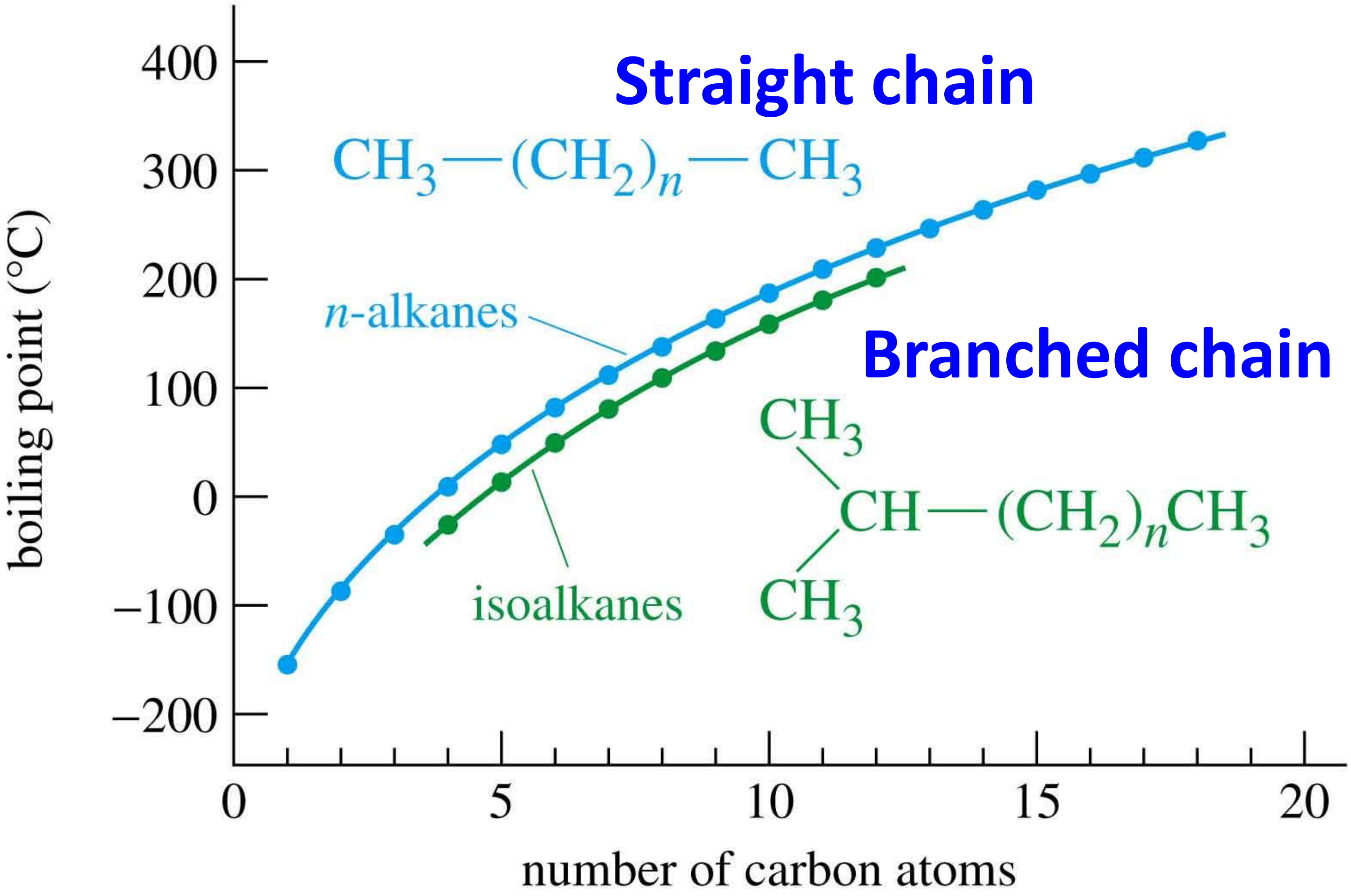
van der Waals Forces



The boiling point of a compound increases with the increase in van der Waals force.

As the number of carbon and hydrogen atoms increase, the additive effects of these weak intermolecular becomes significant, as evidenced by the increase in boiling and melting points from methane to hexane to icosane.

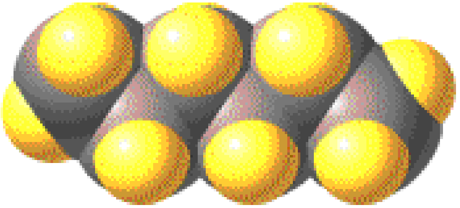
Boiling Points of Alkanes



Straight chain

Branched chain

van der Waals forces depend on the surface of the compounds interacting.

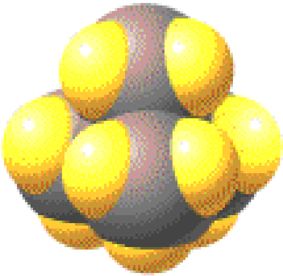


n-pentane

b.p. 36.1°C

2-methylbutane

b.p. 28°C



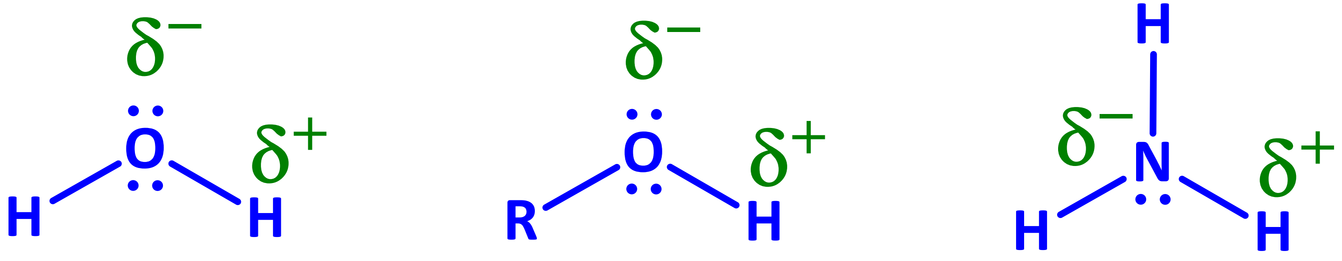
2,2-dimethylpropane

b.p. 9.5°C

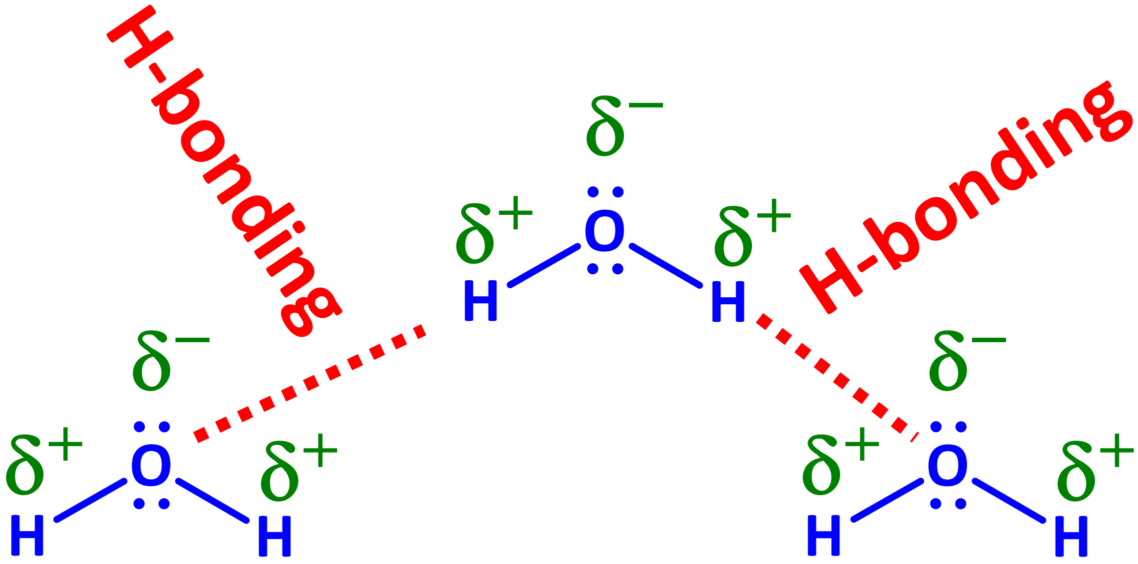
Hydrogen Bonding

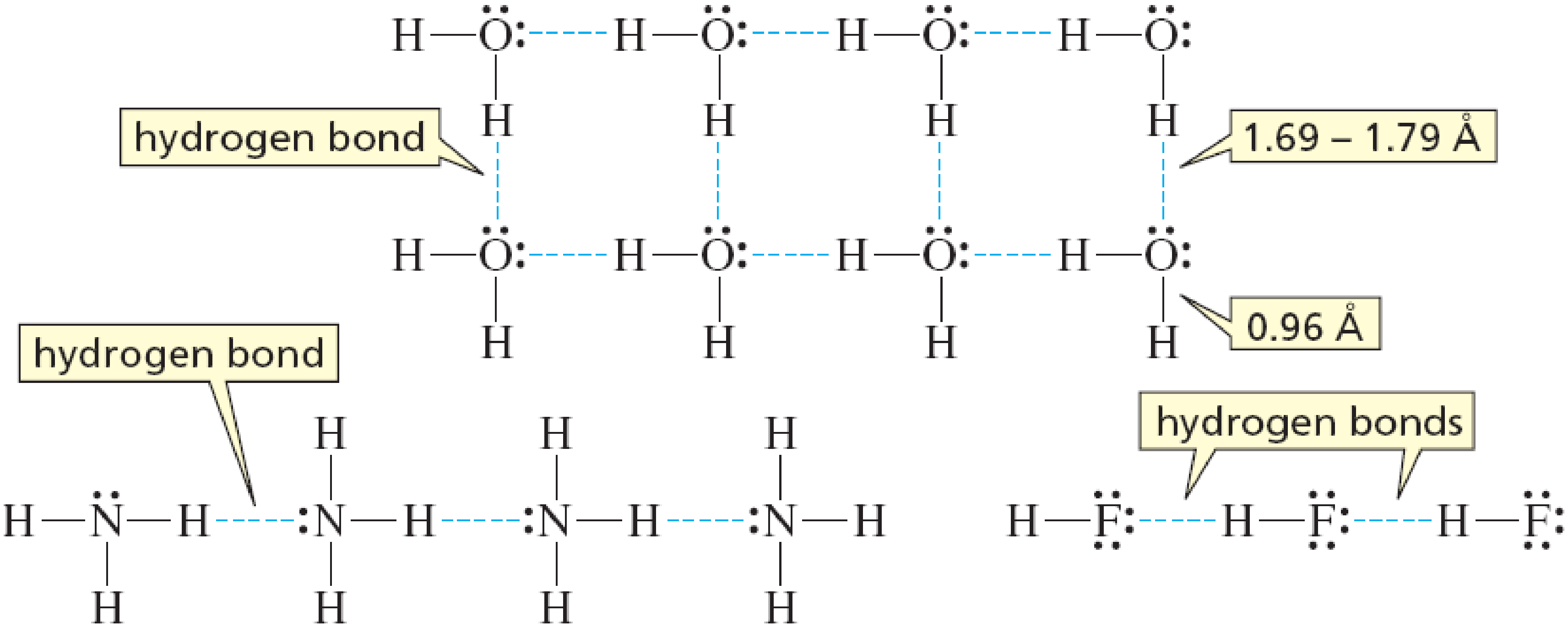
An especially strong type of dipole-dipole interaction occurs between molecules containing a hydrogen atom bonded to fluorine, oxygen or nitrogen. Each of these latter elements are the most electronegative and has unshared valence electrons.

Examples



In the liquid state, the molecules of any of these compounds have strong attractions for one another.



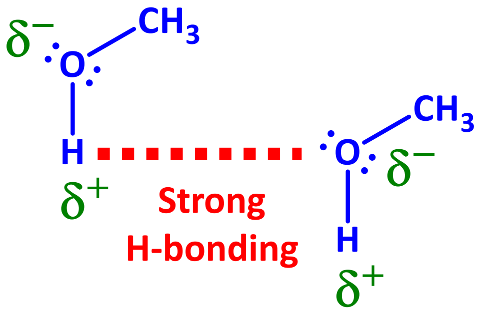

hydrogen bond
1.69 – 1.79 Å
0.96 Å
hydrogen bond
hydrogen bonds

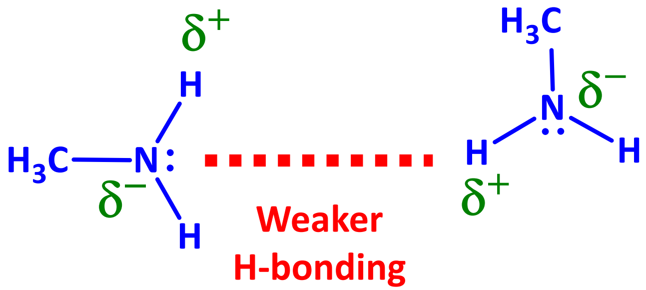
H-bonding is substantially stronger than most dipole-dipole attractions. The reason for this is due to the size of the atoms involved. A hydrogen atom is small compared to other atoms and can occupy a position close to the unshared electrons of the electronegative atom.

Atoms larger than hydrogen can’t occupy such a position; consequently dipole-dipole interactions between other atoms are weaker.

Hydrogen bonds are not all the same strength. An O ---- HO hydrogen bond is stronger than an N ---- HN hydrogen bond.

This is because oxygen is more electronegative than nitrogen; therefore, the O-H group is more polar and has a more positive H. This more positive H is more strongly attracted by a negative centre.

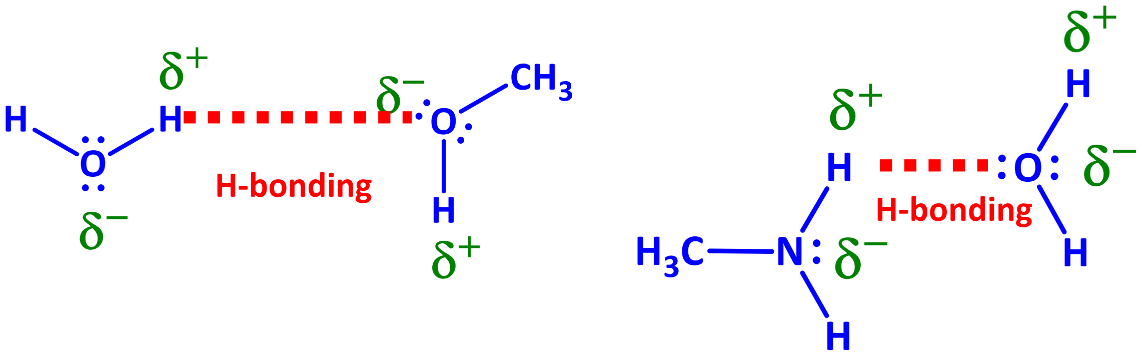




Boiling point 69°C -6.3°C

For all substances, boiling point increases with molecular weight because of increased van der Waals attractions.

- H-bonding may form between two different compounds; such as between CH_3OH and H_2O or between CH_3NH_2 and H_2O.

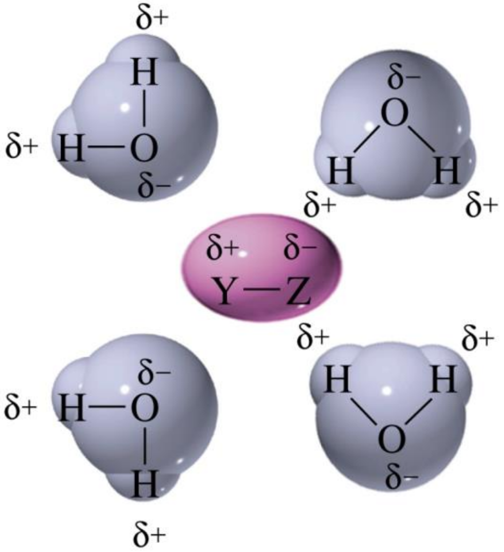


- Solubility of covalent compounds in water is another property affected by H-bonding. A compound that can form H-bonding with water tends to be more soluble in water than a compound that can't.

Like Dissolves Like

Polar compound dissolves in polar solvent

Nonpolar compound dissolves in nonpolar solvent



solvation of a polar compound $\overset{\delta+}{Y}—\overset{\delta-}{Z}$ by water

Problem

Give adequate explanations for the following observations:

I. Methyl iodide (CH_3I) is liquid at room temperature while methane (CH_4) is a gas.

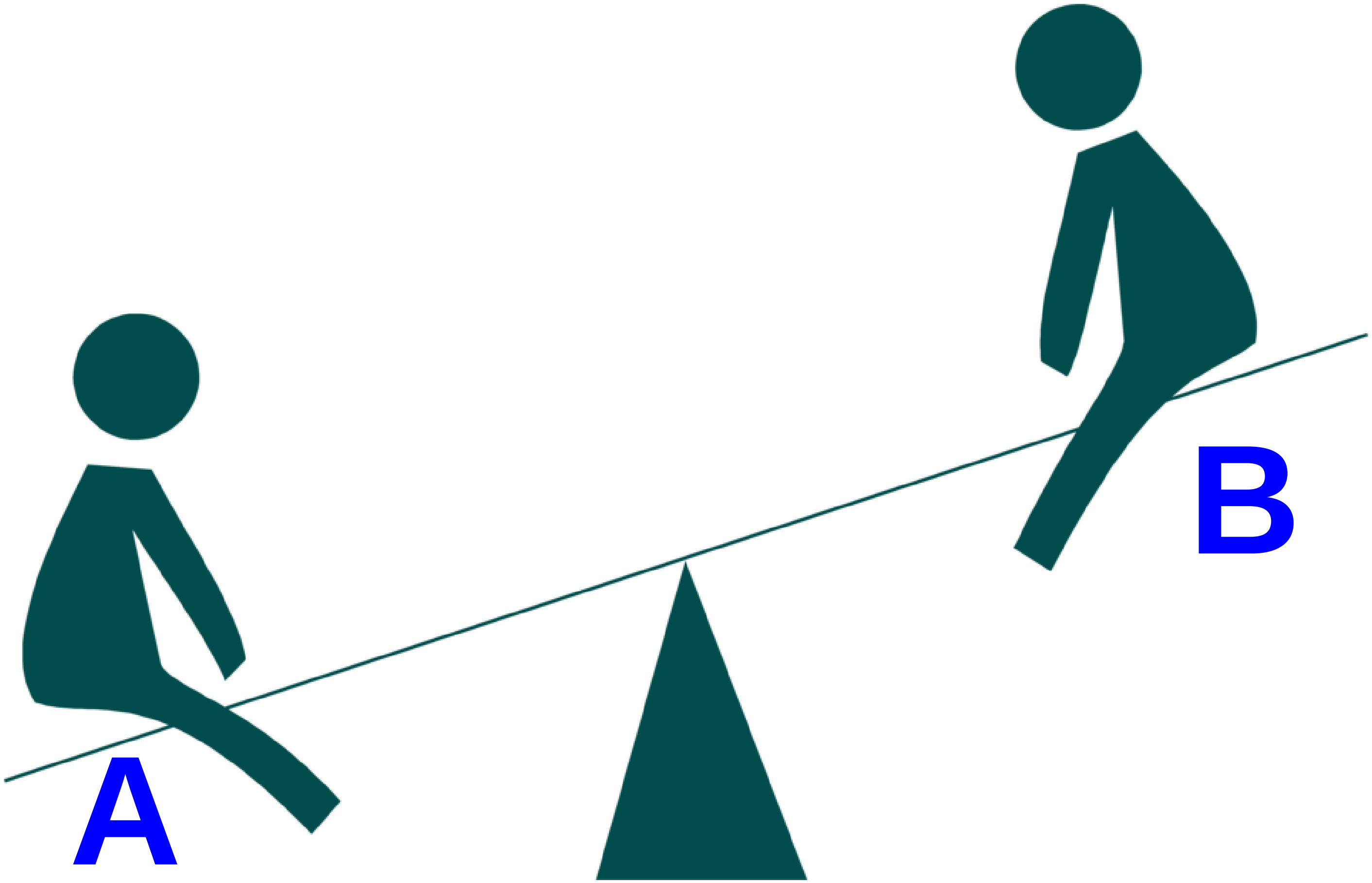
II. Ethanol (C_2H_5OH) boils at 78˚C while diethyl ether (CH_3-O-CH_3) boils at -23.6˚C despite the fact that they have the same molecular weight.

III. Arrange the following compounds in order of increasing polarity (least polar first):

CH_3-CH_2-CH_2-NH_2 CH_3-CH_2-CH_3 CH_3-CH_2-CH_2-OH

$$A \longrightarrow B$$

Irreversible Chemical Reaction



$$A \rightleftharpoons B$$

Reversible Chemical Reaction

Chemical Equilibrium

What is Equilibrium?

- Equilibrium is a state in which there are no observable changes as time goes by.
- When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time, and there are no visible changes in the system.
- However, there is much activity at the molecular level because reactant molecules continue to form product molecules while product molecules react to yield reactant molecules, it is a dynamic situation.

The Concept of Equilibrium and the Equilibrium Constant

Few chemical reactions proceed in only one direction. Most are reversible, at least to some extent.

At the start of a reversible process, the reaction proceeds toward the formation of products.

As soon as some product molecules are formed, the reverse process begins to take place and reactant molecules are formed from product molecules.

The equation of chemical equilibrium can be expressed symbolically as:

$$\textbf{Reactants} \rightleftharpoons \textbf{Products}$$

At equilibrium

- *rate of forward reaction = rate of reverse reaction*
- the concentrations of the reactants and products remain constant.

$$At\ equibrium\ \frac{\Delta[C]}{\Delta t} = \text{Constant}$$

Where [C] is concentration and t is time

For a generalized reversible chemical reaction,

$$aA + bB \rightleftharpoons cC + dD$$

where *a, b, c, and d are the stoichiometric coefficients for the reacting species A, B,* C, and D.

For the reaction at a particular temperature and at equilibrium, the equilibrium constant, K, is given by:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Where [C], [D], [A] and [B] represent the concentrations of reactants and products at equilibrium.

- The equilibrium constant, then, is defined by a *quotient, the numerator of which* is obtained by multiplying together the equilibrium concentrations of the *products, each* raised to a power equal to its stoichiometric coefficient in the balanced equation.
- Applying the same procedure to the equilibrium concentrations of *reactants gives the* denominator.

Examples

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

Note that although the concentrations may vary, as long as a given reaction is at equilibrium and the temperature does not change, the value of K remains constant.

The magnitude of the equilibrium constant tells us whether an equilibrium reaction favors the products or reactants.

If K *is much greater than 1 (that is,* $K >> 1$*), the equilibrium will lie to the right and favors the products.*

Conversely, if the equilibrium constant is much smaller than 1 (that is, $K << 1$*), the equilibrium will lie* to the left and favor the reactants.

Writing Equilibrium Constant Expressions

- The concept of equilibrium constants is extremely important in chemistry. Equilibrium constants are the key to solving a wide variety of stoichiometry problems involving equilibrium systems.
- To use equilibrium constants, we must express them in terms of the reactant and product concentrations.
- However, because the concentrations of the reactants and products can be expressed in different units and because the reacting species are not always in the same phase, there may be more than one way to express the equilibrium constant for the *same reaction.*

To begin with, we will consider reactions in which the reactants and products are in the same phase.

Homogenous equilibrium

Homogenous equilibrium applies to reactions in which all reacting species are in the same phase.

An example of a homogenous gas-phase equilibrium is the dissociation of N_2O_4.

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad K_c = \frac{[NO_2]^2}{[N_2O_4]}$$

The subscript in K_c indicates that the concentration of the reacting species are expressed in molarity or moles per liter.

The concentrations of reactants and products in gaseous reactions can also be expressed in terms of their partial pressures.

The equilibrium constant for the dissociation of N_2O_4 in terms of partial pressures (in atm) of the reacting species can be written as:

$$K_P = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$

Where P_{NO2} and P_{N2O4} are the equilibrium partial pressures (in atm) of NO_2 and N_2O_4, respectively. The subscript in K_P tells us that equilibrium concentration are expressed in terms of pressure.

In general, K_c is not equal to K_p. A simple relationship between K_p and K_c can be derived as follows. Let us consider the following equilibrium in gas phase:

$$a\mathrm{A}(g) \rightleftharpoons b\mathrm{B}(g)$$

The equilibrium constant K_c is given by $$K_C = \frac{[B]^b}{[A]^a}$$

And the expression K_p is given $$K_P = \frac{P_B^b}{P_A^a}$$

For an ideal gas $$\frac{PV}{T} = nR$$

Where P is pressure (in atm), V is volume (in L), T is temperature (in kelvin (K)) *n* is number of moles and R (*R* = 0.08206 L·atm/mol·K) is a gas constant.

The ideal gas equation implies that:

$$P_A = \frac{n_A RT}{V} \text{ and } P_B = \frac{n_B RT}{V}$$

Substituting this in the expression for K_p, we obtain

$$K_P = \frac{(\frac{n_B RT}{V})^b}{(\frac{n_A RT}{V})^a} = \frac{(\frac{n_B}{V})^b}{(\frac{n_A}{V})^a}(RT)^{b-a}$$

Now both n_B/V and n_A/V are number of moles per liters of solution and can be replaced by [B] and [A], so that,

$$K_P = \frac{[B]^b}{[A]^a}(RT)^{b-a} = K_c(RT)^{b-a} = K_c(RT)^{\Delta n} = K_c(0.08206T)^{\Delta n}$$

Δn = moles of gaseous products – moles of gaseous reactants

For the dissociation of N_2O_4 to NO_2,

$$\mathbf{N_2O_4(g) \rightleftharpoons 2NO_2(g)}$$

we can write, $K_P = K_c(0.08206T)^{\Delta n}$

Δn = moles of gaseous products – moles of gaseous reactants = 2 – 1 = 1

Therefore, $K_P = K_c(0.08206\mathrm{T})$

For a generalized reversible chemical reaction,

$$a\mathrm{A(g)} + b\mathrm{B(g)} \rightleftharpoons c\mathrm{C(g)} + d\mathrm{D(g)}$$

$$K_P = K_c(0.08206T)^{\Delta n}$$

Δn = moles of gaseous products – moles of gaseous reactants

= $(c + d) - (a + b)$

As another example of homogeneous equilibrium, let us consider the ionization of acetic acid (CH_3COOH) in water:

$$CH_3COOH\,(aq) + H_2O\,(l) \rightleftharpoons CH_3COO^{\ominus}(aq) + H_3O^{\oplus}(aq)$$

The equilibrium constant is $$K_c' = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

For a dilute aqueous solution, the concentration of water is essentially constant (≈55M)

$$K_a = K_C'[H_2O] = \frac{[CH_3COO^-][H_3O^+]}{[CH_3CO_2H]}$$

↓

Acidity constant (a measure of the strength of an acid)

The concentration of liquids is not included in the expression of the equilibrium constant.

Heterogeneous equilibrium

Heterogeneous equilibrium applies to reactions in which reactants and products are in different phases.

$$\mathrm{CaCO_3\,(s)} \rightleftharpoons \mathrm{CaO\,(s) + CO_2\,(g)}$$

$$K_{c'} = \frac{[CaO][CO_2]}{[CaCO_3]}$$

However, the concentration of solids does not change and therefore $[\mathrm{CaCO_3}]$ and [CaO] is constant.

$$Kc = K_{c'}\frac{[CaCO_3]}{[CaO]} = [CO_2]$$

The concentration of **solids** and **pure liquids** are not included in the expression for the equilibrium constant.

Examples

Write expressions for K_c, and K_P if applicable, for the following reversible reactions at equilibrium:

a) $HF\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^{\oplus}(aq) + F^{\ominus}(aq)$

b) $2NO\ (g) + O_2\ (g) \rightleftharpoons 2NO_2(g)$

Answers

a) Since there are no gases present, K_P does not apply and we have only K'_c:

$$K'_C = \frac{[F^-][H_3O^+]}{[HF][H_2O]}$$

The concentration of the liquid remains constant

$$K_c = \frac{[F^-][H_3O^+]}{[HF]}$$

b) $$K_C = \frac{[NO_2]^2}{[NO]^2[O_2]} \quad \text{and} \quad K_P = \frac{P^2_{NO_2}}{P^2_{NO_2} P_{O2}}$$

Practice Exercise

Write K_c and K_P for the decomposition of nitrogen pentoxide: $2N_2O_5\,(g) \rightleftharpoons 4NO_2(g) + O_2(g)$

Example

The equilibrium concentrations for the reaction between carbon monoxide and molecular chlorine to form $COCl_2$ (g) at 74^0C are [CO] = 0.012 M, $[Cl_2]$ = 0.054 M, and $[COCl_2]$ = 0.14 M. Calculate the equilibrium constants K_c and K_p.

$$CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2(g)$$

Answer

$$K_c = \frac{[COCl_2]}{[CO][Cl_2]} = \frac{0.14}{0.012 \text{ x } 0.054} = 220$$

$K_p = K_c(RT)^{\Delta n}$ $\quad \Delta n = 1 - 2 = -1$ $\quad R = 0.0821$ $\quad T = 273 + 74 = 347$ K

$$K_p = 220 \text{ x } (0.0821 \text{ x } 347)^{-1} = 7.7$$

Example

The equilibrium constant K_P for the reaction given below is 158 at 1000K. What is the equilibrium pressure of O_2 if the P_{NO} = 0.270 atm and P_{NO2} = 0.400 atm?

$$2NO_2\,(g) \rightleftharpoons 2NO(g) + O_2(g)$$

$K_P = \dfrac{P_{NO}^2 P_{O_2}}{P_{NO_2}^2}$, this implies $P_{O_2} = K_P \dfrac{P_{NO_2}^2}{P_{NO}^2}$

$$P_{O_2} = 158\frac{(0.400)^2}{(0.270)^2} = 347 \text{ atm}$$

Practice Problem

1. The following equilibrium process has been studied at 230°C: $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

In one experiment the concentrations of the reacting species at equilibrium are found to be [NO] = 0.0542 M, $[O_2]$= 0.127 M, and $[NO_2]$= 15.5 M. Calculate the equilibrium constant (K_c) of the reaction at this temperature.

2. The equilibrium constant K_P for the decomposition of phosphorus pentachloride to phosphorus trichloride and molecular chlorine is found to be 1.05 at 250°C. If the equilibrium partial pressures of PCl_5 and PCl_3 are 0.875 atm and 0.463 atm, respectively, what is the equilibrium partial pressure of Cl_2 at 250°C?

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Example

Write the equilibrium constant expression K_c, and K_P if applicable, for each of the following heterogeneous systems:

a) $(NH_4)_2Se(s) \rightleftharpoons 2NH_3(g) + H_2Se(g)$

b) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

c) $P_4(s) + 6Cl_2(g) \rightleftharpoons 4PCl_3(l)$

Answer

(a) The equilibrium constant is given by

$$\mathbf{K'_C = \frac{[NH_3]^2[H_2Se]}{[(NH_4)_2Se]}}$$

However, since $(NH_4)_2Se$ is a solid, we write the new equilibrium constant as

$$\mathbf{K_C = [NH_3]^2[H_2Se]}$$

Alternatively, we can express the equilibrium constant K_P in terms of the partial pressures of NH_3 and H_2Se:

$$\mathbf{K_P = P_{NH_3}^2 P_{H_2Se}}$$

b)

$$\mathbf{K'_C} = \frac{[\boldsymbol{Ag^+}][\boldsymbol{Cl^-}]}{[\mathbf{AgCl}]}$$

Again, [AgCl] is incorporated into K_c because AgCl is a solid.

$$\boldsymbol{K_C = [Ag^+][Cl^-]}$$

(c) The equilibrium constant is

$$\mathbf{K'_C = \frac{[PCl_3]^4}{[P_4][Cl_2]^6}}$$

Since pure solids and pure liquids do not appear in the equilibrium constant expression, we write

$$\boldsymbol{K_C = \frac{1}{[\mathrm{Cl}_2]^6}}$$

Alternatively, we can express the equilibrium constant in terms of the pressure of Cl_2:

$$\boldsymbol{K_P = \frac{1}{P^6_{Cl_2}}}$$

Practice Exercise

1. Write equilibrium constant expressions for K_c and K_P for the formation of nickel tetracarbonyl, which is used to separate nickel from other impurities:

$$\mathbf{Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)}$$

2. Consider the following equilibrium at 295 K:

$$\mathbf{NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)}$$

The partial pressure of each gas is 0.265 atm. Calculate K_P and K_c for the reaction.

Multiple Equilibria

The reactions we have considered so far are all relatively simple. A more complicated situation is one in which the product molecules in one equilibrium system are involved in a second equilibrium process:

$$\mathbf{A + B \rightleftharpoons C + D} \qquad K_C' = \frac{[C][D]}{[A][B]}$$

$$\mathbf{C + D \rightleftharpoons E + F} \qquad K_C'' = \frac{[E][F]}{[C][D]}$$

The overall reaction is given by the sum of the two reactions

$$\begin{array}{lll} \mathbf{A + B \rightleftharpoons C + D} & & \mathrm{K}_\mathrm{C}' \\ \underline{\mathbf{C + D \rightleftharpoons E + F}} & & \mathrm{K}_\mathrm{C}' \\ \mathbf{A + B \rightleftharpoons E + F} & & \mathrm{K}_\mathrm{C} \end{array}$$

Overall net reaction

The equilibrium constant K_c for the overall reaction is

$$K_C = \frac{[E][F]}{[A][B]}$$

We obtain the same expression if we take the product of the expressions for K'_c *and* K''_c

$$K_C = \frac{[C][D]}{[A][B]} x \frac{[E][F]}{[C][D]} = \frac{[E][F]}{[A][B]} = K'_C K''_C$$

We can now make an important statement about multiple equilibria:

If a reaction can be expressed as the sum of two or more reactions, the equilibrium constant for the overall reaction is given by the product of the equilibrium constants of the individual reactions.

An examples of multiple of multiple equilibria is the ionization of diprotic acids in aqueous solution . The following equilibrium constants have been determined for carbonic acid at 25°C:

$$H_2CO_3(aq) \rightleftharpoons H^+(aq) + HCO_3^-(aq) \quad K'_C = \frac{[H^+][HCO_3^-]}{[H_2CO_3]} = 4.2 \text{ x } 10^{-7}$$

$$HCO_3^-(aq) \rightleftharpoons H^+(aq) + CO_3^{-2}(aq) \quad K''_C = \frac{[H^+][CO_3^{-2}]}{[HCO_3^-]} = 4.2 \text{ x } 10^{-11}$$

The overall reaction is the sum of the two reactions

$$H_2CO_3(aq) \rightleftharpoons 2H^+(aq) + CO_3^{-2}(aq) \quad K_C = \frac{[H^+]^2[CO_3^{-2}]}{[H_2CO_3]}$$

$$K_C = K'_C K''_C = (4.2 \text{ x } 10^{-7})\,(4.8 \text{ x } 10^{-11}) = 2.0 \text{ x } 10^{-17}$$

Calculating the Equilibrium Concentrations

If we know the equilibrium constant for a particular reaction, we can calculate the concentrations in the equilibrium mixture from the initial concentrations. Commonly, only the initial reactant concentrations are given.

Example 1

A mixture of 0.500 mol H_2 and 0.500 mol I_2 was placed in a 1.00-L stainless-steel flask at 430°C. The equilibrium constant K_c for the reaction is 54.3 at this temperature. Calculate the concentrations of H_2, I_2, and HI at equilibrium.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Solution

Step 1

The stoichiometry of the reaction is 1 mol H_2 reacting with 1 mol I_2 to yield 2 mol HI. Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. It follows that the equilibrium concentration of HI must be 2x. We summarize the changes in concentrations as follows:

Reaction	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial	**0.500**		**0.500**		**0.000**
Change	**-x**		**-x**		**+2x**
Equilibrium	**(0.500 – x)**		**(0.500 – x)**		**2x**

Remember the acronym **RICE**

Step 2: The equilibrium constant is given by

$$\mathbf{K_C = \frac{[HI]^2}{[H_2][I_2]}}$$

Substituting, we get

$$\mathbf{54.3 = \frac{(2x)^2}{(0.500\ - x)(0.500\ - x)}}$$

Taking the square root of both sides, we get

$\mathbf{7.37 = \frac{2x}{(0.500\ - x)}}$, this implies x = 0.393 M

Step 3: At equilibrium, the concentrations are

$[H_2]$ = (0.500 - 0.393) M = 0.107 M

$[I_2]$ = (0.500 - 0.393) M = 0.107 M

[HI] = 2 x 0.393 M = 0.786 M

Example 2

For the same reaction and temperature as in Example 1, suppose that the initial concentrations of H_2, I_2, and HI are 0.00623 M, 0.00414 M, and 0.0224 M, respectively. Calculate the concentrations of these species at equilibrium.

Solution

Step 1: Let x be the depletion in concentration (mol/L) of H_2 and I_2 at equilibrium. From the stoichiometry of the reaction it follows that the increase in concentration for HI must be 2x. Next we write

Reaction	$H_2(g)$	+	$I_2(g)$	$\rightleftharpoons$	$2HI(g)$
Initial	**0.00623**		**0.00414**		**0.0224**
Change	**-x**		**-x**		**+2x**
Equilibrium	**(0.00623 – x)**		**(0.00414 – x)**		**0.0224 + 2x**

Step 2: The equilibrium constant is $\mathbf{K_C = \frac{[HI]^2}{[H_2][I_2]}}$

Substituting, we get

$$\mathbf{54.3 = \frac{(0.0224 + 2x)^2}{(0.00623 - x)(0.00414 - x)}}$$

$54.3(2.58 \times 10^{-5} - 0.0104x + x^2) = 5.02x\ 10^{-4} + 0.0896x + 4x^2$

Collecting terms, we get

$50.3x^2 + 0.654x + 8.98x\ 10^{-4} = 0$

This is a quadratic equation of the form $ax^2 + bx + c = 0$.
The solution for a quadratic equation is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here we have a = 50.3, b = -0.654, and c = 8.98×10^{-4}, so that

$$x = \frac{-0.654 \pm \sqrt{(-0.654)^2 - 4(50.3)(8.98 \text{ x } 10-4)}}{2 \text{ x } 50.3}$$

$x = 0.0114$ M or $x = 0.00156$ M

The first solution is physically impossible since the amounts of H_2 and I_2 reacted would be more than those originally present. The second solution gives the correct answer. Note that in solving quadratic equations of this type, one answer is always physically impossible, so choosing a value for x is easy.

Step 3: At equilibrium, the concentrations are

$[H_2] = (0.00623 - 0.00156)$ M = 0.00467 M
$[I_2] = (0.00414 - 0.00156)$ M = 0.00258 M
$[HI] = (0.0224 + 2 \times 0.00156)$ M = 0.0255 M

PRACTICE EXERCISE

1. At 1280°C the equilibrium constant (K_c) for the reaction given below is 1.1 x 10^{-3}. If the initial concentrations are $[Br_2]$ = 6.3 x 10^{-2} M and [Br] = 1.2 x 10^{-2} M, calculate the concentrations of these species at equilibrium.

$$\mathbf{Br_2(g) \rightleftharpoons 2Br(g)}$$

2. The equilibrium constant K_c for the reaction given below is 54.3 at 430°C.

$$\mathbf{H_2(g) + I_2(g) \rightleftharpoons 2HI(g)}$$

At the start of the reaction there are 0.714 mole of H_2, 0.984 mole of I_2 and 0.886 mole of HI in a 2.40 L reaction chamber. Calculate the concentration of the gases at equilibrium.

Applications of Equilibrium Constant

Equilibrium constant can be used to predict the direction of net reaction.

For a reaction of known K_c value, the direction of net reaction can be predicted by calculating the reaction quotient, Q_c.

Q_c is called the *reaction quotient,* where for a reaction such as: **aA + bB $\rightleftharpoons$ cC + dD**

$$Q_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Q_c has the same expression as K_c , but *it* is calculated using concentrations that are not necessarily at equilibrium.

For any system or reaction:

1. Knowing the equilibrium constant, we can predict whether or not a reaction mixture is at equilibrium, and we can predict the direction of net reaction.

    - $Q_c = K_c$ ➔ equilibrium (no net reaction)

    - $Q_c < K_c$ ➔ a net forward reaction;

    - $Q_c > K_c$ ➔ a net reverse reaction

2. The value of *K* tells us whether a reaction favors the products or the reactants.

Factors That Affect Chemical Equilibrium

Chemical equilibrium represents a balance between forward and reverse reactions. In most cases, this balance is quite delicate. Changes in experimental conditions may disturb the balance and shift the equilibrium position so that more or less of the desired product is formed. When we say that an equilibrium position shifts to the right, for example, we mean that the net reaction is now from left to right. Variables that can be controlled experimentally are concentration, pressure, volume, and temperature.

Le Chatelier’s Principle

There is a general rule that helps us to predict the direction in which an equilibrium reaction will move when a change in concentration, pressure, volume, or temperature occurs.

The rule, known as ***Le Chatelier’s† principle, states that if an external stress*** *is applied to a system at equilibrium, the system adjusts in such a way that the stress is offset.*

The word “stress” here means a change in concentration, pressure, volume, or temperature that removes a system from the equilibrium state.

Factors that Affect Chemical Equilibrium

1) Concentration
2) Pressure
3) Volume
4) Temperature
5) Catalysts- Have No Effect On Position Of Equilibrium

1) Changes in Concentrations

- Increase the yield of product by
  - increasing concentration of reactant
  - removing the product from the equilibrium

Example 1 $$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

0.683 M 8.80 M 1.05 M

Increase the concentration of NH_3 to 3.65*M,* the position of equilibrium shifts to the left

$$Q_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(3.65)^2}{(0.683)(8.80)^3} = 0.0286$$

$$\text{But } K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(1.05)^2}{(0.683)(8.80)^3} = 0.02$$

$Q_C > Kc$, a net reverse reaction (equilibrium shifted to the left)

Example 2

$$\mathbf{BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)}$$

$$K_c = [Ba^{2+}]\,[SO_4^{2-}]$$

- ☐ By adding $Ba^{2+}(aq)$, $[SO_4^{2-}]$ decreases, but $BaSO_4$ (s) increases
- ☐ By add $SO_4^{2-}{}_{(aq)}$, $[Ba^{2+}]$ decreases but $BaSO_4$(s) increases
- ☐ Add $BaSO_4$ (s) no change

2. Changes in Volume and Pressure

- Little effect on reactions in solution
- Effect can be large on reactions in the gas phase
- Increase in pressure shifts the equilibrium to the side with the fewer moles of gas

Example

How does the position of equilibrium change as the pressure is increased?

$$\mathbf{2PbS(s) + 5O_2(g) \rightleftharpoons 2PbO(s) + 2SO_4\ (g)}$$

five moles of gaseous reactant *two moles of gaseous product*

An increase in pressure causes an increase in products

In general, an increase in pressure (decrease in volume) favors the net reaction that decreases the total number of moles of gases, and a decrease in pressure (increase in volume) favors the net reaction that increases the total number of moles of gases. For reactions in which there is no change in the number of moles of gases, a pressure (or volume) change has no effect on the position of equilibrium.

3. Changes in Temperature

Equilibrium constant is dependent on temperature, it changes with change in temperature.

A temperature increase favours an endothermic reaction, and a temperature decrease favours an exothermic reaction.

Example

$N_2O_4(g) + 58kJ \rightleftharpoons 2NO_2\ (g)$ **Endothermic reaction**

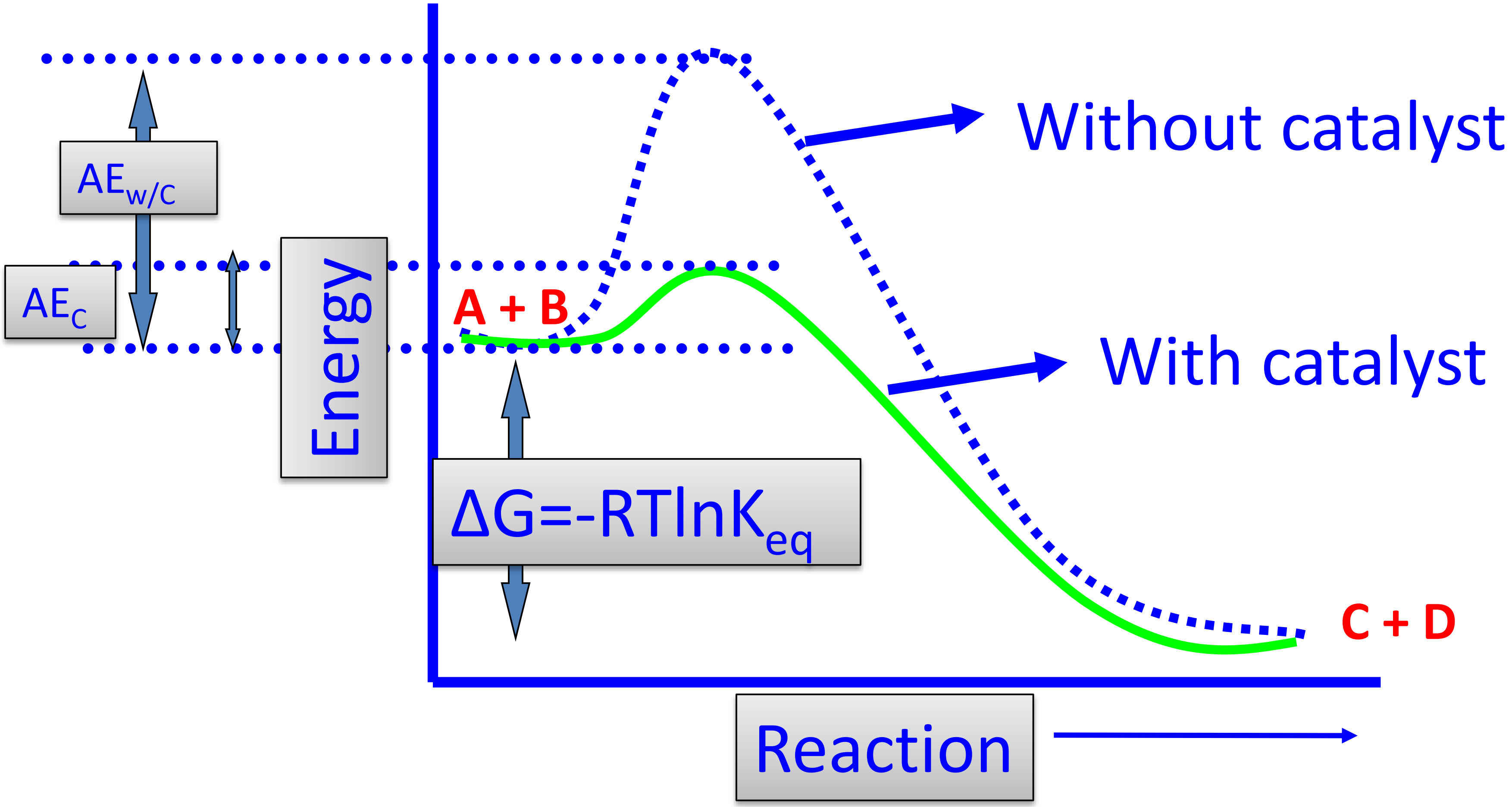
Increase temperature**:** Favours forward reaction

The Effect of a Catalyst

A catalyst enhances the rate of a reaction by lowering the reaction’s activation energy. However, a catalyst lowers the activation energy of the forward reaction and the reverse reaction to the same extent.

We can therefore conclude that the presence of a catalyst does not alter the equilibrium constant, nor does it shift the position of an equilibrium system. Adding a catalyst to a reaction mixture that is not at equilibrium will simply cause the mixture to reach equilibrium sooner. The same equilibrium mixture could be obtained without the catalyst, but we might have to wait much longer for it to happen.

$$a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C} + d\mathrm{D}$$

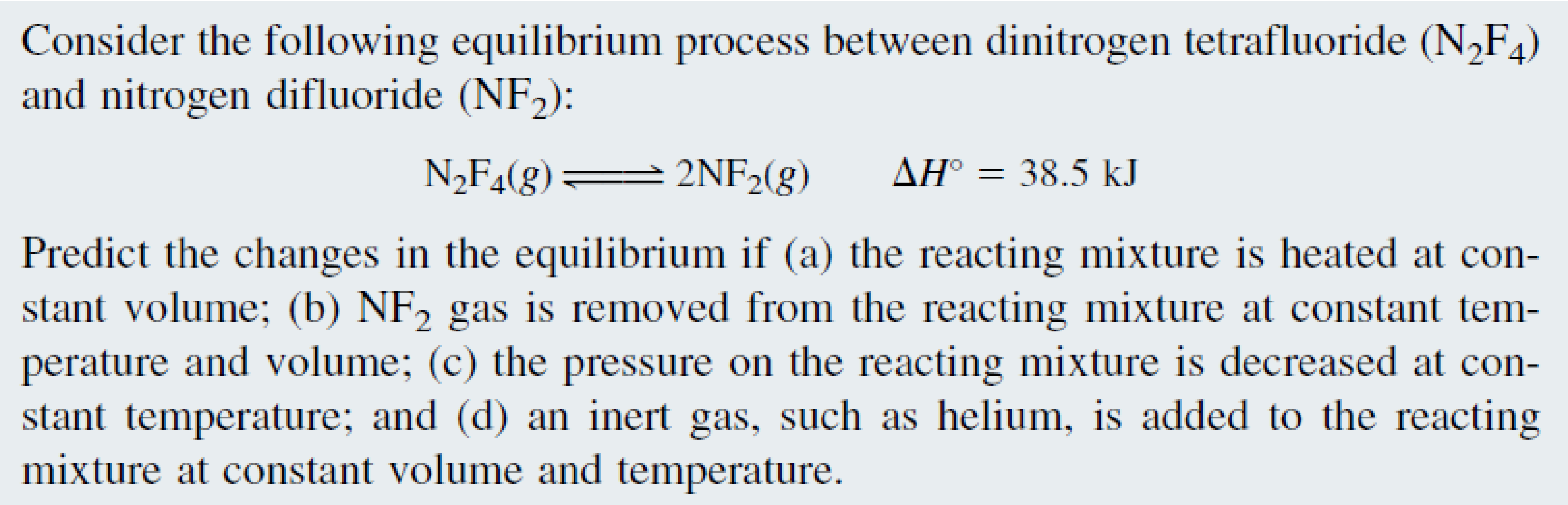


Catalyst lower the activation energy (AE) of reactions and make the reaction faster but does not change the equilibrium constant (K_{eq})

Summary of Factors that Affect the Equilibrium Position

We have considered four ways to affect a reacting system at equilibrium. It is important to remember that, of the four, *only a change in temperature changes the value of the equilibrium constant.* Changes in concentration, pressure, and volume can alter the equilibrium concentrations of the reacting mixture, but they cannot change the equilibrium constant as long as the temperature does not change. A catalyst can speed up the process, but it has no effect on the equilibrium constant or on the equilibrium concentrations of the reacting species.

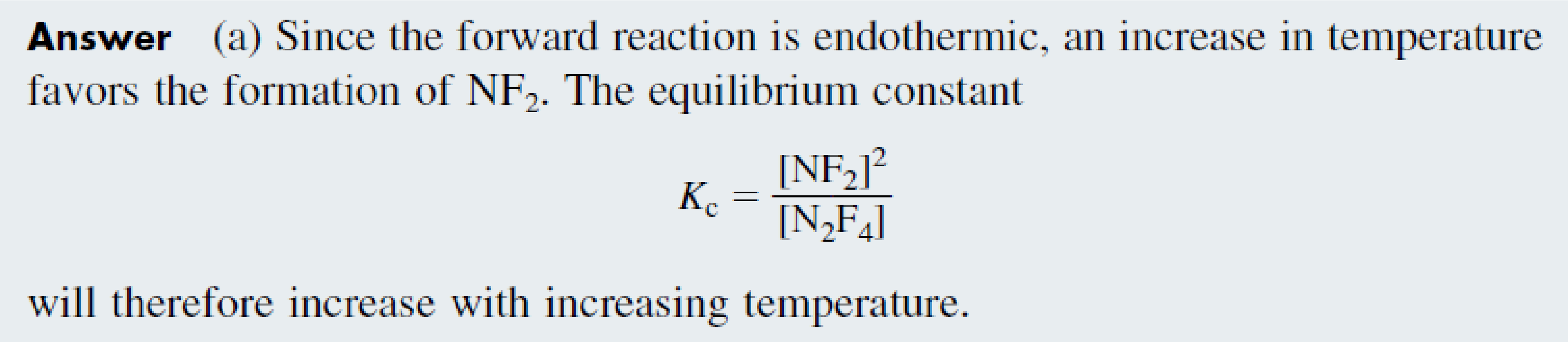
Example



Consider the following equilibrium process between dinitrogen tetrafluoride (N_2F_4) and nitrogen difluoride (NF_2):

$$N_2F_4(g) \rightleftharpoons 2NF_2(g) \qquad \Delta H^\circ = 38.5 \text{ kJ}$$

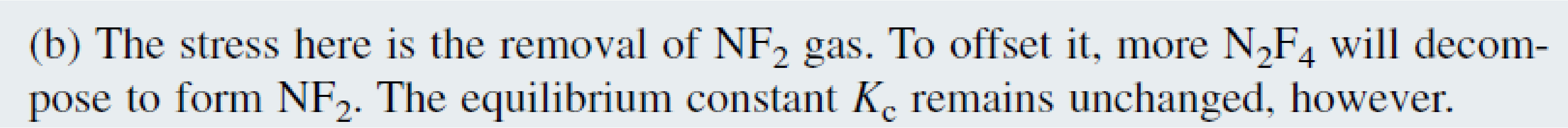
Predict the changes in the equilibrium if (a) the reacting mixture is heated at constant volume; (b) NF_2 gas is removed from the reacting mixture at constant temperature and volume; (c) the pressure on the reacting mixture is decreased at constant temperature; and (d) an inert gas, such as helium, is added to the reacting mixture at constant volume and temperature.



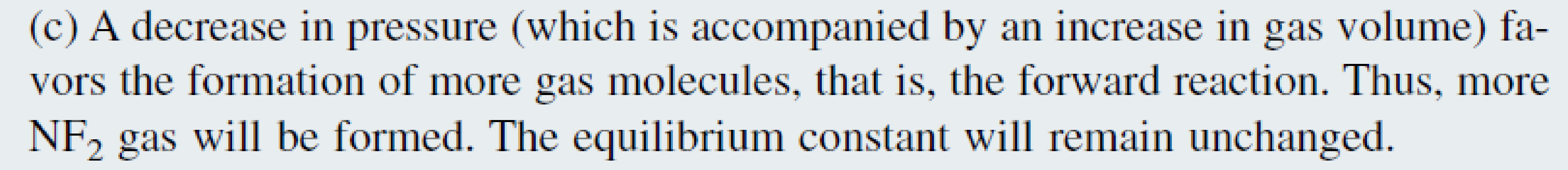
Answer (a) Since the forward reaction is endothermic, an increase in temperature favors the formation of NF_2. The equilibrium constant

$$K_c = \frac{[NF_2]^2}{[N_2F_4]}$$

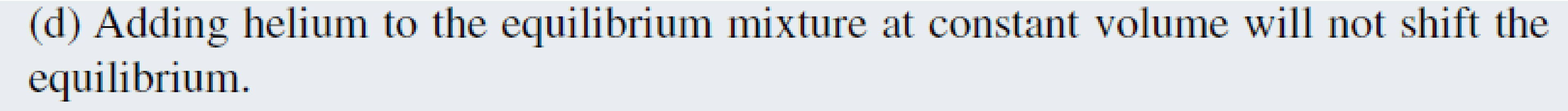
will therefore increase with increasing temperature.



(b) The stress here is the removal of NF_2 gas. To offset it, more N_2F_4 will decompose to form NF_2. The equilibrium constant K_c remains unchanged, however.



(c) A decrease in pressure (which is accompanied by an increase in gas volume) favors the formation of more gas molecules, that is, the forward reaction. Thus, more NF_2 gas will be formed. The equilibrium constant will remain unchanged.



(d) Adding helium to the equilibrium mixture at constant volume will not shift the equilibrium.

Practice problem

1 Consider the equilibrium

$$2\mathrm{I}(g) \rightleftharpoons \mathrm{I}_2(g)$$

What would be the effect on the position of equilibrium of (a) increasing the total pressure on the system by decreasing its volume; (b) adding I_2 to the reaction mixture; and (c) decreasing the temperature?

2 Consider the following equilibrium process:

$$\mathrm{PCl}_5(g) \rightleftharpoons \mathrm{PCl}_3(g) + \mathrm{Cl}_2(g) \qquad \Delta H^\circ = 92.5\ \mathrm{kJ}$$

Predict the direction of the shift in equilibrium when (a) the temperature is raised; (b) more chlorine gas is added to the reaction mixture; (c) some PCl_3 is removed from the mixture; (d) the pressure on the gases is increased; (e) a catalyst is added to the reaction mixture.

Solubility Product

Consider a saturated solution of silver chloride that is in contact with solid silver chloride. The solubility equilibrium can be represented as $\mathrm{AgCl}(s) \rightleftharpoons \mathrm{Ag}^{+}(aq) + \mathrm{Cl}^{-}(aq)$

Because salts such as AgCl are considered as strong electrolytes, all the AgCl that dissolves in water is assumed to dissociate completely into Ag^+ and Cl^- ions. We know that for heterogeneous reactions the concentration of the solid is a constant.

Thus we can write the equilibrium constant for the dissolution of AgCl as

$$K_{\mathrm{sp}} = [\mathrm{Ag}^{+}][\mathrm{Cl}^{-}]$$

where $\mathbf{K_{sp}}$ is called the solubility product constant or simply the solubility product.

In general, the **solubility product** of a compound is the product of the molar concentrations of the constituent ions, each raised to the power of its stoichiometric coefficient in the equilibrium equation.

Because each AgCl unit contains only one Ag^+ ion and one Cl^- ion, its solubility product expression is particularly simple to write. The following cases are more complex:

MgF_2

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq) \qquad K_{sp} = [Mg^{2+}][F^-]^2$$

Ag_2CO_3

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq) \qquad K_{sp} = [Ag^+]^2[CO_3^{2-}]$$

$Ca_3(PO_4)_2$

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \qquad K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

TABLE 16.2 Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [$Al(OH)_3$]	1.8×10^{-33}	Lead(II) chromate ($PbCrO_4$)	2.0×10^{-14}
Barium carbonate ($BaCO_3$)	8.1×10^{-9}	Lead(II) fluoride (PbF_2)	4.1×10^{-8}
Barium fluoride (BaF_2)	1.7×10^{-6}	Lead(II) iodide (PbI_2)	1.4×10^{-8}
Barium sulfate ($BaSO_4$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi_2S_3)	1.6×10^{-72}	Magnesium carbonate ($MgCO_3$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [$Mg(OH)_2$]	1.2×10^{-11}
Calcium carbonate ($CaCO_3$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF_2)	4.0×10^{-11}	Mercury(I) chloride (Hg_2Cl_2)	3.5×10^{-18}
Calcium hydroxide [$Ca(OH)_2$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [$Ca_3(PO_4)_2$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [$Cr(OH)_3$]	3.0×10^{-29}	Silver bromide ($AgBr$)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag_2CO_3)	8.1×10^{-12}
Copper(I) bromide ($CuBr$)	4.2×10^{-8}	Silver chloride ($AgCl$)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [$Cu(OH)_2$]	2.2×10^{-20}	Silver sulfate (Ag_2SO_4)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag_2S)	6.0×10^{-51}
Iron(II) hydroxide [$Fe(OH)_2$]	1.6×10^{-14}	Strontium carbonate ($SrCO_3$)	1.6×10^{-9}
Iron(III) hydroxide [$Fe(OH)_3$]	1.1×10^{-36}	Strontium sulfate ($SrSO_4$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate ($PbCO_3$)	3.3×10^{-14}	Zinc hydroxide [$Zn(OH)_2$]	1.8×10^{-14}
Lead(II) chloride ($PbCl_2$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

For equilibrium reactions involving an ionic solid in aqueous solution, any one of the following conditions may exist:

1) the solution is unsaturated,
2) the solution is saturated, or
3) the solution is supersaturated.

For concentrations of ions that do not correspond to equilibrium conditions we use the reaction quotient, which in this case is called the ion product (Q), to predict whether a precipitate will form.

Note that *Q* has the same form as *K*sp except that the concentrations of ions are *not* equilibrium concentrations. For example, if we mix a solution containing Ag^+ ions with one containing Cl^- ions, then the ion product is given by

$$Q = [\mathrm{Ag}^+]_0[\mathrm{Cl}^-]_0$$

The subscript 0 reminds us that these are initial concentrations and do not necessarily correspond to those at equilibrium.

The possible relationships between *Q* and *K*sp are

- $Q < K_{sp}$, Unsaturated solution
- $Q = K_{sp}$, Saturated solution
- $Q > K_{sp}$, Supersaturated solution;

Molar Solubility and Solubility

There are two ways to express a substance’s solubility: ***molar solubility,*** which is *the number of moles of solute in one liter of a saturated solution (mol/L),* and ***solubility,*** which is *the number of grams of solute in one liter of a saturated solution (g/L).*

Note that both these expressions refer to the concentration of saturated solutions at some given temperature (usually 25°C). Both molar solubility and solubility are convenient to use in the laboratory.

The solubility of calcium sulfate is found experimentally to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulfate.

Answer First we calculate the number of moles of $CaSO_4$ dissolved in 1 L of solution:

$$\frac{0.67\text{ g CaSO}_4}{1\text{ L soln}} \times \frac{1\text{ mol CaSO}_4}{136.2\text{ g CaSO}_4} = 4.9 \times 10^{-3}\text{ mol/L}$$

The solubility equilibrium

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

shows that for every mole of $CaSO_4$ that dissolves, 1 mole of Ca^{2+} and 1 mole of SO_4^{2-} are produced. Thus, at equilibrium

$$[Ca^{2+}] = 4.9 \times 10^{-3}\ M \qquad \text{and} \qquad [SO_4^{2-}] = 4.9 \times 10^{-3}\ M$$

Now we can calculate K_{sp}:

$$\begin{aligned} K_{sp} &= [Ca^{2+}][SO_4^{2-}] \\ &= (4.9 \times 10^{-3})(4.9 \times 10^{-3}) \\ &= 2.4 \times 10^{-5} \end{aligned}$$

PRACTICE EXERCISE

The solubility of lead chromate ($PbCrO_4$) is 4.5×10^{-5} g/L. Calculate the solubility product of this compound.

Using the data in Table 16.2, calculate the solubility of copper(II) hydroxide, $Cu(OH)_2$, in g/L.

Answer

Step 1: When $Cu(OH)_2$ dissociates, the species in solution are Cu^{2+} and OH^- ions.

Step 2: Let s be the molar solubility of $Cu(OH)_2$. Since one unit of $Cu(OH)_2$ yields one Cu^{2+} ion and two OH^- ions, at equilibrium $[Cu^{2+}]$ is s and $[OH^-]$ is $2s$. We summarize the changes in concentrations as follows:

	$Cu(OH)_2(s) \rightleftharpoons$	$Cu^{2+}(aq)$ +	$2OH^-(aq)$
Initial (M):		0.00	0.00
Change (M):		$+s$	$+2s$
Equilibrium (M):		s	$2s$

Step 3:

$$K_{sp} = [Cu^{2+}][OH^-]^2$$

$$2.2 \times 10^{-20} = (s)(2s)^2$$

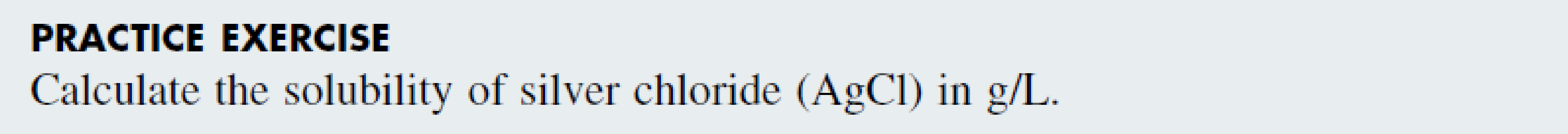
$$s^3 = \frac{2.2 \times 10^{-20}}{4} = 5.5 \times 10^{-21}$$

Solving for s, we get $s = 1.8 \times 10^{-7}\ M$

Knowing that the molar mass of $Cu(OH)_2$ is 97.57 g/mol and knowing its molar solubility, we can calculate the solubility in g/L as follows:

$$\text{solubility of } Cu(OH)_2 = \frac{1.8 \times 10^{-7} \text{ mol } Cu(OH)_2}{1 \text{ L soln}} \times \frac{97.57 \text{ g } Cu(OH)_2}{1 \text{ mol } Cu(OH)_2}$$

$$= 1.8 \times 10^{-5} \text{ g/L}$$



PRACTICE EXERCISE

Calculate the solubility of silver chloride (AgCl) in g/L.

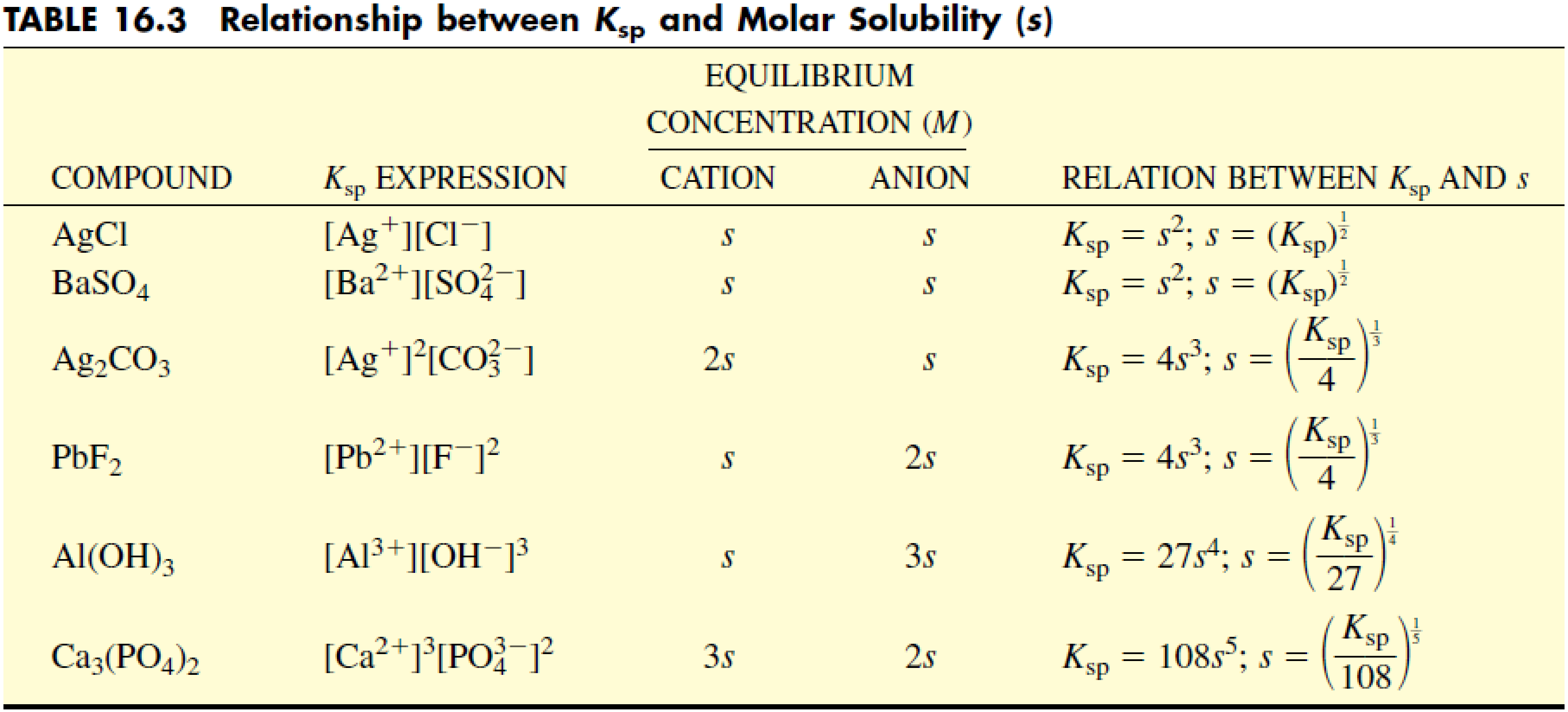


TABLE 16.3 Relationship between K_{sp} and Molar Solubility (s)

COMPOUND	K_{sp} EXPRESSION	EQUILIBRIUM CONCENTRATION (M) CATION	EQUILIBRIUM CONCENTRATION (M) ANION	RELATION BETWEEN K_{sp} AND s
AgCl	$[Ag^+][Cl^-]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	$2s$	s	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
PbF_2	$[Pb^{2+}][F^-]^2$	s	$2s$	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	s	$3s$	$K_{sp} = 27s^4;\ s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
$Ca_3(PO_4)_2$	$[Ca^{2+}]^3[PO_4^{3-}]^2$	$3s$	$2s$	$K_{sp} = 108s^5;\ s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

As the above examples show, solubility and solubility product are related. If we know one, we can calculate the other, but each quantity provides different information.

When carrying out solubility and/or solubility product calculations, keep in mind the following important points:

- ❑ The solubility is the quantity of a substance that dissolves in a certain quantity of water. In solubility equilibria calculations, it is usually expressed as grams of solute per liter of solution. Molar solubility is the number of moles of solute per liter of solution.
- ❑ The solubility product is an equilibrium constant.
- ❑ Molar solubility, solubility, and solubility product all refer to a saturated solution.

Solubility product (Ksp)

- In a saturated solution of a sparingly soluble salt, a dynamic equilibrium exists between the insoluble salt and its dissociated ions
- Example: Adding AgCl to water, a small amount of the salt goes into solution yielding Ag+ and Cl- ions, but the rest remains as excess solid
- Hence the solid AgCl is in equilibrium with Ag+ and Cl- ions
- This can be represented as:

$$AgCl \rightleftharpoons Ag^{+} + Cl^{-}$$

- And can be expressed as

$$K = [Ag^{+}][Cl^{-}]/[AgCl]$$

- Thus Ksp = $[Ag^{+}][Cl^{-}]$

- **Therefore Solubility product (Ksp)** is the product of the activities of the ions in a saturated solution of a sparingly soluble salt
- Since the salt is sparingly soluble, the solution is dilute.
- Ksp = $[Ag^{+}][Cl^{-}]$

- Note: Solubility product is dependent on temperature but nearly independent of the concentration of ions, provided the solution is dilute

Expression for solubility product

- In case where stoichiometric coefficients exist e.g.
- $AxBy_{(s)} \rightleftharpoons xA^{y+} + yB^{x-}$
- Solubility product is given by

  $$Ksp = [A^{y+}]^x[B^{x-}]^y$$

- Example

  $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

  $Ksp = [Ca^{2+}][F^-]^2$

Saturated and unsaturated solutions

- Saturated solution occurs when the ionic product is equal to or greater than the Ksp of the salt
- If ionic product is less than the Ksp, The solution is unsaturated, because more salt can dissolve to raise the concentration of ions
- If ionic product exceeds Ksp, a super saturated solution exists, hence precipitation will occur
- Thus the values of ionic product of a solution can be used to predict whether or not precipitation will occur

Saturated and unsaturated solutions

Example

- Ionic product <Ksp, No precipitation
- Ionic product = Ksp, No precipitation
- Ionic product >Ksp, precipitation occurs

- **Relationship between Ksp and Solubility (s)**
- For a salt e.g. AgCl, if solubility is expressed in mol/L, then [Ag+] and [Cl-] ions is equal to solubility S

- $Ksp = [Ag^+][Cl^-] = S^2$
- Or $s = (Ksp)^{½}$
- Thus, for salt of the type AxBy, if S is the solubility, then from the equation
- $AxBy_{(s)} \rightleftharpoons xA^{y+} + yB^{x-}$
- $[A^{y+}] = xS$, and $[B^{x-}] = yS$
- Thus $Ksp = [xS]^x[yS]^y = x^x y^x S^{(x+y)}$

  Or $S = [Ksp/ x^x y^x]^{(1/(x+y))}$
- Example, For CaF_2

  $[Ca^{2+}] = S$, and $[F-] = 2S$

  $Ksp = (S)(2S)^2 = 4S^3$

  Thus $S = (Ksp/4)^{1/3}$

Examples

- The solubility product of Ag_2CrO_4 is 9 x 10^{-12} at 298 K. Calculate the solubility of Ag_2CrO_4
- Ans: Let the solubility of the salt be S,
- Thus, $[CrO_4^{2-}] = S$, and $[Ag^+] = 2S$
- Thus, 1 mol of $AgCrO_4$ produces 2 moles of Ag+ ions
- $Ksp = [Ag^+]^2[CrO_4^{2-}] = (2S)^2(S) = 9x\ 10^{-12}$

Organic Chemistry

What is organic chemistry?

Organic chemistry is the study of the chemistry of carbon compounds.

The compounds of carbon are the central substances of which all living things on this planet are made.

Every living organism is made of organic chemicals.

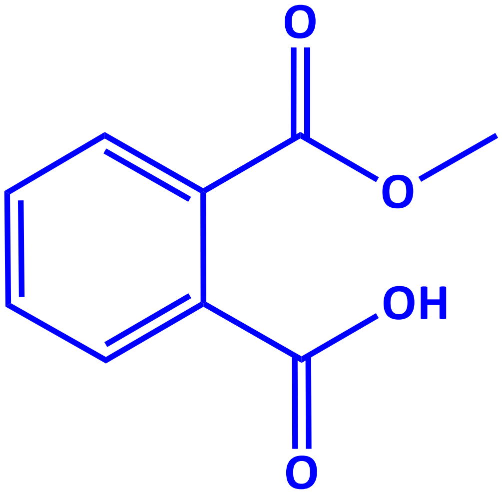
The proteins that make up your hair, skin, and muscles; the DNA that controls your genetic heritage; the foods that nourish you; and the medicines that heal you are all organic chemicals.

Anyone with a curiosity about life and living things, and anyone who wants to be a part of the remarkable advances now occurring in medicine and the biological sciences, must first understand organic chemistry.

Examples of Organic Compounds

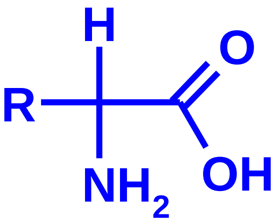
CH_4

Methane
(Chief constituent of natural gas)



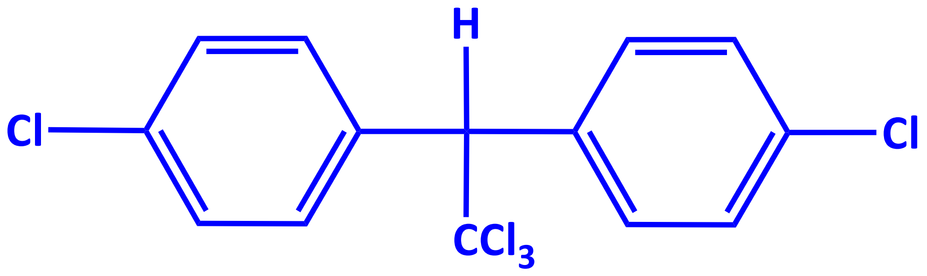
Acetylsalicylic acid
(Aspirin)

(Pain reliever)



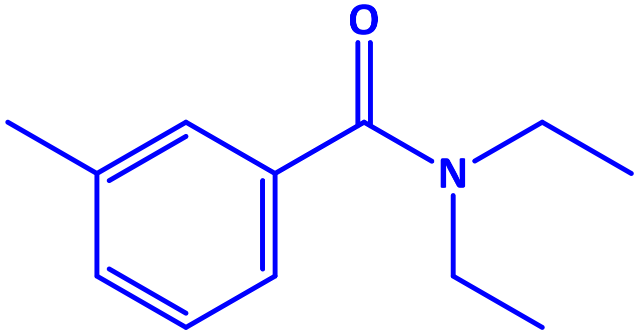
Aminoacids

(The building blocks of proteins)



1,1,1-Trichloro-bis(p-chlorophenyl) ethane (DDT)

(Insecticide)



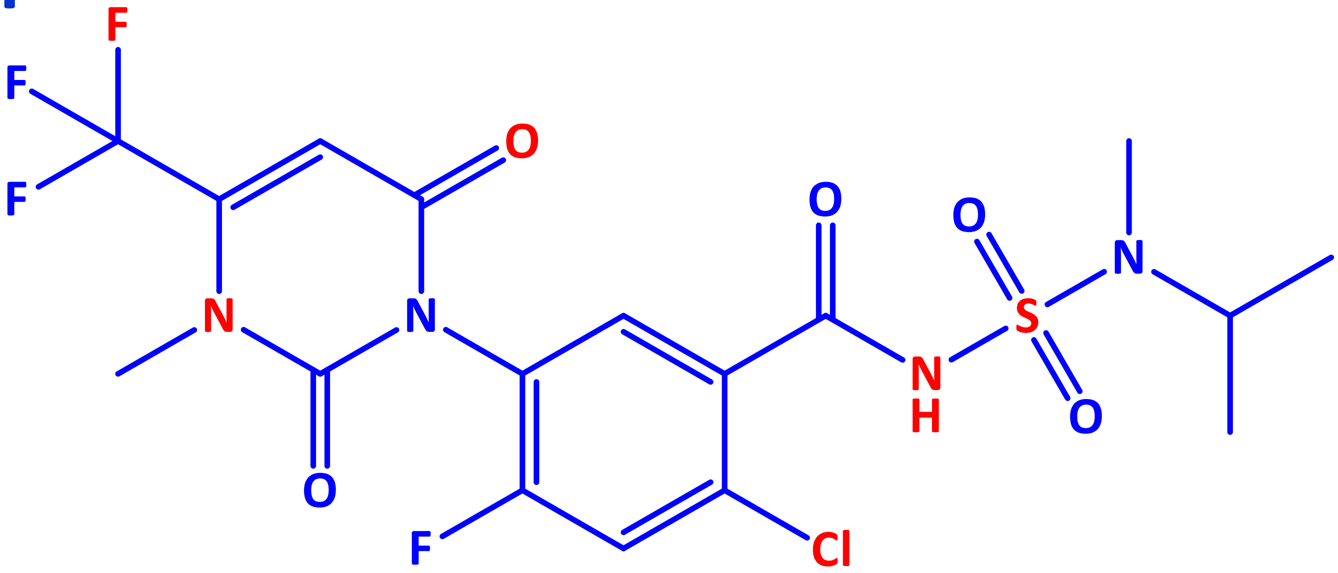
N,N-Diethyl-m-toluamide (DEET)

DEET, the active ingredient in the most widely used insect repellents, is effective against mosquitoes, fleas, and ticks.

Polyethylene

Although carbon is the principal element in organic compounds, most also contain hydrogen, and many contain nitrogen, oxygen, phosphorous, sulfur, halogens or other compounds.

Example

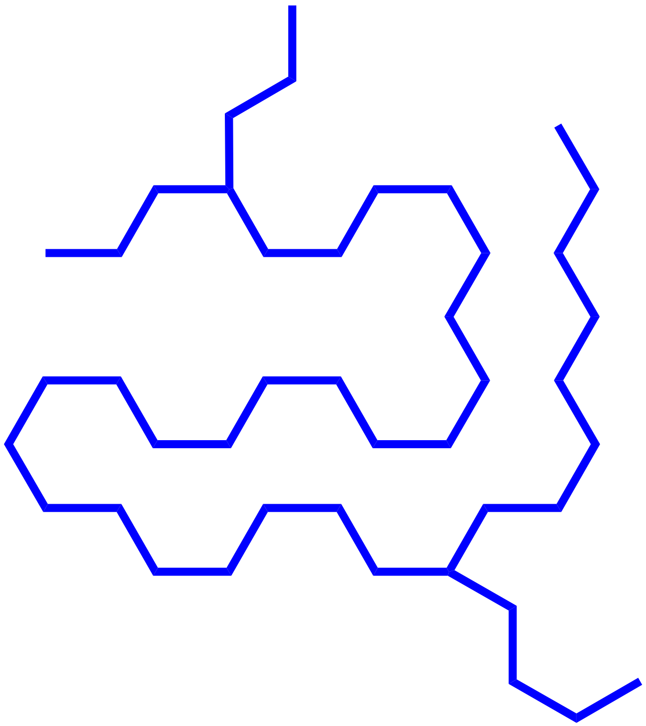


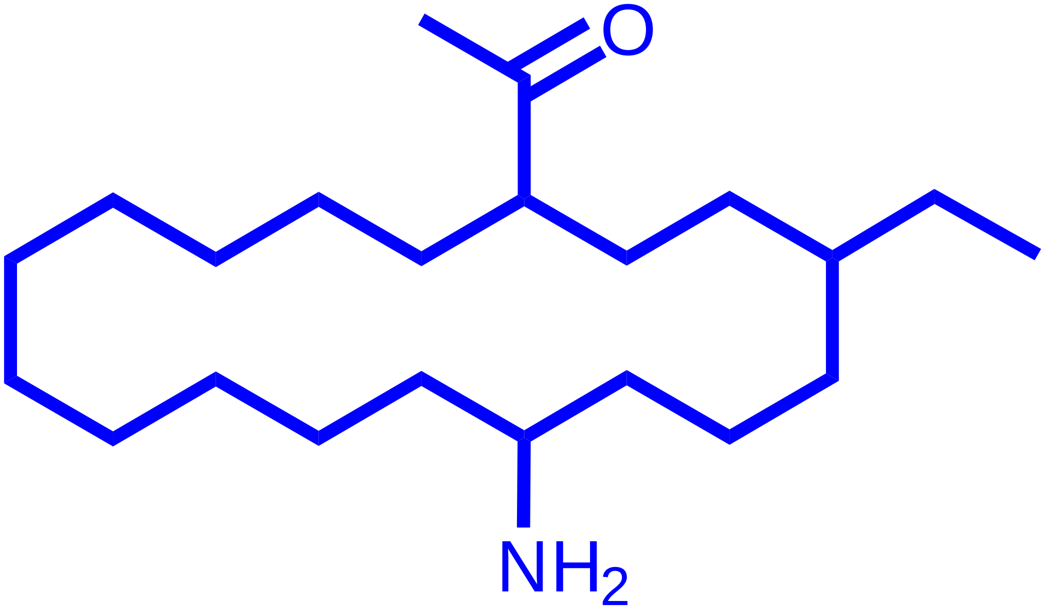
Saflufenacil (Herbicide)

There being over 110 elements in the periodic table, why is carbon so special? What is that sets carbon apart from all other elements in the periodic table?

There are only about 100,000 inorganic compounds but the number of organic compounds is more than 18,000,000!

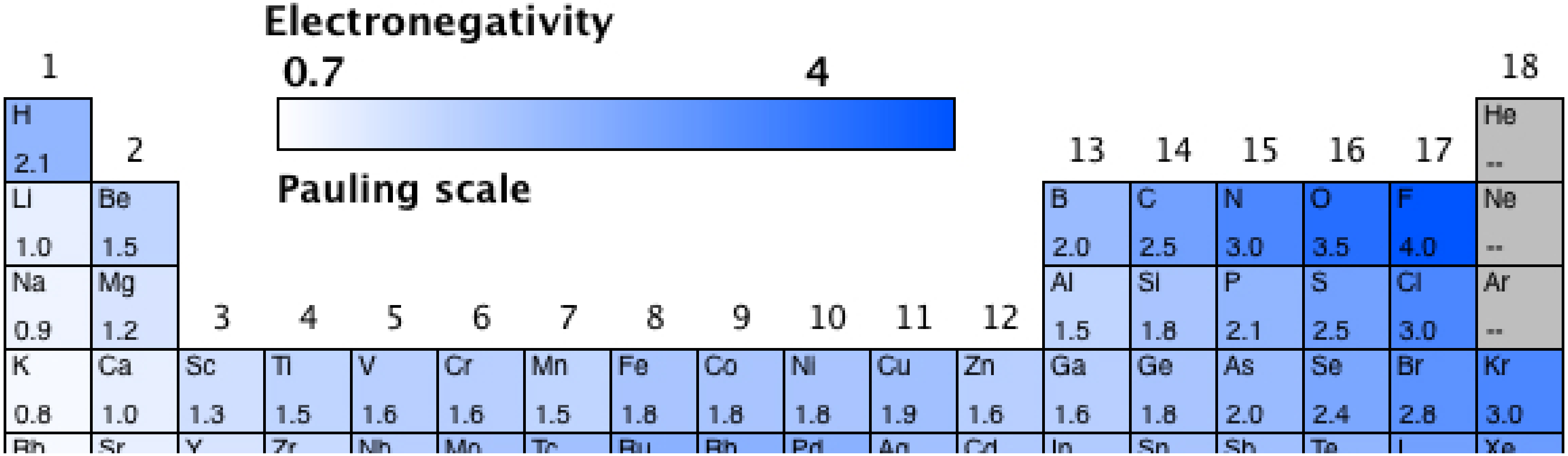
Carbon atoms can attach themselves to one another to an extent not possible for atoms of any other elements.





Each arrangement corresponds to a different compound, and has it own characteristic set of physical and chemical properties.

Carbon in the Periodic Table

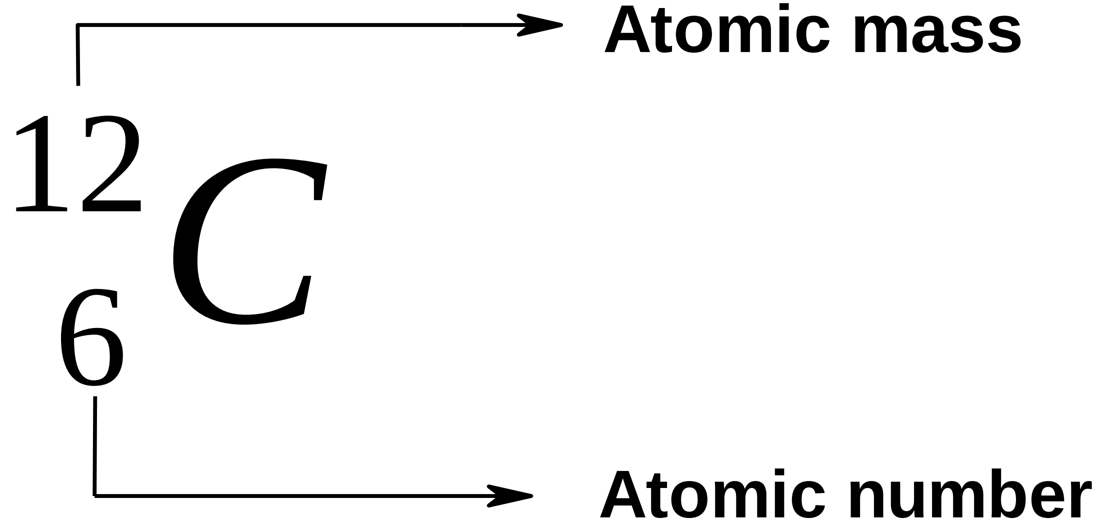


Electronegativity

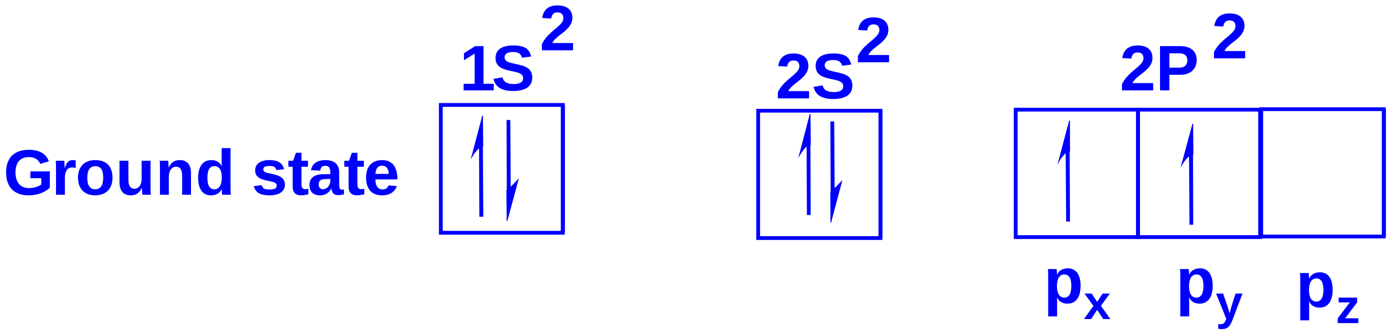
0.7 4

Pauling scale

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H 2.1																	He --
Li 1.0	Be 1.5											B 2.0	C 2.5	N 3.0	O 3.5	F 4.0	Ne --
Na 0.9	Mg 1.2											Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0	Ar --
K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.6	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	Kr 3.0
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe



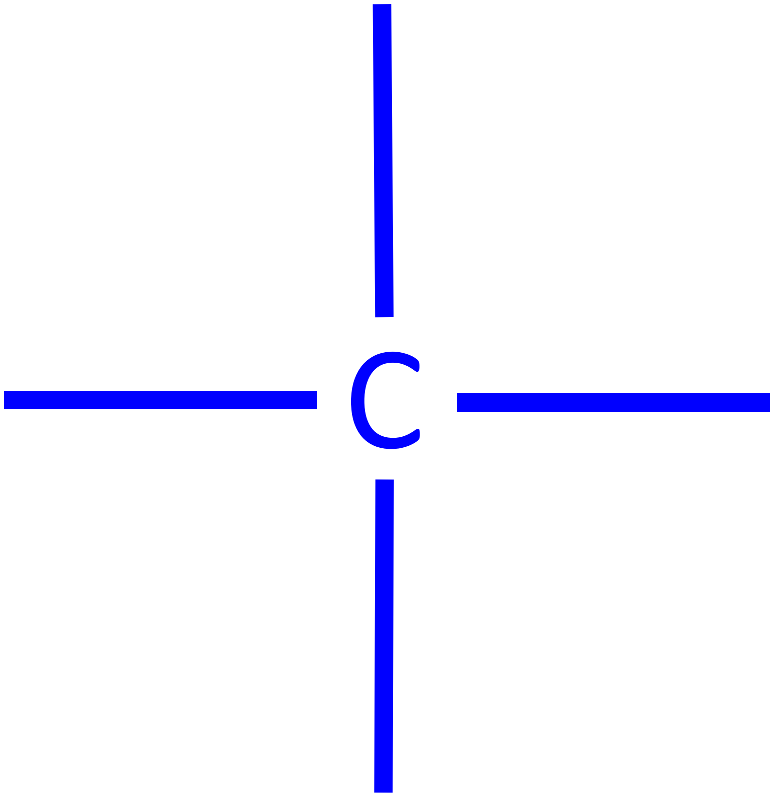
Electronic configuration: $1s^2 2s^2 2p^2$



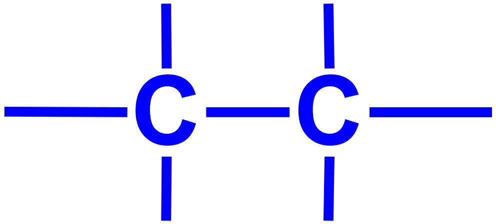
Carbon has four electrons in its outer most shell and requires four more electrons in a covalent bond to have a complete outer shell of electrons.

Bond formation in carbon

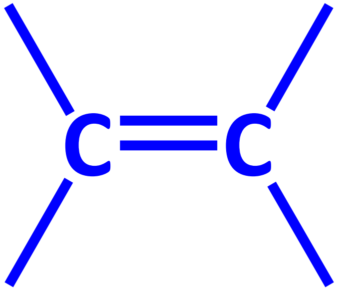
1. Carbon is tetravalent; that is it forms four bonds



2. **A carbon atom can use one or more of its valence electrons to form bonds with other carbon atoms.**



Single bond



Double bond

Triple bond

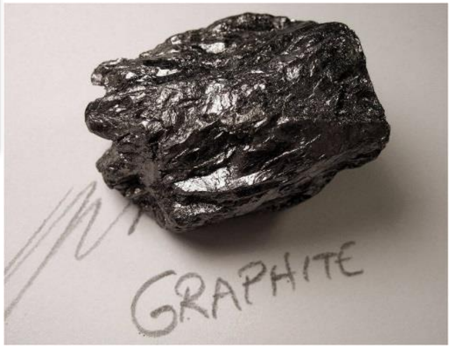
Allotropes of Carbon

When elements can exist in more than one form, these different forms are called allotropes.

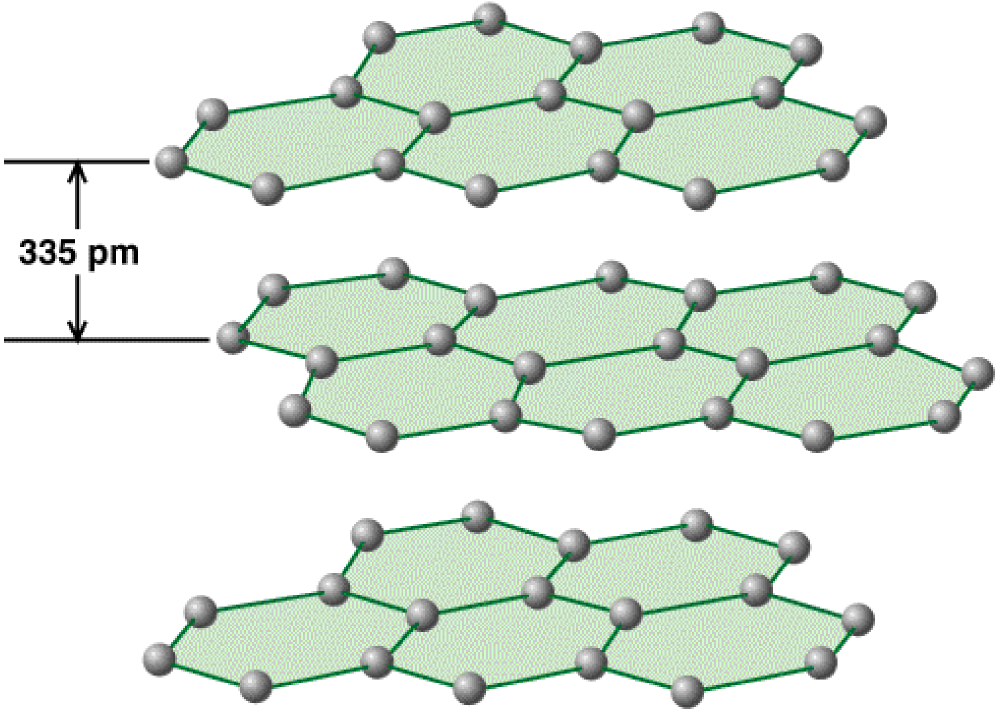
The allotropes of carbon are:

- **Graphite**
- **Diamond**
- **Buckministerfullerene**

Graphite



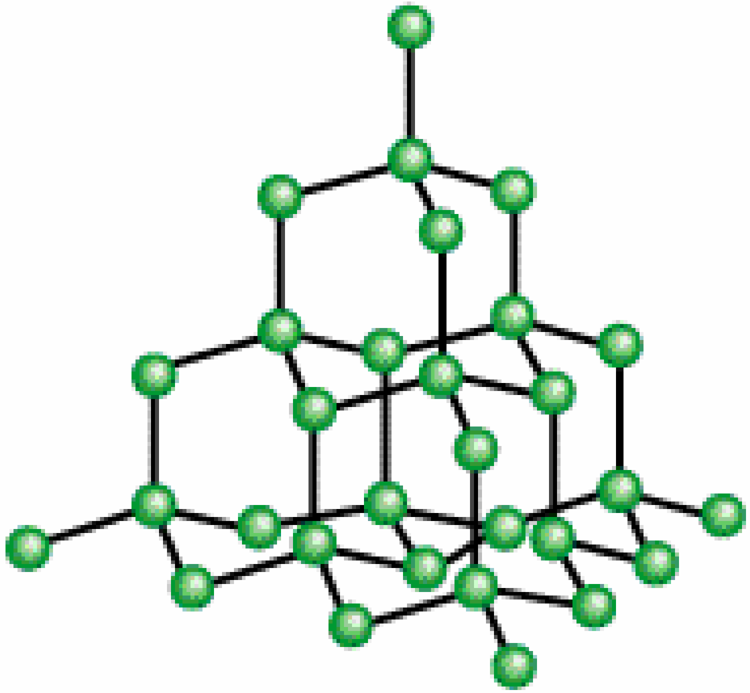
- Graphite is an opaque, dark and greasy solid that is used in the ‘leads’ of pencils, an electrical conductor and as a lubricant.
- In graphite sheets of covalently bonded carbon atoms are held together by weak van der Waals forces, hence making graphite a lubricant.
- Ordinary “lead” pencils actually are made of a form of graphite.



- The sheets form a regular array of hexagons linked together.
- Carbon is capable of forming four covalent bonds.
- In graphite, however, it forms only three bonds. Hence, there are unbonded electrons.
- Some of these become delocalized-meaning, they escape the control of their parent atoms and move around the whole of the crystal. For this reason, graphite is capable of carrying a current.

Diamond

- Diamond is a lustrous crystal and the hardest substance known to man.
- It is used in addition to as jewellery as tips of drills, or other industrial appliances where such strength is required.
- The structure of diamond is based on a tetrahedron. In each tetrahedron a carbon atom sits in the middle surrounded by four other carbons.

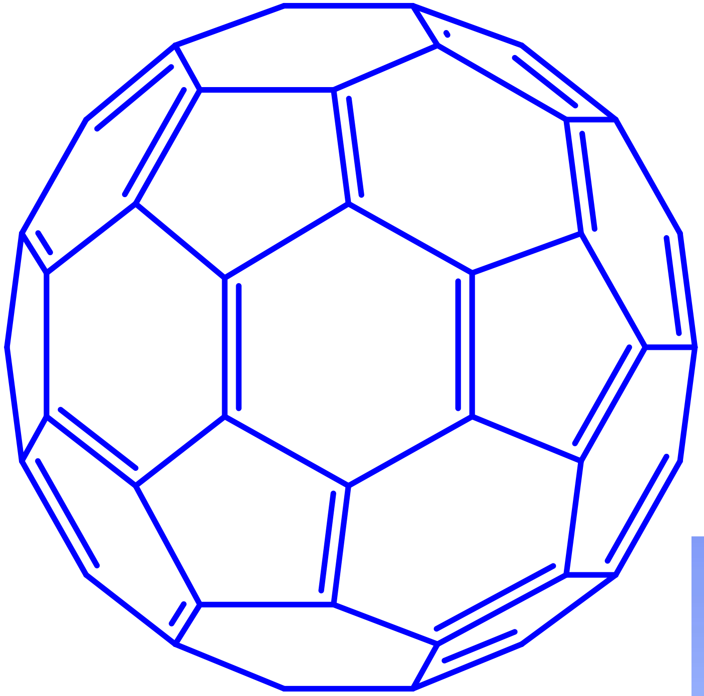


This structure repeats infinitely in all directions.

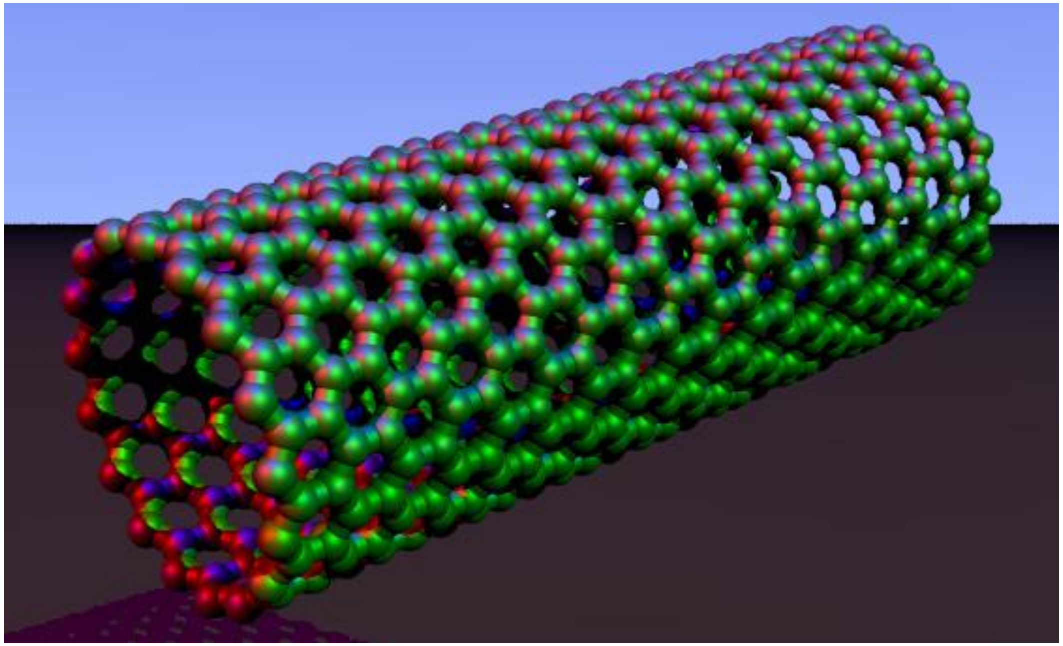
- These tetrahedral interlink form a single crystal.
- Since each carbon is covalently bonded to four others, there are no declocalized electrons, so diamond does not conduct electricity, it is an insulator.

Buckministerfullerene

- In addition to diamond and graphite a third form of pure carbon was discovered in 1985 opening a new era of chemistry (1996 Nobel Prize in chemistry).
- This allotrope of carbon is sometimes called fullerene or bucky ball.
- It consists of a hollow cluster of 60 carbons, and is the most symmetrical large molecule known.



Buckministerfullerene



Nanotubes

Problem

Diamond and graphite are allotropes of carbon.

I. Define the term allotrope

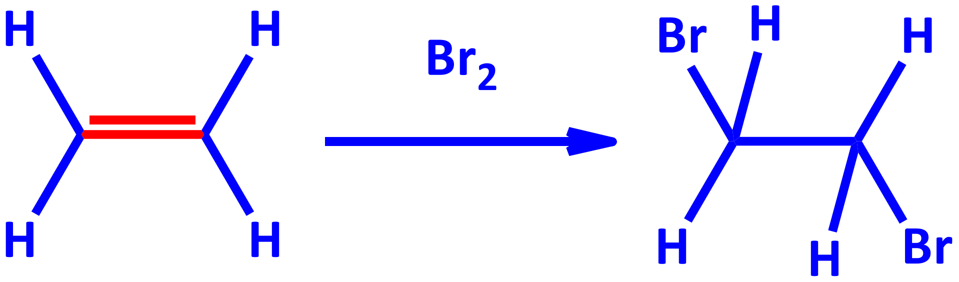
II. Graphite is used to make lubricants for engines. Explain, in terms of its structure, why graphite can act as a lubricant.

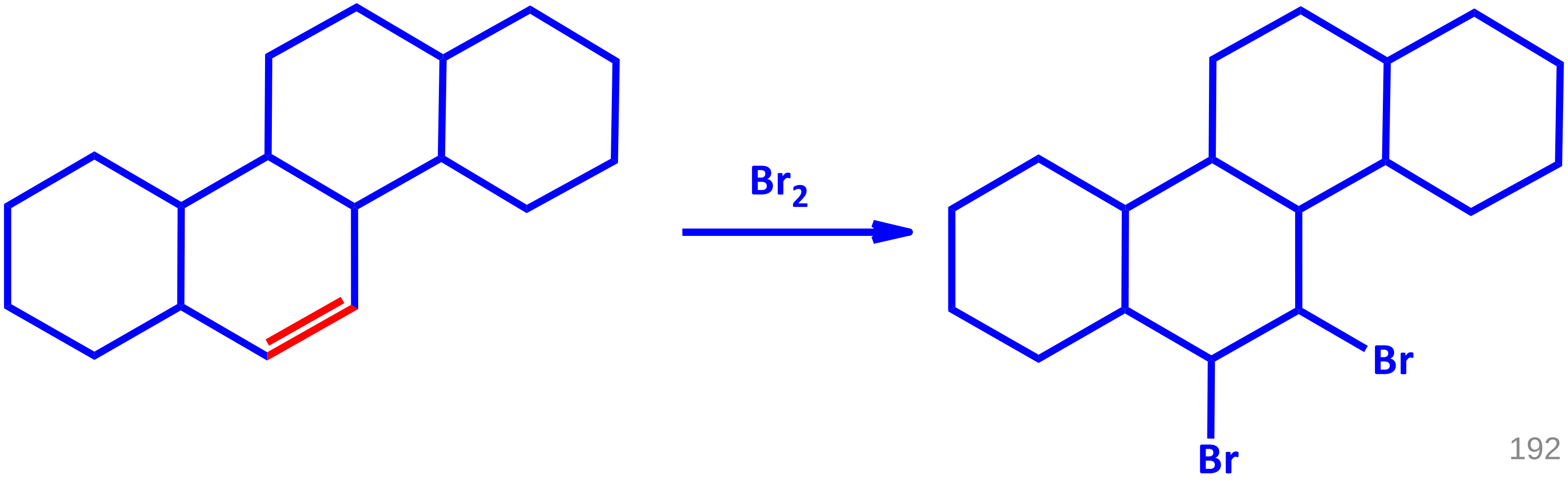
III. Give one use of diamond which depends on its hardness.

Functional Groups

- Chemists have learned through many years of experience that organic compounds can be classified according to their structural features and that members of a given family often have similar physical and chemical behaviour.
- The structural features that make it possible for classify organic compounds by reactivity are called **functional groups**.

- A functional group is part of a molecule where most of its chemical reactions occur. It is the part that effectively the compound’s chemical properties (and most of its physical properties as well).

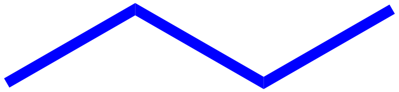




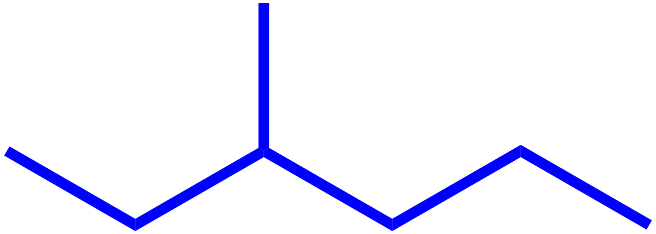
The chemistry of every molecule, regardless of size and complexity, is determined by the functional group it contains.

Alkanes

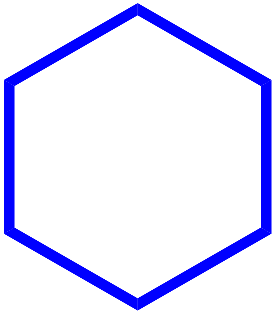
- **They contain only C-C single bonds.**
- **The alkanes are the simplest class of organic molecules because they contain no functional groups. They are extremely unreactive.**



Butane



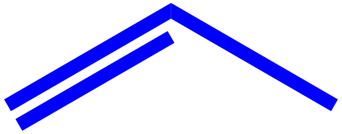
3-Methylhexane



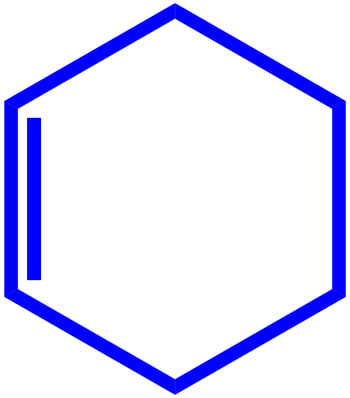
Cyclohexane

Alkenes

- Sometimes called olefins are hydrocarbons which contain C=C double bonds.



Prop-1-ene

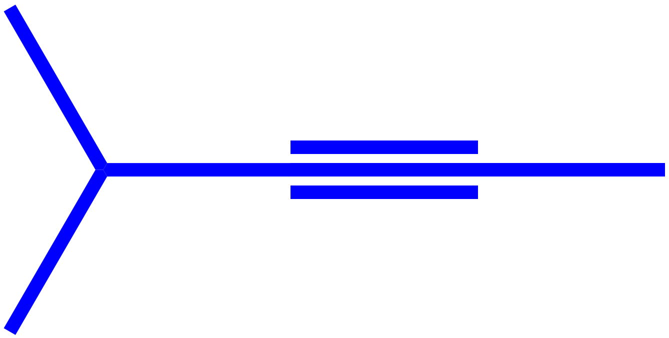


Cyclohexene

Alkynes

- Alkynes are hydrocarbons that contain C≡C triple bond.

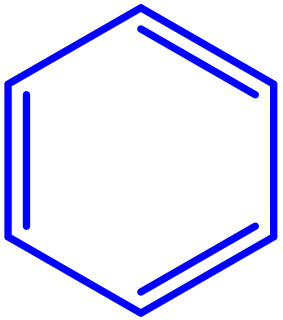
Ethyne (Acetylene)



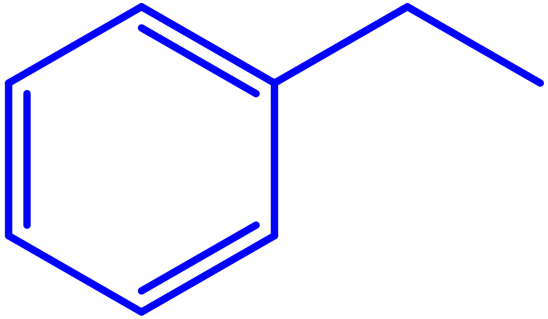
4-Methylpent-2-yne

Aromatic

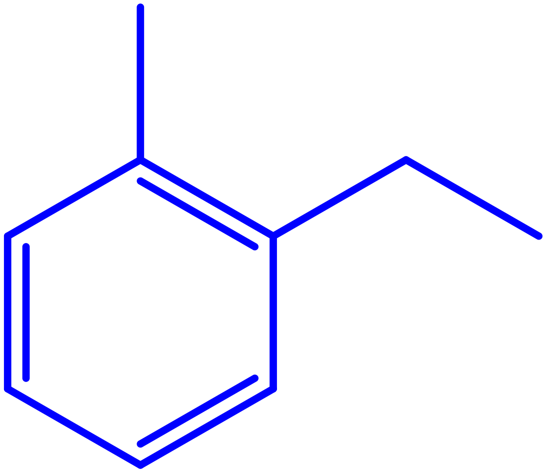
- **Compounds that contain benzene.**



Benzene



Ethylbenzene

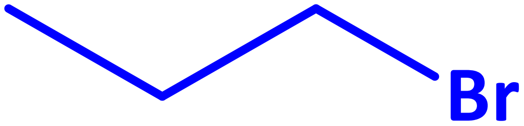


1-Ethyl-2-methylbenzene

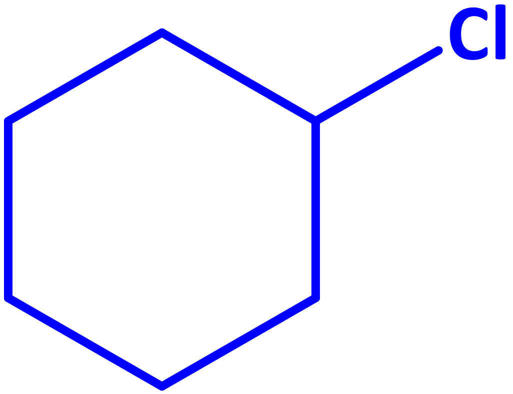
Alkyl Halides

- Contain an alkyl group bonded to F, Cl, Br or I.

R——X where X is a halogen



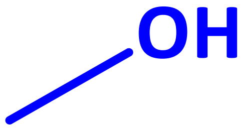
1-Bromopropane



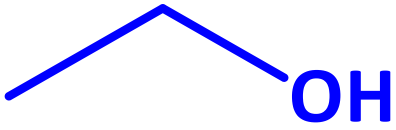
Chlorocyclohexane

Alcohols

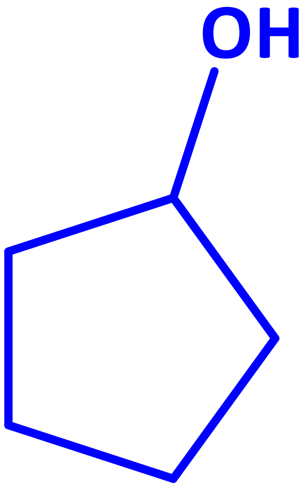
- **Alcohols contain a hydroxyl (OH) group.**



Methanol



Ethanol

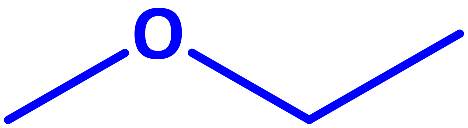


Cyclopentanol

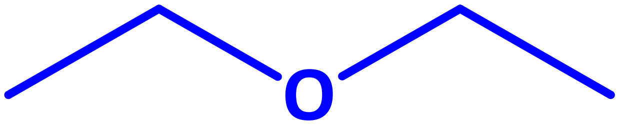
Ethers

- Ethers contain $R_1–O–R_2$. It refers to any compound that has two alkyl groups linked through an oxygen atom.

$$R_1\text{-}O\text{-}R_2$$



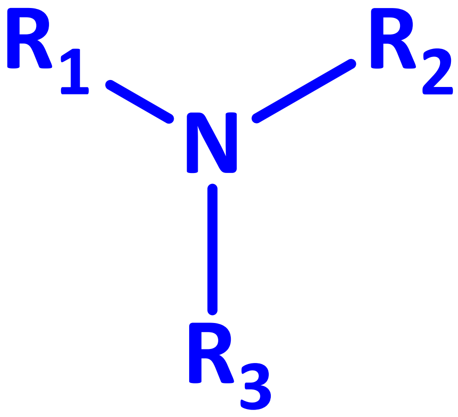
Ethyl methyl ether

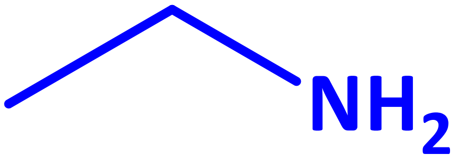


Diethyl ether

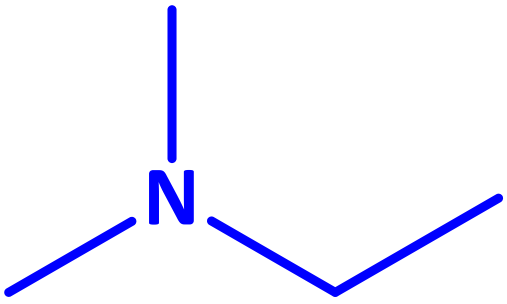
Amines

- **Amines contain the amino ($NR_1R_2R_3$) group, a nitrogen attached to an alkyl group.**





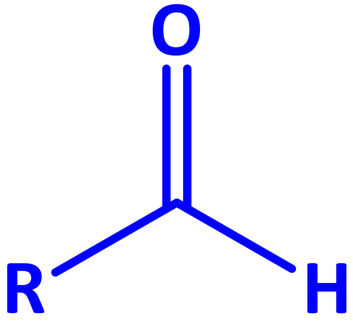
Ethanamine



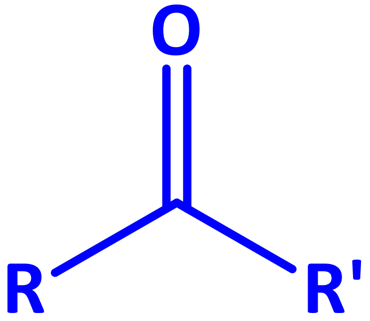
N**,*****N*****-Dimethylethanamine**

Alhdeydes and Ketones

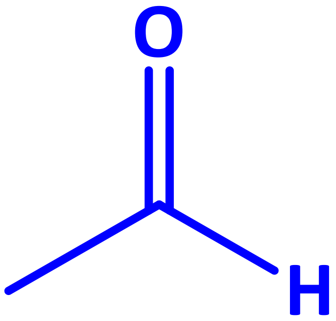
- Aldehydes (R–CHO) and ketones (R_1–CO–R_2) contain the carbonyl group C=O.



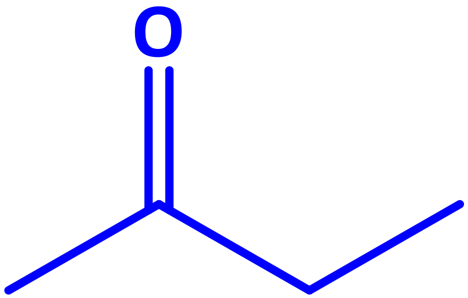
Aldehyde



Ketone



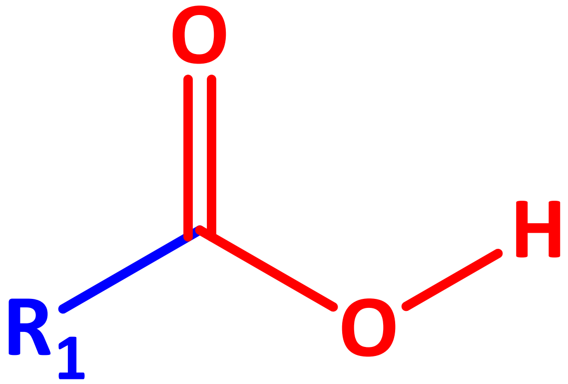
Acetaldehyde

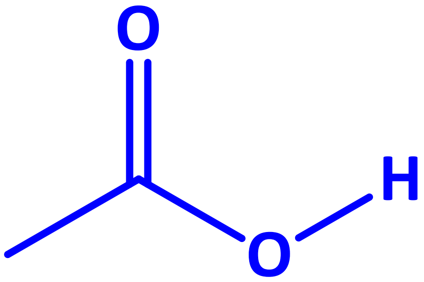


Butan-2-one

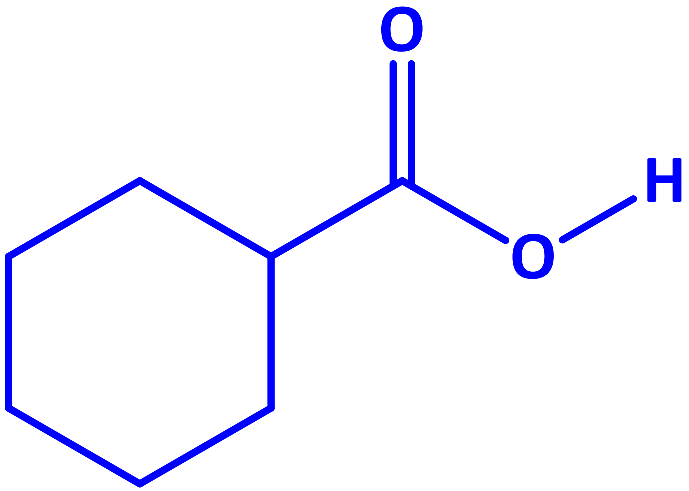
Carboxylic Acids

- Carboxylic acids ($R–CO_2H$) contain the carboxyl group CO_2H.





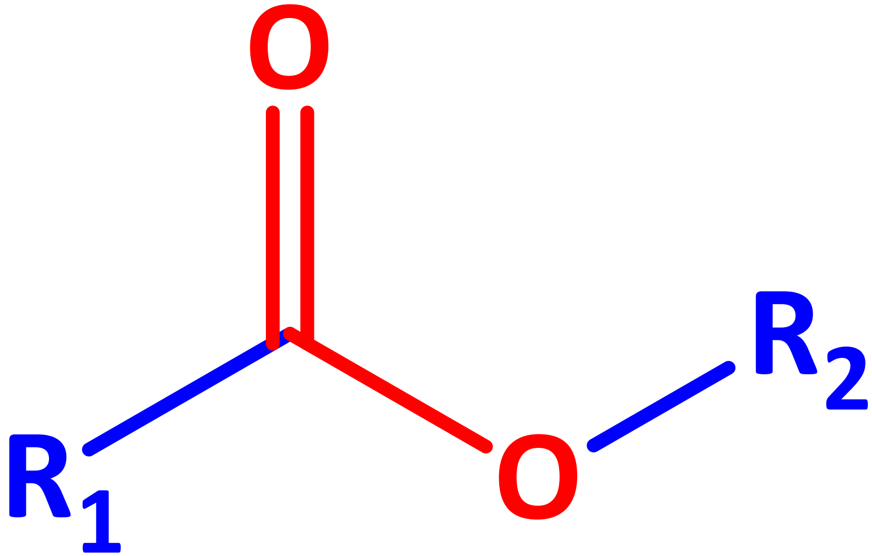
Acetic acid (Vinegar)



Cyclohexanecarboxylic acid

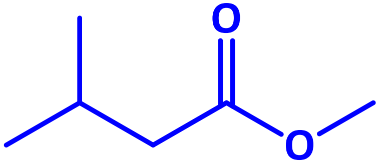
Esters

- Esters ($R_1–CO_2-R_2$) contain a carboxyl group with an extra alkyl group ($-CO_2R$).

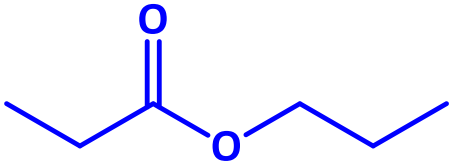


Commercial applications of esters

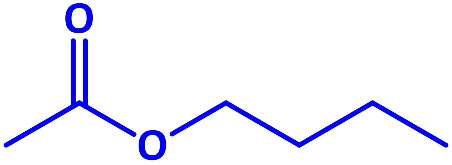
The characteristics fruity smell of esters lead to their use in artificial fruit essences.



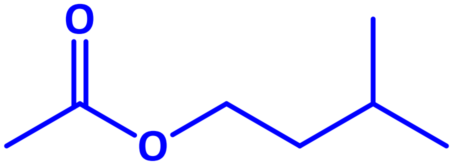
Methyl 3-methylbutanoate



Propyl propionate

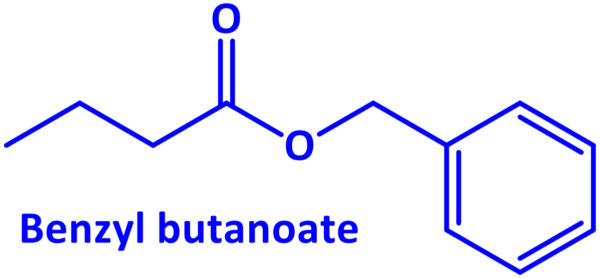


Butyl acetate



3-Methylbutyl acetate

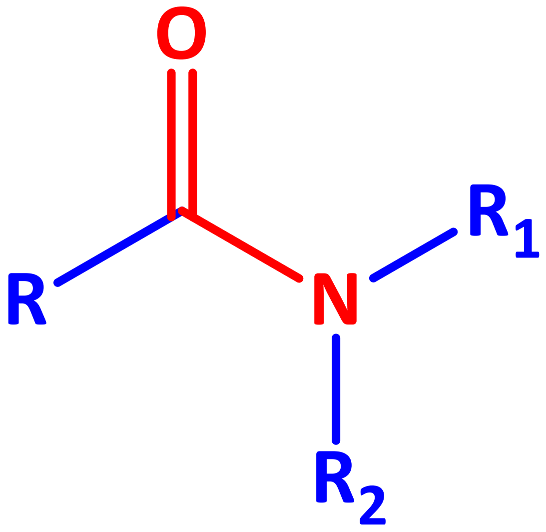
Methyl octanoate

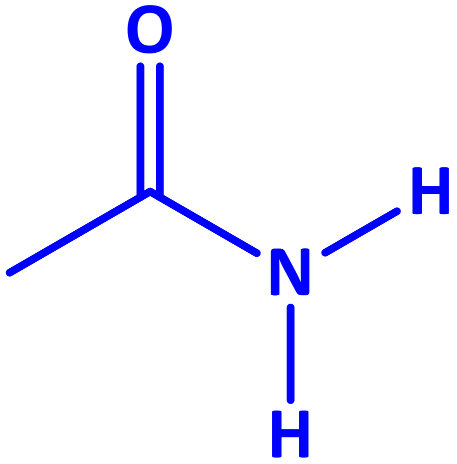


Benzyl butanoate

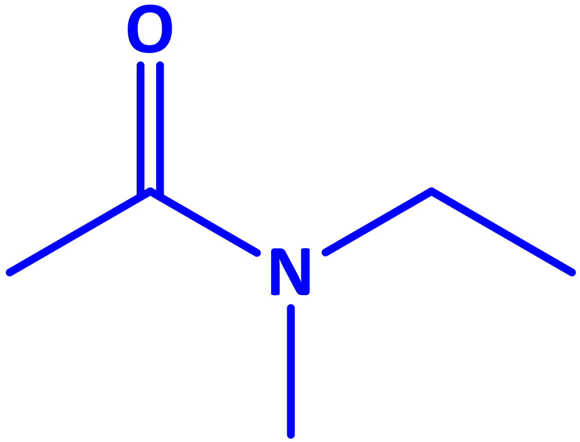
Amides

- **Amides ($RCONR_1R_2$)**



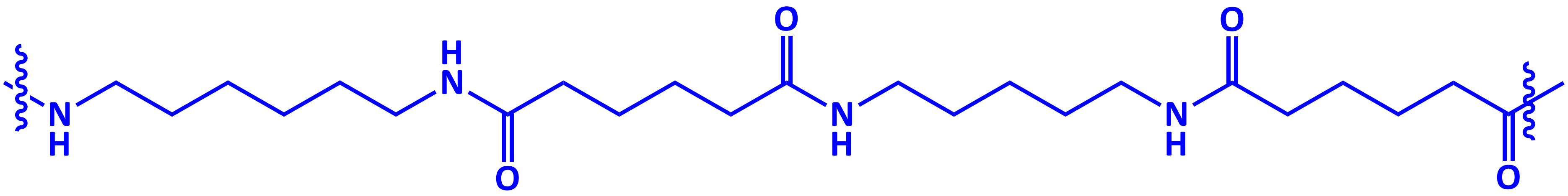


Acetamide



***N*-ethyl-*N*-methylacetamide**

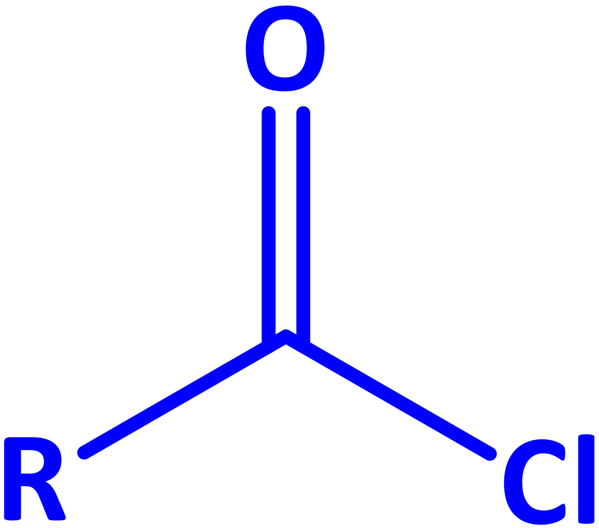
Nylon 6,6

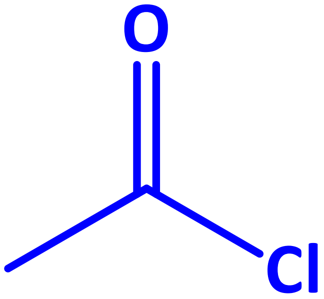


Polymer

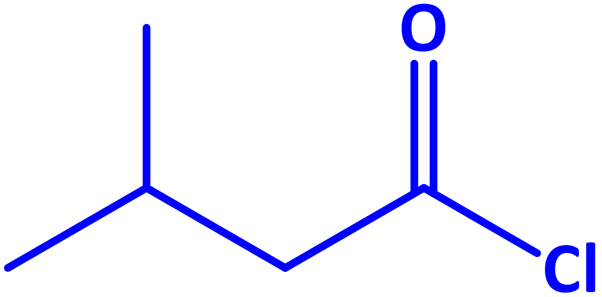
Acid Chlorides

- **Acid chlorides (R–COCl)**

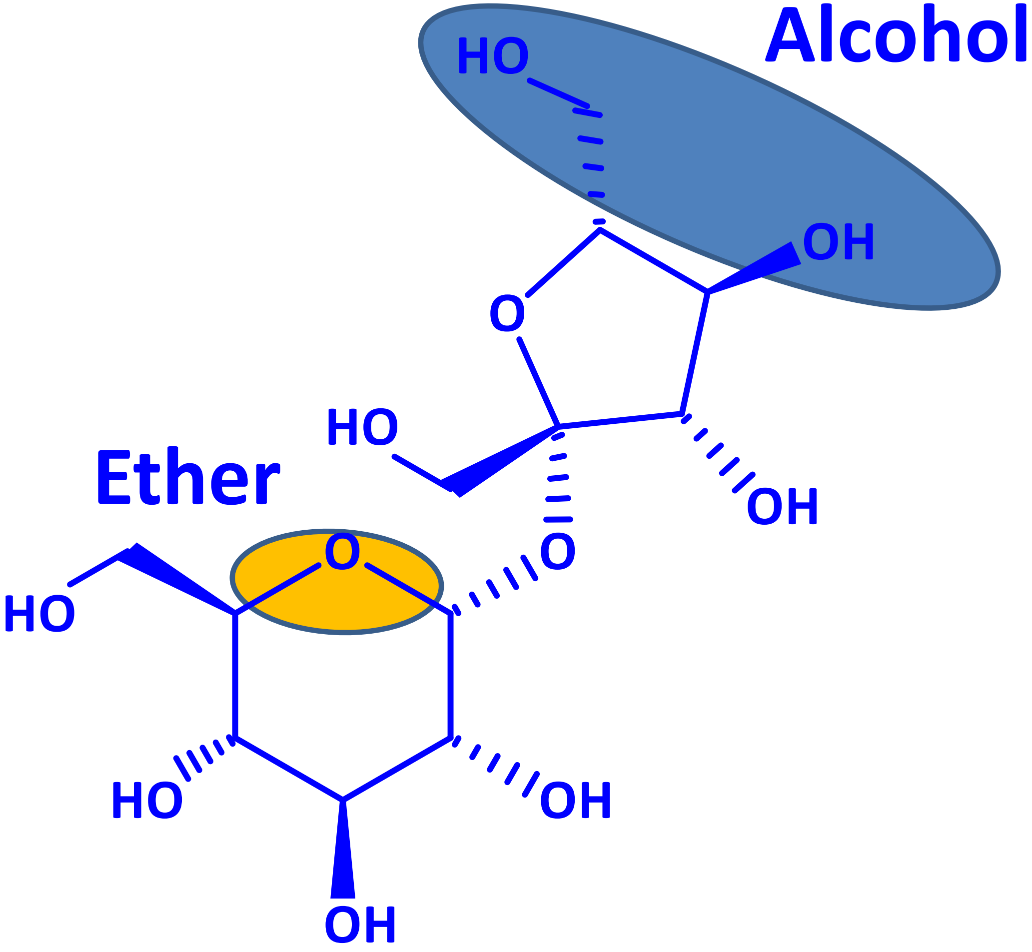




Acetyl chloride

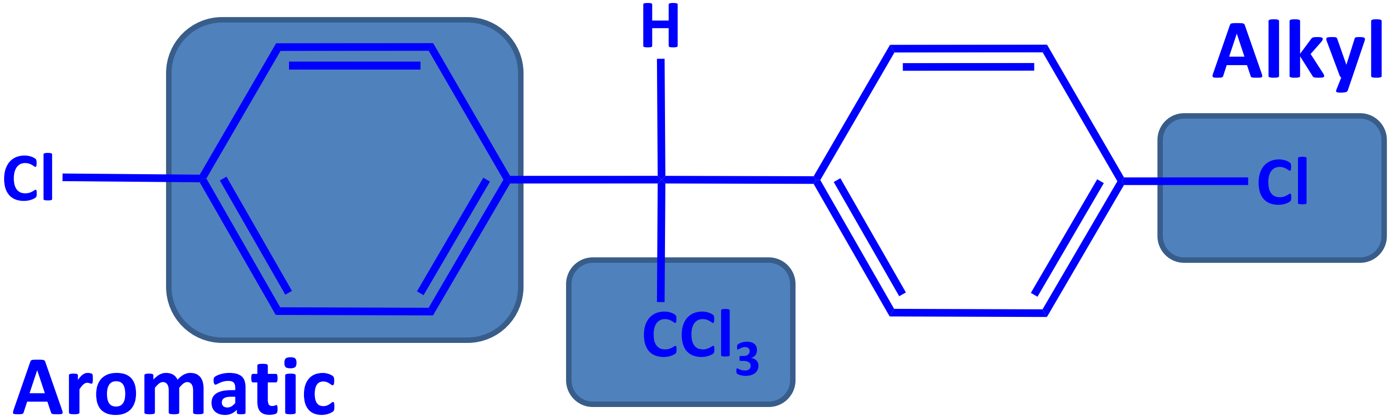


3-Methylbutanoyl chloride



Sucrose

DDT

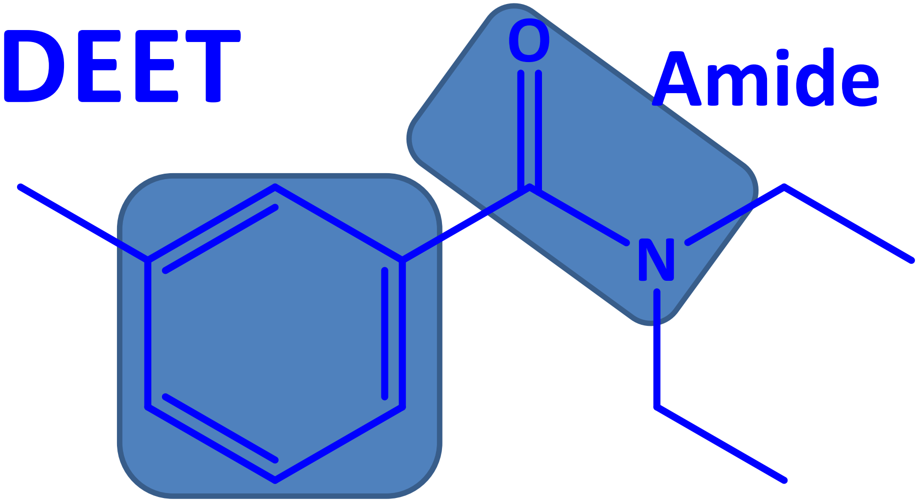


Aromatic

Alkyl halide

Alkyl halide

DEET

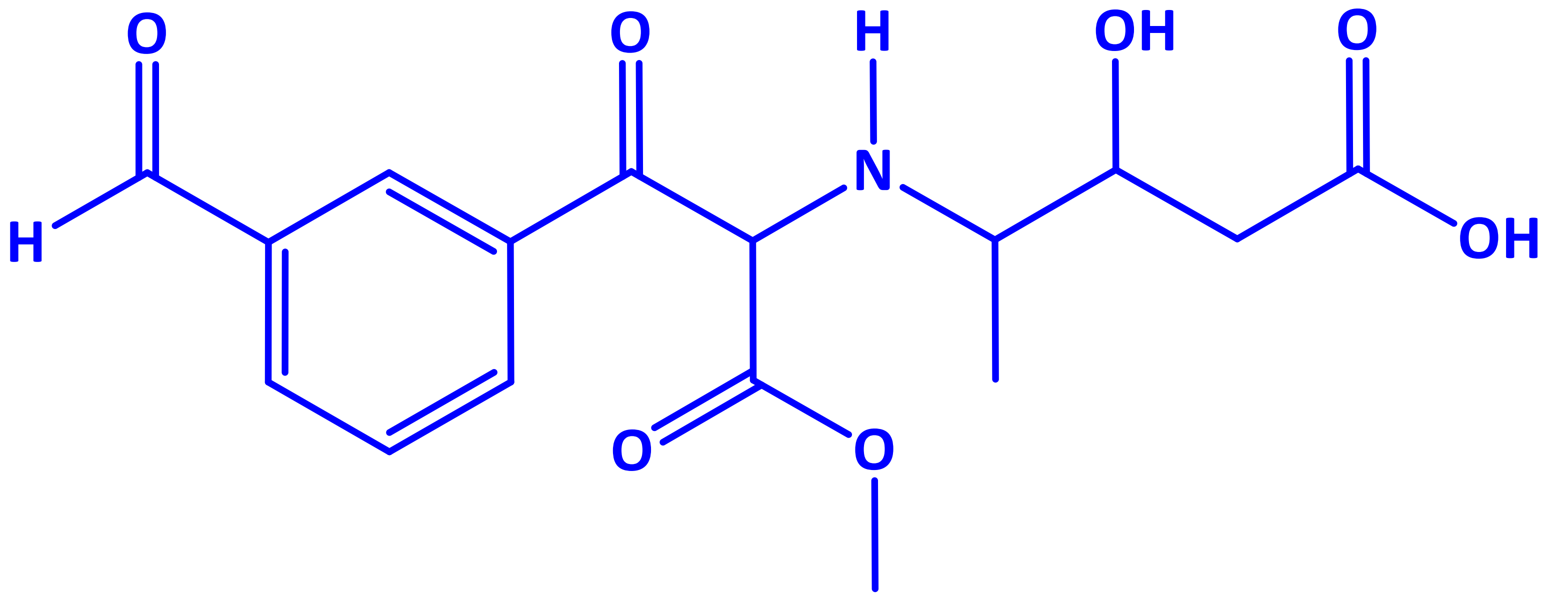


Amide

Aromatic

Problem

In the following structure circle and identify the functional groups.

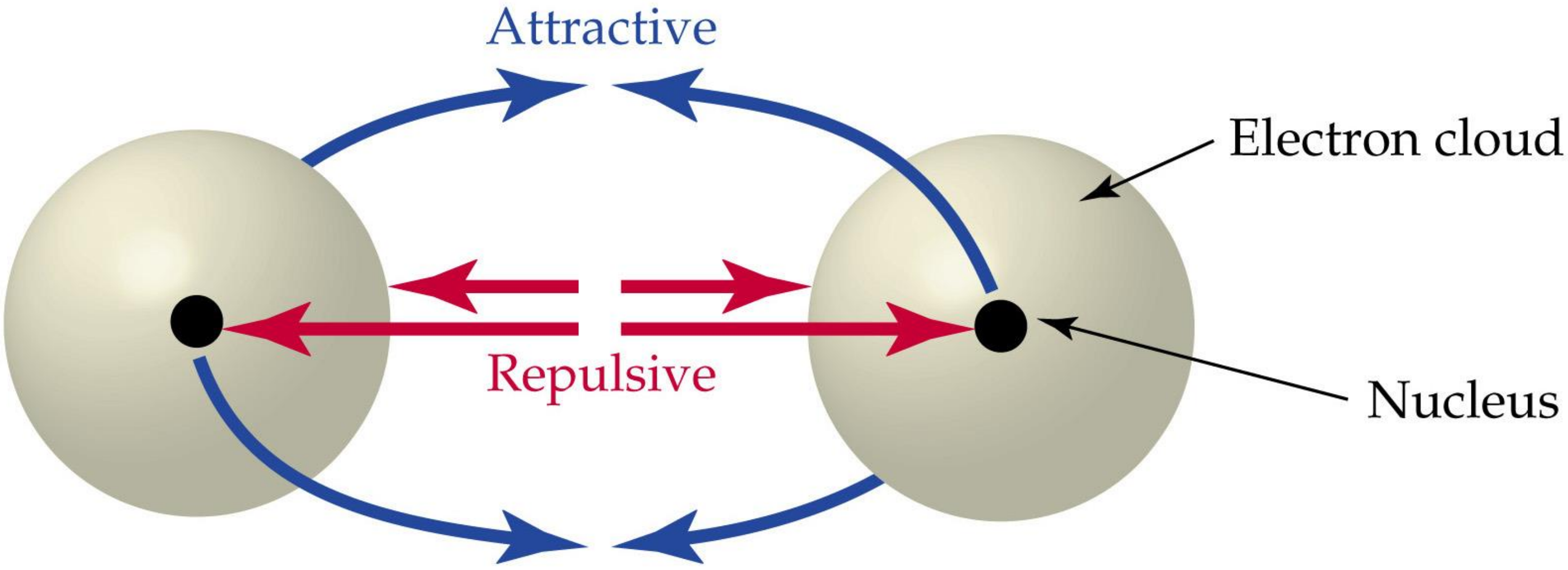


Bonding in carbon compounds
Covalent bond
and
Hybridization

Main-group elements tend to undergo reactions that leave them with eight outer-shell electrons. That is, main-group elements react so that they attain a noble gas electron configuration with filled s and p sublevels in their valence electron shell.

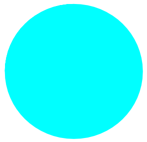
- **Valence e^- play a fundamental role in chemical bonding.**
- **e^- transfer leads to *ionic bonds.***
- **Sharing of e^- leads to *covalent bonds.***
- **e^- are transferred of shared to give each atom a noble gas configuration**
  - ***the octet.***

When bringing together two atoms that are initially very far apart. Three types of interaction occur:

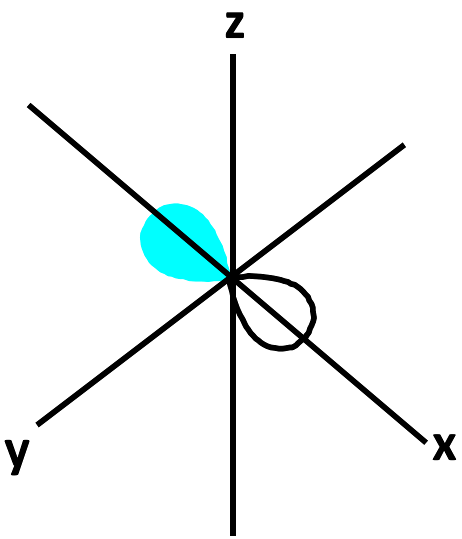


A covalent H-H bond is the net result of attractive and repulsive electrostatic forces.

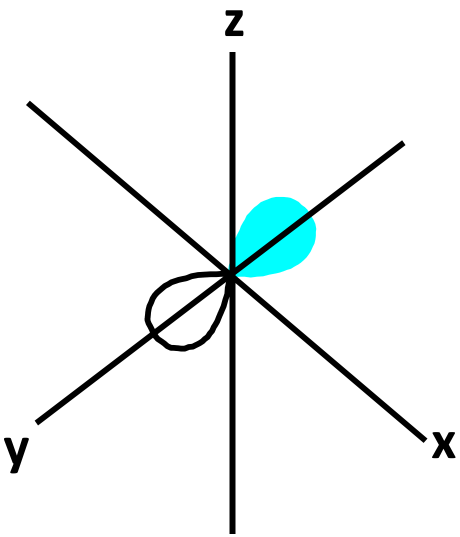
Hybridization of Carbon



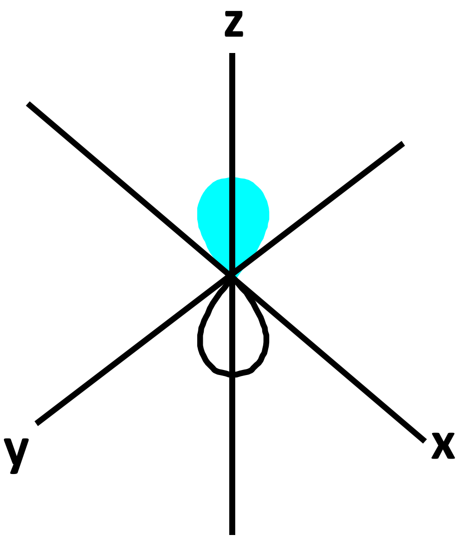
s



p_x



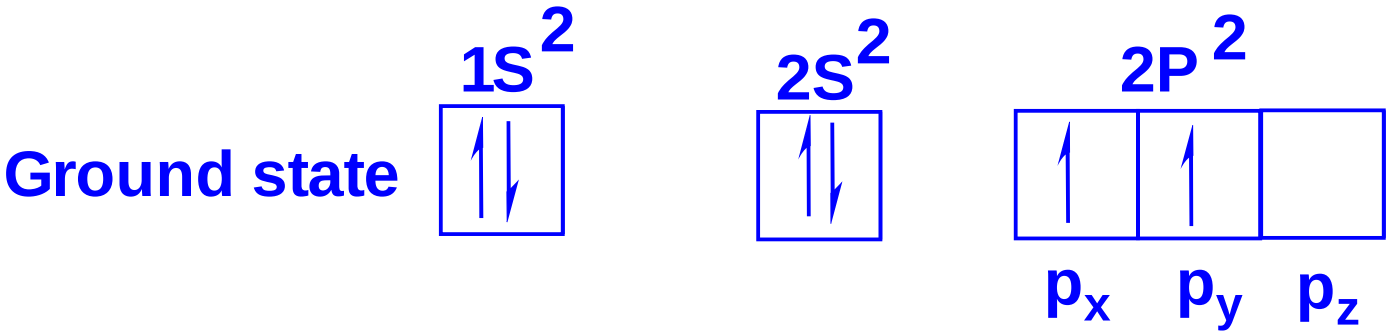
p_y



p_z

Carbon has, outside its nucleus, six electrons and therefore the ground state electronic configuration of carbon is:

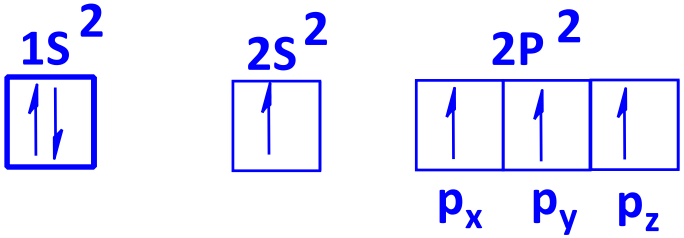
$$1S^2\ 2S^2\ 2P^2$$



This, however, represent the ground state of the carbon atom in which only two unpaired electrons are available for bond formation with other atoms, i.e. at first sight carbon might appear to be only divalent.

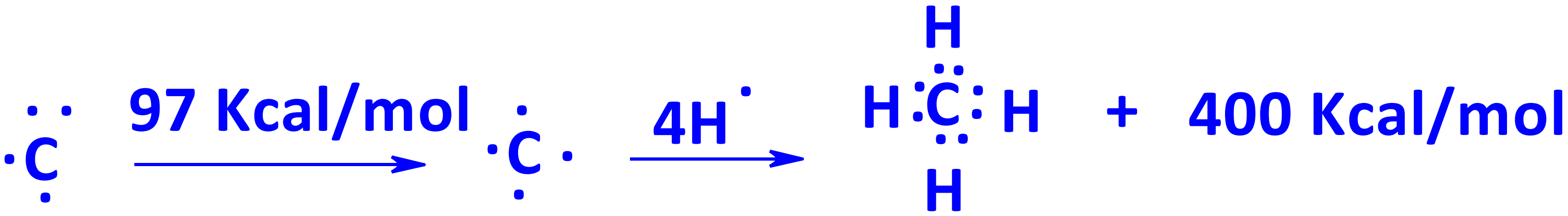
Ground state $\xrightarrow{97\ \text{Kcal/mol}}$ Excited state

Excited state



$1S^2\ 2S^1\ 2P_x^1\ 2P_y^1\ 2P_z^1$

A typical C-H has a bond strength of 100 Kcal/mol



Net-Energy change = (400-97) Kcal/mol = 300 Kcal/mol

In the excited state carbon has four unpaired electrons and can form four bonds with hydrogen.

Methane - sp^3 Hybridized

What is the nature of the four C-H bonds in methane?

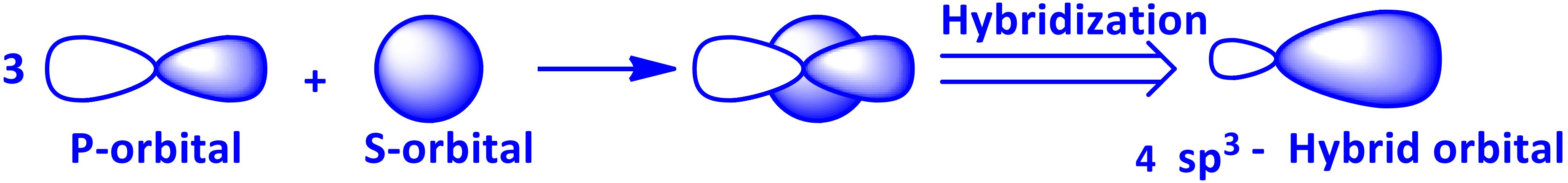
Since excited carbon uses two kinds of orbitals (2s and 2p) for bonding purpose, we might expect methane to have two kinds of C-H bonds.

$$1S^2\ 2S^1\ 2P_x^1\ 2P_y^1\ 2P_z^1$$

In fact this is not the case.

A large amount of evidence show that all four C-H bonds in methane are identical and the bond angles are 109.5°.

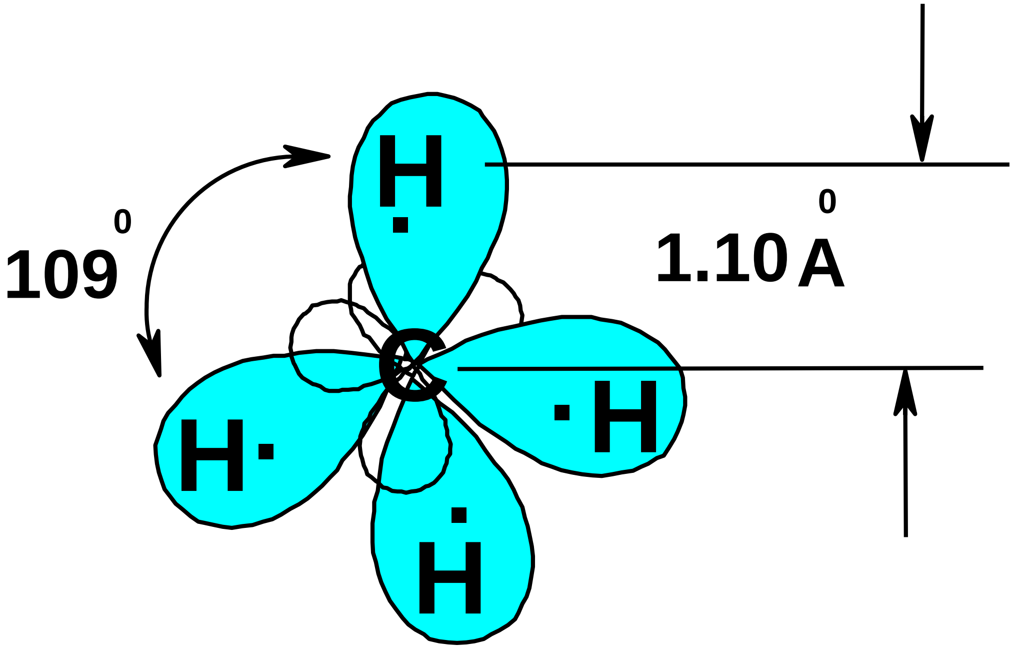
The valence orbitals of a carbon atom are neither s or p but a hybrid or mixture of orbitals.



Hybridization is the combination of two or more atomic orbitals to form the same number of hybrid orbitals, each having the same shape and energy.

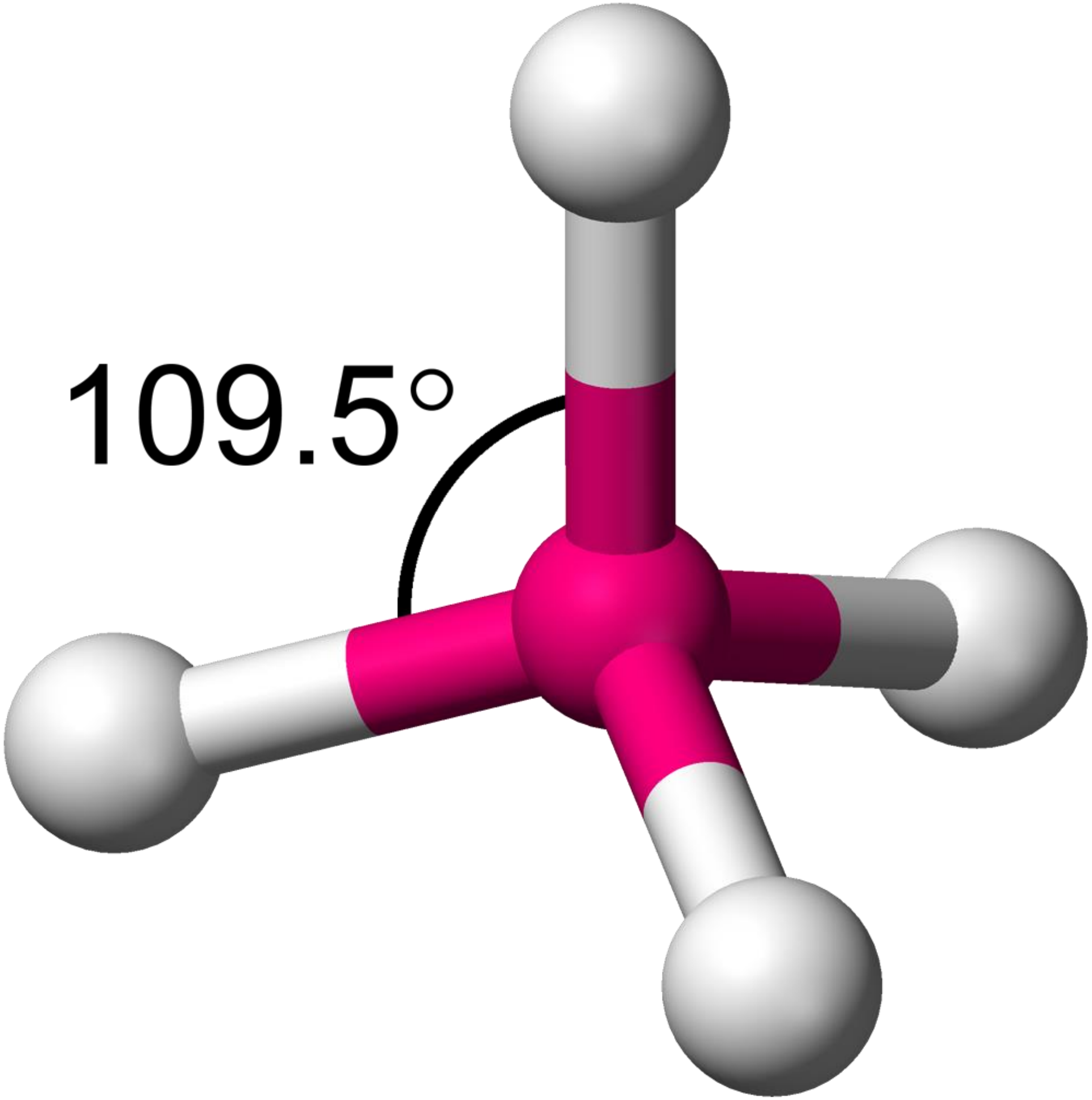
Since three p orbitals are mixed with one s-orbital, we call the hybrid orbitals sp^3, meaning that each of them has one-fourth s-character and three-fourth p-character.

Each bond in CH_4 is formed by overlap of an sp^3 hybrid orbital of carbon with a 1s orbital of hydrogen. These four bonds point to the corners of a tetrahedron.



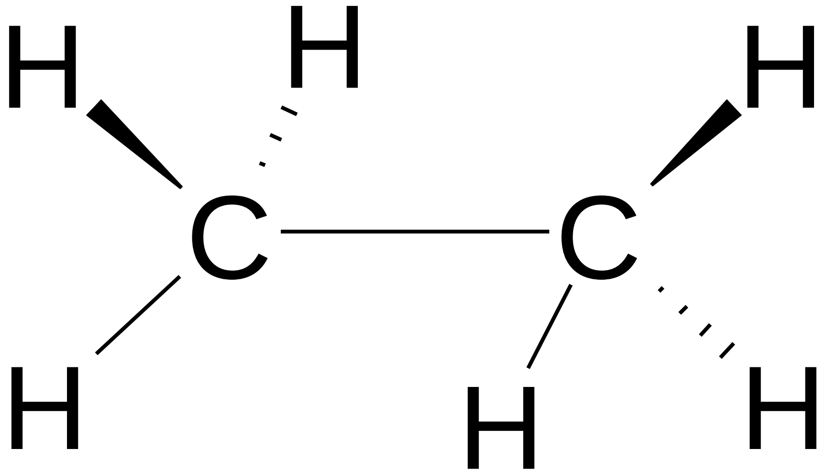
Bond strength = 104 Kcal/mol

The tetrahedral shape of an sp^3 hybridized carbon

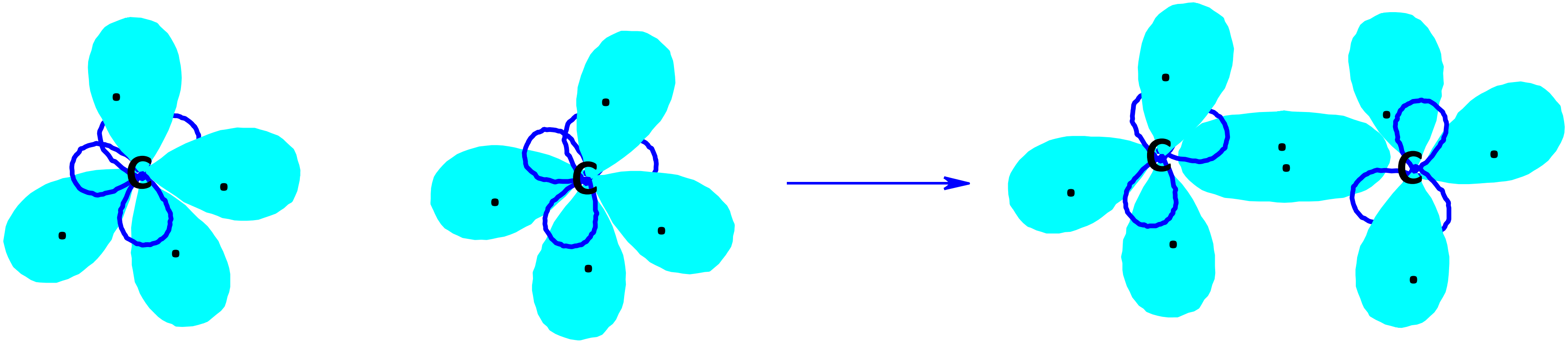


All four C – H bonds in methane are sigma (δ) bonds, because the electron density is concentrated on the axis joining C and H and are formed by head on overlap of orbitals.

Ethane (C_2H_6) – sp^3 Hybridization



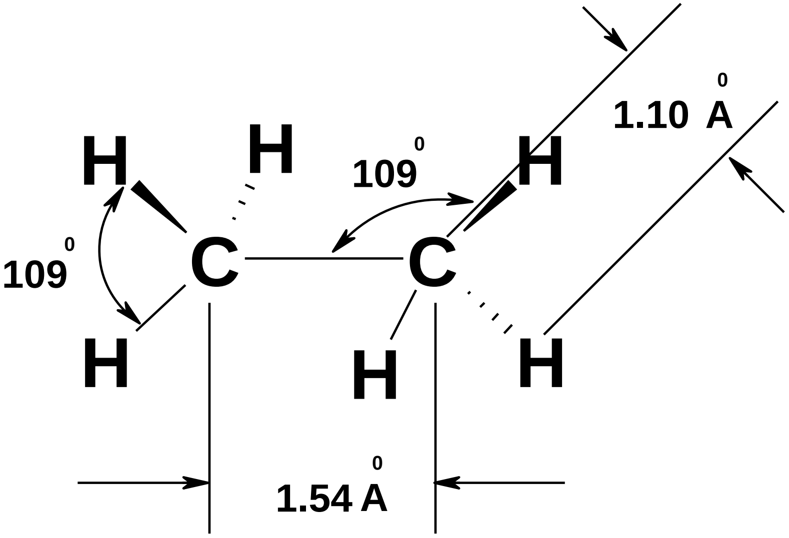
We can picture the ethane molecule by assuming that the two carbon atoms bond to each other by sigma overlap of an sp^3 hybrid orbital from each carbon.



sp^3 carbon

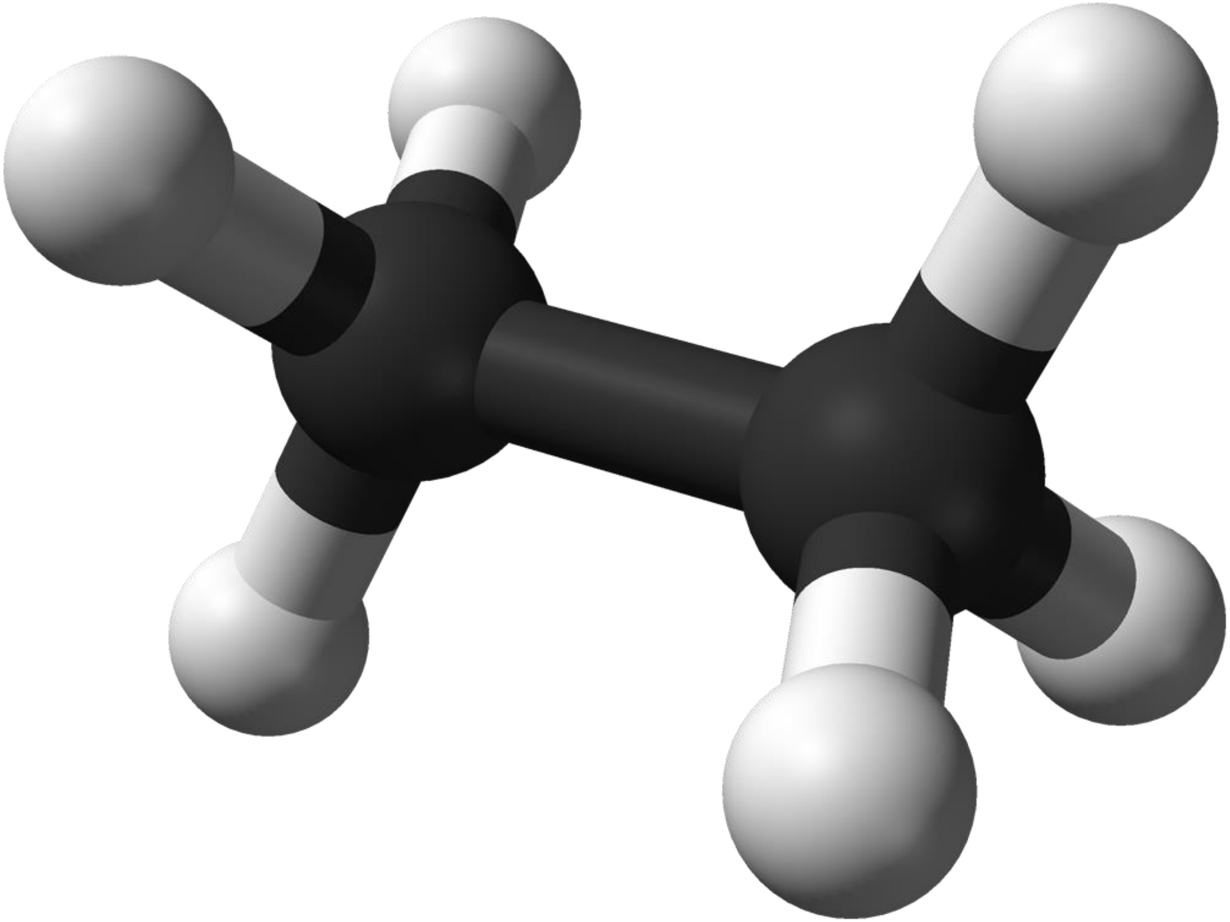
sp^3 carbon

sp^3– sp^3 sigma bond

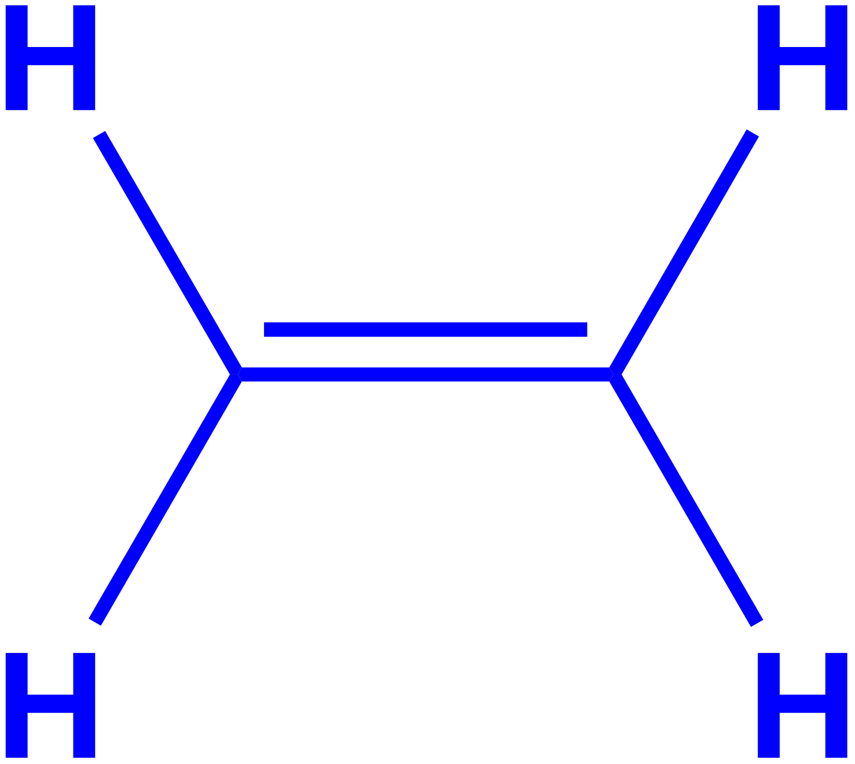


Structure of Ethane

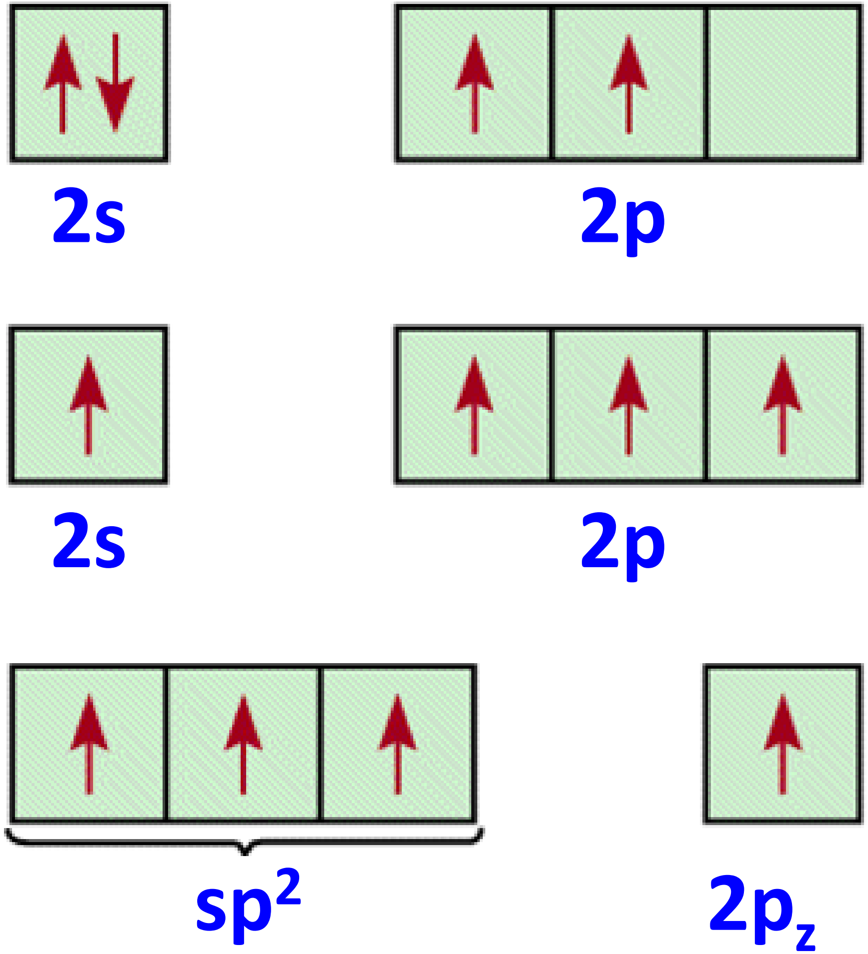
Ethane (C_2H_6) – sp^3 Hybridization



Ethylene (C_2H_4)-sp^2 Hybridization



sp^2 hybridization of a carbon



ground state

2s

2p

excited state

2s

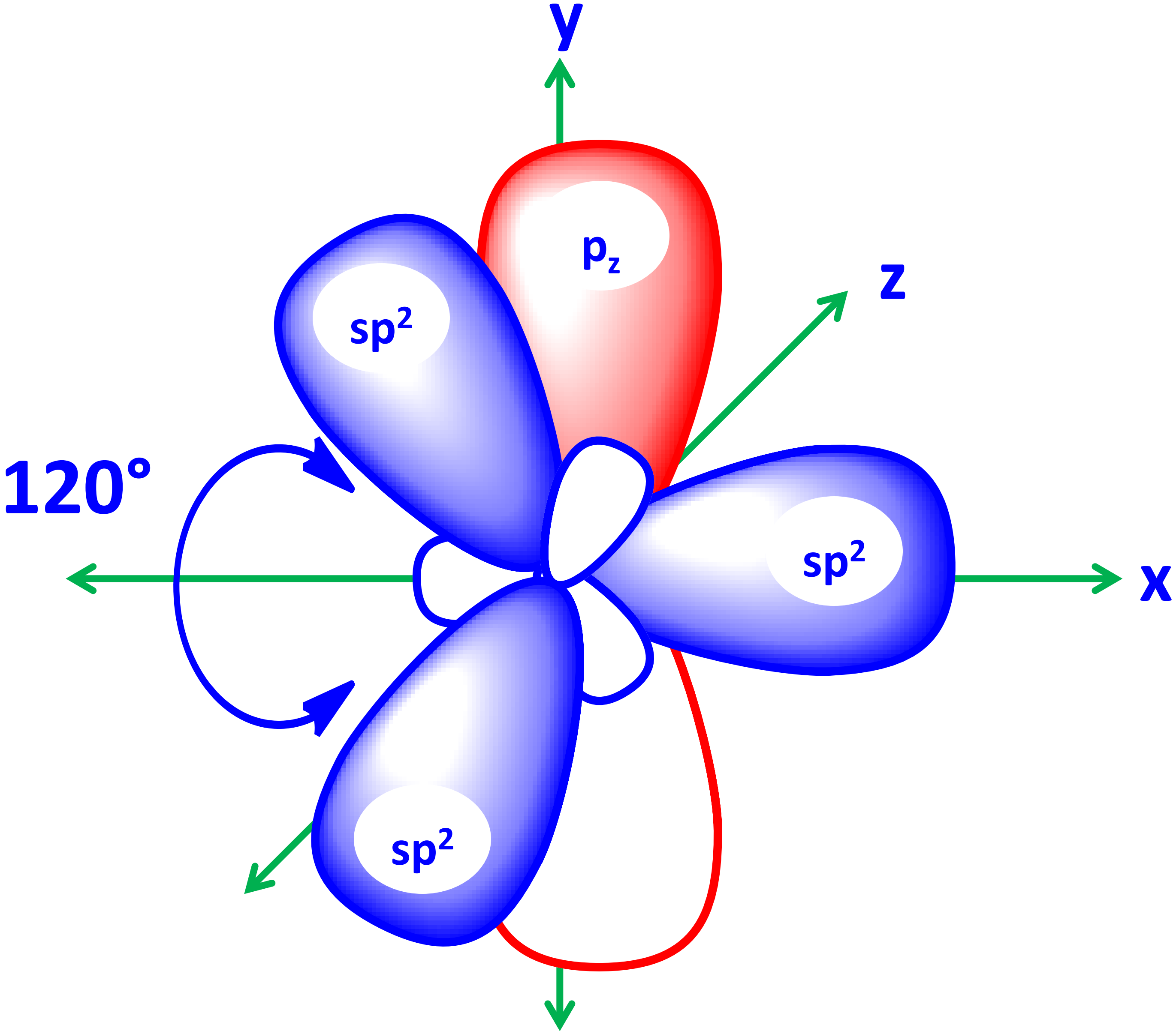
2p

sp^2 hybridized state

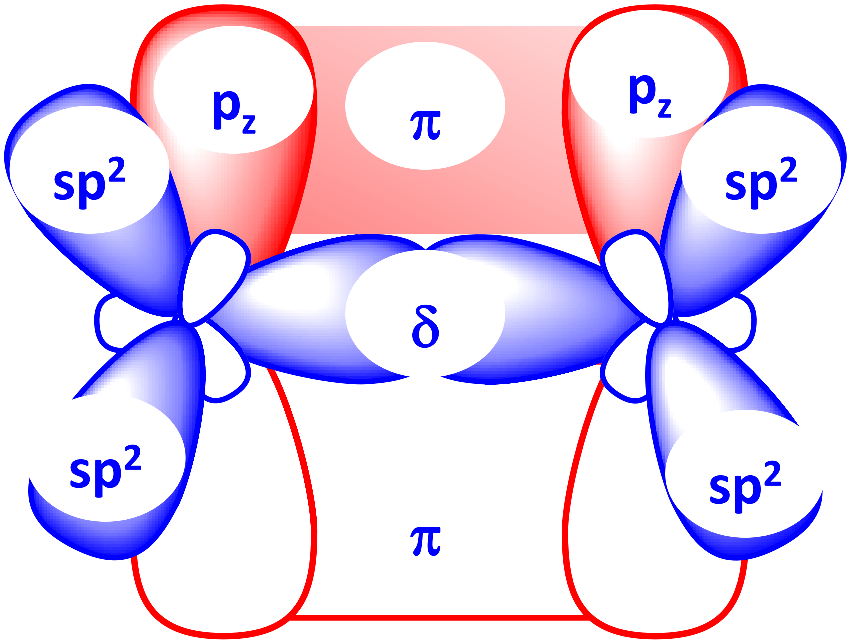
sp^2

$2p_z$

unhybridized p orbital



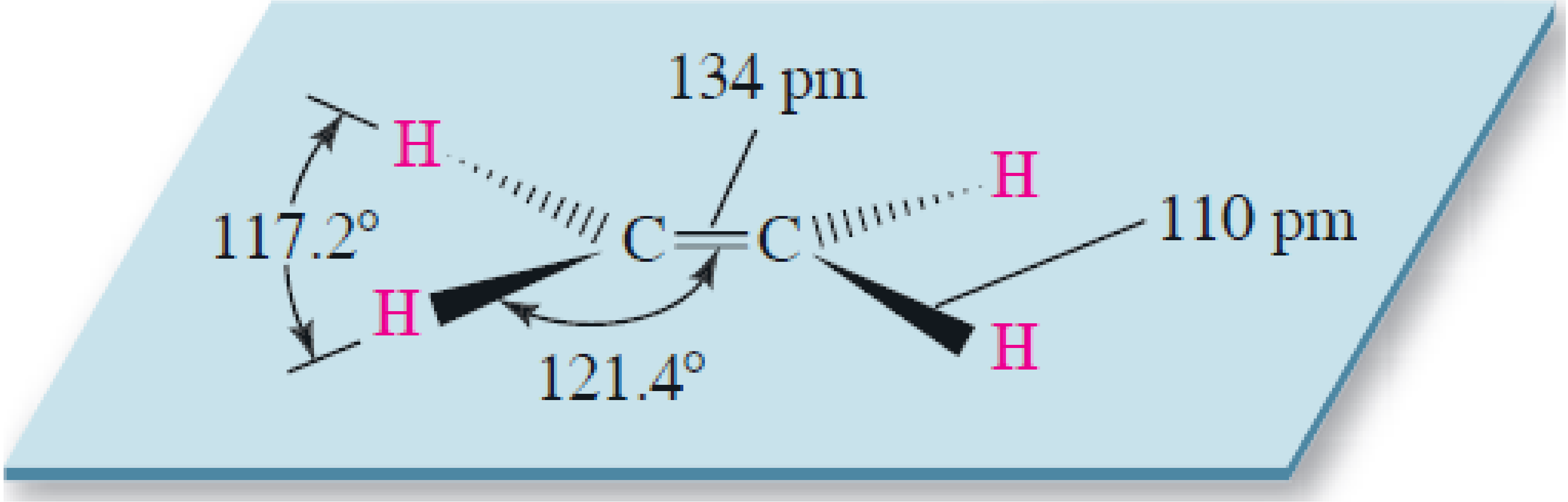
sp^2 hybridized carbon



δ bond, formed by end-on overlap of two sp^2 hybrid orbitals

π bond, formed by side-by-side overlap of two 2p orbitals.

The electron density in a π bond is farther from the two nuclei, π bonds are usually weaker and therefore more easily broken than δ bonds.



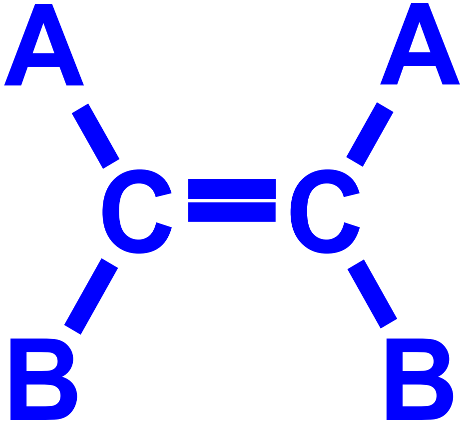
Planar shape

The carbon-carbon double bond is rigid and bond rotation can not occur.

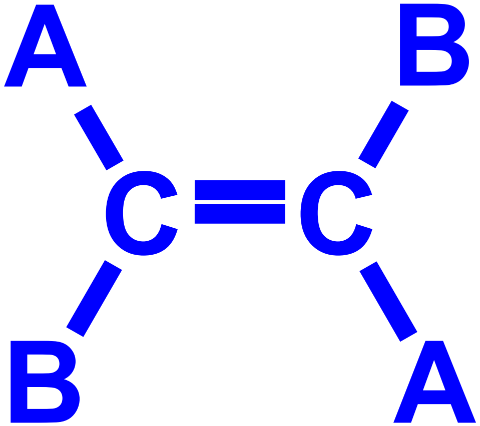
For rotation to occur the π-bond must be broken. The energy barrier for bond rotation in ethene (ethylene) is 235 kJ/mol while for ethane is only 12 kJ/mol.

The rigidity of the double bond gives rise to the possibility of stereoisomerism (geometric isomerism) which is commonly referred to as *cis-trans* isomerism in alkenes.

Cis isomer cannot become trans without a chemical reaction occurring.

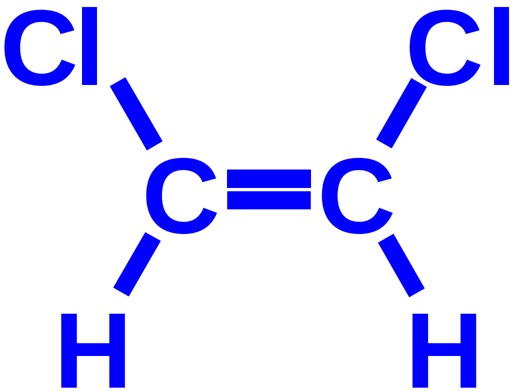


cis = The substituents are on the same side of the double bond.

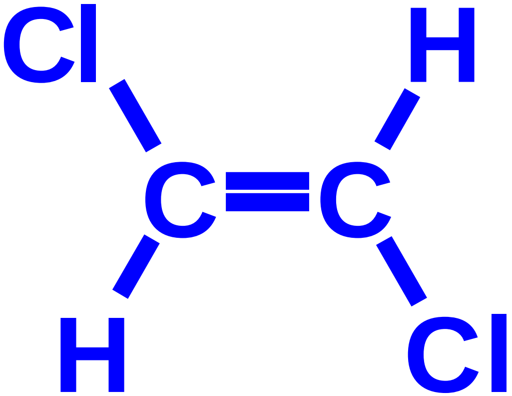


trans = The substituents are on opposite side of the double bond.

Examples



cis-1,2-dichloroethene

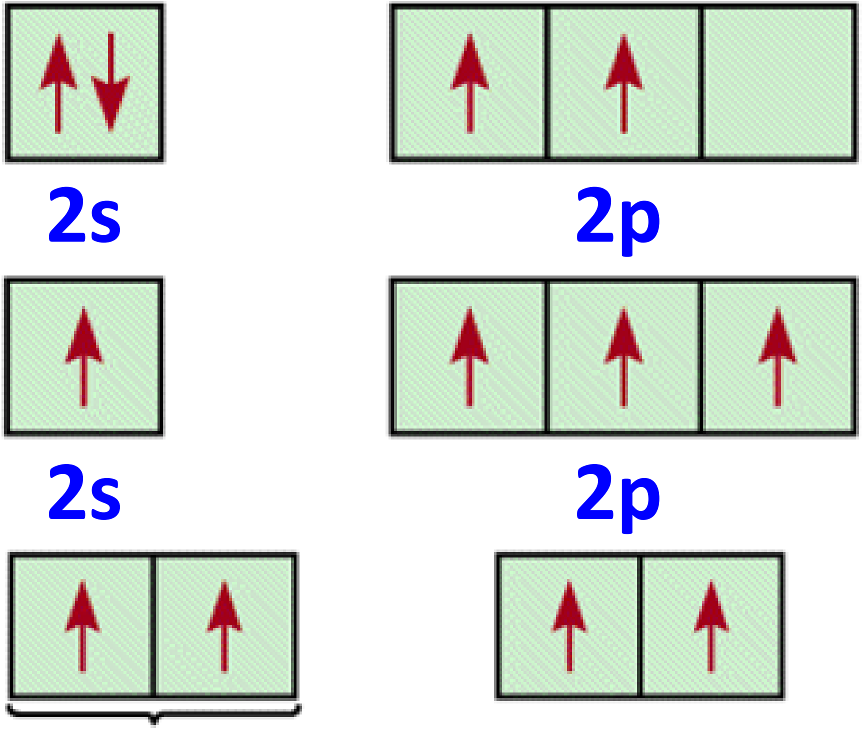


trans-1,2-dichloroethene

Ethyne (C_2H_2)-sp-Hybridization

$$H-C\equiv C-H$$

sp hybridization of a carbon



ground state

2s

2p

excited state

2s

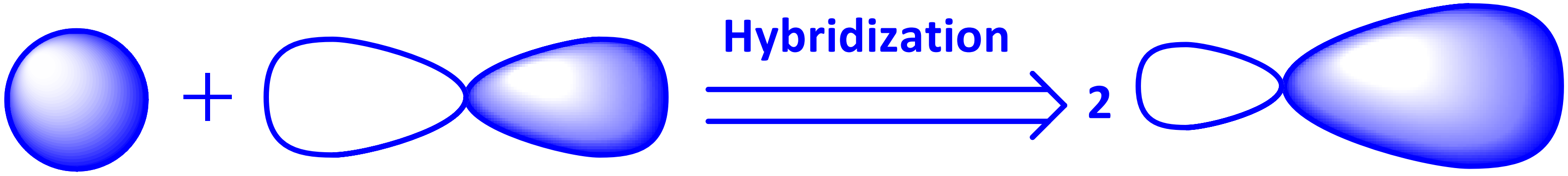
2p

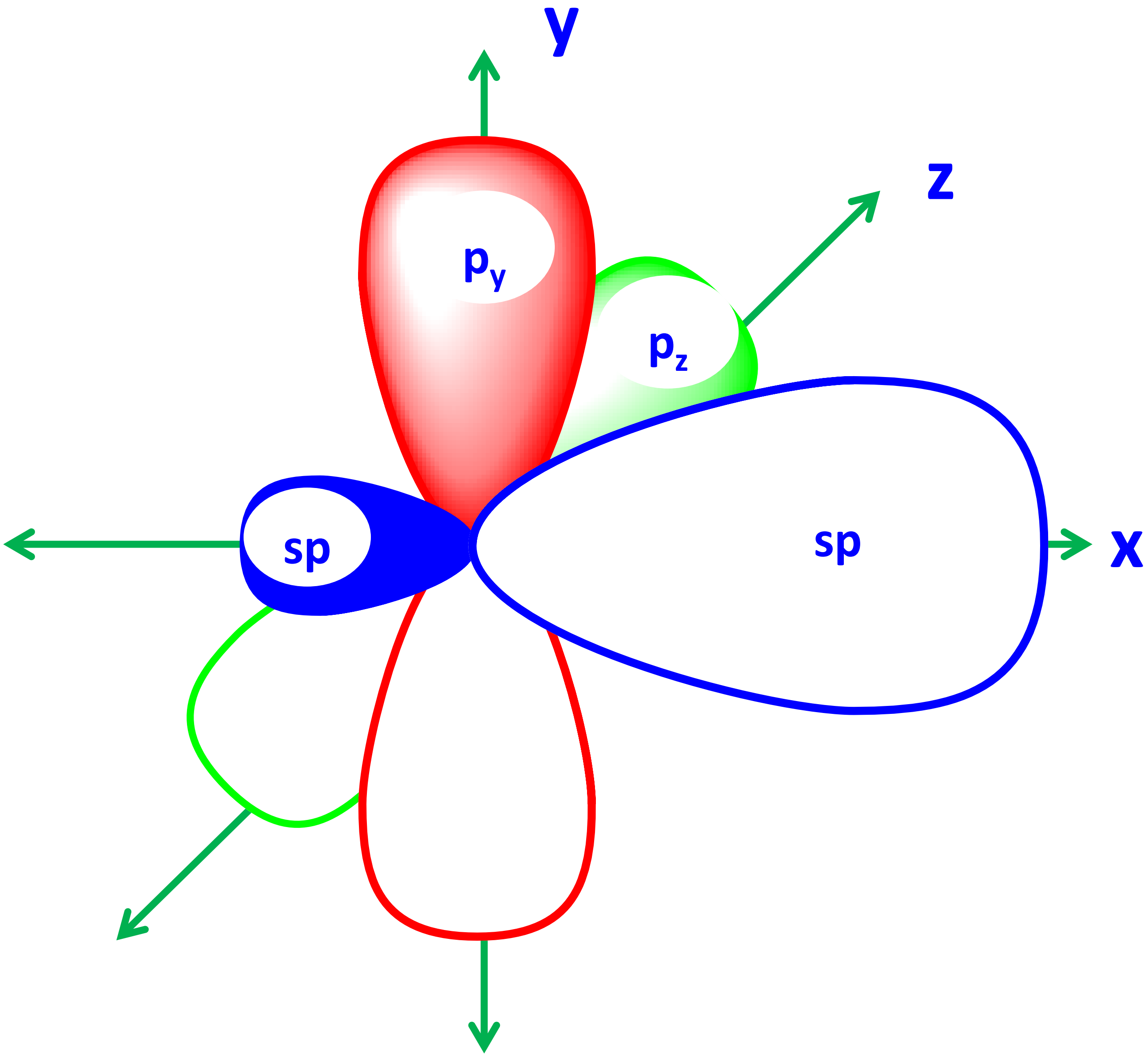
sp hybridized state

sp

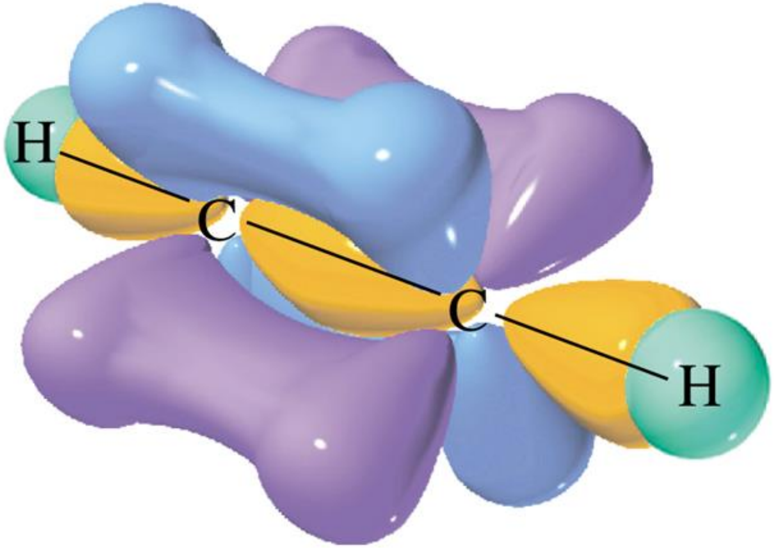
$2p_y$ $2p_z$

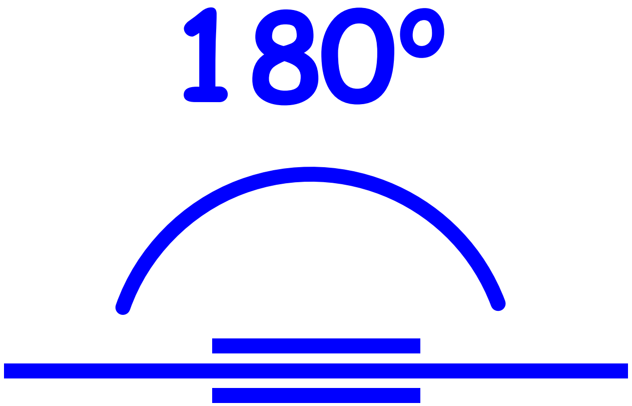
unhybridized p orbitals





sp hybridized carbon

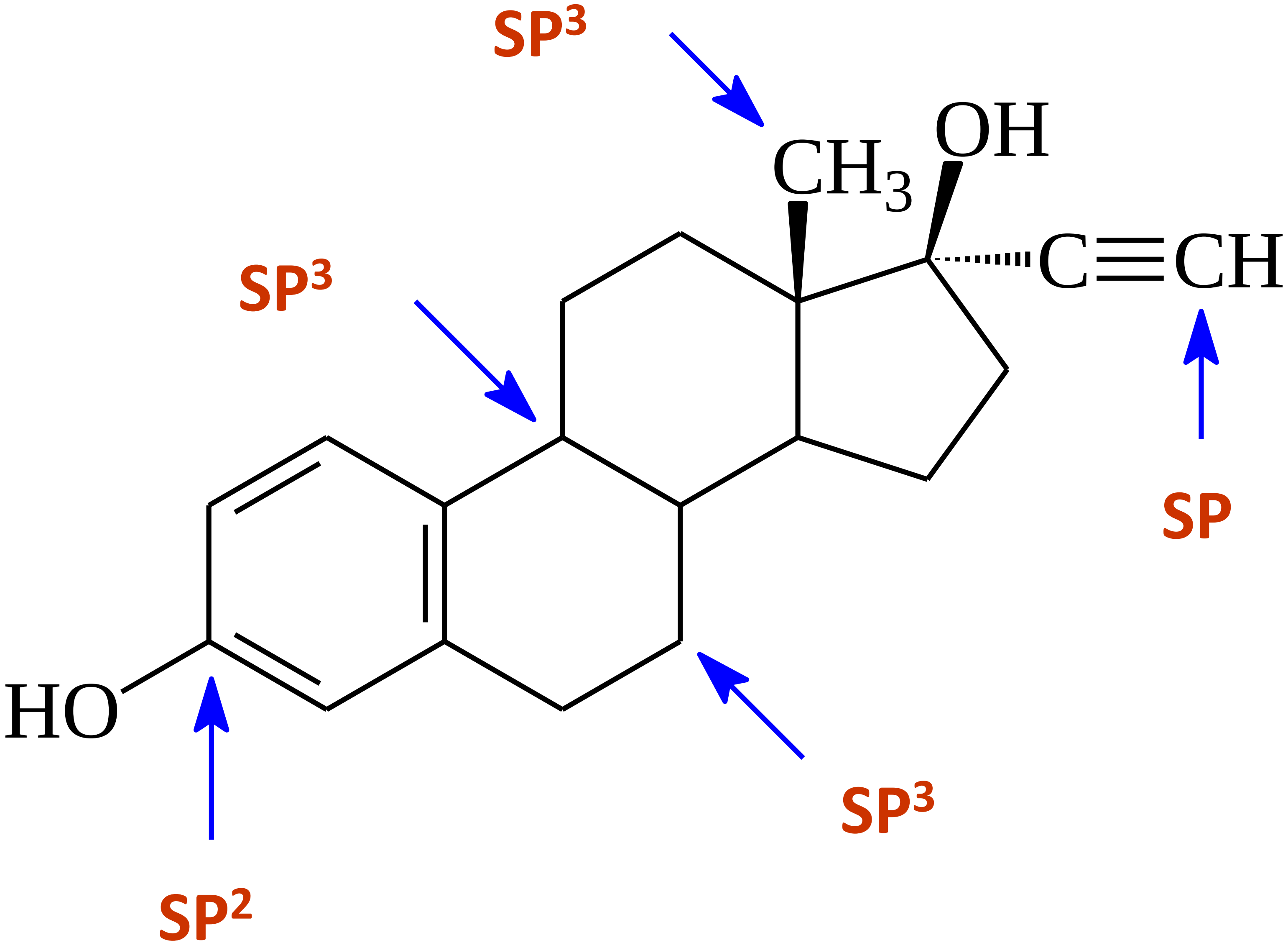




Alkynes have a linear geometry with C-C bond angles of 180°.

Comparison of Carbon-Carbon and Carbon-Hydrogen bonds in methane, ethane, ethylene and ethyne.

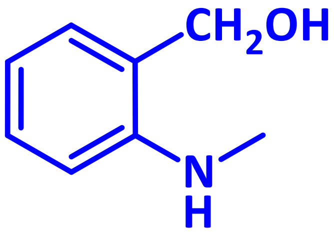
Molecule	Bond	Bond strength (Kcal/mol)	Bond length (Å)	S-character (%)
Methane, CH_4	C_{SP3}-H_{1S}	104	1.10	25
Ethane, CH_3-CH_3	$C_{SP3\ -}\ C_{SP3}$ C_{SP3}-H_{1S}	88 98	1.54 1.10	25
Ethylene, $H_2C{=}CH_2$	$C_{SP2\ -}\ C_{SP2}$ C_{SP2}-H_{1S}	152 103	1.33 1.076	33
Ethyne, $HC{\equiv}CH$	$C_{SP\ -}\ C_{SP}$ C_{SP}-H_{1S}	200 125	1.20 1.06	50


SP³
SP³
CH₃
OH
C≡CH
SP
HO
SP³
SP²

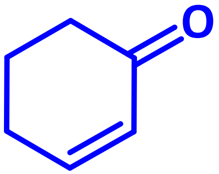
Problem

I. **Locate and identify the functional groups in the following molecules:**

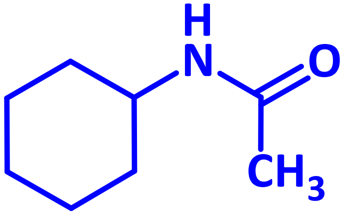
a)



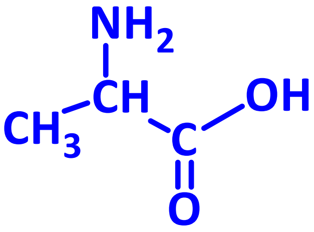
b)



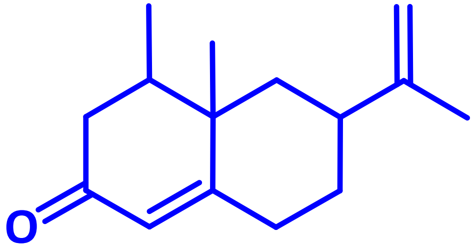
c)



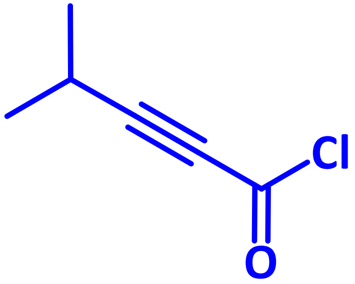
d)



e)

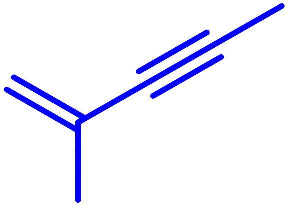


f)

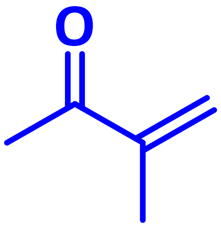


II. **Indicate bond angle at each carbon in the following compounds**

a.



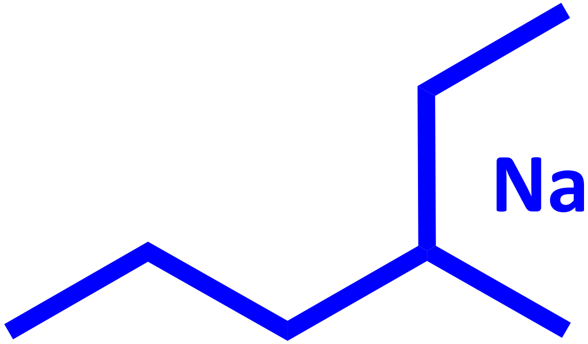
b.



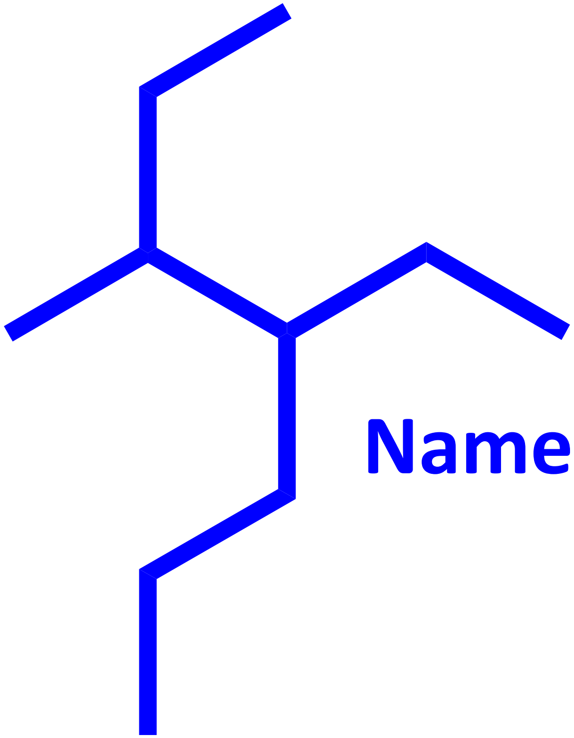
RULES OF NAMING ALKANES

Step I: Find the parent hydrocarbon

a) Find the largest continuous chain of carbon atoms present in the molecule, and use the name of that chain as the parent name. The longest chain may not always be apparent from the manner of writing; you may have to “turn corners”.

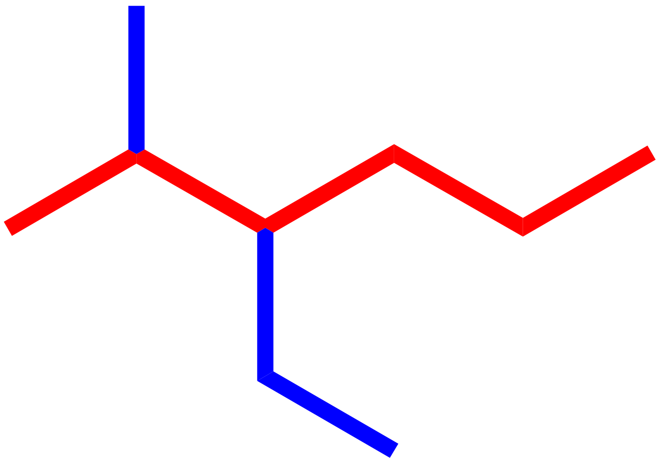


Named as a substituted hexane

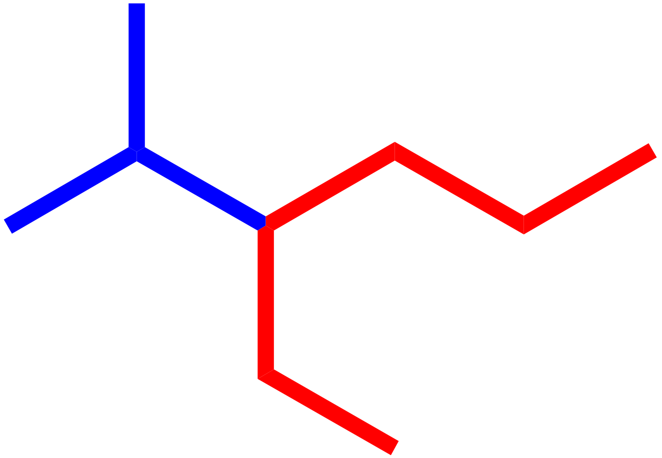


Named as a substituted heptane

b) If two chains of equal length are present, choose the one with the large number of branches points as the parent:



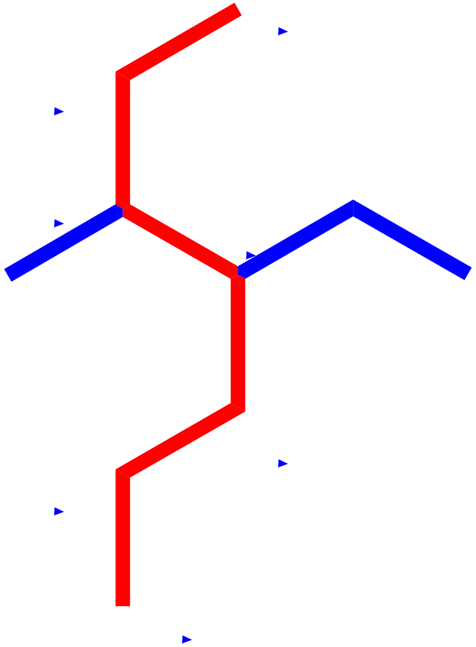
not



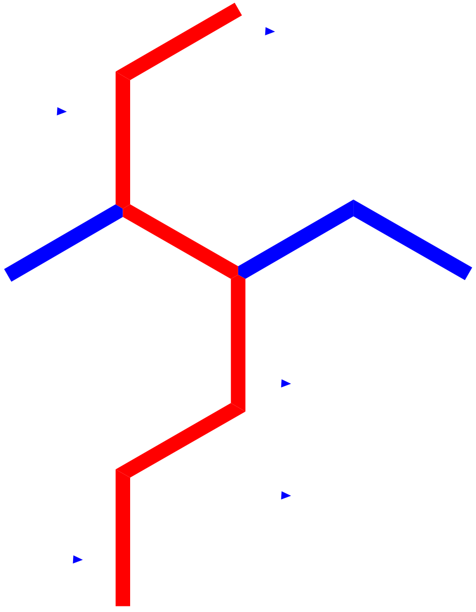
as a hexane with one substituent

Step II: Number the atoms in the main chain

a) Beginning at the end of nearer the first branch point, number each carbon atom in the chain:



NOT

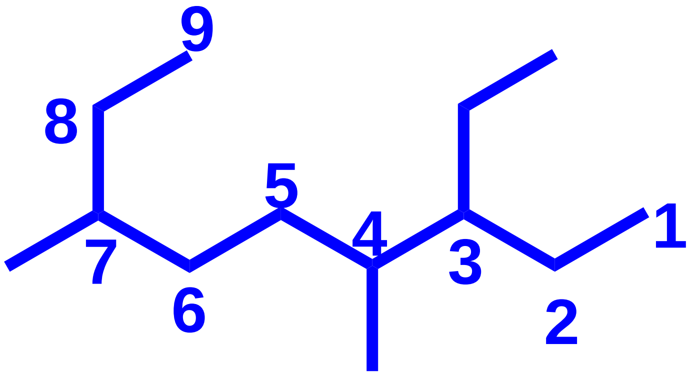


The first branch occurs at C3 in the proper system of numbering, not at C4.

b)If there is branching an equal distance away from both ends of the parent chain, begin numbering at the end nearer the second branch point:

Step III Identify and number the substituents

a) Assign a number to each substituent according to its point of attachment to the main chain:



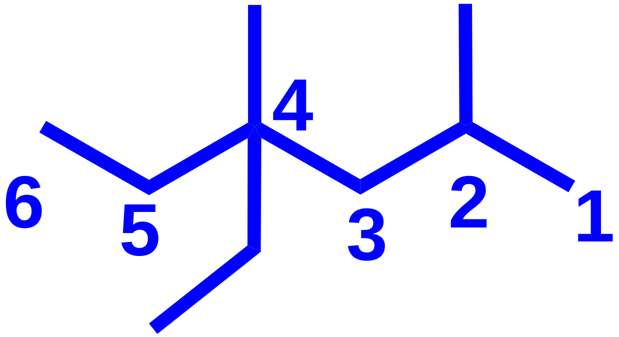
Named as nonane

Substituents: On C3, CH_2CH_3 (3-ethyl)

On C4, CH_3 (4-methyl)

On C7, CH_3 (7-methyl)

b)If there are two substituents on the same carbon, give them both the same number. There must be as many numbers in the name as there are substituents.



Named as hexane

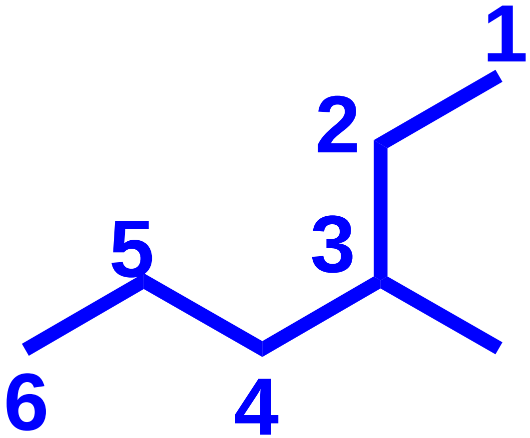
Substituents: On C2, CH_3 (2-methyl)

On C4, CH_3 (4-methyl)

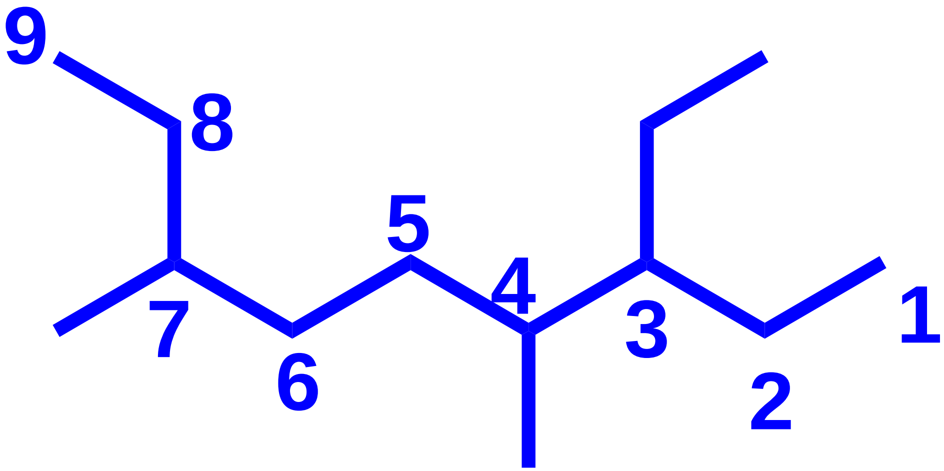
On C4, CH_2CH_3 (4-ethyl)

Step IV: Write the name as a single word

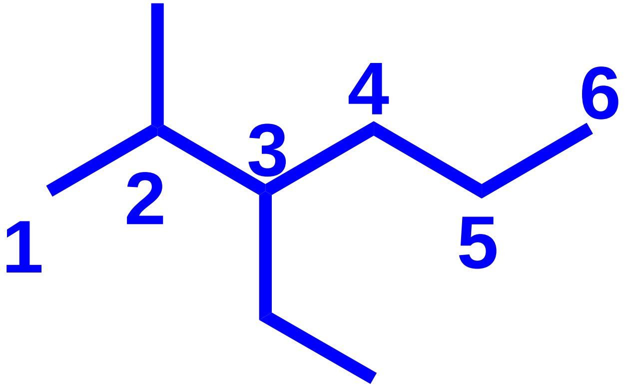
Use hyphens to separate the different prefixes, and use commas to separate numbers. If two or more substituents are present, cite them in alphabetical order. It two or more identical substituents are present, use one of the multiplier prefixes di, tri, tetra and so forth. Do not use these prefixes for alphabetizing purposes, however.



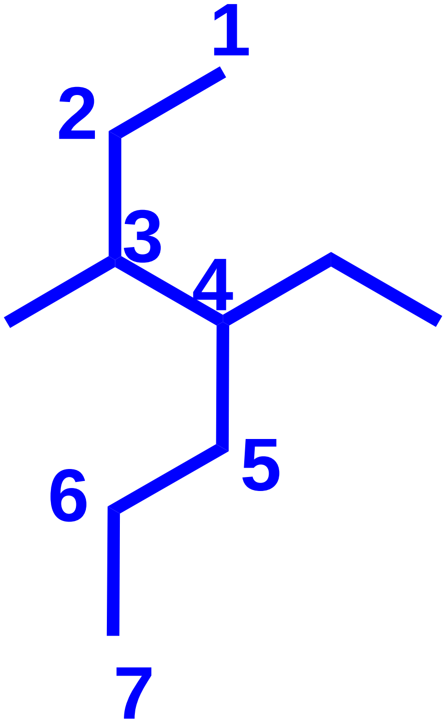
3-Methylhexane



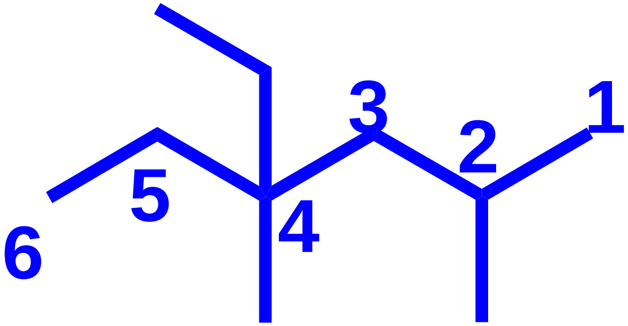
3-Ethyl-4,7-dimethylnonane



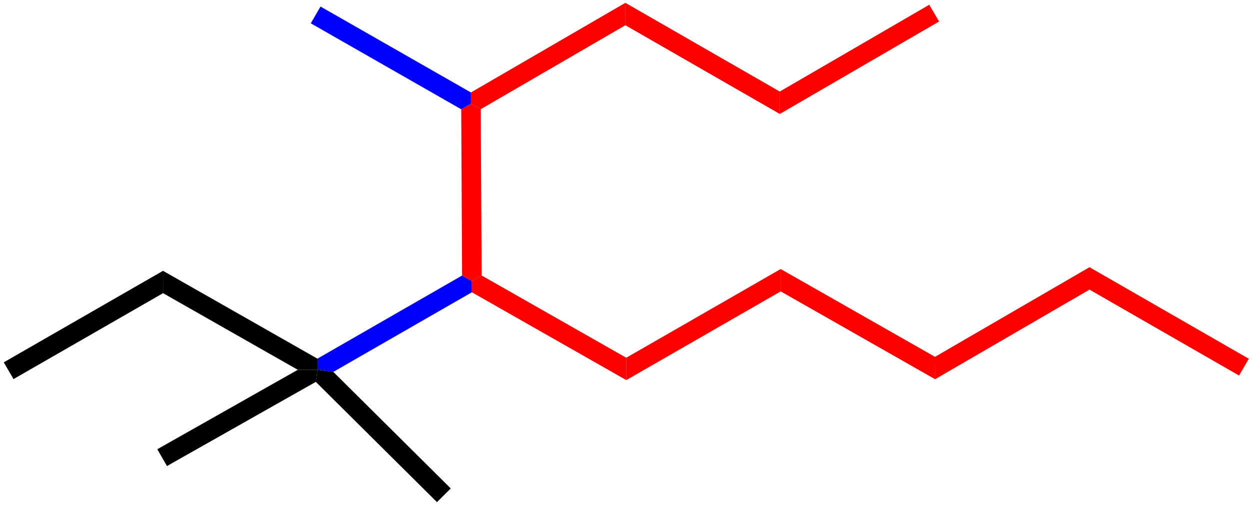
3-Ethyl-2-methylhexane



4-Ethyl-3-methylheptane



4-Ethyl-2,4-dimethylhexane



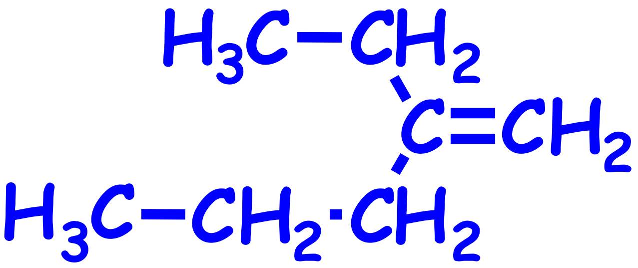
4-Methyl-5-(1,1-dimethylpropyl)decane

Nomenclature of alkenes

Alkenes are named using a series of rules similar to those of alkanes, with the suffix –ene used instead of –ane to identify the family. There are three steps:

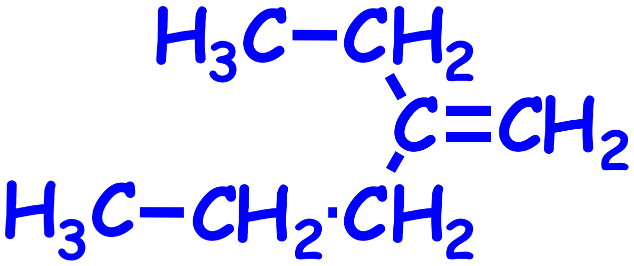
STEP 1: Name the parent hydrocarbon

Find the largest continuous chain containing the double bond, and name the compounds accordingly, using the suffix –ene.



Named as pentene

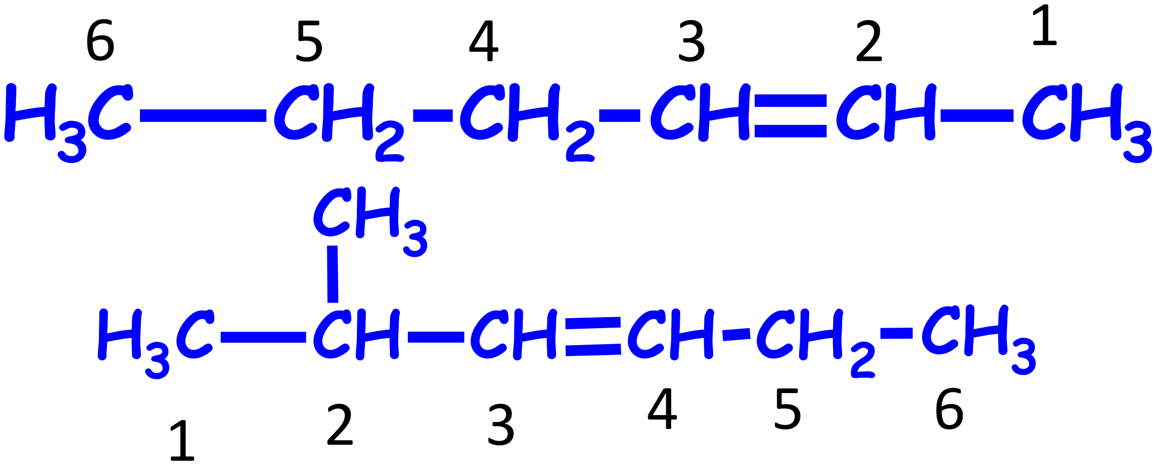
NOT



As hexene, since the double bond is not in the six carbon chain

STEP 2: Number the carbon atoms in the chain

Begin at the end nearer the double bond or, if the double bond is equidistant from two ends, begin numbering at the end nearer the first branch point. This rule ensures that the double bond carbon receives the lowest possible numbers.



$$\overset{6}{H_3C}-\overset{5}{CH_2}-\overset{4}{CH_2}-\overset{3}{CH}=\overset{2}{CH}-\overset{1}{CH_3}$$

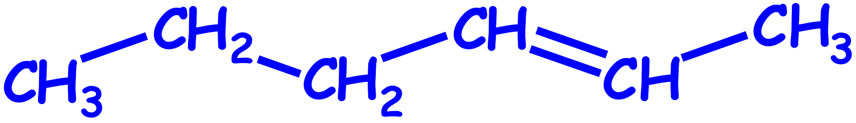
$$\underset{1}{H_3C}-\underset{2}{\overset{\overset{CH_3}{|}}{CH}}-\underset{3}{CH}=\underset{4}{CH}-\underset{5}{CH_2}-\underset{6}{CH_3}$$

STEP 3: Write the full name

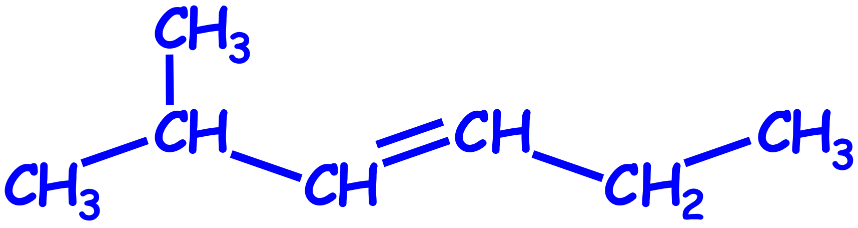
Number the substituents according to their positions in the chain, and list them alphabetically.

Indicate the position of the double bond by giving the number of the first alkene carbon and placing that number immediately before the parent name.

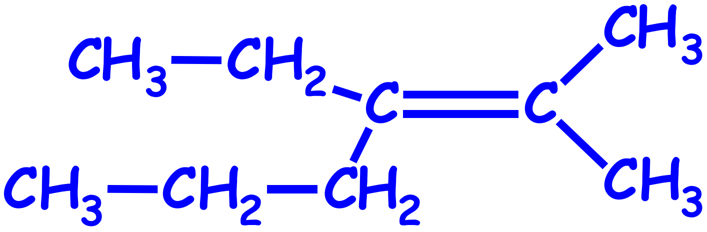
If more than one double bond is present, indicate the position of each, and use one of the suffixes –diene, -triene, and so on.



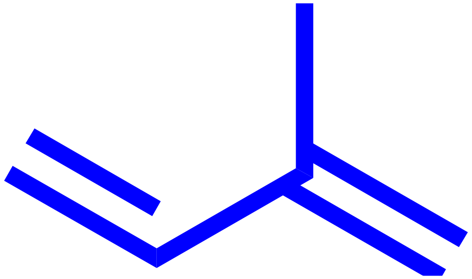
2-Hexene



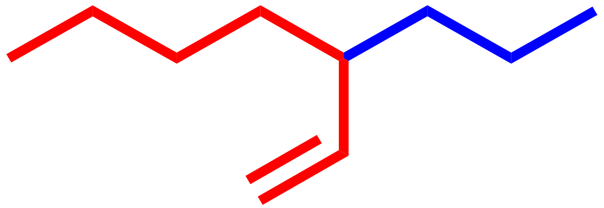
2-Methyl-3-hexene



3-Ethyl-2-methyl-2-hexene



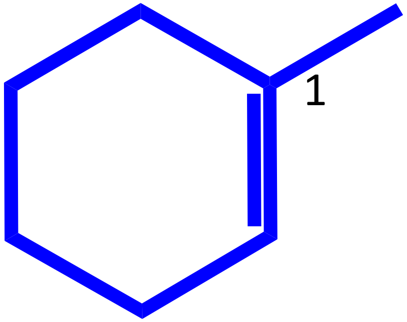
2-Methyl-1,3-butadiene



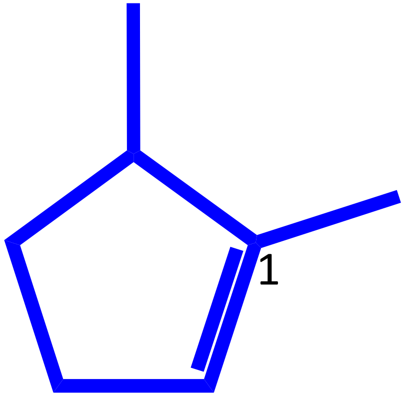
3-Propyl-1-heptene

Cycloalkenes are named similarly, but because there is no chain end to begin from, we number the cycloalkenes so that the double bond is between C-1 and C-2 and the first substituent has a low number as possible.

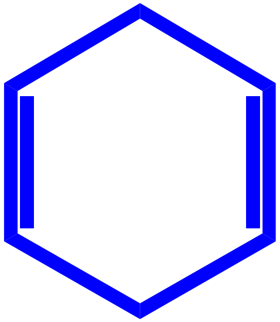
Note that it is not necessary to indicate the position of the double bond in the name because it is always between C-1 and C-2.



1-Methylcyclohexene



1,5-Dimethylcyclopentene

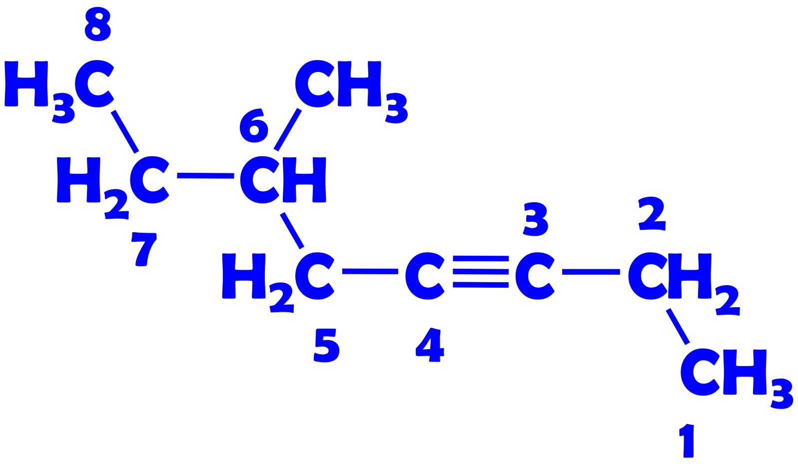


1,4-Cyclohexadiene

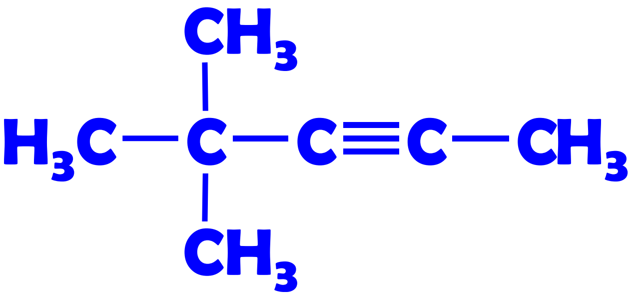
Nomenclature of alkynes

Alkynes follow the general rules of hydrocarbon nomenclature. The -ane ending of the name of the alkane corresponding to the longest continuous chain of carbon atoms that contains the triple bond is changed to –yne. Numbering the main chain begins at the end nearer the triple bond so that the triple bond receives as low a number as possible.

EXAMPLES



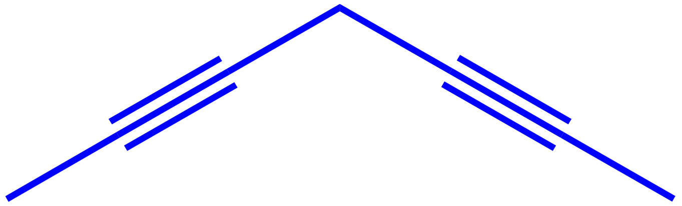
6-Methyl-3-octyne



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-C\equiv C-CH_3$

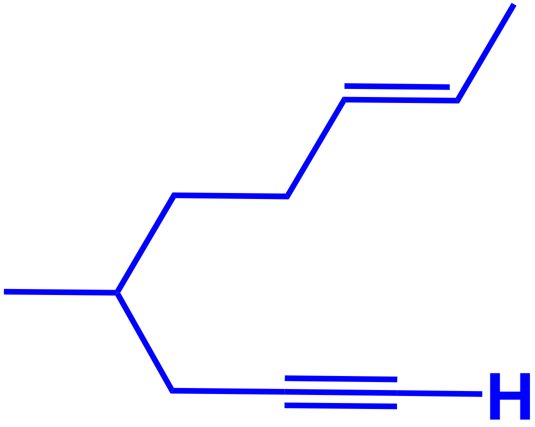
4,4-Dimethyl-2-pentyne

Compounds with more than one triple bond are named as diynes, triynes and so forth.



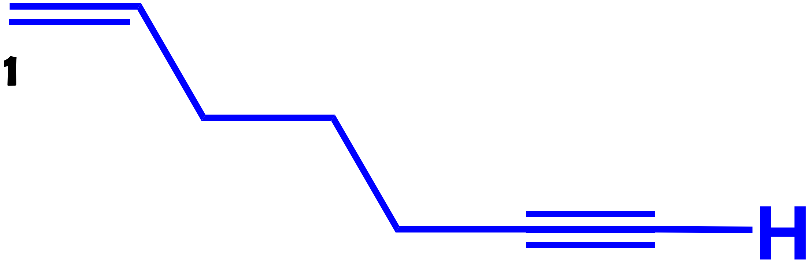
2,5-Heptadiyne

Compounds containing both double and triple bonds are called enynes. Numbering of an enyne chain starts from the end nearer the first multiple bonds, whether double or triple.



Trans-4-Methyl-7-nonen-1-yne

When there is a tie in numbering, double bonds receives the lower number than triple bonds.



1-Hepten-6-yne