CHM 104

Module 4- Chemistry of Group IVA Elements (Carbon Group)

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COLPHYS

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Outline

- **Periodic table**
- **Occurrence and Uses of Group IVA Elements**
- **Some Physical and Chemical Parameters of Group IV Elements**
- **Valency**
- **Some Simple compounds of Group IV elements**
- **Special products/behaviour of some Group IV elements**

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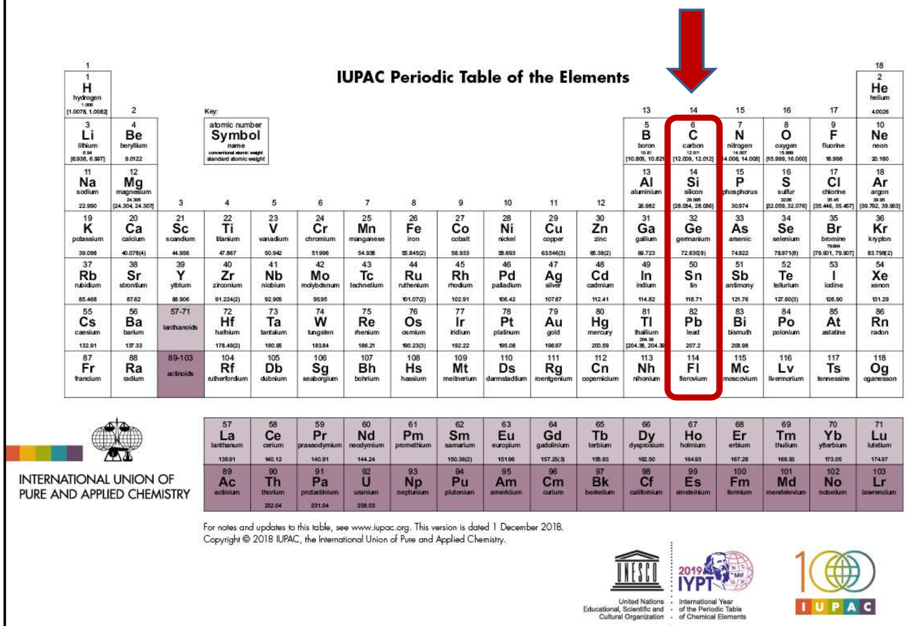

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Occurrence and Uses of Group IVA Elements: Carbon

- **Carbon** occurs as crystalline allotropes (diamond and graphite) and molecular allotrope (fullerenes).
- **Diamond** occurs naturally in igneous rocks which can be found in South Africa.
- **Graphite** occurs naturally in many areas eg. Republic of Korea, Austria, China, Mexico, Madagascar, Germany, Sri Lanka, and Russia.
- **Fullerenes** occur naturally in a number of deposits in Australia, New Zealand and North America.
- Carbon also exists as carbon (IV) oxide (CO_2) at 0.04% of the earth's atmosphere

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What is Allotropy?

- **Allotropy**, the existence of a chemical element in two or more forms, which may differ in the arrangement of atoms in crystalline solids or in the occurrence of molecules that contain different numbers of atoms. *(https://www.britannica.com/science/allotropy, 2019)*

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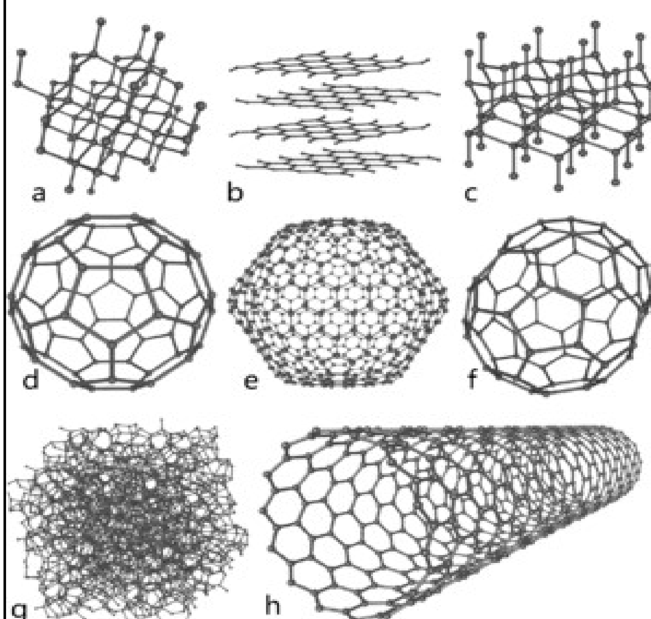
Allotropes of Carbon



Eight allotropes of carbon:
a: Diamond,
b: Graphite,
c: Lonsdaleite,
d: C_{60} (Buckminsterfullerene or buckyball),
e: C_{540},
f: C_{70},
g: Amorphous carbon,
and h: single-walled carbon nanotube or buckytube.

Courtesy :Wikipedia

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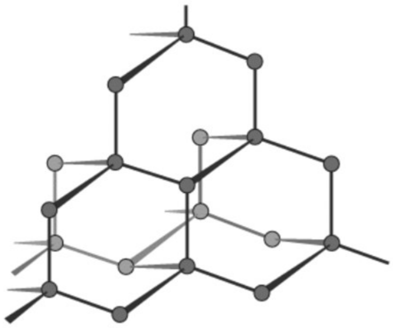
Allotropes of Carbon



The crystal structure of diamond.

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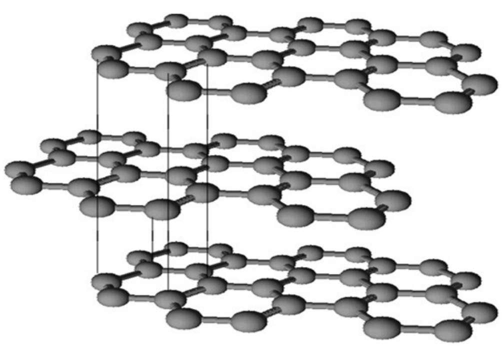
Allotropes of Carbon



Natural Graphite

A view of the planes of atoms in the structure of graphite.

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Allotropes of Carbon

Diamond and graphite are two allotropes of carbon:
pure forms of the same element that differ in structure.

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Allotropes of Carbon

Characteristics	Diamond	Graphite
Density	3.5gcm^{-3}	2.3gcm^{-3}-less dense than diamond because its structure is less compact.
Structure	A three dimensional array of carbon atoms, each atom surrounded tetrahedrally by four other carbons. Each diamond crystal is a giant molecule containing very strong bonds.The structure is highly rigid.	A two dimensional array of carbon atoms, each atom surrounded by three other carbons in the same plane and the bonding is covalent. The sheet of carbon atoms are arranged in regular hexagon and are held by weak van der Waal's forces.
Hardness	Hardest naturally occurring substance	Very soft and slippery because the weak forces holding the individual sheets together are easily broken, the sheets are easily moved relative to one another.
Electrical	Does not conduct electricity	Graphite conducts electricity. Since each carbon atoms is surrounded by three other carbons, thus alternate single and double bonds must be present to complete the octet of each carbon atom. The presence of the double bonds means that mobile electrons are present and these can readily be transferred from one hexagon to another by the application of an electric field.

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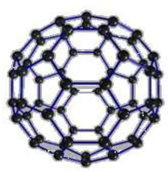
Allotropes of Carbon

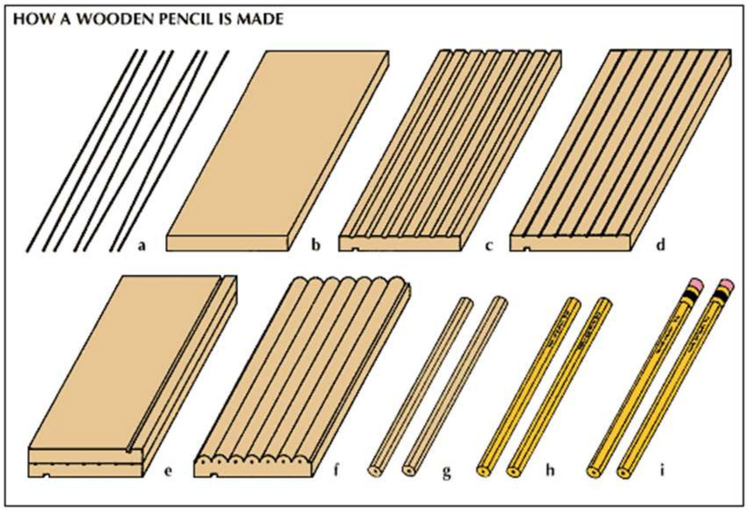
Characteristics	**Fullerenes** *also known as* ***buckminsterfullerene***
Discovery	First discovered in 1985 by Sir Harold W. Kroto of the United Kingdom and by Richard E. Smalley and Robert F. Curl, Jr., of the United States.
Structure	Cagelike molecules composed of 60 carbon atoms (C_{60}) joined together by single and double bonds to form a hollow sphere with 12 pentagonal and 20 hexagonal faces
Properties 	➢It readily accepts and donates electrons ➢The molecule readily adds atoms of hydrogen and of the halogen elements which can be replaced by other groups, such as phenyl-C_6H_5, thus opening useful routes to a wide range of novel fullerene derivatives. ➢Endohedral species of the Fullerenes also exists, in which a metal atom is physically trapped inside a fullerene cage. The resulting compounds (assigned the formulas $M@C_{60}$) have been extensively studied. ➢These derivatives exhibit advanced materials behaviour

Applications of Allotropes of Carbon

- **Diamond** is used as gemstones, cutting tools, abrasives etc

- **Graphite** is used as a lubricant. It is exploited commercially for its inertness, high thermal stability, electrical and thermal conductivities. A single layer of graphite is called graphene and has extraordinary electrical, thermal, and physical properties.

- **Fullerenes** are applied as nanotubes in materials science.[owing to their extraordinary thermal conductivity and mechanical and electrical properties, carbon nanotubes find applications as additives to various structural materials, also for medical uses.]. Has potentials for great uses.



The main parts of a pencil are the **graphite** rods

(Courtesy :Encyclopædia Britannica)

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Occurrence and Uses of Group IVA Elements: Silicon

- Elemental Si does not exist naturally but constitutes 25.7% of the earth's crust in the form of sand, quartz etc

Uses

- Si is utilized in steel industries, electronic and semiconductor industries.
- It is also used as the main component of glass in the form of silica(SiO_2)

Quartz Silicon sand

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Occurrence and Uses of Group IVA Elements: Germanium

- Ge constitutes 1.8ppm of the earth's crust

Uses

- Used as polymerization catalysts for the production of polyethylene; fibre optics, optical devices (GeO_2), as semiconductors in electronic and solar electrical industries.

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Occurrence and Uses of Group IVA Elements: Tin

- Sn occurs naturally as the ore cassiterite (SnO_2)

Uses

- Used for tin plating for example in steel cans to improve corrosion resistance.
- Also used as alloys eg bronze.

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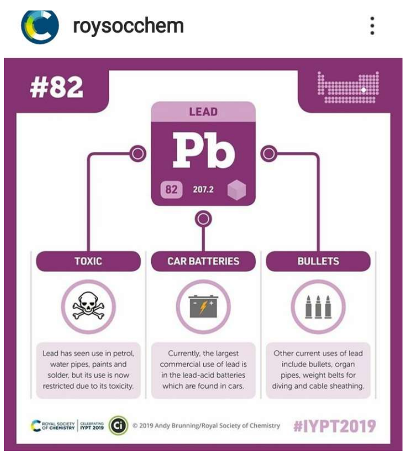
Occurrence and Uses of Group IVA Elements: Lead



- Pb occurs naturally as the ore: galena(PbO), anglesite($PbSO_4$) and cerussite ($PbCO_3$)

Uses

- Used in industry plant; as Lead acid batteries.
- Lead oxides are used in the making of lead crystal glass
- Lead(IV) oxide as an oxidizing agent in the production of dyestuffs, chemicals etc

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Occurrence and Uses of Group IVA Elements: Flerovium

1. It was discovered by Yuri Oganessian and Vladimir Utyonkov in 1998
2. It is named after the Russian physicist Georgy Flerov, the founder of the Joint Institute for Nuclear Research (JINR) where the element was discovered
3. Discovered by the bombarding of plutonium with calcium. The reaction produced a single atom of flerovium-289, the most stable of its isotopes with a half-life of 2.1 seconds
4. At present, it is only used in research.
5. Flerovium can be formed in nuclear reactors

$$^{244}_{94}Pu + \,^{48}_{20}Ca \rightarrow \,^{289}_{114}Fl + 3\,^{1}_{0}n$$

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SOME PHYSICAL AND CHEMICAL PARAMETERS OF GROUP IV ELEMENTS

Element	Carbon C	Silicon Si	Germanium Ge	Tin Sn	Lead Pb
Atomic No	6	14	32	50	82
Electronic Configuration	$1s^2 2s^2 2p^2$	$[Ne]3s^2 3p^2$	$[Ar]4s^2 4p^2$	$[Kr]4d^{10} 5s^2 5p^2$	$[Xe]4f^{14} 5d^{10} 6s^2 6p^2$
Atomic radii (nm)	0.077	0.117	0.122	0.140	0.154
Melting point°C	3730[d]	1410	937	232	327
Boiling point°C	4830[d]	2360	2830	2270	1744
Conductivity	Farily good[gr] Non-cond.[d]	Semi-cond	Semi-cond	Good	Good
First ionization energy/kJ mol^{-1}	1086	787	760	707	715
Type of Structure	Giant molecule	Giant molecule similar to diamond	Giant molecule similar to diamond	Giant metallic	Giant metallic

gr-graphite d-diamond

Some physical properties of Group IV elements

- **Metallic Properties:** Carbon and silicon are non-metallic. Germanium has both metallic and non-metallic properties (metalloid). Tin and lead are definitely metallic.
- **Stucture:** The structure changes from giant molecular lattices in carbon and silicon to giant metallic structure in tin and lead.

Valency

They exhibit a valency of 2 and 4

- carbon and silicon compounds, the 4-valent states are very stable relative to 2-valent state. The 2-valent state is rare and easily oxidised to 4-valent state. CO is reacts very exothermically to form CO_2.
- Germanium forms oxides in both 2-valent and 4-valent state. However, GeO_2 is rather more stable than GeO. GeO_2 does not act as an oxidising agent and GeO is readily converted to GeO_2.

Valency-

- The compounds of Sn and Pb are often predominantly ionic.
- In tin compounds, the 4-valent states are slightly more stable than the 2-valent state

$$Sn^{2+}(aq) + Hg^{2+}(aq) \rightarrow Sn^{4+}(aq) + Hg(l)$$
$$Sn^{2+}(aq) + I_2(aq) \rightarrow Sn^{4+}(aq) + 2I^-(aq)$$

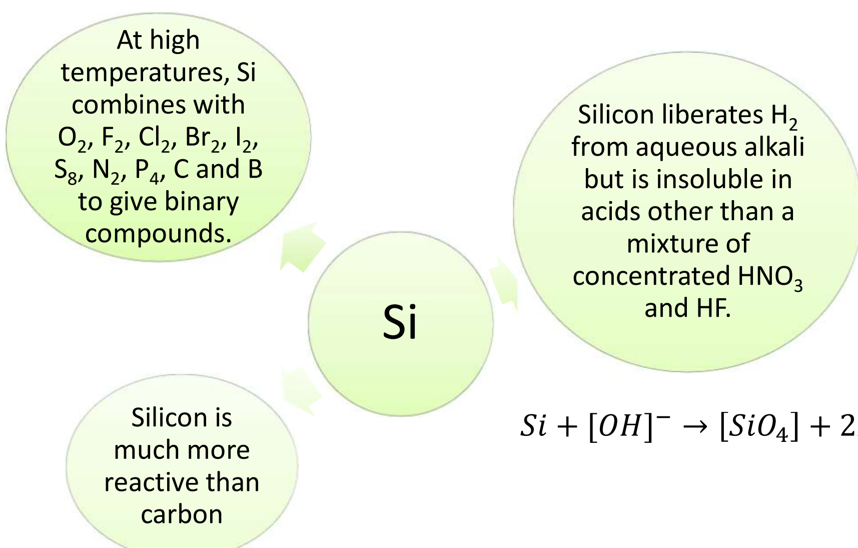
Valency-

- For lead compounds, 2-valent state is the most predominant. PbO_2 is a strong oxidising agent, while PbO is relatively stable.

$$PbO_2(s) + 4HCl(aq) \rightarrow PbCl_2(aq) + Cl_2 + 2H_2O(l)$$
$$2PbO_2(s) + 4H_2S(g) \rightarrow 2PbS(s) + S_2(g) + 4H_2O(l)$$

- ***Inert pair effect*** Ge, Sn and Pb form 2-valent compounds in which the two *s* electrons are inert (inert pair effect- because, as each of the two electrons is removed form p orbital, the remainder in the s-orbital are held more strongly by the increased positive charge-in the s orbital) and the stability increases from Ge to Pb.

Chemical properties: **Silicon**



$$Si + [OH]^- \rightarrow [SiO_4] + 2H_2$$

Chemical properties:**Germanium**

Ge

- Germanium is more electropositive than Silicon and behave like silicon.
- Reacts with Conc HNO_3 to form GeO_2.
- Does not react with aqueous alkali
- Reacts with H_2S to give GeS_2.
- Reacts with HCl to give $GeCl_4$.

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Chemical properties: **Tin**

Sn

- Reacts with dilute HNO_3 to form $Sn(NO_3)_2$ and NH_4NO_3.
- little affected by dilute HCl or H_2SO_4 but when concentrated will yield $SnCl_2$ and $SnSO_4/SO_2$ respectively
- Reacts with O_2 and sulphur at high temp. to give SnO_2 and SnS_2 respectively..
- Reacts readily with halogens to give SnX_4.

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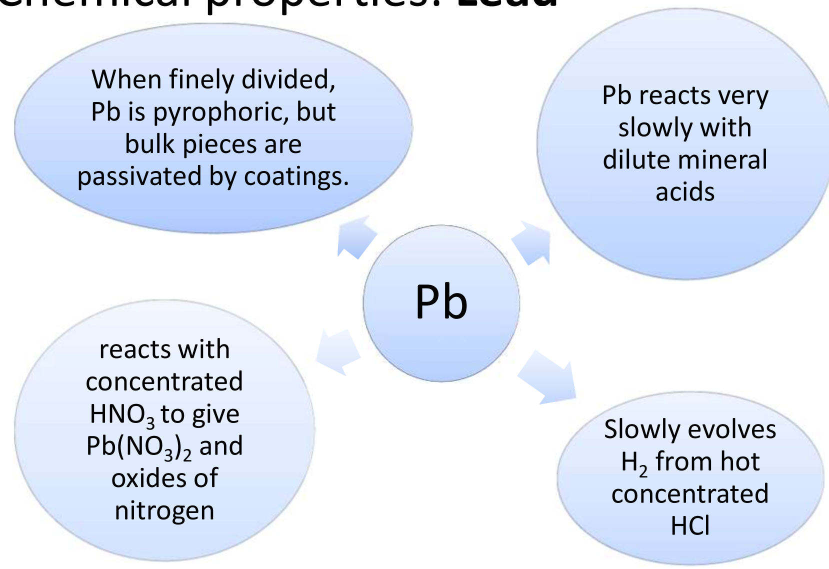
Chemical properties: **Lead**



{A pyrophoric material is spontaneously inflammable}

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Some Simple compounds of Group IV elements

- **Hydrides--**tetravalent hydrides XH_4

  CATENATION is a a unique ability of this group in which they forms stable compounds containing long chains and rings of atoms.

  – ***Hydrocarbons: eg*** alkanes, alkenes and alkynes. The ability of carbon to catenate results from the fact that the C-C bond is almost as strong as the C-O bond [C-C=346 $kJmol^{-1}$, C-O=360 $kJmol^{-1}$].

  – ***Silanes:*** Si-Si bond is much weaker than Si-O bond [Si-Si=226$kJmol^{-1}$, Si-O=464$kJmol^{-1}$], therefore catenated compounds of silicon are energetically unstable with respect to SiO_2 and does not occur naturally. SiH_4 is spontaneously inflammable in air.

  – ***Germane, Stannane And Plumbane:***

  eg GeH_4, SnH_4 and PbH_4

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Some Simple compounds of Group IV elements

- **Halides-----**All the elements in this group react directly with halogens to form the tetrahalides (CCl_4, $SiCl_4$), except lead which forms the dihalides ($PbCl_2$).
- **Oxides----**All members of the group except lead reacts with oxygen on heating to form the dioxide(CO_2, SiO_2). Lead forms the monoxide, PbO.
- **Carbides, silicides:** These are solid state binary compounds that some members of this group form with metals. Examples: metal carbides are CaC_2, K_2C_2.

  Metal silicides; Mg_2Si, Ca_2Si. Ge, Sn and Pb do not form solid state binary compounds with metals

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Carbon dioxide:Greenhouse effect

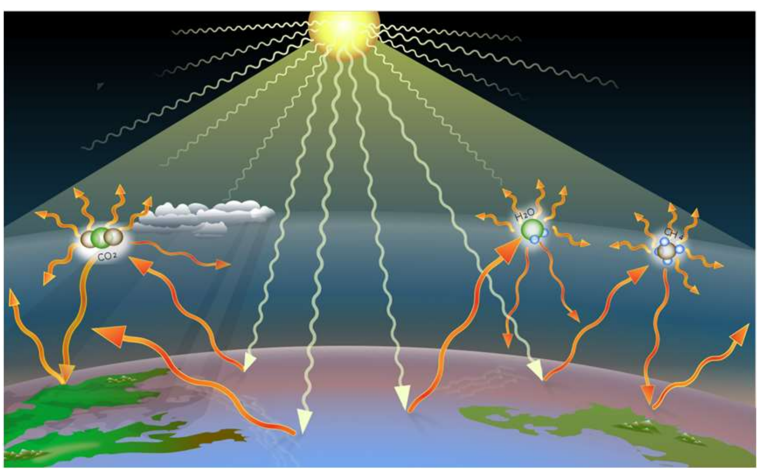

Diagram showing light energy (white arrows) emitted by the sun, warming the earth's surface which then emits the energy as heat (orange arrows), which warms the atmosphere and is then re-emitted as heat by three of the greenhouse gas molecules (water, carbon dioxide, and methane) *(Wikipedia,2019)*

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Carbon dioxide: Dry Ice

- **Dry Ice** is the solid form of carbon dioxide
- **Dry ice** sublimates at 194.65 K at Earth atmospheric pressures
- **Dry ice** is colourless, non-flammable, with a sour zesty odor, and can lower the pH of a solution when dissolved in water, forming carbonic acid (H_2CO_3).

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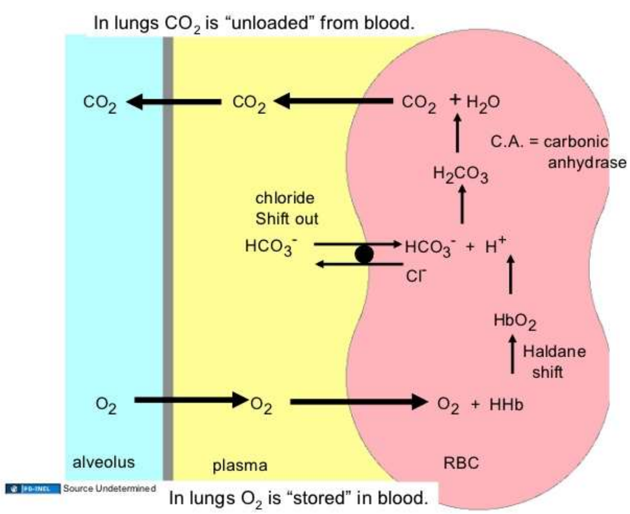
Carbon dioxide: Produced in the blood



Google image, 2019

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Glass: What is glass?

- Glass is a state of matter.
- It is a solid produced by cooling molten material so that the internal arrangement of atoms, or molecules, remains in a random or disordered state, similar to the arrangement in a liquid.

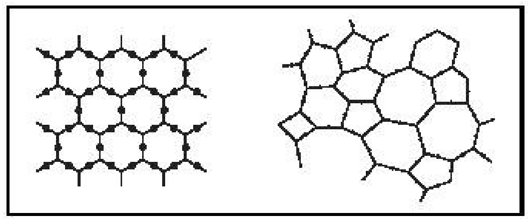

Figure 1. Structures of a typical solid (l.) and glass (r.)

http://www.chemistryexplained.com/Ge-Hy/Glass.html

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Glass: What is glass?

- Pure silica can produce an excellent glass, but it is very high-melting (1,723 ^{o}C, or 3,133 ^{o}F), and the melt is so extremely viscous that it is difficult to handle.
- All common glasses contain other ingredients that make the silica easier to melt and the hot liquid easier to shape.

http://www.chemistryexplained.com/Ge-Hy/Glass.html

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Making of glass

- Glass is made from liquid sand by heating ordinary sand, (which is mostly made of silicon dioxide) sodium carbonate, and limestone until it melts and turns into a liquid.
- Sand melts at the incredibly high temperature of 1700°C (3090°F).

(Google images, 2018)

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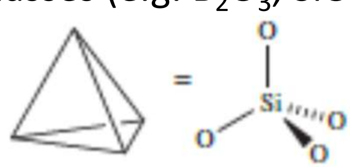
(Google images, 2018)

- When liquid silica cools, it forms a non-crystalline glass consisting of an infinite lattice assembled from SiO_4 tetrahedra connected in a random manner.
- Only a few oxides form glasses (e.g. B_2O_3, SiO_2, GeO_2, P_2O_5 and As_2O_5)



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Types of Glasses

- Quartz glass (formed on cooling fused SiO_2) can withstand sudden temperature changes and has specialist uses.
- Borosilicate glass (Pyrex) contains 10–15% B_2O_3 and has a lower melting point than silica glass. They are chemically unreactive and can stand great changes in temperature without breaking.

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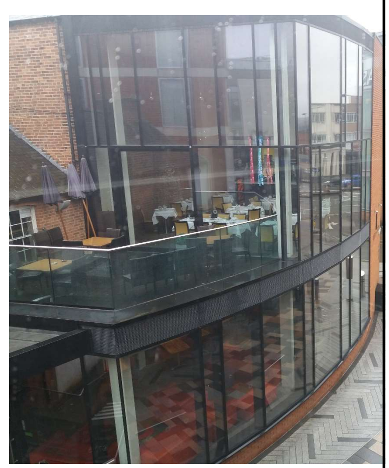
Types of Glasses

- Soda glass contains added alkali which converts some of the Si-O-Si bridges in the silica network into terminal Si=O groups, reducing the melting point below that of borosilicate glass.
- *Lead crystal* and *flint glass* are very dense and highly refractive glasses that are prepared by replacing lime with PbO and Pb_3O_4 .



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Types of glass

- Coloured glasses made by adding additives such as transition metal compounds.

- For example-
  - Cu_2O, a red precipitate has been added to glass, to which it imparts a red color.
  - CuO is used in making blue and green colored glass.

  - CoO gives a blue glass
  - FeO imparts a green color
  - CaF_2 produces an opaque white (milk) glass.

(Google images, 2018)

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Typical glass contains *formers*, *fluxes*, and *stabilizers*.

•**Formers** make up the largest percentage of the mixture to be melted. In typical soda-lime-silica glass the *former* is silica (Silicon dioxide) in the form of sand.

•**Fluxes** lower the temperature at which the formers will melt. Soda (Sodium carbonate) and Potash (Potassium carbonate), both alkalis, are common fluxes. Potash glass is slightly more dense than soda glass.

•**Stabilizers** make the glass strong and water resistant. Calcium carbonate, often called calcined limestone, is a stabilizer. Without a stabilizer, water and humidity attack and dissolve glass.

Glasses begin as mixtures of **oxides**. Their compositions can be represented by listing the weight percentages of their components. Compare the percentages for **1**, a typical, modern soda-lime-silica glass (used to make bottles and windows); **2**, laboratory and some baking ware; **3**, optical, high lead crystal; **4**, 96% silica glass (can withstand very high temperatures); **5**, a typical, ancient Roman soda-lime-silica glass.

https://www.cmog.org/article/chemistry-glass

		1	**2**	**3**	**4**	**5**
Silica	SiO_2	73.6%	80.0%	35.0%	96.5%	67.0%
Soda	Na_2O	16.0	4.	--	--	18.0
Lime	CaO	5.2	--	--	--	8.0
Potash	K_2O	0.6	0.4	7.2	--	1.0
Magnesia	MgO	3.6	--	--	--	1.0
Alumina	Al_2O_3	1.0	2.0	--	0.5	2.5
Iron Oxide	Fe_2O_3	--	--	--	--	0.5
Boric Oxide	B_2O_3	--	13.0	--	3.0	--
Lead Oxide	PbO	--	--	58.0	--	0.01

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Charcoal a form of Carbon

Charcoal

- This is an impure form of graphitic carbon,
- It is obtained as a residue when carbonaceous material is partially burned, or heated with limited access of air.
- Coke, carbon black, and soot may be regarded as forms of charcoal
- Most important use has been as a metallurgical fuel
- **Activated charcoal** is a black, odorless, flavorless powder that has been used since ancient times to treat various ailments.
- Used as an anti-poison remedy, reducing gas and flatulence, lower cholesterol levels and improved kidney function.
- Also used in skin care

Britannica, The Editors of Encyclopaedia. "charcoal". *Encyclopedia Britannica*, 26 Sep. 2022, https://www.britannica.com/science/charcoal. Accessed 3 November 2022.