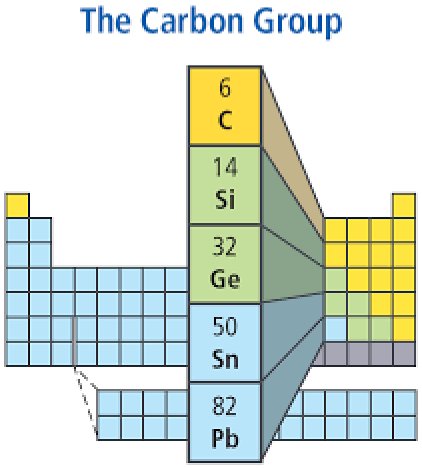
Group 14 – Overview

- The group includes non-metals (C), semi-metals (Si, Ge) and metals (Sn, Pb).
- The most important oxidation states are +2 and +4. The stability of compounds with a +2 oxidation state increases with the atomic number (PbH_4 and $PbCl_4$ are unstable whereas CH_4 and CCl_4 are very stable) .
- Carbon displays a unique π-bonding ability (double bonds) and likes to form chain compounds (→ 'Organic Chemistry').
- The basic character of the hydroxides increases with the atomic number: $Ge(OH)_2$ is slightly acidic, $Sn(OH)_2$ is amphoteric and $Pb(OH)_2$ is slightly basic.



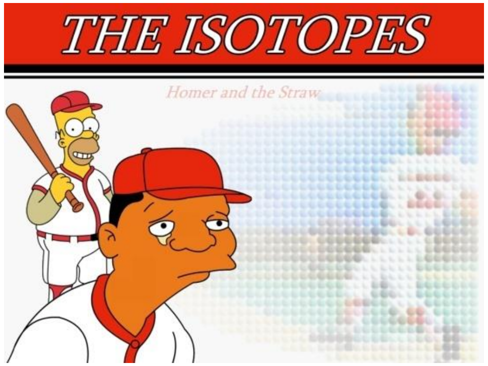
Carbon

- Carbon is the sixth most abundant element in the universe.
- Carbon is most commonly obtained from coal deposits, although it usually must be processed into a form suitable for commercial use.
- Three naturally occurring allotropes of carbon are known to exist: amorphous carbon, graphite and diamond.

Coal

Carbon Isotopes

- In 1961 the International Union of Pure and Applied Chemistry adopted the isotope ^{12}C (natural abundance: 98.93 %) as the basis for atomic weights.
- ^{14}C an isotope with a half-life of 5715 years, has been widely used to date such materials as wood, archaeological specimens, etc.
- ^{13}C is particularly useful for isotopic labeling studies since it is not radioactive, but is a spin I = $^1/_2$ nucleus and therefore a good NMR nucleus (natural abundance: 1.07 %).



Radiocarbon Dating

- ^{14}C is produced in the atmosphere by reaction of ^{14}N and neutrons:

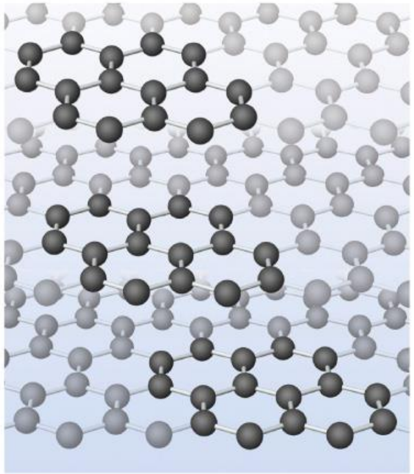
$$^{14}N + n \rightarrow {}^{14}C + p$$

- In all living organisms the ^{14}C concentration is approx. constant. After death of the organism: only decay.
- ^{14}C decays back to ^{14}N by emitting electrons, which can be detected. Limit after ~ 10 half-lifes because few material is left.

Willard F. Libby, Nobel prize in Chemistry 1960 for '*for his method to use Carbon-14 for age determinations in archaeology, geology, geophysics, and other branches of science'.*

Graphite

- sp^2 Hybridized, 2-D sheet structure.
- Hexagonal graphite has a ABAB sheet structure.
- C-C = 142 pm.
- Extremely soft – weak interactions between the sheets.
- Delocalized (p-p)π-bonds: → Conductor (the conductivity along the sheets is 10^4 times higher)
- Uses: electrode material, pencil 'lead', lubricant.
- In air, graphite reacts to CO_2 at T > 700 °C.



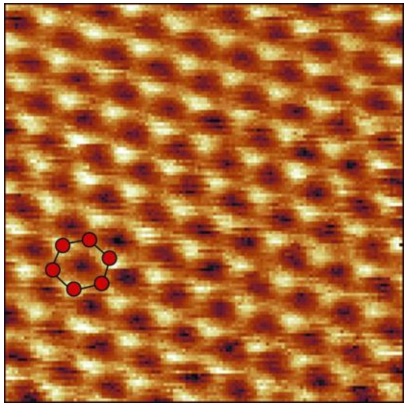


Image of graphite obtained by scanning force microscopy.

Charcoal

Charcoal is usually produced by the heating of wood in the absence of oxygen. The resulting soft, brittle, lightweight, black, porous material resembles coal.

Charcoal pencils

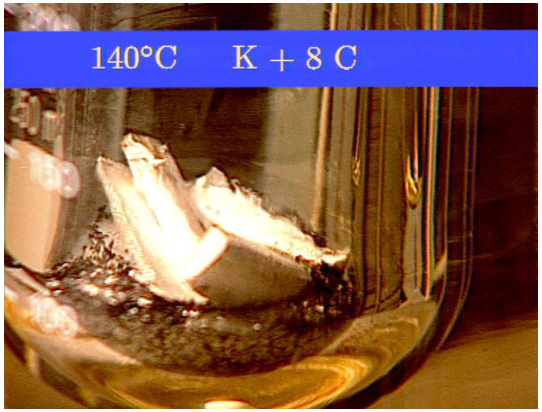
Charcoal

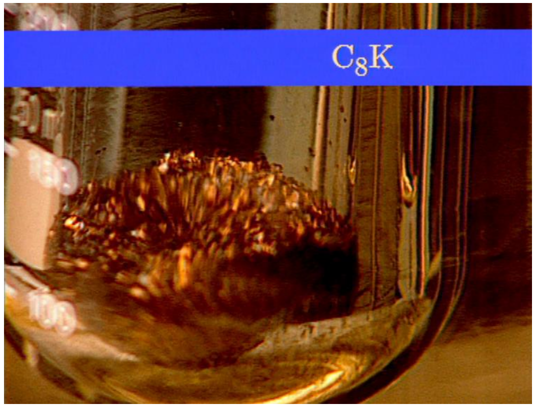
The men and women who made charcoal were called “colliers.” To make charcoal, split billets of wood were stacked as high as 20 feet. A triangular chimney was created in the middle of the mound. The entire pile would then be covered with a layer of loose top soil about 1 foot thick. A small opening would be left for the chimney. For the next few days and nights, the collier would get little sleep as the smoldering mound would need constant watch. If the fire grew to hot, it would consume the entire pit and burn all the fuel. If it burned too slowly the quality would be insufficient.

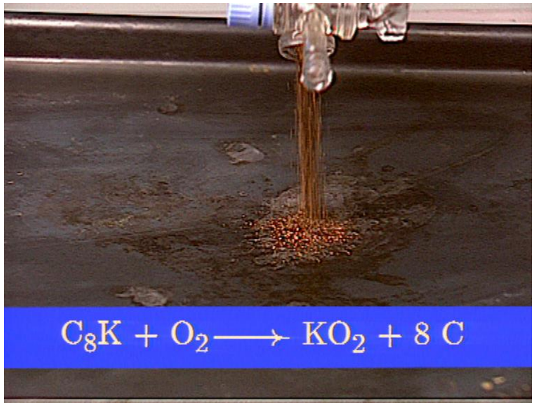
Activated Charcoal

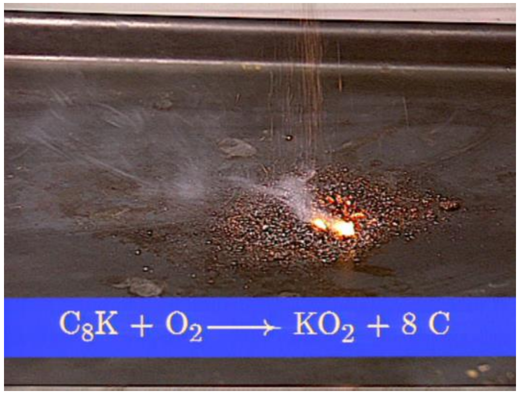
Activated charcoal represents a large surface area for adsorbtion. 1g of activated charcoal has surface of 800 to 2000 m^2. It can absorb 100 to 200 times its own weight in organic chemicals.

Graphite and K



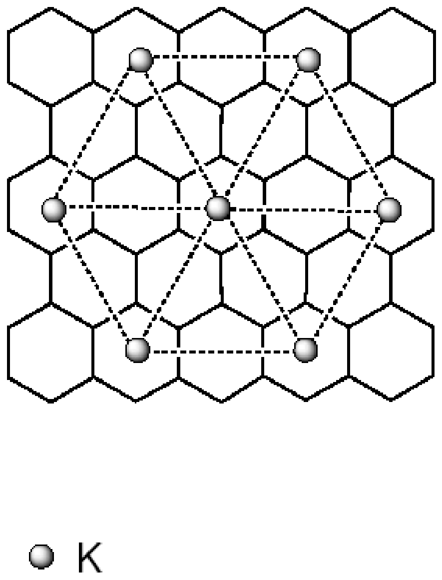


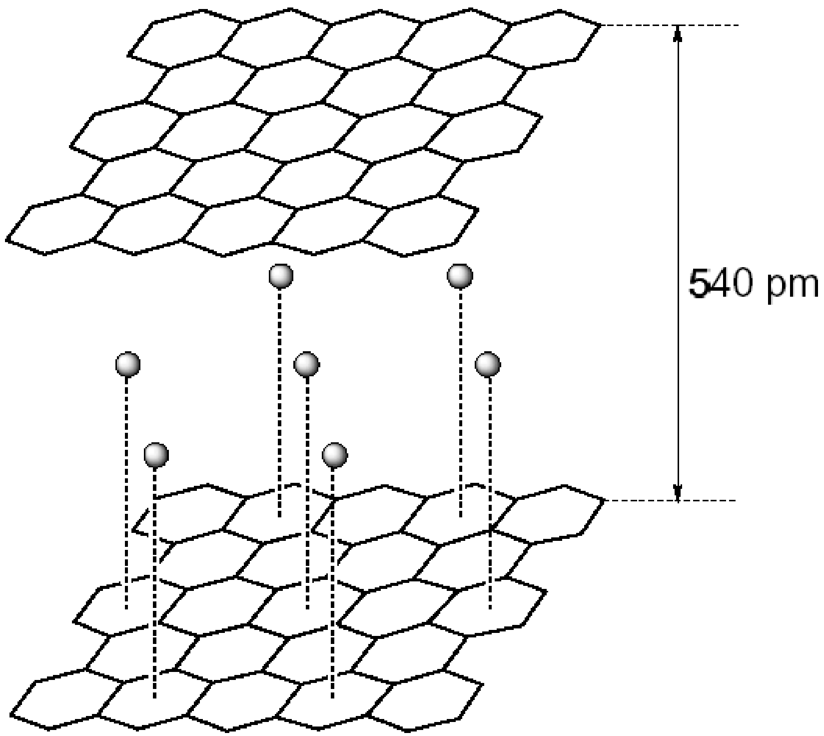




(Video: http://www.cci.ethz.ch)

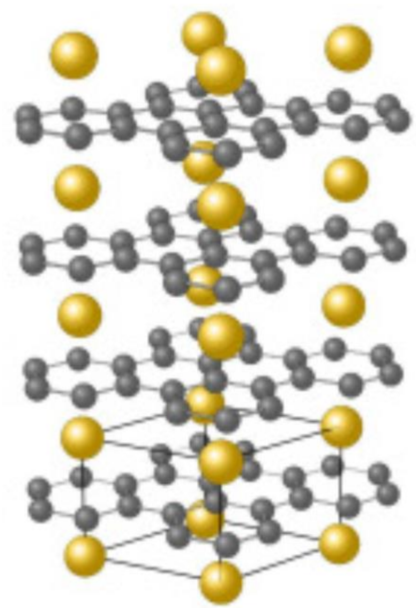
Structure of C_8K

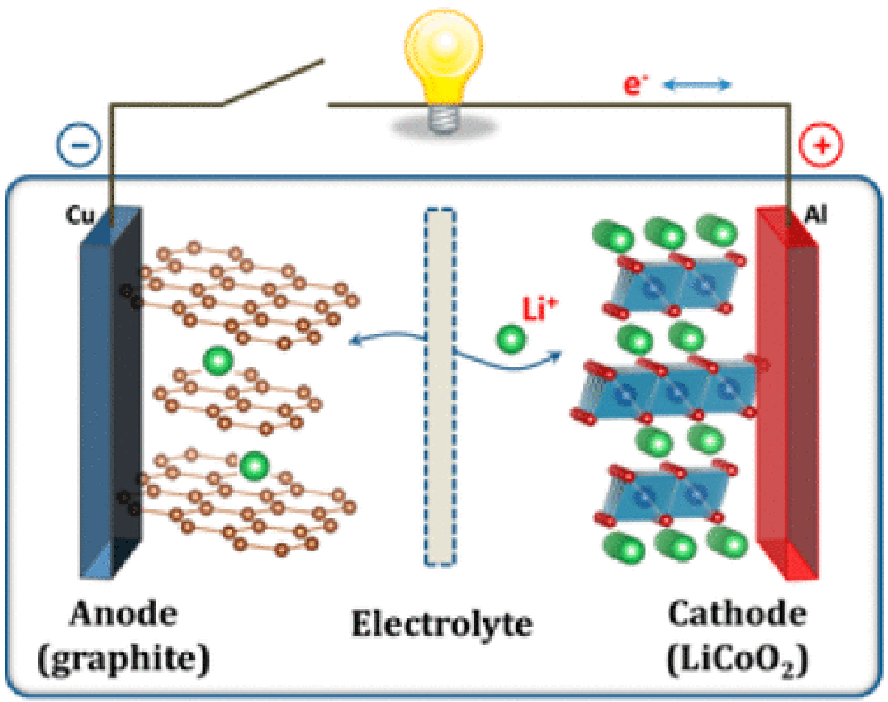




The carbon layers are directly on top of each other; the distance between the layers is 540 pm (graphite: ABA or ABC; 335 pm).

The Lithium Ion Battery

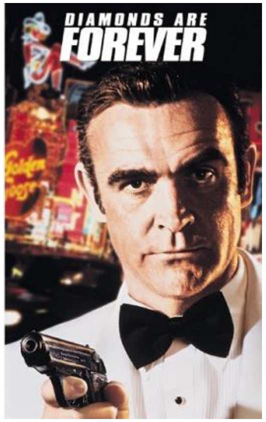




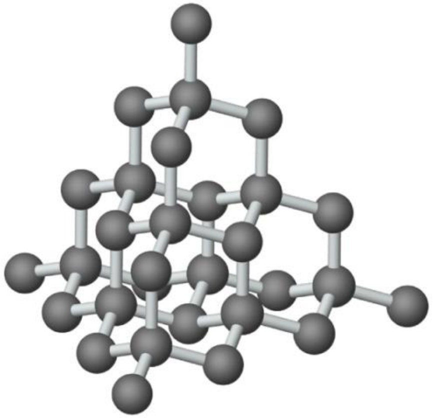
$$\mathrm{LiC_6 + CoO_2 \rightleftharpoons C_6 + LiCoO_2}$$

Discharge →

Diamond

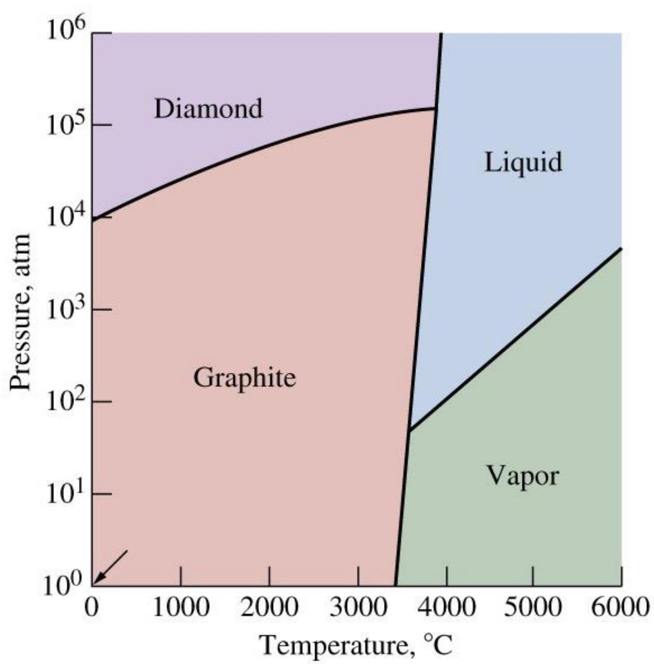


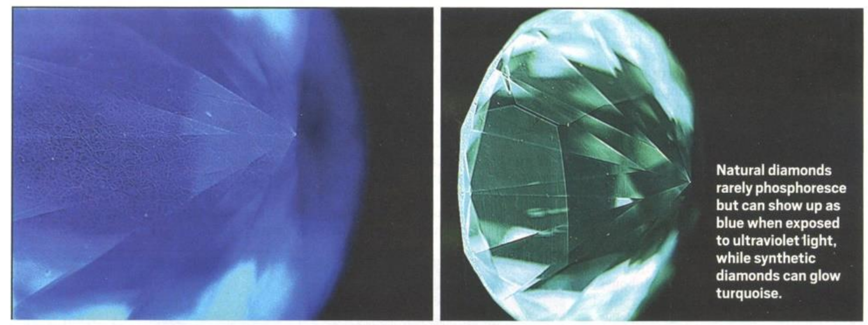
- sp^3 Hybridized, 3-D network solid.
- C-C = 154 pm.
- Because of the high C-C bond energy, diamond is extremely hard and has a high melting point – but it does burn!
- Electric insulator but very high thermal conductivity.
- In air, diamond reacts to CO_2 at T > 800 °C (Davy proved that diamond and graphite are the same by burning them and analyzing the gas produced).



Synthetic Diamonds

- 1955: a team at General Electric claimed credit for the first reproducible transformation of graphite to diamond.
- Typically required: very high pressure and temperature.





MATERIALS

Synthesizing precious gems

Technologies have become so good that man-made stones are being sold as natural

month ranging in size from 1–20 mm. An advantage Tairus has over gem miners is that its stones can be made to order, Barshai says.

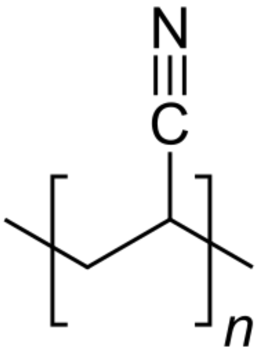
C&EN, Jan. 30, 2017

Diamonds manufactured by Diamond Foundry, a company to market gem-quality synthetic stones.

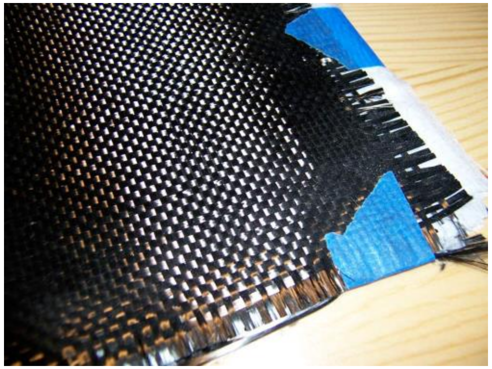
(http://www.diamondfoundry.com)

Carbon Fibers

Carbon fibers are made from organic polymers such as polyacrylonitrile.

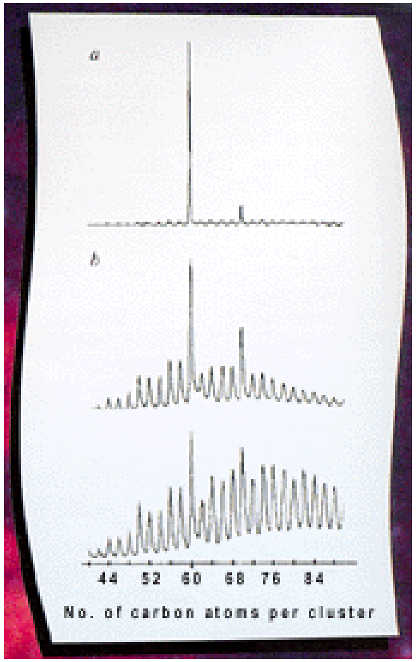


1. Oxidation (~ 300 °C)
2. Carbonization (> 1000 °C)

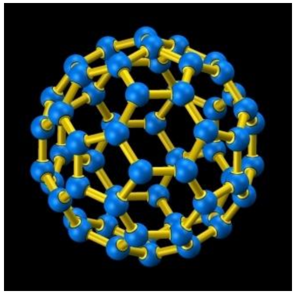


Fullerenes – History

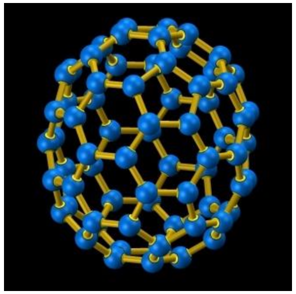
- In 1985, Robert Curl, Harold Kroto and Richard Smalley made the completely unexpected discovery that the element carbon can also exist in the form of very stable spheres. They termed these new carbon balls fullerenes.
- Five years after the discovery of the fullerenes, the astrophysicists D. R. Huffmann and W. Krätschmer and their co-workers managed to produce fullerenes in larger quantities.
- Robert Curl, Harold Kroto and Richard Smalley were awarded the **1996 Nobel Prize in Chemistry** for their roles in the discovery of this class of compounds. (http://nobelprize.org/chemistry/laureates/1996/illpres).



The read-out from the mass spectrometer shows how the peaks corresponding to C_{60} and C_{70} become more distinct when the experimental conditions are optimized.

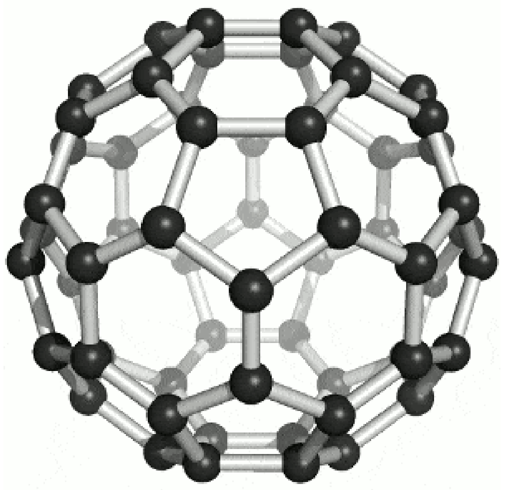


Buckminsterfullerene, C_{60}



C_{70}

Fullerenes – Properties

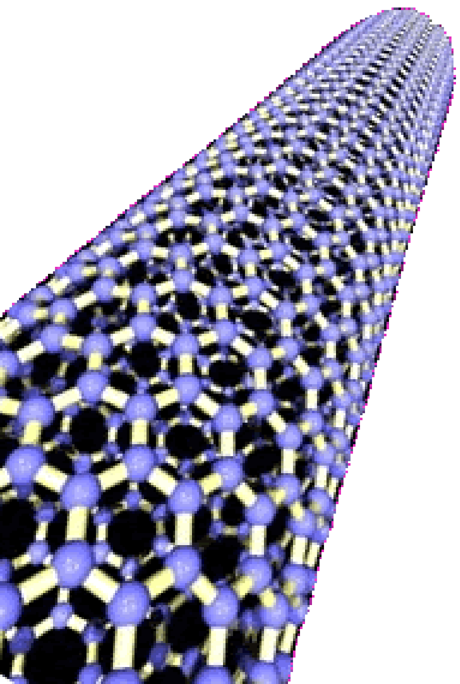


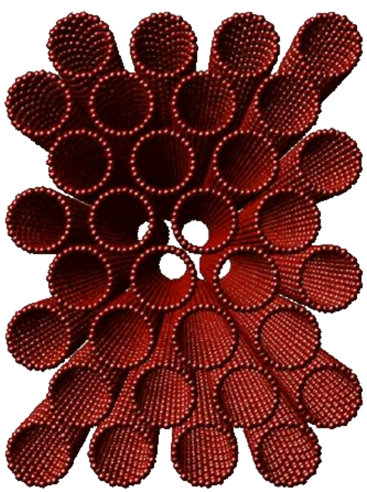
- C_{60} is comprised of 20 six-membered and 12 five-membered rings with all carbon atoms being equivalent.
- Fullerenes are also found in the natural environment, but only in the ppm-range.
- Good solvents for fullerenes are CS_2 and toluene. Fullerenes are unsoluble in water and stable at air.
- Sigma-Aldrich (2023) : 1 g C_{60} = 205.- SFr;
  0.5 g C_{70} = 575.- SFr.

Solution of C_{60} in toluene

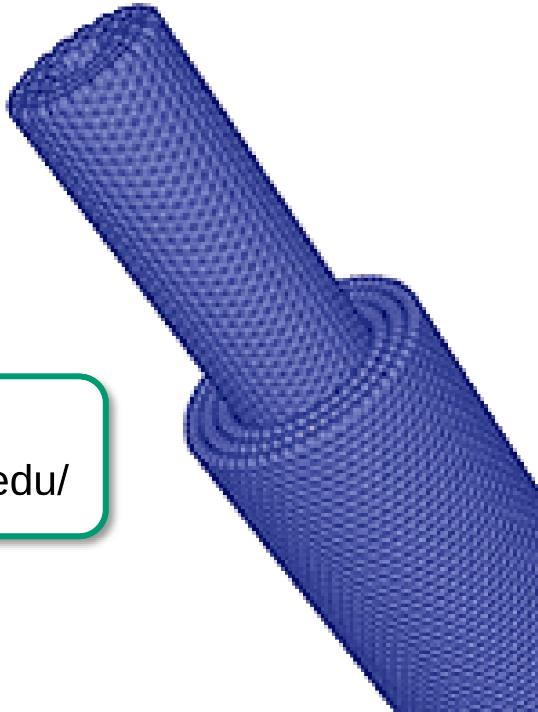
Carbon Nanotubes – History

- Multi-walled carbon nanotubes (MWCN): discovered in 1991 by the Japanese electron microscopist Sumio Iijima who was studying the material deposited on the cathode during the arc-evaporation synthesis of fullerenes (*Nature* **1991**, *354*, 56).
- 1993: First report about single-walled carbon nanotubes (SWNT), also from the Iijima lab *(Nature* **1993**, *363*, 606)*.*

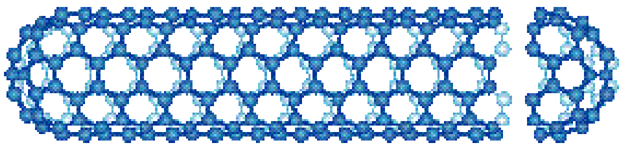




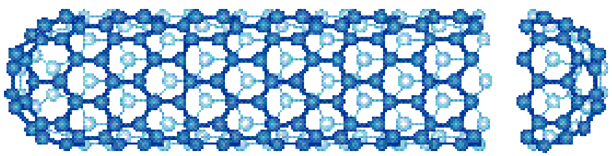
'The Nanotube Site':
http://nanotube.msu.edu/



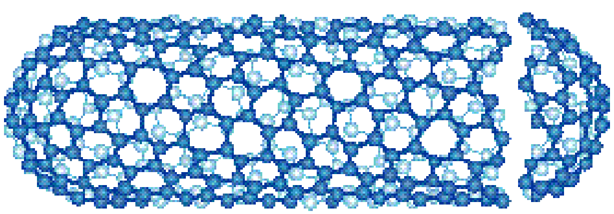
Carbon Nanotubes – Structures



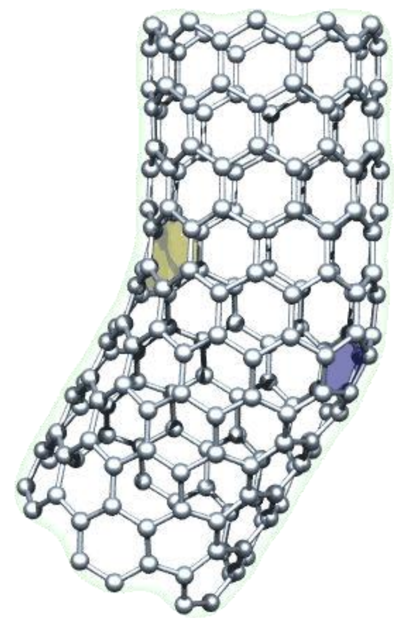
‘Armchair structure’



‘Zigzag structure’



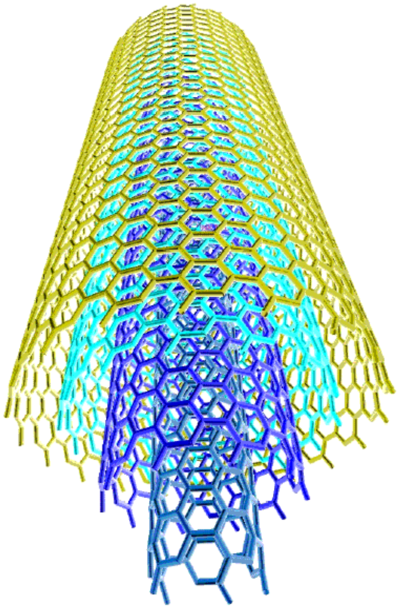
Chiral structure

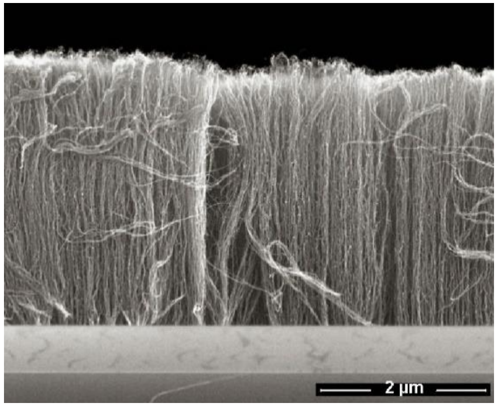


Defects result in bends

Carbon Nanotubes – Properties

- Nanotubes can be metallic or semiconducting depending on their structure (even superconducting at low temperature).
- Nanotubes display a very high thermal conductivity
- Nanotube fibers are very strong.
- Tubes can be filled with a variety of materials including biological molecules.





Carbon Nanotubes – Production

C&EN
CHEMICAL & ENGINEERING NEWS

BUSINESS

NOVEMBER 12, 2007 | VOLUME 85, NUMBER 46 | PP. 29-35

Carbon Nanotubes By The Metric Ton

Axunn

FREESTYLE Bayer's carbon nanotubes combined with epoxy resins by Nanoledge make Axunn's skis stronger.

Arkema

SCALED UP Arkema's carbon nanotube reactor can produce tens of metric tons per year.

Carbon Nanotubes – Applications

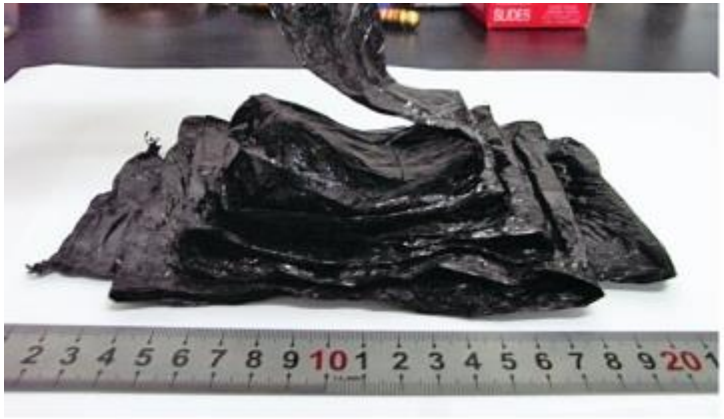
C&EN
CHEMICAL & ENGINEERING NEWS

Latest News
Web Date: January 29, 2016

Strong, Stretchable Carbon Nanotube Films Surpass Kevlar And Carbon Fiber

Nanomaterials: Simple new method yields films of highly aligned, densely packed nanotubes

By ***Prachi Patel***



Nano Letters **2016**, *16*, 946

Graphene

Andre Geim

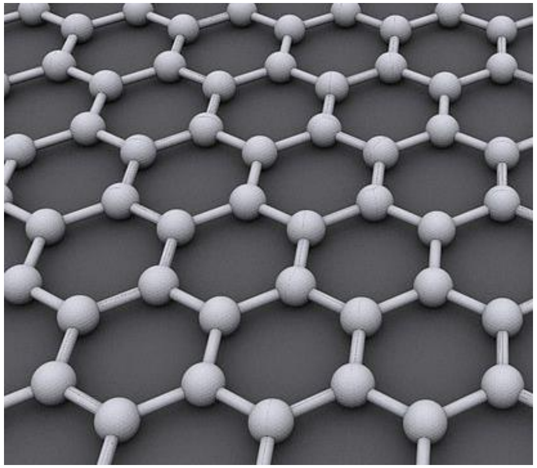
Konstantin Novoselov

The Nobel Prize in Physics 2010 was awarded jointly to Andre Geim and Konstantin Novoselov *"for groundbreaking experiments regarding the two-dimensional material graphene"*

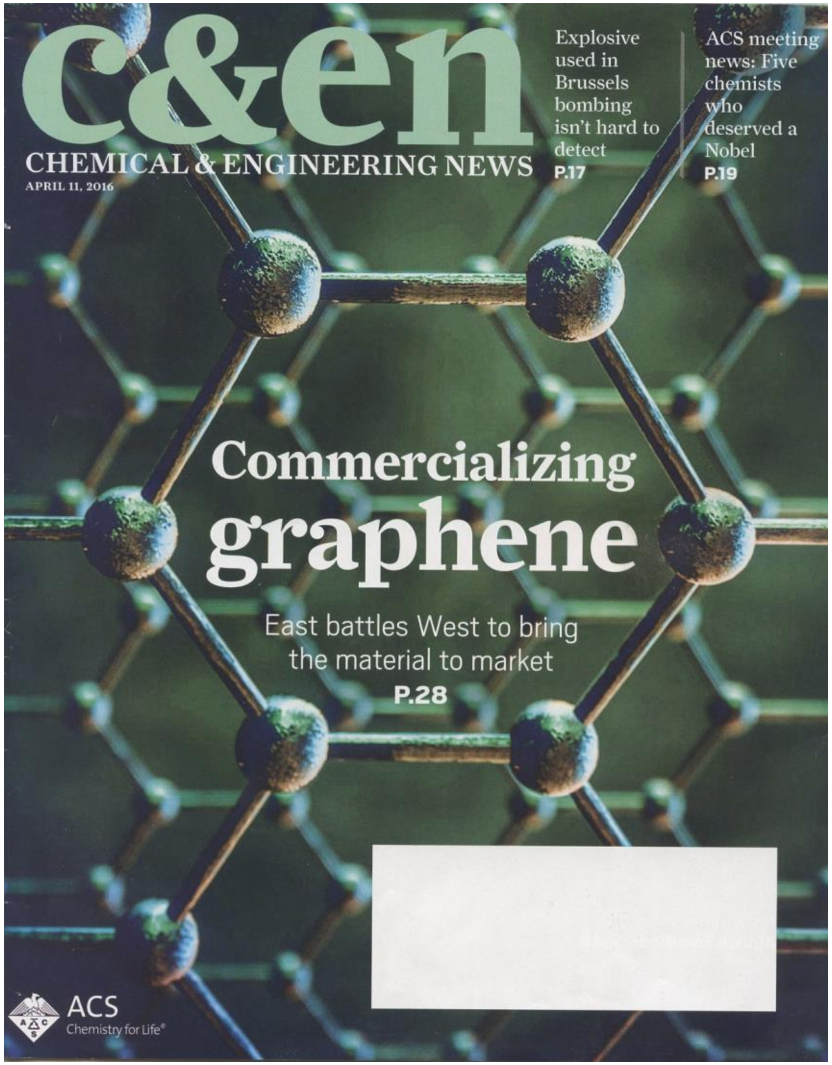
http://www.nobelprize.org/nobel_prizes/physics/laureates/2010/

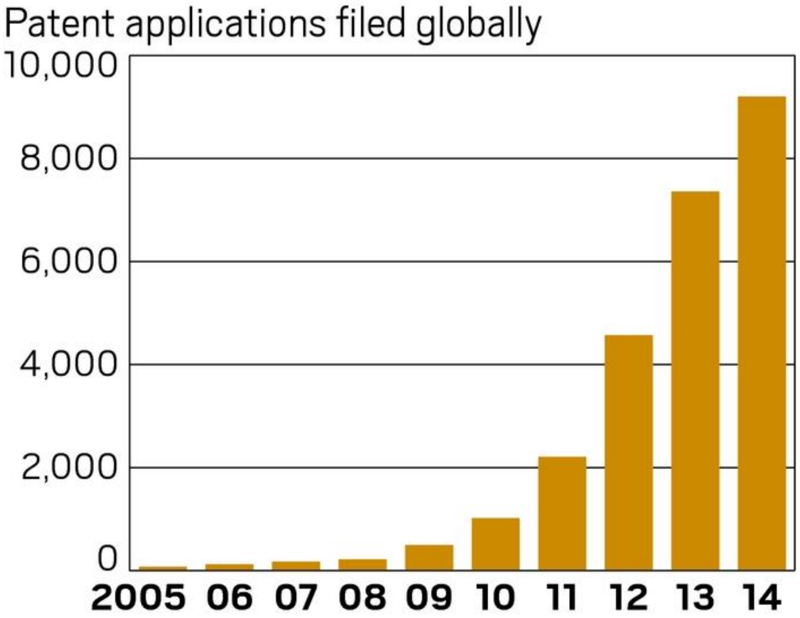
Graphene

- One-atom-thick planar sheets of sp^2-bonded carbon atoms.
- First synthesis by Böhm in 1962.
- In 2004, Geim and Novoselov isolated individual graphene planes by using adhesive tape.
- Graphene has a remarkably high electron mobility and may other unique physical properties.
- Graphene appears to be one of the strongest materials ever tested.
- By now, graphene is produced and sold on a larger scale.



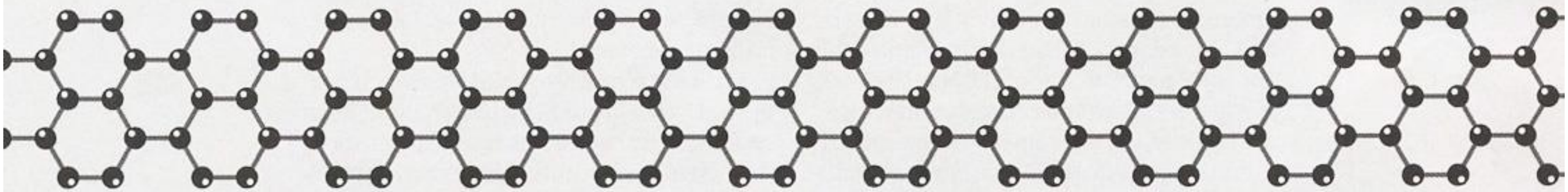
Graphene





C&EN April 11, 2016

Graphene

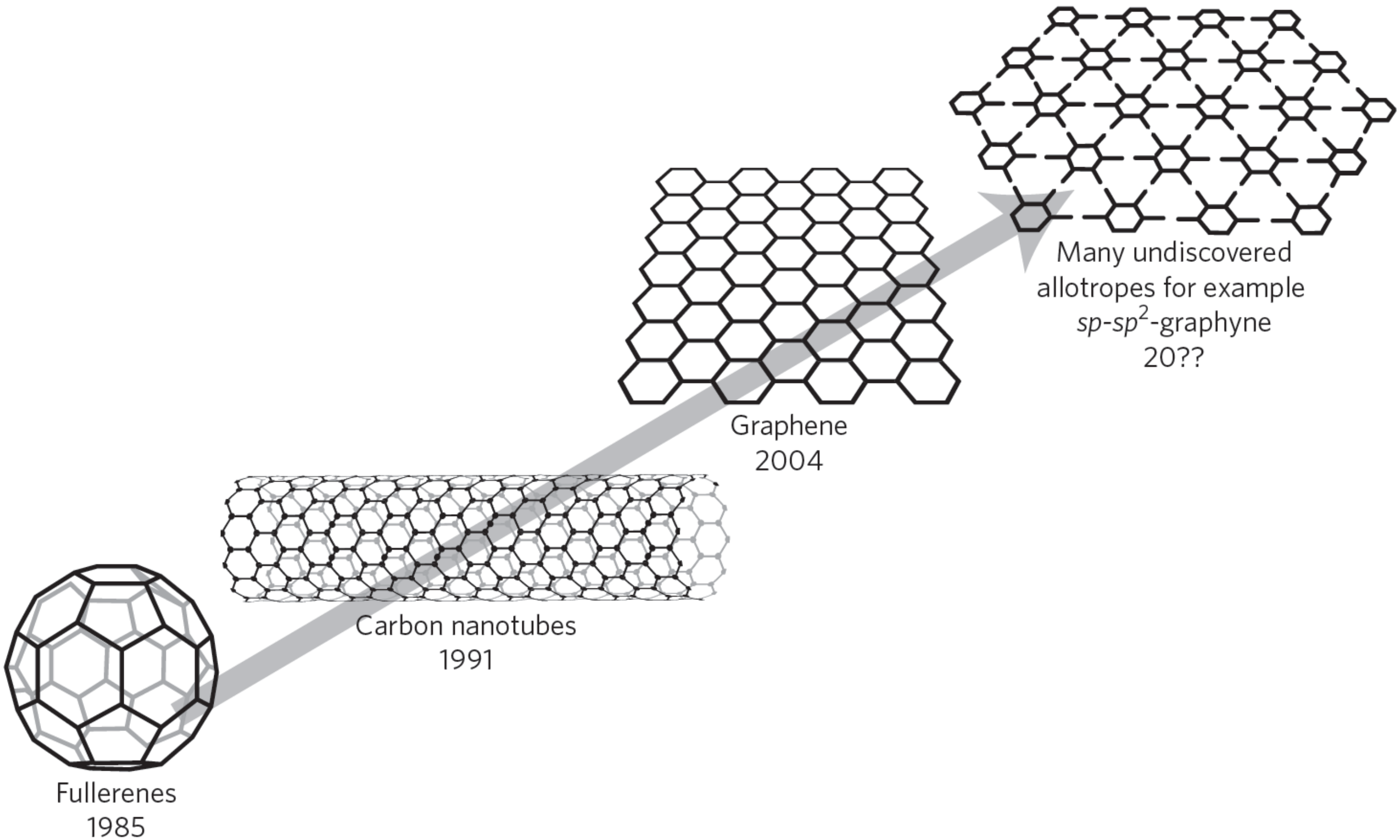


Graphene by the numbers

- **$30 million:** Expected worldwide sales of graphene in 2016
- **>$220 million:** Expected worldwide sales of graphene in 2026
- **6:** How many times graphene is as effective at conducting electricity as copper
- **500:** The number of graphene-related patent families filed by Samsung
- **2003:** The year the University of Manchester's Andre K. Geim and Konstantin S. Novoselov first isolated graphene using sticky tape
- **7:** The number of research papers published daily about graphene
- **$1.1 billion:** The 10-year budget of the European Commission's Graphene Flagship
- **120%:** The amount graphene can be stretched
- **47%:** The share of graphene patents first filed by organizations in China
- **$90 million:** The cost of building the U.K.'s National Graphene Institute at the University of Manchester
- **>26,000:** The number of graphene-related patents filed worldwide to date

C&EN April 11, 2016

What else?

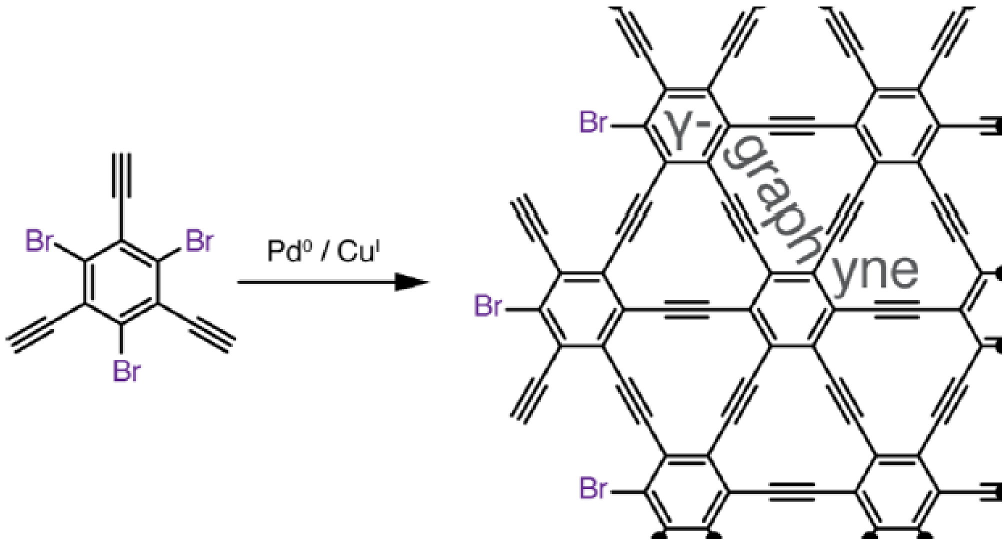


A. Hirsch *Nature Mater.* **2010**, *9*, 868.

Graphyne

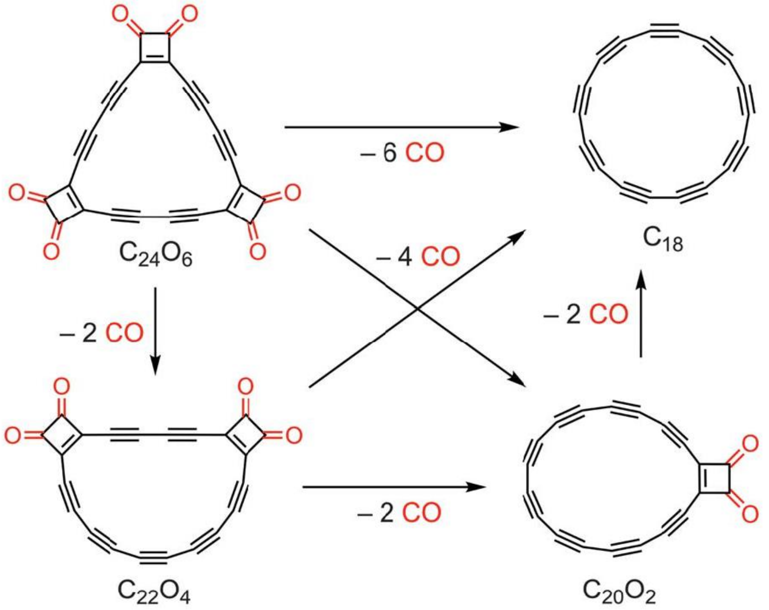
JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS
Article

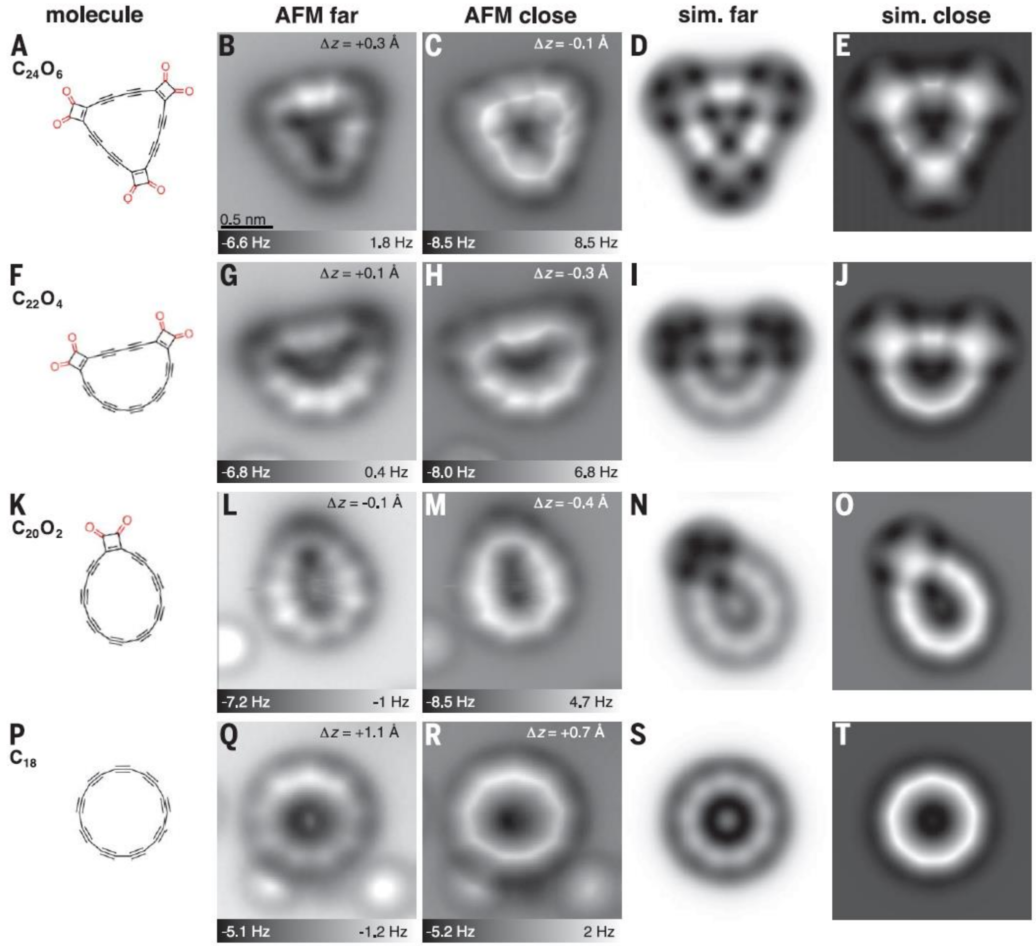
Scalable Synthesis and Characterization of Multilayer γ-Graphyne, New Carbon Crystals with a Small Direct Band Gap



V. O. Rodionov *et al.*, *J. Am. Chem. Soc.* **2022**, *144*, 17999.

Cyclo(18)carbon

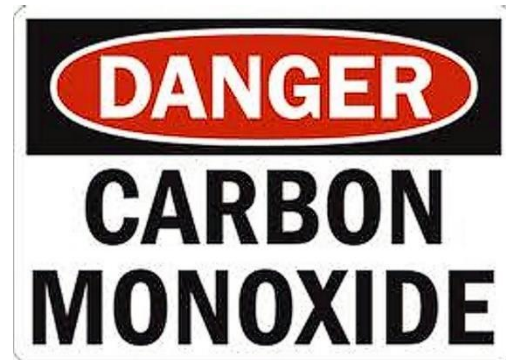


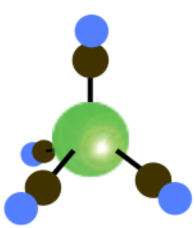


H. L. Anderson *et al.*, *Science* **2019**, *365*, 1299.

Carbon Monoxide (CO)

- Carbon monoxide is an odorless, colorless gas.
- CO is **very toxic**: it interferes with the delivery of oxygen in the blood to the rest of the body.
- CO is formed by incomplete oxidation of carbon. In the laboratory, CO can be obtained by dropping formic acid into warm H_2SO_4.
- CO forms carbonyl complexes with many transition metals.
  (→ 'Organometallic Chemistry')





$Ni(CO)_4$

$$HCOOH \xrightarrow{H_2SO_4} H_2O + CO$$

Carbon Dioxide (CO_2)

- CO_2 is an odorless, colorless gas.
- It is heavier than air and accumulates on the bottom of closed rooms → danger of suffocation.
- In the laboratory, CO_2 can be obtained by reaction of carbonates with acid:

$$CaCO_3 + 2\ HCl \longrightarrow CaCl_2 + H_2O + CO_2$$

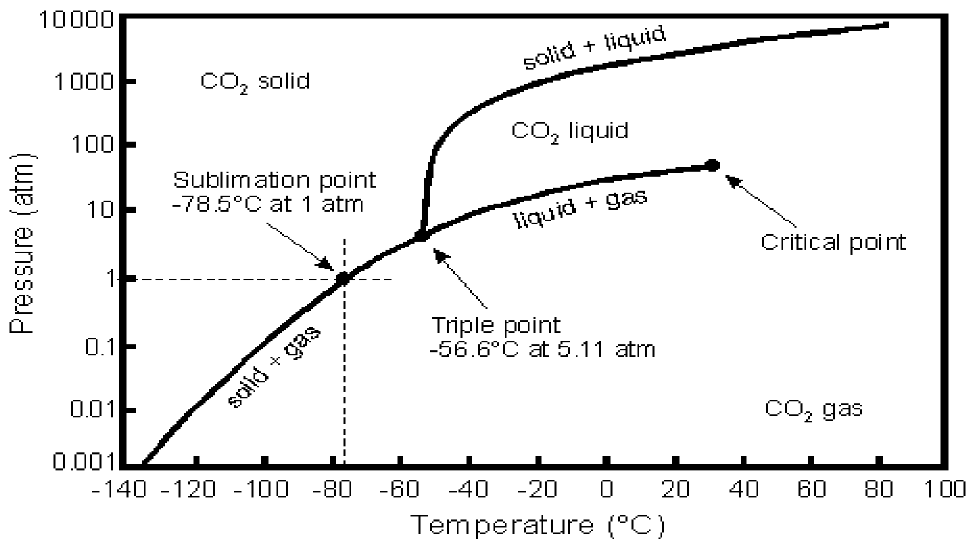
- CO_2 is chemically very stable. Very strong reducing agents are able to reduce CO_2 (Na, Mg).
- Between CO, C and CO_2 exist the '**Boudouard Equilibrium**':

$$CO_2 + C(s) \rightleftharpoons 2\ CO$$

At low temperature, the equilibrium is on the side of CO_2 → CO is metastable at room temperature!

Supercritical CO_2 (SCO_2)

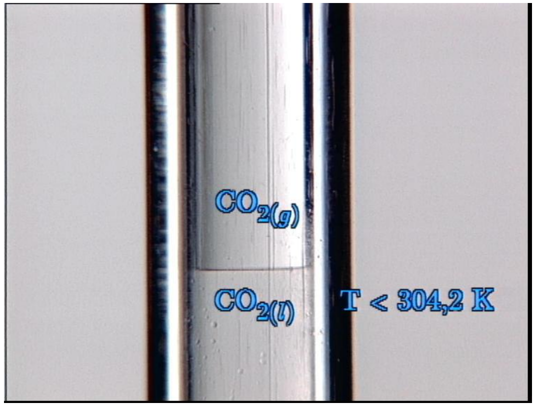
- The critical point of CO_2 is at ***T* = 31 °C** and ***p* = 74 bar**.
- SCO_2 is used for extraction processes on the industrial scale (e.g. decaffeination).



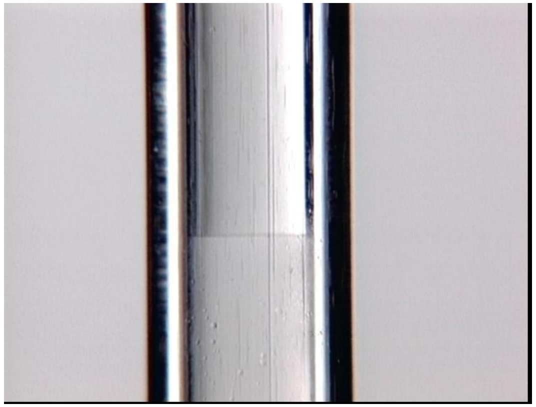
Pressure-Temperature phase diagram for CO_2.

2 x 400 l extraction plant for SCO_2.

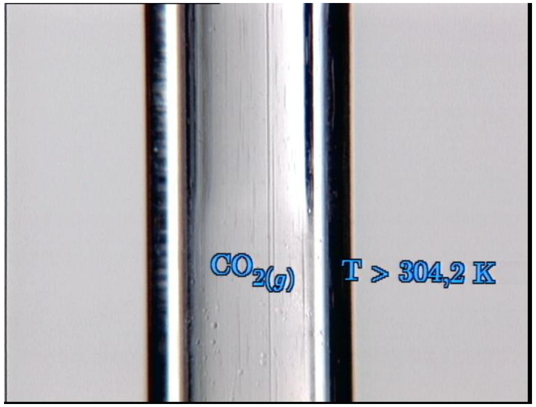
The Critical Point



Liquid and gas phases coexist below 304 K.



While heating the meniscus raises and becomes less sharp.

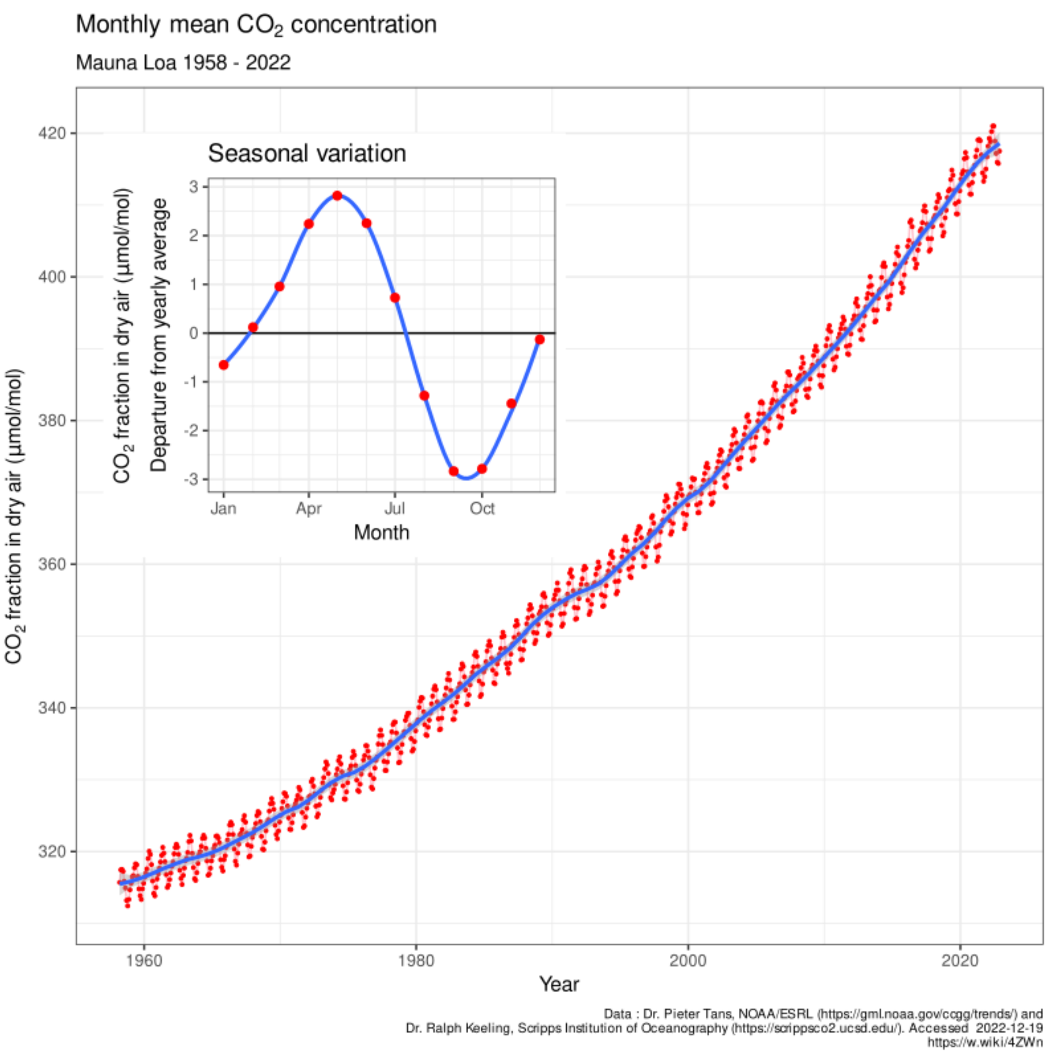


When the critical temperature of CO_2 (304 K) is passed the phase border disappears.

(Video: http://www.cci.ethz.ch)

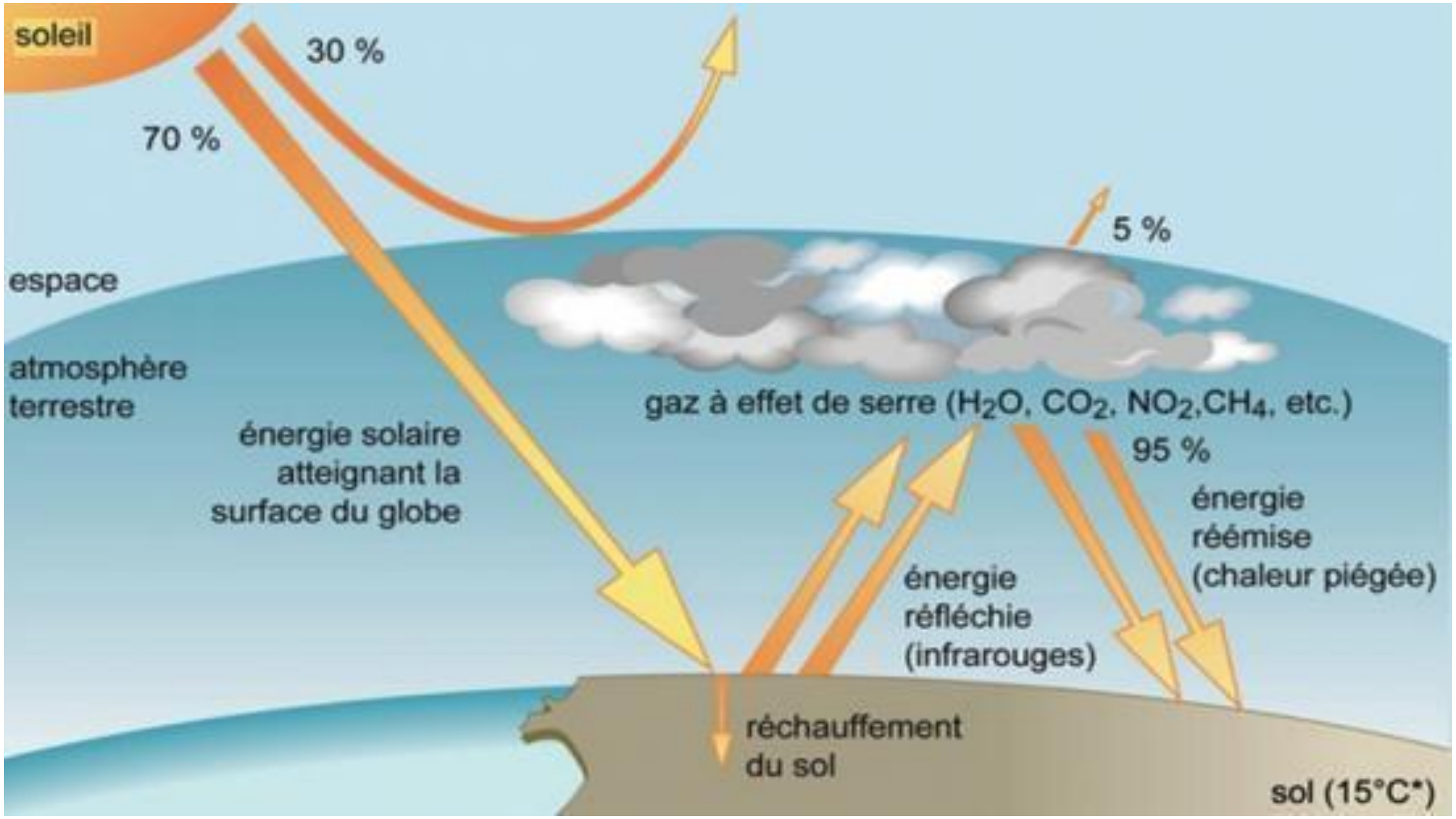
Carbon Dioxide and the Environment

Air contains > 0.04 vol % CO_2 (> 400 ppm).

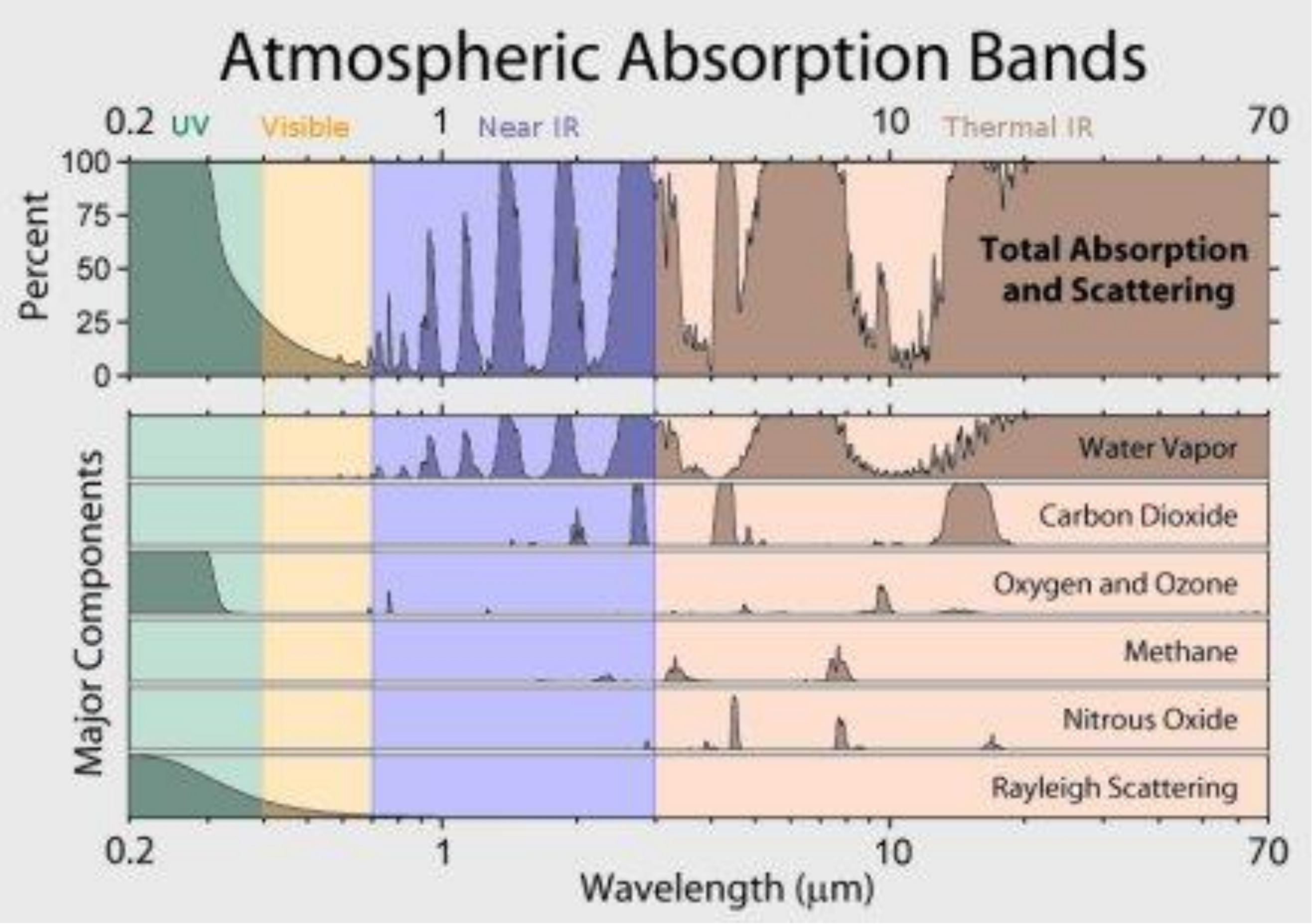


'The Keeling curve'

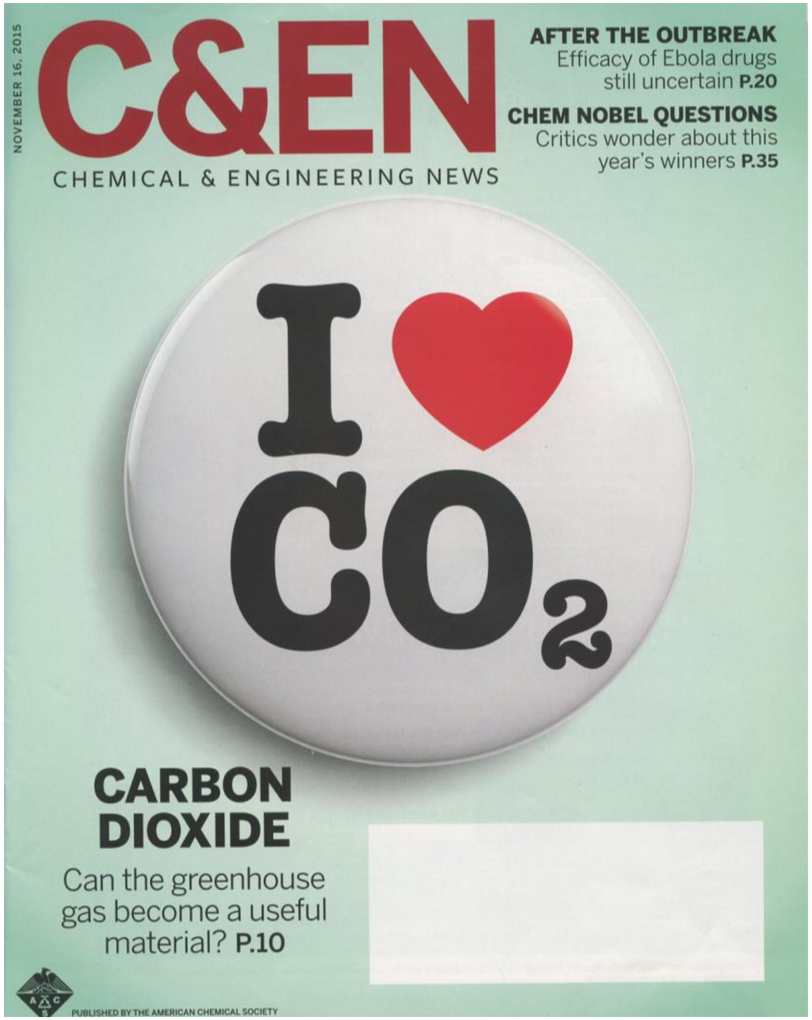
Greenhouse Effect



Greenhouse Effect

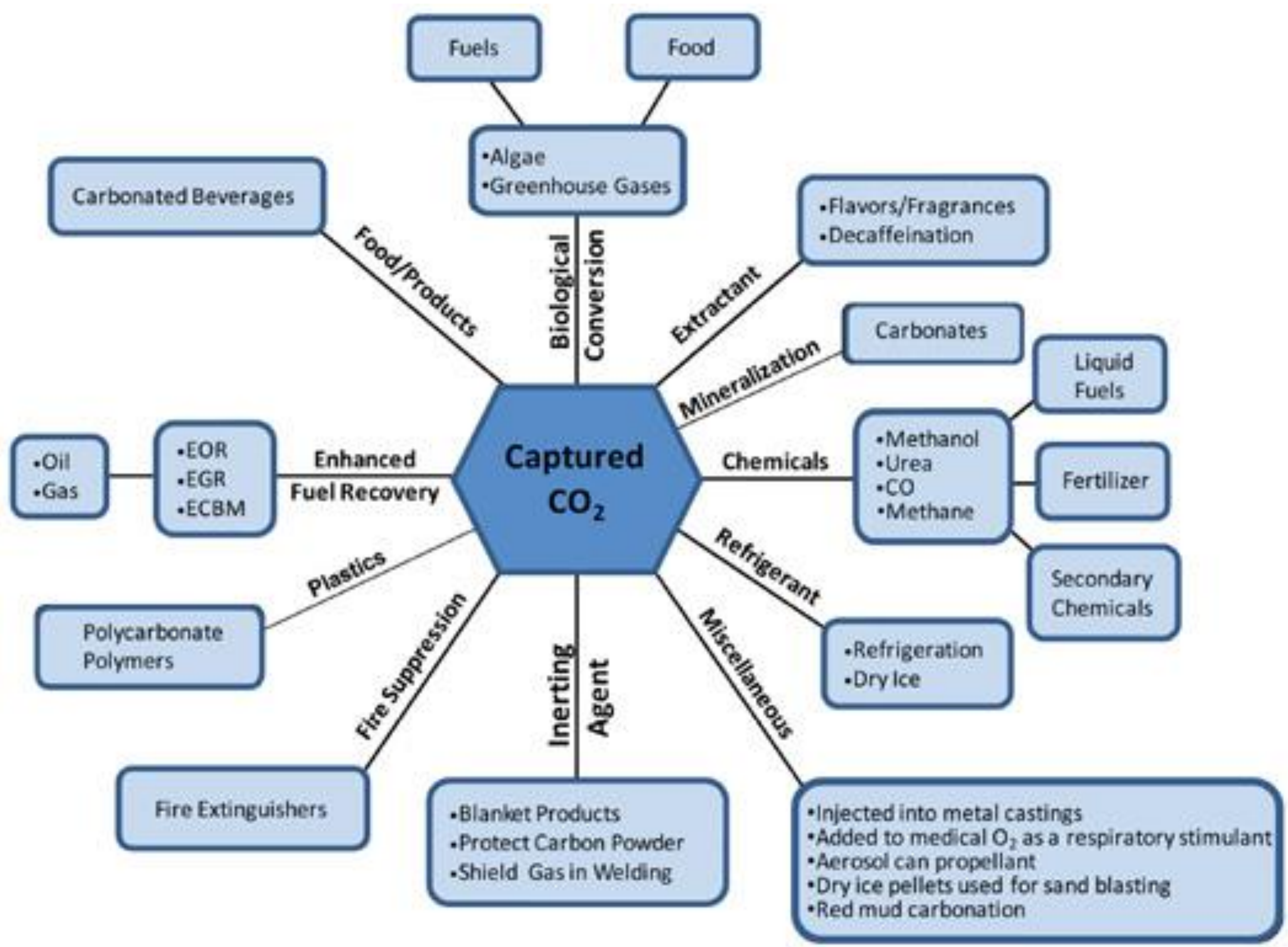


Using Carbon Dioxide



C&EN November 16, 2015

Using Carbon Dioxide



Using Carbon Dioxide – Synthesis of Urea
The Bosch-Meiser Process

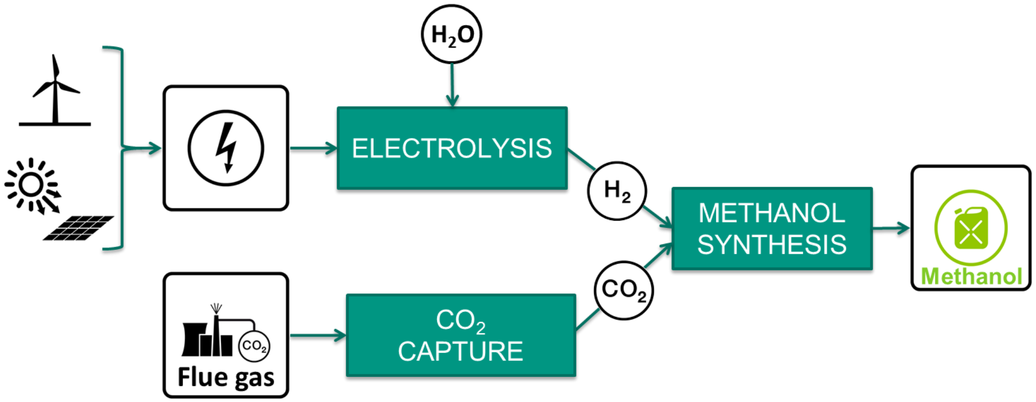
$$2NH_3(g) + CO_2(g) \longrightarrow \underbrace{H_2N{-}CO_2^-\;NH_4^+(s)}_{\textit{ammonium carbamate}}$$

$$\downarrow$$

$$\underbrace{H_2N{-}CO{-}NH_2}_{\textit{urea}} + H_2O(g)$$

~ 200 °C / 200 bar

Using Carbon Dioxide – Synthesis of Methanol



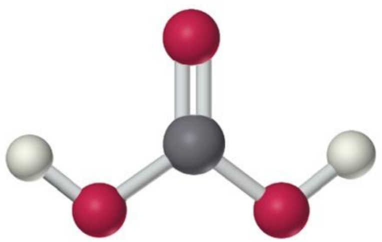
$$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

(October 2022)

→ link

Carbonic Acid

- CO_2 is the anhydride of carbonic acid, H_2CO_3. An aqueous solution of CO_2 reacts slightly acidic (pH = 4-5). The following equilibria are involved:


Carbonic acid

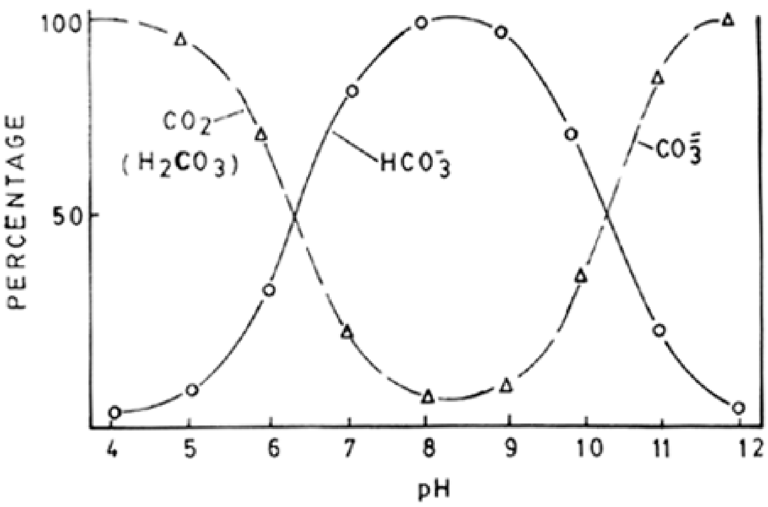
$$CO_2 + H_2O \longrightarrow H_2CO_3$$

$$H_2CO_3 + H_2O \longrightarrow H_3O^+ + HCO_3^- \qquad pK = 6.3$$

$$HCO_3^- + H_2O \longrightarrow H_3O^+ + CO_3^{2-} \qquad pK = 10.3$$

- The first equilibrium is almost completely on the side of CO_2: 99.8 % is in the form of a dissolved CO_2 molecule.

- Two forms of salts with HCO_3^- anions ('**bicarbonates**') and CO_3^{2-} anions ('**carbonates**').



Carbonic Acid

CO2 behaves as an acid

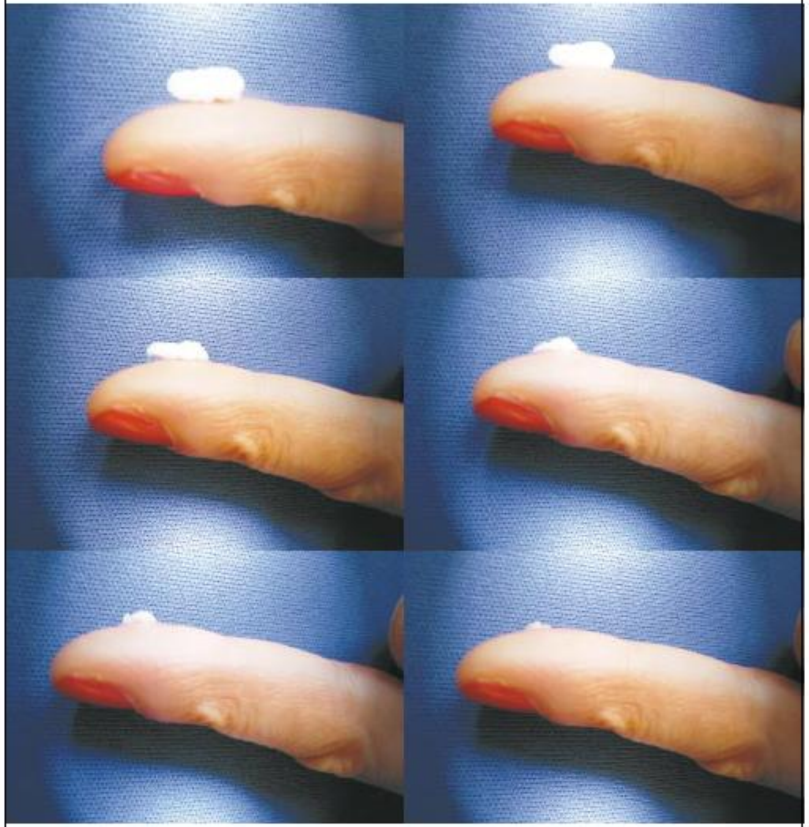
http://www.youtube.com/watch?v=nGZ8j2wHUrs

The Stability of Carbonic Acid

- For a long time the isolation of pure carbonic acid was thought to be impossible.
- Chemists succeeded to isolate and characterize pure carbonic acid. H_2CO_3 can even be sublimed and condensated proving its gase phase stability.
- The decomposition is catalyzed by water. This is an autocatalytic process.

Angew. Chem. Int. Ed. **2000**, *39*, 891.

Carbonic Acid (H_2CO_3) on the Finger Tip



Decay of carbonic acid (H_2CO_3) in an ice matrix on warming from the temperature of liquid nitrogen (77 K) on the finger tip of Ingrid Kohl over a period of about two minutes. More about this on the following pages.

Carbides

Carbides are compounds of carbon and metals or semi-metals → carbon is the more electronegative partner. Three classes of carbides can be distinguished:

- **Ionic carbides**
  Are formed with the most electropositive metals. They can be hydrolyzed to form hydrocarbons. The most common ionic carbides contain a C_2^{2-} ion (CaC_2).

- **Covalent carbides**
  Are formed with elements of similar electronegativity. SiC is very hard (diamond structure) and chemically very resistant.

- **Metallic carbides**
  Carbon fits in the holes of the metal lattice. They are very hard and show high melting temperatures (e.g. WC, Mp. ~ 2700 °C).

A scissor made from WC (http://www.finescience.com/fst/misc/tungsten.html)

Calcium Carbide

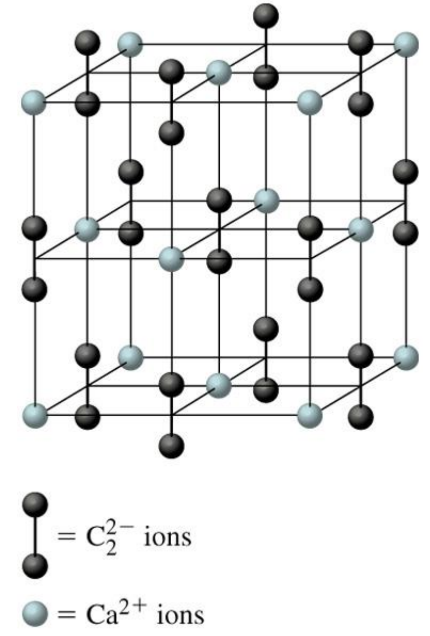
- CaC_2 is produced on a large scale from CaO and C:

$$CaO + 3\,C \xrightarrow{2200\,°C} CaC_2 + CO$$

- Most of it is used for the production of acetylene:

$$CaC_2 + 2\,H_2O \longrightarrow Ca(OH)_2 + HCCH$$

- CaC_2 crystallizes in a distorted NaCl structure.



'Carbide Lamp'

CaC_2

Carbon Disulfide (CS_2)

- Pure carbon disulfide is a colorless liquid with a pleasant odor that is like the smell of chloroform. The impure carbon disulfide that is usually used is a **yellowish liquid with an unpleasant odor**.
- It has been an important industrial chemical because of its ability to solubilize fats, rubbers, phosphorus, sulfur, and other elements (e.g. C_{60}).
- Carbon disulfide evaporates at room temperature, and the gas is more than twice as heavy as air.
- Carbon disulfide easily forms explosive mixtures with air and catches fire very easily.