# Carbon

#### Contents

- 1 Introduction
- 2 Characteristics
  - 2.1 Allotropes
  - 2.2 Occurrence
  - 2.3 Isotopes
  - 2.4 Formation in stars
  - 2.5 Carbon cycle
- 3 Compounds
  - 3.1 Organic compounds
  - 3.2 Inorganic compounds
    - 3.3 Organometallic compounds
- 4 History and etymology
- 5 Production

0

- 5.1 Graphite
  - 5.2 Diamond
- 6 Applications
  - 6.1 Diamonds
- 7 Precautions

#### 1. Introduction :

**Carbon** is the chemical element with symbol **C** and atomic number 6. As a member of group 14 on the periodic table, it is nonmetallic and tetravalent - making four electrons available to form covalent chemical bonds. There are three naturally occurring isotopes, with <sup>12</sup> C and <sup>13</sup> C being stable, while <sup>14</sup> C is radioactive, decaying with a half - life of about 5730 years. Carbon is one of the few elements known since antiquity. The name "carbon" comes from Latin language *carbo*, coal, and, in some Romance and Slavic languages, the word carbon can refer both to the element and to coal.

There are several allotropes of carbon of which the best known are graphite, diamond, and amorphous carbon. The physical properties of carbon vary widely with the allotropic form. For example, diamond is highly transparent, while graphite is opaque and black. Diamond is among the hardest materials known, while graphite is soft enough to form a streak on paper (hence its name, from the Greek word "to write"). Diamond has a very low electrical conductivity, while graphite is a very good conductor. Under normal conditions, diamond has the highest thermal conductivity of all known materials. All the allotropic forms are solids under normal conditions but graphite is the most thermodynamically stable.

All forms of carbon are highly stable, requiring high temperature to react even with oxygen. The most common oxidation state of carbon in inorganic compounds is +4, while +2 is found in carbon monoxide and other transition metal carbonyl complexes. The largest sources of inorganic carbon are limestones, dolomites and carbon dioxide, but significant quantities occur in organic deposits of coal, peat, oil and methane clathrates. Carbon forms more compounds than any other element, with almost ten million pure organic compounds described to date, which in turn are a tiny fraction of such compounds that are theoretically possible under standard conditions.

Carbon is one of the least abundant elements in the Earth's crust, but the fourth most abundant element in the universe by mass after hydrogen, helium, and oxygen. It is present in all known lifeforms, and in the human body carbon is the second most abundant element by mass ( about 18.5 % ) after oxygen. This abundance, together with the unique diversity of organic compounds and their unusual polymerforming ability at the temperatures commonly encountered on Earth, make this element the chemical basis of all known life.

Appearance			
Clear ( diamond ), black ( graphite )			
General			
Name, symbol, number	Carbon, C, 6		
Element category	Non metal		
Group, Period, Block	14,2,p		
Standard atomic weight	$12 \text{ g} \cdot \text{mol}^{-1}$		
Electrons per shell	2,4		

	Physical properties				
Phase		Solid	Solid		
Density		Amorphous : $1.8 - 2.1 \text{ g} \cdot \text{cm}^{-3}$		$g \cdot cm^{-3}$	
Density		Grapl	Graphite: 2.267 g·cm <sup><math>-3</math></sup>		
Density		Diam	Diamond : $3.515 \text{ g} \cdot \text{cm}^{-3}$		
Heat of Fusio	on	117 (graphite) kJ $\cdot$ mol <sup>-1</sup>		$\mathrm{pl}^{-1}$	
Specific Heat	t Capacity		(25 °C) 8.517 (graphite) 6.155 (diamond) $J \cdot mol^{-1} \cdot K^{-1}$		
Atomic properties					
Oxidation sta	ates	<b>4</b> ,3,	<b>4</b> , 3, 2, 1, 0, -1, -2, -3, <b>- 4</b>		
Electrone gat	tivity	2.55 (	(Pauling scale)		
Ionization en	ergies	1st : 1	$1086.5 \text{ kJ} \cdot \text{mol}^{-1}$		
(more)		2nd :	2nd : 2352.6 kJ·mol <sup><math>-1</math></sup>		
		3rd : -	3rd : 4620.5 kJ·mol <sup>-1</sup>		
Covalent Rac	dius	77 (sp	77 (sp <sup>3</sup> ), 73(sp <sup>2</sup> ), 69(sp) pm		
Van der Waa	ls Radius	170 p	m		
Miscellaneo	us				
Magnetic ord	lering	diama	agnetic		
		(300	(300 K) 119-165 (graphite)		
Thermal conductivity		900 -	900 - 2300 ( diamond )		
		W⋅m	$\mathbf{W} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1}$		
Thermal expansion		(25 °C	$(25 \ ^{\circ}C) 0.8$ (diamond)		
Thermal expansion	•	$\mu \mathbf{m} \cdot \mathbf{m}^{-1} \cdot \mathbf{K}^{-1}$			
Mohs hardness			1 - 2 (Graphite)		
	10 ( Diamond )				
Most stable isotopes of carbon					
iso N.A.	half - life	DM	DE (MeV)	<b>DP 15</b>	
<sup>12</sup> C 98.9 %	<sup>12</sup> C is stable				
<sup>13</sup> C 1.1 %					
<sup>14</sup> C trace	5730 y	beta <sup>-</sup>	0.156	<sup>14</sup> N	

#### 2. Characteristics

The different forms or *allotropes* of carbon include the hardest naturally occurring substance, diamond, and also one of the softest known substances, graphite. Moreover, it has an affinity for bonding with other small atoms, including other carbon atoms, and is capable of forming multiple stable covalent bonds with such atoms. As a result, carbon is known to form almost ten million different compounds; the large majority of all chemical compounds.<sup>[11]</sup> Carbon also has the highest melting and sublimation point of all elements. At atmospheric pressure it has no actual melting point as its triple point is at 10 MPa so it sublimates above 4000 K.

Carbon sublimes in a carbon arc which has a temperature of about 5800K. Thus, irrespective of its allotropic form, carbon remains solid at higher temperatures than the highest melting point metals such as tungsten or rhenium. Although thermodynamically prone to oxidation, carbon resists oxidation more effectively than elements such as iron and copper that are weaker reducing agents at room temperature.

Carbon compounds form the basis of all known so far life on Earth, and the carbon-nitrogen cycle provides some of the energy produced by the Sun and other stars. Although it forms an extraordinary variety of compounds, most forms of carbon are comparatively unreactive under normal conditions. At standard temperature and pressure, it resists all but the strongest oxidizers. It does not react with sulfuric acid, hydrochloric acid, chlorine or any alkalis. At elevated temperatures carbon reacts with oxygen to form carbon oxides, and will reduce such metal oxides as iron oxide to the metal. This exothermic reaction is used in the iron and steel industry to control the carbon content of steel:

$$Fe_3O_4 + 4C_{(s)} \rightarrow 3Fe_{(s)} + 4CO_{(g)}$$

with sulfur to form carbon disulfide and with steam in the coal - gas reaction

$$C_{(s)} + H_2O_{(g)} \rightarrow CO_{(g)} + H_{2(g)}.$$

Carbon combines with some metals at high temperatures to form metallic carbides, such as the iron carbide cementite in steel, and tungsten carbide, widely used as an abrasive and for making hard tips for cutting tools. As to 2009, graphene appears the strongest material ever tested . However, the process of separating it from graphite will require some technological development before it is economical enough to be used in industrial processes.

## The system of carbon allotropes spans a range of extremes :

Synthetic nanocrystalline diamond is the hardest materials known.	Graphite is one of the softest materials known.
Diamond is the ultimate abrasive.	Graphite is a very good lubricant.
Diamond is an excellent electrical insulator.	Graphite is a conductor of electricity.
Diamond is the best known naturally occurring thermal conductor	Some forms of graphite are used for thermal insulation (i.e. firebreaks and heat shields)
Diamond is highly transparent.	Graphite is opaque.
Diamond crystallizes in the cubic system.	Graphite crystallizes in the hexagonal system.
Amorphous carbon is completely isotropic.	Carbon nanotubes are among the most anisotropic materials ever produced.

#### 2.1. Allotropes of carbon

Atomic carbon is a very short - lived species and therefore, carbon is stabilized in various multi-atomic structures with different molecular configurations called allotropes. The three relatively well-known allotropes of carbon are amorphous carbon, graphite, and diamond. Once considered exotic, fullerenes are nowadays commonly synthesized and used in research; they include buckyballs, carbon nanotubes, carbon nanobuds and nanofibers. Several other exotic allotropes have also been discovered, such as lonsdaleite, glassy carbon, carbon nanofoam and linear acetylenic carbon.

• The amorphous form, is an assortment of carbon atoms in a non-crystalline, irregular, glassy state, which is essentially graphite but not held in a crystalline macrostructure. It is present as a powder, and is the main constituent of substances such as charcoal, lampblack (soot) and activated carbon.

• At normal pressures carbon takes the form of graphite, in which each atom is bonded trigonally to three others in a plane composed of fused hexagonal rings, just like those in aromatic hydrocarbons. The resulting network is 2 - dimensional, and the resulting flat sheets are stacked and loosely bonded through weak Van der Waals forces. This gives graphite its softness and its cleaving properties ( the sheets slip easily past one another ). Because of the delocalization of one of the outer electrons of each atom to form a  $\pi$  - cloud, graphite conducts electricity, but only in the plane of each covalently bonded sheet. This results in a lower bulk electrical conductivity for carbon than for most metals. The delocalization also accounts for the energetic stability of graphite over diamond at room temperature.

#### Some allotropes of carbon :

a) diamond
b) graphite
c) lonsdaleite
d) amorphous carbon
e) carbon nanotube .

• At very high pressures carbon forms the more compact allotrope diamond, having nearly twice the density of graphite. Here, each atom is bonded tetrahedrally to four others, thus making a 3-dimensional network of puckered six-membered rings of atoms. Diamond has the same cubic structure as silicon and germanium and, thanks to the strength of the carbon-carbon bonds is the hardest naturally occurring substance in terms of resistance to scratching. Contrary to the popular belief that *"diamonds are forever"*, they are in fact thermodynamically unstable under normal conditions and transform into graphite. But due to a high activation energy barrier, the transition into graphite is so extremely slow at room temperature as to be unnoticeable.

• Under some conditions, carbon crystallizes as lonsdaleite. This form has a hexagonal crystal lattice where all atoms are covalently bonded. Therefore, all properties of lonsdaleite are close to those of diamond.

Fullerenes have a graphite-like structure, but instead of purely hexagonal packing, they also contain pentagons ( or even heptagons ) of carbon atoms, which bend the sheet into spheres, ellipses or cylinders. The properties of fullerenes ( split into buckyballs, buckytubes and nanobuds ) have not yet been fully analyzed and represents an intense area of research in nanomaterials. The names "fullerene" and "buckyball" are given after Richard Buckminster Fuller, popularizer of geodesic domes, which resemble the structure of fullerenes. The buckyballs are fairly large molecules formed completely of carbon bonded trigonally, forming spheroids ( the best - known and simplest is the soccerball shaped structure  $C_{60}$ buckminsterfullerene ). Carbon nanotubes are structurally similar to buckyballs, except that each atom is bonded trigonally in a curved sheet that forms a hollow cylinder. Nanobuds were first published in 2007 and are hybrid bucky tube/buckyball materials ( buckyballs are covalently bonded to the outer wall of a nanotube ) that combine the properties of both in a single structure.

• Of the other discovered allotropes, Carbon nanofoam is a ferromagnetic allotrope discovered in 1997. It consists of a low-density cluster-assembly of carbon atoms strung together in a loose three-dimensional web, in which the atoms are bonded trigonally in six- and seven - membered rings. It is among the lightest known solids, with a density of about 2 kg/m<sup>3</sup>. Similarly, glassy carbon contains a high proportion of closed porosity.<sup>[24]</sup> But unlike normal graphite, the graphitic layers are not stacked like pages in a book, but have a more random arrangement. Linear acetylenic carbon has the chemical structure - (C::: C)<sub>n</sub> -

Carbon in this modification is linear with *sp* orbital hybridization, and is a polymer with alternating single and triple bonds. This type of carbyne is of considerable interest to nanotechnology as its Young's modulus is forty times that of the hardest known material – diamond.

## 2.2.Occurrence

Carbon is the fourth most abundant chemical element in the universe by mass after hydrogen, helium, and oxygen. Carbon is abundant in the Sun, stars, comets, and in the atmospheres of most planets. Some meteorites contain microscopic diamonds that were formed when the solar system was still a protoplanetary disk. Microscopic diamonds may also be formed by the intense pressure and high temperature at the sites of meteorite impacts.

" Present day " (1990s) sea surface dissolved inorganic carbon concentration ( from the GLODAP climatology )

In combination with oxygen in carbon dioxide, carbon is found in the Earth's atmosphere (in quantities of approximately 810 gigatonnes) and dissolved in all water bodies (approximately 36,000 gigatons). Around 1,900 gigatons are present in the biosphere. Hydrocarbons (such as coal, petroleum, and natural gas) contain carbon as well — coal "reserves" (not "resources") amount to around 900 gigatons, and oil reserves around 150 gigatons. With smaller amounts of calcium, magnesium, and iron, carbon is a major component in very large masses of carbonate rock (limestone, dolomite, marble etc.).

Coal is a significant commercial source of mineral carbon; anthracite containing 92 - 98 % carbon and the largest source ( 4,000 Gt, or 80 % of coal, gas and oil reserves) of carbon in a form suitable for use as fuel.

Graphite is found in large quantities in New York and Texas, the United States, Russia, Mexico, Greenland, and India.

Natural diamonds occur in the rock kimberlite, found in ancient volcanic "necks," or "pipes". Most diamond deposits are in Africa,

notably in South Africa, Namibia, Botswana, the Republic of the Congo, and Sierra Leone. There are also deposits in Arkansas, Canada, the Russian Arctic, Brazil and in Northern and Western Australia.

Diamonds are now also being recovered from the ocean floor off the Cape of Good Hope. However, though diamonds are found naturally, about 30 % of all industrial diamonds used in the U.S. are now made synthetically.

According to studies from the Massachusetts Institute of Technology, an estimate of the global carbon budget is :

Biosphere, oceans, atmosphere			
$0.45 \times 10^{18}$ kilograms (3.7 x $10^{18}$ moles)			
Crust			
Organic carbon	$13.2 \text{ x } 10^{18} \text{ kg}$		
Carbonates	62.4 x 10 <sup>18</sup> kg		
Mantle			
$1200 \ge 10^{18} \text{ kg}$			

Carbon - 14 is formed in upper layers of the troposphere and the stratosphere, at altitudes of 9 - 15 km, by a reaction that is precipitated by cosmic rays. Thermal neutrons are produced that collide with the nuclei of nitrogen-14, forming carbon - 14 and a proton.

#### 2.3. Isotopes of carbon

Isotopes of carbon are atomic nuclei that contain six protons plus a number of neutrons (varying from 2 to 16). Carbon has two stable, naturally occurring isotopes. The isotope carbon - 12 ( $^{12}$  C) forms 98.93 % of the carbon on Earth, while carbon - 13 ( $^{13}$  C) forms the remaining 1.07 %. The concentration of  $^{12}$  C is further increased in biological materials because biochemical reactions discriminate against  $^{13}$  C. In 1961 the International Union of Pure and Applied Chemistry (IUPAC) adopted the isotope carbon-12 as the basis for atomic weights. Identification of carbon in NMR experiments is done with the isotope  ${}^{13}C$ .

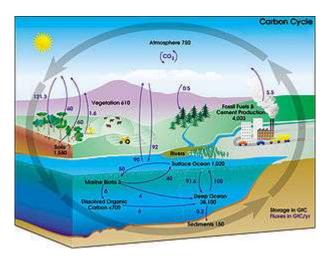
Carbon - 14 (<sup>14</sup> C) is a naturally occurring radioisotope which occurs in trace amounts on Earth of up to 1 part per trillion (0.000000001%), mostly confined to the atmosphere and superficial deposits, particularly of peat and other organic materials. This isotope decays by 0.158 MeV  $\beta$ <sup>-</sup> emission. Because of its relatively short half-life of 5730 years, <sup>14</sup>C is virtually absent in ancient rocks, but is created in the upper atmosphere (lower stratosphere and upper troposphere) by interaction of nitrogen with cosmic rays.<sup>[35]</sup> The abundance of <sup>14</sup>C in the atmosphere and in living organisms is almost constant, but decreases predictably in their bodies after death. This principle is used in radiocarbon dating, invented in 1949, which has been used extensively to determine the age of carbonaceous materials with ages up to about 40,000 years.

There are 15 known isotopes of carbon and the shortest-lived of these is  ${}^{8}C$  which decays through proton emission and alpha decay and has a half-life of  $1.98739 \times 10^{-21}$  s. The exotic  ${}^{19}C$  exhibits a nuclear halo, which means its radius is appreciably larger than would be expected if the nucleus was a sphere of constant density.

# 2.4. Formation in stars( Triple - alpha process & CNO cycle )

Formation of the carbon atomic nucleus requires a nearly simultaneous triple collision of alpha particles (helium nuclei) within the core of a giant or supergiant star. This happens in conditions of temperature and helium concentration that the rapid expansion and cooling of the early universe prohibited, and therefore no significant carbon was created during the Big Bang. Instead, the interiors of stars in the horizontal branch transform three helium nuclei into carbon by means of this triple-alpha process. In order to be available for formation of life as we know it, this carbon must then later be scattered into space as dust, in supernova explosions, as part of the material which later forms second, third - generation star systems which have planets accreted from such dust. The Solar System is one such third - generation star system. One of the fusion mechanisms powering stars is the carbon - nitrogen cycle.

Rotational transitions of various isotopic forms of carbon monoxide (e.g.  $^{12}$ CO,  $^{13}$ CO, and C  $^{18}$ O) are detectable in the submillimeter regime, and are used in the study of newly forming stars in molecular clouds.



# 2.5. Carbon cycle

Diagram of the carbon cycle. The black numbers indicate how much carbon is stored in various reservoirs, in billions of tons ( "GtC" stands for gigatons of carbon; figures are circa 2004 ). The purple numbers indicate how much carbon moves between reservoirs each year. The sediments, as defined in this diagram, do not include the  $\sim$ 70 million GtC of carbonate rock and kerogen.

Under terrestrial conditions, conversion of one element to another is very rare. Therefore, the amount of carbon on Earth is effectively constant. Thus, processes that use carbon must obtain it somewhere and dispose of it somewhere else. The paths that carbon follows in the environment make up the carbon cycle. For example, plants draw carbon dioxide out of their environment and use it to build biomass, as in carbon respiration or the Calvin cycle, a process of carbon fixation. Some of this biomass is eaten by animals, whereas some carbon is exhaled by animals as carbon dioxide. The carbon cycle is considerably more complicated than this short loop; for example, some carbon dioxide is dissolved in the oceans; dead plant or animal matter may become petroleum or coal, which can burn with the release of carbon, should bacteria not consume it .

#### **3**. Compounds

# **3.1.Organic compounds**

Structural formula of methane, the simplest possible organic compound.

Correlation between the *carbon cycle* and formation of organic compounds. In plants, carbon dioxide formed by carbon fixation can join with water in photosynthesis (green) to form organic compounds, which can be utilized and further converted by both plants and animals.

Carbon has the ability to form very long chains of interconnecting C - C bonds. This property is called catenation. Carbon - carbon bonds are strong, and stable. This property allows carbon to form an almost infinite number of compounds; in fact, there are more known carbon-containing compounds than all the compounds of the other chemical elements combined except those of hydrogen ( because almost all organic compounds contain hydrogen too ).

The simplest form of an organic molecule is the hydrocarbon - a large family of organic molecules that are composed of hydrogen atoms bonded to a chain of carbon atoms. Chain length, side chains and functional groups all affect the properties of organic molecules. By IUPAC's definition, all the other organic compounds are functionalized compounds of hydrocarbons.

Carbon occurs in all known organic life and is the basis of organic chemistry. When united with hydrogen, it forms various flammable compounds called hydrocarbons which are important to industry as refrigerants, lubricants, solvents, as chemical feedstock for the manufacture of plastics and petrochemicals and as fossil fuels.

When combined with oxygen and hydrogen, carbon can form many groups of important biological compounds including sugars, lignans, chitins, alcohols, fats, and aromatic esters, carotenoids and terpenes. With nitrogen it forms alkaloids, and with the addition of sulfur also it forms antibiotics, amino acids, and rubber products. With the addition of phosphorus to these other elements, it forms DNA and RNA, the chemical-code carriers of life, and adenosine triphosphate (ATP), the most important energy - transfer molecule in all living cells.

#### **3.2. Inorganic compounds of carbon**

Commonly carbon-containing compounds which are associated with minerals or which do not contain hydrogen or fluorine, are treated separately from classical organic compounds; however the definition is not rigid . Among these are the simple oxides of carbon. The most prominent oxide is carbon dioxide  $(CO_2)$ . This was once the principal constituent of the paleoatmosphere, but is a minor component of the Earth's atmosphere today.<sup>[41]</sup> Dissolved in water, it forms carbonic acid  $(H_2CO_3)$ , but as most compounds with multiple single-bonded oxygens on a single carbon it is unstable. Through this intermediate. though, resonance-stabilized carbonate ions are produced. Some important minerals are carbonates, notably calcite. Carbon disulfide  $(CS_2)$  is similar.

The other common oxide is carbon monoxide (CO). It is formed by incomplete combustion, and is a colorless, odorless gas. The molecules each contain a triple bond and are fairly polar, resulting in a tendency to bind permanently to hemoglobin molecules, displacing oxygen, which has a lower binding affinity. Cyanide (CN<sup>-</sup>), has a similar structure, but behaves much like a halide ion (pseudohalogen). For example it can form the nitride cyanogen molecule ((CN)<sub>2</sub>), similar to diatomic halides. Other uncommon oxides are carbon suboxide (C<sub>3</sub>O<sub>2</sub>), the unstable dicarbon monoxide (C<sub>2</sub>O) , carbon trioxide (CO<sub>3</sub>) , cyclopentanepentone (C<sub>5</sub>O<sub>5</sub>), cyclo hexane hexone (C<sub>6</sub>O<sub>6</sub>), and mellitic anhydride (C<sub>12</sub>O<sub>9</sub>).

With reactive metals, such as tungsten, carbon forms either carbides ( $C^{4-}$ ), or acetylides ( $C^{2-2}$ ) to form alloys with high melting points. These anions are also associated with methane and acetylene, both very weak acids. With an electronegativity of 2.5, carbon prefers

to form covalent bonds. A few carbides are covalent lattices, like carborundum (SiC), which resembles diamond.

#### **3.3.** Organo metallic compounds

Organometallic compounds by definition contain at least one carbon-metal bond. A wide range of such compounds exist; major classes include simple alkyl-metal compounds (e.g. tetra ethyl lead),  $\eta^2$ -alkene compounds (e.g. Zeise's salt, and  $\eta^3$ -allyl compounds (e.g. allyl palladium chloride dimer; metallocenes containing cyclo pentadienyl ligands (e.g. ferrocene); and transition metal carbene complexes. Many metal carbonyls exist (e.g. tetra carbonyl nickel); some workers consider the carbon monoxide ligand to be purely inorganic, and not organometallic.

While carbon is understood to exclusively form four bonds, an interesting compound containing an octahedral hexacoordinated carbon atom has been reported. The cation of the compound is [ ( $Ph_3PAu$ )  $_6C$ ]<sup>2+</sup>. This phenomenon has been attributed to the aurophilicity of the gold ligands.

#### 4 . History and etymology

The English name *carbon* comes from the Latin *carbo* for coal and charcoal, and hence comes from the French *charbon*, meaning charcoal. In German, Dutch and Danish, the names for carbon are *Kohlenstoff, koolstof* and *kulstof* respectively, all literally meaning coal - substance.

Carbon was discovered in prehistory and was known in the forms of soot and charcoal to the earliest human civilizations. Diamonds were known probably as early as 2500 BCE in China, while carbon in the form of charcoal was made around Roman times by the same chemistry as it is today, by heating wood in a pyramid covered with clay to exclude air.

In 1722, René A. F. de Réaumur demonstrated that iron was transformed into steel through the absorption of some substance, now known to be carbon.<sup>[56]</sup> In 1772, Antoine Lavoisier showed that

diamonds are a form of carbon, when he burned samples of carbon and diamond then showed that neither produced any water and that both released the same amount of carbon dioxide per gram. Carl Wilhelm Scheele showed that graphite, which had been thought of as a form of lead, was instead a type of carbon. In 1786, the French scientists Claude Louis Berthollet, Gaspard Monge and C. A. Vandermonde then showed that this substance was carbon. In their publication they proposed the name carbone (Latin carbonum) for this element. Antoine Lavoisier listed carbon as an element in his 1789 textbook.

A new allotrope of carbon, fullerene, that was discovered in 1985<sup>[60]</sup> includes nanostructured forms such as buckyballs and nano tubes . Their discoverers ( Curl, Kroto, and Smalley ) received the Nobel Prize in Chemistry in 1996. The resulting renewed interest in new forms lead to the discovery of further exotic allotropes, including glassy carbon, and the realization that "amorphous carbon" is not strictly amorphous .

# **5**. Production :

# 5.1. Graphite :

Commercially viable natural deposits of graphite occur in many parts of the world, but the most important sources economically are in China, India, Brazil, and North Korea. Graphite deposits are of metamorphic origin, found in association with quartz, mica and feldspars in schists, gneisses and metamorphosed sandstones and limestone as lenses or veins, sometimes of a meter or more in thickness. Deposits of graphite in Borrowdale, Cumberland, England were at first of sufficient size and purity that, until the 1800s, pencils were made simply by sawing blocks of natural graphite into strips before encasing the strips in wood. Today, smaller deposits of graphite are obtained by crushing the parent rock and floating the lighter graphite out on water.

According to the USGS, world production of natural graphite in 2006 was 1.03 million tons and in 2005 was 1.04 million tons (revised), of which the following major exporters produced: China

produced 720,000 tons in both 2006 and 2005, Brazil 75,600 tons in 2006 and 75,515 tons in 2005 (revised), Canada 28,000 tons in both years, and Mexico (amorphous) 12,500 tons in 2006 and 12,357 tons in 2005 (revised). In addition, there are two specialist producers: Sri Lanka produced 3,200 tons in 2006 and 3,000 tons in 2005 of lump or vein graphite, and Madagascar produced 15,000 tons in both years, a large portion of it "crucible grade" or very large flake graphite. Some other producers produce very small amounts of "crucible grade".

According to the USGS, U.S. (synthetic) graphite electrode production in 2006 was 132,000 tons valued at \$495 million and in 2005 was 146,000 tons valued at \$391 million, and high-modulus graphite (carbon) fiber production in 2006 was 8,160 tons valued at \$172 million and in 2005 was 7,020 tons valued at \$134 million.

#### **5.2.Diamond**:

The diamond supply chain is controlled by a limited number of powerful businesses, and is also highly concentrated in a small number of locations around the world .

Only a very small fraction of the diamond ore consists of actual diamonds. The ore is crushed, during which care has to be taken in order to prevent larger diamonds from being destroyed in this process and subsequently the particles are sorted by density. Today, diamonds are located in the diamond-rich density fraction with the help of X-ray fluorescence, after which the final sorting steps are done by hand. Before the use of X - rays became commonplace, the separation was done with grease belts; diamonds have a stronger tendency to stick to grease than the other minerals in the ore .

Historically diamonds were known to be found only in alluvial deposits in southern India . India led the world in diamond production from the time of their discovery in approximately the 9th century  $BCE^{[65]}$  to the mid-18th century AD, but the commercial potential of these sources had been exhausted by the late 18th century and at that time India was eclipsed by Brazil where the first non - Indian diamonds were found in 1725.

Diamond production of primary deposits (kimberlites and lamproites) only started in the 1870s after the discovery of the Diamond fields in South Africa. Production has increased over time and now an accumulated total of 4.5 billion carats have been mined since that date. Interestingly 20 % of that amount has been mined in the last 5 years alone and during the last ten years 9 new mines have started production while 4 more are waiting to be opened soon. Most of these mines are located in Canada, Zimbabwe, Angola, and one in Russia .

In the United States, diamonds have been found in Arkansas, Colorado, and Montana. In 2004, a startling discovery of a microscopic diamond in the United States led to the January 2008 bulk-sampling of kimberlite pipes in a remote part of Montana.

Today, most commercially viable diamond deposits are in Russia, Botswana, Australia and the Democratic Republic of Congo. In 2005, Russia produced almost one - fifth of the global diamond output, reports the British Geological Survey. Australia boasts the richest diamantiferous pipe with production reaching peak levels of 42 metric tons (41 LT; 46 ST) per year in the 1990s.

There are also commercial deposits being actively mined in the Northwest Territories of Canada, Siberia (mostly in Yakutia territory, for example Mir pipe and Udachnaya pipe), Brazil, and in Northern and Western Australia. Diamond prospectors continue to search the globe for diamond-bearing kimberlite and lamproite pipes.

#### **6** . Applications

Carbon is essential to all known living systems, and without it life as we know it could not exist . The major economic use of carbon other than food and wood is in the form of hydrocarbons, most notably the fossil fuel methane gas and crude oil (petroleum). Crude oil is used by the petrochemical industry to produce, amongst others, gasoline and kerosene, through a distillation process, in refineries. Cellulose is a natural, carbon-containing polymer produced by plants in the form of cotton, linen, and hemp. Cellulose is mainly used for maintaining structure in plants. Commercially valuable carbon polymers of animal origin include wool, cashmere and silk. Plastics are made from synthetic carbon polymers, often with oxygen and nitrogen atoms included at regular intervals in the main polymer chain. The raw materials for many of these synthetic substances come from crude oil.

The uses of carbon and its compounds are extremely varied. It can form alloys with iron, of which the most common is carbon steel. Graphite is combined with clays to form the 'lead' used in pencils used for writing and drawing. It is also used as a lubricant and a pigment, as a molding material in glass manufacture, in electrodes for dry batteries and in electroplating and electroforming, in brushes for electric motors and as a neutron moderator in nuclear reactors.

Charcoal is used as a drawing material in artwork, for grilling, and in many other uses including iron smelting. Wood, coal and oil are used as fuel for production of energy and space heating. Gem quality diamond is used in jewelry, and Industrial diamonds are used in drilling, cutting and polishing tools for machining metals and stone. Plastics are made from fossil hydrocarbons, and carbon fiber, made by pyrolysis of synthetic polyester fibers is used to reinforce plastics to form advanced, lightweight composite materials. Carbon fiber is made by pyrolysis of extruded and stretched filaments of polyacrylonitrile (PAN) and other organic substances. The crystallographic structure and mechanical properties of the fiber depend on the type of starting material, and on the subsequent processing. Carbon fibers made from PAN have structure resembling narrow filaments of graphite, but thermal processing may re-order the structure into a continuous rolled sheet. The result is fibers with higher specific tensile strength than steel.

Carbon black is used as the black pigment in printing ink, artist's oil paint and water colours, carbon paper, automotive finishes, India ink and laser printer toner. Carbon black is also used as a filler in rubber products such as tyres and in plastic compounds. Activated charcoal is used as an absorbent and adsorbent in filter material in applications as diverse as gas masks, water purification and kitchen extractor hoods and in medicine to absorb toxins, poisons, or gases from the digestive system. Carbon is used in chemical reduction at high temperatures. Coke is used to reduce iron ore into iron. Case hardening of steel is achieved by heating finished steel components in carbon powder. Carbides of silicon, tungsten, boron and titanium, are among the hardest known materials, and are used as abrasives in cutting and grinding tools. Carbon compounds make up most of the materials used in clothing, such as natural and synthetic textiles and leather, and almost all of the interior surfaces in the built environment other than glass, stone and metal.

#### 6.1. Diamonds

The diamond industry can be broadly separated into two basically distinct categories: one dealing with gem - grade diamonds and another for industrial-grade diamonds. While a large trade in both types of diamonds exists, the two markets act in dramatically different ways.

A large trade in gem - grade diamonds exists. Unlike precious metals such as gold or platinum, gem diamonds do not trade as a commodity: there is a substantial mark-up in the sale of diamonds, and there is not a very active market for resale of diamonds.

The market for industrial - grade diamonds operates much differently from its gem - grade counterpart. Industrial diamonds are valued mostly for their hardness and heat conductivity, making many of the gemological characteristics of diamond, including clarity and color, mostly irrelevant. This helps explain why 80 % of mined diamonds (equal to about 100 million carats or 20,000 kg annually), unsuitable for use as gemstones and known as bort, are destined for industrial use . In addition to mined diamonds, synthetic diamonds found industrial applications almost immediately after their invention in the 1950s; another 3 billion carats ( 600 metric tons ) of synthetic diamond is produced annually for industrial use. The dominant industrial use of diamond is in cutting, drilling, grinding, and polishing. Most uses of diamonds in these technologies do not require large diamonds; in fact, most diamonds that are gem-quality except for their small size, can find an industrial use. Diamonds are embedded in drill tips or saw blades, or ground into a powder for use in grinding and polishing applications. Specialized applications include use in laboratories as containment for high pressure experiments , high - performance bearings, and limited use in specialized windows. With the continuing advances being made in the production of synthetic diamonds, future applications are beginning to become feasible. Garnering much excitement is the possible use of diamond as a semiconductor suitable to build microchips from, or the use of diamond as a heat sink in electronics .

## 7. Precautions

Pure carbon has extremely low toxicity and can be handled and even ingested safely in the form of graphite or charcoal. It is resistant to dissolution or chemical attack, even in the acidic contents of the digestive tract, for example. Consequently if it gets into body tissues it is likely to remain there indefinitely. Carbon black was probably one of the first pigments to be used for tattooing, and Ötzi the Iceman was found to have carbon tattoos that survived during his life and for 5200 years after his death. However, inhalation of coal dust or soot (carbon black) in large quantities can be dangerous, irritating lung tissues and causing the congestive lung disease coalworker's pneumoconiosis. Similarly, diamond dust used as an abrasive can do harm if ingested or inhaled. Microparticles of carbon are produced in diesel engine exhaust fumes, and may accumulate in the lungs.<sup>[81]</sup> In these examples, the harmful effects may result from contamination of the carbon particles, with organic chemicals or heavy metals for example, rather than from the carbon itself.

Carbon may also burn vigorously and brightly in the presence of air at high temperatures, as in the Windscale fire, which was caused by sudden release of stored Wigner energy in the graphite core. Large accumulations of coal, which have remained inert for hundreds of millions of years in the absence of oxygen, may spontaneously combust when exposed to air, for example in coal mine waste tips.

The great variety of carbon compounds include such lethal poisons as tetrodotoxin, the lectin ricin from seeds of the castor oil plant *Ricinus communis*, cyanide ( $CN^-$ ) and carbon monoxide; and such essentials to life as glucose and protein.

# **Carbon dioxide**

# Contents

- 1 Introduction
- 2 Chemical and physical properties
- 3 History of human understanding
- 4 Isolation and production
  - 4.1 Industrial production
- 4. • 5 Uses
  - 5.1 Drinks
  - 5.2 Foods
  - 5.3 Pneumatic systems
  - 5.4 Fire extinguisher
  - 5.5 Welding
  - 5.6 Caffeine removal
  - 5.7 Pharmaceutical and other chemical processing
  - 5.8 Agriculture / Biological applications
  - 5.9 Lasers
  - 5.10 Polymers and plastics
  - 5.11 Oil recovery
  - 5.12 As refrigerants
  - 5.13 Coal bed methane recovery
  - 5.14 Wine making
  - 5.15 pH control
- 6 In the Earth's atmosphere
- 7 In the oceans
- 8 Biological role
  - 8.1 Role in photosynthesis
  - 8.2 Toxicity
  - 8.3 Human physiology

# 1. Introduction :

**Carbon dioxide** ( chemical formula :  $CO_2$  ) is a chemical compound composed of two oxygen atoms covalently bonded to a single carbon atom. It is a gas at standard temperature and pressure and exists in Earth's atmosphere in this state.

Carbon dioxide is used by plants during photosynthesis to make sugars, which may either be consumed in respiration or used as the raw material to produce other organic compounds needed for plant growth and development. It is produced during respiration by plants, and by all animals, fungi and microorganisms that depend either directly or indirectly on plants for food. It is thus a major component of the carbon cycle. Carbon dioxide is generated as a by-product of the combustion of fossil fuels or the burning of vegetable matter, among other chemical processes. Large amounts of carbon dioxide are emitted from volcanoes and other geothermal processes such as hot springs and geysers and by the dissolution of carbonates in crustal rocks.

As of March 2009, carbon dioxide in the Earth's atmosphere is at a concentration of 387 ppm by volume.<sup>[1]</sup> Atmospheric concentrations of carbon dioxide fluctuate slightly with the change of the seasons, driven primarily by seasonal plant growth in the Northern Hemisphere. Concentrations of carbon dioxide fall during the northern spring and summer as plants consume the gas, and rise during the northern autumn and winter as plants go dormant, die and decay. Carbon dioxide is a greenhouse gas as it transmits visible light but absorbs strongly in the infrared and near-infrared.

Carbon dioxide has no liquid state at pressures below 5.1 atmospheres. At 1 atmosphere (near mean sea level pressure), the gas deposits directly to a solid at temperatures below -78 °C and the solid sublimes directly to a gas above -78 °C. In its solid state, carbon dioxide is commonly called dry ice.

 $CO_2$  is an acidic oxide: an aqueous solution turns litmus from blue to pink. It is the anhydride of carbonic acid, an acid which is unstable and is known to exist only in aqueous solution.

$$CO_2 + H_2O H_2CO_3$$

 $CO_2$  is toxic in higher concentrations: 1 % (10,000 ppm) will make some people feel drowsy. Concentrations of 7 % to 10 % cause dizziness, headache, visual and hearing dysfunction, and unconsciousness within a few minutes to an hour.

Carbonic acid gas Carbonic anhydride Dry ice ( solid )
CO <sub>2</sub>
44.010 g / mol
Colorless, Odorless Gas
* 1.562 g / mL ( solid at 1 atm and -78.5 ° C ) * 0.770 g / mL ( liquid at 56 atm and 20 ° C ) * 1.977 g / L ( gas at 1 atm and 0 ° C ) * 849.6 g / L ( supercritical fluid at 150 atm and 30 ° C
- 78 °C
- 57 °C ( at 5.185 bar )
1.45 g / L at 25 ° C
6.35, 10.33
1.1120
0.07 cP at -78 °C
zero

#### 2. Chemical and physical properties

Carbon dioxide pressure-temperature phase diagram showing the triple point and critical point of carbon dioxide

Small pellets of dry ice subliming in air.

For more details on this topic, see Carbon dioxide .

Carbon dioxide is colorless. At low concentrations, the gas is odorless. At higher concentrations it has a sharp, acidic odor. It will act as an asphyxiant and an irritant. When inhaled at concentrations much higher than usual atmospheric levels, it can produce a sour taste in the mouth and a stinging sensation in the nose and throat. These effects result from the gas dissolving in the mucous membranes and saliva, forming a weak solution of carbonic acid. This sensation can also occur during an attempt to stifle a burp after drinking a carbonated beverage. Amounts above 5,000 ppm are considered very unhealthy, and those above about 50,000 ppm ( equal to 5 % by volume ) are considered dangerous to animal life .

At standard temperature and pressure, the density of carbon dioxide is around  $1.98 \text{ kg} / \text{m}^3$ , about 1.5 times that of air. The carbon dioxide molecule (O = C = O) contains two double bonds and has a linear shape. It has no electrical dipole, and as it is fully oxidized, it is moderately reactive and is non-flammable, but will support the combustion of metals such as magnesium.

At  $-78.51^{\circ}$  C or  $-109.3^{\circ}$  F, carbon dioxide changes directly from a solid phase to a gaseous phase through sublimation, or from gaseous to solid through deposition. Solid carbon dioxide is normally called "dry ice", a generic trademark. It was first observed in 1825 by the French chemist Charles Thilorier. Dry ice is commonly used as a cooling agent, and it is relatively inexpensive. A convenient property for this purpose is that solid carbon dioxide sublimes directly into the gas phase leaving no liquid. It can often be found in grocery stores and laboratories, and it is also used in the shipping industry. The largest non-cooling use for dry ice is blast cleaning.

Liquid carbon dioxide forms only at pressures above 5.1 atm; the triple point of carbon dioxide is about 518 kPa at -56.6 °C . The critical point is 7.38 MPa at 31.1 °C.

An alternative form of solid carbon dioxide, an amorphous glasslike form, is possible, although not at atmospheric pressure . This form of glass, called *carbonia*, was produced by super cooling heated  $CO_2$  at extreme pressure (40 - 48 GPa or about 400,000 atmospheres ) in a diamond anvil. This discovery confirmed the theory that carbon dioxide could exist in a glass state similar to other members of its elemental family, like silicon (silica glass) and germanium. Unlike silica and germania glasses, however, carbonia glass is not stable at normal pressures and reverts back to gas when pressure is released.

#### 3. History of human understanding

Carbon dioxide was one of the first gases to be described as a substance distinct from air. In the seventeenth century, the Flemish chemist Jan Baptist van Helmont observed that when he burned charcoal in a closed vessel, the mass of the resulting ash was much less than that of the original charcoal. His interpretation was that the rest of the charcoal had been transmuted into an invisible substance he termed a "gas" or "wild spirit" (*spiritus sylvestre*).

The properties of carbon dioxide were studied more thoroughly in the 1750s by the Scottish physician Joseph Black. He found that limestone (calcium carbonate) could be heated or treated with acids to yield a gas he called "fixed air." He observed that the fixed air was denser than air and did not support either flame or animal life. Black also found that when bubbled through an aqueous solution of lime (calcium hydroxide), it would precipitate calcium carbonate. He used this phenomenon to illustrate that carbon dioxide is produced by animal respiration and microbial fermentation. In 1772, English chemist Joseph Priestley published a paper entitled *Impregnating Water with Fixed Air* in which he described a process of dripping sulfuric acid (or *oil of vitriol* as Priestley knew it) on chalk in order to produce carbon dioxide, and forcing the gas to dissolve by agitating a bowl of water in contact with the gas.

Carbon dioxide was first liquefied (at elevated pressures) in 1823 by Humphry Davy and Michael Faraday.<sup>[8]</sup> The earliest description of solid carbon dioxide was given by Charles Thilorier, who in 1834 opened a pressurized container of liquid carbon dioxide, only to find that the cooling produced by the rapid evaporation of the liquid yielded a "snow" of solid CO<sub>2</sub>.

#### 4. Isolation and production

Carbon dioxide may be obtained from air distillation. However, this yields only very small quantities of  $CO_2$ . A large variety of chemical reactions yield carbon dioxide, such as the reaction between most acids and most metal carbonates. For example, the reaction

between hydrochloric acid and calcium carbonate (limestone or chalk) is depicted below:

 $2 \text{ HCl} + \text{CaCO}_3 \rightarrow \text{CaCl}_2 + \text{H}_2\text{CO}_3$ 

The  $H_2CO_3$  then decomposes to water and  $CO_2$ . Such reactions are accompanied by foaming or bubbling, or both. In industry such reactions are widespread because they can be used to neutralize waste acid streams.

The production of quicklime (CaO) a chemical that has widespread use, from limestone by heating at about 850 °C also produces  $CO_2$ :

 $CaCO_3 \rightarrow CaO + CO_2$ 

The combustion of all carbon containing fuels, such as methane (natural gas), petroleum distillates (gasoline, diesel, kerosene, propane), but also of coal and wood, will yield carbon dioxide and, in most cases, water. As an example the chemical reaction between methane and oxygen is given below.

 $CH_4 + 2 O_2 \rightarrow CO_2 + 2 H_2O$ 

Iron is reduced from its oxides with coke in a blast furnace, producing pig iron and carbon dioxide:

 $2 \operatorname{Fe}_2 \operatorname{O}_3 + 3 \operatorname{C} \rightarrow 4 \operatorname{Fe} + 3 \operatorname{CO}_2$ 

Yeast metabolizes sugar to produce carbon dioxide and ethanol, also known as alcohol, in the production of wines, beers and other spirits, but also in the production of bioethanol:

 $\mathrm{C_6H_{12}O_6} \rightarrow 2\ \mathrm{CO_2} + 2\ \mathrm{C_2H_5OH}$ 

All aerobic organisms produce  $CO_2$  when they oxidize carbohydrates, fatty acids, and proteins in the mitochondria of cells. The large number of reactions involved are exceedingly complex and not described easily. Refer to (cellular respiration, anaerobic respiration and photosynthesis). Photo autotrophs ( i.e. plants, cyanobacteria ) use another *modus operandi*: Plants absorb  $CO_2$  from the air, and, together with water, react it to form carbohydrates:

$$n \operatorname{CO}_2 + n \operatorname{H}_2 \operatorname{O} \rightarrow (\operatorname{CH}_2 \operatorname{O}) n + n \operatorname{O} 2$$

Carbon dioxide is soluble in water, in which it spontaneously interconverts between CO<sub>2</sub> and H<sub>2</sub>CO<sub>3</sub> ( carbonic acid ). The relative concentrations of CO<sub>2</sub>, H<sub>2</sub>CO<sub>3</sub>, and the deprotonated forms HCO<sub>3</sub><sup>-</sup> (bicarbonate) and CO<sub>3</sub><sup>2-</sup> ( carbonate ) depend on the pH. In neutral or slightly alkaline water ( pH > 6.5 ), the bicarbonate form predominates ( >50 % ) becoming the most prevalent ( >95 % ) at the pH of seawater, while in very alkaline water ( pH > 10.4 ) the predominant ( > 50 %) form is carbonate. The bicarbonate and carbonate forms are very soluble, such that air-equilibrated ocean water (mildly alkaline with typical pH = 8.2 – 8.5 ) contains about 120 mg of bicarbonate per liter.

# **4.1. Industrial production**

Carbon dioxide is produced mainly from six processes :

1. From combustion of fossil fuels and wood;

2. As a by - product of hydrogen production plants, where methane is converted to  $CO_2$ ;

3. As a by - product of fermentation of sugar in the brewing of beer, whisky and other alcoholic beverages;

4. From thermal decomposition of lime stone,  $CaCO_3$ , in the manufacture of lime , CaO;

5. As a by - product of sodium phosphate manufacture;

6. Directly from natural carbon dioxide springs, where it is produced by the action of acidified water on limestone or dolomite.

# 5. Uses

Carbon dioxide is used by the food industry, the oil industry, and the chemical industry. It is used in many consumer products that require pressurized gas because it is inexpensive and nonflammable, and because it undergoes a phase transition from gas to liquid at room temperature at an attainable pressure of approximately 60 bar (870 psi, 59 atm), allowing far more carbon dioxide to fit in a given container than otherwise would. Life jackets often contain canisters of pressured carbon dioxide for quick inflation. Aluminum capsules are also sold as supplies of compressed gas for airguns, paintball markers, for inflating bicycle tires, and for making seltzer. Rapid vaporization of liquid carbon dioxide is used for blasting in coal mines. High concentrations of carbon dioxide can also be used to kill pests, such as the Common Clothes Moth.

#### 5.1. Drinks

Carbon dioxide is used to produce carbonated soft drinks and soda water. Traditionally, the carbonation in beer and sparkling wine comes about through natural fermentation, but some manufacturers carbonate these drinks artificially.

## **5.2. Foods**

A candy called Pop Rocks is pressurized with carbon dioxide gas at about 40 bar (600 psi). When placed in the mouth, it dissolves (just like other hard candy) and releases the gas bubbles with an audible pop. Leavening agents produce carbon dioxide to cause dough to rise. Baker's yeast produces carbon dioxide by fermentation of sugars within the dough, while chemical leaveners such as baking powder and baking soda release carbon dioxide when heated or if exposed to acids.

#### **5.3.** Pneumatic systems

Carbon dioxide is one of the most commonly used compressed gases for pneumatic ( pressurized gas ) systems in portable pressure tools and combat robots.

#### **5.4.** Fire extinguisher

Carbon dioxide extinguishes flames, and some fire extinguishers, especially those designed for electrical fires, contain liquid carbon dioxide under pressure. Carbon dioxide has also been widely used as

an extinguishing agent in fixed fire protection systems for total flooding of a protected space, (National Fire Protection Association Code 12). International Maritime Organisation standards also recognise carbon dioxide systems for fire protection of ship holds and engine rooms. Carbon dioxide based fire protection systems have been linked to several deaths. A review of CO2 systems (Carbon Dioxide as a Fire Suppressant: Examining the Risks, US EPA) identified 51 incidents between 1975 and the date of the report, causing 72 deaths and 145 injuries.

## 5.5.Welding

Carbon dioxide also finds use as an atmosphere for welding, although in the welding arc, it reacts to oxidize most metals. Use in the automotive industry is common despite significant evidence that welds made in carbon dioxide are more brittle than those made in more inert atmospheres, and that such weld joints deteriorate over time because of the formation of carbonic acid. It is used as a welding gas primarily because it is much less expensive than more inert gases such as argon or helium.

#### 5.6.Caffeine removal

Liquid carbon dioxide is a good solvent for many lipophilic organic compounds, and is used to remove caffeine from coffee. First, the green coffee beans are soaked in water. The beans are placed in the top of a column seventy feet (21 m) high. Then supercritical carbon dioxide in fluid form at about 93 degrees Celsius enters at the bottom of the column. The caffeine diffuses out of the beans and into the carbon dioxide

#### 5.7. Pharmaceutical and other chemical processing

Carbon dioxide has begun to attract attention in the pharmaceutical and other chemical processing industries as a less toxic alternative to more traditional solvents such as organo chlorides. It's used by some dry cleaners for this reason. In the chemical industry, carbon dioxide is used for the production of urea, carbonates and bicarbonates, and sodium salicylate.

## **5.8.** Agriculture / Biological applications

Plants require carbon dioxide to conduct photosynthesis. Because of low current atmospheric concentration, carbon dioxide is practically the limiting factor of the Earth life, as compare to two other similarly important components - water and sun light. While plants "in wild" are optimized for this, plant-intense greenhouses may (and of large size - must) enrich their atmospheres with additional  $CO_2$ to sustain plant life and growth, because the low present-day atmosphere concentration of  $CO_2$  is just above the "suffocation" level for green plants. A photosynthesis-related drop (by a factor less than two) in carbon dioxide concentration in a greenhouse compartment would kill green plants, or, at least, completely stop their growth. At very high concentrations (a factor of 100 or more higher than its atmospheric concentration), carbon dioxide can be toxic to animal life, so raising the concentration to 10,000 ppm (1 %) or higher for several hours will eliminate pests such as whiteflies and spider mites in a greenhouse. It has been proposed that carbon dioxide from power generation be bubbled into ponds to grow algae that could then be converted into biodiesel fuel. Carbon dioxide is already increasingly used in greenhouses as the main carbon source for Spirulina algae. In medicine, up to 5 % carbon dioxide (factor 150 as compare to atmospheric concentration) is added to pure oxygen for stimulation of breathing after apnea and to stabilize the  $O_2/CO_2$  balance in blood.

#### 5.9. Lasers

A common type of industrial gas laser is the carbon dioxide laser.

#### 5.10. Polymers and plastics

Carbon dioxide can also be combined with limonene oxide from orange peels or other epoxides to create polymers and plastics.<sup>[12]</sup>

#### 5.11. Oil recovery

Carbon dioxide is used in enhanced oil recovery where it is injected into or adjacent to producing oil wells, usually under supercritical conditions. It acts as both a pressurizing agent and, when dissolved into the underground crude oil, significantly reduces its viscosity, enabling the oil to flow more rapidly through the earth to the removal well. In mature oil fields, extensive pipe networks are used to carry the carbon dioxide to the injection points.

#### 5.12. As refrigerants

Liquid and solid carbon dioxide are important refrigerants, especially in the food industry, where they are employed during the transportation and storage of ice cream and other frozen foods. Solid carbon dioxide is called "dry ice" and is used for small shipments where refrigeration equipment is not practical.

Liquid carbon dioxide (industry nomenclature R744 or R-744) was used as a refrigerant prior to the discovery of R - 12 and is likely to enjoy a renaissance due to environmental concerns. Its physical properties are highly favorable for cooling, refrigeration, and heating purposes, having a high volumetric cooling capacity. Due to its operation at pressures of up to 130 bars,  $CO_2$  systems require highly resistant components that have been already developed to serial production in many sectors. In car air conditioning, in more than 90% of all driving conditions, R744 operates more efficiently than systems using R - 134a. Its environmental advantages (GWP of 1, non - ozone depleting, non - toxic, non – flammable ) could make it the future working fluid to replace current HFCs in cars, supermarkets, hot water heat pumps, among others. Some applications: Coca - Cola has fielded  $CO_2$ -based beverage coolers and the U.S. Army is interested in  $CO_2$  refrigeration and heating technology.

By the end of 2007, the global car industry is expected to decide on the next-generation refrigerant in car air conditioning.  $CO_2$  is one discussed option .)

#### **5.13.** Coal bed methane recovery

In enhanced coal bed methane recovery, carbon dioxide is pumped into the coal seam to displace methane .

#### 5.14. Wine making

Carbon dioxide in the form of dry ice is often used in the wine making process to cool down bunches of grapes quickly after picking to help prevent spontaneous fermentation by wild yeasts. The main advantage of using dry ice over regular water ice is that it cools the grapes without adding any additional water that may decrease the sugar concentration in the grape must, and therefore also decrease the alcohol concentration in the finished wine.

Dry ice is also used during the cold soak phase of the wine making process to keep grapes cool. The carbon dioxide gas that results from the sublimation of the dry ice tends to settle to the bottom of tanks because it is heavier than regular air. The settled carbon dioxide gas creates an hypoxic environment which helps to prevent bacteria from growing on the grapes until it is time to start the fermentation with the desired strain of yeast.

Carbon dioxide is also used to create a hypoxic environment for carbonic maceration, the process used to produce Beaujolais wine.

Carbon dioxide is sometimes used to top up wine bottles or other storage vessels such as barrels to prevent oxidation, though it has the problem that it can dissolve into the wine, making a previously still wine slightly fizzy. For this reason, other gasses such as nitrogen or argon are preferred for this process by professional wine makers.

#### 5.15. pH control

Carbon dioxide can be used as a mean of controlling the pH of swimming pools, by continuously adding gas to the water, thus keeping the pH level from rising. Among the advantages of this is the avoidance of handling (more hazardous) acids.

#### 6. In the Earth's atmosphere

Carbon dioxide in earth's atmosphere is considered a trace gas currently occurring at an average concentration of about 385 parts per million by volume or 582 parts per million by mass. The total mass of atmospheric carbon dioxide is  $3.0 \times 10^{15}$  kg (3,000 gigatonnes). Its concentration varies seasonally and also considerably on a regional basis, especially near the ground. In urban areas concentrations are generally higher and indoors they can reach 10 times background levels. Carbon dioxide is a greenhouse gas.

Yearly increase of atmospheric  $CO_2$ : In the 1960s, the average annual increase was 37 % of the 2000 - 2007 average .

Five hundred million years ago carbon dioxide was 20 times more prevalent than today, decreasing to 4 - 5 times during the Jurassic period and then slowly declining with a particularly swift reduction occurring 49 million years ago. Human activities such as the combustion of fossil fuels and deforestation have caused the atmospheric concentration of carbon dioxide to increase by about 35% since the beginning of the age of industrialization.

Up to 40 % of the gas emitted by some volcanoes during subaerial volcanic eruptions is carbon dioxide. It is estimated that volcanoes release about 130 - 230 million tonnes (145 - 255 million tons) of CO<sub>2</sub> into the atmosphere each year. Carbon dioxide is also produced by hot springs such as those at the Bossoleto site near Rapolano Terme in Tuscany, Italy. Here, in a bowl - shaped depression of about 100 m diameter, local concentrations of CO<sub>2</sub> rise to above 75% overnight, sufficient to kill insects and small animals, but warm rapidly when sunlit and disperse by convection during the day.<sup>[22]</sup> Locally high concentrations of CO<sub>2</sub> are thought to have caused 37 fatalities at Lake Monoun, Cameroon in 1984 and 1700 casualties at Lake Nyos, Cameroon in 1986. Emissions of CO<sub>2</sub> by human activities are currently more than 130 times greater than the quantity emitted by volcanoes, amounting to about 27 billion tonnes per year.

#### 7. In the oceans :

There is about 50 times as much carbon dissolved in the oceans in the form of  $CO_2$  and carbonic acid, bicarbonate and carbonate ions as exists in the atmosphere. The oceans act as an enormous carbon sink, and have taken up about a third of  $CO_2$  emitted by human activity.<sup>[25]</sup> Gas solubility decreases as the temperature of water increases and therefore the rate of uptake from the atmosphere decreases as ocean temperatures rise.

Most of the  $CO_2$  taken up by the ocean forms carbonic acid in equilibrium with bicarbonate and carbonate ions. Some is consumed in photosynthesis by organisms in the water, and a small proportion of that sinks and leaves the carbon cycle. Increased  $CO_2$  in the atmosphere has led to decreasing alkalinity of seawater and there is some concern that this may adversely affect organisms living in the water. In particular, with decreasing alkalinity, the availability of carbonates for forming shells decreases.

## 8. Biological role

Carbon dioxide is an end product in organisms that obtain energy from breaking down sugars, fats and amino acids with oxygen as part of their metabolism, in a process known as cellular respiration. This includes all plants, animals, many fungi and some bacteria. In higher animals, the carbon dioxide travels in the blood from the body's tissues to the lungs where it is exhaled. In plants using photosynthesis, carbon dioxide is absorbed from the atmosphere.

#### 8.1. Role in photosynthesis

Overview of photosynthesis and respiration. Carbon dioxide together with water, form oxygen and organic compounds by photosynthesis, which can be respired to water and  $(CO_2)$ .

Plants remove carbon dioxide from the atmosphere by photosynthesis, also called carbon assimilation, which uses light energy to produce organic compounds (cellulose, lipids, and various proteins) by combining carbon dioxide and water. Free oxygen is released as gas from the decomposition of water molecules, while the hydrogen is split into its protons and electrons and used to generate chemical energy via photophosphorylation. This energy is required for the fixation of carbon dioxide in the Calvin cycle to make 3 - phospho glycerate that is used in metabolism, to construct sugars that can be used as an energy source within the plant through respiration and as

the raw material for the construction of more complex organic molecules, such as polysaccharides, nucleic acids and proteins during growth.

Even when greenhouses are vented, carbon dioxide must be introduced into them to maintain plant growth, as the concentration of carbon dioxide can fall during daylight hours to as low as 200 ppm (a limit of C3 carbon fixation photosynthesis). Plants can grow up to 50 percent faster in concentrations of 1,000 ppm CO<sub>2</sub> when compared with ambient conditions, though this assumes no change in climate and no limitation on other nutrients . Some people (for example David Bellamy) believe that as the concentration of CO<sub>2</sub> rises in the atmosphere that it will lead to faster plant growth and therefore increase food production. Such views are too simplistic; studies have shown that increased CO<sub>2</sub> leads to fewer stomata developing on plants<sup>[29]</sup> which leads to reduced water usage.<sup>[30]</sup> Studies using FACE have shown that increases in CO<sub>2</sub> lead to decreased concentration of micronutrients in crop plants. This may have knock-on effects on other parts of ecosystems as herbivores will need to eat more food to gain the same amount of protein.

Plants also emit  $CO_2$  during respiration, and so the majority of plants and algae, which use C3 photosynthesis, are only net absorbers during the day. Though a growing forest will absorb many tons of  $CO_2$  each year, the World Bank writes that a mature forest will produce as much  $CO_2$  from respiration and decomposition of dead specimens (e.g. fallen branches) as is used in biosynthesis in growing plants. However six experts in biochemistry, biogeology, forestry and related areas writing in the science journal Nature that "Our results demonstrate that old - growth forests can continue to accumulate carbon, contrary to the long-standing view that they are carbon neutral." Mature forests are valuable carbon sinks, helping maintain balance in the Earth's atmosphere. Additionally, and crucially to life on earth, photosynthesis by phytoplankton consumes dissolved  $CO_2$  in the upper ocean and thereby promotes the absorption of  $CO_2$  from the atmosphere.

#### 8.2. Toxicity

Main symptoms of Carbon dioxide toxicity, by increasing volume percent in air.

Carbon dioxide content in fresh air (averaged between sea-level and 10 hPa level, i.e. about 30 km altitude) varies between 0.036% (360 ppm) and 0.039 % (390 ppm), depending on the location .

Prolonged exposure to moderate concentrations can cause acidosis and adverse effects on calcium phosphorus metabolism resulting in increased calcium deposits in soft tissue. Carbon dioxide is toxic to the heart and causes diminished contractile force.

Toxicity and its effects increase with the concentration of  $CO_2$ , here given in volume percent of  $CO_2$  in the air:

• 1 %, as can occur in a crowded auditorium with poor ventilation, can cause drowsiness with prolonged exposure.<sup>[2]</sup>

• At 2 % it is mildly narcotic and causes increased blood pressure and pulse rate, and causes reduced hearing.

• At about **5** % it causes stimulation of the respiratory centre, dizziness, confusion and difficulty in breathing accompanied by headache and shortness of breath.

• At about **8** % it causes headache, sweating, dim vision, tremor and loss of consciousness after exposure for between five and ten minutes .

A natural disaster linked to  $CO_2$  intoxication occurred during the limnic eruptions in the  $CO_2$  - rich lakes of Monoun and Nyos in the Okun range of North - West Cameroon: the gas was brutally expelled from the mountain lakes and leaked into the surrounding valleys, killing most animal forms. During the Lake Nyos tragedy of 1988, 1700 villagers and 3500 livestock died.

Due to the health risks associated with carbon dioxide exposure, the U.S. Occupational Safety and Health Administration says that average exposure for healthy adults during an eight-hour work day should not exceed 5,000 ppm (0.5%). The maximum safe level for

infants, children, the elderly and individuals with cardio-pulmonary health issues is significantly less. For short - term (under ten minutes) exposure, the U.S. National Institute for Occupational Safety and Health (NIOSH) and American Conference of Government Industrial Hygienists (ACGIH) limit is 30,000 ppm (3 %). NIOSH also states that carbon dioxide concentrations exceeding 4% are immediately dangerous to life and health.

Adaptation to increased levels of  $CO_2$  occurs in humans. Continuous inhalation of  $CO_2$  can be tolerated at three percent inspired concentrations for at least one month and four percent inspired concentrations for over a week. It was suggested that 2.0 percent inspired concentrations could be used for closed air spaces ( e.g. a submarine) since the adaptation is physiological and reversible. Decrement in performance or in normal physical activity does not happen at this level.

These figures are valid for pure carbon dioxide. In indoor spaces occupied by people the carbon dioxide concentration will reach higher levels than in pure outdoor air. Concentrations higher than 1,000 ppm will cause discomfort in more than 20 % of occupants, and the discomfort will increase with increasing  $CO_2$  concentration. The discomfort will be caused by various gases coming from human respiration and perspiration, and not by  $CO_2$  itself. At 2,000 ppm the majority of occupants will feel a significant degree of discomfort, and many will develop nausea and headaches. The  $CO_2$  concentration between 300 and 2,500 ppm is used as an indicator of indoor air quality.

Acute carbon dioxide toxicity is sometimes known by the names given to it by miners: blackdamp ( also called *choke damp* or *stythe* ). Miners would try to alert themselves to dangerous levels of carbon dioxide in a mine shaft by bringing a caged canary with them as they worked. The canary would inevitably die before  $CO_2$  reached levels toxic to people.

Carbon dioxide ppm levels (CDPL) are a surrogate for measuring indoor pollutants that may cause occupants to grow drowsy, get headaches, or function at lower activity levels. To eliminate most indoor air quality complaints, total indoor CDPL must be reduced to below 600. NIOSH considers that indoor air concentrations that exceed 1,000 are a marker suggesting inadequate ventilation. ASHRAE recommends they not exceed 1,000 inside a space.

#### 8.3. Human physiology

 $CO_2$  is carried in blood in three different ways. ( The exact percentages vary depending whether it is arterial or venous blood ).

• Most of it ( about 70 % – 80 %) is converted to bicarbonate ions  $HCO_3^-$  by the enzyme carbonic anhydrase in the red blood cells , by the reaction  $CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$ .

• 5 % - 10 % is dissolved in the plasma<sup>+</sup>

- 5 % – 10 % is bound to hemoglobin as carbamino compounds  $\dot{}$ 

Hemoglobin, the main oxygen-carrying molecule in red blood cells, carries both oxygen and carbon dioxide. However, the  $CO_2$  bound to hemoglobin does not bind to the same site as oxygen. Instead, it combines with the N-terminal groups on the four globin chains. However, because of allosteric effects on the hemoglobin molecule, the binding of  $CO_2$  decreases the amount of oxygen that is bound for a given partial pressure of oxygen. The decreased binding to carbon dioxide in the blood due to increased oxygen levels is known as the Haldane Effect, and is important in the transport of carbon dioxide from the tissues to the lungs. Conversely, a rise in the partial pressure of  $CO_2$  or a lower pH will cause offloading of oxygen from hemoglobin, which is known as the Bohr Effect.

Carbon dioxide is one of the mediators of local autoregulation of blood supply. If its levels are high, the capillaries expand to allow a greater blood flow to that tissue.

Bicarbonate ions are crucial for regulating blood pH . A person's breathing rate influences the level of  $CO_2$  in their blood. Breathing that is too slow or shallow causes respiratory acidosis, while breathing

that is too rapid leads to hyperventilation, which can cause respiratory alkalosis.

Although the body requires oxygen for metabolism, low oxygen levels do not stimulate breathing. Rather, breathing is stimulated by higher carbon dioxide levels. As a result, breathing low-pressure air or a gas mixture with no oxygen at all ( such as pure nitrogen ) can lead to loss of consciousness without ever experiencing air hunger. This is especially perilous for high - altitude fighter pilots. It is also why flight attendants instruct passengers, in case of loss of cabin pressure, to apply the oxygen mask to themselves first before helping others otherwise one risks going unconscious .

Typically the gas we exhale is about 4 % to 5 % carbon dioxide and 4 % to 5 % less oxygen than was inhaled.

Breathing produces approximately 2.3 pounds (  $1\ \rm kg$  ) of carbon dioxide per day per person.

# **Carbon Monoxide**

#### Contents

- 1 Introduction
- 2 History
- 3 Molecular Properties
- 4 Biological and physiological properties
  - 4.1 Toxicity
  - 4.2 Human Physiology
  - 4.3 Microbiology
- 5 Occurrence
  - 5.1 Atmospheric presence
  - 5.2 Urban pollution
    - 5.3 Indoor pollution
- 6 Production
  - 6.1 Laboratory preparation
    - 6.2 Industrial production
- 7 Coordination chemistry
- 8 Organic and main group chemistry
- 9 Uses

0

0

- 9.1 Chemical industry
- 9.2 Meat coloring
- 9.3 Medicine

# 1. Introduction :

**Carbon monoxide**, with the chemical formula CO, is a colorless, odorless and tasteless, yet highly toxic gas. Its molecules consist of one carbon atom and one oxygen atom, connected by a covalent double bond and a dative covalent bond. It is the simplest oxo carbon , and can be viewed as the anhydride of formic acid  $(CH_2O_2)$ .

Carbon monoxide is produced from the partial oxidation of carbon-containing compounds; it forms in preference to the more usual carbon dioxide ( $CO_2$ ) when there is a reduced availability of oxygen, such as when operating a stove or an internal combustion

engine in an enclosed space. Carbon monoxide has significant fuel value, burning in air with a characteristic blue flame, producing carbon dioxide. Despite its serious toxicity, it was once widely used (as the main component of coal gas) for domestic lighting, cooking and heating, and in the production of nickel. Carbon monoxide still plays a major role in modern technology, in industrial processes such as iron smelting and as a precursor to myriad products.

Other Names	Carbonic Oxide
Molecular Formula	СО
Molar Mass	28 g / mol
Appearance	Colourless, odorless gas
Density	0.789 g / mL, liquid 1.250 g / L at 0 ° C , 1 atm 1.145 g / L at 25 °C , 1 atm
Melting Point	−205 °C
Boiling Point	−191.5 °C
Solubility in Water	0.0026 g / 100 mL ( 20 °C )
Solubility	soluble in chloroform , acetic acid , ethyl acetate , ethanol , ammonium hydroxide
Flash Point	- 191 ° C
Autoignition temperature	609 ° C
Thermo dynamic data	Phase behaviour : Solid , liquid , gas

## 2. History

Carbon monoxide has been unknowingly used by humans since prehistoric times, for the smelting of iron and other metallic ores.<sup>1</sup> The gas was used for executions by the Greek and Romans in Classical Antiquity, and was described by the Spanish doctor Arnaldus de Villa Nova in the 11th century In 1776 the French chemist de Lassone produced CO by heating zinc oxide with coke, but mistakenly concluded that the gaseous product was hydrogen as it burned with a blue flame. The gas was identified as a compound containing carbon and oxygen by the English chemist William Cumberland Cruikshank in the year 1800. Its toxic properties on dogs were thoroughly investigated by Claude Bernard around 1846.

During World War II, carbon monoxide was used to keep motor vehicles running in parts of the world where gasoline was scarce. External charcoal or wood burners were fitted, and the carbon monoxide produced by gasification was piped to the carburetor.<sup>[citation needed]</sup> The CO in this case is known as "wood gas". Carbon monoxide was also reportedly used on a small scale during the Holocaust at some Nazi extermination camps (most notably by gas vans in Chelmno), and in the Action T4 "euthanasia" program.<sup>[citation needed]</sup>

#### **3**. Molecular properties

The carbon monoxide molecule consists of one atom of carbon and one atom of oxygen, covalently bonded by a double bond and a dative covalent bond. Its bond length is 112.8 pm. The effects of atomic formal charge and electronegativity result in a small bond dipole moment with its negative end on the carbon atom<sup>[3]</sup>. The reason for this, despite oxygen's greater electronegativity, is that the highest occupied molecular orbital has an energy much closer to that of carbon's p orbitals, meaning that greater electron density is found near the carbon. In addition, carbon's lower electro negativity creates a much more diffuse electron cloud, enhancing the polarize ability . This is also the reason that almost all chemistry involving carbon monoxide occurs through the carbon atom, and not the oxygen.

The bond length of CO is consistent with a partial triple bond, and the molecule can be represented by three resonance structures:

In this classical model, the leftmost structure contributes the most. As such, carbon monoxide resembles molecular nitrogen, and in addition, it has nearly the same molecular mass. Indeed, their physical properties (boiling point, melting point, etc.) are very similar.

## 4 . Biological and physiological properties

#### 4.1. Toxicity

Carbon monoxide poisoning is the most common type of fatal poisoning in many countries.<sup>[4]</sup> Carbon monoxide is colorless and odorless, but extremely toxic: it combines with hemoglobin in the blood to produce carboxy hemoglobin ( Hb CO ), which is ineffective for delivering oxygen to the body tissues (a condition known as anoxemia). Concentrations as low as 667 ppm can cause up to 50 % of the body's hemoglobin to convert to Hb CO. In the United States, OSHA limits long-term workplace exposure levels to 50 ppm.<sup>[5]</sup>

The most common symptoms of CO poisoning can resemble the flu, including headache, nausea and vomiting, dizziness, lethargy and a feeling of weakness. Infants may be irritable and feed poorly. Neurological signs include confusion, disorientation, visual disturbance, syncope and seizures.

In his pioneering 1846 study, Claude Bernard observed that that the blood of poisoned dogs was more *rutilant* ("gleaming" or "glowing") in all the vessels, a fact now known to be due to the formation of HbCO. Some classic descriptions of CO poisoning cite also retinal hemorrhages, bright reddish skin, and an abnormal " cherry-red" blood hue; but in most clinical diagnoses these signs are seldom seen.

Carbon monoxide is believed to compromise other important molecules such as myoglobin, and mitochondrial cytochrome oxidase Exposures can lead to significant damage to the heart and central nervous system, especially to the globus pallidus , often with longterm sequelae. Carbon monoxide can also have severe effects on the fetus of a pregnant woman.

## 4.2. Human Physiology

Carbon monoxide is produced naturally in the human body as part of normal metabolism, such as the breakdown of heme (a part of the hemoglobin molecule) by the enzyme heme oxygenase to CO, biliverdin and a  $Fe^{3+}$  cation. The endogenously produced CO may have important physiological roles in the body, such as a neurotransmitter or a blood vessels relaxant. In the neuronal system it has been shown to be involved in learning and memory and odor response, among others. It provides cardiac protection in the circulatory system. It also has roles in the immune, respiratory, reproductive, and gastrointestinal systems, as well as in the kidneys and liver. Because of its expansive role, abnormalities in CO metabolism have been linked to a variety of disease processes, including neuro degenerations , hypertension, heart failure, and inflammation. In addition CO regulates inflammatory reactions in a manner that prevents the development of several diseases such as atherosclerosis or severe malaria.

## 4.3. Microbiology

CO is a nutrient for methanogenic bacteria , a building block for acetyl coenzyme A. This theme is the subject for the emerging field of bio organo metallic chemistry. In bacteria, CO is produced via the reduction of carbon dioxide via the enzyme carbon monoxide dehydrogenase, an Fe – Ni – S - containing protein .

A heme - based CO - sensor protein, CooA , is known. The scope of its biological role is still unclear, it is apparently part of a signaling pathway in bacteria and archaea, but its occurrence in mammals is not established.

## 5. Occurrence

Carbon monoxide commonly occurs in various natural and artificial environments. Here are some typical concentrations:

- 0.1 ppm natural background atmosphere level (MOPITT)
- 0.5 to 5 ppm average background level in homes

• 5 to 15 ppm - levels near properly adjusted gas stoves in homes

- 100 200 ppm Mexico City central area from autos etc .
- 5,000 ppm chimney of a home wood fire

• 7,000 ppm - undiluted warm car exhaust - without catalytic converter

#### **5.1.** Atmospheric presence

Carbon monoxide has always been present as a minor constituent of the atmosphere, chiefly as a product of volcanic activity but also from natural and man-made fires ( such as forest and bushfires, burning of crop residues, and sugarcane fire – cleaning ) and the burning of fossil fuels. It occurs dissolved in molten volcanic rock at high pressures in the earth's mantle. Carbon monoxide contents of volcanic gases vary from less than 0.01 % to as much as 2% depending on the volcano. Because natural sources of carbon monoxide are so variable from year to year, it is extremely difficult to accurately measure natural emissions of the gas.

Carbon monoxide has an indirect radiative forcing effect by elevating concentrations of methane and tropospheric ozone through chemical reactions with other atmospheric constituents ( e.g., the hydroxyl radical, OH<sup>•</sup>) that would otherwise destroy them. Through natural processes in the atmosphere, it is eventually oxidized to carbon dioxide. Carbon monoxide concentrations are both short-lived in the atmosphere and spatially variable.

#### 5.2. Urban pollution

Carbon monoxide is a major atmospheric pollutant in urban areas, chiefly from exhaust of internal combustion engines (including vehicles, portable and back-up generators, lawn mowers, power washers, etc.), but also from improper burning of various other fuels (including wood, coal, charcoal, oil, kerosene, propane, natural gas, and trash). Along with aldehydes, it reacts photo chemically to produce peroxy radicals. Peroxy radicals react with nitrogen oxide to increase the ratio of NO<sub>2</sub> to NO, which reduces the quantity of NO that is available to react with ozone.

## **5.3. Indoor pollution**

In closed environments, the concentration of carbon monoxide can easily rise to lethal levels. On average, about 170 people in the United States die every year from CO produced by non-automotive consumer products. These products include malfunctioning fuelburning appliances such as furnaces, ranges, water heaters and room heaters; engine-powered equipment such as portable generators; fireplaces; and charcoal that is burned in homes and other enclosed areas. In 2005 alone, CPSC staff is aware of at least 94 generatorrelated CO poisoning deaths. Forty - seven of these deaths were known to have occurred during power outages due to severe weather, including Hurricane Katrina. Still others die from CO produced by non -consumer products, such as cars left running in attached garages. The Centers for Disease Control and Prevention estimates that several thousand people go to hospital emergency rooms every year to be treated for CO poisoning.

Carbon monoxide is also a constituent of tobacco smoke.

#### 6. Production

Carbon monoxide is so fundamentally important that many methods have been developed for its production .

#### 6.1. Laboratory preparation

Carbon monoxide is conveniently produced in the laboratory by the dehydration of formic acid, for example with sulfuric acid. Another method is heating an intimate mixture of powdered zinc metal and calcium carbonate, which releases CO and leaves behind zinc oxide and calcium oxide:

$$Zn + CaCO_3 \rightarrow Zn O + Ca O + CO$$

#### **6.2. Industrial production**

A major industrial source of CO is producer gas, a mixture containing mostly carbon monoxide and nitrogen, formed by combustion of carbon in air at high temperature when there is an excess of carbon. In an oven, air is passed through a bed of coke. The initially produced  $CO_2$  equilibrates with the remaining hot carbon to give CO. The reaction of  $O_2$  with carbon to give CO is described as the Boudouard equilibrium. Above 800 °C, CO is the predominant product:

$$O_2 + 2 C \rightarrow 2 CO (\Delta H = -221 kJ / mol)$$

Another important source is "water gas", a mixture of hydrogen and carbon monoxide produced via the endothermic reaction of steam and carbon:

$$H_2O + C \rightarrow H_2 + CO (\Delta H = 131 \text{ kJ/mol})$$

Other similar "synthesis gases" can be obtained from natural gas and other fuels.

Carbon monoxide is also is a byproduct of the reduction of metal oxide ores with carbon, shown in a simplified form as follows:

$$MO + C \rightarrow M + CO$$

Since CO is a gas, the reduction process can be driven by heating, exploiting the positive (favorable) entropy of reaction. The Ellingham diagram shows that CO formation is favored over  $CO_2$  in high temperatures.

#### 7. Coordination chemistry

Most metals form coordination complexes containing covalently attached carbon monoxide. Only those in lower oxidation states will complex with carbon monoxide ligands. This is because there must be sufficient electron density to facilitate back donation from the metal  $d_{xz}$ -orbital, to the  $\pi^*$  molecular orbital from CO. The lone pair on the carbon atom in CO, also donates electron density to the  $d_{x^2-y^2}$  on the metal to form a sigma bond. In nickel carbonyl, Ni(CO)<sub>4</sub> forms by the direct combination of carbon monoxide and nickel metal at room temperature. For this reason, nickel in any tubing or part must not come into prolonged contact with carbon monoxide (corrosion). Nickel carbonyl decomposes readily back to Ni and CO upon contact with hot surfaces, and this method was once used for the industrial purification of nickel in the Mond process .

In nickel carbonyl and other carbonyls, the electron pair on the carbon interacts with the metal; the carbon monoxide donates the electron pair to the metal. In these situations, carbon monoxide is called the **carbonyl** ligand. One of the most important metal carbonyls is iron penta carbonyl, Fe (CO)<sub>5</sub>:

Many metal - CO complexes are prepared by decarbonylation of organic solvents, not from CO. For instance, iridium tri chloride and tri phenyl phosphine react in boiling 2 – methoxy ethanol or DMF to afford Ir Cl (CO) (PPh<sub>3</sub>)<sub>2</sub>.

## 8. Organic and main group chemistry

In the presence of strong acids and water, carbon monoxide reacts with olefins to form carboxylic acids in a process known as the Koch-Haaf reaction. In the Gattermann - Koch reaction, arenes are converted to benzaldehyde derivatives in the presence of AlCl<sub>3</sub> and HCl.<sup>[20]</sup> Organolithium compounds, e.g. butyl lithium react with CO, but this reaction enjoys little use.

Although CO reacts with carbocations and carbanions, it is relatively unreactive toward organic compounds without the intervention of metal catalysts .

With main group reagents, CO undergoes several noteworthy reactions. Chlorination of CO is the industrial route to the important compound phosgene. With boron CO forms an adduct,  $H_3BCO$ , which is iso electronic with the acylium cation  $[H_3CCO]^+$ . CO reacts with sodium to give products resulting from C - C coupling such as  $Na_2C_2O_2$  (sodium acetylene diolate), and potassium to give  $K_2C_2O_2$  (potassium acetylene diolate) and  $K_2C_6O_6$  (potassium rhodizonate ).

The compounds cyclo hexane hexone or tri quinoyl ( $C_6O_6$ ) and cyclo penta nepentone or leuconic acid ( $C_5O_5$ ), which so far have been obtained only in trace amounts, can be regarded as polymers of carbon monoxide.

At high pressure (over 5 gigapascals), carbon monoxide disproportionates into carbon dioxide  $CO_2$  and a solid polymer of carbon and oxygen (in 3:2 atomic ratio).

#### 9. Uses

#### 9.1. Chemical industry

Carbon monoxide is a major industrial gas that has many applications in bulk chemicals manufacturing .

Large quantities of aldehydes are produced by the hydro formylation reaction of alkenes, CO, and  $H_2$ . In one of many applications of this technology, hydro formylation is coupled to the Shell Higher Olefin Process to give precursors to detergents. Methanol is produced by the hydrogenation of CO. In a related reaction, the hydrogenation of CO is coupled to C-C bond formation, as in the Fischer-Tropsch process where CO is hydrogenated to liquid hydrocarbon fuels. This technology allows coal or biomass to be converted to diesel.

In the Monsanto process, carbon monoxide and methanol react in the presence of a homogeneous rhodium catalyst and hydroiodic acid to give acetic acid. This process is responsible for most of the industrial production of acetic acid.

An industrial scale use for pure carbon monoxide is purifying nickel in the Mond process.

#### 9.2. Meat coloring

Carbon monoxide is used in modified atmosphere packaging systems in the US, mainly with fresh meat products such as beef, pork, and fish, to keep them looking red and fresh. The CO combines with myoglobin to form carboxy myoglobin, a bright cherry red pigment. Carboxymyoglobin is more stable than the oxygenated form of myoglobin, oxymyoglobin, which can become oxidized to the brown pigment, metmyoglobin. This stable red color can persist much longer than in normally packaged meat. Typical levels of CO used are 0.4 % to 0.5 %.

The technology was first given "generally recognized as safe" (GRAS) status by the U.S. Food and Drug Administration (FDA) in 2002 for use as a secondary packaging system, and does not require labeling. In 2004 the FDA approved CO as primary packaging method, declaring that CO does not mask spoilage odor.<sup>[26]</sup> Despite this ruling, the technology remains controversial in the US for fears that it is deceptive and masks spoilage. In 2007 a bill<sup>[28]</sup> was introduced to the United States House of Representatives to label modified atmosphere carbon monoxide packaging as a "color additive"; however, the bill died in subcommittee. The practice is banned in many other countries, including Canada, Japan, Singapore and the European Union.

#### 9.3. Medicine

CO is also currently being studied in several research laboratories throughout the world for its anti - inflammatory and cyto protective properties that can be used therapeutically to prevent the development of a series of pathologic conditions such as ischemia reperfusion injury, transplant rejection, atherosclerosis, sepsis, severe malaria or autoimmunity. However, there are yet no clinical applications of CO in humans.