

AI Properties of CO₂ and carbon-based fuels

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CONTENTS

AI.1	Introduction to Appendix I	3
AI.2	Carbon dioxide	3
AI.2.1	Physical properties of CO ₂	3
AI.2.2	Chemical properties of CO ₂	4
AI.2.3	Health and safety aspects of exposure to CO ₂	6
AI.2.4	Established uses for CO ₂	8
AI.3	Conversion factors	9
AI.4	Fuels and emissions	9
AI.4.1	Carbonaceous fuels	9
AI.4.2	Examples of emissions from carbonaceous fuels	11
REFERENCES		13
TABLES		15
FIGURES		23

AI.1 Introduction to Appendix I

This Appendix presents data about the relevant physical and chemical properties of CO₂ together with an outline of the effects of CO₂ on human health and a summary of some of the typical recommendations for avoiding harm to humans. Established uses for CO₂ are listed and some common conversion factors relevant to this report are presented. An introduction is also provided to the main types of fossil fuels and other carbon-containing fuels, as background to considering how their use produces CO₂.

AI.2 Carbon dioxide

Carbon dioxide is a chemical compound of two elements, carbon and oxygen, in the ratio of one to two; its molecular formula is CO₂. It is present in the atmosphere in small quantities (370 ppm) and plays a vital role in the Earth's environment as a necessary ingredient in the life cycle of plants and animals. During photosynthesis plants assimilate CO₂ and release oxygen. Anthropogenic activities which cause the emission of CO₂ include the combustion of fossil fuels and other carbon-containing materials, the fermentation of organic compounds such as sugar and the breathing of humans. Natural sources of CO₂, including volcanic activity, dominate the Earth's carbon cycle.

CO₂ gas has a slightly irritating odour, is colourless and is denser than air. Although it is a normal, if minor, constituent of air, high concentrations of CO₂ can be dangerous.

AI.2.1 *Physical properties of CO₂*

AI.2.1.1 *General*

At normal temperature and pressure, carbon dioxide is a gas. The physical state of CO₂ varies with temperature and pressure as shown in Figure AI.1 – at low temperatures CO₂ is a solid; on warming, if the pressure is below 5.1 bar, the solid will sublime directly into the vapour state. At intermediate temperatures (between –56.5°C, the temperature of the triple point, and 31.1°C, the critical point), CO₂ may be turned from a vapour into a liquid by compressing it to the corresponding liquefaction pressure (and removing the heat produced).

At temperatures higher than 31.1°C (if the pressure is greater than 73.9 bar, the pressure at the critical point), CO₂ is said to be in a supercritical state where it behaves as a gas; indeed under high pressure, the density of the gas can be very large, approaching or even exceeding the density of liquid water (also see Figure AI.2.). This is an important aspect of CO₂'s behaviour and is particularly relevant for its storage.

Figure AI.2. Variation of CO₂ density as a function of temperature and pressure (Bachu, 2003).

Heat is released or absorbed in each of the phase changes across the solid-gas, solid-liquid and liquid-gas boundaries (see Figure AI.1). However, the phase changes from the supercritical condition to liquid or from supercritical to gas do not require or release heat. This property is useful for the design of CO₂ compression facilities since, if this can be exploited, it avoids the need to handle the heat associated with the liquid-gas phase change.

AI.2.1.2 Specific physical properties

There is a substantial body of scientific information available on the physical properties of CO₂. Selected physical properties of CO₂ are given in Table AI.1. The phase diagram for CO₂ is shown in Figure AI.1. Many authors have investigated the equation of state for CO₂ (e.g., Span and Wagner, 1996). The variation of the density of CO₂ as a function of temperature and pressure is shown in Figure AI.2, the variation of vapour pressure of CO₂ with temperature in Figure AI.3, and the variation of viscosity with temperature and pressure in Figure AI.4. Further information on viscosity can be found in Fenghour *et al.* (1998). The pressure-enthalpy chart for CO₂ is shown in Figure AI.5. The solubility of CO₂ in water is described in Figure AI.6.

Table AI.1. Physical properties of CO₂.

Figure AI.1. Phase diagram for CO₂ (based on Shakhshiri).

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Figure AI.3. Vapour pressure of CO₂ as a function of temperature (Span and Wagner, 1996).

Figure AI.4. Variation of CO₂ viscosity as a function of temperature and pressure (Bachu, 2003).

Figure AI.5. Pressure-Enthalpy chart for CO₂.

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Figure AI.6. Solubility of CO₂ in water (Kohl and Nielsen, 1997).

*AI.2.2 Chemical properties of CO₂**AI.2.2.1 General*

Some thermodynamic data for CO₂ and a few related compounds are given in Table AI.2.

Table AI.2. Thermodynamic data for selected carbon-containing compounds (ref. Cox *et al.*, 1989 and other sources).

In an aqueous solution CO₂ forms carbonic acid, which is too unstable to be easily isolated. The solubility of CO₂ in water (Figure AI.6) decreases with increasing temperature and increases with increasing pressure. The solubility of CO₂ in water also decreases with increasing water salinity by as much as one order of magnitude (Figure AI.7). The following empirical relation (Enick and Klara, 1990) can be used to estimate CO₂ solubility in brackish water and brine:

$$w_{\text{CO}_2, b} = w_{\text{CO}_2, w} \cdot (1.0 - 4.893414 \cdot 10^{-2} \cdot S + 0.1302838 \cdot 10^{-2} \cdot S^2 - 0.1871199 \cdot 10^{-4} \cdot S^3) \quad (1)$$

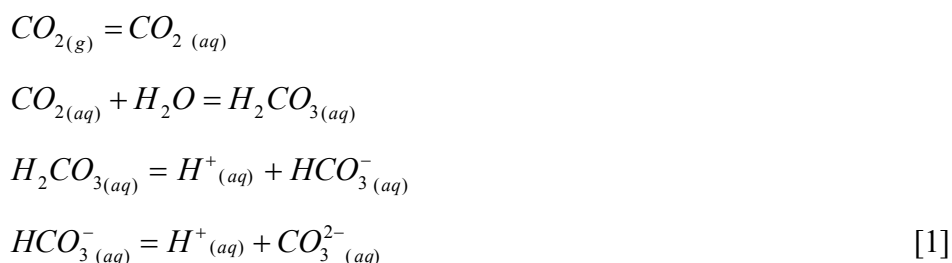
where w_{CO_2} is CO₂ solubility, S is water salinity (expressed as total dissolved solids in % by weight) and the subscripts *w* and *b* stand for pure water and brine, respectively.

Figure AI.7. Solubility of CO₂ in brine relative to that in pure water, showing experimental points reported by Enick and Klara, 1990 and correlation developed by those authors. (TDS stands for total dissolved solids).

A solid hydrate separates from aqueous solutions of CO₂ that are chilled (below about 11°C) at elevated pressures. A hydrate is a crystalline compound consisting of the host (water) plus guest molecules. The host is formed from a tetrahedral hydrogen-bonding network of water molecules; this network is sufficiently open to create pores (or cavities) that are large enough to contain a variety of other small molecules (the guests). Guest molecules can include CH₄ and CO₂. CO₂ hydrates have similar (but not identical) properties to methane hydrates, which have been extensively studied due to their effects on natural gas production and their potential as future sources of hydrocarbons. CO₂ hydrates have not been studied as extensively.

AI.2.2.2 Impact of CO₂ on pH of water

The dissolution of CO₂ in water (this may be sea water, or the saline water in geological formations) involves a number of chemical reactions between gaseous and dissolved carbon dioxide (CO₂), carbonic acid (H₂CO₃), bicarbonate ions (HCO₃⁻) and carbonate ions (CO₃²⁻) which can be represented as follows:



Addition of CO₂ to water initially leads to an increase in the amount of dissolved CO₂. The dissolved CO₂ reacts with water to form carbonic acid. Carbonic acid dissociates to form bicarbonate ions, which can further dissociate into carbonate ions. The net effect of dissolving *anthropogenic* CO₂ in water is the removal of carbonate ions and production of bicarbonate ions, with a lowering in pH.

Figure AI.8 shows the dependence of pH on the extent to which CO₂ dissolves in sea water at temperatures of 0°C and 25°C based on theoretical calculations (IEA Greenhouse Gas R&D Programme, 2000) by iterative solution of the relationships (Horne, 1969) for the carbonic acid/bicarbonate/carbonate equilibria combined with activity coefficients for the bicarbonate and carbonate ions in sea water. The temperature dependence of the ionization of water and the bicarbonate equilibria were also included in this calculation. This gives values for the pH of typical sea water of 7.8–8.1 at 25°C and 8.1–8.4 at 0°C. These values, which are strongly dependent on carbonate/bicarbonate buffering, are in line with typical data for sea water (Figure AI.8 shows two experimental data points reported by Nishikawa *et al.*, 1992).

Figure AI.8. Dependence of pH on CO₂ concentration in sea water.

Figure AI.8 also shows that there is a small effect of temperature on the reduction in pH that results from dissolution of CO₂. A minor pressure dependence of water ionization is also reported (Handbook of Chemistry and Physics, 2000). The effect on water ionization of an increase in pressure from atmospheric to 250 bar (equivalent to 2500 m depth) is minor and about the same as would result from increasing temperature by about 2°C. The effect of pressure can therefore be ignored.

AI.2.3 Health and safety aspects of exposure to CO₂

As a normal constituent of the atmosphere, where it is present in low concentrations (currently 370 ppm), CO₂ is considered harmless. CO₂ is non-flammable.

As it is 1.5 times denser than air at normal temperature and pressure, there will be a tendency for any CO₂ leaking from pipework or storage to collect in hollows and other low-lying confined spaces which could create hazardous situations. The hazardous nature of the release of CO₂ is enhanced because the gas is colourless, tasteless and is generally considered odourless unless present in high concentrations.

When contained under pressure, escape of CO₂ can present serious hazards, for example asphyxiation, noise level (during pressure relief), frostbite, hydrates/ice plugs and high pressures (Jarrell *et al.*, 2002). The handling and processing of CO₂ must be taken into account during the preparation of a health, safety and environment plan for any facility handling CO₂.

AI.2.3.1 Effects of exposure to CO₂

At normal conditions, the atmospheric concentration of CO₂ is 0.037%, a non-toxic amount. Most people with normal cardiovascular, pulmonary-respiratory and neurological functions can tolerate exposure of up to 0.5–1.5% CO₂ for one to several hours without harm.

Higher concentrations or exposures of longer duration are hazardous – either by reducing the concentration of oxygen in the air to below the 16% level required to sustain human life¹, or by entering the body, especially the bloodstream, and/or altering the amount of air taken in during breathing; such physiological effects can occur faster than the effects resulting from the displacement of oxygen, depending on the concentration of CO₂. This is reflected in, for example, the current US occupational exposure standard of 0.5% for the maximum allowable concentration of CO₂ in air for eight hours continuous exposure; the maximum concentration to which operating personnel may be exposed for a short period of time is 3.0%.

The impact of elevated CO₂ concentrations on humans depends on the concentration and duration of exposure. At concentrations up to 1.5%, there are no noticeable physical consequences for healthy adults at rest from exposure for an hour or more (Figure AI.9); indeed, exposure to slightly elevated concentrations of CO₂, such as in re-breathing masks on aeroplanes at high altitude, may produce beneficial effects (Benson *et al.*, 2002). Increased activity or temperature may affect how the exposure is perceived. Longer exposure, even to less than 1% concentration, may significantly affect health. Noticeable effects occur above this level, particularly changes in respiration and blood pH level that can lead to increased heart rate, discomfort, nausea and unconsciousness.

Figure AI.9. Effects of CO₂ exposure on humans (Fleming *et al.*, 1992).

It is noted (Rice, 2004) that most studies of the effects of CO₂ have involved healthy young male subjects, especially in controlled atmospheres such as submarines. Carbon dioxide tolerance in susceptible subgroups, such as children, the elderly, or people with respiratory deficiency, has not been studied to such an extent.

¹ Signs of asphyxia will be noted when atmospheric oxygen concentration falls below 16%. Unconsciousness, leading to death, will occur when the atmospheric oxygen concentration is reduced to ≤8% although, if strenuous exertion is being undertaken, this can occur at higher oxygen concentrations (Rice, 2004).

Acute exposure to CO₂ concentrations at or above 3% may significantly affect the health of the general population. Hearing loss and visual disturbances occur above 3% CO₂. Healthy young adults exposed to more than 3% CO₂ during exercise experience adverse symptoms, including laboured breathing, headache, impaired vision and mental confusion. CO₂ acts as an asphyxiant in the range 7–10% and can be fatal at this concentration; at concentrations above 20%, death can occur in 20 to 30 minutes (Fleming *et al.*, 1992). The effects of CO₂ exposure are summarized in Table AI.3, which shows the consequences at different concentrations.

Table AI.3. Some reports of reactions to exposure to elevated concentrations of CO₂.

Health risks to the population could therefore occur if a release of CO₂ were to produce:

- relatively low ambient concentrations of CO₂ for prolonged periods;
- or intermediate concentrations of CO₂ in relatively anoxic environments;
- or high concentrations of CO₂.

CO₂ intoxication is identified by excluding other causes, as exposure to CO₂ does not produce unique symptoms.

AI.2.3.2 Occupational standards

Protective standards have been developed for workers who may be exposed to CO₂ (Table AI.4 shows US standards but similar standards are understood to apply in other countries). These standards may or may not be relevant for protection of the general population against exposure to CO₂. Nevertheless, the occupational standards exist and provide a measure of the recommended exposure levels for this class of individual.

Table AI.4. Occupational exposure standards.

Site-specific risk assessments using these and other health data are necessary to determine potential health risks for the general population or for more sensitive subjects.

AI.2.3.3 Sensitive populations

Rice (2004) has indicated that there may be certain specific groups in the population which are more sensitive to elevated CO₂ levels than the general population. Such groups include those suffering from certain medical conditions (including cerebral disease as well as patients in trauma) medicated patients and those experiencing panic disorder, as well as individuals with pulmonary disease resulting in acidosis, children and people engaged in complex tasks.

CO₂ is a potent cerebrovascular dilator and significantly increases the cerebral blood flow. CO₂ exposure can seriously compromise patients in a coma or with a head injury, with increased intracranial pressure or bleeding, or with expanding lesions. An elevated partial pressure of CO₂ in arterial blood can further dilate cerebral vessels already dilated by anoxia.

Anoxia and various drugs (Osol and Pratt, 1973) can depress the stimulation of the respiratory centre by CO₂. In such patients, as well as patients with trauma to the head, the normal compensatory mechanisms will not be effective against exposure to CO₂ and the symptoms experienced will not necessarily alert the individuals or their carers to the presence of high CO₂ levels.

Patients susceptible to panic disorder may experience an increased frequency of panic attacks at 5% CO₂ (Woods *et al.*, 1988). Panic attack and significant anxiety can affect the ability of the individual to exercise appropriate judgment in dangerous situations.

CO₂ exposure can increase pulmonary pressure as well as systemic blood pressure and should be avoided in individuals with systemic or pulmonary hypertension. The rise in cardiac work during CO₂ inhalation could put patients with coronary artery disease or heart failure in jeopardy (Cooper *et al.*, 1970).

Infants and children breathe more air than adults relative to their body size and they therefore tend to be more susceptible to respiratory exposures (Snodgrass, 1992). At moderate to high CO₂ concentrations, the relaxation of blood vessels and enhanced ventilation could contribute to rapid loss of body heat in humans of any age. Carbon dioxide can significantly diminish an individual's performance in carrying out complex tasks.

AI.2.3.4 CO₂ control and response procedures

Suitable control procedures have been developed by industries which use CO₂, for example, minimizing any venting of CO₂ unless this cannot be avoided for safety or other operational reasons. Adequate ventilation must be provided when CO₂ is discharged into the air to ensure rapid dispersion.

Due its high density, released CO₂ will flow to low-levels and collect there, especially under stagnant conditions. High concentrations can persist in open pits, tanks and buildings. For this reason, monitors should be installed in areas where CO₂ might concentrate, supplemented by portable monitors. If CO₂ escapes from a vessel, the consequent pressure drop can cause a hazardous cold condition with danger of frostbite from contact with cold surfaces, with solid CO₂ (dry ice) or with escaping liquid CO₂. Personnel should avoid entering a CO₂ vapour cloud not only because of the high concentration of CO₂ but also because of the danger of frostbite.

Hydrates, or ice plugs, can form in the piping of CO₂ facilities and flowlines, especially at pipe bends, depressions and locations downstream of restriction devices. Temperatures do not have to fall below 0°C for hydrates to form; under elevated pressures this can occur up to a temperature of 11°C.

AI.2.4 Established uses for CO₂

A long-established part of the industrial gases market involves the supply of CO₂ to a range of industrial users (source: Air Liquide). In several major industrial processes, CO₂ is manufactured on site as an intermediate material in the production of chemicals. Large quantities of CO₂ are used for enhanced oil recovery. Other uses of CO₂ include:

- Chemicals
 - Carbon dioxide is used in synthesis chemistry and to control reactor temperatures. CO₂ is also employed to neutralize alkaline effluents.
 - The main industrial use of CO₂ is in the manufacture of urea, as a fertilizer.
 - Large amounts of CO₂ are also used in the manufacture of inorganic carbonates and a lesser amount is used in the production of organic monomers and polycarbonates.
 - Methanol is manufactured using a chemical process which makes use of CO₂ in combination with other feedstocks.
 - CO₂ is also used in the manufacture of polyurethanes.
- Pharmaceuticals

- CO₂ is used to provide an inert atmosphere, for chemical synthesis, supercritical fluid extraction and for acidification of waste water and for product transportation at low temperature (–78°C).
- Food and Beverage
 - CO₂ is used in the food business in three main areas: Carbonation of beverages; packaging of foodstuffs and as cryogenic fluid in chilling or freezing operations or as dry ice for temperature control during the distribution of foodstuffs.
- Health care
 - Intra-abdominal insufflation during medical procedures to expand the space around organs or tissues for better visualization.
- Metals industry
 - CO₂ is typically used for environmental protection; for example for red fume suppression during scrap and carbon charging of furnaces, for nitrogen pick-up reduction during tapping of electric arc furnaces and for bottom stirring.
 - In non-ferrous metallurgy, carbon dioxide is used for fume suppression during ladle transfer of matte (Cu/Ni production) or bullion (Zn/Pb production).
 - A small amount of liquid CO₂ is used in recycling waters from acid mine drainage.
- Pulp and paper
 - CO₂ enables fine-tuning of the pH of recycled mechanical or chemical pulps after an alkaline bleaching. CO₂ can be used for increasing the performance of paper production machines.
- Electronics
 - CO₂ is used in waste water treatment and as a cooling medium in environmental testing of electronic devices. CO₂ can also be used to add conductivity to ultra-pure water and, as CO₂ snow, for abrasive cleaning of parts or residues on wafers; CO₂ can also be used as a supercritical fluid for removing photoresist from wafers, thus avoiding use of organic solvents.
- Waste treatment
 - Injection of CO₂ helps control the pH of liquid effluents.
- Other applications
 - CO₂ snow is used for fire extinguishers, for pH control and for regulation of waste waters in swimming pools.

AI.3 Conversion factors

Some conversion factors relevant to CO₂ capture and storage are given in Table AI.5. Other, less precise conversions and some approximate equivalents are given in Table AI.6.

Table AI.5. Some conversion factors.

Table AI.6. Approximate equivalents and other definitions.

AI.4 Fuels and emissions

AI.4.1 Carbonaceous fuels

Carbonaceous fuels can be defined as materials rich in carbon and capable of producing energy on oxidation. From a historical perspective, most of these fuels can be viewed as carriers of solar energy, having been derived from plants which depended on solar energy for growth. Thus, these fuels can be distinguished by the time taken for their formation, which is millions of years for fossil

fuels, hundreds of years for peat and months-to-years for biofuels. On the scale of the human lifespan, fossil fuels are regarded as non-renewable carbonaceous fuels while biofuels are regarded as renewable. Coal, oil and natural gas are the major fossil fuels. Wood, agro-wastes, etcetera are the main biofuels for stationary uses but, in some parts of the world, crops such as soya, sugar cane and oil-seed plants are grown specifically to produce biofuels, especially transport fuels such as bioethanol and biodiesel. Peat is close to being a biofuel in terms of its relatively short formation time compared with fossil fuels.

AI.4.1.1 Coal

Coal is the most abundant fossil fuel present on Earth. Coal originated from the arrested decay of the remains of plant life which flourished in swamps and bogs many millions of years ago in a humid, tropical climate with abundant rainfall. Subsequent action of heat and pressure and other physical phenomena metamorphosed it into coal. Because of various degrees of metamorphic change during the process, coal is not a uniform substance; no two coals are the same in every respect. The composition of coal is reported in two different ways: The proximate analysis and the ultimate analysis, both expressed in % by weight. In a proximate analysis, moisture, volatile matter, fixed carbon and ash are measured using prescribed methods, which enable the equipment designer to determine how much air is to be supplied for efficient combustion, amongst other things. An ultimate analysis determines the composition in terms of the elements that contribute to the heating value, such as carbon, hydrogen, nitrogen, sulphur, the oxygen content (by difference), as well as ash. Along with these analyses, the heating value (expressed as kJ kg^{-1}) is also determined.

Carpenter (1988) describes the various coal classification systems in use today. In general, these systems are based on hierarchy and rank. The rank of a coal is the stage the coal has reached during the coalification² process – that is its degree of metamorphism or maturity. Table AI.7 shows the classification system adopted by the American Society for Testing Materials (ASTM), D388-92A (Carpenter, 1988; Perry and Green, 1997). This rank-based system is extensively used in North America and many other parts of the world. This system uses two parameters to classify coals by rank, fixed carbon (dry, mineral-matter-free) for the higher rank coals and gross calorific value (moist, mineral-matter-free) for the lower rank coals. The agglomerating character of the coals is used to differentiate between adjacent coal groups.

Table AI.7. Characterization of coals by rank (according to ASTM D388-92A).

AI.4.1.2 Oil and petroleum fuels

During the past 600 million years, the remains of incompletely decayed plant have become buried under thick layers of rock and, under high pressure and temperature, have been converted to petroleum which may occur in gaseous, liquid or solid form. The fluid produced from petroleum reservoirs may be crude oil (a mixture of light and heavy hydrocarbons and bitumen) or natural gas liquids. Hydrocarbons can also be extracted from tar sands or oil shales; this takes place in several parts of the world.

Fuels are extracted from crude oil through fractional distillation, with subsequent conversion and upgrading. Such fuels are used for vehicles (gasoline, jet fuel, diesel fuel and liquefied petroleum gases (LPG)), heating oils, lighting oils, solvents, lubricants and building materials such as asphalts, plus a variety of other products. The compositions of heating fuels may differ in their composition,

² Coalification refers to the progressive transformation of peat through lignite/brown coal, to sub-bituminous, bituminous and anthracite coals.

density, etcetera but general categories are recognized worldwide: Kerosene-type vaporizing fuel, distillate (or 'gas oil') and more viscous blends and residuals. Tables AI.8 and AI.9 provide typical specifications of some common fuels (Perry and Green, 1997; Kaantee *et al.*, 2003).

AI.4.1.3 Natural gas

Natural gas is combustible gas that occurs in porous rock of the Earth's crust; it is often found with or near accumulations of crude oil. It may occur in separate reservoirs but, more commonly, it forms a gas cap entrapped between the petroleum and an impervious, capping rock layer in a petroleum reservoir. Under high-pressure conditions, it becomes partially mixed with or dissolved in the crude oil. Methane (CH₄) is the main component of natural gas, usually making up more than 80% of the constituents by volume. The remaining constituents are ethane (C₂H₆), propane (C₃H₈), butane (C₄H₁₀), hydrogen sulphide (H₂S) and inerts (N₂, CO₂ and He). The amounts of these compounds can vary greatly depending on location. Natural gas is always treated prior to use, mainly by drying, and by removing H₂S and, depending on the amount present, CO₂. There are no universally accepted specification systems for marketed natural gas; however a typical composition of natural gas is given in Table AI.10 (Spath and Mann, 2000).

Table AI.10. Typical natural gas composition.

AI.4.1.4 Biofuels

Biofuels may be defined as fuels produced from organic matter or combustible oils produced by plants (IPCC, 2001). Dedicated energy crops, including short-rotation woody crops such as hardwood trees and herbaceous crops such as switch grass, are agricultural crops that are solely grown for use as biofuels. These crops have very fast growth rates and can therefore provide a regular supply of fuel. The category of biofuels also includes wood from trees and wood waste products (e.g., sawdust, wood chips, etc.), crop residues (e.g., rice husks, bagasse, corn husks, wheat chaff, etc.). This category of fuel is often taken to include some types of municipal, animal and industrial wastes (e.g., sewage sludge, manure, etc.). These would be combusted in stationary plants. Chemical properties of typical biofuels, including peat, are given in Table AI.11 (Sami *et al.*, 2001; Hower, 2003).

Table AI.11. Chemical analysis and properties of some biomass fuels (Sami *et al.*, 2001; Hower, 2003).

Biomass-derived fuels can also be manufactured for use as transport fuels, for example ethanol from fermentation of plant material or biodiesel produced by transesterification of vegetable oils. The energy efficiency of fermentation systems can be improved by combustion of the solid residues to produce electricity.

AI.4.2 Examples of emissions from carbonaceous fuels

Depending on the fuel type and application, the utilization of carbonaceous fuels causes direct and indirect emissions of one or more of the following: SO_x, NO_x, particulate matter, trace metals and elements, volatile organic carbons and greenhouse gases (e.g., CO₂, CH₄, N₂O). Direct emissions are usually confined to the point of combustion of the fuel. Indirect emissions include those that arise from the upstream recovery, processing and distribution of the fuel. Life cycle analysis (LCA) can be used to account for all emissions (direct as well as indirect) arising from the recovery, processing, distribution and end-use of a fuel. Table AI.12 (Cameron, 2002) and Table AI.13 (EPA, 2004) give an idea of some direct and indirect emissions anticipated, but these should only be viewed as examples due to the considerable variation there can be in many of these values.

Table AI.12. Direct emissions of non-greenhouse gases from two examples of coal and natural gas plants based on best available control technology, burning specific fuels (Cameron, 2002).

Table AI.13. Direct CO₂ emission factors for some examples of carbonaceous fuels.

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Tables

Table AI.1. Physical properties of CO₂.

Property	Value
Molecular weight	44.01
Critical temperature	31.1°C
Critical pressure	73.9 bar
Critical density	467 kg m ⁻³
Triple point temperature	-56.5°C
Triple point pressure	5.18 bar
Boiling (sublimation) point (1.013 bar)	-78.5°C
<i>Gas Phase</i>	
Gas density (1.013 bar at boiling point)	2.814 kg m ⁻³
Gas density (@ STP)	1.976 kg m ⁻³
Specific volume (@ STP)	0.506 m ³ kg ⁻¹
C _p (@ STP)	0.0364 kJ (mol.K) ⁻¹
C _v (@ STP)	0.0278 kJ (mol.K) ⁻¹
C _p /C _v (@ STP)	1.308
Viscosity (@ STP)	13.72 μN.s m ⁻² (or μPa.s)
Thermal conductivity (@ STP)	14.65 mW (m.K) ⁻¹
Solubility in water (@ STP)	1.716 vol/vol
Enthalpy (@ STP)	21.34 kJ mol ⁻¹
Entropy (@ STP)	117.2 J (mol.K) ⁻¹
Entropy of formation	213.8 J (mol.K) ⁻¹
<i>Liquid Phase</i>	
Vapour pressure (at 20°C)	58.5 bar
Liquid density (at -20°C and 19.7 bar)	1032 kg m ⁻³
Viscosity (@ STP)	99 μN.s/m ² (or μPa.s)
<i>Solid Phase</i>	
Density of carbon dioxide snow at freezing point	1562 kg m ⁻³
Latent heat of vaporization (1.013 bar at sublimation point)	571.1 kJ kg ⁻¹

where STP stands for Standard Temperature and Pressure, which is 0°C and 1.013 bar

Sources: Air Liquide gas data table; Kirk-Othmer (1985); NIST (2003).

Table AI.2. Thermodynamic data for selected carbon-containing compounds (ref. Cox *et al.*, 1989 and other sources).

Compound	Heat of Formation	Gibbs free energy of formation	Entropy of Formation
	ΔH_f° kJ mol ⁻¹	ΔG_f° kJ mol ⁻¹	S_f° J mol ⁻¹ K ⁻¹
CO (g)	-110.53	-137.2	197.66
CO ₂ (g)	-393.51	-394.4	213.78
CO ₂ (l)		-386	
CO ₂ (aq)	-413.26		119.36
CO ₃ ²⁻ (aq)	-675.23		-50.0
CaO (s)	-634.92		38.1
HCO ₃ ⁻ (aq)	-689.93	-603.3	98.4
H ₂ O (l)	-285.83		69.95
H ₂ O (g)	-241.83		188.84
CaCO ₃ (s)	-1207.6 (calcite)	-1129.1	91.7
	-1207.8 (aragonite)	-1128.2	88
MgCO ₃ (s)	-1113.28 (magnesite)	-1029.48	65.09
CH ₄ (g)	-74.4	-50.3	186.3
CH ₃ OH (l)	-239.1	-166.6	126.8
(g)	-201.5	-162.6	239.8

Table AI.3. Some reports of reactions to exposure to elevated concentrations of CO₂.

CO ₂ Conc.	Exposure Reactions	
	Air Products (2004)	Rice (2004)
1%	Slight increase in breathing rate.	Respiratory rate increased by about 37%
2%	Breathing rate increases to 50% above normal level. Prolonged exposure can cause headache, tiredness.	Ventilation rate raised by about 100%. Respiratory rate raised by about 50%; Increased brain blood flow.
3%	Breathing increases to twice normal rate and becomes laboured. Weak narcotic effect. Impaired hearing, headache, increase in blood pressure and pulse rate.	Exercise tolerance reduced in workers when breathing against inspiratory & expiratory resistance.
4–5%	Breathing increases to approximately four times normal rate; symptoms of intoxication become evident and slight choking may be felt.	Increase in ventilation rate by ~200%; Respiratory rate doubled, dizziness, headache, confusion, dyspnoea.
5–10%	Characteristic sharp odour noticeable. Very laboured breathing, headache, visual impairment and ringing in the ears. Judgment may be impaired, followed within minutes by loss of consciousness.	At 8–10%, severe headache, dizziness, confusion, dyspnoea, sweating, dim vision At 10%, unbearable dyspnoea, followed by vomiting, disorientation, hypertension, and loss of consciousness.
50–100%	Unconsciousness occurs more rapidly above 10% level. Prolonged exposure to high concentrations may eventually result in death from asphyxiation.	

Table AI.4. Occupational exposure standards.

	Time-Weighted Average (8 hour day/ 40 hour week)	Short-Term Exposure Limit (15 minute)	Immediately Dangerous to Life and Health
Permissible Exposure Limit ^a	5000 ppm (0.5%)		
Recommended Exposure Limit ^b	5000 ppm (0.5%)	30,000 ppm (3%)	40,000 ppm (5%)
Threshold Limit Value ^c	5000 ppm (0.5%)		

^a OSHA US Occupational Safety and Health Administration (1986)

^b NIOSH US National Institute of Occupational Safety and Health (1997)

^c ACGIH American Conference of Governmental Industrial Hygienists.

Table AI.5. Some conversion factors.

To convert:	Into the following units:	Multiply by:
US gallon	litre	3.78541
barrels (bbl)	m ³	0.158987
ton (Imperial)	tonne	1.01605
short ton (US)	tonne	0.907185
lbf	N	4.44822
kgf	N	9.80665
lbf in ⁻²	Bar	0.0689476
Bar	MPa	0.1
Btu	MJ	0.00105506
Btu	kWh	0.000293071
kWh	MJ	3.60000
Btu lb ⁻¹	MJ kg ⁻¹	0.00232600
Btu ft ⁻³	MJ m ⁻³	0.0372589
Btu/h	kW	0.000293071
Btu (lb.°F) ⁻¹	kJ (kg.°C) ⁻¹	4.18680
Btu (ft ² .h) ⁻¹	kW m ⁻²	0.00315459
Btu (ft ³ .h) ⁻¹	kW m ⁻³	0.0103497
Btu (ft ² .h.°F) ⁻¹	W (m ² .°C) ⁻¹	5.67826
1 MMT ^a	million tonnes	0.907185
°F	°C	$^{\circ}C = \frac{(^{\circ}F - 32)}{1.8}$

^a The abbreviation MMT is used in the literature to denote both Millions of short tons and Millions of metric tonnes. The conversion given here is for the former.

Table AI.6. Approximate equivalents and other definitions.

To convert	Into the following units	Multiply by	
1 t C	t CO ₂	3.667	
1 t CO ₂	m ³ CO ₂ (at 1.013 bar and 15 °C)	534	
1 t crude oil	Bbl	7.33	
1 t crude oil	m ³	1.165	
Fractions retained			
Release rate (fraction of stored amount released per year)	Fraction retained over 100y	Fraction retained over 500 years	Fraction retained over 5000 years
0.001	90%	61%	1%
0.0001	99%	95%	61%
0.00001	100%	100%	95%
Other definitions			
Standard Temperature and Pressure	0 °C and 1.013 bar		

Table AI.7. Characterization of coals by rank (according to ASTM D388-92A).

	Fixed Carbon Limits (dmmf basis) ^a %		Volatile Matter Limits (dmmf basis) ^a %		Gross Calorific Value Limits (mmmf basis) ^b MJ kg ⁻¹		
Class Group	Equal to or greater than	Less than	Greater than	Equal to or less than	Equal to or greater than	Less than	Agglomerating Character
<i>Anthracite</i>							
Meta -anthracite	98	-	-	2	-	-	Non-agglomerating
Anthracite	92	98	2	8	-	-	
Semi -anthracite ^{††}	86	92	8	14	-	-	
<i>Bituminous coal</i>							
Low volatile	78	86	14	22	-	-	Commonly agglomerating
Medium volatile	69	78	22	31	-	-	
High volatile A	-	69	31	-	32.6 [‡]	-	
High volatile B	-	-	-	-	30.2 [‡]	32.6	
High volatile C	-	-	-	-	26.7	30.2	
					24.4	26.7	Agglomerating
<i>Sub-bituminous coal</i>							
A	-	-	-	-	24.4	26.7	Non-agglomerating
B	-	-	-	-	22.1	24.4	
C	-	-	-	-	19.3	22.1	
<i>Lignite</i>							
A	-	-	-	-	14.7	19.3	
B	-	-	-	-	-	14.7	

^a mmmf indicates moist mineral-matter-free basis; moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal. [#] indicates dry-mineral-matter-free basis (dmmf). ^{††} If agglomerating, classified in the low volatile group of the bituminous class.

^b Coals having 69% or more fixed carbon (dmmf) are classified according to fixed carbon, regardless of gross calorific value.

Table AI.8. Typical specifications of petroleum-based heating fuels.

Specifier	Number	Category
Canadian Government Specification Board, Department of Defense Production, Canada	3-GP-2	Fuel oil, heating
Deutsches Institut für Normung e.V., Germany	DIN 51603	Heating (fuel) oils
British Standards Institution, UK	B.S. 2869	Petroleum fuels for oil engines and burners
Japan	JIS K2203	Kerosene
	JIS K2204	Gas oil
	JIS K2205	Fuel oil
Federal Specifications, United States	ASTM D 396	Fuel oil, burner

Table AI.9. Typical ultimate analysis of petroleum-based heating fuels.

Composition %	No. 1 fuel oil (41.5° API ^a)	No. 2 fuel oil (33° API ^a)	No. 4 fuel oil (23.2° API ^a)	Low sulphur, No. 6 fuel oil (33° API ^a)	High sulphur, No. 6 fuel oil (15.5° API ^a)	Petroleum coke ^b
Carbon	86.4	87.3	86.47	87.26	84.67	89.5
Hydrogen	13.6	12.6	11.65	10.49	11.02	3.08
Oxygen	0.01	0.04	0.27	0.64	0.38	1.11
Nitrogen	0.003	0.006	0.24	0.28	0.18	1.71
Sulphur	0.09	0.22	1.35	0.84	3.97	4.00
Ash	<0.01	<0.01	0.02	0.04	0.02	0.50
C/H Ratio	6.35	6.93	7.42	8.31	7.62	29.05

^a Degree API = (141.5/s) – 131.5; where s is the specific density at 15°C;^b reference: Kaantee *et al.* (2003).**Table AI.10.** Typical natural gas composition.

Component	Pipeline composition used in analysis	Typical range of wellhead components (mol%)	
	Mol% (dry)	Low value	High value
Carbon dioxide CO ₂	0.5	0	10
Nitrogen N ₂	1.1	0	15
Methane CH ₄	94.4	75	99
Ethane C ₂ H ₆	3.1	1	15
Propane C ₃ H ₈	0.5	1	10
Isobutane C ₄ H ₁₀	0.1	0	1
N-butane C ₄ H ₁₀	0.1	0	2
Pentanes + (C ₅ ⁺)	0.2	0	1
Hydrogen sulphide (H ₂ S)	0.0004	0	30
Helium (He)	0.0	0	5
Heat of combustion (LHV)	48.252 MJ kg ⁻¹	-	-
Heat of combustion (HHV)	53.463 MJ kg ⁻¹	-	-

Table AI.11. Chemical analysis and properties of some biomass fuels (Sami *et al.*, 2001; Hower, 2003).

	Peat	Wood (saw dust)	Crop Residues (sugar cane bagasse)	Municipal Solid Waste	Energy Crops (Eucalyptus)
Proximate Analysis					
Moisture	70–90	7.3	-	16–38	-
Ash	-	2.6	11.3	11–20	0.52
Volatile matter	45–75	76.2	-	67–78	-
Fixed carbon	-	13.9	14.9	6–12	16.9
Ultimate Analysis					
C	45–60	46.9	44.8	-	48.3
H	3.5–6.8	5.2	5.4	-	5.9
O	20–45	37.8	39.5	-	45.1
N	0.75–3	0.1	0.4	-	0.2
S	-	0.04	0.01	-	0.01
Heating Value, MJ kg⁻¹, (HHV)	17–22	18.1	17.3	15.9–17.5	19.3

Table AI.12. Direct emissions of non-greenhouse gases from two examples of coal and natural gas plants based on best available control technology, burning specific fuels (Cameron, 2002).

Emissions	Coal (supercritical PC with best available emission controls)	Natural gas (NGCC with SCR)
NO _x , g GJ ⁻¹	4–5	5
Sox, g GJ ⁻¹	4.5–5	0.7
Particulates, g GJ ⁻¹	2.4–2.8	2
Mercury, mg GJ ⁻¹	0.3–0.5	N/A

Table AI.13. Direct CO₂ emission factors for some examples of carbonaceous fuels.

Carbonaceous Fuel	Heat Content (HHV) MJ kg⁻¹ ^a	Emission Factor gCO₂ MJ⁻¹ ^a
Coal		
Anthracite	26.2	96.8
Bituminous	27.8	87.3
Sub-bituminous	19.9	90.3
Lignite	14.9	91.6
Biofuel		
Wood (dry)	20.0	78.4
Natural Gas	kJ m⁻³	
	37.3	50
Petroleum Fuel	MJ m⁻³	
Distillate Fuel Oil (#1, 2 & 4)	38,650	68.6
Residual Fuel Oil (#5 & 6)	41,716	73.9
Kerosene	37,622	67.8
LPG (average for fuel use)	25,220	59.1
Motor Gasoline	-	69.3

^a Reported values converted to SI units (NIES, 2003).

Figures

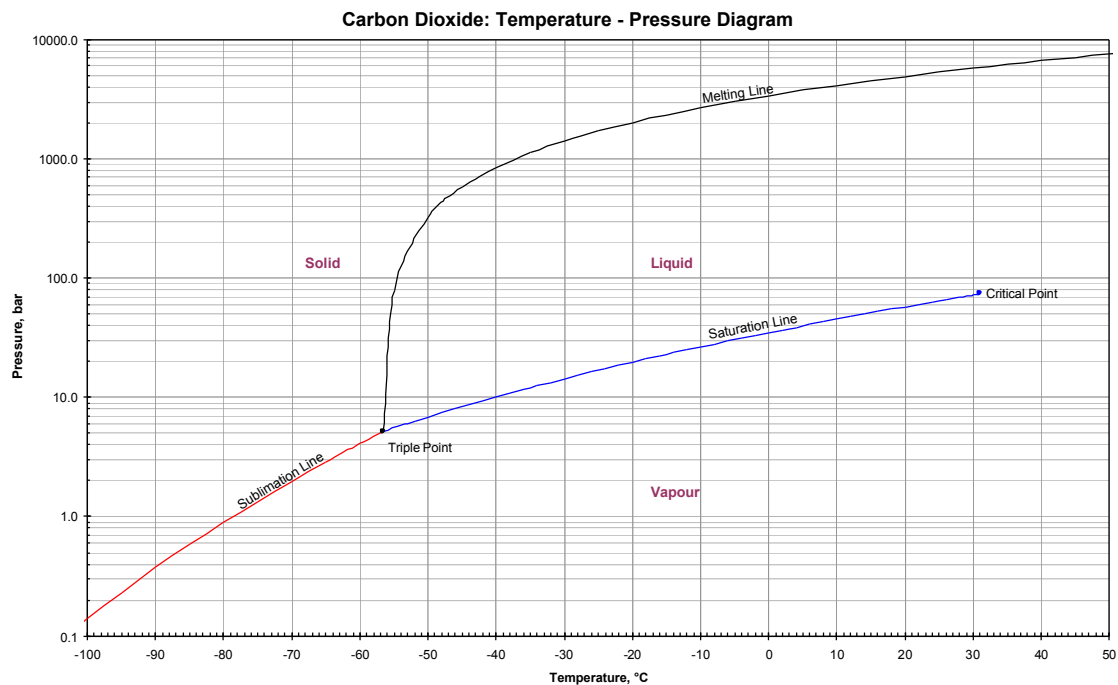


Figure AI.1. Phase diagram for CO₂ (based on Shakhshiri).

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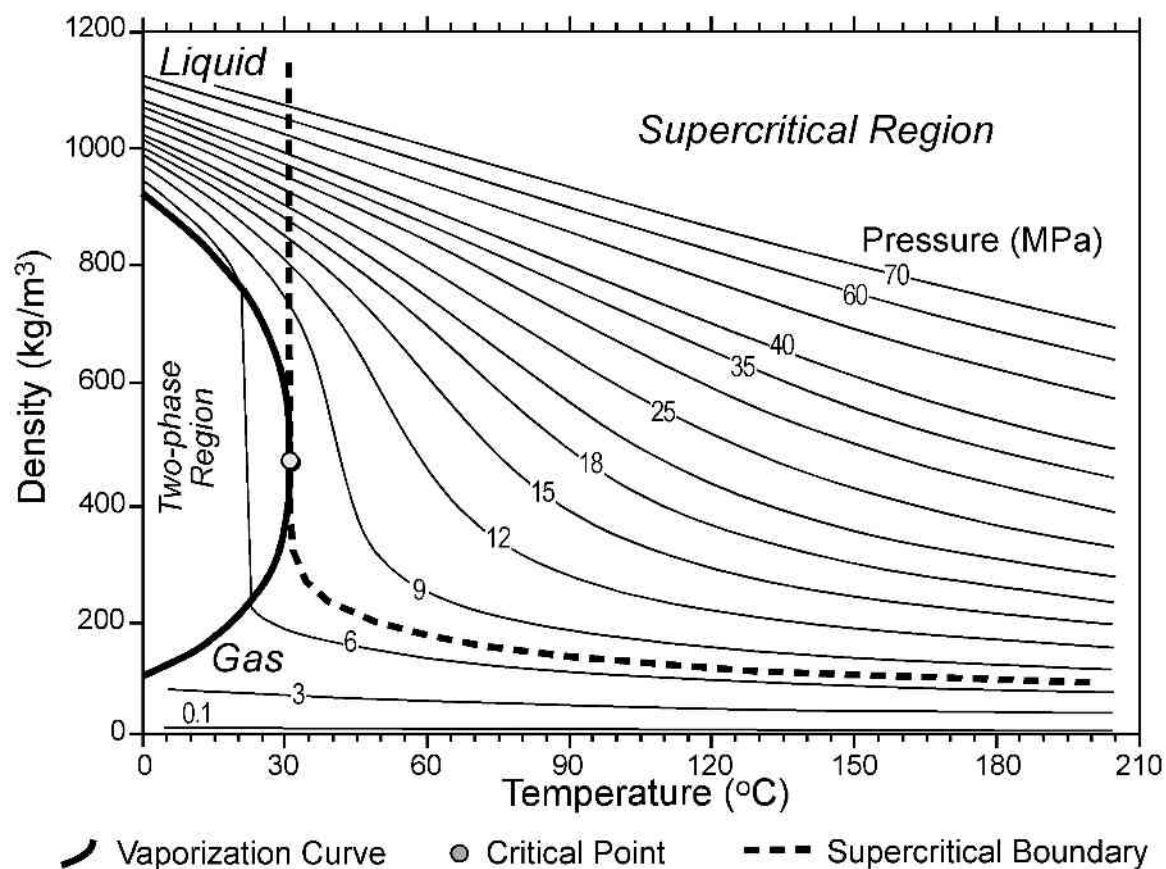
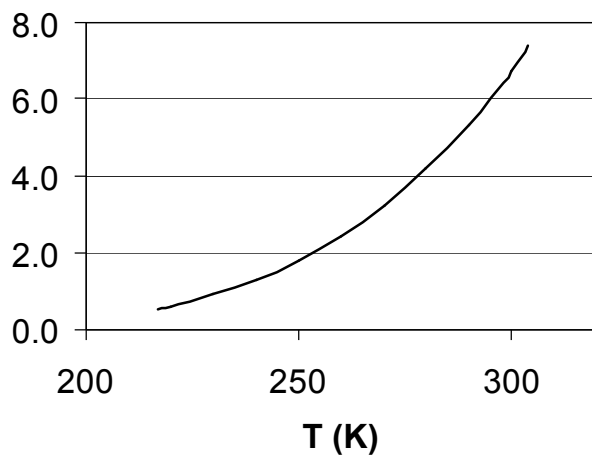
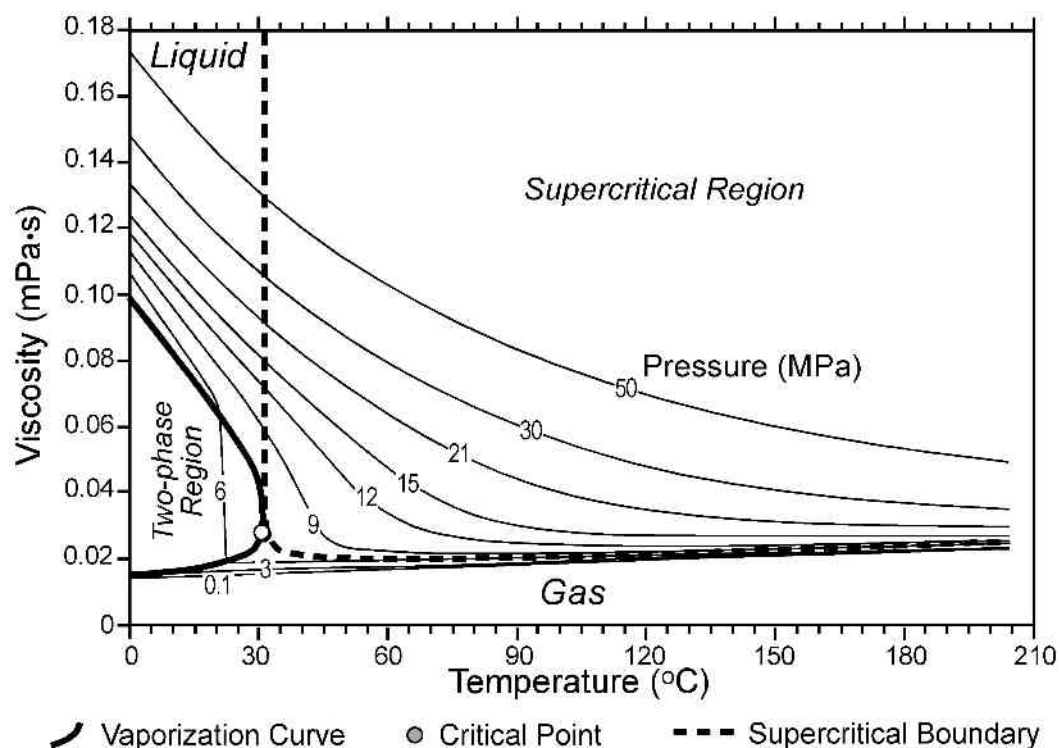


Figure AI.2. Variation of CO₂ density as a function of temperature and pressure (Bachu, 2003).**Vapour pressure (MPa)****Figure AI.3.** Vapour pressure of CO₂ as a function of temperature (Span and Wagner, 1996).**Figure AI.4.** Variation of CO₂ viscosity as a function of temperature and pressure (Bachu, 2003).

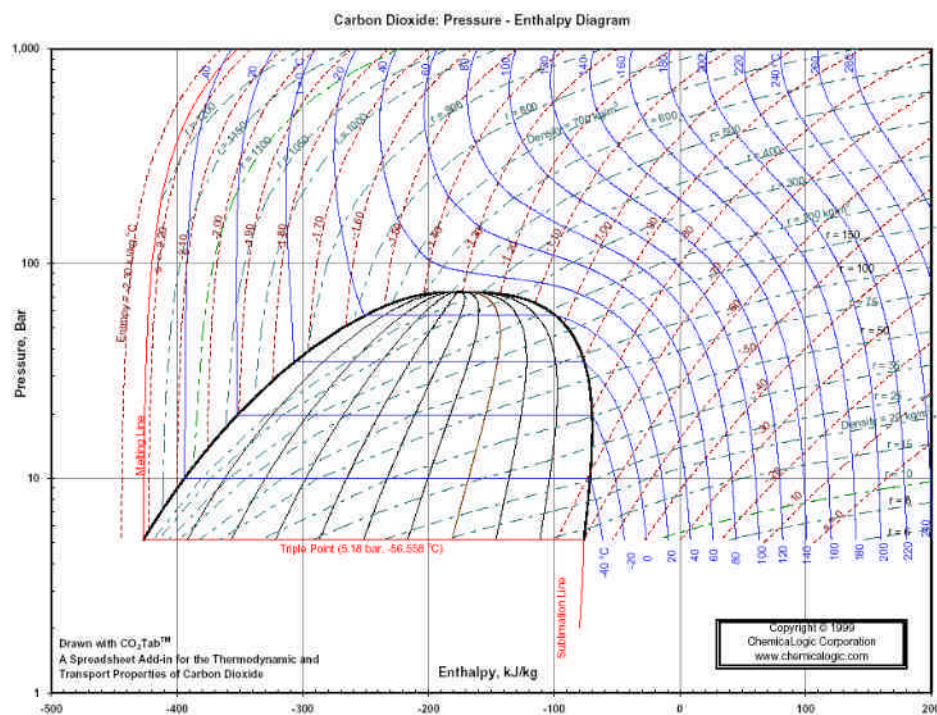


Figure AI.5. Pressure-Enthalpy chart for CO₂.

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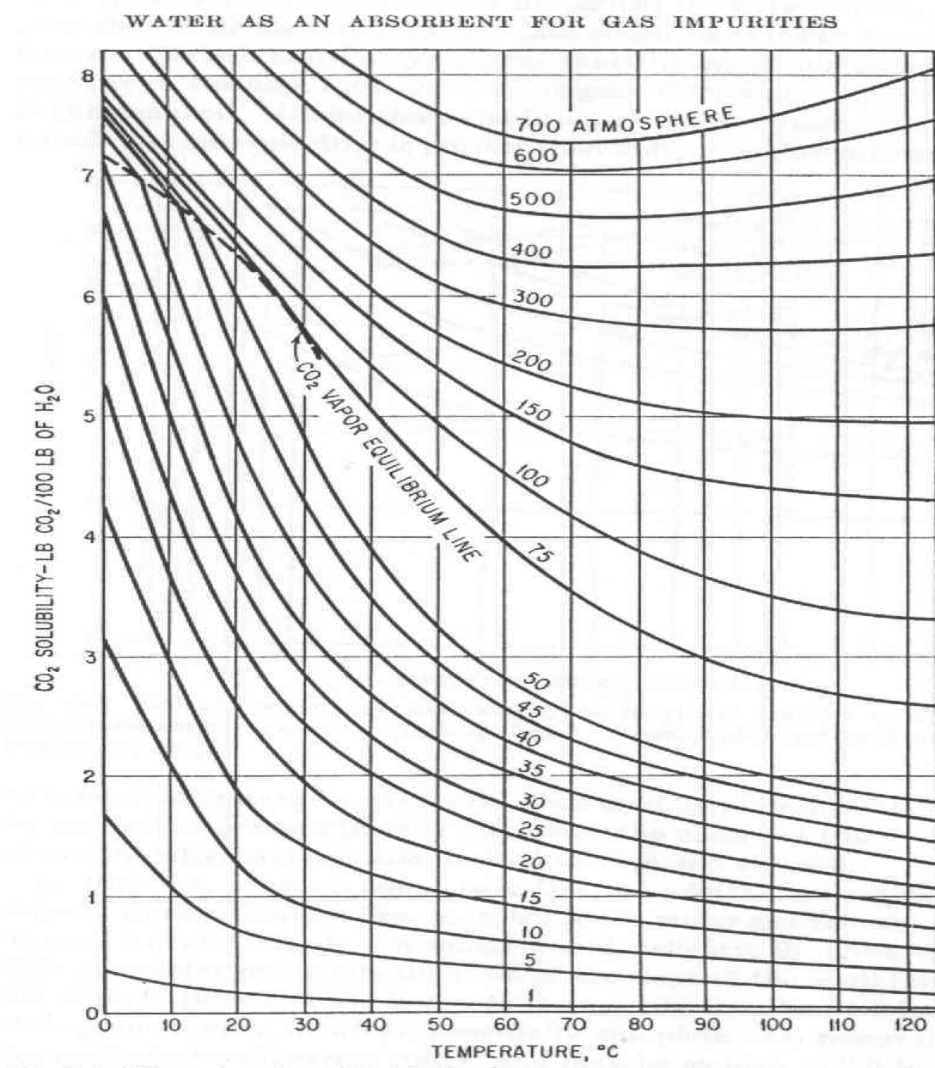


Figure AI.6. Solubility of CO₂ in water (Kohl and Nielsen, 1997).

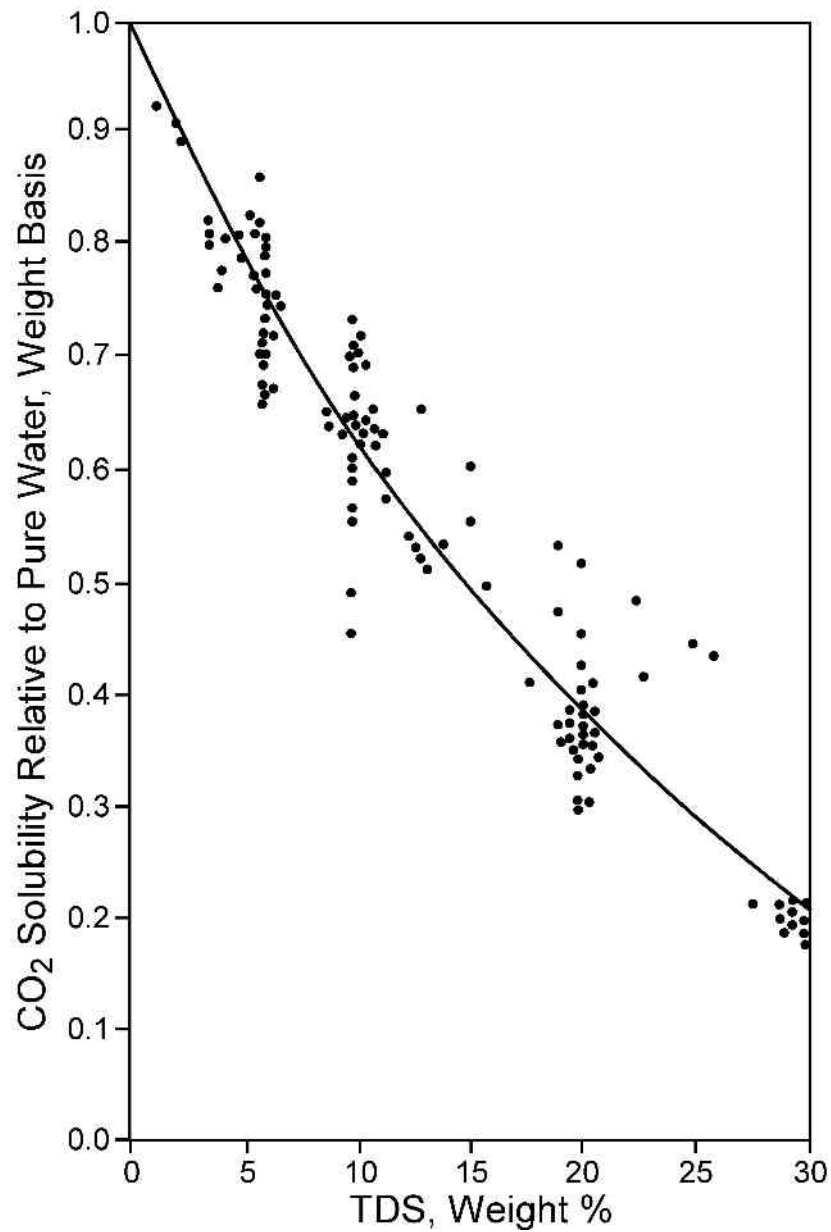


Figure AI.7. Solubility of CO₂ in brine relative to that in pure water, showing experimental points reported by Enick and Klara, 1990 and correlation developed by those authors. (TDS stands for total dissolved solids).

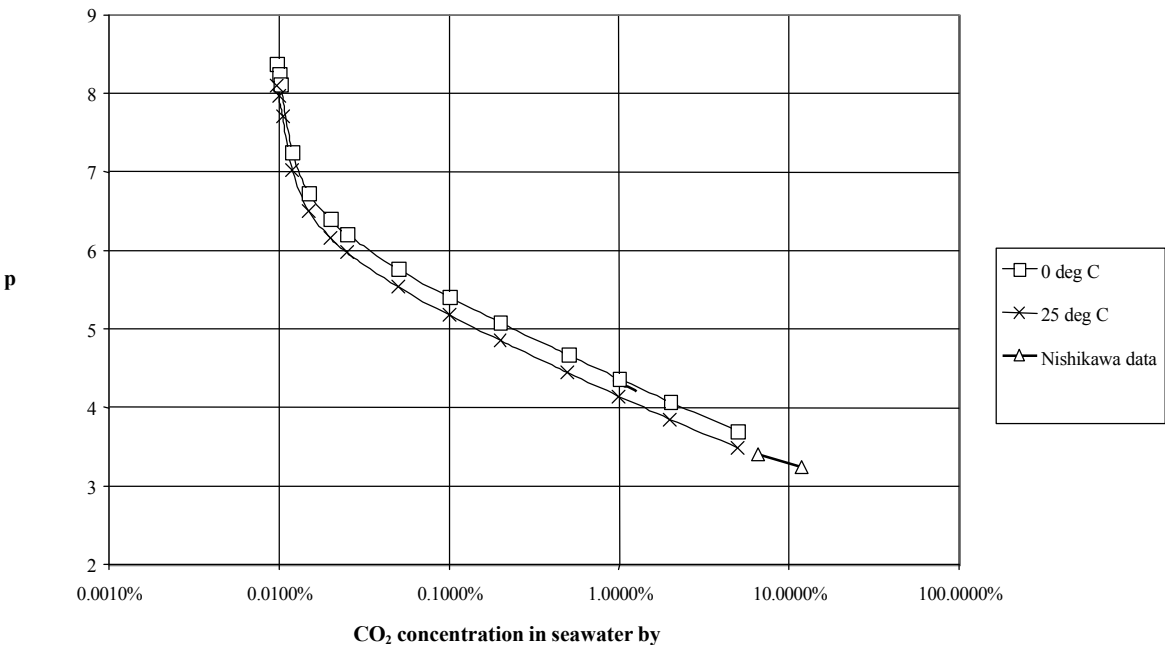


Figure AI.8. Dependence of pH on CO₂ concentration in sea water.

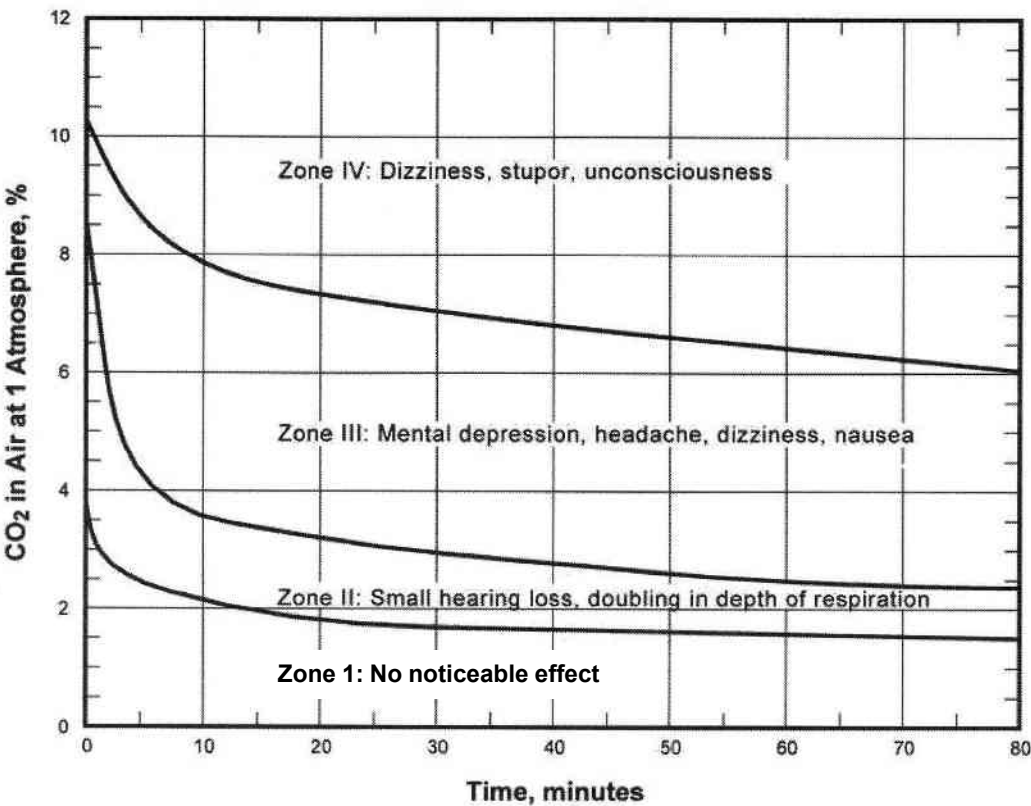


Figure AI.9. Effects of CO₂ exposure on humans (Fleming *et al.*, 1992).