CARBON DIOXIDE

1. Introduction

Carbon dioxide [124-38-9], CO_2, is a colorless gas with a faintly pungent odor and acid taste first recognized in the sixteenth century as a distinct gas through its presence as a by-product of both charcoal combustion and fermentation. Today carbon dioxide is a by-product of many commercial processes: synthetic ammonia production, hydrogen production, substitute natural gas production, fermentation, limestone calcination, certain chemical syntheses involving carbon monoxide (qv), and reaction of sulfuric acid with dolomite. Generally present as one of a mixture of gases, carbon dioxide is separated, recovered, and prepared for commercial use as a solid (dry ice), liquid, or gas.

Carbon dioxide is also found in the products of combustion of all carbonaceous fuels, in naturally occurring gases, as a product of animal metabolism, and in small quantities, about 0.03 vol %, in the atmosphere. Its many applications include beverage carbonation, chemical manufacture, firefighting, food freezing, foundry-mold preparation, greenhouses, mining operations, oil well secondary recovery, rubber tumbling, therapeutical work, welding, and extraction processes. Although it is present in the atmosphere and the metabolic processes of animals and plants, carbon dioxide cannot be recovered economically from these sources.

2. Physical Properties

Some values of physical properties of CO_2 appear in Table 1. An excellent pressure–enthalpy diagram (a large Mollier diagram) over 260 to 773 K and 70–20,000 kPa (10–2,900 psi) is available (1). The thermodynamic properties of saturated carbon dioxide vapor and liquid from 178 to the critical point, 304 K, have been tabulated (2). Also given are data for superheated carbon

Table 1. **Properties of Carbon Dioxide**

Property	Value
sublimation point at 101.3 kPa[a], °C	−78.5
triple point at 518 kPa[b] °C	−56.5
critical temperature, °C	31.1
critical pressure, kPa[b]	7383
critical density, g/L	467
latent heat of vaporization, J/g[c]	
at the triple point	353.4
at 0°C	231.3
gas density at 273 K and 101.3 kPa[a], g/L	1.976
liquid density	
at 273 K, g/L	928
at 298 K and 101.3 kPa[a] CO_2, vol/vol	0.712
viscosity at 298 K and 101.3 kPa[a], mPa · s(=cP)	0.015
heat of formation at 298 K, kJ/mol[d]	393.7

[a] 101.3 kPa = 1 atm.
[b] To convert kPa to psia, multiply by 0.145.
[c] To convert J/g to Btu/lb, multiply by 0.4302.
[d] To convert kJ/mol to Btu/mol, multiply by 0.9487.

dioxide vapor from 228 to 923 K at pressures from 7 to 7,000 kPa (1–1,000 psi). A graphical presentation of heat of formation, free energy of formation, heat of vaporization, surface tension, vapor pressure, liquid and vapor heat capacities, densities, viscosities, and thermal conductivities has been provided (3). Compressibility factors of carbon dioxide from 268 to 473 K and 1,400–69,000 kPa (203–10,000 psi) are available (4).

Available data on the thermodynamic and transport properties of carbon dioxide have been reviewed and tables compiled giving specific volume, enthalpy, and entropy values for carbon dioxide at temperatures from 255 K to 1088 K and at pressures from atmospheric to 27,600 kPa (4,000 psia). Diagrams of compressibility factor, specific heat at constant pressure, specific heat at constant volume, specific heat ratio, velocity of sound in carbon dioxide, viscosity, and thermal conductivity have also been prepared (5).

Equations for viscosity at different temperatures, pressures, and thermal conductivity have also been provided (5). The vapor pressure function for carbon dioxide in terms of reduced temperatures and pressure is as follows:

$$\log P_R = 4.2397 - \frac{4.4229}{T_R} - 5.3795 \log T_R + 0.1832 \frac{P_R}{T_R^2}$$

where P_R equals reduced pressure, which equals P/P_c (P_c, critical pressure 7.38 MPa or 72.85 atm), and T_R equals reduced temperature, which equals T/T_c (T_c, critical temperature, 304.2 K) (6). This equation gives accurate vapor pressure values from the triple point to the critical point. A table of reduced density values for carbon dioxide covering the range of reduced pressures from 0.3 to 500 kPa (0.044–72.5 psi) and reduced temperatures from 0.712 to 20 K is also supplied (6). Enthalpy values for carbon dioxide in the critical region, and with

Table 2. **Vapor Pressure of Solid Carbon Dioxide**[a]

Temperature,°C	Pressure, Pa	Temperature,°C	Pressure, Pa
−188°C	1.333×10^{-4}	−148°C	1.333×10^{1}
−182°C	1.333×10^{-3}	−136°C	1.333×10^{2}
−175°C	1.333×10^{-2}	−120°C	1.333×10^{3}
−167°C	1.333×10^{-1}	−100°C	1.333×10^{4}
−159°C	1.333	−65°C	1.333×10^{5}

[a] To convert Pa to mm Hg, divide by 1.333×10^{2}.

temperatures from 423 to 923 K and pressures from 0 to 20 MPa (0–200 atm), have been computed (7,8).

Diagrams of isobaric heat capacity (C_p) and thermal conductivity for carbon dioxide covering pressures from 0 to 13,800 kPa (0–2,000 psi) and 311 to 1088 K have been prepared. Viscosities at pressures of 100–10,000 kPa (1–100 atm) and temperatures from 311 to 1088 K have been plotted (9).

Vapor pressure data for solid carbon dioxide are given in Table 2 (10). The sublimation temperature of solid carbon dioxide, 194.5 K at 101 kPa (1 atm), was selected as one of the secondary fixed points for the International Temperature Scale of 1948.

The solubility of carbon dioxide in water is given in Figure 1 (11). Over the temperature range 273–393 K, the solubilities at pressures below 20 MPa (200 atm) decrease with increasing temperature. From 30 to 70 MPa (300–700 atm) a solubility minimum is observed between 343 and 353 K, with solubilities increasing as temperature increases to 393 K. Information on the solubility of carbon dioxide in pure water and synthetic seawater over the range 268 to 298 K and 101–4,500 kPa pressure (1–44 atm) is available (12,13).

The following tables of properties of carbon dioxide are available: enthalpy, entropy, and heat capacity at 0 and 5 MPa (0 and 50 atm, respectively) from 273 to 1273 K; pressure–volume product (PV), enthalpy, and isobaric heat capacity (C_p) from 373 to 1273 K at pressures from 5 to 140 MPa (50–1,400 atm) (14).

A more recent compilation includes tables giving temperature and PV as a function of entropies from 0.573 to 0.973 (zero entropy at 0°C, 101 kPa (1 atm) and pressures from 5 to 140 MPa (50–1400 atm) (15). Joule-Thomson coefficients, heat capacity differences (C_p–C_v), and isochoric heat capacities (C_v) are given for temperatures from 373 to 1273 K at pressures from 5 to 140 MPa.

3. Chemical Properties

Carbon dioxide, the final oxidation product of carbon, is not very reactive at ordinary temperatures. However, in water solution it forms carbonic acid [463-79-6], H_2CO_3, which forms salts and esters through the typical reactions of a weak acid. The first ionization constant is 3.5×10^{-7} at 291 K; the second is 4.4×10^{-11} at 298 K. The pH of saturated carbon dioxide solutions varies from 3.7 at 101 kPa (1 atm) to 3.2 at 2,370 kPa (23.4 atm). A solid hydrate [27592-78-5], $CO_2 \cdot 8H_2O$, separates from aqueous solutions of carbon dioxide that are chilled at elevated pressures.

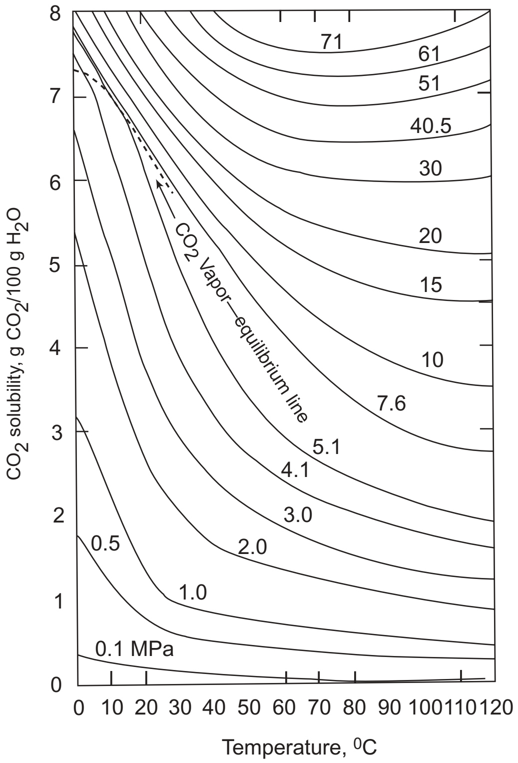

Fig. 1. Solubility of carbon dioxide in water at various pressures in MPa. To convert MPa to atm, multiply by 10.

Although carbon dioxide is very stable at ordinary temperatures, when it is heated above 1700°C the reaction forming CO proceeds to the right to an appreciable extent (15.8%) at 2500 K. This reaction also proceeds to the right to a limited extent in the presence of ultraviolet light and electrical discharges.

$$2\,CO_2 \rightleftarrows 2\,CO + O_2$$

Carbon dioxide may be reduced by several means. The most common of these is the reaction with hydrogen.

$$CO_2 + H_2 \longrightarrow CO + H_2O$$

This is the reverse of the water–gas shift reaction in the production of hydrogen and ammonia (qv). Carbon dioxide may also be reduced catalytically with various hydrocarbons and with carbon itself at elevated temperatures. The latter reaction occurs in almost all cases of combustion of carbonaceous fuels and is generally employed as a method of producing carbon monoxide.

$$CO_2 + C \longrightarrow 2\,CO$$

Carbon dioxide reacts with ammonia as the first stage of urea manufacture to form ammonium carbamate [1111-78-0].

$$CO_2 + 2\ NH_3 \longrightarrow NH_2COONH_4$$

The ammonium carbamate then loses a molecule of water to produce urea [57-13-6], $CO(NH_2)_2$. Commercially, this is probably the most important reaction of carbon dioxide and it is used worldwide in the production of urea (qv) for synthetic fertilizers and plastics (see AMINO RESINS; CARBAMIC ACID).

3.1. Radioactive Carbon. In addition to the common stable carbon isotope of mass 12, traces of a radioactive carbon isotope of mass 14 with a half-life estimated at 5568 years are present in the atmosphere and in carbon compounds derived from atmospheric carbon dioxide. Formation of radioactive ^{14}C is thought to be caused by cosmic irradiation of atmospheric nitrogen. The concentration of carbon-14 [14762-75-5] in atmospheric carbon dioxide is approximately constant throughout the world. The ratio of $^{14}CO_2$ [51-90-1] to $^{12}CO_2$ in the atmosphere, although constant for several hundred years, has decreased in the last sixty years by about 3% because of the influx of carbon dioxide in the atmosphere from the burning of fossil fuels, ie, coal, petroleum, and natural gas. Procedures have been developed for estimating the age of objects containing carbon or carbon compounds by determining the amount of radioactive ^{14}C present in the material as compared with that present in carbon-containing substances of current botanical origin (16). Ages of materials up to 45,000 years have been estimated with the radiocarbon dating technique.

Carbon dioxide containing known amounts of ^{14}C has been used as a tracer in studying botanical and biological problems involving carbon and carbon compounds and in organic chemistry to determine the course of various chemical reactions and rearrangements. It has also been used in testing gaseous diffusion theory with mixtures of CO_2 and $^{14}CO_2$ at elevated pressures (17).

3.2. Environmental Chemistry. Carbon dioxide plays a vital role in the earth's environment. It is a constituent in the atmosphere and, as such, is a necessary ingredient in the life cycle of animals and plants.

In animal metabolism, oxygen from the atmosphere reacts with sugars in the body to produce energy according to the overall formula:

$$C_6H_{12}O_6 + 6\ O_2 \longrightarrow 6\ CO_2 + 6\ H_2O + \text{energy}$$

The by-product CO_2 is released to the atmosphere. In plant metabolism, carbon dioxide from the air is taken into the leaves of the plant. Using energy from light, carbon dioxide reacts with water in the presence of enzymes to produce sugar. This reaction, photosynthesis, is the reverse of the above reaction.

The balance between animal and plant life cycles as affected by the solubility of carbon dioxide in the earth's water results in the carbon dioxide content in the atmosphere of about 0.03 vol %. However, carbon dioxide content of the atmosphere seems to be increasing as increased amounts of fossil fuels are burned. There is some evidence that the rate of release of carbon dioxide to the atmosphere may be greater than the earth's ability to assimilate it. Measurements from the U.S. Water Bureau show an increase of 1.36% in the CO_2 content of the atmosphere in a five-year period and predictions indicate that at present the content may have increased by 25% (see AIR POLLUTION).

The effects of such an increase, if it occurs, are not known. It could result in a warmer temperature at the earth's surface by allowing the short heat waves from the sun to pass through the atmosphere while blocking larger waves that reflect back from the earth. If the earth's average temperature were to increase by several degrees, portions of the polar ice caps could melt causing an increase in the level of the oceans, or air circulation patterns could change, altering rain patterns to make deserts of farmland or vice versa.

On the other hand, it has been demonstrated that the addition of CO_2 to greenhouses increases the growth rate of plants so that an increase in the partial pressure of CO_2 in the air could stimulate plant growth making possible shorter growing seasons and increased consumption of carbon dioxide from the air. CO_2 is also used in water-treatment applications. Because it is significantly safer than mineral acids, it can be used to reduce the alkalinity of treated water.

4. Manufacture

Sources of carbon dioxide for commercial carbon dioxide recovery plants are (*1*) synthetic ammonia and hydrogen plants in which methane or other hydrocarbons are converted to carbon dioxide and hydrogen ($CH_4 + 2\ H_2O \longrightarrow CO_2 + 4\ H_2$); (*2*) flue gases resulting from the combustion of carbonaceous fuels; (*3*) fermentation in which a sugar such as dextrose is converted to ethyl alcohol and carbon dioxide ($C_6H_{12}O_6 \longrightarrow 2\ C_2H_5OH + 2\ CO_2$); (*4*) lime-kiln operation in which carbonates are thermally decomposed ($CaCO_3 \longrightarrow CaO + CO_2$); (*5*) sodium phosphate manufacture ($3\ Na_2CO_3 + 2\ H_3PO_4 \longrightarrow 2\ Na_3PO_4 + 3\ CO_2 + 3\ H_2O$); and (*6*) natural carbon dioxide gas wells.

4.1. Ammonia and Hydrogen Plants. More carbon dioxide is generated and recovered from ammonia and hydrogen plants than from any other source. Both plants produce hydrogen and carbon dioxide from the reaction between hydrocarbons and steam. In the case of hydrogen plants, the hydrogen is recovered as a pure gas. For ammonia plants the hydrogen is produced in the presence of air, controlled to give the volume ratio between hydrogen and nitrogen required to synthesize ammonia. In order to produce either product it is necessary to remove the carbon dioxide (18). The annual synthetic ammonia production capacity in the United States was about 15.9×10^6 t in 2001 (see AMMONIA). For each ton of ammonia produced, more than a ton of carbon dioxide is generated. Hence the available carbon dioxide supply from this source is several times as large as the total commercial production of carbon dioxide. A substantial amount of the carbon dioxide recovered from ammonia plants is used for urea production.

4.2. Flue Gases. In a typical plant for producing gaseous carbon dioxide from coke, coal, fuel oil, or gas the fuel is burned under a standard water-tube boiler for the production of 1400–1800 kPa (200–260 psi) steam. At 613 K flue gases containing 10–18% carbon dioxide leave the boiler and pass through two packed towers where they are cooled and cleaned by water. The gases are then passed through a booster blower into the base of the absorption tower. The

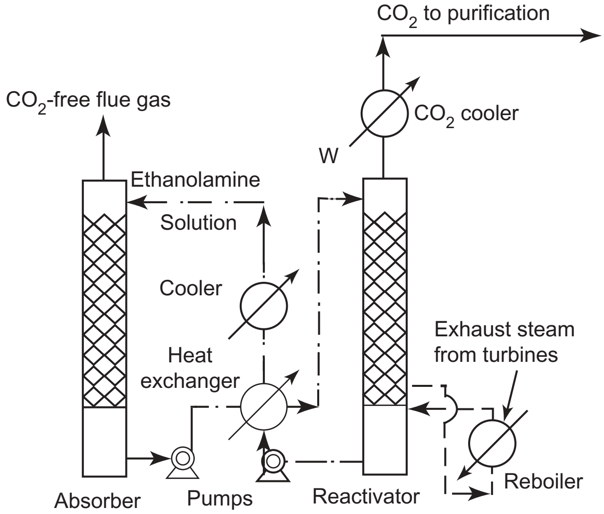

Fig. 2. Recovery of carbon dioxide using a Girbotol recovery unit.

recovery system shown in Figure 2 is the Girbotol amine process (19) although an alkaline carbonate system may also be used (Fig. 2). In the tower, carbon dioxide is absorbed selectively by a solution of ethanol amines passing countercurrent to the gas stream (see ALKANOLAMINES). The carbon dioxide-free flue gases pass out of the top of the tower into the atmosphere, the carbon dioxide-bearing solution passes out from the bottom of the tower, through pumps and heat exchangers, into the top of a reactivation tower. Here heat strips the carbon dioxide from the amine solution and the reactivated solution returns through the heat-exchanger equipment to the absorption tower. Carbon dioxide and steam pass through the top of the reactivation tower into a gas cooler in which the steam condenses and returns to the tower as reflux. The carbon dioxide at this point is available as a gas at a pressure of about 200 kPa (2 atm). If liquid or solid carbon dioxide is desired it may be further purified for odor removal before compression.

The steam balance in the plant shown in Figure 2 enables all pumps and blowers to be turbine-driven by high pressure steam from the boiler. The low pressure exhaust system is used in the reboiler of the recovery system and the condensate returns to the boiler. Although there is generally some excess power capacity in the high pressure steam for driving other equipment, eg, compressors in the carbon dioxide liquefaction plant, all the steam produced by the boiler is condensed in the recovery system. This provides a well-balanced plant in which few external utilities are required and combustion conditions can be controlled to maintain efficient operation.

4.3. Fermentation Industry. Large quantities of carbon dioxide are present in gases given off in the fermentation of organic substances such as molasses, corn, wheat, and potatoes in the production of beer, distilled beverages, and industrial alcohol. These gases may contain impurities such as aldehydes, acids, higher alcohols, glycerol, furfural, glycols, and hydrogen sulfide. Two processes are in general use for removing these contaminants and preparing the carbon dioxide for use. In one process, this is accomplished by the use of activated-carbon adsorbers; the other process is a chemical purification process (see BEER; BEVERAGE SPIRITS, DISTILLED; ETHANOL; FERMENTATION). A very small percentage of commercial CO_2 is produced by this process.

The Backus process (20,21) uses active carbon. Carbon dioxide gases from the top of the fermentors are collected in a low pressure gas holder to even out the flow. Roots-Connersville-type blowers force the gases through Feld scrubbers where they are washed with water to remove the bulk of entrained material, alcohols, aldehydes, etc. The washed gases pass through active-carbon purifiers, which adsorb the balance of impurities, and then to the compressors. The adsorption process gives off heat, which is removed by water coils embedded in the carbon. Periodically, the carbon beds must be reactivated to remove accumulated impurities. This is accomplished by passing live steam through the carbon bed and water coils. After steaming, the carbon beds are dried by passing air through them; they are then ready for reuse. In general, two sets of active-carbon purifiers are used, one on-stream and the other being reactivated (see ADSORPTION, GAS SEPARATION).

The Reich process (22,23) uses chemical processes to remove impurities. Carbon dioxide from the fermentors is bubbled through a wash box, or catchall, which removes entrained liquids and mash. The gases pass through three packed scrubbing towers. In the first, dilute alcohol solution is passed countercurrent to the gases for de-alcoholizing the gases. The other two towers use water for further removal of alcohol. The alcohol is returned to the alcohol plant for distillation or use in the fermentors. The washed gas passes through a gas holder and blower, which boosts it through the balance of the purification plant. The first stage in this section is a potassium dichromate washer for the oxidation of organic impurities and the removal of hydrogen sulfide. Next, the gas is passed countercurrent to concentrated sulfuric acid for dehydration and dichromate removal. Entrained sulfuric acid is removed by a dry solid ash tower and the residual oxidized material is removed by countercurrent scrubbing with a light oil. The gas is then ready for compression. In some installations the first stage of compression is inserted before the dichromate washer and the purification operations are carried out at 600–800 kPa (87–116 psi).

4.4. Lime-Kiln Operation. Gases containing up to 40% carbon dioxide from the lime kiln pass through a cyclone separator, which removes the bulk of entrained dust. The gas is then blown through the two scrubbers, which remove the finer dust, cooled, and passes into an absorption tower. Here carbon dioxide may be recovered by the sodium carbonate or Girbotol process.

4.5. Sodium Phosphate Manufacturing. Some pure carbon dioxide gas is available as a by-product in plants manufacturing sodium phosphate from sodium carbonate [497-19-8] and phosphoric acid [7664-38-2]. Two carbon dioxide plants were installed prior to 1962 to utilize this by-product gas.

4.6. Natural Gas Wells. Natural gas, containing high percentages of carbon dioxide, has been found in a number of locations including New Mexico, Colorado, Utah, and Washington. Several small plants have been in operation for a number of years producing commercial solid and liquid carbon dioxide from these sources (see GAS, NATURAL). Several large CO_2 plants are in operation using well gas as a source of CO_2.

There are a number of methods of recovering carbon dioxide from industrial or natural gases. The potassium carbonate and ethanolamine processes are most common. In all these processes the carbon dioxide-bearing gases are passed countercurrent to a solution that removes the carbon dioxide by absorption and retains it until it is desorbed in separate equipment. All of these processes are in commercial use and the most suitable choice for a given application depends on individual conditions. Water could be used as the absorbing medium, but this is uncommon because of the relatively low solubility of carbon dioxide in water at normally encountered pressures. The higher solubility in the alkali carbonate and ethanolamine solutions is the result of a chemical combination of the carbon dioxide with the absorbing medium.

Sodium Carbonate Process. This process of recovering pure carbon dioxide from gas containing other diluents, such as nitrogen and carbon monoxide, is based on the reversibility of the following reaction:

$$Na_2CO_3 + H_2O + CO_2 \rightleftharpoons 2\ NaHCO_3$$

This reaction proceeds to the right at low temperatures and takes place in the absorber where the carbon dioxide-bearing gases are passed countercurrent to the carbonate solution. The amount of carbon dioxide absorbed in the solution varies with temperature, pressure, partial pressure of carbon dioxide in the gas, and solution strength. Operating data on this reaction have been obtained by numerous investigators (24). The reaction proceeds to the left when heat is applied. The reaction takes place in a lye boiler. A heat exchanger preheats the strong lye approaching the boiler and cools the weak lye returning to the absorber. A lye cooler further cools weak lye to permit the reaction to proceed further to the right in the absorber. The carbon dioxide gas and water vapor released from the solution in the boiler pass through a steam condenser where the water condenses and returns to the system. The cool carbon dioxide proceeds to the gas holder and compressors. The absorber is generally a carbon–steel tower filled with coke, Raschig rings, or steel turnings. The weak solution is distributed evenly over the top of the bed and contacts the gas on the way down. Some plants operate with the tower full of sodium carbonate solution and allow the gas to bubble up through the liquid. Although this may afford a better gas-to-liquid contact, an appreciable amount of power is required to force the gas through the tower.

The lye boiler is usually steam heated but may be direct-fired. Separation efficiency may be increased by adding a tower section with bubble-cap trays. To permit the bicarbonate content of the solution to build up, many plants are designed to recirculate the lye over the absorber tower with only 20–25% of the solution flowing over this tower passing through the boiler. Several absorbers may also be used in series to increase absorption efficiencies.

The sodium carbonate process is used in a number of dry-ice plants in the United States, although its operating efficiency is generally not as high as that of processes using other solutions. These plants obtain the carbon dioxide from flue gases as well as lime-kiln gases.

Potassium Carbonate Process. The potassium carbonate process is similar to the sodium carbonate process. However, as potassium bicarbonate

[298-14-6] is more soluble than the corresponding sodium salt, this process permits a more efficient absorption than the other. The equipment layout is the same and the operation technique is similar.

There are several variations of the potassium carbonate process. The hot potassium carbonate process does not involve cooling of the solution flowing from the boiler to the absorber (25). Absorption takes place at essentially the same temperature as solution regeneration. In its simplest form this process uses an absorption column, a regeneration column, a heated boiler or reboiler, and a circulating pump. This arrangement minimizes energy requirements and capital costs but the higher absorbing temperature does not allow the carbon dioxide removal to be as complete as with lower temperatures. One modification that improves removal is the use of a split stream flow to the absorber. Part of the solution is cooled and used at the top of the absorber. The balance of the solution, uncooled, is added part way down the absorber. The combined solution from the absorber then flows to the regenerator. In another modification two-stage absorption and regeneration is used. The carbonate solution from the absorber flows to the regeneration column. Part of the solution is withdrawn from the column at some intermediate point and pumped, uncooled, to an intermediate point in the absorber. The remaining solution undergoes a more complete regeneration and is cooled and pumped to the top of the absorber.

Three commercial processes that use these various hot carbonate flow arrangements are the promoted Benfield process, the Catacarb process, and the Giammarco-Vetrocoke process (26–29). Each uses an additive described as a promoter, activator, or catalyst, which increases the rates of absorption and desorption, improves removal efficiency, and reduces the energy requirement. The processes also use corrosion inhibitors, which allow use of carbon–steel equipment. The Benfield and Catacarb processes do not specify additives. Vetrocoke uses boric acid, glycine, or arsenic trioxide, which is the most effective.

These processes have been used in many plants to remove carbon dioxide from ammonia synthesis gas or natural gas. They are most effective if the gas stream being treated is at elevated pressures (1700 kPa (17 atm) or higher). This increases the carbon dioxide partial pressure so that the hot potassium carbonate solution absorbs a substantial amount of carbon dioxide. The stripping tower or regenerator operates at or near atmospheric pressure.

Ethanolamines may also be added to carbonate solutions to improve their performance (30). Vapor pressure-equilibrium data for the K_2CO_3–$KHCO_3$–CO_2–H_2 system are given (31).

Girbotol Amine Process. This process developed by the Girdler Corporation is similar in operation to the alkali carbonate processes. However, it uses aqueous solutions of an ethanolamine, ie, either mono-, di-, or triethanolamine. The operation of the Girbotol process depends on the reversible nature of the reaction of CO_2 with monoethanolamine [141-43-5] to form monoethanolamine carbonate [21829-52-7].

$$2\,HOCH_2CH_2NH_2 + H_2O + CO_2 \rightleftharpoons (HOCH_2CH_2NH_3)_2CO_3^{2-}$$

The reaction proceeds in general to the right at low temperatures (300–338 K) and absorbs the carbon dioxide from the gas in the absorber as shown in

Figure 2. The amine solution, rich in carbon dioxide, passes from the bottom of the tower through a heat exchanger, where it is preheated by hot, lean solution returning from the reactivator. On passing into the reactivator the solution passes countercurrent to a stream of carbon dioxide and steam, which strips the carbon dioxide out of the solution. By the time the solution reaches the bottom of the tower, where heat is supplied by a steam-heated or direct-fired reboiler, it has been reactivated. This hot solution (373–423 K) passes out of the tower, through the heat exchanger and cooler, and returns to the absorber tower.

The amine process or one of the various carbonate processes is used in the majority of CO_2-removal applications. At low pressures the amine process has clear advantages in removal efficiency and installed cost. At higher pressures the increased carbon dioxide partial pressures favor a higher CO_2 content in the absorbing solution, whether carbonate or amine, which permits a lower steam usage per unit of carbon dioxide stripped from the absorbent. Until recently, amine systems have not been able to take full advantage of the benefits of higher absorber pressure because of corrosion problems. The CO_2-rich amine solution is inherently more corrosive than potassium carbonate solutions so that the stronger the amine solution and the greater the carbon dioxide content the worse the corrosion potential. To hold corrosion to a minimum, amine solution designs have been limited to a maximum solution strength of 20 wt% with a maximum CO_2 content of about 0.0374 m^3/L (5 ft^3/gal) of solution. Even then, some plants experience severe corrosion problems requiring replacement of some carbon-steel equipment with stainless steel. Carbonate solutions pick up more CO_2 per unit of solution than the amines, resulting in a lower circulation rate and a correspondingly lower heat regeneration requirement.

Overall comparison between amine and carbonate at elevated pressures shows that the amine usually removes carbon dioxide to a lower concentration at a lower capital cost but requires more maintenance and heat. The impact of the higher heat requirement depends on the individual situation. In many applications, heat used for regeneration is from low temperature process gas, suitable only for boiler feed water heating or low pressure steam generation, and it may not be useful in the overall plant heat balance.

Union Carbide has developed Amine Guard, which essentially eliminates corrosion in amine systems (32–35). It permits the use of substantially higher amine concentrations and greater carbon dioxide pick-up rates without corrosive attack. This results in an energy requirement comparable to that of the carbonate process and allows the use of smaller equipment for a specific CO_2-removal application thereby reducing the capital cost.

Solubility of carbon dioxide in ethanolamines is affected by temperature, amine solution strength, and carbon dioxide partial pressure. Information on the performance of amines is available in the literature and from amine manufacturers. Values for the solubility of carbon dioxide and hydrogen sulfide mixtures in monoethanolamine and for the solubility of carbon dioxide in diethanolamine are given (36,37). Solubility of carbon dioxide in monoethanolamine is provided (38). The effects of catalysts have been studied to improve the activity of amines and provide absorption data for carbon dioxide in both mono- and diethanolamine solutions with and without sodium arsenite as a catalyst (39). Absorption kinetics over a range of contact times for carbon dioxide in monoethanolamine have also been investigated (40).

Sulfinol Process. The Sulfinol process was developed during the 1960s to remove carbon dioxide and other acidic gas from gas streams at high partial pressures. It uses a circulating solution with a flow pattern similar to those in the amine and carbonate processes. Regeneration occurs at low pressure, and heat is exchanged between the regenerated solution and the solution from the absorber. The Sulfinol solution is a mixture of sulfolane [126-33-0] (tetrahydrothiophene 1,1-dioxide), an alkanolamine, and water.

The process is capable of achieving higher solubilities of CO_2 in the solution without the corrosion problems encountered with amine systems before the advent of Amine Guard. The Sulfinol process is used in over 50 plants worldwide; nevertheless, it is used less often than the amine or carbonate processes.

Rectisol Process. This is one of several processes that use a solvent for removing carbon dioxide from gas streams. In the Rectisol process, the solvent is usually methanol and the operating temperature of the absorber is about 273 K. The process uses an absorption column and stripping column with intermediate pumps and heat exchangers. It is necessary to cool the process gas to the absorbing temperature. Split flow of the solvent stream to the absorber is used, with partially stripped solvent from the midsection of the stripper being used at the top of the absorber. Stripping is accomplished by pressure release, heat, and contact with an inert stripping gas, which is blown through the column.

The processes using physical absorption require a solvent circulation proportional to the quantity of process gas, inversely proportional to the pressure, and nearly independent of the carbon dioxide concentration. Therefore, high pressures could favor the use of these processes. The Recitsol process requires a refrigeration system and more equipment than the other processes. This process is primarily used in coal gasification for simultaneous removal of H_2S, COS, and CO_2.

Purisol Process. This is a solvent process which uses *N*-methyl-2-pyrrolidinone [872-50-4] as the solvent and benefits from high pressure, 7000 kPa (69 atm) or higher. All commercial installations are at pressures above 4000 kPa (39 atm).

Fluor Process. This is a solvent process that uses propylene carbonate [108-32-7]. Propylene carbonate has a high solubility for CO_2, a low solubility for other light gases, is chemically stable, and noncorrosive to carbon steel. Physical solvent plants represent a higher capital cost than the carbonate or amine process plants but may result in reducing operating costs where high pressures are involved. Seven plants using the Fluor process for removal of acidic gases were in existence by 1970; five natural gas plants, one hydrogen, and one ammonia plant.

Pressure Swing Adsorption. A number of processes based on Pressure Swing Adsorption (PSA) technology have been used in the production of carbon dioxide. In one version of the PSA process, CO_2 is separated from CH_4 using a multibed adsorption process (41). In this process both CH_4 and CO_2 are produced. The process requires the use of five adsorber vessels. Processes of this type can be used for producing CO_2 from natural gas wells, landfill gas, or from oil wells undergoing CO_2 flooding for enhanced oil recovery (see ADSORPTION, GAS SEPARATION).

4.7. Methods of Purification. Although carbon dioxide produced and recovered by the methods outlined above has a high purity, it may contain traces of hydrogen sulfide and sulfur dioxide, which cause a slight odor or taste. The fermentation gas recovery processes include a purification stage, but carbon dioxide recovered by other methods must be further purified before it is acceptable for beverage, dry ice, or other uses. The most commonly used purification methods are treatments with potassium permanganate, potassium dichromate, or active carbon.

Potassium Permanganate. Probably the most widely used process for removing traces of hydrogen sulfide from carbon dioxide is to scrub the gas with an aqueous solution saturated with potassium permanganate [7722-64-7]. Sodium carbonate is added to the solution as buffer. The reaction is as follows:

$$3\,H_2S + 2\,KMnO_4 + 2\,CO_2 \longrightarrow 3\,S + 2\,MnO_2 + 2\,KHCO_3 + 2\,H_2O$$

The precipitated manganese dioxide and sulfur are discarded. The solution is used until it becomes spent or so low in potassium permanganate that it is no longer effective and is discarded and replaced. It is customary to place two scrubbers in series, with the liquid flow countercurrent to the gas flow, to more efficiently use the permanganate solution. When the solution in the first scrubber is spent, with respect to the gas, the positions of the scrubbers are reversed and the spent scrubber is recharged with fresh solution.

Two types of scrubbers are used. The simpler consists of a vessel half or two-thirds full of solution. The gas feeds into the bottom of the vessel and bubbles up through the solution. The other scrubber is a small packed tower through which the gas stream is passed countercurrent to a recirculating shower of potassium permanganate and soda ash solution. The latter requires a circulating pump and a solution mix chamber, but has the advantage of reducing the pressure drop through the equipment to a minimum. The solution is used until spent and then discarded. Two scrubbers of this type may also be used to improve efficiency.

Potassium Dichromate. This method is similar in application to the potassium permanganate method.

$$K_2Cr_2O_7 + 3\,H_2S + H_2O + 2\,CO_2 \longrightarrow 3\,S + 2\,Cr(OH)_3 + 2\,KHCO_3$$

The precipitated chromic hydroxide and sulfur are discarded. This process is used to purify carbon dioxide from fermentation in the Reich process and as a final cleanup after the alkali carbonate or ethanolamine recovery processes (22,23).

Active Carbon. The process of adsorbing impurities from carbon dioxide on active carbon or charcoal has been described in connection with the Backus process of purifying carbon dioxide from fermentation processes. Space velocity and reactivation cycle vary with each application. The use of active carbon need not be limited to the fermentation industries but, where hydrogen sulfide is the only impurity to be removed, the latter two processes are usually employed (see ACTIVATED CARBON).

4.8. Methods of Liquefaction and Solidification. Carbon dioxide may be liquefied at any temperature between its triple point (216.6 K) and its critical point (304 K) by compressing it to the corresponding liquefaction pressure, and removing the heat of condensation. There are two liquefaction processes. In the first, the carbon dioxide is liquefied near the critical temperature; water is used for cooling. This process requires compression of the carbon dioxide gas to pressures of about 7600 kPa (75 atm). The gas from the final compression stage is cooled to about 305 K and then filtered to remove water and entrained lubricating oil. The filtered carbon dioxide gas is then liquefied in a water-cooled condenser.

The second liquefaction process is carried out at temperatures from 261 to 296 K, with liquefaction pressures of about 1600–2400 kPa (16–24 atm). The compressed gas is precooled to 277 to 300 K, water and entrained oil are separated, and the gas is then dehydrated in an activated alumina, bauxite, or silica gel drier, and flows to a refrigerant-cooled condenser (see DRYING AGENTS). The liquid is then distilled in a stripper column to remove noncombustible impurities. Liquid carbon dioxide is stored and transported at ambient temperature in cylinders containing up to 22.7 kg. Larger quantities are stored in refrigerated insulated tanks maintained at 255 K and 2070 kPa (20 atm), and transported in insulated tank trucks and tank rail cars.

Solidification. Liquid carbon dioxide from a cylinder may be converted to "snow" by allowing the liquid to expand to atmospheric pressure. This simple process is used only where very small amounts of solid carbon dioxide are required because less than one-half of the liquid is recovered as solid.

Solid carbon dioxide is produced in blocks by hydraulic presses. Standard presses produce blocks 25 × 25 × 25 cm, 50 × 25 × 25 cm, or 50 × 50 × 25 cm. A 25-cm cube of dry ice weighs 23 kg, allowing for about 10% sublimation loss during storage and shipment (some 27-kg blocks are also produced). Dry ice is about 1.7 times as dense as water ice, whereas its net refrigerating effect on a weight basis is twice that of water ice. Automation and improved operating cycles have increased dry-ice press capacities so that one 50 × 50 × 30 cm press can produce more than thirty metric tons of dry-ice blocks per day (42).

Liquid carbon dioxide from a supply tank at 700 kPa (7 atm) and 227 K is fed to the press chamber through an automatic feed valve. The pressure in the press is maintained slightly above the triple point (480–550 kPa or 70–80 psi). The quantity fed to the press may be controlled by a timer, or a device that measures the level of liquid in the press chamber. The pressure is reduced and the evolved CO_2 vapor is returned to a recycle system. When the pressure falls below the triple point (518 kPa or 75 psi), the liquid CO_2 solidifies to form carbon dioxide snow. Heat-exchange units are used to cool the liquid CO_2 with cold vapors from the press. About 50% of the liquid fed to the press remains as snow when the pressure has dropped close to atmospheric. The hydraulic rams then press the snow to a solid block of dry ice. The block moves along a conveyor and is cut by band saws into four blocks, which are subsequently carried through automatic weighing and packaging machines.

Carbon dioxide is ordinarily dehydrated during the liquefaction cycle to prevent freeze-ups in the condenser and flow valves in the liquid lines. In some cases brittle or crumbly blocks of dry ice have been formed. This difficulty has been overcome either by varying the residual moisture content of the liquid carbon dioxide, or by injecting minute quantities of colorless mineral oil or diethylene glycol into the liquid carbon dioxide entering the press. If the dry ice is to be used for edible purposes, the additive must meet FDA specifications.

Although liquid carbon dioxide may be stored without loss in tanks and cylinders, dry ice undergoes continuous loss in storage because of sublimation. This loss can be minimized by keeping the dry ice in insulated boxes or bins. Special insulated rail cars and trucks are used for hauling dry-ice blocks. Most plants produce the material at the time it is sold to avoid storage losses and rehandling costs.

5. Economic Aspects

In 1998, 35×10^6t of gaseous carbon dioxide was consumed. Liquid carbon dioxide consumption was 6.6×10^6t. Gaseous carbon dioxide is used for enhanced oil recovery and, thus, it exceeded liquid use.

In the United States, 27.9×10^6t of gaseous carbon dioxide was used in the oil fields and 5.8×10^6t was used in urea production. Western Europe consumed 3.5×10^6t. Growth in the U.S. and Western Europe is expected at the rate of 3–4% through 2003. In Japan, a 2% growth rate is expected (43).

Much more carbon dioxide is generated daily than is recovered (44). The decision whether or not to recover by-product carbon dioxide often depends on the distance and cost of transportation between the carbon dioxide producer and consumer. For example, it has become profitable to recover more and more carbon dioxide from CO_2-rich natural gas wells in Texas as the use of carbon dioxide in secondary oil recovery has increased. The production levels for enhanced oil recovery are generally not reported because of the captive nature of the application.

6. Health and Safety Factors

Although carbon dioxide is a constituent of exhaled air, high concentrations are hazardous. Up to 0.5 vol% carbon dioxide in air is not considered harmful, but carbon dioxide concentrates in low spots because it is one and one-half times as heavy as air. Five vol% carbon dioxide in air causes a threefold increase in breathing rate and prolonged exposure to concentrations higher than 5% may cause unconsciousness and death. Ventilation sufficient to prevent accumulation of dangerous percentages of carbon dioxide must be provided where carbon dioxide gas has been released or dry ice has been used for cooling.

The ACGIH TLV (TWA) is 5000 ppm (9000 mg/m^3) with a STEL of 30,000 ppm (54,000 mg/m^3). However, the documentation of the threshold limit values and biological exposure indices stated that “medically fit” persons in special circumstances may tolerate daily exposure to 1.5% (15,000 ppm). The definition of "medically fit" excludes all persons over the age of 65 and persons with current endocrine disorders. The National Institute for Occupational Safety and Health has recommended a TWA of 5000 ppm as a limit, with short-term excursions up to 3% (30,000 ppm) for 10 min (45).

7. Uses

A large portion of the carbon dioxide recovered is used at or near the location where it is generated as an ingredient in a further processing step. In this case, the gaseous form is most often used. Low temperature liquid and solid carbon dioxide are used for refrigeration. Where the producer and the consumer are distant, carbon dioxide may be liquified to reduce transportation cost and revaporized at the point of consumption.

About 51% of the carbon dioxide consumed in the United States is used in the food industry. It is generally purchased in liquid form but may be used in any form. It is generally used for food freezing or chilling. Numerous patents on applications and equipment for these applications have been received.

Approximately 18% of carbon dioxide output is used for beverage carbonation. Both soft drinks and beer production consume the largest quantity of CO_2 for carbonation (see CARBONATED BEVERAGES).

About 10% of the carbon dioxide produced is for chemical manufacturing. Sold as a liquid, it is used as a raw material, for inerting and pressurizing, and for cooling. Other applications include metal working (4%) and oil and gas recovery (6%).

7.1. Dry Ice.

Refrigeration of foodstuffs, especially ice cream, meat products, and frozen foods, is the principal use for solid carbon dioxide. Dry ice is especially useful for chilling ice cream products because it can be easily sawed into thin slabs and leaves no liquid residue upon evaporation. Crushed dry ice may be mixed directly with other products without contaminating them and is widely used in the processing of substances that must be kept cold. Dry ice is mixed with molded substances that must be kept cold. For example, dry ice is mixed with molded rubber articles in a tumbling drum to chill them sufficiently so that the thin flash or rind becomes brittle and breaks off. It is also used to chill golf-ball centers before winding. A device and process for generating carbon dioxide snow has been reported (46).

Dry ice is used to chill aluminum rivets. These harden rapidly at room temperature, but remain soft if kept cold with dry ice. It has found numerous uses in laboratories, hospitals, and airplanes as a convenient and readily available low temperature coolant.

7.2. Liquid Carbon Dioxide.

The rapid increase in the use of liquid carbon dioxide is the result of new applications as well as improved facilities for transporting, storing, and handling liquid carbon dioxide. Carbon dioxide manufacturers have developed refrigerated bulk-liquid storage systems that they install and maintain for large consumers. These systems are available in sizes from 2 to 50 tons and have an insulated storage tank, maintained at 2080 kPa (20.5 atm) and 255 K by a Freon refrigeration unit, with a refrigeration coil in the upper part of the storage tank. An external vaporizer is provided when gaseous carbon dioxide is needed. Liquid-level and pressure relief valves, and a safety rupture disk, are provided. The entire assembly is enclosed in a sheet-steel housing mounted on a steel base, and requires nominal power. A 12-ton unit is supplied with a 1500-W (two-horsepower) refrigeration unit. Vaporizers can be heated by electricity or steam. One kg of steam vaporizes approximately 6 kg of CO_2. The storage tanks are refilled by the CO_2 supplier, either by tank truck or rail car delivery.

Ready availability and easy application of bulk liquid carbon dioxide have caused it to replace dry ice in many cases. Liquid CO_2 can be stored without loss and is easily measured or weighed. Liquid carbon dioxide is also used, along with dry ice, for direct injection into chemical reaction systems to control temperature.

Liquid carbon dioxide provides the most readily available method of rapid refrigeration and is used for rapid chilling of loaded trucks and rail cars before shipment. A two to four minute injection of liquid carbon dioxide into a loaded ice cream truck causes the temperature to drop as much as 70°C, flushing the warm air out of the truck and leaving a layer of carbon dioxide snow in the truck, which sublimes slowly to provide additional refrigeration. This greatly reduces the load on the truck's mechanical refrigeration system and eliminates the time lag in cooling the truck contents to a safe storage temperature. Test chambers for environmental studies have been effectively cooled at temperatures to $-80°C$ with liquid carbon dioxide, either by direct injection, or by using the liquid to chill circulating refrigerant liquids. The speed with which chilling may be obtained and the low equipment cost required have been the main factors in the selection of liquid carbon dioxide for this service.

Liquid carbon dioxide has been used for many years in the Long-Airdox blasting system for mining coal. A steel cartridge containing liquid carbon dioxide is placed in a hole drilled in the coal seam. A heating mixture in the cartridge is ignited electrically. This vaporizes the carbon dioxide, causing the pressure to increase enough to burst a steel rupture disk and release the carbon dioxide, which shatters the coal. The cartridge is then recovered and reused.

Liquid carbon dioxide is used as a source of power in certain applications. The vapor pressure of liquid carbon dioxide (7290 kPa or 72 atm at 294 K) may be used for operating remote signaling devices, spray painting, and gas-operated firearms. Carbon dioxide in small cylinders is also used for inflating life rafts and jackets.

Fire-extinguishing equipment, ranging from hand-type extinguishers to permanent installations in warehouses, chemical plants, ships, and airplanes, uses liquid carbon dioxide. In addition to its snuffing action liquid carbon dioxide exerts a pronounced cooling effect helpful in fire extinguishing. It may be used on all types of fires and leaves no residue, but care must be exercised to safeguard against suffocation of personnel.

Carbon dioxide is sometimes added to irrigation water, in the same manner as fertilizer ammonia, in hard water regions. Carbon dioxide is also used with other gases in treating respiratory problems and in anesthesia.

In addition to chemical synthesis and enhanced oil recovery, gaseous carbon dioxide is used in the carbonated beverage industry. Carbon dioxide gas under pressure is introduced into rubber and plastic mixes, and on pressure release a foamed product is produced. Carbon dioxide and inert gas mixtures rich in carbon dioxide are used to purge and fill industrial equipment to prevent the formation of explosive gas mixtures.

The addition of small amounts of carbon dioxide to the atmosphere in greenhouses greatly improves the growth rate of vegetables and flowers.

Carbon dioxide is widely used in the hardening of sand cores and molds in foundries. Sand is mixed with a sodium silicate binder to form the core or mold after which it is contacted with gaseous carbon dioxide. Carbon dioxide reacts with the sodium silicate to produce sodium carbonate and bicarbonate, plus silicic acid, resulting in hardening of the core or mold without baking.

The use of carbon dioxide gas for shielded arc welding with semiautomatic microwire welding equipment has led to welding speeds up to 10 times those obtainable within conventional equipment. No cleaning or wire brushing of the welds is required (45) (see WELDING).

Carbon dioxide gas is used to immobilize animals prior to slaughtering them (46). In addition to providing a humane slaughtering technique, this results in better quality meat. The CO_2 increases the animal's blood pressure, thereby increasing blood recovery. The increased accuracy obtainable in the killing operation reduces meat losses because of cut shoulders.

As a weak acid (in aqueous solution) carbon dioxide neutralizes excess caustic in textile manufacturing operations. It does not injure fabrics and is easy to use. Carbon dioxide is also used for neutralizing alkaline wastewaters, treating skins in tanning operations, and carbonating treated water to prevent scaling.

Carbon dioxide is used as a chemical reagent in the manufacture of sodium salicylate, basic lead carbonate or white lead, and sodium, potassium, and ammonium carbonates and bicarbonates.

A device or sachet for maintaining or modifying the atmosphere in a package suitable for meat, beef, lamb, pork, etc, the device including at least two containing layers, a moisture activated chemical substance contained by the containing layers, and at least one absorbent layer has been reported. Moisture within the package is soaked up by the absorbing layer. The moisture is then transferred from the absorbing layer to permeate through a micro-porous layer as water vapor and activate the chemicals. The gas produced by the chemicals then passses through the sachet and into the package's atmosphere. This modifies the atomosphere to ensure that there is an adequate quantity of CO_2 for achieving the desired shelf life of the packaged food (49).

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