CO_2 fundamentals and safety

Part one: Information that may save your life and prevent damage to equipment

By Keith Hall, Premier Cryogenics Services

The carbon dioxide (CO_2) molecule is composed of one carbon atom covalently bonded to two oxygen atoms. At less than 0.04%, carbon dioxide is still the fourth most common gas present in the earth's atmosphere. Natural sources of CO_2 include volcanic outgassing, forest fires, biomass decay, animal respiration, and oceanic evaporation. In its vapor and liquid states CO_2 is colorless with a slightly pungent odor and a biting taste (which you all recognize if you have tasted a fountain drink that was dispensed with no flavoring). In its solid state, dry ice is white.

CO_2 is heavier than air and gathers in low places. To state that CO_2 is not just a simple asphyxiant but is one of the most overlooked of all toxic gases, may be a surprise to many safety professionals. A concentration of 19.5% oxygen is the hazardous condition threshold for oxygen deficiency in most jurisdictions. In the case of CO_2 in a confined space, with an oxygen meter reading of 19.5%, the concentration of CO_2 could be much higher than the generally accepted workplace exposure limit. "The bottom line is that if you wait until the oxygen deficiency alarm is activated, and the deficiency is due to the presence of CO_2, you will have substantially exceeded the toxic exposure limit." (Robert E. Henderson, https://ohsonline.com/Articles/2006/07/Carbon-Dioxide-Measures-Up-as-a-Real-Hazard.aspx?m=1&Page=2). While low-concentrations are not harmful, higher concentrations can affect respiratory function, cause excitation and depression of the central nervous system.

Pressure versus temperature

When dealing with CO_2 we should understand how temperature and pressure are directly related (if the pressure increases the temperature also increases, and vice-versa) and how they affect the solid, liquid, gaseous and supercritical states.

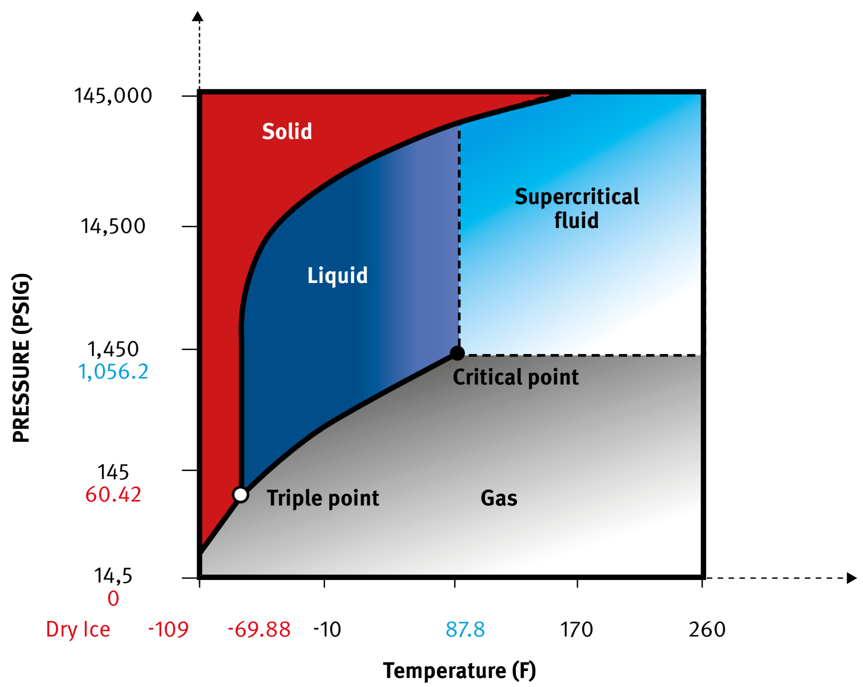
CO_2 cannot exist as a liquid at atmospheric pressure; only as a solid (dry ice at -109°F) or as a vapor. At atmospheric pressure, sublimation occurs as solid dry ice skips the liquid phase and changes directly into vapor (in contrast evaporation occurs when a liquid changes state to a vapor).

With 60.42 psig pressure exerted on it (corresponding temperature is -69.88°F), CO_2 can exist simultaneously as a solid, liquid, or vapor. This singular temperature and pressure condition is known as the 'triple point'.

As seen on the Pressure-Temperature Equilibrium Curve in Figure 1, CO_2 can only exist as a liquid in the range shown in dark blue above the triple point, between 60.42 psig and 1,056.2 psig and corresponding -69.88°F to 87.8°F. At pressure and temperature conditions shown in red, CO_2 exists as a solid, and as a vapor as shown by the gray area. Above the triple point CO_2 can exist as a solid, liquid, vapor, or super critical fluid, depending upon the pressure-temperature conditions.

Supercritical fluids (SCF) held below the pressure required to be compressed into a solid do not have distinct liquid or gas phases; they have no surface tension, and no phase boundaries exist. SCFs expand to fill their container like a gas, while having the density of a liquid. CO_2 becomes a supercritical fluid when held at or above its critical point (critical temperature of 87.8°F and critical pressure of 1,056.2 psig) in the area shown in light blue. Supercritical fluids can defuse through solids like a ▸

Figure 1. Phase Diagram of carbon dioxide



(Sources: https://commons.wikimedia.org/wiki/File%3ACarbon_dioxide_pressure-temperature_phase_diagram.svg (units changed).
Thermophysical Properties of Carbon Dioxide, Vukalovich and Altunin, 1965)

gas, and dissolve materials like a liquid. A handy pressure versus temperature reference table is included in Figure 2.

Key CO_2 safety points that may save your life

1. *Safe practices and personal protective equipment* — Avoid death, injury, and/or equipment damage by learning about safety and proper equipment operation before working with or around carbon dioxide. Always follow safe CO_2 practices and follow company and industry safety precautions. Always wear personal safety protective equipment (PPE) when working around CO_2. At a minimum, this includes gloves, eye and ear protection, a hard hat, and proper clothing.
2. *Asphyxiation* — Carbon dioxide gas can suffocate you! CO_2 is heavier than air and sinks downward. It displaces air by pushing air up and out of its way, and it concentrates in low and confined spaces. Always use safety equipment and follow safety procedures before entering a location where a hazard like CO_2 could exist. Get an entry permit before going into a confined space; and do not depend on measured oxygen content of the air alone because elevated levels of carbon dioxide can be toxic, even when adequate oxygen for life support exists (reference Compressed Gas Association, CGA G-6.7). Air is composed of 21% oxygen, 78% nitrogen, and 1% argon, CO_2, helium, other trace gases, and pollution. If an oxygen meter measures a confined space atmosphere to be 19.6% oxygen you may think that is safe. But what if the remaining 80.4% contains high levels of CO_2 or other hazardous gases? Even with sufficient oxygen, you could be breathing dangerous or lethal amounts of CO_2 and not know it.
3. *Freeze Burns* — At atmospheric pressure CO_2 is solid (dry ice) at minus 109°F. At this temperature, contact between exposed skin and dry ice will cause frost bite, resulting in severe tissue damage which will blister, similar to a burn; both are thermal injuries. Contact of exposed skin with cold piping can also result in tissue damage. Always wear gloves and long sleeve shirts when working around CO_2.
4. *Shotgun and cannon ball effect* — Liquid CO_2 will flash-freeze into dry ice particles if depressurized below 60.4 psig. These solid particles act like shotgun pellets if vented from a piping circuit or hose. Severe injury can result. The only silver-lining to being shot with dry-ice pellets is that the surgeon patching you back up (if you are still alive), will not have to remove the pellets from your wounds; they will sublime and turn to vapor. Dry ice particles can also build-up within, and plug-up, a piping circuit or hose. As the upstream temperature warms, so does the upstream line pressure. As the dry ice particles, or plug, warm they expand into CO_2 gas, contributing to an upstream pressure rise. This pent-up high-pressure, upstream of the blockage, may result in the piping or hose exploding like a bomb. Alternately the dry ice plug may eject like a cannon ball when the piping or hose is vented. These dry ice plugs tend to lodge tightly in low places and hose ends. Try to keep low spots out of hoses and take time to carefully drain them at the conclusion of a job. If your job set-up requires low-points, always use a low-line pressure union between two hoses, at the lowest point. The low-line pressure union must be equipped with a safety line relief valve and a pressurized drain vent.
Dry ice plugs tend to form most frequently when you depressurize a line to disconnect after a job. Never permit a line with liquid in it to fall below 215 psig. Never drain a line without using 215 psig minimum gaseous pressure to blow the line clean of liquid. Always wear proper safety PPE and carefully follow standard procedure for venting down a tank or piping circuit. At 215 psig and above liquid CO_2 will never fall below the minimum metal design temperature of the tank and piping circuits.
It is better to be safe than ride in a hearse!
5. *Aim CO_2 Equipment Away from People and Stand Aside* — Disconnecting improperly depressurized transfer hoses causes many injuries. Treat hose ends, fill connection openings, vent/drain ports, etc. the same as you would the end of the barrel on a gun. If depressurized incorrectly, dry ice pellets or plugs will form and can be ejected from the piping or hose with lethal force, as described above. Avoid injury and equipment damage from the "shotgun and cannon" effects by never permitting anyone to stand in front of an open hose connection, hose end, valve, or other opening. Such openings should never be directed toward equipment. Exercise extreme care when attaching or removing a CO_2 transfer hose and keep the cylinder heads of high-pressure pumps aimed away from people. Ensure hoses are properly secured on both ends to avoid whipping of a loose end if the hose were to be accidentally pressurized.
6. *Never permit pressure on liquid CO_2 to drop below 215 psig* — Just like the ill-fated Titanic, carbon steel CO_2 vessels, piping, fittings, and elastomeric hoses embrittle when exposed to cold temperatures. At 200 psig liquid CO_2 is approximately minus 20°F. To avoid potential catastrophe, always maintain the pressure on liquid CO_2 above 215 psig. Should a vessel, line, or hose ever be depressurized below 200 psig the resulting temperature drops below minus 20°F. A corresponding decrease in the temperature of the product results in the system operating below it Minimum Design Metal Temperature (MDMT) and the containment vessel material could fail at or below its Nil Ductility Transition Temperature (NDTT). Carbon steel piping and fittings, and elastomeric hoses rated for standard CO_2 temperatures, become less ductile (embrittle) and fail when stressed at cold temperatures. Stress is caused by internal pressure, but could also result from an impact (i.e., hammering a hose connection), from a bending load on improperly supported piping, from flexing an elastomeric hose when it is cold, and from other situations.
Rule of thumb to remember - never permit a line with liquid in it to fall below 215 psig.
7. *Get CO_2 equipment training* — Never operate any type of equipment in CO_2 service without first being trained in CO_2 safety. You should understand the basics of CO_2 and feel comfortable with safe and correct operational procedures for any given piece of equipment or CO_2 system. It is recommended that an experienced operator be present, as an instructor, the first few times you operate a new piece of CO_2 equipment. gw

"Never operate any type of equipment in CO_2 service without first being trained in CO_2 safety"

Figure 2. Handy CO_2 Pressure vs Temperature, Reference Table

	Pressure (psig)	Temperature (°F)
Critical Point	1056.2	87.8
	350	10.7
	325	6.4
	300	1.7
	291	0
	275	−3.2
	250	−8.4
	225	−14
Minimum Recommended Use Temp	**215**	**−16.4**
	200	−20
	130	−40
	103	−50
Triple Point	60.42	−69.88
Solid Dry Ice	0	−109.3

CO_2 Trivia

- At atmospheric pressure, -109°F dry ice sublimes from a solid to a vapor. The vapor is so cold that humidity in the air condenses on it (just like when you see your breath in the wintertime), creating a fog effect. This is sometimes used for special effect in movies and at performances.
- Supercritical CO_2 is used to remove as much as 99% of the caffeine from green coffee beans.
- Supercritical CO2 is also is used as a solvent in dry cleaning.
- Supercritical CO2 is used in more applications than the supercritical phase of any other substance.
- CO2 is used for fighting fires in some applications It cools while denying the fire of oxygen.

Part 2 of this article will run in our January issue

ABOUT THE AUTHOR

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CO_2 fundamentals and safety

Part two: The minimum you should know about CO_2 that may save your life and prevent damage to equipment

By Keith Hall, Premier Cryogenics Services

Last month in part one of this article, we discussed the makeup of carbon dioxide (CO_2) and the four phases or states of matter for CO_2 that we typically deal with (solid, liquid, vapor, and supercritical fluid). On a pressure-temperature phase diagram we learned where these states occur. We learned about the triple and critical points of C02. And we learned some interesting facts about CO_2. Most importantly, seven basic things to know about CO_2 that may save your life, were laid out.

In this issue we will learn some more fun things about CO_2, and several basic things to prevent damage

Nine steps to prevent damage to equipment

In addition to the safety procedures outlined in Part one of this article, below are ways to prevent damage to expensive equipment and avoid downtime. These also help prevent injuries.

1. Inspect Equipment – All equipment should be in good repair and free of defects. Before beginning any job or using any piece of CO_2 equipment, visually, carefully inspect all equipment involved in each operation. Look for cleanliness, cracks, wear, damage, or other signs of potential failure. Note that hoses wear and degrade over time. One typical location where hoses often fail is at either end near the connections. Degradation occurs from the weight of a sagging hose when connected and not properly supported. For safety and to extend the life of your hoses, only buy hoses with 18-inch armor cuffs on each end which serve as strain-reliefs.
   Make sure Compressed Gas Association (CGA) guidelines are observed for the construction materials for CO_2 hoses, including temperature and pressure ratings, tags/markings, outer-skin perforations, and usage age.
2. Practice Preventive Maintenance – Cracks may develop in metallic components in the threads. Use standard QC inspection processes and tools, i.e., magnetic particle, ultrasonic, X-ray, and other inspection techniques as necessary, or required by preventive maintenance schedules and procedures, to ensure that all equipment is in good condition. Verify that all preventive maintenance tasks have been performed before operating any equipment involved in CO_2 service. Also, verify that oil, coolant levels, etc., in equipment are at their safe operating levels.
3. Get CO_2 Equipment Training – Never operate any type of equipment in CO_2 service without first being trained in CO_2 safety. You should understand the basics of CO_2 and feel comfortable with safe and correct operational procedures for any given piece of equipment or CO_2 system. It is recommended that an experienced operator be present, as an instructor, the first few times you operate a new piece of CO_2 equipment.

Take carbon dioxide seriously! Lives have been lost, people hurt, and equipment damaged due to the lack of knowledge of CO_2, proper training, and not following basic CO_2 safety and proper methods for operating CO_2 equipment.

4. Locate Equipment Carefully – It is important to treat the location of equipment almost as carefully as the people who operate it. Hose-ends, fill connection openings, vent/drain ports, etc. can rupture and be explosive; make sure they are not directed at equipment. The venting of cold liquid onto an adjacent piece of equipment could cause embrittlement, damage, or component failure. Improperly depressurized CO_2 vessels, lines, components, or equipment could cause the formation of dry ice pellets or a dry ice plug. These pellets or plugs, as discussed previously, can be ejected like a cannon, damaging any equipment located in front of the opening. Avoid equipment layouts with low-points in piping or hoses where dry ice plugs may tend to form when the circuit is depressurized.
5. Stake Down/Secure – Stake down and secure high-pressure discharge lines and hoses before pressurizing. Make sure hoses are properly connected before pressurizing. Make sure drain/vent valves are closed before you pressurize. Failure to do so could result in a hose, secured only at one end, whipping dangerously around. ***It is better to correct an unsafe friend that to bury one!***
6. Never Permit the Pressure on CO_2 Liquid to Drop Below 215 psig – Carbon steel CO_2 vessels, pumps, piping, and fittings embrittle when exposed to cold temperatures. At 200 psig, liquid CO_2 is approximately minus 20°F. To avoid potential catastrophe, always maintain the pressure on liquid CO_2 above 215 psig.
   Some CO_2 vessels are constructed from stainless steel alloys rated for cryogenic service temperatures, i.e. beverage carbonation liquid cylinders. However, the vast majority of CO_2 vessels are made from special carbon steel alloys and are only rated to the minus 20 to minus 50°F range (*see Figure 1*). As the temperature and pressure of CO_2 are directly related, the lower the pressure, the lower the temperature of the liquid CO_2, hence the lower required design temperature rating of its vessel of containment (*see Figure 2*). When

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Figure 1. Common CO_2 Vessel Alloys

Alloy	Minimium Design Metal Temperature (°F)
SA516-70N	-20
A612-N	-20
SA517-B	-40 to -50*
SA517-E	-50
*Often Charpy Impact tested to -50	

Figure 2. Handy CO_2 Pressure vs Temperature Reference Table

	Pressure (psig)	Temperature (°F)
Critical Point	1056.2	87.8
	350	10.7
	325	6.4
	300	1.7
	291	0
	275	-3
	250	-8.4
	225	-14
Min Recommended Use	**215**	**-16.4**
	200	-20
	130	-40
	103	-50
Triple Point	60.42	-69.88
Solid Dry Ice	0	-109.3

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using vessels rated for use at lower than minus 20°F, it is important to be aware that downstream carbon steel piping, fittings, hoses, and connections used in adjacent systems may not be rated to operate in that temperature range and will embrittle and fail dangerously.

7. Hammer Carefully – As carbon steel fittings embrittle when cold, hammer carefully on cold pipe connections, low-line unions, etc. Always wear eye protection as pieces may chip away and hit you.
8. Properly Pressure Drain and Depressurize Hoses, Piping Circuits, and Storage Vessels – Carefully follow drain and blowdown procedures to avoid the formation of dry ice pellets or a plug. Be aware of low points in the piping or hoses where dry ice plugs may tend to form. Immediately use vapor pressure to drain any line that becomes isolated when a valve is closed. Gaseous CO_2 under pressure no less than 215 psig must be used to blow the liquid from lines, hoses, equipment, and piping circuits. Simply opening a vent/drain valve to drain a line will cause solid dry ice to quickly form within the line, often plugging it, and creating a dangerous situation. If gaseous CO_2 pressure is not available, the line should be vented little by little as the liquid boils off as it warms. Carefully monitor a pressure gauge to ensure that the line pressure stays well above 215 psig until all liquid has boiled off.

   Always ensure that a safety relief valve, properly rated for pressure and flow rate, is installed on every line where liquid could be trapped. A temperature versus pressure table for CO_2 from part one of this article is included here again as a handy reference tool.
9. Do Not Overfill –When liquid CO_2 is stored in a vessel and no product is withdrawn, heat from the environment leaking into the liquid will cause the temperature and pressure of the CO_2 to rise. Like other materials that expand when heated, liquid CO_2 expands in volume, occupying more space in the storage vessel. For this reason the "full" level in a tank takes into consideration the expansion volume of the liquid; it assures that there is sufficient vapor space in the top of the vessel to contain the expanded liquid without the pressure relief device opening to discharge liquid instead of vapor. Overfilling the vessel could cause hydrostatic over-pressurization of the vessel and result in a catastrophic rupture. The potential also exists for dry ice formation and plugging of the relief devices, which could also result in catastrophic rupture of the containment vessel.

© PCS | **Trick-or-Treaters enjoy witch's brew as it bubbles and old vapor falls from the sides of the container. This homemade root beer is chilled and carbonated with dry ice (-109°F).**

CO_2 Witch's brew for Halloween
Recipe for homemade dry ice root beer

- Fill a 5-gallon insulated water cooler with tap water
- Use a long-handled spoon to stir in and dissolve 5 pounds of sugar
- Stir in one bottle of root beer concentrate (be sure the bottle makes 5 gallons as there is some root beer concentrate available that makes root beer by the cupful).
  Root beer concentrate is sold in some large supermarkets and can be found near the vanilla. You can also order it on-line. McCormick Root Beer Concentrate in 2-ounce bottles is what I use.
- Bust 10 pounds of dry ice into small chunks (double bag, wear safety glasses, and hit with a hammer).
- Use clean gloves to avoid freeze burns, and add a few chucks of dry ice every few minutes.
- The dry ice sublimes and makes the root beer bubble with vapor like witch's brew until it is good and cold and carbonated after about 45-minutes. It is especially delicious when root beer slush forms on the surface. If you get in a hurry to taste the root beer, it will still taste good but be flat until properly carbonated. gw

Warning – never hold dry ice bare-handed. Never swallow even a small piece of dry ice!

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