



CARBON DIOXIDE

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1 Introduction

This publication is one of a series compiled by the Compressed Gas Association, Inc. (CGA), to satisfy the demand for information relative to the production, storage, transportation, safe handling and use of compressed and liquefied gases, cryogenic liquids, and related products.

As part of the programme of harmonization of industry standards, the Asia Industrial Gases Association (AIGA) has adopted the original CGA standard G-6 as AIGA 068/10. This standard is intended as an international harmonized standard for the use and application by members of CGA, EIGA, JIMGA and AIGA. This edition has the same content as the CGA edition except for editorial changes in formatting, units, spelling and references to AIGA documents.

2 Scope and purpose

2.1 Scope

The scope includes the physical and chemical properties, physiology, toxicity, special hazards, production, regulations, storage, handling, and applications of carbon dioxide.

2.2 Purpose

The purpose of this publication is to provide information on carbon dioxide. It should be useful to carbon dioxide users, producers, and distributors. Detailed information on the various aspects of carbon dioxide and its transportation and use may be found in sources listed in the reference section.

3 Definitions

For the purposes of this publication, the following definitions apply.

3.1 Carbon dioxide

A chemical compound consisting of one atom of carbon bonded to two atoms of oxygen expressed by the chemical formula CO_2 . The shipping name for carbon dioxide in uninsulated cylinders in the United States and Canada is Carbon Dioxide.

3.2 Container

An insulated pressure vessel, ASME-coded for the storage of carbon dioxide.

3.3 Critical point

The highest pressure and temperature for a pure gas at which the liquid and vapor phases can exist in equilibrium. For carbon dioxide, this occurs at a temperature of 87.9 °F (31.1 °C) and a pressure of 1070.6 psia (7381.8 kPa, abs).^{1, 2}

3.4 Critical pressure

The pressure that must be exerted to produce liquefaction at the critical temperature. For carbon dioxide the critical pressure is 1070.6 psia (7381.8 kPa, abs).

3.5 Critical temperature

The temperature above which a pure gas cannot be liquefied regardless of the degree of compression. For carbon dioxide the critical temperature is 87.9 °F (31.1 °C).

¹ kPa shall indicate gauge pressure unless otherwise noted as (kPa, abs) for absolute pressure or (kPa, differential) for differential pressure. All kPa values are rounded off per CGA P-11, *Metric Practice Guide for the Compressed Gas Industry* [1].

² References are shown by bracketed numbers and are listed in order of appearance in the reference section.

3.6 Cylinder

See insulated cylinder (3.8) and uninsulated cylinder (3.14).

3.7 Dry ice

The common name for solid carbon dioxide. Its temperature is -109.3°F (-78.5°C) at atmospheric pressure.

3.8 Insulated cylinder

A DOT-approved cylinder with a water capacity not more than 120 U.S. gal (454 L) or 1000 lb (454 kg) and a service pressure rating of at least 40 psia (276 kPa, abs) but not more than 500 psig (3448 kPa), or a TC-approved cylinder with a water capacity not more than 450 L and a service pressure rating from 3.0 bar to 35.0 bar

3.9 Maximum allowable working pressure (MAWP)

The maximum gauge pressure permissible at the top of a container in its operating position for a designated temperature [2].

3.10 Saturated condition

The condition at which the pressure and temperature of all existing physical states are at equilibrium.

3.11 Sublimation

The process of changing from the solid phase directly to the gas phase without passing through the liquid phase.

3.12 Supercritical fluid

A substance that is at a pressure and a temperature equal to or greater than its critical point. A substance that has complete mutual solubility of the liquid and the gas.

3.13 Triple point

The temperature and pressure at which a material exists simultaneously as a solid, liquid, and gas. For carbon dioxide the triple point is -69.9°F (-56.6°C) and 75.1 psia (518 kPa, abs).

3.14 Uninsulated cylinder

A cylindrically shaped pressure-containing device with a minimum rated service pressure of 1800 psig (124 bar) and a water capacity no greater than 120 U.S. gal (454 L). The minimum service pressure of 1800 psig (124 bar) is specific to carbon dioxide.

3.15 Upset condition

Any condition outside the normal design parameters.

4 Carbon dioxide

4.1 Physical and chemical properties

Carbon dioxide is a colorless, odorless, slightly acid gas that is approximately 50% heavier than air. It is non-flammable and will not support combustion. The physical constants of carbon dioxide are summarized in Table 1. Carbon dioxide can exist as a solid, liquid, gas, or supercritical fluid depending upon conditions of temperature and pressure.

Carbon dioxide at its triple point exists simultaneously as a liquid, gas, and solid at -69.9°F (-56.6°C) and 75.1 psia (518 kPa, abs). Any change in pressure or temperature causes carbon dioxide to revert to a two-phase condition (see Figure 1).

Carbon dioxide at its critical point exists simultaneously as a liquid, gas, and supercritical fluid at 87.9°F (31.1°C) and 1070.6 psia (7381.8 kPa). At pressures and temperatures greater than the critical point, carbon dioxide exists only as a supercritical fluid. The solubility of carbon dioxide in water varies with temperature and pressure as shown in Table 2 [3]. Table 2 shows the volume of carbon dioxide measured at 32°F (0°C) and 0 psig (0 kPa) that dissolves in one volume of water at the pressure and temperature indicated.

See Tables 3 and 4 and Figure 2 for the thermodynamic and physical properties of carbon dioxide.

Table 1—Physical constants of carbon dioxide

(See Tables 3 and 4 for other properties)

| Chemical Name: | Carbon dioxide | |
|--|--|---------------------------------|
| Synonym: | Carbon anhydride, carbonic acid gas, carbonic anhydride, dry ice | |
| CAS Registry Number: | 124–38–9 | |
| | U.S. Units | SI Units |
| Chemical formula | CO ₂ | CO ₂ |
| Molecular weight | 44.01 | 44.01 |
| Vapor pressure ¹⁾ at 2 °F (–16.7 °C) | 302 psig | 2082 kPa |
| Specific gravity of the gas at 70 °F (21.1 °C) and 1 atm | 1.522 | 1.522 |
| Solid to gas expansion ratio (specific volume of the gas) at 70 °F (21.1 °C) and 1 atm | 8.741 ft ³ /lb | 0.5457 m ³ /kg |
| Density of the gas at 70 °F (21.1 °C) and 1 atm | 0.1144 lb/ft ³ | 1.833 kg/m ³ |
| Density of the liquid saturated at 2 °F (–16.7 °C) | 63.3 lb/ft ³ (8.46 lb/gal) | 1014 kg/m ³ |
| Density of solid (dry ice) at 1 atm and –109.3 °F (–78.5 °C) | 97.6 lb/ft ³ | 1563 kg/m ³ |
| Sublimation temperature at 1 atm | –109.3 °F | –78.5 °C |
| Critical temperature | 87.9 °F | 31.1 °C |
| Critical pressure | 1070.6 psia | 7381.8 kPa |
| Critical density | 29.2 lb/ft ³ | 468 kg/m ³ |
| Triple point | –69.9 °F at <u>75.1 psia</u> | –56.6 °C at <u>518 kPa, abs</u> |
| Latent heat of vaporization at 2 °F (–16.7 °C) | 119.0 Btu/lb | 276.8 kJ/kg |
| Latent heat of fusion at 1 atm and –69.9 °F (–56.6 °C) | 85.6 Btu/lb | 199 kJ/kg |
| Latent heat of sublimation at 1 atm and –109.3 °F (–78.5 °C) | 245.5 Btu/lb | 571.0 kJ/kg |
| Specific heat of the gas at 77 °F (25.0 °C) and 1 atm | | |
| C _p | 0.203 Btu/(lb)(°F) | 0.850 kJ/(kg)(°C) |
| C _v | 0.157 Btu/(lb)(°F) | 0.657 kJ/(kg)(°C) |
| Ratio of specific heats (C _p /C _v) at 59 °F (15.0 °C) | 1.304 | 1.304 |
| Solubility in water, vol/vol at 68 °F (20.0 °C) | 0.90 | 0.90 |
| Viscosity of saturated liquid at 2 °F (–16.7 °C) | 0.287 lb/(ft)(hr) | 0.000119 Pa·s |
| ¹⁾ All psig values are referenced to 14.696 psia (101.325 kPa, abs). | | |

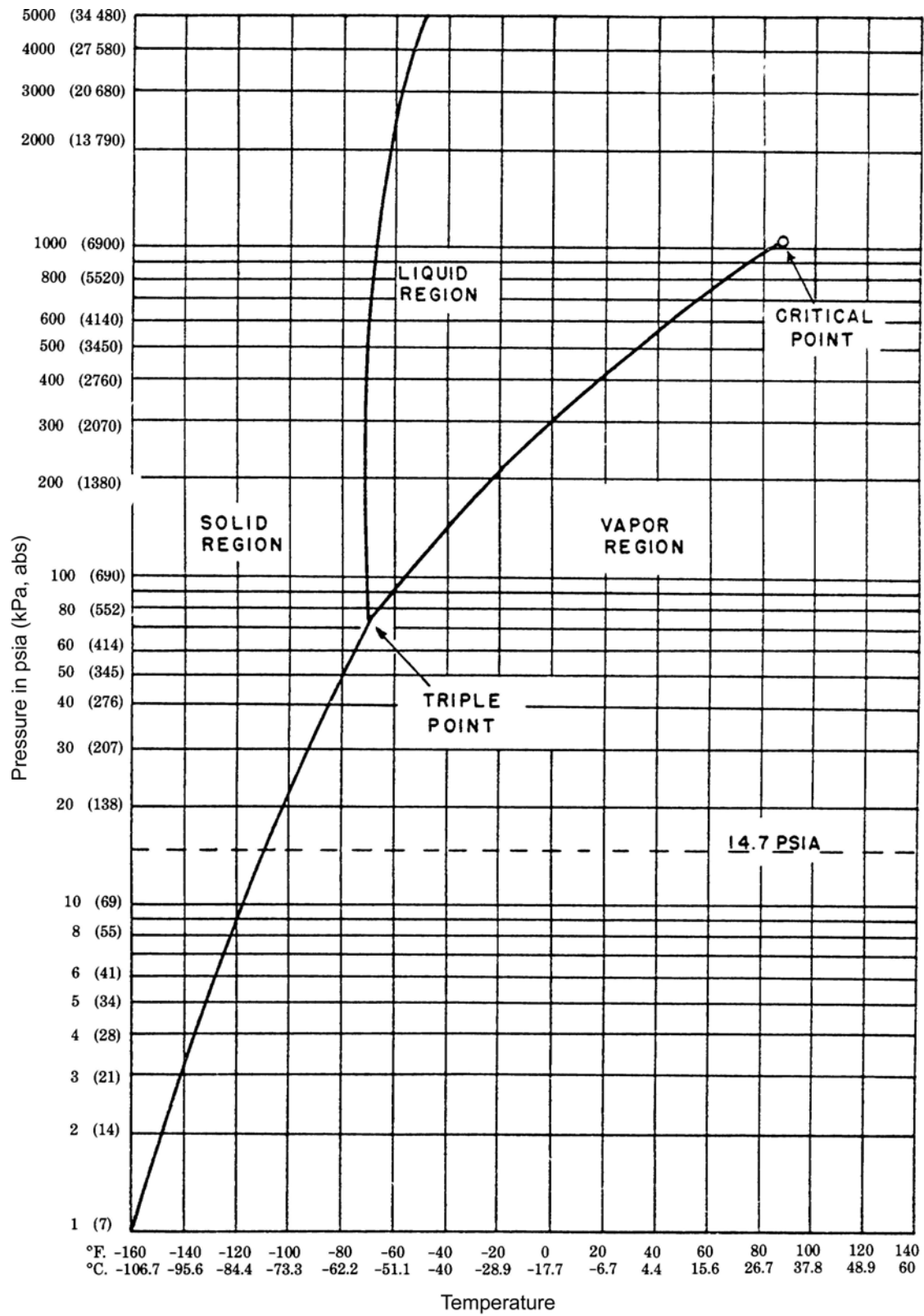


Figure 1—Carbon dioxide phase diagram

Table 2—Solubility of carbon dioxide in water [3]

| Pressure psig (kPa) | Temperature °F (°C) | | | | | | | | | | | | |
|------------------------|---------------------|-------------|-------------|-------------|-------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| | 32 (0) | 36 (2.2) | 40 (4.4) | 44 (6.7) | 48 (8.9) | 55 (12.8) | 60 (15.6) | 65 (18.3) | 70 (21.1) | 75 (23.9) | 80 (26.7) | 85 (29.4) | 90 (32.2) |
| 15 (103) | 3.46 | 3.19 | 2.93 | 2.70 | 2.50 | 2.20 | 2.02 | 1.86 | 1.71 | 1.58 | 1.48 | 1.35 | 1.27 |
| 20 (138) | 4.04 | 3.73 | 3.42 | 3.15 | 2.92 | 2.57 | 2.36 | 2.17 | 2.00 | 1.84 | 1.69 | 1.58 | 1.48 |
| 25 (172) | 4.58 | 4.27 | 3.92 | 3.61 | 3.35 | 2.95 | 2.69 | 2.48 | 2.29 | 2.10 | 1.93 | 1.80 | 1.70 |
| 30 (207) | 5.21 | 4.81 | 4.41 | 4.06 | 3.77 | 3.31 | 3.03 | 2.80 | 2.58 | 2.37 | 2.18 | 2.03 | 1.91 |
| 35 (241) | 5.80 | 5.35 | 4.91 | 4.52 | 4.19 | 3.69 | 3.37 | 3.11 | 2.86 | 2.63 | 2.42 | 2.26 | 2.13 |
| 40 (276) | 6.37 | 5.89 | 5.39 | 4.97 | 4.61 | 4.05 | 3.71 | 3.42 | 3.15 | 2.89 | 2.67 | 2.49 | 2.34 |
| 45 (310) | 6.95 | 6.43 | 5.88 | 5.43 | 5.03 | 4.43 | 4.06 | 3.74 | 3.44 | 3.16 | 2.91 | 2.72 | 2.56 |
| 50 (345) | 7.53 | 6.95 | 6.36 | 5.89 | 5.45 | 4.80 | 4.40 | 4.05 | 3.73 | 3.42 | 3.16 | 2.94 | 2.77 |
| 55 (379) | 8.11 | 7.48 | 6.86 | 6.34 | 5.87 | 5.17 | 4.74 | 4.37 | 4.02 | 3.69 | 3.40 | 3.17 | 2.99 |
| 60 (414) | 8.71 | 8.02 | 7.35 | 6.79 | 6.29 | 5.53 | 5.08 | 4.68 | 4.31 | 3.95 | 3.64 | 3.39 | 3.20 |
| 70 (483) | 9.86 | 9.09 | 8.33 | 7.70 | 7.13 | 6.27 | 5.76 | 5.30 | 4.89 | 4.49 | 4.14 | 3.86 | 3.63 |
| 80 (552) | 11.02 | 10.17 | 9.31 | 8.61 | 7.98 | 7.00 | 6.43 | 5.92 | 5.46 | 5.02 | 4.62 | 4.31 | 4.06 |
| 90 (621) | 12.18 | 11.25 | 10.30 | 9.52 | 8.82 | 7.74 | 7.11 | 6.54 | 6.04 | 5.55 | 5.12 | 4.77 | 4.49 |
| 100 (690) | 13.34 | 12.33 | 11.29 | 10.43 | 9.66 | 8.40 | 7.79 | 7.18 | 6.62 | 6.08 | 5.60 | 5.22 | 4.91 |

4.2 Manufacture

Large quantities of carbon dioxide for commercial use are primarily obtained from one of the following processes:

- combustion;
- wells/geothermal;
- fermentation;
- hydrogen;
- ammonia;
- phosphate rock;
- coal gasification;
- ethylene oxide; and
- acid neutralization.

Carbon dioxide is typically refined to the required purity by scrubbing, distillation, adsorption/desorption, oxidation, and/or filtration. For carbon dioxide purity specifications, see CGA G-6.2, *Commodity Specification for Carbon Dioxide* [4].

Carbon dioxide is generally liquefied by compression and refrigeration for storage or shipment. It is stored and shipped as a liquid at pressures and temperatures ranging from 200 psig and –20 °F (1380 kPa and –29 °C) to 350 psig and 11 °F (2410 kPa and –12 °C).

Solid carbon dioxide is manufactured by decreasing the pressure of the liquid below its triple point forming dry ice (snow) and cold vapor (see CGA G-6.9, *Dry Ice*) [5].

Solid carbon dioxide can be compressed into blocks of dry ice or extruded into pellets. Dry ice blocks are commercially available in 10-in (25.4-cm) nominal size cubes weighing 50 lb to 60 lb (23 kg to 27 kg) and having a density of approximately 94 lb/ft³ (1500 kg/m³). Pellets are available in various sizes (see Figure 3).

Table 3—Thermodynamic properties of saturated carbon dioxide solid, liquid, and vapor phases (U.S. customary units)

| Temp °F | | Pressure | | Density | Specific volume | Enthalpy ¹⁾ | | Entropy ¹⁾ | |
|------------------|--------|----------|---------------------|--------------------|---------------------|------------------------|--------|-----------------------|--------|
| | | psia | psig | lb/ft ³ | ft ³ /lb | Btu/lb | | Btu/(lb)(°R) | |
| | | | | solid or liquid | vapor | solid or liquid | vapor | solid or liquid | vapor |
| Solid and Vapor | −150 | 1.793 | 26.26 ²⁾ | 99.7 | 41.81 | 53.55 | 305.50 | 0.3394 | 1.1530 |
| | −140 | 3.171 | 23.46 ²⁾ | 99.2 | 24.41 | 56.36 | 306.90 | 0.3483 | 1.1318 |
| | −130 | 5.405 | 18.92 ²⁾ | 98.8 | 14.69 | 59.22 | 308.30 | 0.3571 | 1.1126 |
| | −120 | 8.923 | 11.75 ²⁾ | 98.3 | 9.131 | 62.15 | 309.62 | 0.3658 | 1.0945 |
| | −110 | 14.34 | 7.725 ²⁾ | 97.5 | 5.829 | 65.16 | 310.81 | 0.3743 | 1.0770 |
| | −109.3 | 14.70 | 0.000 | 97.5 | 5.683 | 65.38 | 310.90 | 0.3748 | 1.0758 |
| | −105 | 17.94 | 3.244 | 97.2 | 4.708 | 66.69 | 311.45 | 0.3786 | 1.0687 |
| | −100 | 22.28 | 7.584 | 96.9 | 3.814 | 68.24 | 312.01 | 0.3829 | 1.0606 |
| | −95 | 27.67 | 12.97 | 96.6 | 3.103 | 69.80 | 312.50 | 0.3872 | 1.0527 |
| | −90 | 34.14 | 19.44 | 96.2 | 2.531 | 71.41 | 312.89 | 0.3915 | 1.0449 |
| | −85 | 41.63 | 26.93 | 95.7 | 2.074 | 73.01 | 313.11 | 0.3959 | 1.0372 |
| | −80 | 50.58 | 35.88 | 95.3 | 1.714 | 74.63 | 313.22 | 0.4002 | 1.0292 |
| | −75 | 61.72 | 47.02 | 94.9 | 1.418 | 76.28 | 313.29 | 0.4045 | 1.0215 |
| | −70 | 74.76 | 60.06 | 94.4 | 1.182 | 77.96 | 313.42 | 0.4089 | 1.0151 |
| | −69.9 | 75.13 | 60.43 | 94.4 | 1.157 | 78.01 | 313.42 | 0.4112 | 1.0150 |
| Triple point | | | | | | | | | |
| Liquid and Vapor | −69.9 | 75.13 | 60.43 | 73.53 | 1.157 | 163.6 | 313.42 | 0.6308 | 1.0150 |
| | −68 | 78.48 | 63.78 | 73.30 | 1.117 | 164.4 | 313.49 | 0.6318 | 1.0128 |
| | −66 | 82.34 | 67.64 | 73.05 | 1.060 | 165.3 | 313.58 | 0.6340 | 1.0107 |
| | −64 | 86.35 | 71.65 | 72.79 | 1.011 | 166.1 | 313.67 | 0.6362 | 1.0088 |
| | −62 | 90.50 | 75.80 | 72.54 | 0.9659 | 167.0 | 313.76 | 0.6384 | 1.0070 |
| | −60 | 94.76 | 80.06 | 72.28 | 0.9254 | 167.9 | 313.85 | 0.6406 | 1.0053 |
| | −58 | 99.15 | 84.45 | 72.01 | 0.8876 | 168.8 | 313.94 | 0.6427 | 1.0038 |
| | −56 | 103.7 | 89.00 | 71.76 | 0.8501 | 169.6 | 314.03 | 0.6448 | 1.0024 |
| | −54 | 108.4 | 93.70 | 71.49 | 0.8145 | 170.5 | 314.12 | 0.6469 | 1.0010 |
| | −52 | 113.2 | 98.50 | 71.23 | 0.7809 | 171.4 | 314.23 | 0.6490 | 0.9996 |
| | −50 | 118.2 | 103.50 | 70.97 | 0.7489 | 172.3 | 314.33 | 0.6511 | 0.9982 |
| | −48 | 123.4 | 108.70 | 70.71 | 0.7184 | 173.2 | 314.44 | 0.6533 | 0.9967 |
| | −46 | 128.8 | 114.10 | 70.44 | 0.6896 | 174.1 | 314.57 | 0.6555 | 0.9952 |
| | −44 | 134.3 | 119.60 | 70.16 | 0.6622 | 175.0 | 314.68 | 0.6577 | 0.9938 |
| | −42 | 140.0 | 125.30 | 69.88 | 0.6361 | 175.9 | 314.78 | 0.6599 | 0.9924 |
| | −40 | 145.9 | 131.20 | 69.60 | 0.6113 | 176.8 | 314.89 | 0.6621 | 0.9910 |
| | −38 | 152.0 | 137.30 | 69.33 | 0.5876 | 177.7 | 314.98 | 0.6642 | 0.9897 |
| | −36 | 158.1 | 143.40 | 69.04 | 0.5648 | 178.7 | 315.09 | 0.6663 | 0.9883 |
| | −34 | 164.6 | 149.90 | 68.76 | 0.5432 | 179.6 | 315.20 | 0.6684 | 0.9869 |
| | −32 | 171.2 | 156.50 | 68.48 | 0.5227 | 180.5 | 315.31 | 0.6704 | 0.9855 |
| | −30 | 178.0 | 163.30 | 68.20 | 0.5031 | 181.4 | 315.40 | 0.6725 | 0.9842 |
| | −28 | 184.9 | 170.20 | 67.92 | 0.4844 | 182.3 | 315.49 | 0.6746 | 0.9829 |
| | −26 | 192.1 | 177.40 | 67.64 | 0.4665 | 183.2 | 315.58 | 0.6767 | 0.9817 |
| | −24 | 199.6 | 184.90 | 67.35 | 0.4492 | 184.3 | 315.67 | 0.6788 | 0.9805 |
| | −22 | 207.2 | 192.50 | 67.06 | 0.4325 | 185.2 | 315.74 | 0.6810 | 0.9793 |
| | −20 | 215.0 | 200.30 | 66.77 | 0.4166 | 186.1 | 315.81 | 0.6831 | 0.9781 |
| | −18 | 223.1 | 208.40 | 66.47 | 0.4014 | 187.0 | 315.86 | 0.6852 | 0.9769 |
| | −16 | 231.3 | 216.60 | 66.17 | 0.3868 | 188.1 | 315.92 | 0.6873 | 0.9756 |
| | −14 | 239.8 | 225.10 | 65.87 | 0.3731 | 189.0 | 315.95 | 0.6894 | 0.9743 |
| | −12 | 248.7 | 234.00 | 65.56 | 0.3599 | 189.9 | 315.99 | 0.6916 | 0.9730 |
| | −10 | 257.6 | 242.90 | 65.25 | 0.3473 | 191.0 | 316.01 | 0.6937 | 0.9717 |
| | −8 | 266.9 | 252.20 | 64.93 | 0.3351 | 191.9 | 316.01 | 0.6958 | 0.9704 |
| | −6 | 276.3 | 261.6 | 64.62 | 0.3233 | 193.0 | 316.01 | 0.6979 | 0.9691 |

| Temp °F | Pressure | | Density | Specific volume | Enthalpy ¹⁾ | | Entropy ¹⁾ | |
|------------|----------|-------|--------------------|---------------------|------------------------|--------|-----------------------|--------|
| | psia | psig | lb/ft ³ | ft ³ /lb | Btu/lb | | Btu/(lb)(°R) | |
| | | | solid or liquid | vapor | solid or liquid | vapor | solid or liquid | vapor |
| −4 | 285.8 | 271.1 | 64.29 | 0.3119 | 193.9 | 315.99 | 0.7000 | 0.9678 |
| −2 | 295.7 | 281.0 | 63.96 | 0.3010 | 194.9 | 315.95 | 0.7022 | 0.9666 |
| + 0 | 305.8 | 291.1 | 63.63 | 0.2906 | 195.8 | 315.92 | 0.7043 | 0.9654 |
| 2 | 316.3 | 301.6 | 63.30 | 0.2805 | 196.9 | 315.88 | 0.7064 | 0.9642 |
| 4 | 327.0 | 312.3 | 62.97 | 0.2707 | 198.0 | 315.83 | 0.7085 | 0.9629 |
| 6 | 337.9 | 323.2 | 62.64 | 0.2613 | 198.9 | 315.76 | 0.7106 | 0.9616 |
| 8 | 349.0 | 334.3 | 62.30 | 0.2523 | 200.0 | 315.68 | 0.7127 | 0.9603 |
| 10 | 360.5 | 345.8 | 61.99 | 0.2436 | 200.9 | 315.59 | 0.7148 | 0.9589 |
| 12 | 372.2 | 357.5 | 61.69 | 0.2353 | 202.0 | 315.50 | 0.7169 | 0.9575 |
| 14 | 384.3 | 369.6 | 61.32 | 0.2273 | 203.0 | 315.40 | 0.7190 | 0.9561 |
| 16 | 396.5 | 381.8 | 61.02 | 0.2196 | 204.1 | 315.27 | 0.7211 | 0.9547 |
| 18 | 409.0 | 394.3 | 60.67 | 0.2122 | 205.2 | 315.13 | 0.7232 | 0.9533 |
| 20 | 421.9 | 407.2 | 60.32 | 0.2050 | 206.3 | 314.96 | 0.7253 | 0.9520 |
| 22 | 435.1 | 420.4 | 59.91 | 0.1980 | 207.4 | 314.80 | 0.7275 | 0.9507 |
| 24 | 448.7 | 434.0 | 59.57 | 0.1911 | 208.4 | 314.62 | 0.7297 | 0.9493 |
| 26 | 462.5 | 447.8 | 59.17 | 0.1845 | 209.5 | 314.42 | 0.7319 | 0.9479 |
| 28 | 476.6 | 461.9 | 58.78 | 0.1783 | 210.6 | 314.19 | 0.7341 | 0.9465 |
| 30 | 490.8 | 476.1 | 58.40 | 0.1722 | 211.7 | 313.90 | 0.7363 | 0.9450 |
| 32 | 505.5 | 490.8 | 58.02 | 0.1663 | 212.8 | 313.58 | 0.7385 | 0.9434 |
| 34 | 520.5 | 505.8 | 57.59 | 0.1602 | 214.0 | 313.20 | 0.7407 | 0.9417 |
| 36 | 536.0 | 521.3 | 57.12 | 0.1542 | 215.1 | 312.77 | 0.7429 | 0.9399 |
| 38 | 551.7 | 537.0 | 56.70 | 0.1482 | 216.4 | 312.28 | 0.7452 | 0.9380 |
| 40 | 567.7 | 553.0 | 56.29 | 0.1425 | 217.4 | 311.76 | 0.7475 | 0.9360 |
| 42 | 584.0 | 569.3 | 55.89 | 0.1372 | 218.7 | 311.20 | 0.7598 | 0.9340 |
| 44 | 600.8 | 586.1 | 55.44 | 0.1321 | 220.0 | 310.63 | 0.7521 | 0.9321 |
| 46 | 617.8 | 603.1 | 54.95 | 0.1273 | 221.2 | 310.05 | 0.7544 | 0.9302 |
| 48 | 635.2 | 620.5 | 54.43 | 0.1226 | 222.5 | 309.47 | 0.7568 | 0.9283 |
| 50 | 652.9 | 638.2 | 53.91 | 0.1181 | 223.7 | 308.90 | 0.7593 | 0.9264 |
| 52 | 671.2 | 656.5 | 53.45 | 0.1138 | 225.0 | 308.32 | 0.7618 | 0.9246 |
| 54 | 689.7 | 675.0 | 52.95 | 0.1095 | 226.4 | 307.75 | 0.7643 | 0.9227 |
| 56 | 708.6 | 693.9 | 52.37 | 0.1054 | 227.7 | 307.13 | 0.7668 | 0.9207 |
| 58 | 727.9 | 713.2 | 51.81 | 0.1014 | 229.1 | 306.49 | 0.7694 | 0.9187 |
| 60 | 747.6 | 732.9 | 51.17 | 0.09752 | 230.6 | 305.78 | 0.7720 | 0.9166 |
| 62 | 767.7 | 753.0 | 50.47 | 0.09372 | 232.0 | 305.03 | 0.7746 | 0.9145 |
| 64 | 788.3 | 773.6 | 49.78 | 0.08999 | 233.5 | 304.22 | 0.7773 | 0.9123 |
| 66 | 809.3 | 794.6 | 49.08 | 0.08631 | 235.1 | 303.35 | 0.7801 | 0.9100 |
| 68 | 830.8 | 816.1 | 48.39 | 0.08261 | 236.7 | 302.45 | 0.7830 | 0.9077 |
| 70 | 852.7 | 838.0 | 47.62 | 0.07894 | 238.3 | 301.52 | 0.7861 | 0.9053 |
| 72 | 875.0 | 860.3 | 46.80 | 0.07535 | 240.3 | 300.51 | 0.7894 | 0.9030 |
| 74 | 897.8 | 883.1 | 45.90 | 0.07173 | 242.1 | 299.39 | 0.7930 | 0.9006 |
| 76 | 921.1 | 906.4 | 44.94 | 0.06811 | 244.3 | 298.10 | 0.7970 | 0.8982 |
| 78 | 945.1 | 930.4 | 43.90 | 0.06411 | 246.4 | 296.57 | 0.8013 | 0.8957 |
| 80 | 969.5 | 954.8 | 42.67 | 0.06013 | 248.9 | 294.75 | 0.8060 | 0.8924 |
| 82 | 994.5 | 979.8 | 41.23 | 0.05603 | 251.5 | 292.46 | 0.8112 | 0.8881 |
| 84 | 1020 | 1005 | 39.59 | 0.05171 | 254.7 | 289.67 | 0.8170 | 0.8821 |
| 86 | 1046 | 1031 | 37.03 | 0.04711 | 259.0 | 285.64 | 0.8249 | 0.8737 |
| 87.9 | 1071 | 1056 | 29.21 | 0.03423 | 272.7 | 272.70 | 0.8483 | 0.8483 |

¹⁾ Based on 0 for the perfect crystal at absolute zero temperature, −459.67 °F (−273.15 °C).

²⁾ Inches of mercury below atmospheric pressure.

Table 4—Thermodynamic properties of saturated carbon dioxide solid, liquid, and vapor phases (SI units)

| Temp °C | | Pressure | | Density | Specific volume | Enthalpy ¹⁾ | | Entropy | |
|------------------|-------|-----------------|--------------|--------------------|---------------------------------------|------------------------|-------|--------------------|-------|
| | | kPa absolute | kPa gauge | kg/m ³ | m ³ /kg x 10 ⁻³ | kJ/kg | | kJ/(kg)(K) | |
| | | | | solid or liquid | vapor | solid or liquid | vapor | solid or liquid | vapor |
| Solid and Vapor | -102 | 11.36 | -89.97 | 1597 | 2837 | 123.5 | 710.1 | 1.415 | 4.841 |
| | -100 | 13.97 | -87.36 | 1595 | 2327 | 125.8 | 711.3 | 1.428 | 4.809 |
| | -98 | 17.15 | -84.18 | 1593 | 1916 | 128.2 | 712.4 | 1.442 | 4.777 |
| | -96 | 20.95 | -80.38 | 1591 | 1583 | 130.5 | 713.6 | 1.455 | 4.746 |
| | -94 | 25.49 | -75.84 | 1588 | 1314 | 132.9 | 714.8 | 1.469 | 4.716 |
| | -92 | 30.89 | -70.44 | 1585 | 1095 | 135.3 | 715.9 | 1.482 | 4.687 |
| | -90 | 37.27 | -64.06 | 1582 | 917.3 | 137.7 | 717.1 | 1.495 | 4.658 |
| | -88 | 44.76 | -56.57 | 1579 | 771.9 | 140.2 | 718.2 | 1.508 | 4.630 |
| | -86 | 53.53 | -47.80 | 1576 | 651.3 | 142.6 | 719.3 | 1.521 | 4.603 |
| | -84 | 63.77 | -37.56 | 1573 | 550.7 | 145.1 | 720.4 | 1.534 | 4.376 |
| | -82 | 75.72 | -25.61 | 1569 | 467.1 | 147.6 | 721.4 | 1.548 | 4.550 |
| | -80 | 89.62 | -11.71 | 1565 | 397.7 | 150.1 | 722.4 | 1.561 | 4.523 |
| | -78.5 | 101.3 | 0.0 | 1562 | 354.7 | 152.1 | 723.1 | 1.569 | 4.504 |
| | -78 | 105.7 | 4.4 | 1561 | 339.8 | 152.7 | 723.4 | 1.574 | 4.498 |
| | -76 | 124.2 | 22.9 | 1558 | 291.1 | 155.3 | 724.4 | 1.586 | 4.473 |
| | -74 | 145.6 | 44.3 | 1554 | 249.9 | 157.9 | 725.4 | 1.599 | 4.449 |
| | -72 | 170.0 | 68.7 | 1549 | 215.1 | 160.5 | 726.3 | 1.612 | 4.425 |
| | -70 | 198.1 | 96.8 | 1545 | 185.7 | 163.1 | 727.1 | 1.625 | 4.402 |
| | -68 | 230.2 | 128.9 | 1541 | 160.8 | 165.8 | 727.7 | 1.638 | 4.378 |
| | -66 | 267.0 | 165.7 | 1536 | 139.5 | 168.4 | 728.1 | 1.651 | 4.353 |
| | -64 | 308.9 | 207.6 | 1532 | 121.1 | 171.1 | 728.4 | 1.664 | 4.328 |
| | -62 | 356.7 | 255.4 | 1527 | 105.1 | 173.9 | 728.6 | 1.677 | 4.304 |
| | -60 | 409.8 | 308.5 | 1522 | 91.23 | 176.7 | 728.7 | 1.690 | 4.281 |
| | -58 | 467.1 | 365.8 | 1517 | 81.00 | 179.5 | 728.8 | 1.703 | 4.262 |
| | -56.6 | 518.0 | 416.7 | 1513 | 72.22 | 181.4 | 729.0 | 1.722 | 4.250 |
| Triple point | | | | | | | | | |
| Liquid and Vapor | -56.6 | 518.0 | 416.7 | 1178 | 72.22 | 380.5 | 729.0 | 2.641 | 4.250 |
| | -56 | 531.7 | 430.4 | 1176 | 71.10 | 381.5 | 729.1 | 2.643 | 4.244 |
| | -54 | 578.9 | 477.6 | 1168 | 64.72 | 385.2 | 729.5 | 2.659 | 4.229 |
| | -52 | 629.5 | 528.2 | 1161 | 59.78 | 388.9 | 729.8 | 2.675 | 4.215 |
| | -50 | 683.6 | 582.3 | 1154 | 55.41 | 392.5 | 730.2 | 2.691 | 4.203 |
| | -48 | 741.0 | 639.7 | 1146 | 51.36 | 396.2 | 730.6 | 2.707 | 4.192 |
| | -46 | 801.9 | 700.6 | 1139 | 47.63 | 399.9 | 731.1 | 2.723 | 4.181 |
| | -44 | 866.3 | 865.0 | 1131 | 44.20 | 403.7 | 731.5 | 2.739 | 4.170 |
| | -42 | 934.3 | 833.0 | 1123 | 41.05 | 407.5 | 732.0 | 2.756 | 4.160 |
| | -40 | 1006 | 904.7 | 1115 | 38.16 | 411.3 | 732.4 | 2.772 | 4.149 |
| | -38 | 1082 | 981 | 1107 | 35.52 | 415.1 | 732.9 | 2.788 | 4.139 |
| | -36 | 1162 | 1061 | 1099 | 33.11 | 419.0 | 733.3 | 2.803 | 4.129 |
| | -34 | 1246 | 1145 | 1091 | 30.90 | 422.9 | 733.7 | 2.819 | 4.119 |
| | -32 | 1335 | 1234 | 1083 | 28.87 | 426.8 | 734.1 | 2.835 | 4.109 |
| | -30 | 1429 | 1328 | 1074 | 27.00 | 430.8 | 734.4 | 2.851 | 4.100 |
| | -28 | 1527 | 1426 | 1066 | 25.27 | 434.8 | 734.7 | 2.867 | 4.091 |
| | -26 | 1630 | 1529 | 1057 | 23.66 | 438.8 | 734.9 | 2.883 | 4.081 |
| | -24 | 1739 | 1638 | 1048 | 22.16 | 442.8 | 735.0 | 2.899 | 4.072 |
| | -22 | 1852 | 1751 | 1039 | 20.76 | 446.9 | 735.0 | 2.915 | 4.062 |
| | -20 | 1971 | 1870 | 1030 | 19.45 | 451.0 | 735.0 | 2.931 | 4.053 |
| | -18 | 2095 | 1994 | 1021 | 18.24 | 455.1 | 734.9 | 2.947 | 4.044 |
| | -16 | 2226 | 2125 | 1011 | 17.13 | 459.3 | 734.7 | 2.963 | 4.034 |
| | -14 | 2362 | 2261 | 1002 | 16.09 | 463.6 | 734.4 | 2.979 | 4.024 |

| Temp °C | | Pressure | | Density | Specific volume | Enthalpy ¹⁾ | | Entropy | |
|------------------|------|-----------------|--------------|--------------------|---------------------------------------|------------------------|-------|--------------------|-------|
| | | kPa absolute | kPa gauge | kg/m ³ | m ³ /kg x 10 ⁻³ | kJ/kg | | kJ/(kg)(K) | |
| | | | | solid or liquid | vapor | solid or liquid | vapor | solid or liquid | vapor |
| Liquid and Vapor | -12 | 2503 | 2402 | 991.9 | 15.11 | 467.8 | 734.1 | 2.994 | 4.014 |
| | -10 | 2649 | 2548 | 982.0 | 14.19 | 472.2 | 733.6 | 3.010 | 4.004 |
| | -8 | 2804 | 2703 | 971.8 | 13.34 | 476.6 | 733.0 | 3.027 | 3.993 |
| | -6 | 2964 | 2863 | 961.5 | 12.54 | 481.1 | 732.2 | 3.043 | 3.983 |
| | -4 | 3131 | 3030 | 951.5 | 11.79 | 485.6 | 731.4 | 3.059 | 3.973 |
| | -2 | 3305 | 3204 | 940.7 | 11.07 | 490.3 | 730.5 | 3.076 | 3.962 |
| | 0.0 | 3485 | 3384 | 929.4 | 10.38 | 495.0 | 729.4 | 3.092 | 3.950 |
| | 2.0 | 3673 | 3572 | 917.4 | 9.703 | 499.8 | 727.7 | 3.109 | 3.937 |
| | 4.0 | 3869 | 3768 | 905.0 | 9.046 | 504.7 | 725.4 | 3.126 | 3.923 |
| | 6.0 | 4071 | 3970 | 892.1 | 8.435 | 509.8 | 723.1 | 3.143 | 3.908 |
| | 8.0 | 4282 | 4181 | 878.0 | 7.878 | 515.0 | 720.8 | 3.161 | 3.894 |
| | 10.0 | 4501 | 4400 | 863.6 | 7.375 | 520.4 | 718.5 | 3.179 | 3.879 |
| | 12.0 | 4730 | 4629 | 848.2 | 6.900 | 525.9 | 716.1 | 3.198 | 3.864 |
| | 14.0 | 4966 | 4865 | 831.9 | 6.446 | 531.6 | 713.5 | 3.217 | 3.849 |
| | 16.0 | 5210 | 5109 | 814.3 | 6.006 | 537.6 | 710.5 | 3.236 | 3.833 |
| | 18.0 | 5464 | 5363 | 795.5 | 5.577 | 543.8 | 707.2 | 3.256 | 3.817 |
| | 20.0 | 5727 | 5626 | 775.2 | 5.157 | 550.4 | 703.5 | 3.278 | 3.800 |
| | 22.0 | 6001 | 5900 | 753.6 | 4.745 | 557.8 | 699.4 | 3.303 | 3.783 |
| | 24.0 | 6285 | 6184 | 728.9 | 4.337 | 566.0 | 694.6 | 3.331 | 3.765 |
| | 26.0 | 6581 | 6480 | 696.4 | 3.914 | 575.4 | 688.2 | 3.364 | 3.745 |
| 28.0 | 6890 | 6789 | 655.7 | 3.460 | 586.3 | 679.1 | 3.403 | 3.710 | |
| 30.0 | 7211 | 7110 | 593.1 | 2.910 | 602.5 | 664.4 | 3.454 | 3.658 | |
| 31.1 | 7382 | 7281 | 467.9 | 2.137 | 634.3 | 634.3 | 3.552 | 3.552 | |

¹⁾ Based on 0 for the perfect crystal at zero kelvin (−273.15 °C).

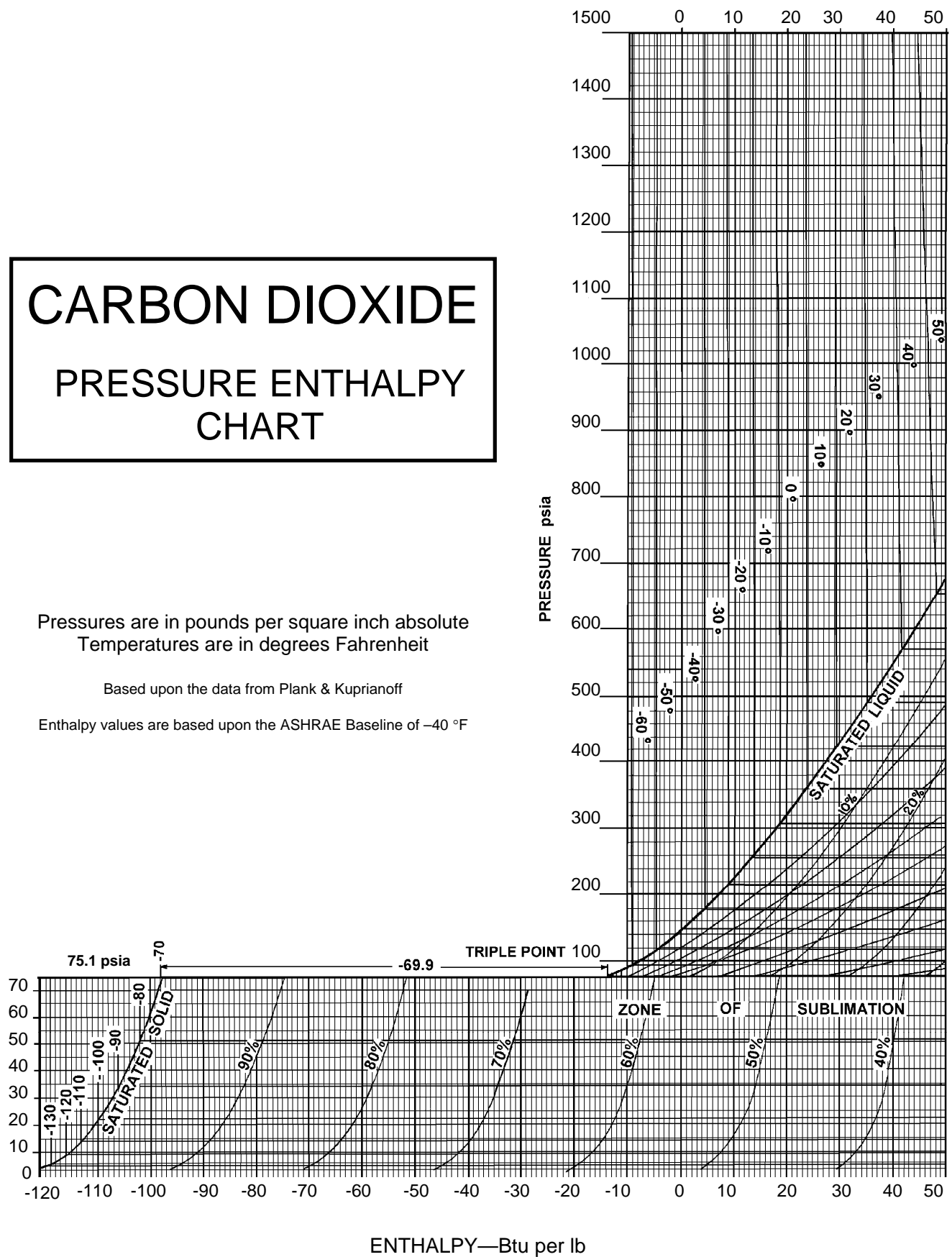
CARBON DIOXIDE

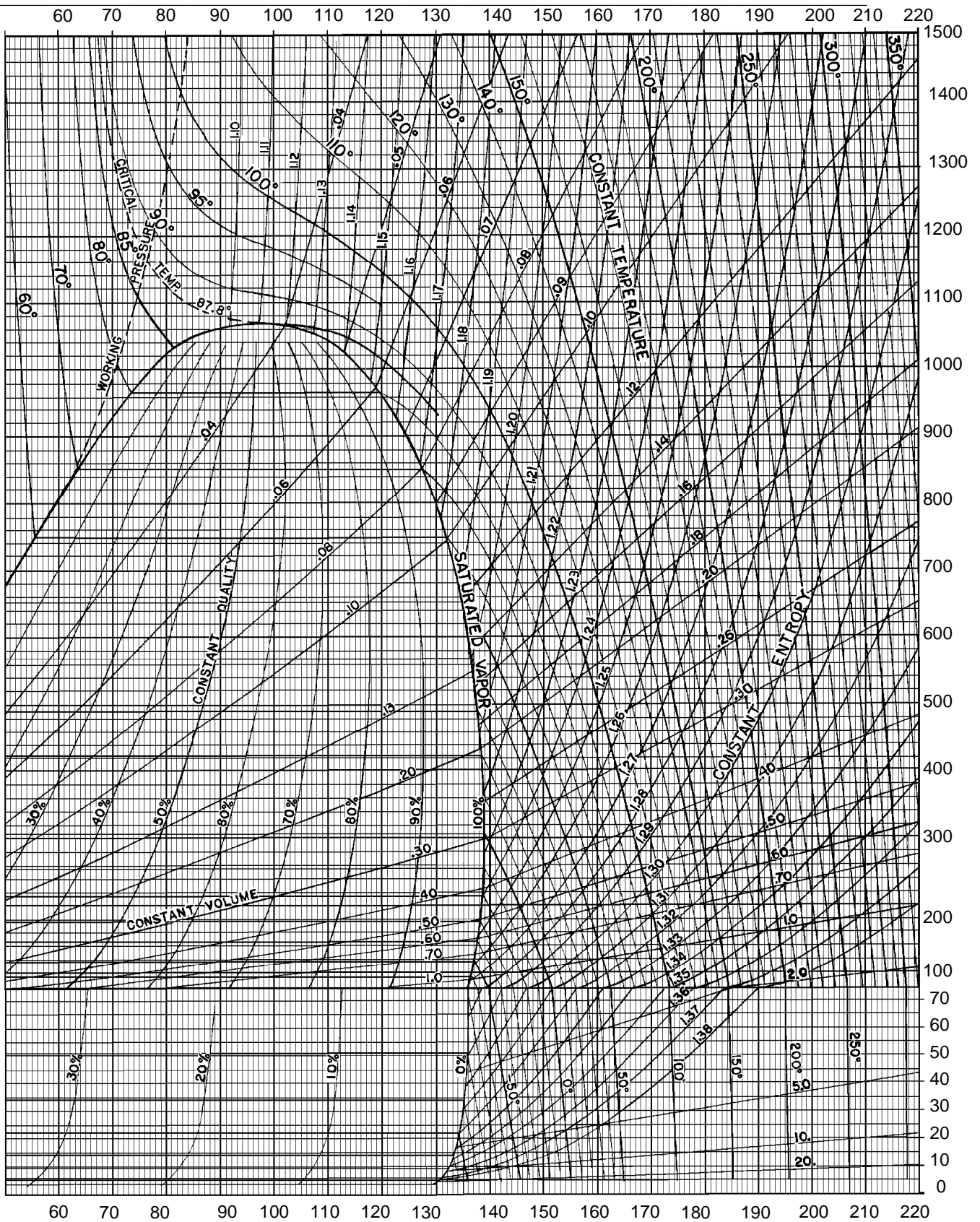
PRESSURE ENTHALPY CHART

Pressures are in pounds per square inch absolute
Temperatures are in degrees Fahrenheit

Based upon the data from Plank & Kuprianoff

Enthalpy values are based upon the ASHRAE Baseline of -40°F





ENTHALPY—Btu per lb

Figure 2b—Pressure enthalpy chart (Part 2)



Figure 3—Production of dry ice disks for airline food module refrigeration

5 Special hazards

5.1 General

Personnel handling liquid carbon dioxide should be thoroughly familiar with its associated hazards. There are several conditions in which extreme danger to personnel and equipment may exist. The following describes these conditions and offers procedures and guidelines to prevent dangerous conditions from developing.

5.2 Personal protective equipment

Always wear heavy gloves and eye protection when handling equipment containing vapor, liquid, and solid carbon dioxide. Contact between exposed skin and cold piping or carbon dioxide vapor can cause frost burns. Dry ice particles formed by depressurizing liquid carbon dioxide are extremely cold and can cause severe damage to unprotected eyes or skin.

5.3 Dry ice blocking

Liquid carbon dioxide in a hose or pipe flows like water. However, when the pressure is reduced below 75.1 psia (518 kPa, abs), the liquid changes into a mixture of vapor and solid carbon dioxide. Solid carbon dioxide, when formed in a pipe or hose, may create a plug and prevent depressurization that creates a safety hazard. The dry ice can be compacted into a plug that can trap gas.

The pressure behind or within a plug can increase as the dry ice sublimates until the plug is forcibly ejected or the hose or pipe ruptures. A dry ice plug can be ejected from any open end of a hose or pipe with enough force to cause serious injury to personnel, from the impact of the dry ice plug or the sudden whip of the hose or pipe as the plug ejects or both.

5.3.1 Liquid line depressurization

To prevent dry ice blockage, the liquid carbon dioxide must be purged from the hose or pipe with vapor greater than 200 psig (1380 kPa) before reducing the pressure below 75.1 psia (518 kPa, abs). This can be done by supplying carbon dioxide vapor to one end of the hose or piping system to maintain the pressure above the triple point while removing the liquid from the other end. This can be accomplished by using a crossover line.

5.3.2 Liquid line pressurization to prevent dry ice blockage when liquid is introduced

To prevent dry ice blocking, liquid piping must be pressurized with carbon dioxide gas to *more* than 200 psig (1380 kPa) before introducing liquid carbon dioxide.

Flexing elastomer hoses containing residual dry ice inside can lead to fracturing of the inner liner, which can lead to catastrophic failure.

5.3.3 Low temperature effects on materials

Depressurization of a liquid carbon dioxide system can result in low temperature liquid carbon dioxide and/or the formation of dry ice placing the container, piping, and hoses in an upset condition below the system design temperatures. For further information, see CGA G-6.7, *Safe Handling of Liquid Carbon Dioxide Containers That Have Lost Pressure* [6].

Many materials safe to use at normal liquid carbon dioxide temperatures may become brittle and fail if stressed when subjected to dry ice temperatures ($-109.3\text{ }^{\circ}\text{F}$ [$-78.5\text{ }^{\circ}\text{C}$]). Materials used in the construction of carbon dioxide transfer systems including hoses must be compatible with carbon dioxide and the temperature and pressure conditions encountered.

Piping systems subject to operating temperatures below ambient will contract. Allowances shall be made in piping and support systems to compensate for these changes in dimensions. Commonly used copper tubing will shrink approximately 1 in (2.5 cm) per 100 ft (30.5 m) for every $100\text{ }^{\circ}\text{F}$ ($55.6\text{ }^{\circ}\text{C}$) reduction in temperature.

For further information on piping systems, see G-6.1, *Standard for Insulated Liquid Carbon Dioxide Systems at Consumer Sites* [7].

5.4 Cylinders

Carbon dioxide cylinders are currently fabricated from steel or aluminum with a minimum rated service pressure of 1800 psig (124 bar). The U.S. Department of Transportation (DOT) and Transport Canada (TC) are the recognized regulatory agencies in the United States and Canada that regulate the manufacture of carbon dioxide cylinders [8, 9]. Typical dimensions and capacities of the most commonly used carbon dioxide cylinders are listed in Table 5.

Aluminum cylinders subjected to heat or fire shall not be used again. Temperatures in excess of $350\text{ }^{\circ}\text{F}$ ($177\text{ }^{\circ}\text{C}$) will irreversibly change the properties of the aluminum and the cylinder must be condemned. If there is any evidence or suspicion of exposure to excessive heat, condemn the cylinder.

5.5 Trapped liquid

When liquid carbon dioxide is forced to occupy a fixed volume such as between two closed valves or within a valve, its pressure will increase as it warms and expands. As long as there is vapor space in the valve or pipe, the pressure rises about 5 psi per $^{\circ}\text{F}$ (62 kPa per $^{\circ}\text{C}$). When the pipe or valve becomes liquid full, the hydrostatic pressure rises at the rate of 850 psi per $^{\circ}\text{F}$ (10 550 kPa per $^{\circ}\text{C}$). As the temperature continues to increase, the pressure of the trapped liquid can exceed what the piping and hoses can withstand. This will cause rupture of the hose or piping with possible injury and property damage.

To prevent trapped liquid from becoming a hazard, all liquid carbon dioxide piping and transfer lines shall be equipped with pressure relief devices located in all parts of the system in which liquid can be trapped such as between valves, check valves, and pumps. These pressure relief devices shall be set to discharge within the design pressure of the part of the system they protect and should discharge into a well-ventilated area (see CGA G-6.5, *Standard for Small, Stationary, Insulated Carbon Dioxide Supply Systems*) [10].

To prevent trapped liquid from becoming a hazard in ball- and gate-type valves, they shall be adequately designed to prevent liquid carbon dioxide from being trapped within the valve.

Table 5—Typical dimensions and capacities of carbon dioxide cylinders

| Nominal carbon dioxide capacity lb | Internal volume in³ | Water weight capacity lb | Overall length in | Outside diameter in |
|---|---|---|----------------------------------|------------------------------------|
| 0.22 (3.5 oz) | 9 | 0.32 | 5.3 | 2.0 |
| 0.45 (7 oz) | 18 | 0.65 | 9.4 | 2.0 |
| 0.66 (10.5 oz) | 27 | 0.97 | 13.0 | 2.0 |
| 0.75 (12 oz) | 31 | 1.1 | 9.4 | 2.5 |
| 1.0 | 41 | 1.5 | 7.8 | 3.2 |
| 1.25 | 51 | 1.6 | 9.4 | 3.2 |
| 1.5 | 61 | 2.2 | 11.1 | 3.2 |
| 1.75 | 71 | 2.6 | 12.5 | 3.2 |
| 2 | 84 | 3.0 | 9.3 | 4.4 |
| 5 | 205 | 7.4 | 14.8 | 5.3 |
| 10 | 408 | 14.7 | 16.8 | 6.9 |
| 15 | 612 | 22.1 | 23.4 | 6.9 |
| 20 | 816 | 29.4 | 23.6 | 8.0 |
| 35 | 1429 | 51.5 | 38.6 | 8.0 |
| 50 | 2040 | 73.5 | 46.6 | 8.6 |
| 50 | 2370 | 85.2 | 51 | 8.5 |
| 50 or 60 | 2675 | 96.0 | 51 | 9.0 |
| 75 | 3055 | 110.3 | 56 | 9.3 |
| 100 | 4080 | 147.3 | 58 | 10.6 |

5.6 Personnel overexposure

When carbon dioxide is used in an enclosed area, it is necessary to ventilate the area adequately to maintain a safe working environment for personnel. Carbon dioxide in the gaseous state is colorless, odorless, and not easily detected. Gaseous carbon dioxide is 1.5 times denser than air and will, therefore, be found in greater concentrations at low elevations. Ventilation systems should be designed to exhaust from the lowest elevation and allow make-up air to enter at a higher elevation. Do not depend solely on measuring the oxygen content of the air because higher concentrations of carbon dioxide can be dangerous, even with adequate oxygen for life support. For additional information, see 6.2.

5.7 Overfilling containers

When liquid carbon dioxide is stored in a container with no product withdrawal, heat leak causes the temperature and pressure to rise and the liquid to expand. As long as there is vapor space in the container, the pressure rises about 5 psi per °F (62 kPa per °C). When the container becomes liquid full, the hydrostatic pressure rises at the rate of 850 psi per °F (10 550 kPa per °C). Table 6 and Figure 4 illustrate this phenomenon with data for pressure rise in a container originally filled to 93% with –20 °F (–28.9 °C) liquid carbon dioxide. Although storage containers are generally equipped with refrigeration systems to maintain the liquid temperature at 0 °F (–17.8 °C), power failures can occur. Small and portable containers are not equipped with refrigeration; all storage containers can potentially become liquid full.

To prevent undue stresses to the container and nuisance cycling of the pressure relief device with consequent product loss, liquid carbon dioxide storage containers should not be filled to a level that allows them to become liquid full before reaching the pressure relief device setting, which is generally 350 psig (2410 kPa).

The safe filling level depends on the temperature of the liquid being transferred into the container. The colder the liquid, the more vapor space required for liquid expansion. Figure 4 shows safe filling levels for a range of liquid temperatures. Filling above this line leads to an overfilled condition. Please note that Figure 4 only applies to filling of insulated containers with pressure relief devices set at 350 psig (2410 kPa) or less. Those

quantities would be a significant overfill of uninsulated high pressure cylinders and also would exceed the maximum filling density allowed for DOT-4L/TC-4LM containers with pressure relief devices set above 350 psig (2410 kPa). DOT tables for filling density go as high as a maximum 625 psig (4310 kPa) pressure relief device setting with an 86% maximum filling density (see 173.304a(e)(2)[8]. For TC, the table in CSA B340, *Selection and Use of Cylinders, Spheres, Tubes, and Other Containers for the Transportation of Dangerous Goods, Class 2*, goes up to a 4300 kPa pressure control valve setting at 86% maximum filling density [11].

Table 6—Volume expansion upon warming of liquid carbon dioxide saturated at 200 psig (1380 kPa) for a container with a 350 psig (2410 kPa) MAWP

| Pressure | | Temperature | | Volume occupied by liquid carbon dioxide ¹⁾ |
|----------|------|-------------|--------------|--|
| psig | kPa | °F | °C | % |
| 200 | 1380 | −20 | −28.9 | 92.6 |
| 210 | 1450 | −18 | −27.8 | 93.1 |
| 220 | 1520 | −15 | −26.1 | 93.5 |
| 230 | 1590 | −13 | −25.0 | 94.1 |
| 240 | 1650 | −11 | −23.9 | 94.6 |
| 250 | 1720 | −8 | −22.2 | 95.1 |
| 260 | 1790 | −6 | −21.1 | 95.6 |
| 270 | 1860 | −4 | −20.0 | 96.1 |
| 280 | 1930 | −2 | −18.9 | 96.6 |
| 290 | 2000 | 0 | −17.8 | 97.1 |
| 300 | 2070 | 2 | −16.7 | 97.6 |
| 310 | 2140 | 4 | −15.6 | 98.1 |
| 320 | 2210 | 5 | −15.0 | 98.6 |
| 330 | 2280 | 7 | −13.9 | 99.0 |
| 340 | 2340 | 9 | −12.8 | 99.5 |
| 350 | 2410 | <u>11</u> | <u>−11.7</u> | 100.0 |

¹⁾ The percent liquid full is the percent of total vessel volume and should not be confused with the liquid level gauge reading.

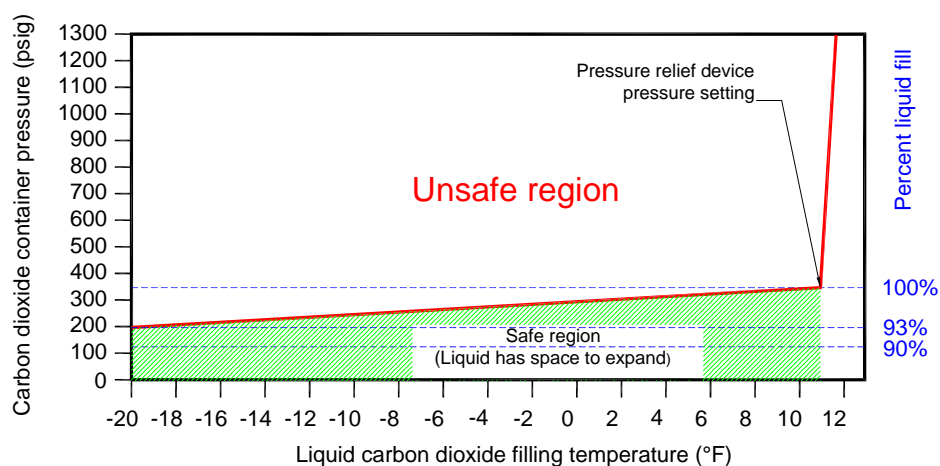


Figure 4—Safe filling volumes for 350 psig carbon dioxide containers

5.8 **Static electricity**

The manufacturing of solid dry ice produces static electricity charges (> 100 000 volts). This may lead to a discharge of the static electricity to any grounded object or person.

Use of carbon dioxide snow or solid dry ice in combustible environments should be carefully evaluated. Liquid carbon dioxide should not be used for inerting combustible atmospheres because of the extremely high static charges produced during the formation of dry ice. Gaseous carbon dioxide can be used for inerting combustible atmospheres without the risk of generating static charges. See CGA SB-33, *Static Electricity Hazards of Liquid or Solid Carbon Dioxide* for additional information [12].

6 **Physiological effects of carbon dioxide**

6.1 **General**

The physiological effects of carbon dioxide are unique because it is a product of normal metabolism, a requirement of the body's normal internal chemical environment, and an active messenger substance in the linking of respiration, circulation, and vascular response to the demands of metabolism both at rest and in exercise.

The respiratory control system maintains carbon dioxide pressure at a relatively high level of about 50 mm Hg pressure in the arterial blood and tissue fluids. This maintains the acidity of the tissue and cellular fluids at the proper level for essential metabolic reactions and membrane functions. Changes in the normal carbon dioxide tissue pressure can be damaging. If tissue pressure becomes excessively low, which can occur from hyperventilation, failure of critical neuromuscular function or loss of consciousness can occur.

Inhaled carbon dioxide produces the same physiological effects as metabolically produced carbon dioxide. As the carbon dioxide tissue pressure rises from inhaling carbon dioxide, the body responds by using respiratory and adaptive processes to adjust to the change. These adaptive processes are limited and cannot cope with severe exposures, which cause pH change to the body fluids. Toxic effects of carbon dioxide, namely severe and disruptive acidosis, occur when high concentrations of carbon dioxide are inhaled.

The blood and cellular fluids are actually solutions of sodium bicarbonate containing numerous other substances. Severe exposure to carbon dioxide forms carbonic acid in the blood for which the sodium bicarbonate is not very effective as a buffer. The decrease in pH has a rapid toxic effect because the neural control systems are excessively driven. It is important to note that these effects are independent of the amount of oxygen in the atmosphere being breathed.

The effects produced by low and moderate concentrations of carbon dioxide are physiological and reversible, *but the effects of high concentrations are toxic and damaging* [13].

6.2 **Physiological effects of carbon dioxide**

The response to carbon dioxide inhalation depends on degree and duration of exposure, and it varies greatly even in healthy, normal individuals. The medical term for the physiological effects of excess carbon dioxide in the blood is hypercapnia. Carbon dioxide can be toxic even when normal oxygen levels are present. Low concentrations of inspired carbon dioxide can be tolerated for a considerable period of time without noticeable effect, or may merely cause an unnatural feeling of shortness of breath. Sustained exposure to 5% carbon dioxide produces stressful rapid breathing. When the level of inspired carbon dioxide exceeds 7%, the rapid breathing becomes labored (dyspnea) and restlessness, faintness, severe headache, and dulling of consciousness occur. At 15%, unconsciousness accompanied by rigidity and tremors occurs in less than 1 minute, and in the 20% to 30% range it produces unconsciousness and convulsions in less than 30 seconds. The reason these effects occur quickly is that carbon dioxide diffuses in the tissue fluids at a rate approximately 20 times more rapidly than oxygen. High concentrations of carbon dioxide can asphyxiate quickly without warning and with no possibility of self-rescue regardless of the oxygen concentration.

6.3 **Physical effects of overexposure to carbon dioxide**

Skin, mouth, or eye contact with solid carbon dioxide that has a temperature of -109.3°F (-78.5°C) can cause severe frostbite, skin lesions, corneal burn, or more serious injury from deep-freezing of the tissues. Liquid dis-

charging from a container produces high velocity carbon dioxide snow particles that are abrasive in addition to being cold and will cause similar injuries.

6.4 Regulatory standards

Carbon dioxide is present in the atmosphere at about 350 ppm (0.035%) by volume. The Occupational Safety and Health Administration (OSHA) standard, found in Title 29 of the U.S. *Code of Federal Regulations* (29 CFR) 1910.1000, specifies that employee exposure to carbon dioxide in any 8-hour shift of a 40-hour work-week shall not exceed the 8-hour time-weighted average (TWA-PEL) of 5000 ppm (0.5%) (9000 mg/m³) [14]. According to the American Conference of Governmental Industrial Hygienists (ACGIH), the short-term exposure limit (STEL/Ceiling) for 15 minutes or less is 30 000 ppm (3%) (54 000 mg/m³) [15]. In Canada, similar limits are mandated by provincial legislation.

6.5 Safety precautions

Appropriate warning signs should be placed at the entrance to confined areas where high concentrations of carbon dioxide gas can accumulate. A typical warning is shown below:

CAUTION—CARBON DIOXIDE GAS
Ventilate the area before entering. A high carbon dioxide gas concentration can occur in this area and can cause asphyxiation.

Carbon dioxide monitoring should be carried out before entering any confined space or low area in which carbon dioxide gas may have accumulated. The carbon dioxide shall be removed by ventilation to a concentration below 3% or a supplied-air respirator shall be donned before entering the confined space or low area (see CGA SB-15, *Avoiding Hazards in Confined Work Spaces During Maintenance, Construction and Similar Activities*) [16].

6.6 Rescue and first aid

Do not attempt to remove anyone exposed to high concentrations of carbon dioxide without using proper rescue equipment or you may also become a casualty. Rescuers account for over 60% of confined space fatalities. If the exposed person is unconscious, obtain assistance and use established emergency procedures.

If a person has inhaled large amounts of carbon dioxide and is exhibiting adverse effects, move the exposed individual to fresh air at once. If breathing has stopped, perform artificial respiration. Only qualified personnel may give oxygen to the victim. Keep the affected person warm and at rest. Get medical attention as soon as possible. Fresh air and assisted breathing is appropriate for all cases of overexposure to gaseous carbon dioxide. With prompt response to a carbon dioxide emergency, recovery is usually complete and uneventful.

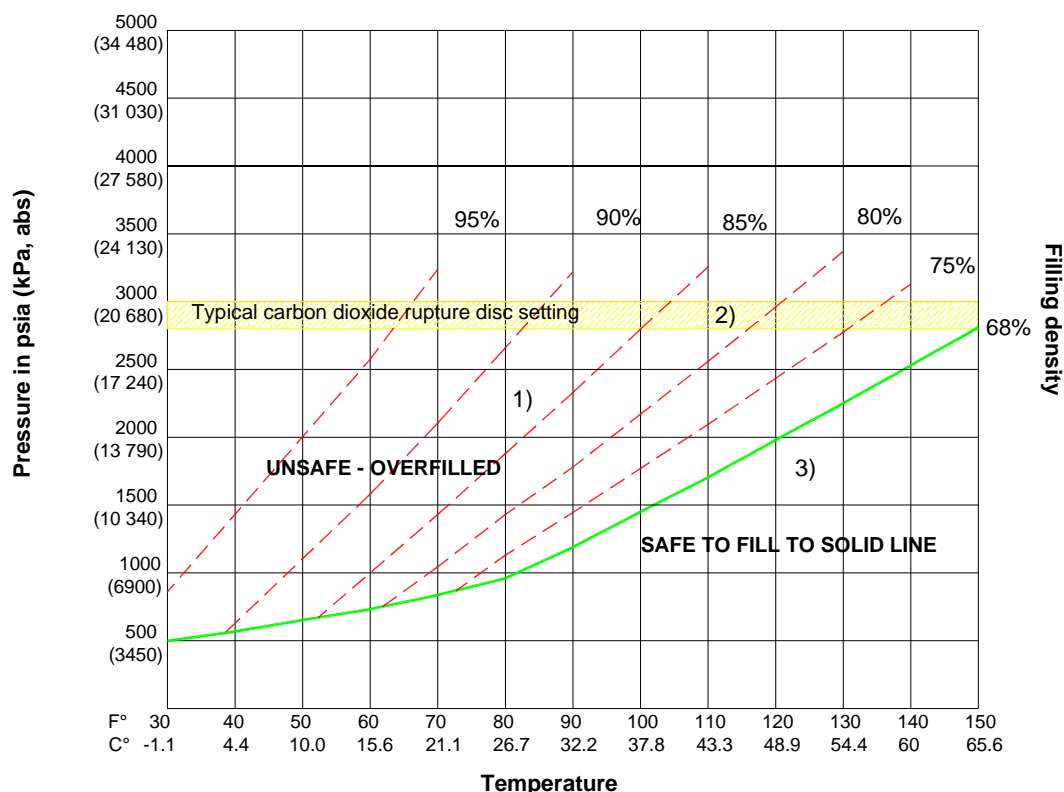
If dry ice or compressed carbon dioxide gas comes in contact with the skin or mouth, stop the exposure immediately. If frostbite has occurred, obtain medical attention. Do not rub the area. Immerse in warm water, 100 °F to 105 °F (37.8 °C to 40.6 °C).

7 Transportation of carbon dioxide

7.1 General

Cylinders and containers used for the transportation of carbon dioxide are either insulated or uninsulated. Insulated liquid containers commonly have a working pressure between 200 psig and 500 psig (1380 kPa and 3450 kPa). They may be refrigerated to compensate for heat gained by the contents during transport. These containers include insulated liquid cylinders, tank cars, portable tanks, and cargo tanks.

Uninsulated cylinders have a design pressure that will safely contain carbon dioxide at normal ambient temperatures. The pressure in these cylinders varies with ambient temperature (see Figure 5).



NOTE—This chart is based upon a cylinder filled to its correct maximum liquid carbon dioxide capacity of 68% of the total volume (water weight capacity). An overfilled cylinder obviously experiences enormous internal pressures from expansion of the liquid carbon dioxide as it warms to higher temperatures after filling.

- 1) Dashed lines indicate temperature-pressure relationship when the cylinder is overfilled.
- 2) A correctly installed carbon dioxide cylinder rupture disk functions at 2800 psig to 3000 psig (19 310 kPa to 20 680 kPa) depending on design.
- 3) Maximum permitted filling capacity is 68%.

Figure 5—Approximate pressure in carbon dioxide cylinders filled to indicated densities at selected temperature

The product shipping names and product identification numbers for the three forms of carbon dioxide shipped are carbon dioxide, UN 1013; carbon dioxide, refrigerated liquid, UN 2187; and carbon dioxide, solid or dry ice, UN 1845.

The DOT and TC hazard classification for carbon dioxide and carbon dioxide refrigerated liquid is 2.2 (non-flammable gas). Under DOT, carbon dioxide solid is Class 9 (miscellaneous hazardous materials) when transported by air or water and unclassified when transported by rail or highway. In Canada, it is Class 9 (miscellaneous dangerous goods) regardless of mode of transportation.

CGA's recommended hazard ratings for carbon dioxide gas and liquid are as follows in accordance with the National Fire Protection Association (NFPA) rating system and the National Paint and Coatings Association's (NPCA) Hazardous Material Identification System, Third Edition (HMIS® III) as referenced in CGA P-19 *CGA Recommended Hazard Ratings for Compressed Gases* and CGA P-24 *Guide to the Preparation of Material Safety Data Sheets* [17, 18, 19, 20]:

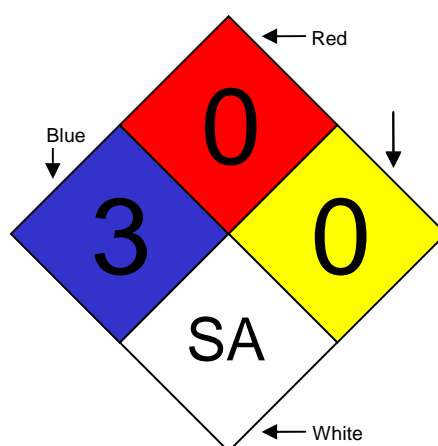
| NFPA ¹⁾ | | HMIS® III ¹⁾ | |
|--------------------|---|-------------------------|---|
| Gas | | Gas | |
| Health | 1 | Health | 1 |
| Flammability | 0 | Flammability | 0 |
| Instability | 0 | Physical Hazard | 3 |

| | | | |
|--------------|------------------|-----------------|----------|
| Special | SA ²⁾ | | |
| Liquid | | Liquid | |
| Health | 3 | Health | 3 |
| Flammability | 0 | Flammability | 0 |
| Instability | 0 | Physical Hazard | <u>2</u> |
| Special | SA ²⁾ | | |
| Solid | | Solid | |
| Health | 3 | Health | 3 |
| Flammability | 0 | Flammability | 0 |
| Instability | 0 | Physical Hazard | <u>0</u> |
| Special | SA ²⁾ | | |

¹⁾ CGA's recommended rating of carbon dioxide using NFPA's rating system and HMIS[®] III.

²⁾ CGA recommends SA to designate a simple asphyxiant.

For an example of an NFPA hazard label, see Figure 6.



Copyright © 2002, 13th Edition, National Fire Protection Association, Quincy, MA 02269. This warning system is intended to be interpreted and applied only by properly trained individuals to identify fire, health, and stability hazards of chemicals. The user is referred to the recommended classifications of certain chemicals in the NFPA *Fire Protection Guide to Hazardous Materials*, which should be used as a guideline only [21]. Whether the chemicals are classified by NFPA or not, anyone using the NFPA 704 system to classify chemicals does so at their own risk [17].

Figure 6—NFPA hazard label for liquid carbon dioxide
Yellow

7.2 Regulations applying to containers and cylinders

In the United States, the transportation of carbon dioxide in interstate commerce by rail, highway, air, and water is governed by federal authority under regulations promulgated by DOT [8]. In Canada, TC regulates all modes of transport through the *Transportation of Dangerous Goods Act and Regulations* [9]. The Canadian Regulations adopt these standards:

- For rail transport
 - Canadian General Standards Board CGSB 43.147–2005, *Construction, Modification, Qualification, Maintenance, and Selection and Use of Means of Containment for the Handling, Offering for Transport, or Transporting of Dangerous Goods by Rail* [22];
- For cylinder shipments
 - CSA B339, *Cylinders, Spheres, and Tubes for the Transportation of Dangerous Goods* [23]
 - CSA B340 [11]; and
- For bulk shipments by road
 - CSA B620, *Highway Tanks and Portable Tanks for the Transportation of Dangerous Goods* [24]

- CSA B622, *Selection and Use of Highway Tanks, Multi-Unit Tank Car Tanks, and Portable Tanks for the Transportation of Dangerous Goods, Class 2* [25].

The specifications of these regulatory authorities require, among other things, that the materials used for carbon dioxide containers and cylinders meet certain chemical and physical requirements, pass specified hydrostatic pressure tests, and be protected by adequate pressure relief devices.

7.3 Uninsulated cylinders

7.3.1 General

Uninsulated steel cylinders shall comply with DOT specifications 3, 3A-1800, 3AX-1800, 3AA-1800, 3AAX-1800, 3E1800, 3T1800, 3HT2000, or 39. Aluminum cylinders shall comply with DOT-3AL1800.

In Canada, uninsulated steel cylinders shall comply with TC specifications TC-3AM138, CTC-3A1800, TC-3AXM138, CTC-3AX1800, TC-3AAM138, CTC-3AA1800, TC-3AAXM138, CTC-3AAX1800, TC-3EM124, CTC-3E1800, ICC-3, TC-3TM138, TC-39M, CTC-39, TC-3HTM138, CTC-3HT2000, or TC-3ASM138. Aluminum cylinders shall comply with specifications TC-3ALM124 or CTC-3AL1800. Since 1993, Canadian cylinders have been made to metric units as indicated by the letter M in the specification with the service pressure expressed in bar. One bar equals 100 kPa, or approximately 14.5 psi.

7.3.2 Cylinder valves

Carbon dioxide cylinder valve connection standards have been adopted by CGA and recognized as United States and Canadian standards [26]. Carbon dioxide cylinders use a CGA 320 outlet connection. Small medical carbon dioxide cylinders equipped with a yoke-type valve use a CGA 940 outlet connection.

7.3.3 Cylinder pressure relief devices

Carbon dioxide cylinders, with certain exceptions, shall be equipped with pressure relief devices designed to release excessive pressure that can occur from overfilling, exposure to fire, or high temperatures. The minimum permissible service pressure rating for uninsulated cylinders in carbon dioxide service is 1800 psig (12 410 kPa). They shall have a rupture disk designed to rupture at no higher than the minimum required test pressure of the cylinder (e.g. 5/3 of the service pressure for DOT cylinders). Details of pressure relief device requirements are in CGA S-1.1, *Pressure Relief Device Standards—Part 1—Cylinders for Compressed Gases* [27].

7.3.4 Filling limits

Uninsulated carbon dioxide cylinders shall be filled by weight. Care shall be exercised to avoid overfilling, which can contribute to catastrophic failure. DOT limits the weight of carbon dioxide that may be charged into a cylinder to 68% of the weight of water the cylinder will hold at 60 °F, and CSA B340 specifies a maximum permitted filling density of 68% at 15 °C [8, 11]. If a cylinder is filled over 68%, a rise in temperature could cause the cylinder to become liquid full. The pressure in a cylinder filled with carbon dioxide to various percentages of its water capacity is given in Table 2. For detailed information on filling carbon dioxide cylinders, see CGA G-6.3, *Carbon Dioxide Cylinder Filling and Handling Procedures* [28].

7.3.5 Retesting

Carbon dioxide cylinders (except specification 3HT, 3E, and 39) are required by DOT and TC regulations to be requalified for continued service every 5 years by an authorized retester. Specification 3HT cylinders shall be retested every 3 years. Specification 3E cylinders do not require retesting because they are smaller than 2 in (5 cm) in diameter and 24 in (61 cm) in length. Specification 39 cylinders may not be refilled.

This requalification includes a thorough external and internal visual inspection as well as an internal hydrostatic pressure test (see CGA C-6, *Standards for Visual Inspection of Steel Compressed Gas Cylinders*; CGA C-6.1, *Standards for Visual Inspection of High Pressure Aluminum Compressed Gas Cylinders*; CGA C-8, *Standard for Requalification of DOT-3HT, CTC-3HT, and TC-3HTM Seamless Steel Cylinders*; and CGA C-1, *Methods for Hydrostatic Testing of Compressed Gas Cylinders*) [29, 30, 31, 32]. For DOT cylinders and older Canadian (CTC, BTC, or CRC) cylinders, the hydrostatic test shall be performed at 5/3 of the stamped service pressure.

For metric TC cylinders, the hydrostatic test shall be performed at 1.5 times the marked service pressure. The internal visual inspection shall be carefully performed to detect harmful corrosion because wet carbon dioxide can rapidly corrode a steel cylinder.

Cylinders that have evidence of physical damage (dents, pitting, cracks, arc burns, fire/heat damage, damaged threads, bulges, or any other signs of physical damage) or fail the hydrostatic test shall be removed from service.

Each requalified cylinder shall be plainly and permanently stamped with the month and year of the test with the retester's identification number (RIN) between the month and year of the retest date. In the United States, the cylinder owner shall keep a record of the inspection and retest data on all cylinders until the next requalification. In Canada, the cylinder owner shall keep a copy of the requalification report for 10 years.

7.3.6 Marking and labeling

The following marks are required by DOT and TC to be plainly stamped on the shoulder, top head, or neck of all carbon dioxide cylinders:

- DOT or TC specification number followed by the service pressure, for example, DOT-3A1800 or TC-3AM138;
- Serial number and identifying symbol of the cylinder manufacturer. The symbol shall be registered with DOT or TC, or both; and
- Independent inspector's (third party) official mark and the manufacturing test date. The word SPUN and/or PLUG shall be added when an end closure is made by the spinning process or affected by plugging (see 49 CFR, Part 178, Subpart C, *Specifications for cylinders*, or CSA B339) [8, 23].

The required markings on cylinders shall not be changed except as prescribed in DOT or TC regulations. The serial number and identifying symbol of the maker shall never be obliterated or changed and shall be kept in a legible condition.

In addition to the required marking listed previously, carbon dioxide cylinders shall be labeled with the following:

- Product shipping name—Carbon Dioxide;
- Product identification number—UN 1013. These markings shall be by means of stenciling, printing, or labeling; shall not be readily removable; and shall be in accordance with 49 CFR or Canadian regulations [8, 9];
- A 100-mm (3.9-in) green diamond-shaped nonflammable gas label with a cylinder symbol in the upper corner and the hazard class number, 2, in the bottom corner shall be used on every cylinder. In the United States, the use of NONFLAMMABLE GAS on the label is optional. In Canada, its use is not authorized; and
- Alternately, DOT regulations (see 49 CFR 172.400a) allow the use of 30 mm (1.25-in) square-on-point labels as long as the cylinder(s) are not overpacked and are durably and legibly marked in accordance with CGA C-7, *Guide to the Preparation of Precautionary Labeling and Marking of Compressed Gas Cylinders*, Appendix A [8, 33].
- In Canada, the general requirement is for each side of a label to be at least 100 mm in length with a line running 5 mm inside the edge. However, if that size label, together with the shipping name, technical name, and UN number, cannot be displayed because of the irregular shape or size of the small means of containment, each side of the label may be reduced in length by the same amount to the point where the label, together with the shipping name, technical name, and UN number, will fit that small means of containment, but must not be reduced to less than 30 mm. See subsection 4.10(4) of the *Transportation of Dangerous Goods Regulations* [9].

For additional details on United States and Canadian marking and labeling, see CGA G-6.3 and CGA C-7 [28, 33].

Cylinders equipped with a dip or siphon tube, allowing withdrawal of liquid when the cylinder is upright, shall be clearly identified on the exterior of the cylinder by the words siphon, dip tube, or other descriptive phrase. This

does not apply to fire extinguishing cylinders. A gas pressure regulator shall never be attached to a cylinder with a siphon tube.

7.4 Insulated liquid cylinders

DOT and TC authorize the shipment of liquid carbon dioxide in vacuum-insulated cylinders manufactured to the 4L specification.

7.5 Tank cars

7.5.1 General

DOT regulations governing the shipment of liquid carbon dioxide are found in 49 CFR 173.314 and 49 CFR 173.31[8]. TC regulations are found in CGSB-43.147-2005 [21]. Both authorize shipments in DOT or TC specification 105A500W, 105S500W, and 105J500W tank cars (see Figure 7) [8].



Figure 7—Liquid carbon dioxide tank car

7.5.2 Pressure relief devices

The pressure relief devices for DOT 105A500 and DOT/TC 105A500W tank cars consist of a primary pressure relief device set to open at 375 psig (2590 kPa) or lower, a rupture disk designed to burst at a pressure less than the tank test pressure [500 psig (3450 kPa)], and two pressure regulating devices set to open at 350 psig (2410 kPa). These devices shall be approved by the Association of American Railroad's Committee on Tank Cars [see 49 CFR 173.314(b)(4) and 173.314(c)] [8]. Personnel such as railroad employees should be made aware that one or both of the pressure regulating devices routinely open during transportation. The carbon dioxide escaping during such a valve opening may create a sound that an untrained person may believe to be a hazardous leak. This is normal operation and such railroad tank cars may be safely moved. Railroad tank cars in liquid carbon dioxide service should display a stencil that reads REGULATING VALVES VENTING NORMAL.

7.5.3 Filling limits

DOT and Canadian regulations require that railroad tank cars be filled so the liquid portion of the gas at 0 °F (−17.8 °C) does not completely fill the tank (see 49 CFR 173.314, Note 5 and CGSB 43.147-2005) [8, 22]. A relationship of volume to temperature in containers is shown in Figure 5.

7.5.4 Retesting and requalification

Tank cars in liquid carbon dioxide service shall be requalified at least once every 10 years (see 49 CFR 180.509(c) and CGSB 43.147-2005) [8, 22]. Pressure relief devices shall be requalified every 5 years (See 49 CFR 180.509(c)(3)(ii)) and 180.509(h) [8]. The dates of requalification of the tank and pressure relief devices shall be stenciled on the tank car.

7.6 Portable tanks

7.6.1 General

DOT authorizes the shipment of liquefied carbon dioxide in portable tanks complying with DOT specification 51 as well as certain other portable tanks as outlined in 49 CFR 173.32(b). For further details, refer to 49 CFR 173.315 [8]. In Canada, TC 51 portable tanks may be used in accordance with CSA B622 or CGSB 43.147–2005 [25, 22].

7.6.2 Pressure relief device

Each portable tank shall be provided with one or more pressure relief devices of the pilot-operated or spring-loaded type. A portable tank may also be provided with a pressure-controlling device that regulates the internal pressure by venting when the pressure reaches a preset point below the start-to-discharge pressure of the pressure relief device [see 49 CFR 173.315(i)(9) and (11)] [8]. Details of pressure relief device requirements are contained in CGA S-1.2, *Pressure Relief Device Standards—Part 2—Portable Containers for Compressed Gases* [34].

7.6.3 Filling limits

DOT regulations prohibit filling portable tanks in excess of 95% of their volumetric capacity, which is typically determined during the filling operation by using fixed-length internal dip tubes or by weighing [8]. Depending upon the temperature of the carbon dioxide being loaded, it may be necessary to fill to a lower percentage level to prevent them from becoming liquid full before reaching the start-to-discharge pressure of the pressure relief device (see 49 CFR 173.315) [8]. A relationship of volume to temperature in containers is shown in Figure 5.

7.6.4 Retesting

Portable tanks in carbon dioxide service shall be subjected to a hydrostatic pressure test at least once every 5 years. The retest pressure shall be a minimum of 1.5 times the design pressure. For a specification TC/DOT-51 portable tank, the minimum design pressure is 200 psig (1380 kPa). A portable tank that has been out of service for a period of 1 year or more shall be retested before being returned to service (see 49 CFR 180.605(b) or CSA B620) [8, 23]. The date of the most recent retest shall be marked on the portable tank on or near the metal certification plate [see 49 CFR 180.605(k) or CSA B620] [8, 24].

7.7 Cargo tanks

7.7.1 General

DOT authorizes the shipment of liquid carbon dioxide in cargo tanks complying with specifications MC-330 and TC/MC-331 [8]. In Canada, TC authorizes the shipment of liquid carbon dioxide in TC 331 or TC 338 highway tanks as outlined in CSA B622 (see Figures 8 and 9) [25].



Figure 8—Liquid carbon dioxide cargo tank



Figure 9—Liquid carbon dioxide cargo tank (straight truck)

7.7.2 Pressure relief devices

Each cargo tank shall be provided with one or more pressure relief devices of the spring-loaded type and may be equipped with a rupture disk-type device rated between 1.5 and 2 times the design pressure. A cargo tank may also be provided with a pressure-controlling device, which regulates the internal pressure by venting when the pressure reaches a preset point below the start-to-discharge pressure of the pressure relief device [see 49 CFR 173.315(i)(9) and (10) and CSA B620] [8, 24]. Details of pressure relief device requirements are contained in CGA S-1.2 [34].

7.7.3 Filling limits

DOT regulations prohibit filling cargo tanks in excess of 95% of their volumetric capacity, which is typically determined during the filling operation by using fixed-length internal dip tubes or by weighing. It may be necessary to fill to a lower percentage level depending upon the temperature of the carbon dioxide being loaded to prevent them from becoming liquid full before reaching the start-to-discharge pressure of the pressure relief device

(see 49 CFR 173.315 and CSA B620) [8, 24]. A relationship of volume to temperature in containers is shown in Figure 5.

7.7.4 Retesting

Cargo tanks in carbon dioxide service shall be subjected to a hydrostatic or pneumatic pressure test by an authorized inspector at least once every 5 years. In the United States, external visual inspection is also required every 5 years. In Canada, external inspection is required annually, and internal inspection of TC 331 highway tanks is required every 5 years [24]. The retest pressure for a specification MC-330 and TC/MC-331 cargo tank shall be a minimum of 1.5 times the design pressure. A written report of the retest should be retained in the vehicle file for at least 5 years. The month and year of the last test shall be durably and legibly marked on the cargo tank jacket in letters at least 1.25 in (32 mm) high near the metal certification plate (see 49 CFR 180.407 and CSA B620) [8, 24].

MC-330 and TC/MC-331 cargo tanks in carbon dioxide service shall also be subjected to an annual leakage test. The month and year of the test shall be durably and legibly marked on the cargo tank jacket in letters at least 1.25 in (32 mm) high near the metal certification plate (see 49 CFR 180.407(h) and CSA B620) [8, 24].

A cargo tank that has been out of service for a period of 1 year or more shall be retested before being returned to service [see 49 CFR 180.407(b)(3) and CSA B620] [8, 24].

8 Storage and handling of carbon dioxide

8.1 Uninsulated cylinders

8.1.1 Storage precautions

Cylinders always should be stored in a definitely assigned location (see CGA P-1, *Safe Handling of Compressed Gases in Containers*) [35]. It is important to remember that liquid carbon dioxide in uninsulated cylinders is stored at about 850 psig (5860 kPa) at room temperature, and cylinder failure can result in a violent release of energy. Carbon dioxide vapor is approximately 1.5 times heavier than air. Gas escaping from a cylinder will tend to collect in low areas or confined spaces and can cause asphyxiation.

Cylinders should never be subjected to temperatures in excess of 125 °F (51.7 °C) because of the excessive pressure that will occur. Cylinders should never be stored in direct sunlight, near furnaces, radiators, or any other source of heat. Steel cylinders subjected to fire or high heat shall either be condemned or returned to the cylinder manufacturer for examination to determine their suitability for continued service. Aluminum cylinders that have been subjected to heat or fire shall not be used again. Temperatures in excess of 350 °F (177 °C) will irreversibly change the properties of the aluminum, and the cylinder shall be condemned (see CGA G-6.3) [28].

Cylinders shall not be dropped or otherwise subjected to abnormal mechanical shock that could damage the cylinder, valve, or pressure relief device. Cylinders should not be stored near elevators or gangways or in locations where heavy moving objects may strike them or fall on them. Cylinders should be secured to a wall or other suitable structure to prevent them from falling over.

Cylinders should be stored in a dry, well-ventilated location above ground level. External corrosion can be the cause of cylinder failure, and cylinders should not be stored in plating rooms or other locations that may have a corrosive atmosphere.

8.1.2 Handling precautions

Personnel should be trained in the proper handling and use of carbon dioxide cylinders. They also should be made aware of the hazards involved when approved procedures are bypassed, altered, or ignored. For additional information, see CGA G-6.3, CGA P-1, and CGA P-24 [28, 35, 20].

The internal pressure of carbon dioxide cylinders varies with ambient temperature. For example, under equilibrium conditions at -40 °F (-40 °C) the pressure would be approximately 131 psig (900 kPa); and at 85 °F (29.4 °C) the pressure would be 1018 psig (7020 kPa). Extreme care should be exercised when connecting, disconnecting, filling, discharging, and maintaining cylinders.

The piping system to the use point shall be designed to safely accommodate the pressures encountered. Piping or tubing shall be adequately braced and protected from mechanical damage. Examples of acceptable piping specifications are:

- Ferrous piping—ASTM *Iron and Steel Products*, Volume 01.06, and ASTM A53, *Specifications for Pipe, Steel Black and Hot-Dipped, Zinc-Coated, Welded and Seamless* [36, 37];
- Nonferrous piping—ASTM B88, *Specification for Seamless Copper Water Tube* [38];
- Flexible metallic hose—UL 536, *Flexible Metal Hose* [39].

Adequate pressure relief devices shall be provided where liquid carbon dioxide can become trapped (see 5.5).

CAUTION: *Ordinary cast iron pipe and malleable iron and steel pipe conforming to ASTM A120 shall not be used because they might fracture upon impact, especially under cold conditions.*

Gas pressure-reducing regulators should be specifically designed for carbon dioxide service. Neoprene, nylon, ethylene-propylene diene monomer (EPDM), and polytetrafluoroethylene (PTFE) are commonly used in both carbon dioxide regulators and cylinder valves. Avoid using materials that absorb carbon dioxide and swell or deform such as certain formulations of Buna-N and natural rubber. High consumption rates may require a regulator preheater.

The valves on empty cylinders should be tightly closed to prevent air or moisture from entering while they are being returned for refilling.

8.2 Insulated liquid cylinders

8.2.1 Storage precautions

Cylinders should always be stored in an assigned location. These cylinders are designed to vent carbon dioxide gas to limit the pressure as the contents warm. Therefore, the location shall be well ventilated, out of traffic patterns, and above ground away from cellars or low areas where the heavy carbon dioxide gas (1.5 times heavier than air) may collect. Storage should be away from excessive heat sources.

8.2.2 Handling precautions

Liquid carbon dioxide cylinders (liquid cylinders) have an inner container suspension system designed to minimize heat input. Liquid cylinders depend upon the vacuum in the insulation space to provide the required degree of insulation. Loss of this vacuum will cause excessive amounts of gaseous carbon dioxide to be vented through the pressure relief devices. In such cases, the liquid cylinder should be immediately moved outdoors and the liquid cylinder supplier should be notified. Liquid cylinders should never be subjected to shocks, falls, or impact and shall always be kept upright (see Figure 10).



Figure 10—Insulated liquid carbon dioxide cylinder

Full liquid cylinders are very heavy and shall be moved only on a four-wheel cart designed for that purpose. Rolling of full liquid cylinders is extremely hazardous because, should the cylinder fall, the inner container might fail, releasing full pressure to the vacuum space causing a catastrophic failure of the outer shell. Also, a falling liquid cylinder can cause severe injuries from its weight alone.

Never lift a liquid cylinder by the handling ring because the ring is not designed for that purpose and could be damaged. If a cylinder must be moved with a hoist, forklift, etc., attach the hooks to the lifting lugs provided for that purpose using an appropriate spreader bar.

8.2.3 Operating precautions

Many liquid cylinders have a vaporizer in the vacuum space to provide gaseous carbon dioxide at near ambient temperatures. Should the use rate become excessive, the outer shell of the cylinder will frost heavily and the withdrawn carbon dioxide may become extremely cold. Never apply heat to the liquid cylinder to correct this condition; instead, reduce the use rate or manifold additional cylinders.

A liquid cylinder is equipped with a filling/liquid-use valve, a gas-use valve, a pressure-building valve, a vent valve, a pressure gauge, a liquid-level gauge, and various regulators and pressure relief devices. The gas- and liquid-use valves, the pressure-building valve, the liquid-level gauge, and the pressure gauge are the only devices intended for customer use.

8.3 Bulk liquid carbon dioxide storage containers (containers)

Containers shall be designed, constructed, and tested in accordance with the requirements of the *ASME Boiler & Pressure Vessel Code* (ASME Code), Section VIII, Division 1, current at the time the vessel is constructed (see Figure 11) [2].

Containers shall be designed and constructed to minimize the risk of overfilling. Containers shall never be allowed to become completely liquid full (see Table 6).

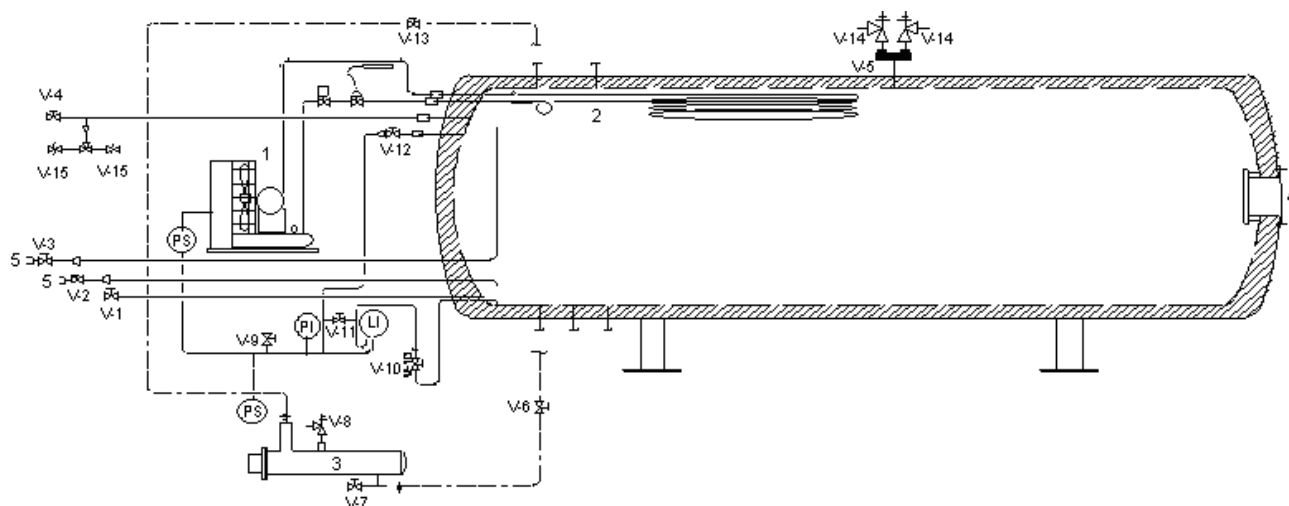
Containers shall be adequately insulated and may be equipped with refrigerating and vaporizing systems to maintain the pressure within the design pressure and temperature limitations. See Figure 12 for a typical piping schematic for carbon dioxide storage systems.

Carbon dioxide storage quantities greater than 10 000 lb (4536 kg) are covered in 40 CFR, Part 370, and by Title III of the *Superfund Amendments and Reauthorization Act* (SARA), Section 312, Tier II Hazardous

Chemical Inventory Report requirements [40]. It is the responsibility of the user to file the appropriate government reports by March 1 of each calendar year. Tier II reports should be sent to the appropriate State Emergency Response Commission (SERC), the appropriate Local Emergency Planning Committee (LEPC), and the local fire department.



Figure 11—Bulk liquid carbon dioxide container



| Equipment | Symbols | Valve number/sequence | |
|---|-------------------------|---|---|
| 1. Refrigeration system | PI = Pressure indicator | V-1 Liquid process | V-9 Instrumentation blowdown |
| 2. Refrigeration coil | LI = Level indicator | V-2 Liquid fill | V-10 Instrumentation isolation |
| 3. Pressure-building vaporizer (optional) | PS = Pressure switch | V-3 Vapor balance | V-11 Instrumentation equalization |
| 4. Manway | | V-4 Vapor process | V-12 Instrumentation isolation |
| 5. Fixed-end CGA fitting | | V-5 Switching valve—3-way diverter valve (shall conform to pressure loss requirements of ASME Code) | V-13 Vaporizer isolation |
| | | V-6 Vaporizer isolation | V-14 Vessel pressure relief device 350 psig (2410 kPa) set pressure. Discharge piped to weather protected tee arrangement |
| | | V-7 Vaporizer blowdown | V-15 Pressure control device 350 psig (2410 kPa) |
| | | V-8 Vaporizer pressure relief device | |

Figure 12—Typical piping schematic for carbon dioxide storage system

8.4 Pressure relief devices for stationary containers

8.4.1 General

Containers shall be equipped with properly sized pressure relief devices compatible with carbon dioxide. Sizing of the primary pressure relief device shall be sufficient to maintain safe pressure in the event of a major external heat input such as fire. See CGA S-1.3, *Pressure Relief Device Standards—Part 3—Stationary Storage Containers for Compressed Gases* and the ASME Code for sizing requirements [41, 2].

The pressure relief device shall access the highest point in the vapor space in the container. Piping to the pressure relief device shall not pass through the liquid phase of the container to prevent the condensation of moisture or freezing of moisture in the pressure relief device. The maximum allowable pressure drop from the vapor phase of the container to the inlet of the relief device should not exceed 3% of start-to-discharge pressure 10.5 psig (72 kPa) for a MAWP of 350 psig (2410 kPa)] under full-flow condition [2].

Use of a three-way selector valve and pressure relief devices with external field test connections is recommended but not required. These allow for periodic maintenance and valve testing as required in CGA S-1.3 without removing the container from service [41].

Pressure relief device discharge piping shall be designed so it cannot accumulate moisture, water, ice, or any other foreign material that would restrict its proper operation.

Sizing and design of all pressure relief device discharge piping shall meet the requirements of Appendix M of the ASME Code and CGA S-1.3 [2, 41]. The maximum pressure restriction allowed on the pressure relief device discharge piping is 10% of the start-to-discharge pressure. For example, the maximum allowable pressure (back pressure) in the discharge piping would be 35 psig (241 kPa) for a 350 psig (2410 kPa) pressure relief device setting.

A rupture disk-type pressure relief device may be used but is not recommended to meet sizing requirements. A ruptured disk will result in the complete depressurization of the container causing the formation of dry ice at -109.3°F (-78.5°C). To return the container to service, repressurize the container using one of CGA's recommended procedures (see CGA G-6.7) [6].

The pressure relief device shall be clearly marked to show the pressure and flow capacity at which it is set to operate. It shall have a means of sealing the start-to-discharge pressure adjustment and be ASME certified. It shall be located and arranged to prevent tampering or damage as much as possible.

The pressure relief device shall discharge into a well-ventilated area to prevent asphyxiation. Carbon dioxide is 1.5 times heavier than air and accumulates in low or poorly ventilated areas.

The use of an adjustable back-pressure regulator or bleeder valve is recommended but not required. It is typically sized to maintain the container pressure due to normal heat input should the refrigeration unit fail. The pressure setting is above the normal operating pressure and below the pressure relief valve start-to-discharge pressure setting, typically 325 psig (2240 kPa).

8.4.2 Indoor installations

Most carbon dioxide containers are designed for outdoor installation. Indoor installations are discouraged, but if necessary, require increasing the pressure relief device capacity as required by CGA S-1.3 [41]. All pressure relief devices shall be piped externally to a safe location. Container fill connections as well as level and pressure gauges should be piped to an outdoor location readily accessible to the person responsible for filling the container with carbon dioxide. Monitoring carbon dioxide concentrations is recommended for all indoor installations.

8.5 Refrigeration system

A mechanical refrigeration system may be used to maintain the desired operating pressure during periods of low usage or increased heat input.

The refrigeration unit removes heat from the contents by condensing carbon dioxide vapor, which results in a corresponding decline in pressure. The refrigeration evaporator coil is installed in the vapor space of the container. The refrigeration system automatically operates to maintain a preset maximum pressure, typically 290 psig to 310 psig (2000 kPa to 2140 kPa). Failure of the refrigeration system could lead to a gradual loss of carbon dioxide vapor through the pressure relief system.

The refrigeration system is designed and sized based on the normal heat entry into the container as well as any extra heat load due to the process being used. Examples of other heat loads are a circulating loop or a cylinder filling pump returning liquid to the container.

8.6 Vaporizer system

A pressure-building vaporizing system may be required to maintain the desired operating pressure during periods of vapor usage or high liquid withdrawal. A cooling effect takes place as product is withdrawn from the container resulting in a decrease of pressure and temperature.

The pressure-building vaporizer system is designed to prevent the pressure in the container from dropping below a preset value. A small portion of the liquid is vaporized and returned to the vapor space of the container.

The vaporizer should be sized for the expected vapor withdrawal rate. Typical electrically operated vaporizers range in capacities from 9 kW to 56 kW. Larger capacities are available using steam or hot water as the heat source.

The vaporizer system operates at preset pressures, typically 245 psig to 255 psig (1690 kPa to 1760 kPa), to maintain a preset minimum pressure.

CAUTION: Failure of the vaporizer system could cause the container temperature to drop below the minimum design metal temperature. Continued product withdrawal after such a failure could cause the contents of the container to convert to dry ice.

8.7 Transfer hoses

Hoses used in the transfer of liquid and gaseous carbon dioxide between containers, cargo tanks, and tank cars are typically elastomer hoses designed specifically for the transfer of liquid carbon dioxide. These hoses shall meet or exceed the requirements of CGA G-6.6, *Standard for Elastomer-Type Carbon Dioxide Bulk Transfer Hose* (see Figures 13 and 14) [42]. Hoses of this type are to be inspected and requalified for continued service once every 6 months with a recommended maximum service life of 4 years in accordance with CGA P-7, *Standard for Requalification of Cargo Tank Hose Used in the Transfer of Carbon Dioxide Refrigerated Liquid* [43].



Figure 13—Liquid cylinder fill hose



Figure 14—Bulk liquid transfer hose

Hoses used in the transfer of liquid carbon dioxide into DOT-4L and TC-4LM specification liquid cylinders shall be designed with a MAWP of at least 1000 psig (6900 kPa) and a minimum design temperature of -65°F (-53.9°C). The hose material shall be compatible with the transfer of liquid carbon dioxide.

Hoses used in the transfer of carbon dioxide into uninsulated cylinders are recommended to be in accordance with CGA E-9, *Standard for Flexible PTFE-Lined Pigtails for Compressed Gas Service* [44]. Hoses used in the transfer of carbon dioxide should be restrained at the ends to prevent whipping in the event of a hose connection failure.

8.8 Solid carbon dioxide (dry ice)

8.8.1 General

Dry ice in equilibrium with its vapor at 1 atmosphere is at -109.3°F (-78.5°C). It is typically used as an expendable refrigerant, and it absorbs heat rapidly from its surroundings and sublimates into carbon dioxide gas. For additional information on dry ice and labeling, see CGA G-6.9 [5].

8.8.2 Storage boxes

Storage boxes for dry ice are well insulated on the bottom and sides with either an open or closed top. If the top can be tightly closed, the container shall be designed to prevent pressure buildup due to sublimation. Open-top boxes are usually covered with an insulating blanket fitted tightly enough at the edges to eliminate the intrusion of air while still allowing the escape of carbon dioxide vapor. Proper storage and shielding from moisture in the air minimizes the accumulation of frost.

8.8.3 Location of storage area

Dry ice storage boxes should be stored in a cool, well-ventilated area.

8.8.4 Handling precautions

Dry ice should not be handled with bare hands. Heavy insulated gloves are recommended. Dry ice blocks may be moved with steel tongs.

Dry ice should be disposed of only in an area that is not accessible to passers-by.

Do not transport dry ice in automobiles or other passenger vehicles without sufficient ventilation to prevent excessive exposure of carbon dioxide vapors to the occupants. Driving with windows, trunk lids, and hatches open is recommended. Never leave dry ice in a parked passenger vehicle. Dry ice in a closed passenger vehicle can result in the accumulation of dangerous concentrations of carbon dioxide vapor. It can be safely trans-

ported in closed cargo areas in trucks without special ventilation provided passengers are restricted to the truck cabs. Special shipping requirements are applicable when dry ice is transported by water or air (see 49 CFR 173.217 and TC regulations) [8, 9].

9 Carbon dioxide applications

9.1 Expendable refrigerants

- food freezing;
- chilling;
- transportation of chilled and frozen products;
- shrink fitting;
- environmental testing;
- cryogenic grinding;
- plastic blow mold chilling;
- rubber deflashing; and
- dry ice blast cleaning.

9.2 Carbonation

- soft drinks;
- beer and wine; and
- beverage dispensing.

9.3 Chemical reactant

- manufacturing of carbonates;
- methanol;
- urea; and
- foundry cores.

9.4 Pressurizing/solvent medium

- enhanced oil recovery;
- aerosol propellant; and
- blowing agents.

9.5 pH control

- potable water treatment; and
- swimming pool and caustic waste neutralization.

9.6 Fire suppression

9.7 Controlled atmospheres

- welding;
- shielding gas;

- inerting and blanketing; and
- greenhouse atmospheric enrichment.

9.8 Other

- grain fumigation;
- medical respiratory therapy mixtures; and
- supercritical extraction.

10 References

Unless otherwise specified, the latest edition shall apply.

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