



# **SAFE HANDLING OF LIQUID CARBON DIOXIDE CONTAINERS THAT HAVE LOST PRESSURE**

**Doc 164/20**

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# SAFE HANDLING OF LIQUID CARBON DIOXIDE CONTAINERS THAT HAVE LOST PRESSURE

As part of a programme of harmonisation of industry standards, the European Industrial Gases Association (EIGA) has issued EIGA Doc 164, *Safe Handling of Liquid Carbon Dioxide Containers that have Lost Pressure*, jointly produced by members of the International Harmonisation Council and originally published by the Compressed Gas Association (CGA) as CGA G-6.7, *Safe Handling of Liquid Carbon Dioxide Containers that have Lost Pressure*.

This publication is intended as an international harmonised standard for the worldwide use and application of all members of the Asia Industrial Gases Association (AIGA), Compressed Gas Association (CGA), European Industrial Gases Association (EIGA), and Japan Industrial and Medical Gases Association (JIMGA). Each Association's technical content is identical, except for regional regulatory requirements and minor changes in formatting and spelling.

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### Amendments to 164/10

Section	Change
	Editorial to align style with IHC associations
	Extensive technical update
8.4	Removal of ACGIH reference

Note: Technical changes from the previous edition are underlined.

Note: Appendices A, B and C (Informative) are for information only.

## 1 Introduction

This publication is one of a series compiled by the Compressed Gas Association, Inc. (CGA) the European Industrial Gases Association (EIGA), Asia Industrial Gases Association (AIGA), and Japan Industrial and Medical Gases Association (JIMGA) to satisfy the demand for information on the production, handling, storage, transportation, and use of compressed and liquefied gases, cryogenic liquids, and related products.

## 2 Scope and purpose

### 2.1 Scope

The scope of this publication is concerned primarily with the safe re-pressurisation of stationary or transportable liquid carbon dioxide containers made of low alloy carbon steels and having a minimum design metal temperature (MDMT) greater than  $-78.9\text{ }^{\circ}\text{C}$  ( $-110\text{ }^{\circ}\text{F}$ ).

### 2.2 Purpose

The purpose of this publication is to provide information to personnel to ensure that carbon dioxide containers that have lost pressure and could contain solid carbon dioxide (dry ice) or liquid carbon dioxide at temperatures less than the MDMT are safely re-pressurised before being returned to service.

Examples are given of re-pressurisation procedures for containers manufactured under the *ASME Boiler & Pressure Vessel Code*, Section VIII, Division 1 (ASME Code), EN 13445-3, *Unfired pressure vessels Part 3 Design*, EN 13458-2, *Cryogenic vessels—Static vacuum insulated vessels—Part 2 Design, fabrication, inspection and testing*, and AD 2000 Code [1, 2, 3, 4].<sup>1</sup>

## 3 Definitions

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

### 3.1 Publication terminology

#### 3.1.1 Shall

Indicates that the procedure is mandatory. It is used wherever the criterion for conformance to specific recommendations allows no deviation.

#### 3.1.2 Should

Indicates that a procedure is recommended.

#### 3.1.3 May

Indicates that the procedure is optional.

#### 3.1.4 Will

Is used only to indicate the future, not a degree of requirement.

#### 3.1.5 Can

Indicates a possibility or ability.

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<sup>1</sup> References are shown by bracketed numbers and are listed in order of appearance in the reference section.

## **3.2 Technical definitions**

### **3.2.1 Auto-refrigeration**

Lowering of the temperature of carbon dioxide as the pressure reduces to maintain temperature and pressure equilibrium.

### **3.2.2 Brittle**

Property of a material that causes it to break under load with little or no deformation.

### **3.2.3 Coincident temperature**

Corresponding temperature for a substance at a given pressure at equilibrium.

### **3.2.4 Compressed gas**

Substance existing only as a gas at a given temperature and pressure.

### **3.2.5 Condensation**

Process by which a gas converts to a liquid.

### **3.2.6 Container**

Insulated pressure vessel manufactured in accordance with a design standard, for example the ASME Code for the storage of liquid carbon dioxide, EN 13458, or EN 13445 [1, 3, 2].

NOTE Container is interchangeable with vessel or tank.

### **3.2.7 Critical size**

Size of a flaw in the container material that causes an uncontrolled increase of the length of a crack while under constant stress.

### **3.2.8 De-pressurisation**

Reduction of pressure in a container resulting in a container temperature less than the minimum design metal temperature (MDMT) or the solidification of the carbon dioxide.

NOTE Typical causes are the overdrawing of a pressure building vaporiser, leaks, or a pressure relief device that did not reseal properly.

### **3.2.9 Dry ice**

Common name for solid carbon dioxide.

NOTE Its temperature is  $-78.5\text{ }^{\circ}\text{C}$  ( $-109.3\text{ }^{\circ}\text{F}$ ) at atmospheric pressure.

### **3.2.10 Ductile**

Property of a material that defines its ability to deform under load without breaking.

### **3.2.11 Elastic**

Property of a material that defines its ability to deform under load without being permanently deformed.

**3.2.12 Equilibrium**

Physical state of a substance where the temperature and pressure will not change without an energy exchange.

**3.2.13 Low-alloy carbon steel**

Steel relatively low in carbon containing small amounts of other elements to enhance strength, ductility, and toughness.

**3.2.14 Maximum allowable working pressure (MAWP)**

Maximum gauge pressure permissible at the top of a vessel in its operating position for a designated temperature.

**3.2.15 Melting**

Process by which dry ice converts to a liquid.

**3.2.16 Minimum design metal temperature (MDMT)**

Lowest temperature at which a container is designed to operate at a given pressure.

**3.2.17 Nil ductility transition temperature (NDTT)**

Temperature less than which metals are brittle enough to fracture.

**3.2.18 Plastic deformation**

Deformation of a material that will remain permanent after removal of the load that caused it.

**3.2.19 Pressure building vaporiser**

Heat exchanger that vaporises liquid carbon dioxide from the container and returns it to the container as vapour to increase or maintain the pressure.

**3.2.20 Qualified carbon dioxide technician**

Person who by reason of education, training, and experience knows the properties of carbon dioxide; is familiar with the equipment used to store, transfer, and use carbon dioxide; and understands the precautions necessary to safely use carbon dioxide equipment.

**3.2.21 Re-pressurisation**

Process of restoring a container to its design parameters when it has lost pressure and is less than its MDMT.

**3.2.22 Sublimation**

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

**3.2.23 Toughness**

Ability of a metal to absorb energy and undergo plastic deformation before fracturing.

### 3.2.24 Transportable container

Liquid carbon dioxide container meeting the requirement of a local or national authority that allows the container to be moved on public roads and highways while under pressure.

### 3.2.25 Triple point

Temperature and pressure at which a material exists simultaneously as a solid, liquid, and gas.

NOTE For carbon dioxide, the triple point is  $-56.6^{\circ}\text{C}$ ,  $(-69.9^{\circ}\text{F})$  and 416 kPa (60.4 psia).<sup>2</sup>

### 3.2.26 Ultimate tensile strength

Maximum stress level a material can sustain without fracturing.

### 3.2.27 Upset condition

Any condition outside the normal design parameters.

### 3.2.28 Vaporisation

Process by which liquid carbon dioxide is converted to a gas.

### 3.2.29 Yield strength

Stress at which a material exhibits a specified limiting deviation from the proportionality of stress to strain. The deviation is expressed in terms of strain, percent offset, total extension under load, etc. [6, 7].

## 4 Basis

The basis for this publication is actual testing performed under the auspices of CGA, who sponsored extensive testing on a horizontal 50-ton capacity carbon dioxide storage container in 1992 and 1993. The purpose of the testing was to obtain pressure, temperature, and flow rate data to allow CGA to evaluate prospective procedures that could be used to return a de-pressurised carbon dioxide container to normal service. Many different re-pressurisation procedures were in use by the carbon dioxide industry, and the purpose of the testing was to evaluate their safety. Many years of experience in both North America and Europe support the testing done by CGA in 1992 and 1993.

These procedures and recommendations are intended to be the best available knowledge of carbon dioxide and its safe use by the industry. No single re-pressurisation technique or procedure can be used for every container in service.

## 5 Warning

It is critical that persons attempting to return a carbon dioxide container from an upset condition (low pressure) be aware of the hazards involved, the metallurgical properties of the container, the quantity of liquid in the container before the upset, and the physical site conditions in order to choose the safest and best procedure for the circumstances.

A carbon dioxide container that has cooled less than its MDMT should be re-pressurised only by a qualified carbon dioxide technician. Knowledge of the container metallurgy and the properties of carbon dioxide are essential. The potential for catastrophic failure of a de-pressurised container being re-pressurised is much greater than normal if not properly handled.

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<sup>2</sup> 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, *Guideline for Metric Practice for the Compressed Gas Industry* [5].



## 6 Properties of carbon dioxide

Carbon dioxide is a colourless, odourless, slightly acidic gas that is approximately 50% heavier than air. It is non-flammable and will not support combustion. The physical constants of carbon dioxide are summarised 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  $-56.6\text{ }^{\circ}\text{C}$  and 518 kPa, abs ( $-69.9\text{ }^{\circ}\text{F}$  and 75.1 psia). 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  $31.1\text{ }^{\circ}\text{C}$  and 7381.8 kPa, abs ( $87.9\text{ }^{\circ}\text{F}$  and 1070.6 psia). At pressures and temperatures greater than the critical point, carbon dioxide exists only as a supercritical fluid.

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

At temperatures and pressures less than the triple point, carbon dioxide can be either a solid (dry ice) or a gas, depending upon conditions. Dry ice at a temperature of  $-78.5\text{ }^{\circ}\text{C}$  ( $-109.3\text{ }^{\circ}\text{F}$ ) and at atmospheric pressure transforms directly to a gas (sublimes) without passing through the liquid phase. Lower temperatures result if dry ice sublimes at pressures less than atmospheric.

At temperatures and pressures greater than the triple point and less than  $31.1\text{ }^{\circ}\text{C}$  ( $87.9\text{ }^{\circ}\text{F}$ ), carbon dioxide liquid and gas can exist in equilibrium in a closed container. Within this temperature range, the pressure in a closed container holding carbon dioxide liquid and gas in equilibrium bears a definite relationship to the temperature. Carbon dioxide cannot exist as a liquid greater than its critical temperature of  $31.1\text{ }^{\circ}\text{C}$  ( $87.9\text{ }^{\circ}\text{F}$ ), regardless of the pressure.

Table 1 Physical constants of carbon dioxide

	U.S. Units	SI Units
Chemical formula	CO <sub>2</sub>	CO <sub>2</sub>
Molecular weight	44.01 lb/lb-mol	44.01 kg/kg-mol
Vapour pressure		
at 70 °F (21.1 °C)	838 psi	5778 kPa
at 32 °F (0 °C)	491 psi	3385 kPa
at 2 °F (–16.7 °C)	302 psi	2082 kPa
at –20 °F (–28.9 °C)	200 psi	1379 kPa
at –69.9 °F (–56.6 °C)	60.4 psi	416 kPa
at –109.3 °F (–78.5 °C)	0 psi	0 kPa
Density of the gas		
at 70 °F (21.1 °C) and 1 atm	0.1144 lb/ft <sup>3</sup>	1.833 kg/m <sup>3</sup>
at 32 °F (0 °C) and 1 atm	0.1234 lb/ft <sup>3</sup>	1.977 kg/m <sup>3</sup>
Specific gravity of the gas		
at 70 °F (21.1 °C) and 1 atm (air = 1)	1.522	1.522
at 32 °F (0 °C) and 1 atm (air = 1)	1.524	1.524
Specific volume of the gas		
at 70 °F (21.1 °C) and 1 atm	8.741 ft <sup>3</sup> /lb	0.5457 m <sup>3</sup> /kg
at 32 °F (0 °C) and 1 atm	8.104 ft <sup>3</sup> /lb	0.5059 m <sup>3</sup> /kg
Density of liquid, saturated		
at 70 °F (21.1 °C)	47.6 lb/ft <sup>3</sup>	762 kg/m <sup>3</sup>
at 32 °F (0 °C)	58.0 lb/ft <sup>3</sup>	929 kg/m <sup>3</sup>
at 2 °F (–16.7 °C)	63.3 lb/ft <sup>3</sup>	1014 kg/m <sup>3</sup>
at –20 °F (–28.9 °C)	66.8 lb/ft <sup>3</sup>	1070 kg/m <sup>3</sup>
at –69.9 °F (–56.6 °C)	73.5 lb/ft <sup>3</sup>	1177 kg/m <sup>3</sup>
Sublimation temperature (1 atm)	–109.3 °F	–78.5 °C
Critical temperature	87.9 °F	31.1 °C
Critical pressure	1070.6 psia	7381.8 kPa, abs
Critical density	29.2 lb/ft <sup>3</sup>	468 kg/m <sup>3</sup>
Triple point	–69.9 °F at 75.1 psia	–56.6 °C at 518 kPa, abs
Latent heat of vaporisation		
at 32 °F (0 °C)	100.8 Btu/lb	234.5 kJ/kg
at 2 °F (–16.7 °C)	119.0 Btu/lb	276.8 kJ/kg
at –20 °F (–28.9 °C)	129.6 Btu/lb	301.4 kJ/kg
Latent heat of fusion at –69.9 °F (–56.6 °C)	85.6 Btu/lb	199 kJ/kg
Weight of liquid at 2 °F (–16.7 °C)	8.46 lb/gal	1014 kg/m <sup>3</sup>
Latent heat of sublimation at –109.3 °F (–78.5 °C)	245.5 Btu/lb	571.0 kJ/kg

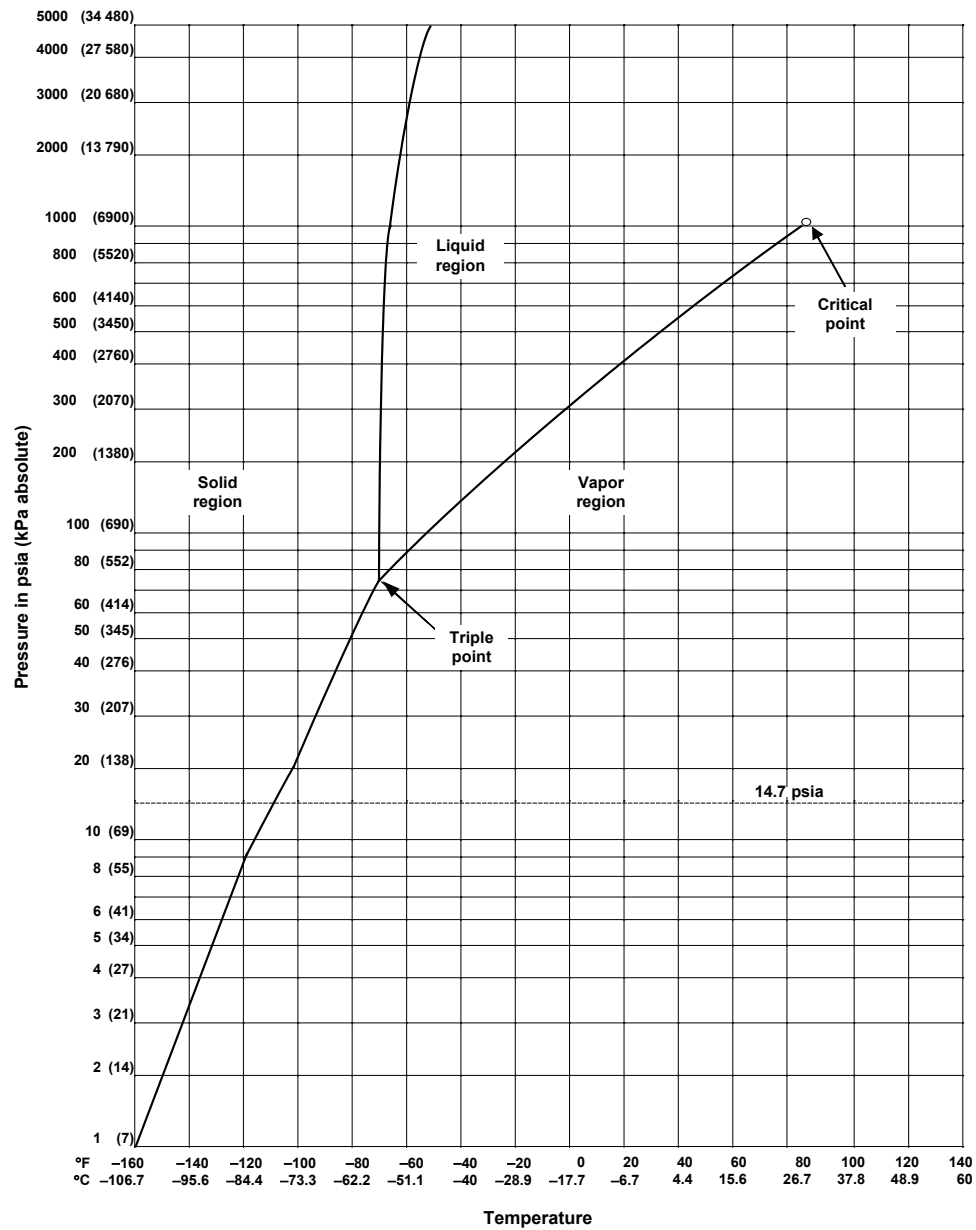


Figure 1 Phase diagram for carbon dioxide

**Table 2 Thermodynamic properties of saturated carbon dioxide solid, liquid and vapour phases (U.S. customary units)**

Temp °F		Pressure		Density	Specific volume	Enthalpy <sup>1)</sup>		Entropy <sup>1)</sup>	
		psia	psi	lb/ft <sup>3</sup>	ft <sup>3</sup> /lb	Btu/lb		Btu/(lb)(°R)	
				solid or liquid	vapour	solid or liquid	vapour	solid or liquid	vapour
Solid and Vapour	-150	1.793	26.26 <sup>2)</sup>	99.7	41.81	53.55	305.50	0.3394	1.1530
	-140	3.171	23.46 <sup>2)</sup>	99.2	24.41	56.36	306.90	0.3483	1.1318
	-130	5.405	18.92 <sup>2)</sup>	98.8	14.69	59.22	308.30	0.3571	1.1126
	-120	8.923	11.75 <sup>2)</sup>	98.3	9.131	62.15	309.62	0.3658	1.0945
	-110	14.34	7.725 <sup>2)</sup>	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 Vapour	-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
	-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

Temp °F	Pressure		Density	Specific volume	Enthalpy <sup>1)</sup>		Entropy <sup>1)</sup>		
	psia	psi	lb/ft³	ft³/lb	Btu/lb		Btu/(lb)(°R)		
			solid or liquid	vapour	solid or liquid	vapour	solid or liquid	vapour	
Liquid and Vapour	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, −273.15 °C (−459.67 °F).

2)

Inches of mercury below atmospheric pressure.

**Table 3 Thermodynamic properties of saturated carbon dioxide solid, liquid and vapour phases (SI units)**

Temp °C		Pressure		Density	Specific volume	Enthalpy <sup>1)</sup>		Entropy	
		kPa absolute	kPa gauge	kg/m³	m³/kg x 10 <sup>-3</sup>	kJ/kg		kJ/(kg)(K)	
				solid or liquid	vapour	solid or liquid	vapour	solid or liquid	vapour
Solid and Vapour	−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

Temp °C		Pressure		Density	Specific volume	Enthalpy <sup>1)</sup>		Entropy	
		kPa absolute	kPa gauge	kg/m <sup>3</sup>	m <sup>3</sup> /kg x 10 <sup>-3</sup>	kJ/kg		kJ/(kg)(K)	
				solid or liquid	vapour	solid or liquid	vapour	solid or liquid	vapour
Solid and Vapour	-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 Vapour	-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	933.0	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
	-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

<sup>1)</sup> Based on 0 for the perfect crystal at zero Kelvin (-273.15 °C).

## 7 Temperature and pressure

The temperature of liquid carbon dioxide and its container decreases as the pressure decreases due to auto-refrigeration. The temperature and phases of the container contents during de-pressurisation can be accurately determined by using the known pressure and the phase diagram shown in Figure 1. A conversion from liquid to dry ice begins to occur at 416 kPa (60.4 psi) with a coincident temperature of  $-56.6\text{ }^{\circ}\text{C}$  ( $-69.9\text{ }^{\circ}\text{F}$ ). This is the triple point where gas, liquid, and dry ice exist in equilibrium. As gas continues venting, energy is extracted from the liquid to generate the gas and solid required to maintain equilibrium. This converts more liquid to a solid. This process continues as long as venting occurs with temperature and pressure remaining constant, until only gas and dry ice remain. Continued venting less than the triple point causes the pressure and temperature to continue to decline until at 0 kPa (0 psi) a temperature of  $-78.5\text{ }^{\circ}\text{C}$  ( $-109.3\text{ }^{\circ}\text{F}$ ) is reached.

Container pressure losses can be caused by such things as a relief valve opening and failing to reclose, the rapid withdrawal of large volumes of carbon dioxide vapour, or the failure of a pressure building vaporiser. In the case of road tankers, pressure loss can occur due to single hose filling at customer tanks.

Carbon dioxide container owners and operators need to understand that the pressure/temperature equilibrium relationship does not apply when a container is being re-pressurised to return to normal service. It is possible for a container to be at 2070 kPa (300 psi) and to have liquid and dry ice at  $-56.6\text{ }^{\circ}\text{C}$  ( $-69.9\text{ }^{\circ}\text{F}$ ) in the container because it is not at equilibrium. The liquid temperature will eventually warm up and the vapour pressure will decrease until they stabilise, but this can take days or weeks to occur.

Carbon dioxide storage containers are typically designed and constructed in accordance with the ASME Code, which is the recognised standard for pressure vessel construction in the United States and Canada [1]. The ASME Code provides a safety factor of 3.5, which means that at its maximum working pressure, the material is stressed to only 28.6% of its ultimate tensile strength. Carbon dioxide containers are typically fabricated using low-alloy carbon steels.

Low-alloy carbon steels at design operating conditions are both strong (have high tensile strength) and ductile. These materials remain strong as they become cold but become less ductile. A decrease in operating temperature can result in the container reaching its nil ductility transition temperature (NDTT). This means that a material that is normally considered ductile becomes brittle at temperatures less than the NDTT. This condition is fully reversible when the metal temperature rises greater than the NDTT. As the temperature decreases, the container material also shrinks and can produce localised stresses. Ductile materials can accommodate localised stresses by slight deformation. The material will stretch in that area and not fail. Brittle materials are not able to stretch locally at low temperatures and can catastrophically fail. If a crack or material defect reaches a critical size in a pressurised brittle container, there is a greater likelihood of a total container failure similar to breaking a glass jar. Ductile materials can fail, but generally not catastrophically because the material tends to stretch, possibly crack and leak, but does not come apart.

Carbon dioxide is stored in insulated containers as a liquefied compressed gas. Normal container operating pressures range from 1380 kPa to 2070 kPa (200 psi to 300 psi), which corresponds to an equilibrium temperature of  $-28.9\text{ }^{\circ}\text{C}$  ( $-20\text{ }^{\circ}\text{F}$ ) and  $-16.1\text{ }^{\circ}\text{C}$  ( $3\text{ }^{\circ}\text{F}$ ) respectively.

In North America, the majority of the containers in refrigerated carbon dioxide service are fabricated using low-alloy carbon steels such as SA-212, SA-515, SA-516, and SA-612. Containers manufactured before 1990 typically had an MDMT of  $-28.9\text{ }^{\circ}\text{C}$  ( $-20\text{ }^{\circ}\text{F}$ ). When the container wall is at an operating temperature colder than the MDMT, it is out of its intended operating condition.

## 8 Physiological effects of carbon dioxide

### 8.1 General

The physiological effects of carbon dioxide are unique because carbon dioxide 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 approximately 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 the 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 that 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.

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 toxic effect because the neural control systems are excessively driven, and this toxic effect is rapid. It is important to note that these effects are independent of the amount of oxygen in the atmosphere being breathed.

The effects produced by inhaling low and moderate concentrations of carbon dioxide are physiological and reversible, but the effects of high concentrations are toxic and damaging [8].

## **8.2 Effects of inhaled 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 dangerous even when normal oxygen levels are present. Low concentrations of inspired carbon dioxide can be tolerated for a considerable period without noticeable effect, or 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 laboured (dyspnoea) and restlessness, faintness, severe headache, and dulling of consciousness occurs. 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 the 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.

## **8.3 Physical effects of overexposure to carbon dioxide**

Skin, mouth, or eye contact with dry ice, which has a temperature of  $-78.5^{\circ}\text{C}$  ( $-109.3^{\circ}\text{F}$ ) can cause severe frostbite, skin lesions, corneal burn, or more serious injury from deep freezing of the tissues. Liquid discharging from a container produces high-velocity carbon dioxide snow particles, which are abrasive in addition to being cold and can cause similar injuries.

## **8.4 Regulatory standard**

Carbon dioxide is naturally present in the atmosphere at about 0.035% by volume. The Occupational Safety and Health Administration (OSHA) standard for maximum allowable concentration, in air in the workplace is 0.5% for 8 continuous hours of exposure. OSHA lists an 8-hour Time-Weighted Average–Permissible Exposure Limit (TWA–PEL) of 5000 ppm (9000 mg/m<sup>3</sup>) for carbon dioxide [9]. TWA–PEL is the exposure limit that shall not be exceeded by the 8-hour time-weighted average in any 8-hour work shift of a 40-hour work week. See Title 29 of the U.S. *Code of Federal Regulations* (29 CFR) Parts 1910.1000, Table Z-1 [9].

Also, exposures greater than the TLV–TWA up to the STEL should not be longer than 15 minutes and should not occur more than 4 times per day. There should be at least 60 minutes between successive exposures in this range [9]. In Canada, similar limits are mandated by provincial legislation.

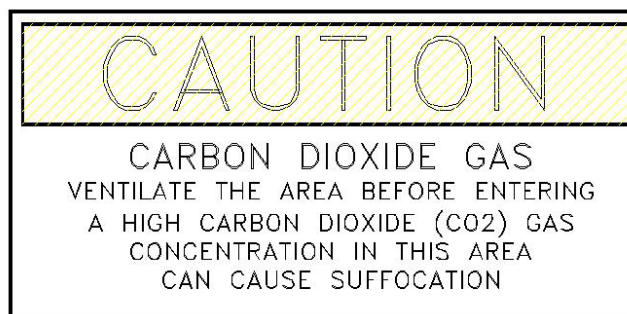


For more information, see the gas supplier's safety data sheet [10].

Rationale for exposure limits being less than those for a simple asphyxiant can be found in EIGA SI 24/17 *Carbon Dioxide Physiological Hazards – “Not just an Asphyxiant”* [11].

## 8.5 Safety precautions

Appropriate warning signs shall be placed at the entrance to confined areas where high concentrations of carbon dioxide gas can accumulate. Some countries regulate the minimum size of the sign. For example, in the United States, NFPA 55, Compressed Gases and Cryogenic Fluids Code, requires the sign to be at least 200 mm (8 in) wide and 150 mm (6 in) high see Figure 2 [12].



**Figure 2 Typical caution sign**

Carbon dioxide monitoring shall be performed prior to entering any confined space or low area in which carbon dioxide gas could have accumulated. The carbon dioxide shall be removed by ventilation to a concentration below 3% (see 8.4) or a supplied-air respirator shall be donned before entering the confined space or low area (see 29 CFR 1910.146) [9]. For further information see personnel overexposure in CGA G-6, Carbon Dioxide [13].

**NOTE** The 3% concentration is for U.S. jurisdictions with exposure time not to exceed 15 minutes. Lower concentrations would apply for longer exposure times in the U.S. The maximum allowed concentrations can be different in other jurisdictions.

***WARNING: Supplied-air respirators shall only be used by authorised personnel with appropriate training and qualification for use of these respirators. Cartridge-style respirators shall not be substituted for supplied-air respirators.***

## 8.6 Rescue and first aid

Do not attempt to remove anyone exposed to high concentrations of carbon dioxide without using proper rescue equipment or you can also become a casualty. According to OSHA rescuers account for over 60% of confined space fatalities. If the exposed person is unconscious, obtain assistance and use the 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 (38 °C to 41 °C [100 °F to 105 °F]), until it appears to be back to the normal skin tone and feels warm.

## **9 Specific hazards**

### **9.1 General**

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

### **9.2 Dry ice blocking**

Liquid carbon dioxide in a hose or pipe flows like water. However, when the pressure is reduced to less than the triple point, the liquid changes into a mixture of vapour and dry ice. Dry ice can create a blockage or plug when formed in a pipe or hose.

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. To prevent dry ice blockage, the liquid carbon dioxide shall be purged from the hose or pipe before reducing the pressure less than the triple point. This can be done by supplying carbon dioxide vapour to one end of the hose or piping system to maintain the pressure greater than the triple point while removing the remaining liquid from the other end.

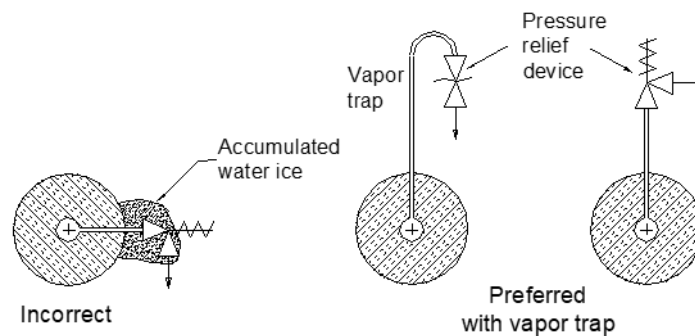
### **9.3 Low temperature effects on materials**

The low temperature effect caused by reducing the pressure of a saturated liquid carbon dioxide (auto-refrigeration) is another hazard. If the pressure is reduced to atmospheric pressure, the temperature can be as low as that of dry ice [ $-78.5\text{ }^{\circ}\text{C}$  ( $-109.3\text{ }^{\circ}\text{F}$ )]. At dry ice temperatures, many materials used in hose and piping systems can become brittle and fail if highly stressed. Materials used in the construction of carbon dioxide transfer systems including hoses should be compatible with liquid carbon dioxide and the temperature and pressure conditions encountered.

### **9.4 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 increases as it warms and expands. As the temperature continues to increase, the pressure of the trapped liquid can exceed what the piping and hoses can withstand. This can cause the hose or piping to rupture with possible injury and property damage.

All liquid carbon dioxide piping shall be equipped with pressure relief devices (PRDs) if the piping is located in the part of the system where liquid can be trapped such as between manual valves, control valves, check valves, etc. Trapping can occur through manual isolation during maintenance or by operation of automatic devices. These PRDs 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. The PRDs shall be installed on a riser pipe extended from the cold liquid piping to create a vapour trap and prevent water ice from accumulating inside the PRD and allow any condensation to drain, see Figure 3.



**Figure 3 Examples of incorrect and preferred pressure relief device installations on liquid carbon dioxide piping**

### 9.5 Overfilling containers

When liquid carbon dioxide is stored in a container and there is no product withdrawal, heat leak causes the temperature and pressure to rise and the liquid to expand. For a given temperature increase, the pressure rises at a faster rate if the container is liquid full compared to a container that still has a vapour space. These characteristics shall be considered while planning re-pressurisation of the container.

### 9.6 Personnel overexposure

When carbon dioxide is used in an enclosed area, ventilate the area adequately to maintain a safe working environment for personnel. Carbon dioxide in the gaseous state is colourless and odourless and not easily detectable. Since gaseous carbon dioxide is 1.5 times denser than air, it will be found in greater concentrations in confined areas or low levels. Therefore, ventilation systems should be designed to exhaust from the lowest level and allow make-up air to enter at a higher point. Do not depend on measuring the oxygen content of the air because carbon dioxide can be dangerous even with adequate oxygen for life support. For additional information, see Section 8.

### 9.7 Thermal expansion and contraction

For conventionally insulated (i.e., polyurethane insulation, not vacuum insulated) tanks on saddles, provisions should exist to accommodate the thermal movements caused by the low temperature cycle. The provisions to include making sure the sliding saddle is free to accommodate both expansion and contraction and that the connected piping has sufficient flexibility for the expected movement. Restricting the movement of these tanks can cause excessive stress to the tank saddles and shell wall.

## 10 Hazards of carbon dioxide container re-pressurisation

### 10.1 Movement of transportable containers

Prior to the start of any re-pressurisation process, transportable containers should be in a secure and suitably equipped location, to allow re-pressurisation in accordance with one of the re-pressurisation methods in this publication. If it is necessary to move a transportable container to a secure and suitably equipped location when the container or portions of it are less than its MDMT, an assessment should be made whether the transportable container can be safely moved. The amount of lading, internal pressure, component temperature, container support configuration, stresses during movement, distance to be moved, etc., shall be included in the assessment. It is recommended that any remaining liquid be discharged before movement, leaving only a residual pressure of approximately 34.5 kPa (5 psi) during movement. This assessment should also consider placing the container and running gear on a flatbed trailer during transport to minimise structural stress on the container.

## 10.2 Hazards

De-pressurisation of a container and the resulting auto-refrigeration that occur will not likely result in the brittle fracture of an otherwise sound container. The highest stresses in the container are caused by the internal pressure exerted by the product. As the pressure and temperature decrease, the pressure-induced stresses also decrease.

Table 4 shows the relationship of the container wall stress and the internal pressure for both an ASME and EN carbon dioxide container. The ASME container is constructed from SA 516-70N having a tensile strength of 70 000 psi (483 MPa) with an MAWP of 350 psi (23.8 bar). The ASME Code requires a safety factor of 3.5; therefore the maximum allowable stress at MAWP is  $70\,000/3.5 = 20\,000$  psi. The EN example is constructed from a material having a guaranteed yield strength of 355 MPa (51 500 psi). EN 13458-2 uses a safety factor of 2.8; therefore the maximum allowable stress at the MAWP of 22 bar (319 psi) is 225.6 MPa [3].

NOTE The yield strength is the stress value corresponding to the 0.2% of the proof stress for carbon steel.

A pressure vessel risk assessment shall be performed by a qualified carbon dioxide technician prior to choosing a container re-pressurisation technique. This assessment shall include the following: the design code of the container, the ductility of the materials of construction, and wall stresses. Those users with vessels other than ASME-designed vessels shall perform a comparable assessment to ensure safe re-pressurisation. See Appendix A for an example of an assessment for an EN-designed vessel and Appendix B for an ASME-designed vessel.

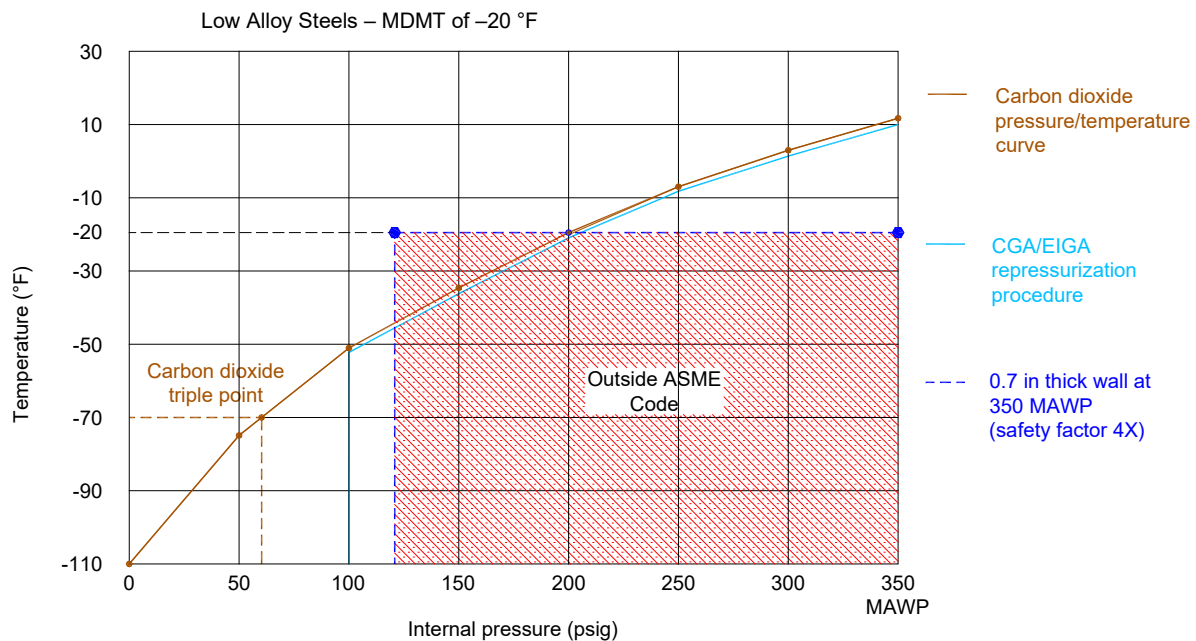
**Table 4 Carbon dioxide container pressure/wall stress relationships**

Internal pressure			Equilibrium carbon dioxide temperature		Wall stress in container due to internal pressure		
psi	kPa	Bar	°F	°C	ASME <sup>1) 3)</sup>		EN <sup>2) 3)</sup>
					psi	MPa	MPa
350	2413	24.1	13	−11	20 000	138	—
319	2199	22	5	−15	18 250	125.8	225.6
300	2069	20.7	3	−16	17 143	118	212.2
250	1724	17.2	−8	−22	14 286	98.4	176.8
200	1379	13.8	−20	−29	11 429	78.8	141.4
150	1034	10.3	−35	−37	8571	59.1	106.1
100	690	6.9	−53	−47	5714	39.4	71.8
60	414	4.1	−69	−56	3429	23.6	56.1
0	0	0	−110	−78.9	0	0	0

<sup>1)</sup> At lower equilibrium temperatures/pressures and using the ASME Code and Figure UCS 66.1, it can be shown that the allowable reduction in MDMT is colder than the equilibrium temperature at reduced pressures [1]. See Figures 4 and 5 as examples for typical liquid carbon dioxide containers, which show the allowable temperature as a function of reduced pressure.

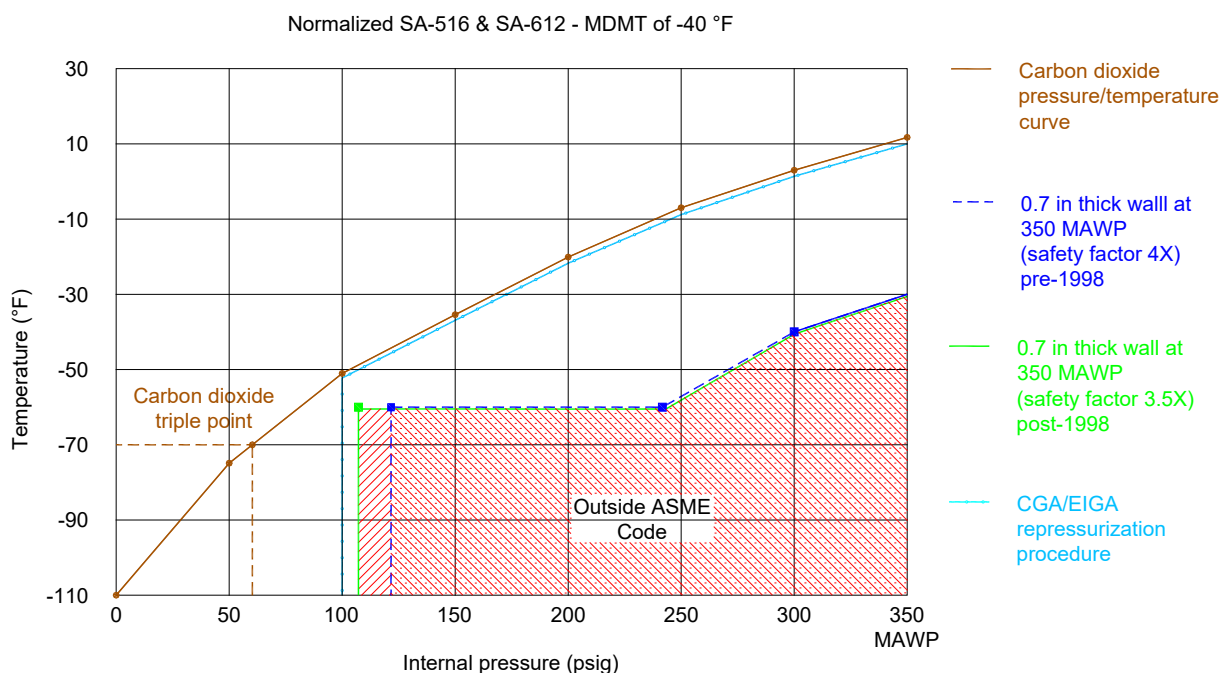
<sup>2)</sup> See Figure A-1 for additional information for EN-designed vessels.

<sup>3)</sup> ASME example is for SA-516-70 with an MAWP of 350 psi (23.8 bar) and safety factor of 3.5. EN example is for EN 13458-2 with an MAWP of 22 bar and safety factor of 2.8 [3]. The result is that the EN tank has a thinner wall and stresses are higher for the same diameter and a given pressure.



NOTE Steels used for carbon dioxide containers included SA-212, SA-515, SA-516 (as rolled), and SA-612 (as rolled).

**Figure 4 Allowable pressure temperatures in an ASME liquid carbon dioxide container (pre-1976 safety factor 4X)**



**Figure 5 Allowable pressure temperature in an ASME liquid carbon dioxide container (pre-1998 safety factor 4X, post-1998 safety factor 3.5X)**

### 10.3 Specific precautions

Dangerous conditions can be caused by artificially increasing the pressure in a container that is de-pressurised and auto-refrigerated to less than the container material's NDTT. A carbon dioxide container at a pressure less than 416 kPa (60.4 psi) should be assumed to be at a temperature less than -69.9 °F (-56.6 °C) in a brittle condition and should be protected from impact. Movement of stationary containers should be avoided. Movement of transportable containers in brittle condition is addressed in 10.1.

Most carbon dioxide containers fabricated before 1976 in North America used coarse grain steels that have poor low temperature characteristics (see Figure 4). These containers remain in service and require special care when performing re-pressurisation. Consideration should be given to installing backpressure control valves to prevent excessive vapour withdrawal, which is a common cause of de-pressurisation. CGA recommends that the life of these vessels not be extended by overhauling, see CGA PS-5, *CGA Position Statement on the Suitability of Carbon Steel Containers for Stationary Carbon Dioxide Storage* [14].

These containers were manufactured using SA-212 or SA-515 low-alloy steels with an MAWP of 2410 kPa to 2500 kPa (350 psi to 363 psi) in accordance with the ASME Code, which allowed MDMTs of  $-29^{\circ}\text{C}$  ( $-20^{\circ}\text{F}$ ) without any impact testing. The ASME Code was revised in 1987 to reflect the fact that similar low-alloy steels did not have adequate ductility at temperatures colder than  $-12^{\circ}\text{C}$  ( $10^{\circ}\text{F}$ ). They were, and still are, within the ASME Code to operate at temperatures as cold as  $-29^{\circ}\text{C}$  ( $-20^{\circ}\text{F}$ ).

Figure 4 illustrates where the pressure/temperature equilibrium curve for carbon dioxide passes through the zone outside the ASME Code at equilibrium temperatures between  $-20^{\circ}\text{F}$  and  $-44^{\circ}\text{F}$  ( $-29^{\circ}\text{C}$  and  $-42^{\circ}\text{C}$ ) and corresponding equilibrium pressures of 200 psi and 120 psi (1380 kPa to 830 kPa).

Nevertheless, the re-pressurisation procedure outlined in Section 13, Method 1 followed by Method 2 are acceptable for the following reasons:

- The pressure vessel safety factor of these containers is 4:1 versus the 3.5:1 safety factor adopted in 1987, which provides an additional level of safety;
- The stress level in the container wall from 830 kPa to 1380 kPa (120 psi to 200 psi) ranges from 33% to 55% of the design stress of the vessel. This means that even if operating in a brittle condition, the stress level is less than 8.3% to 13.7% of the ultimate strength of the material;
- The containers were typically fabricated with fractional inch thickness plate compared to the present day rolled to thickness plate. This effectively increased the container wall thickness thereby increasing the factor of safety beyond the minimum 4:1 required by ASME;
- The containers are protected from impact and external damage by insulation and an outer jacket, reducing the potential risk of a brittle failure caused by external stresses; and
- There have been no known failures or incidents on containers that have used these re-pressurisation methods.

In addition, the following conditions shall be met:

- re-pressurisation procedure is performed by a qualified carbon dioxide technician;
- procedure is continuously attended and monitored for unusual circumstances; and
- after completing the procedure, do not fill the container over 80% of rated capacity the first time (see Section 13).

**CAUTION:** *Improper re-pressurisation of a container that is in a brittle condition can result in catastrophic failure.*

Escaping carbon dioxide can create an asphyxiation hazard in poorly ventilated spaces. Take adequate precautions before entering such an area (see Section 9).

## 11 Preliminary procedures for returning de-pressurised containers to service

Prior to the start of the re-pressurisation of a container, follow these procedures:

- Discontinue all carbon dioxide withdrawal;
- Close all service withdrawal valves and do not return the container to service until it is equal to or greater than the MDMT;
- Shut off all pressure building vaporiser(s) and do not introduce pressure from another source;
- Do not move stationary, fixed location containers;
- Do not subject the de-pressurised container to impact;

- Verify that provisions to accommodate the thermal movements caused by the low temperature cycle have not been compromised (for example, by rust on sliding plates). This applies to conventionally insulated tanks on saddles (i.e., polyurethane insulation, not vacuum insulated), where visible;
- Verify piping attached to a vessel does not show signs of unusual movement; and
- Determine if the container has residual liquid in addition to the expected dry ice.

### 11.1 Personnel requirements

A qualified carbon dioxide technician should determine the reason for loss of pressure and correct the problem before proceeding with re-pressurisation procedures.

Re-pressurisation should only be attempted by a qualified carbon dioxide technician or persons knowledgeable in the container design and physical properties of carbon dioxide. Safe, tested procedures should be developed for each case before proceeding with re-pressurisation.

### 11.2 Provisions for alternate source

Returning a container to service can be a lengthy process, so arrangements may have to be made for an alternate source of carbon dioxide. Depending on the amount of dry ice in the container and the size of the container, a considerable amount of carbon dioxide can be required for the re-pressurisation procedure. An evaluation should be made and an adequate source of carbon dioxide provided for this procedure.

### 11.3 De-pressurised container evaluation

The container and its related piping, markings, Manufacturer's Data Report (U-1A), recent fill records, recent product use records, and events leading up to de-pressurisation should be investigated before proceeding with re-pressurisation. The ASME data plate can be found on the container in one of a number of locations such as on the legs, head, or manway. For an example of a de-pressurised container evaluation form see Figure 6.

Manufacturer _____	Year Built _____	Man. Serial No. _____
Natl Bd No. _____	Type Material _____	MAWP _____
Minimum Design Metal Temp _____ °F	At _____	psi Impact Test _____
ASME Code _____	Capacity _____	Pressure In Container _____
Liquid Level _____	External Appearance _____	
Piping External Appearance (e.g., frosted/water ice build-up or ambient temperature) _____		
Signs of Product Discharge or Leakage _____		
Last Known Contents Level _____	Date _____	Time _____
Last Known Pressure _____	Date _____	Time _____
Known Use Since Last Known Contents Level _____		
Estimated Product Withdrawal Since Last Known Contents Level _____		

**Figure 6 De-pressurised container evaluation form**

### 11.4 Facts to consider in evaluating re-pressurisation methods

Approximately 50% of the carbon dioxide in the container is lost during a complete de-pressurisation.

To re-liquefy and warm 0.45 kg (1 lb) of dry ice to approximately 1030 kPa (150 psi) saturated liquid, 4.1 kg to 4.5 kg of 1720 kPa (9 lb to 10 lb of 250 psi) saturated liquid is required.

Approximately 0.45 kg of -17.8 °C (1 lb of 0 °F) carbon dioxide vapour is required to return 0.45 kg (1 lb) of dry ice to about 1030 kPa (150 psi) saturated liquid. Some of the dry ice in the container melts and changes to liquid. The liquid level increases until the residual dry ice becomes completely submerged in the liquid. At this point, the container pressure increases, and continued addition of vapour

can result in unsafe container pressures greater than the triple point as the heat transfer is reduced because the vapour is no longer in direct contact with the dry ice. Additional energy is required to melt the remaining solid and warm the liquid and the container wall.

The liquid level gauge (using differential pressure or floats) cannot be relied upon when a container has been de-pressurised less than its design temperature and contains dense liquid, snow, or dry ice.

Several carbon dioxide cargo tanks can be required to supply sufficient carbon dioxide vapour to complete the re-pressurisation procedure (see Table 5).

A heat exchanger, a pump, and a source of energy can be required to complete the procedure outlined in 13.2.

During re-pressurisation, dry ice becomes submerged in liquid carbon dioxide at pressures greater than 60.4 psi (416 kPa); therefore pressure can no longer be used as an indicator of container temperature.

Pressure greater than that calculated using the ASME Code and Figure UCS 66.1 should not be applied to a vessel if the vessel's material is likely to be colder than the MDMT [1].

**Table 5—Typical quantities of carbon dioxide and times needed for container re-pressurisation**

Quantity of liquid CO <sub>2</sub> in container before de-pressurisation	CO <sub>2</sub> vapour required to pressurise to 690 kPa (100 psi) (Section 13.2)		Number of full 20 ton CO <sub>2</sub> cargo tanks required	Time to re-liquefy residual dry ice and warm the liquid to -28.8 °C (-20 °F) 1380 kPa (200 psi) using a 6 kW heater (Section 13.2)	Quantity of liquid CO <sub>2</sub> in container after re-pressurisation	Time required to warm the liquid from -45.6 °C to -29 °C (-50 °F to -20 °F) 690 kPa to 1380 kPa (100 psi to 200 psi) using a 6 kW heater (Section 13.3) (No dry ice present)
6 ton	1110 lb	503 kg	0.5	10 hr	3.3 ton	4.2 hr
14 ton	2590 lb	1175 kg	1.2	23.3 hr	7.6 ton	10.3 hr
30 ton	5550 lb	2517 kg	2.5	50 hr	16.3 ton	22 hr
50 ton	9250 lb	4196 kg	4.2	83.3 hr	27.1 ton	36.5 hr
<p><b>NOTES</b></p> <p>1 Container fully de-pressurised to atmosphere.</p> <p>2 Flow rates as high as 54 kg/min (120 lb/min) were observed in tests using cargo tanks as the vapour source. To complete this step, approximately 185 lb of vapour is required per ton of liquid carbon dioxide (92.3 kg/tonne) that was in the container before de-pressurisation. If full 20 ton cargo tanks are the vapour supply source, then 0.084 cargo tanks per ton of liquid de-pressurised is required.</p> <ul style="list-style-type: none"> <li>Example: 50 tons of liquid de-pressurised to 0 psi would require: 185 lb/ton (83.9 kg/0.91 tonne) x 50 ton (45.4 tonnes) = 9250 lb of carbon dioxide vapour (4096 kg) (column 2); or 0.084 x 50 = 4.2 cargo tanks to pressurise to 100 psi (690 kPa) (column 3).</li> <li>Example: A container that is totally de-pressurised should require about 10 kWh/ton liquid to melt all the dry ice and warm the liquid to 200 psi (1380 kPa), i.e., a container with 30 tons of liquid fully de-pressurised can be returned to 200 psi (1380 kPa) using a 6 kW heater in about 50 hrs: 10 kWh/ton x 30 ton/6 kW = 50 hr (column 4).</li> <li>Example: The energy required to warm liquid carbon dioxide is approximately 0.28 kWh/ton °F. A container with 10 tons of liquid at 131 psi (900 kPa) (-40 °F/-40 °C) requires 112 kWh to warm up to 291 psi (2010 kPa) (0 °F/-17.8 °C). (Temperature difference is 40 °F): 0.28 kWh/ton °F x (0 - [-40] °F) x 10 ton = 112 kWh.</li> </ul>						

## 12 Guidelines for evaluation of the condition of a de-pressurised container

A container that is less than the pressure corresponding to its MDMT, typically 1380 kPa (200 psi), needs to be evaluated before proceeding. It is possible that the container is empty (no liquid) or it could hold cold liquid, a mixture of cold liquid and dry ice, or just dry ice. One of the most common causes of container pressures declining to less than 1380 kPa (200 psi) is an empty container. All of the liquid is consumed and only vapour pressure remains in the container. An empty container is not an upset condition but shall be treated as such until a proper evaluation is completed. The following guidelines



should be used by a qualified carbon dioxide technician before proceeding with re-pressurisation and a return to normal service.

Pressure cannot be the sole determinant of pressure vessel wall temperature during re-pressurisation (see 11.4). Dry ice and colder liquid tend to settle to the bottom of the container. This could maintain the temperature of the pressure vessel steel at the bottom of the container at the triple point when the coincident pressure/temperature charts would predict otherwise. Industry testing has shown that the shell and head metal, away from the nozzles being used to warm the tank, can be 10° C (50 °F) or more colder than that predicted by the coincident carbon dioxide temperature charts corresponding to the tank's pressure gauge reading. This sets up the potential for tank failure if a slow and gradual procedure is not used while raising the tank's pressure.

### **12.1 Container pressure greater than 1380 kPa (200 psi)**

The container is probably acceptable for normal service. However, if the container was de-pressurised earlier and the pressure continues to decrease over time with no product removal, cold liquid or dry ice are likely present. Do not maintain in normal service until all facts are known (see Section 11).

### **12.2 Container pressure less than 1380 kPa (200 psi) but greater than 416 kPa (60.4 psi)**

The following procedure should be performed to determine whether the container is empty (no liquid present):

- a) Check the consumption records to determine whether the container could possibly be empty;
- b) Check liquid valve and piping for signs of frost, which can indicate the presence of liquid carbon dioxide or dry ice; and
- c) Confirm that the container is empty by opening either the liquid fill valve or a liquid use valve. If ONLY vapour exits, the container is empty and can be filled in accordance with CGA G-6.4, *Safe Transfer of Liquefied Carbon Dioxide in Insulated Cargo Tanks, Tank Cars, and Portable Containers* [15]. If liquid exits from either liquid valve or, if the piping is obstructed by dry ice blockages, then low-temperature liquid and/or dry ice are present. See 13.1, 13.2, and 13.3 for further guidance.

#### **12.2.1 Container minimum design metal temperature of –29 °C (–20 °F)**

Containers holding liquid at pressures less than 1380 kPa (200 psi) are in an upset condition and are colder than the minimum design condition. Re-pressurise using the procedures outlined in 13.4 and 13.5.

#### **12.2.2 Container minimum design metal temperature of –40.0 °C (–40 °F)**

Containers with pressures greater than 970 kPa (140 psi) can be returned to service. Containers with pressures less than 970 kPa (140 psi) are in an upset condition and require the re-pressurisation procedures as outlined in 13.4 and 13.5.

#### **12.2.3 Container minimum design metal temperature of –46 °C (–50 °F)**

Containers with pressures greater than 724 kPa (105 psi) can be returned to service. Containers with pressures less than 720 kPa (105 psi) are in an upset condition and require the re-pressurisation procedures in 13.4 and 13.5.

#### **12.2.4 Containers with other minimum design metal temperature values**

Containers with other MDMT values can be returned to service at pressures greater than the corresponding equilibrium carbon dioxide pressure (see Figure 1). Containers with temperatures less than the MDMT are in an upset condition and require the re-pressurisation procedures in 13.2 and 13.3.

### 12.3 Container pressure less than 416 kPa (60.4 psi)

The container could be empty of all liquid with vapour pressure only. The following procedure should be performed to determine whether the container is empty (no dry ice present):

- a) Check the consumption records to determine whether the container could possibly be empty;
- b) Check liquid valve and piping for signs of frost, which can indicate the presence of liquid carbon dioxide or dry ice;
- c) Check the pressure and liquid level gauge for accuracy. Pulsations in the liquid level gauge can be an indication of the presence of dry ice;
- d) Pressurise the container to 690 kPa (100 psi) with vapour (see 13.2). If the container pressure stays at 414 kPa (60 psi) for any length of time during this pressurisation, dry ice is present inside the container; and
- e) Open either the liquid fill valve or a liquid use valve and see if only vapour exits. If the liquid piping is obstructed by dry ice or discharges liquid, then the tank contains dry ice and shall be re-pressurised using methods given in Section 13.

### 12.4 Special low-temperature containers

Containers made of materials that remain ductile at  $-78.5^{\circ}\text{C}$  ( $-109.3^{\circ}\text{F}$ ) (for example TC/DOT-4L containers made of type 304 stainless steel) may be returned to service without some of the precautions necessary for containers made of materials that do experience a loss of ductility less than  $-28.9^{\circ}\text{C}$  ( $-20^{\circ}\text{F}$ ). The ASME data plate of such vessels should clearly identify them as having an MDMT colder than  $-78.5^{\circ}\text{C}$  ( $-109.3^{\circ}\text{F}$ ).

Testing has demonstrated that dry ice still exists although the pressure is greater than the point where it would exist if the contents were in an equilibrium condition. Even though some dry ice exists in the container, it is likely that the pressure building vaporiser can be activated and the container returned to service. *Do not fill to the normal liquid carbon dioxide level.* The first fill after a container has lost pressure should not exceed 80% of normal full. This allows room for any residual dry ice to melt and convert to liquid that will expand close to the normal 100% fill level. A container with residual dry ice will be overfull at designed conditions if filled to the normal fill settings. *The procedures suggested in this section only apply to containers with an MDMT less than  $-78.5^{\circ}\text{C}$  ( $-109.3^{\circ}\text{F}$ ).*

### 12.5 Uninterruptible applications

There are special carbon dioxide container applications where large volumes of liquid or vapour are discharged for fire protection, inerting, and purging. The design intent for fire prevention applications is to discharge either a large portion or the entire liquid contents, of the container contents during a short period. The container pressure will decrease while product is removed if no additional vaporisation is provided. The typical range to which the pressure would decrease would be 1724 kPa (250 psi) to as low as 1034 kPa (150 psi). This is typically a designed and expected condition, that may be less than the MDMT, and is tolerable due to the coincident lower pressure and the low frequency of occurrence. Operators of such systems shall use procedures in this publication to return any container that has decreased to less than its MDMT to a safe and normal condition prior to refilling the container or returning to normal service.

Some vapour inerting and purging applications protect containers or processes storing flammable or explosive mixtures, which cannot withstand a supply interruption. Those systems typically have back up measures to protect the container or process, but the designer should consider the expected failure modes of the system and design accordingly. For some examples, see NFPA 86, *Standard for Ovens and Furnaces*; API Standard 2000, *Venting Atmospheric and Low-pressure Storage Tanks*; or ATEX Directive 2014/34/EU, *Equipment and protective systems intended for use in potentially explosive atmospheres* [16, 17, 18].

## 13 Recommended re-pressurisation methods

### 13.1 Recommendations and continuous monitoring

The following recommendations are provided based on the information available at the time of publication. Each instance needs to be evaluated by a qualified carbon dioxide technician. The de-pressurisation of a container is an upset condition. The assumption is made that only a pressure gauge, contents-level gauge, and liquid/vapour fill lines are available to the technician. It is also assumed that little or no instrumentation is available; limited electric power or alternate heat sources exist; cargo tanks are probably the only external sources of carbon dioxide vapour; and the container needs to be returned to normal service as rapidly as possible.

Monitoring by a qualified carbon dioxide technician is required during re-pressurisation. Any sign of leakage, unusual noise, or other unexplained occurrence during these procedures is reason to discontinue re-pressurisation and take other appropriate action.

Method 1 followed by Method 2 is the preferred method under most circumstances. Methods 3 and 4 are alternatives that may be appropriate in some circumstances such as when Methods 1 and 2 are not safe or practical given the container, site conditions, and equipment available.

The flow chart in Appendix C is provided as an aid in deciding the best method to use for re-pressurisation.

### 13.2 Carbon dioxide gas pressurisation up to 690 kPa (100 psi) (Method 1)

**NOTE** This re-pressurising method can be used on most ASME-designed tanks but may not be applicable for EN or other design codes with lower factors of safety. The user shall determine if this technique is acceptable (see the examples in 10.2, Appendix A, and Appendix B to determine the extent of the safe domain).

This procedure is step one of a two-step process outlined here and in 13.3. It is used to partially liquefy any dry ice inside a container when the pressure has decreased less than 416 kPa (60.4 psi).

Connect a hose from the vapour phase of a supply tank to the liquid phase of a de-pressurised container. A manifold similar to Figure 7 is suggested. The de-pressurised container pressure control regulator should be set at 690 kPa (100 psi), and the pressure relief regulator on the supply tank should be set no less than 621 kPa (90 psi) or at the pressure coincident with the supply tank MDMT. Full-time monitoring of pressure gauges and manual control of pressure and flow is an acceptable alternative (Figure 7 alternative manual method). Purge the hose and manifold.

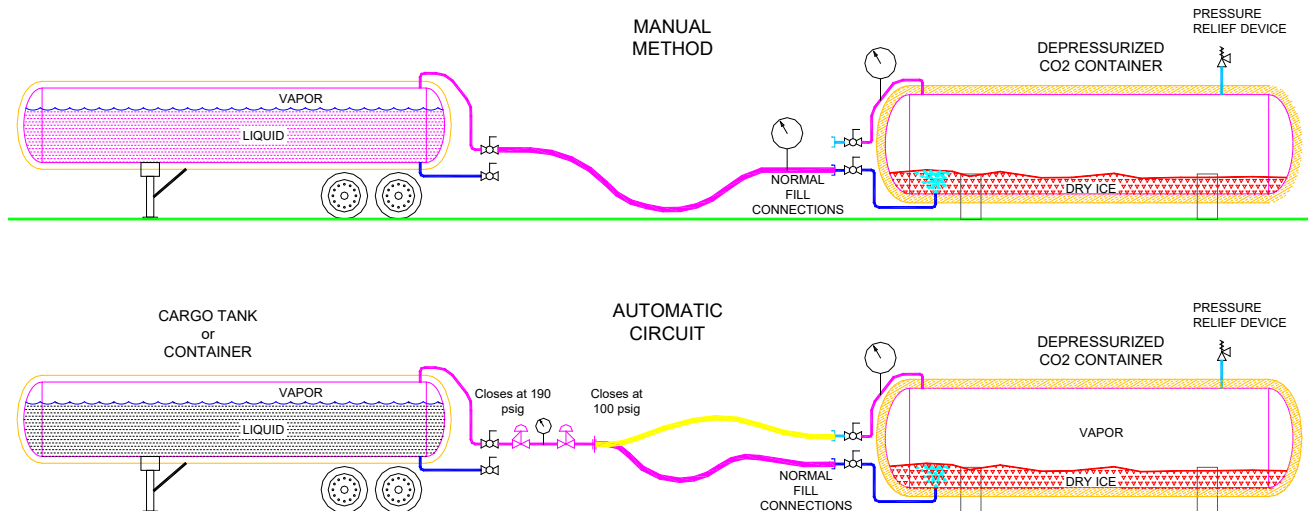
Pressurise the container to 690 kPa (100 psi) with carbon dioxide vapour from cargo tank(s) or other external vapour source (see Table 5 for typical quantities/cargo tanks required). The pressure in the cargo tank will decrease rapidly if there is no vaporiser, which is the reason that multiple cargo tanks may be required. The residual liquid in the cargo tank will auto-refrigerate and should be maintained at a pressure that will not subject the next delivery customer's container to liquid colder than its MDMT.

Slowly open the valves connecting the supply tank and the de-pressurised container. A single supply tank and vaporiser may be used as a vapour source instead of several cargo tanks.

**CAUTION:** Do not let the supply tank pressure fall below the pressure coincident with the MDMT of the supply tank. Without an external pressure building vaporiser, the supply tank pressure can fall to the point that the re-pressurisation operation must be stopped until the supply tank pressure is restored. Large quantities of carbon dioxide can be required (see Table 5).

The external vapour can be added as fast as the piping and hoses allow. If the container liquid piping is blocked by dry ice, the vapour equalisation line should be used (see Figure 7). The vapour condenses, which causes the dry ice to melt. Adding vapour alone does not guarantee re-liquefying all of the dry ice. The liquid level rises until all of the exposed dry ice is submerged. At this point, the container pressure increases rapidly because the incoming vapour cannot contact the dry ice directly. The carbon dioxide technician completing this step should expect the container pressure to increase to the triple point (416.4 kPa [60.4 psi]) and hold at that pressure for an extended period of time and then rapidly increase to the final 100 psi (689.5 kPa). The liquid level gauge could show a reading but is probably not accurate.

When the vapour pressure in the de-pressurised container approaches 690 kPa (100 psi), do not assume that the dry ice is completely melted. The container will have a significant amount of dry ice at  $-56.6\text{ }^{\circ}\text{C}$  ( $-69.9\text{ }^{\circ}\text{F}$ ) remaining. The rising pressure seems to indicate the entire contents are greater than  $-56.6\text{ }^{\circ}\text{C}$  ( $-69.9\text{ }^{\circ}\text{F}$ ), but experimentation has shown that the rate of condensation slows and the pressure begins to rise when the dry ice becomes covered with liquid. As long as dry ice remains in the container, the container is likely to be colder than its MDMT and should be treated accordingly.



**Figure 7 Method 1, Step 1 partial reliquification of solid carbon dioxide (dry ice) container pressurisation with vapour up to 690 kPa (100 psi)**

(Refer to 13.2 and 15.1)

The vapour pressurisation step described in the previous paragraph should not be used to increase the container pressure greater than 690 kPa (100 psi), and the vapour supply container shall be maintained greater than its MDMT. The first step of the re-pressurisation is now complete and the second phase can begin (see 13.3).

The advantages of carbon dioxide gas pressurisation up to 690 kPa (100 psi) are:

- Carbon steel pressure vessels subject to pressure levels less than 690 kPa (100 psi) are unlikely to fail in a catastrophic manner at dry ice temperatures. Table 4 indicates that a container with a 2410 kPa (350 psi) MAWP and a pressure of 690 kPa (100 psi) has a stress level in the steel wall of 39.4 MPa (5714 psi). Therefore, it is safe to pressurise such a container to 690 kPa (100 psi) with no risk of brittle fracture. At 690 kPa (100 psi), testing shows that there is enough liquid in the container to allow liquid to be pumped as recommended in 13.3; and
- No lost product.

The disadvantages of carbon dioxide gas pressurisation up to 100 psi (690 kPa) are:

- Requires large volumes of vapour to partially re-liquefy the dry ice. To pressurise a container from atmospheric pressure to 690 kPa (100 psi), the vapour required per unit mass of de-pressurised liquid is 92.3 kg/tonne (185 lb/ton). In most cases, electric vaporisers are not large enough to complete this step rapidly;
- Only practical carbon dioxide vapour source readily available is from cargo tanks. Typical cargo tanks do not have a vaporiser or auxiliary heat source available, and therefore have a limited quantity of vapour available. Full cargo tanks are the best source but can deliver no more than 50 kg of vapour per tonne of liquid (100 lb/ton). The vapour removed from cargo tanks is supplied by the auto-refrigeration of the liquid carbon dioxide. Vapour removal shall be limited to keep the pressure greater than the corresponding cargo tank MDMT; and
- Insufficient warming of liquid. It does not provide the circulation of the liquid to ensure that all the dry ice is melted in a reasonable time, so recirculating liquid as described in 13.3 is necessary.

### 13.3 Recirculation of warmed liquid (Method 2)

This procedure is step two and shall be preceded by the one listed in Section 13.2 unless the container pressure is equal to or greater than 690 kPa (100 psi).

**NOTE** Valves, nozzles, and piping can be blocked (or become blocked) with dry ice even after carbon dioxide in the container is partially liquefied (see 9.2).

***WARNING: Re-circulation of liquid causes the temperature and pressure of containers fabricated with coarse grain steels to pass through the zone outside the ASME Code as illustrated in Figure 4 [1]. This procedure requires continuous supervision by a qualified carbon dioxide technician to monitor pump flow, heat input, and vessel protection from shock and/or impact for a slow, controlled pressure rise.***

Liquid carbon dioxide is pumped from either the liquid fill or a liquid use line through a vaporiser/vapour heater. The warmed liquid is returned to the container through the vapour fill connection (see Figure 8). Typical pump capacities range from 7.6 l/min to 37.9 l/min (2 gal/min to 10 gal/min) and typical heater capacities range from 3 kW to 18 kW. The preferred procedure is to pump liquid from one end of the container and to return the warmed liquid to the opposite end, if such a connection is available.

The circulating operation should continue until the container pressure exceeds the pressure coincident with the MDMT or 1380 kPa (200 psi). The product heating and circulation can be discontinued at this time. When the pressure remains stable for 2 hours or is rising, the container contents should be at or near equilibrium. The container then may be returned to service.

The container level gauge is typically not accurate until all the dry ice has melted.

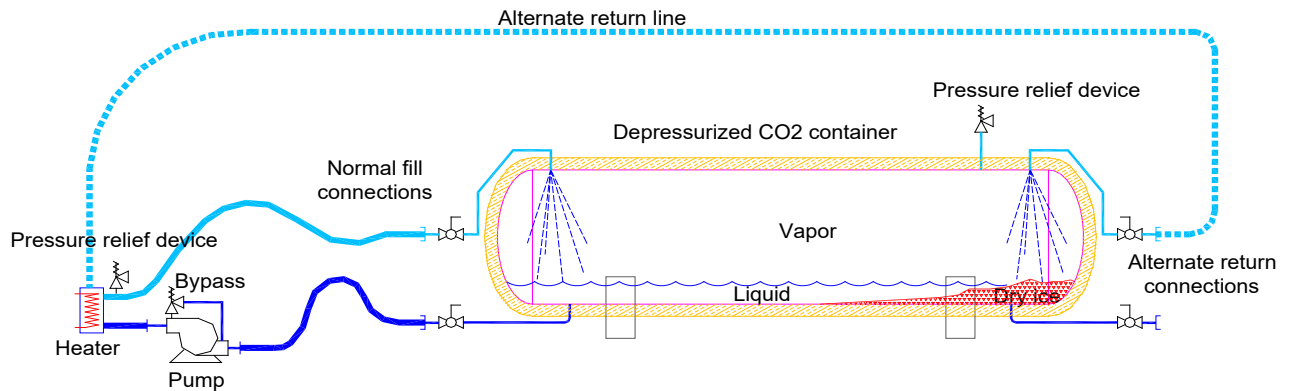
Do not fill the container over 80% of rated capacity the first time after completing this procedure. This allows sufficient volume for the expansion of the cold liquid if residual dry ice remains inside the container. The container pressure and level should be monitored until normal operation is observed.

The advantages to re-circulation of warmed liquid are:

- Minimises the possibility that the vapour pressure in the container will exceed the equilibrium pressure of the circulated liquid. Any dry ice in the container will gradually melt. The liquid circulation causes a mixing action minimising temperature gradients throughout the container;
- Relatively fast – a container can be returned to normal service in one or more days;
- Uses equipment readily available within the carbon dioxide industry. This procedure can be accomplished using only the two fill connections; and
- No lost product.

The disadvantages of recirculation of warm liquid are:

- Requires bringing extra equipment to the site, which adds set up time;
- Requires a compatible electric or energy supply with sufficient capacity to supply the pump and heater. Most carbon dioxide containers have an electric supply for the refrigeration unit that can be temporarily disconnected and used for the process; and
- Requires time varying from hours to days depending on the circumstances.



**Figure 8 Recirculation of warmed liquid to 1380 kPa (200 psi)**

### 13.4 Hot gas warming at no pressure (Method 3)

This procedure is the safest for containers fabricated with coarse grain steels because it does not go into the unsafe zone as illustrated in Figure 4.

Remove the container from service. If the container is greater than 416 kPa (60.4 psi), remove all the remaining liquid carbon dioxide through a liquid connection (see 9.2). De-pressurise completely through a vapour connection.

Inject large quantities of warm, dry air or gas through an open manway or product-use connections and vent to the atmosphere.

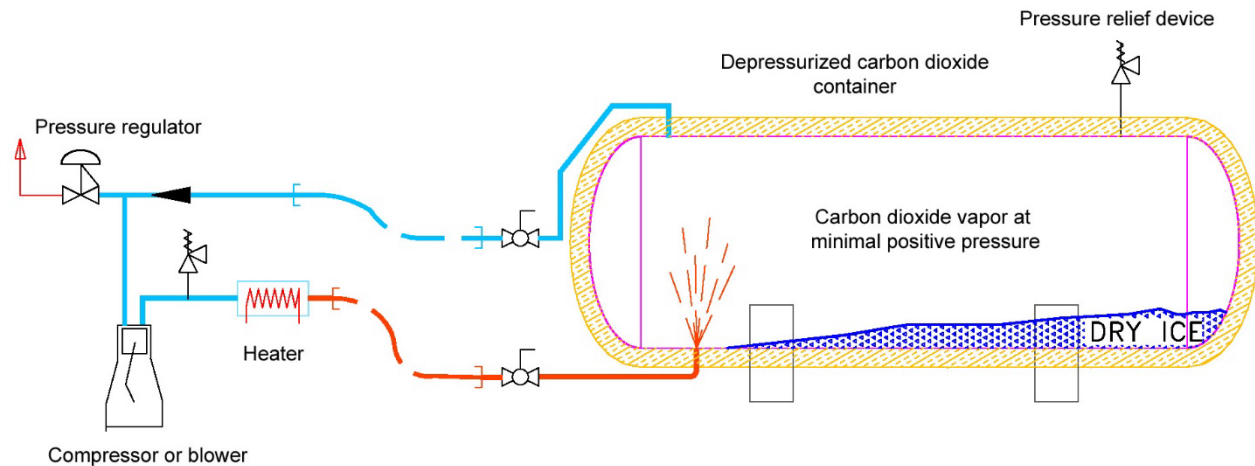
Drain condensed moisture from the container and piping. Dry, clean, and purge after all the dry ice has sublimed. Pressurise the container with carbon dioxide vapour and fill as required for a first fill (see CGA G-6.4) [15].

The advantage of hot gas warming at no pressure is there are no container rupture hazards during the heating process.

The disadvantages of hot gas warming at no pressure are:

- discharges all remaining carbon dioxide;
- can create large volumes of carbon dioxide gas creating a possible asphyxiation hazard;
- requires approximately 276 800 kJ/tonne (238 000 Btu/ton) of liquid in the container before de-pressurisation if complete conversion to dry ice has occurred;
- requires cleaning and purging of the container to remove moisture and contaminants; and
- may require entry through the manway with confined space entry safety restrictions and procedures.

A variation of hot gas warming at little or no pressure is to reduce the tank pressure to near atmospheric pressure and then use a compressor or blower to circulate and heat carbon dioxide vapour in a closed loop. The pressure will increase as the dry ice sublimates, but the pressure rise is limited by a pressure regulator set to near ambient pressure, relieving to atmosphere. See Figure 9.



**Figure 9 Circulation of warm vapour at no pressure to sublime dry ice (Method 3)**

### 13.5 Unassisted natural re-pressurisation (Method 4)

Remove the container from service, close all valves, and install a pressure control device to maintain the container's pressure at 690 kPa (100 psi). Ambient heat entering through the insulation will melt the dry ice and warm the resulting liquid to normal operating conditions.

This is a slow and gradual process. Pressure cannot be used to determine the liquid temperature during re-pressurisation because dry ice and colder liquid tend to settle to the bottom of the container. This could maintain the temperature at the bottom of the container at the triple point irrespective of the pressure. This method should only be used if the pressure in the container is limited to 690 kPa (100 psi) (see Note 1 and 2 of Table 4).

The advantage of unassisted natural re-pressurisation is that it is self-regulating.

The disadvantages of unassisted natural re-pressurisation are:

- It is extremely slow;
- May require up to 30 days depending upon the quantity of product, the ambient temperature, and the quality of the insulation; and
- May take longer in a vertical container than in a horizontal container. While both types of containers can stratify (cold liquid or dry ice below a warm upper layer of liquid), vertical containers are especially prone to this condition.

## 14 Re-pressurisation methods—not recommended

Some of the following procedures are known to have been used for re-pressurisation in the past. Actual tests performed by CGA indicated that they are ineffective or unsafe and are therefore not recommended.

### 14.1 Transfer liquid carbon dioxide into the container to melt the dry ice and warm the liquid—not recommended

The reasons that this method is not recommended are:

- Only works with partially filled containers (approximately 10% full before de-pressurisation). More than a full 20 tonne carbon dioxide trailer is required to restore a 50 tonne container back to service if it contains 10% of liquid just before de-pressurisation;
- No assurance that all the dry ice will melt after the liquid is added. The container can become overfilled after the dry ice melts; and
- May not be able to inject liquid through lines blocked by dry ice.

**14.2 Pressure building vaporiser/internal heater method only—not recommended**

The reasons that this method is not recommended are:

- Dry ice can still exist in areas away from the heater. The container pressure will not reliably indicate product and container temperature;
- Can rapidly increase the vapour pressure in the container without melting the dry ice or warming the liquid in areas away from the heater;
- No liquid circulation to melt dry ice or warm liquid away from the vaporiser; and
- Can cause the heating element to overheat or burn out inside an extremely cold and brittle container. Dry ice in the liquid supply piping (see 9.2) to an external vaporiser or the bridging of dry ice surrounding the internal heater could prevent the heater from being properly submerged in liquid causing overheating.

**14.3 Transferring carbon dioxide vapour into the vapour connection of the de-pressurised container—not recommended**

The reasons that this method is not recommended are:

- Will warm up container contents only when incoming vapour can directly contact dry ice or snow. The pressure rises rapidly when dry ice is covered by liquid, and further melting of the dry ice or warming of the liquid is extremely slow;
- Cannot restore container to service by this method alone; and
- Does not promote any mixing of the liquid.

**14.4 Remove liquid carbon dioxide from the container and transfer to cargo tanks—not recommended**

The reasons that this method is not recommended are:

- requires contents to be in a liquid state before transfer;
- requires cargo tanks with a suitable MDMT; and
- requires a container with a suitable MDMT to receive the cold liquid from the cargo tank.

**14.5 Manual removal of dry ice—not recommended**

The reasons that this method is not recommended are:

- freezing and asphyxiation hazards to personnel; and
- requires confined space entry procedures

**15 Suggested measures to prevent container de-pressurisation**

Owners and operators of carbon dioxide containers should consider installing safeguards and alarm measures to avoid a loss of pressure. Most of these events are caused by excessive vapour withdrawal from the container which in many cases is linked to a loss of vaporisation capacity. Depending on the application and equipment specifications, one or more of the following measures may be considered for installation, see Figure 10.

**15.1 Backpressure regulating valve**

Install a back-pressure regulating valve on the vapour use line, set greater than or equal to a pressure corresponding to the MDMT of the container (1379 kPa [200 psi] setpoint for an MDMT of  $-28^{\circ}\text{C}$  [ $-20^{\circ}\text{F}$ ]). The regulator would close at container pressures no less than the corresponding minimum designed allowable operating temperature, shutting off flow of carbon dioxide from the container.



## 15.2 Direct to process vaporiser

System designers should consider use of direct to process vaporisers for high vapour use. Withdrawing vapour from the top of the container relies on the pressure building vaporiser. The pressure building vaporiser may not be adequate to maintain container pressure at high vapour withdrawal rates.

## 15.3 Low pressure alarm

Install an audible and/or visual low-pressure alarm connected to the container head space to locally alert the operator of low container pressure. This is typically set at a pressure corresponding to a temperature greater than the MDMT and less than the pressure building vaporiser range to allow the operator time to apply corrective action.

## 15.4 Remote monitoring

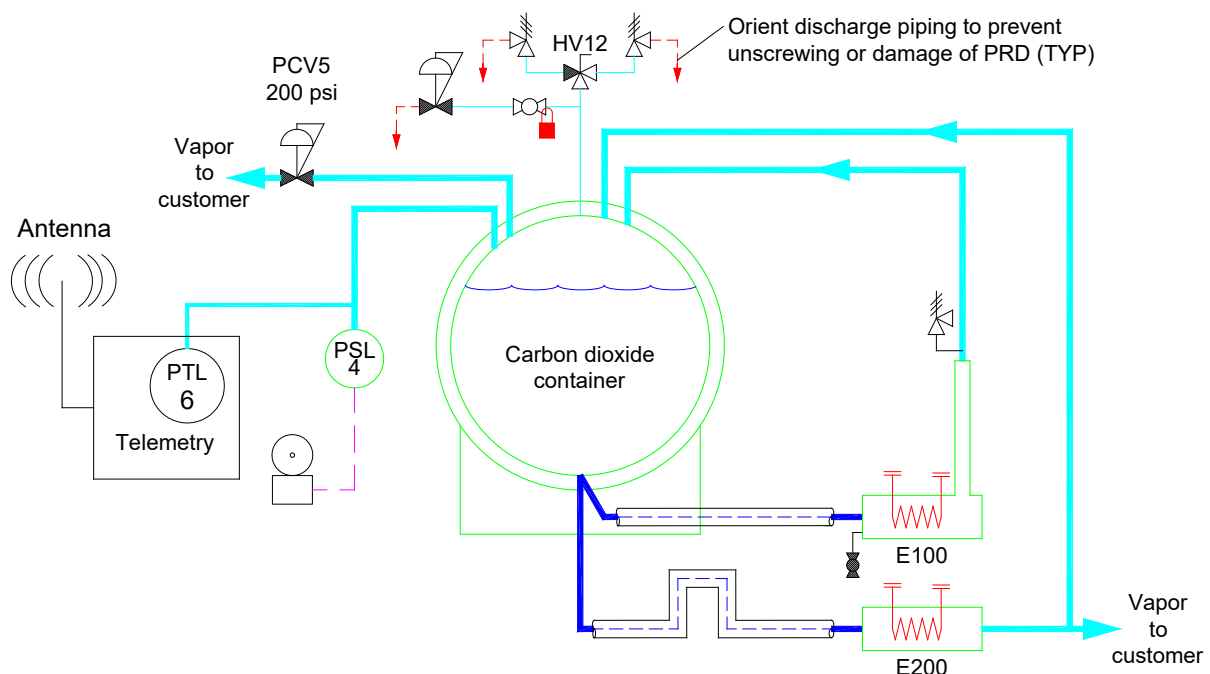
Install local or external telemetry that will generate a low-pressure alarm at a monitored location in order to dispatch a carbon dioxide technician to diagnose the cause of the low container pressure.

## 15.5 Diverter valve on pressure relief devices

Replace a single PRD with a 3-way diverter valve and dual PRDs to allow isolation of a defective PRD failed in the open position. This is in reference to the main container PRD, not ancillary PRDs such as PRDs on the pressure building vaporiser.

## 15.6 Pressure relief device discharge piping design

Evaluate discharge piping orientation and configuration on PRDs to prevent thrust caused by discharging PRDs from unscrewing or damaging the PRDs. This could cause the PRDs to detach from the container or fail in the open position, resulting in the loss of container pressure.



NOTE For additional details and equipment, see CGA G-6.1, *Standard for Insulated Liquid Carbon Dioxide Systems at Consumer Sites* [19].

TAG No	Item	Function
E100	Pressure building vaporiser	Allows limited vapour withdrawal
E200	Direct-to-process vaporiser	Allows high vapour withdrawal
PCV5	Back pressure regulating valve	Stop vapour removal at low pressure

PSL4	Low pressure alarm	Alert user to low pressure
PTL6	External telemetry	Alert technician of low pressure
HV12	3-way diverter	Allows relief device replacement

**Figure 10 Typical protective measures to prevent container de-pressurisation**

### 15.7 Signage

Install warning signage on the container indicating normal operating pressure and the dangers of low operating pressure/temperature. Examples of a sign appropriate for a tank with an MDMT of  $-29^{\circ}\text{C}$  ( $-20^{\circ}\text{F}$ ) are shown in Figure 11.



**Figure 11 Examples of caution signage**

## 16 References

Unless otherwise specified, the latest edition shall apply.

- [1] ASME Boiler & Pressure Vessel Code, American Society of Mechanical Engineers, [www.asme.org](http://www.asme.org)
- [2] EN 13445-3 *Unfired pressure vessels. Part 3 Design*, [www.cen.eu](http://www.cen.eu)
- [3] EN 13458-2, *Cryogenic vessels—Static vacuum insulated vessels—Part 2 Design, fabrication, inspection and testing*, [www.cen.eu](http://www.cen.eu)
- [4] AD 2000 Merkblatt W10 Werkstoffe für tiefe Temperaturen Eisenwerkstoffe, Carl Heymanns Verlag KG, Luxemburger Strasse 449, D-50939 Cologne
- [5] CGA P-11, *Guideline for Metric Practice in the Compressed Gas Industry*, Compressed Gas Association, Inc. [www.cganet.com](http://www.cganet.com)
- [6] ASTM A370, *Standard Test Methods and Definitions for Mechanical Testing of Steel Products*, ASTM International. [www.astm.org](http://www.astm.org) [PC 27576]
- [7] EN 10028-1, *Flat products made of steels for pressure purposes - Part 1: General requirements* [www.cen.eu](http://www.cen.eu)
- [8] Quinn, E.L. and Charles L Jones, *Carbon Dioxide*, p. 97, American Chemical Society Monograph Series, Reinhold Publishing Corp. [www.umi.com](http://www.umi.com)
- [9] *Code of Federal Regulations*, Title 29 (Labor) Part 1910, U.S. Government Printing Office. [www.gpo.gov](http://www.gpo.gov)
- [10] EIGA Doc 919, *Guidelines for the Preparation of Safety Data Sheets*, European Industrial Gases Association, Inc. [www.eiga.eu](http://www.eiga.eu)
- [11] EIGA SI 24 *Carbon Dioxide Physiological Hazards – “Not just an Asphyxiant”*, European Industrial Gases Association, Inc. [www.eiga.eu](http://www.eiga.eu)
- [12] NFPA 55, *Compressed Gases and Cryogenic Fluids Code*, National Fire Protection Association. [www.nfpa.org](http://www.nfpa.org)

- [13] CGA G-6, *Carbon Dioxide*, Compressed Gas Association, [www.cganet.com](http://www.cganet.com)
- [14] CGA PS-5, *CGA Position Statement on the Suitability of Carbon Steel Containers for Stationary Carbon Dioxide Storage*, Compressed Gas Association, Inc. [www.cganet.com](http://www.cganet.com)
- [15] CGA G-6.4, *Safe Transfer of Liquefied Carbon Dioxide in Insulated Cargo Tanks, Tank Cars, and Portable Containers*, Compressed Gas Association, Inc. [www.cganet.com](http://www.cganet.com)
- [16] NFPA 86, *Standard for Ovens and Furnaces*, National Fire Protection Association. [www.nfpa.org](http://www.nfpa.org)
- [17] API Standard 2000, *Venting Atmospheric and Low-pressure Storage Tanks*, American Petroleum Institute. [www.api.org](http://www.api.org)
- [18] ATEX Directive 2014/34/EU, *Equipment for potentially explosive atmospheres*, European Commission. [www.ec.europa.eu](http://www.ec.europa.eu)
- [19] CGA G-6.1, *Standard for Insulated Liquid Carbon Dioxide Systems at Consumer Sites*, Compressed Gas Association. [www.cganet.com](http://www.cganet.com)
- [20] EN 13445-2, *Unfired pressure vessels – Part 2: Materials*, [www.cen.eu](http://www.cen.eu)
- [21] EN 10028-3, *Flat products made of steels for pressure purposes—Part 3: Weldable fine grain steels, normalized*, [www.cen.eu](http://www.cen.eu)

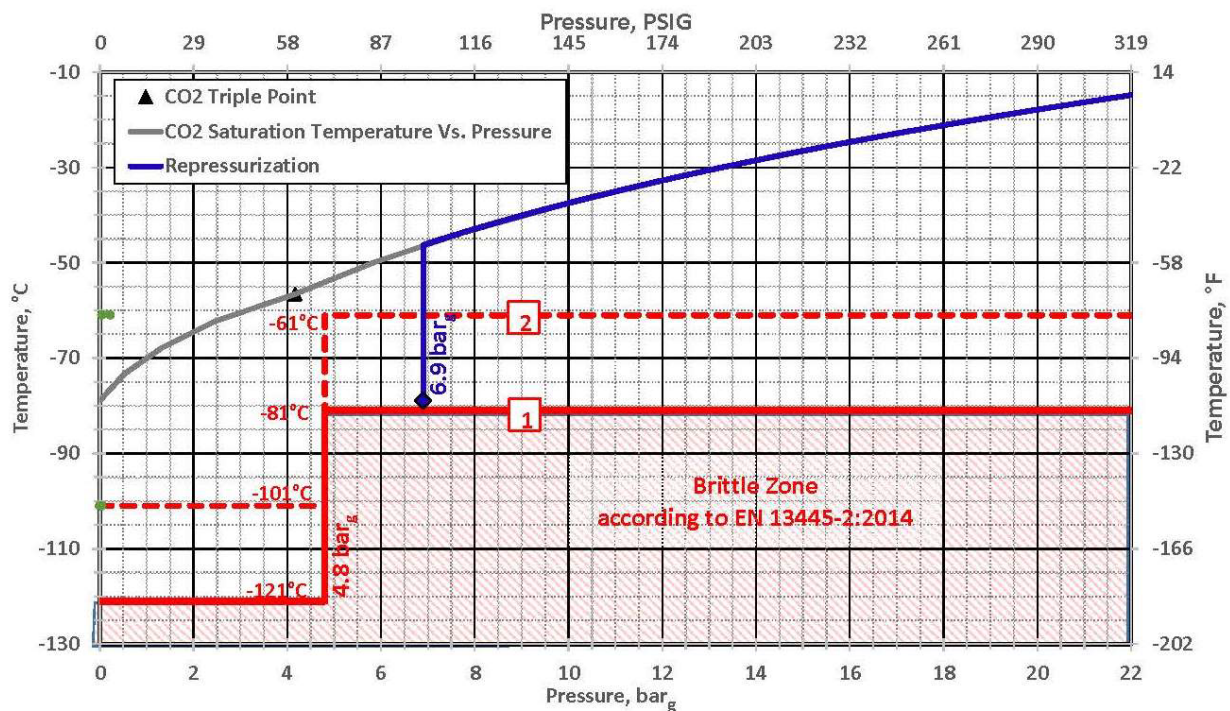
## 17 Additional references

- EN 14197 Parts 1-3, *Cryogenic vessels—Static non-vacuum insulated vessels*, [www.cen.eu](http://www.cen.eu)
- EIGA Doc 66, *Refrigerated CO<sub>2</sub> storage at users' premises*, European Industrial Gases Association. [www.eiga.eu](http://www.eiga.eu)

## Appendix A—EN pressure vessel material design information (Informative)

### A1 EN standard pressure vessel

Both EN examples in Figure A-1 illustrate a 33 ton carbon dioxide pressure vessel, service pressure = 22 bar, outside diameter = 2460 mm, minimum wall thickness = 11.8 mm. Example 1 is manufactured with a steel having a minimum impact value of 27 J at  $-40^{\circ}\text{C}$  with an MDMT of  $-81^{\circ}\text{C}$  based upon Figure A-2. Example 2 is manufactured with a steel having a minimum impact value of 27 J at  $-20^{\circ}\text{C}$  with an MDMT of  $-61^{\circ}\text{C}$  based upon Figure A-2. Information for Examples 1 and 2 are labelled with a number 1 and number 2 inside of a red rectangle in the diagrams. In both cases, the vessels have not been post weld heat treated.



**Figure A-1—EN allowable MDMT conditions for a carbon dioxide container being re-pressurised**

Determine the guaranteed impact properties of the steel at the lowest temperature in the material certificate or the material standard; in Example 1 it is 27 J at  $-40^{\circ}\text{C}$  and in Example 2 it is 27 J at  $-20^{\circ}\text{C}$ .

Determine the wall thickness of the tank, the guaranteed yield stress ( $R_e$ ) of the steel used and whether the vessels has been heat treated after welding; for both examples given in Figure A-1 with no post weld heat treatment,  $R_e = 355 \text{ N/mm}^2$  and thickness equal to 11.8 mm.

For Example 1, the vessel can be operated at temperatures lower than  $-81^{\circ}\text{C}$ , but only when the stress levels are less than 50 MPa per EN 13445-2, *Unfired pressure vessels – Part 2: Materials* [20]. For Example 2, the vessel can be operated at temperatures lower than  $-61^{\circ}\text{C}$ , but only when the stress levels are less than 50 MPa in accordance with EN 13445-2 [20].

The pressure that corresponds to a stress ( $S$ ) of 50 MPa can be determined using the following formula:

$$P = \frac{S \cdot 2e}{D}$$

Where:

$P = 0.48 \text{ MPa}$  (4.8 bar) internal pressure

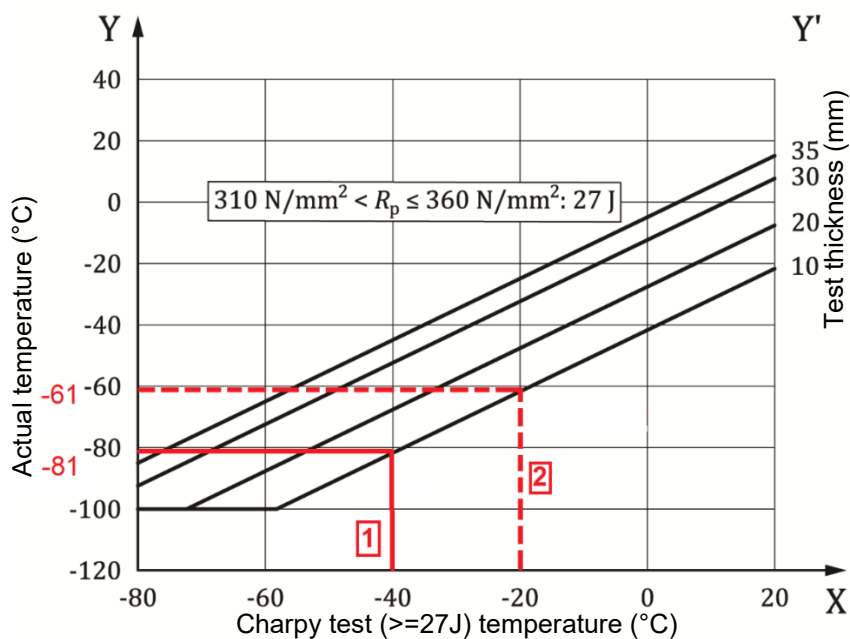
$S = 50 \text{ MPa}$  (stress level where lower operating temperature is allowed)

$e = 11.8 \text{ mm}$  wall thickness

$D = 2460 \text{ mm}$  diameter

EN 13445-2 allows the operation of pressure vessels 40 °C colder than the MDMT as long as the wall stresses are less than 50 MPa [20]. The vessel in Example 1 could operate as cold as  $-121 \text{ °C}$  at pressures less than 4.8 barg, which is well below the coldest dry ice temperature of  $-78 \text{ °C}$  (i.e.,  $-81 \text{ °C}$  MDMT – 40 °C allowable temperature reduction =  $-121 \text{ °C}$  minimum operating temperature at reduced pressure). The vessel in Example 2 could operate as cold as  $-101 \text{ °C}$  at pressures less than 4.8 barg, which is well below the coldest dry ice temperature of  $-78 \text{ °C}$  (i.e.,  $-61 \text{ °C}$  MDMT – 40 °C allowable temperature reduction =  $-101 \text{ °C}$  minimum operating temperature at reduced pressure).

The labelled lines in Figure A-1 were determined using EN 13445-2. Any operating conditions colder than  $-81 \text{ °C}$  (for Example 1) and greater than 4.8 barg would be in the brittle zone according to the EN 13445-2. Any operating conditions colder than  $-61 \text{ °C}$  (for Example 2) and greater than 4.8 barg would be in the brittle zone according to EN 13445-2 [20]. The brittle zone as shown by the shaded area, for Example 1, in Figure A-1 shall be below the temperature/pressure curve for carbon dioxide (red dotted line) to allow safe operation of the tank during re-pressurisation. As shown in Figure A-1, for Example 1, the blue line is above the shaded area: Method 1 can be used in this example. As shown in Figure A-1, for Example 2, the blue line starts below the shaded area: Method 1 cannot be used in this example; either Method 3 or 4 shall be used.



**Figure A-2—Design reference and impact test temperatures as welded condition for and EN pressure vessel,  $310 \text{ N/mm}^2 < R_p \leq 360 \text{ N/mm}^2 : 27 \text{ J}$**

$310 \text{ N/mm}^2 < R_p \leq 360 \text{ N/mm}^2 : 27 \text{ J}$

$R_p =$  proof stress

NOTE In example 1, the minimum acceptable temperature according to the material certificate is  $-40 \text{ °C}$ , but because the wall thickness of the tank is approximately 10 mm, the tank can be used at normal stress (or service pressure) down to  $-81 \text{ °C}$ . In example 2, the minimum acceptable temperature according to the material certificate is  $-20 \text{ °C}$ , but because the wall thickness of the tank is approximately 10 mm, the tank can be used at normal stress (or service pressure) down to  $-61 \text{ °C}$ .

**A2 AD 2000 Merkblatt pressure vessel**

Check the type of the tank material and guaranteed impact properties of the steel at the lowest temperature in the material certificate or the material standard; for example, fine grained steel P355ML1 its impact properties are 27 J at  $-40\text{ }^{\circ}\text{C}$  [4].

Check the MAWP and wall thickness of the tank and if the tank has been heat treated after welding; for example, no heat treatment and thickness equal 11.8 mm.

Select the load case for the lowest expected operation temperature for the tank material on AD 2000 Merkblatt W10, Table 1, Column 4, 5, or 6 which will be  $-78.5\text{ }^{\circ}\text{C}$  if dry ice is in the tank: for example, load case II has to be considered for the material P355NL1 because it allows a lowest operation temperature of  $-110\text{ }^{\circ}\text{C}$  [4].

NOTE Load case II may be selected for all low temperature fine grained steels of the grades P355NL1/2 or P355ML1/2 according to EN 10028-3, *Flat products made of steels for pressure purposes—Part 3: Weldable fine grain steels, normalized*, because their allowable operating temperature is less than  $-90\text{ }^{\circ}\text{C}$  [21].

Select the allowable pressure loads for the tank based on the wall thickness of the tank shell and their heat treatment according to AD 2000 Merkblatt W10, Table 2 and/or Clause 3 [4]. As a general rule heat treatment is not required for wall thicknesses less than 20 mm if the test certificate shows sufficient impact properties for low temperature as required in the material standard.

The required test temperature is also indicated in Table 1, Column 9 of AD 2000 Merkblatt W10 [4]. Example for the material P355NL1 is  $-40\text{ }^{\circ}\text{C}$ .

For wall thicknesses equal or less than 10 mm the allowable pressure load is limited up to 75% of the calculation pressure (MAWP).

For wall thicknesses greater than 10 mm and equal or less than 20 mm the allowable pressure load is limited up to 50% of the calculation pressure (MAWP): for example, a tank with a thickness of 11.8 mm and a MAWP of 22 bar may be pressurised up to 11 bar.

NOTE Load case I is allowed for temperatures less than the triple point for some materials. Nevertheless, the allowable pressure in the tank should be only increased during the re-pressurisation procedure if the temperature of the tank wall is measured and well above the allowable value.

## **Appendix B—ASME Boiler and Pressure Vessel Code, Section VIII, Division 1** **Rules for Construction of Pressure Vessels [1] (Informative)**

### **B1 General**

An assessment of an ASME coded vessel to determine if the re-pressurisation methods in this publication are suitable for a given pressure vessel can be performed using industry experience or more formal methods. For carbon steel vessels a common assessment method would be to use the UCS-66 “Materials” section of the ASME Code. That is the method this appendix will discuss, as the resources and personnel to perform this analysis are widely available. When appropriate, an assessment using methods such as API-579, ASME Code Section XI or other brittle fracture mechanics analysis method can be performed.

ASME Code stamped pressure vessels currently in service vary in the Edition and Addenda they were built to. The materials of construction also vary. The first step in assessing an ASME coded vessel is to acquire information regarding the construction, manufacture, repair, or alteration of the vessel. This shall include a copy of the ASME Data Report and a copy of any National Board Reports on Repairs or Alterations. This could also include a photo of the ASME nameplate and a photo of any Repair or Alteration nameplates. A copy of the fabrication drawing is very useful, but unless the Data Report is unclear, not necessary. Obtaining other information on the size of the vessel, horizontal or vertical, etc. will allow judgements to be made about the accuracy of the information acquired.

This appendix discusses pressure vessels manufactured using carbon steel shell and head materials, permitted by section UCS of the ASME Code. Pressure vessels manufactured using materials permitted by section UHT of the ASME Code can be assessed using similar methods to those used for UCS material but are outside the scope of this appendix. Section UHT materials are more likely to be encountered in cargo tank applications than in stationary tank applications. Pressure vessels using austenitic stainless steel for the shell and heads frequently have lower MDMTs than carbon steels and are beyond the scope of this appendix. Section UHA of the ASME code should be consulted for austenitic stainless-steel vessels.

When assessing an ASME pressure vessel to determine the applicability of this document, it is best to obtain guidance from someone familiar with the code and in particular UCS-66 since the ASME Code has varied over the years. The example in this appendix is specific to a particular edition/addenda of the code. In evaluating other designs, other editions/addenda of the code may apply.

Pre-1987 carbon steel pressure vessels, including for carbon dioxide service, were assigned a generic MDMT of  $-20^{\circ}\text{F}$ . Prior to 1987, the ASME Code required the material to be Charpy impact tested for any pressure vessel that had an MDMT colder than  $-20^{\circ}\text{F}$ . When a generic  $-20^{\circ}\text{F}$  MDMTs has been applied, a more sophisticated analysis may need to be performed.

The thickness, material specification and heat treatment of each of the materials in the pressure vessel must be determined prior to using UCS-66. The heat treatment of usual concern is whether the material is normalised or not, and whether the vessel is post weld heat treated. If normalizing has not been performed the steel is considered as-rolled. SA-612 and SA-516 are available either as-rolled or normalised and both have been used in vessels for liquid carbon dioxide service. If the ASME Data Report does not state the material is normalised it is considered as-rolled.

At equilibrium conditions, for liquid carbon dioxide service, the colder the vessel's internal temperature, the lower the vessel's internal pressure. The lower vessel internal pressure produces a lower required thickness in the vessel components. Since the wall thickness does not change, this can allow lower MDMTs at lower pressures, which may be colder than the MDMT shown on the pressure vessel data plate.

When assessing each component of a pressure vessel, it is necessary to determine the Figure UCS-66 curve its material belongs to. See Table B-1 for the curve listed for the material/heat treatment condition combinations listed.



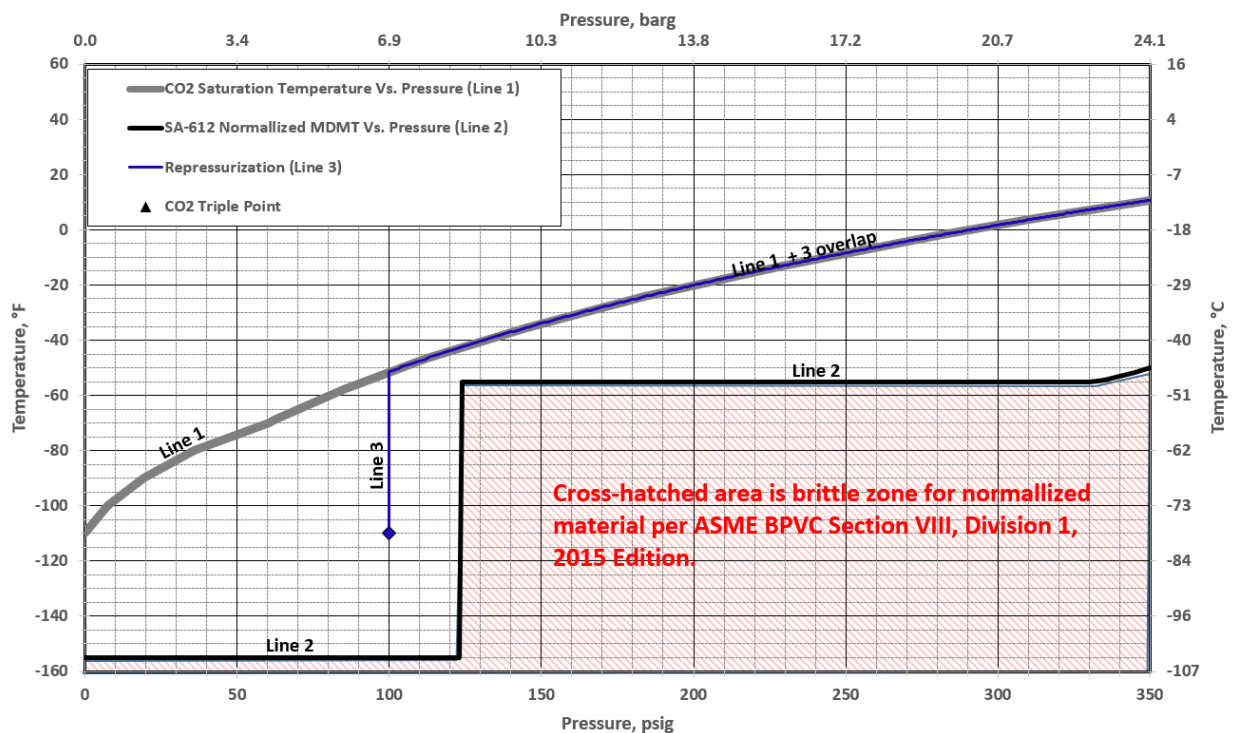
NOTE SA-212 is a material removed from the ASME Code long before UCS-66 was added to the code. Its assignment to Curve A is based on industry reference material. The use of UCS-66 for a vessel made using SA-212, would need the concurrence of the person performing the UCS-66 assessment.

**Table B-1— Example on UCS-66 curve selection**

Material Specification	Heat Treatment Status	UCS-66 Curve
SA-212	As-rolled	Curve A
SA-515-70	As-rolled	Curve A
SA-516-70	As-rolled	Curve B
SA-612	As-rolled	Curve B
SA-516-70	Normalized	Curve D
SA-612	Normalized	Curve D

## B2 UCS-66 Example

The ASME Code example in Figure B-1 illustrates a UCS-66 review of a horizontal 30 ton pressure vessel in liquid carbon dioxide service, manufactured to the 2015 Edition of the ASME Code. The pressure vessel has a MAWP of 350 psi with a normal operating pressure in the 280 psi to 310 psi range. The inside diameter is 78 in with the shell having a nominal thickness of 0.61 in and the 2:1 elliptical heads having a minimum thickness of 0.60 in. Radiography has been performed to allow the shell long seams and heads to have a joint efficiency of 1.0. In this example, the pressure vessel was designed with no corrosion allowance (corrosion allowance equals 0.0 in). The shell and heads are made of SA-612, normalised steel (no impact testing performed). SA-612 normalised steel is listed as a Curve D material in the notes to Figure UCS – 66 “Impact Test Exemption Curves”.



**Figure B-1—Allowable MDMT conditions for the carbon dioxide container in this example being re-pressurised**

The MDMT of this vessel at 350 psi using UCS-66 is  $-51^{\circ}\text{F}$ . In this example the shell governs for MDMT, i.e. the shell is the component with the warmest MDMT and all other pressure parts have an equal or colder MDMT. Per Figure UCS-66, 0.61 in Curve D material has a MDMT of  $-49.7^{\circ}\text{F}$ . The required shell thickness for this vessel with a MAWP of 350 psi plus a hydraulic head of 3 psi is



0.6015 in. Figure UCS-66.1 allows a colder MDMT when the ratio of the required thickness to the nominal/minimum thickness is less than 1.0. Using the ratio of  $0.6015/.61 = .98606$ , Figure UCS-66-1 allows a further reduction of 1.5 °F in the MDMT. The final MDMT at 350 psi is  $-49.7 + -1.5 = -51.2$  which is rounded to  $-51$  °F.

Line 2 in Figure B-1 follows the same process in the previous paragraph, only increments of lower pressure are used to determine the required shell thickness at each pressure increment. The ASME code only allows MDMTs of  $-55$  °F and warmer until the stress level is reduced to 35% of allowable stress. Line 1 in Figure B-1 is a plot of the coincident saturation temperature of liquid carbon dioxide versus the pressure at that temperature. For liquid carbon dioxide service, the colder the vessel's internal temperature, the lower the vessel's internal pressure. The lower vessel internal pressure produces a lower required thickness in the vessel components which can allow lower MDMTs, at the lower pressures, than the MDMT shown on the pressure vessel data plate.

The 2015 Edition of the ASME Code allows a MDMT no lower than  $-155$  °F when the ratio of required thickness to nominal/ minimum thickness is 35% or less. (The 35% ratio applies to the vessels built to the 1998 Edition, 1999 Addenda through the current code. A 0.40 ratio would apply to vessels built to the 1987 Edition, No Addenda through the 1998 Edition, No Addenda). For this example, 35% of 0.61 = 0.2135 in. This vessel at 0.2135 in thickness would allow a design pressure of 126 psi, minus a 3 psi hydraulic head, would give us a pressure gauge reading of 123 psi. Therefore, Line 2 in Figure B-1 has a vertical drop from  $-55$  °F to  $-155$  °F at 123 psi.

A review of Figure B-1 shows the pressure vessel's ASME allowable MDMT boundary (Line 2) is colder than the pressure/temperature relationship for this re-pressurisation procedure shown in Line 3. Therefore any of the methods for re-pressurisation presented in this publication could be used on this pressure vessel.

## Appendix C—Flow chart for Methods 1 through 4

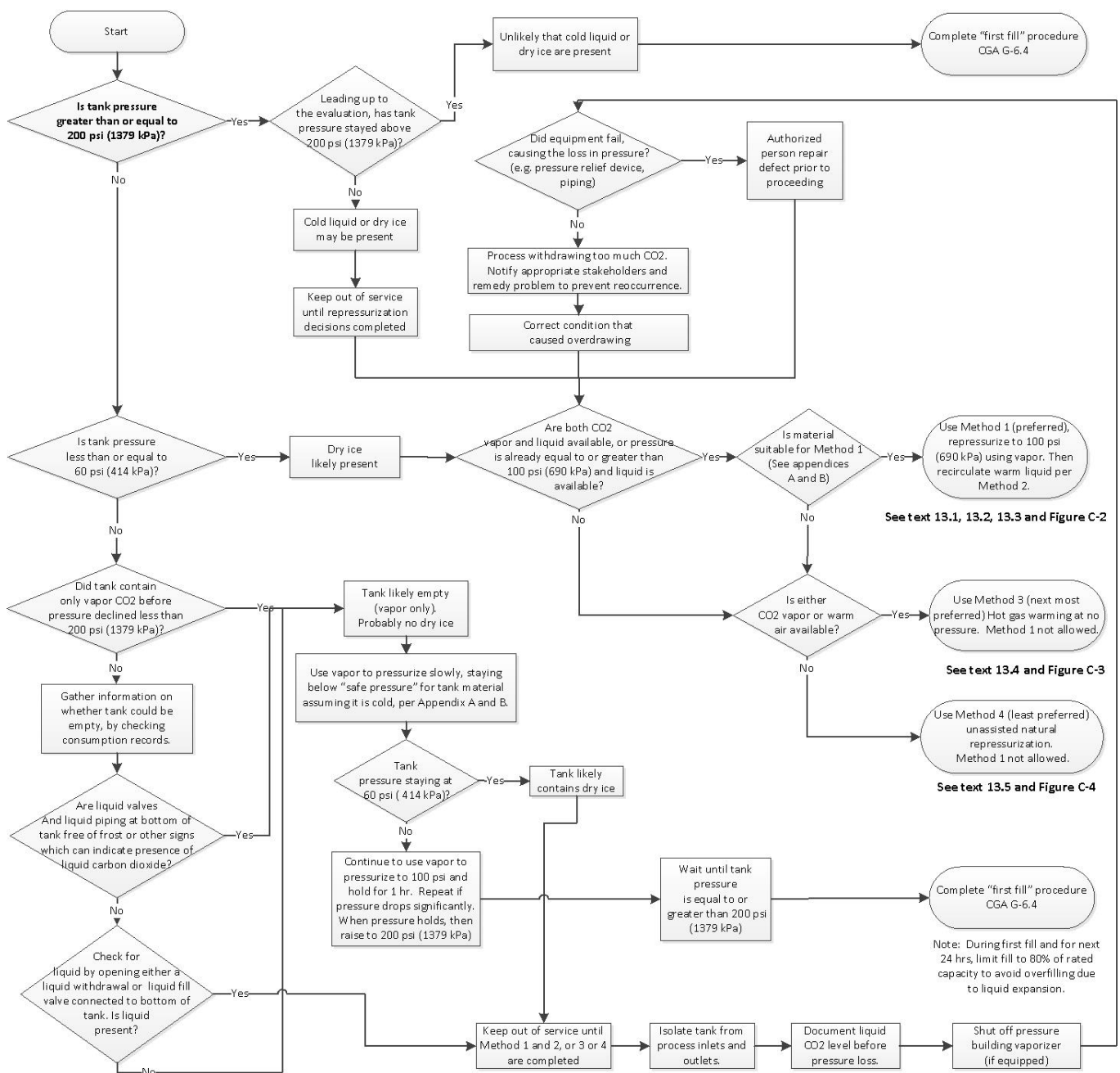
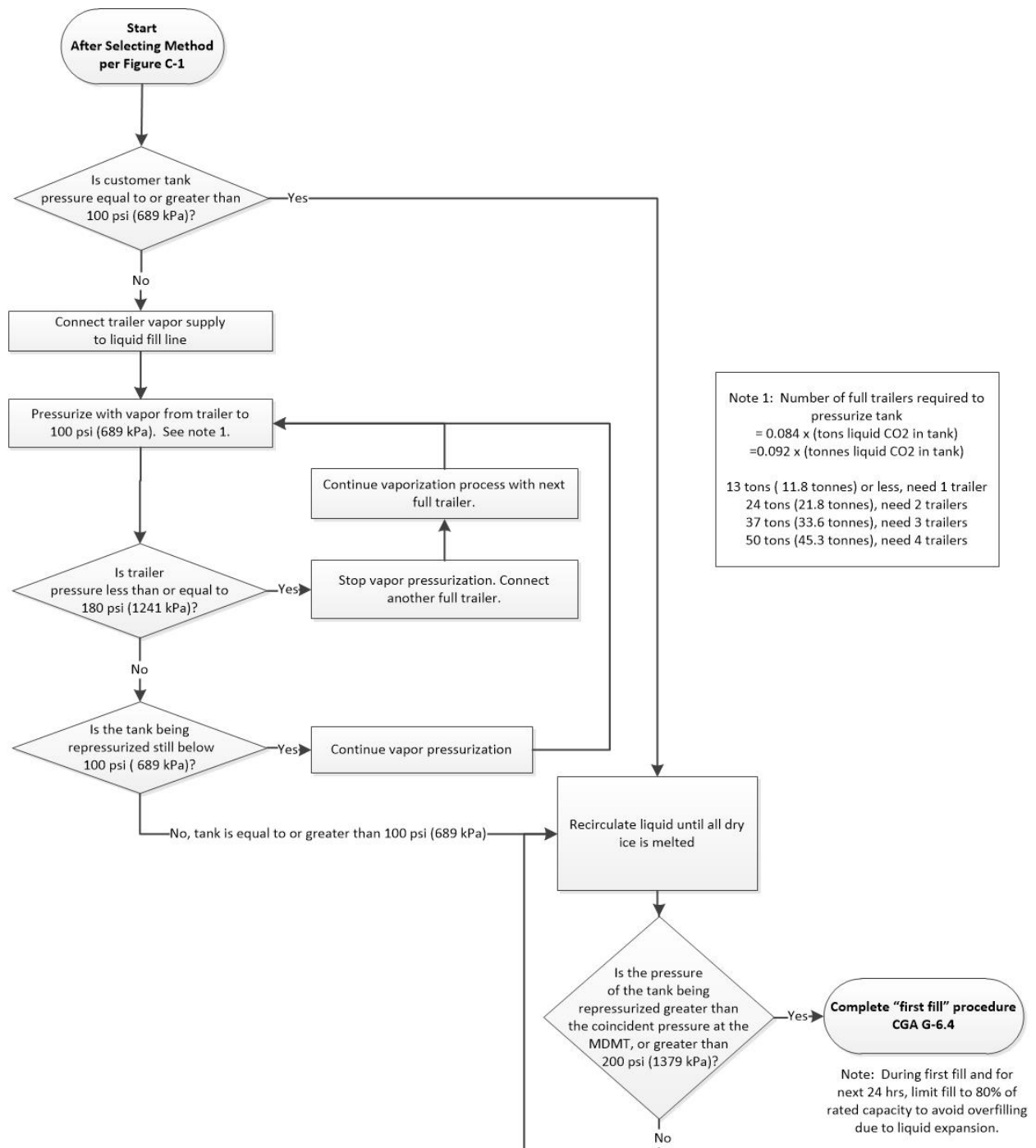
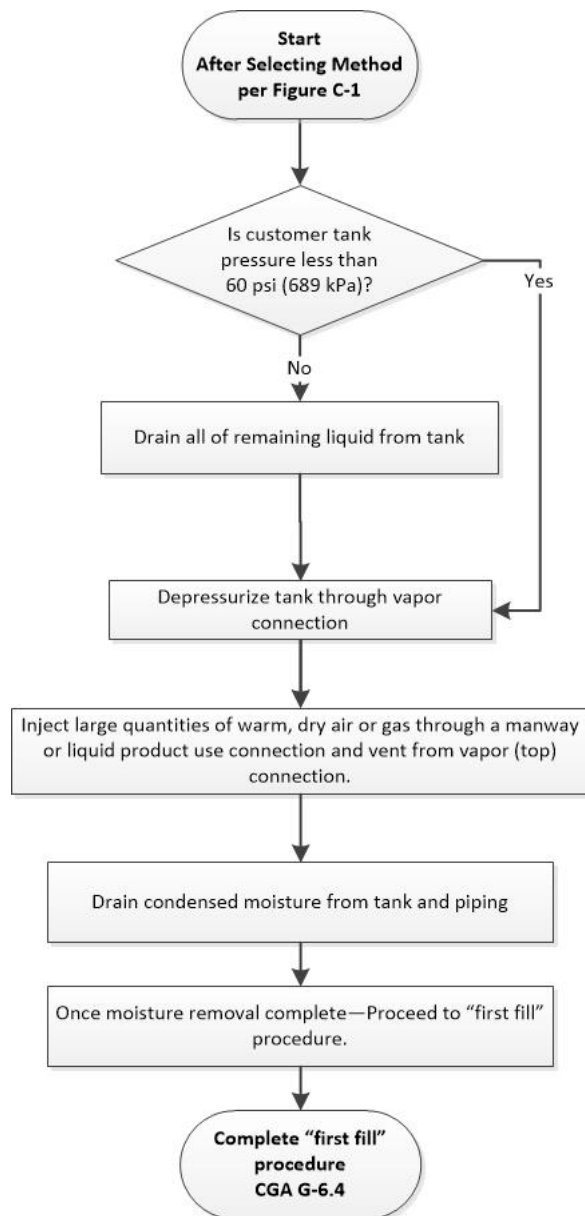


Figure C-1—Decision process for tank re-pressurisation per Section 12 and 13



**Figure C-2—Method 1 re-pressurisation with vapour then Method 2, circulate liquid per 13.2 and 13.3**



Note: During first fill and for next 24 hrs,  
limit fill to 80% of rated capacity to avoid  
overfilling due to liquid expansion.

**Figure C-3—Method 3 re-pressurisation by hot warming at no pressure per 13.4**

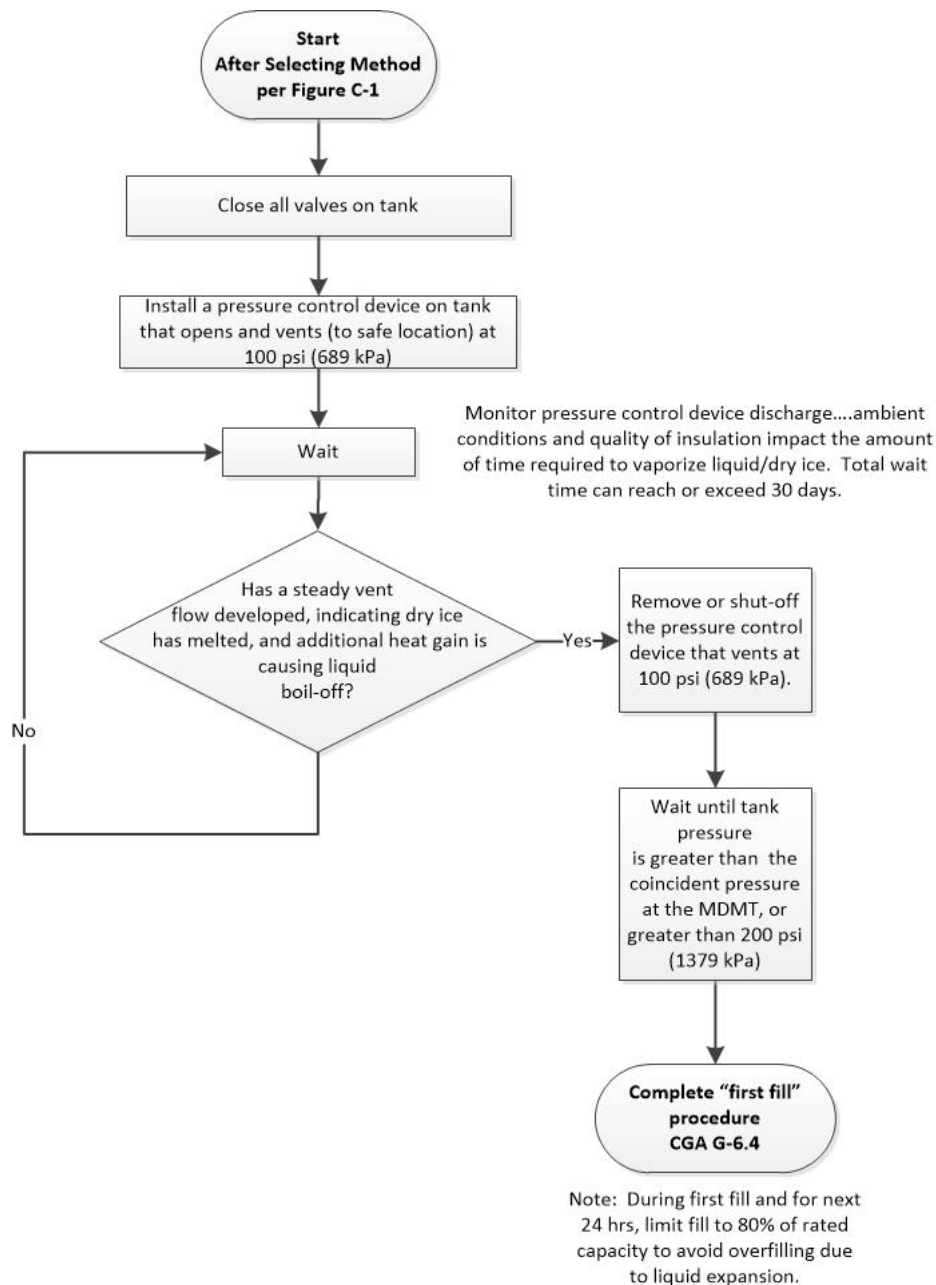


Figure C-4—Method 4 re-pressurisation by natural ambient heat gain per 13.5