THE LINDE GROUP

# Safety Advice.
## 12 – Working with Carbon dioxide $CO_2$.

### 1. Introduction

Working safely with carbon dioxide means understanding the characteristics of this gas and taking suitable safety precautions. This Safety Advice is a recommendation based on practical experience; it supplements, but does not replace, mandatory safety stipulations.
Carbon dioxide is sometimes referred to as "carbonic acid". In this Safety Advice, the term "carbonic acid" is used only to refer to an aqueous solution of carbon dioxide ($CO_2$ in $H_2O$).

### 2. Properties

#### Chemical Properties

Carbon dioxide is non-flammable and, under atmospheric conditions, chemically stable and inert. Combustion reactions are inhibited or completely suppressed by $CO_2$.

Carbon dioxide can react vigorously with certain substances, such as ammonia or amines.

Carbon dioxide dissolves in water to produce carbonic acid, which reacts as a weak acid and has a corrosive effect on carbon steel and a few non-ferrous metals.

#### Physical Properties

As a gas at atmospheric pressure, carbon dioxide is approximately 1.5 times as heavy as air. $CO_2$ therefore tends to flow downward, and can collect in pits, basements, or natural depressions. If there is little air movement, these pools of $CO_2$ can persist for many hours.

The physical states of carbon dioxide, which depend on pressure and temperature, deserve particular attention:

- At atmospheric pressure, $CO_2$ is gaseous.
- At temperatures between –56.6 and +31.1°C, and pressures of at least 5.2 bar, $CO_2$ can exist in liquid form. Liquid $CO_2$ cannot exist at atmospheric pressure (1 bar).
- At temperatures below –56.6°C, $CO_2$ can occur in the solid state.
- All three physical states are possible only at the "triple point" (-56.6°C, 5.2 bar).

#### These physical states can easily change:

In the gas cylinder $CO_2$ is in the liquid state, i.e. "under pressure liquefied." The pressure in the cylinder is approximately 57 bar at 20°C. When $CO_2$ is withdrawn from the cylinder through a regulator set at an outlet pressure of less than 5.2 bar, gaseous $CO_2$ is produced: 1 kg of liquid expands to about 550 litres of gas at atmospheric pressure.

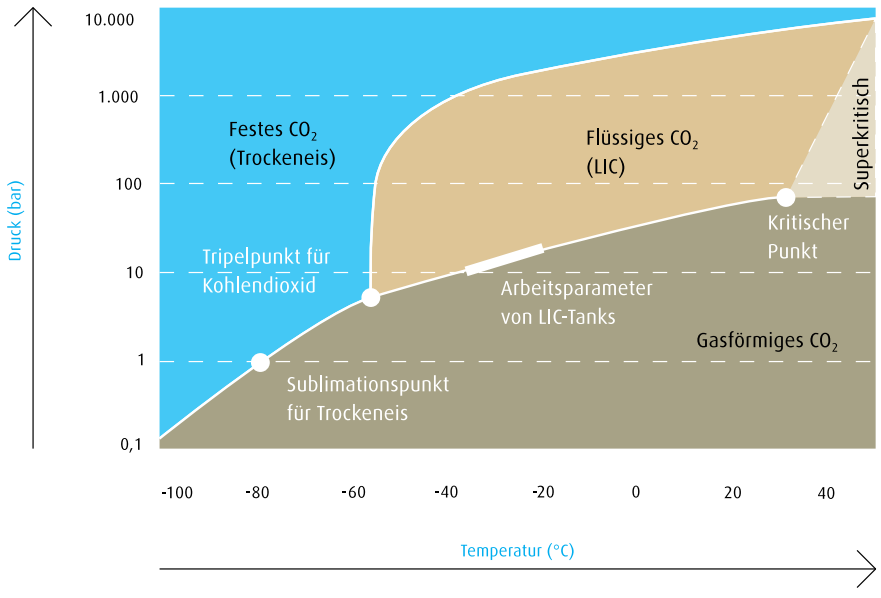
Under certain conditions it is also possible to withdraw $CO_2$ from the cylinder in liquid form (see section 3). If liquid $CO_2$ is abruptly depressurised during withdrawal, it is intensively cooled, producing a mixture of $CO_2$ gas and $CO_2$ snow.

#### Physiological Effects

As a gas, carbon dioxide is colourless and essentially odourless and tasteless. It is therefore practically impossible to detect with the human senses.

Carbon dioxide is considered nontoxic. It is not a hazardous substance as defined by the Dangerous Substances resp. Preparations Directive. The air we brethe contains about 0.03 vol.% carbon dioxide. This concentration is essential for life, since it stimulates the respiratory centre and controls the volume and rate at which we breathe. At higher concentrations, $CO_2$ can

States of aggregation depending on pressure and temperature



be unhealthy. When the air we breathe contains 3 – 5 vol.% $CO_2$, we experience headache, respiratory disturbances and discomfort. At 8 – 10 vol.%, cramps, unconsciousness, respiratory arrest, and death can occur.At this point the oxygen content of the air is still 19 vol.%, which is still sufficient. The physiologically harmful effect of these high $CO_2$ concentrations therefore results not from lack of oxygen, but from the direct effect of carbon dioxide. A maximum workplace concentration (equivalent to TLV) of 0.5 vol.% has therefore been defined for $CO_2$.

Caution: Danger of asphyxiation

Carbon dioxide can also be dangerous to humans because of cold. When cryogenic liquefied $CO_2$, or $CO_2$ that has been cooled by expansion, comes in contact with human skin as a spray or snow, it can produce painful "cryogenic burns." Sensitive tissues such as the cornea are particularly at risk. Large areas of freeze burning can cause death. (See Linde Safety Advice 1, "Handling of cryogenic liquefied gases" )

### Properties of Dry Ice

Dry ice consists of compressed $CO_2$ snow that has been produced by depressurising liquid $CO_2$. At atmospheric pressure the temperature of dry ice is –79°C. When dry ice heats up at atmospheric pressure, it does not melt but instead evaporates completely ("sublimes") to form gaseous cabron dioxide hence the name "dry ice." Depending on how much it is compressed, 1 kg of dry ice yields 300 – 400 litres of $CO_2$ gas. A considerable pressure build-up can therefore occur if dry ice evaporates in a gas-tight vessel.

## 3. Safety Measures

### Health Precautions

Inhalation of $CO_2$ in concentrated form is dangerous to humans. $CO_2$ therefore must not be present in high concentrations in the air. The following safety precautions are advisable:

- Keep $CO_2$ systems gas-tight. Seal any leaks immediately.
- Any $CO_2$ discharge from an operating facility of a safety valve must be vented outdoors.
- Rooms containing $CO_2$ systems must have effective ventilation.
- Rooms in which large quantities of $CO_2$ have collected must be entered only with self-contained breathing apparatus. This applies even if persons have been overcome and urgently require assistance.
- If a sudden $CO_2$ emission occurs, give priority to immediate evacuation of low-lying areas (pits, basements), where the danger of $CO_2$ accumulation is especially severe.
- Fixed $CO_2$ extinguishing systems must be operated, for testing or actual use, only when no one is present in the threatened area. If the carbon dioxide can reach other rooms through ducts, wall openings, ventilation, or air-conditioning systems, these are also considered part of the threatened area.

### Handling of $CO_2$ Cylinders

Important advice for working with any type of gas cylinder is provided in Linde Safety Advice 7 "Safe handling of gas cylinders and cylinder bundles", and 8 "(Re-) Filling Gases".

For $CO_2$ cylinders, also note the following:

Unauthorised transfer of carbon dioxide from one gas cylinder to another constitutes a safety risk, for the following reasons: Cylinders being filled must meet certain requirements so they can reliably withstand the pressure. In general, only the properly trained personnel of an authorised filling facility can determine whether a cylinder is suitable for use. In addition, it is absolutely mandatory that the contents be monitored and defined by weighing during filling. According to the Pressure Vessel Code, a cylinder may contain a maximum of 0,75 kg $CO_2$ per litre of cylinder volume. This fill factor guarantees that the pressure in the $CO_2$ cylinder will not reach the test pressure of 250 bar below a temperature of 65°C. If the filling factor is exceeded, the pressure inside the cylinder increases substantially with even a slight rise in temperature. An overfilled $CO_2$ cylinder can burst if it is merely exposed to sunlight. It is highly inadvisable to transfer carbon dioxide from one cylinder to another.

The pressure in a $CO_2$ cylinder depends solely on temperature. At 20°C, for example, it is 57 bar. Even an almost empty $CO_2$ cylinder remains at 57 bar at 20°C, as long as it contains the liquid phase. This means that the contents of a $CO_2$ cylinder cannot be determined by measuring its pressure, but only by weighing.

$CO_2$ cylinders are generally made of carbon steel. This material is corroded by carbonic acid ($CO_2$ dissolved in $H_2O$) a dangerous loss of strength. $CO_2$ cylinders must therefore be protected from water or aqueous fluids (beer, lemonade, etc.).

In the filling plant, $CO_2$ cylinders must be checked for water prior to filling, and dried if necessary. But users should also make sure that liquids do not enter their $CO_2$ cylinders. One possible safety precaution is to install a backflow preventer.
There is another, very simple safety precaution, which can keep moisture out of $CO_2$ cylinders: they should be emptied only down to a residual pressure of about 5 bar; then keep the cylinder valves closed. This prevents moist air from entering into the cylinder.

$CO_2$ cylinder valves shall have a overpressure safety device in the form of a bursting disk that is secured to the valve with a coupling nut. To prevent inadvertent and dangerous discharge of $CO_2$, this device must never be tampered with.

### Withdrawing Gas from $CO_2$ Dip Tube Cylinders

$CO_2$ dip tube cylinders contain a dip tube which extends from the cylinder valve to just above the bottom of the cylinder. Provided it remains vertical, a dip tube cylinder always yields $CO_2$ in liquid form. Note the following particular characteristics when using these cylinders:

- $CO_2$ dip tube cylinders are clearly marked as such by the filling plant. The user must specifically note that the cylinder is a $CO_2$ dip tube cylinder.
- $CO_2$ dip tube cylinders must be used only when the user intends to withdraw liquid carbon dioxide.
- $CO_2$ dip tube cylinders must not be fitted with a regulator, sine the pressure drop woul cause the liquid caarbon dioxide to solidify into $CO_2$ snow, clogging the regulator and disabling it.
- $CO_2$ dip tube cylinders must be standing upright while gas is being withdrawn, so that the opening of the dip tube remains below the $CO_2$ liquid level. Thsi is the only way in which almost the entire contents of the cylinder can be withdrawn in liquid form as intended.
- Liquid carbon dioxide emerges from a $CO_2$ dip tube cylinder at full cylinder pressure. The withdrawal device must therefore be appropriately pressure-

resistant and designed for liquid $CO_2$. It would be potentially fatal, for example, to connect a $CO_2$ dip tube cylinder to a beer keg without a regulator. The keg would be completely incapable of withstanding the pressure of the evaporating liquid $CO_2$, and would burst.

- Pipe sections for liquid $CO_2$ equipped with shutoff devices must also be equipped with a safety valve.
- When liquid carbon dioxide withdrawn from a dip tube cylinder expands to atmospheric pressure, $CO_2$ snow is produced. Dip tube cylinders are therefore used primarily in instances where $CO_2$ snow is required, for example to refrigerate foodstuffs. $CO_2$ snow can be dangerous in several ways. If it contacts human skin while emerging, there is a danger of cryogenic burns. Minimum protection should therefore consist of safety glasses for the eyes. The $CO_2$ snow can also clog the supply system. When a plug of $CO_2$ snow is suddenly loosened, for example by striking the supply hose, the backedup liquid $CO_2$ abruptly deprssurises. This can cause the hose to fly around or burst, injuring people of damaging property.
- A very specific hazard can arise when $CO_2$ is used to inert flammable gases or vapours. In a flowing mixture of gaseous $CO_2$ and $CO_2$ snow,the "snowflakes" can become electrostatically charged and can ignite an explosive gas / air mixture by sparking. $CO_2$ should therefore never be sprayed directly into a cloud of flammable gas or vapour. This important instruction applies to $CO_2$ cylinders with or without a dip tube.

### Withdrawing Gas from $CO_2$ Cylinders Without Dip Tubes

In $CO_2$ cylinders without dip tubes, carbon dioxide is withdrawn from the top of the cylinder. When the cylinder valve is opened, the pressure in the cylinder decreases. $CO_2$ continously evaporates from the liquid phase and emerges as a gas. One important application for $CO_2$ cylinders without dip tubes is in beverage dispensing.
$CO_2$ cylinders without dip tubes must be used with a regulator to dispense gas, so the pressure can be reduced to a level appropriate for the intended purpose.
$CO_2$ cylinders without dip tubes must be vertical while gas is being withdrawn. A horizontal cylinder would release liquid $CO_2$, which might cause the supply apparatus to clog up with $CO_2$ snow.
The rate at which $CO_2$ can be withdrawn from cylinders without dip tubes is limited,

Low temperature warning

since the $CO_2$ must evaporate from the liquid phase. This process absorbs heat from the environment, which means that the gas cylinder and especially the valve can ice up. This may make the valve difficult to operate. To prevent this, multiple cylinders should be used when large amounts of $CO_2$ are needed, or the cylinder can be heated with warm water (maximum 50°C). The cylinder should never be heated with a flame.

### Handling of Dry Ice

Because of its low temperature and the formation of gaseous $CO_2$, a few special safety precautions must be taken when handling dry ice:

- Dry ice is not edible. Do not lick it or place it directly in beverages. The cold and subsequent pressure might have unpleasant effects on the human body. Keep dry ice out of the reach of children!
- Because of its low temperature, dry ice must not be handled with bare hands. Wearing gloves or using appropriate tongs will protect against freeze burning. When manually chopping up dry ice with a suitable implement, protect the eyes from flying particles by wearing safety glasses.
- Dry ice must not be stored or transported in tightly sealed containers. The pressure


resulting from evaporation could burst the container.

- No one should enter a room in which dry ice is being stored until the accompanying gaseous $CO_2$ has been removed by adequate ventilation.
- Dry ice in larger quantities must be transported only in vehicle cargo compartments that are isolated in a gas-tight manner from the cab or passenger compartment.

## 4. Conclusion

Carbon dioxide, in all its forms, can be used for many purposes. it is important to use its capabilities correctly in order to achieve the desired effect and eliminate hazards. Our gas specialists can tell you how to do that.
Consultation in all business and technical problems is made available by the experts of our Sales Offices.

Linde AG
Linde Gas Division, Linde Gas Germany, Seitnerstraße 70, 82049 Pullach
Phone 018 03.85 000-0*, Fax 018 03.85 000-1, www.linde-gas.com