1,3-Butadiene

IDENTIFICATION

1,3-Butadiene
Biethylene
Biethylene Bivinyl
Bivinyl butadiene
Diethylene Divinyl
Divinyl biethylene
Divinyl butadiene
Erythrene
Pyrrolylene
Vinylethylene

ZVG No: 11430
CAS No: 106-99-0
EC No: 203-450-8
INDEX No: 601-013-00-X

CHARACTERISATION

SUBSTANCE GROUP CODE

140120 Hydrocarbons, aliphatic, unsaturated
162000 Organic gases

STATE OF AGGREGATION

The substance is gaseous.

PROPERTIES

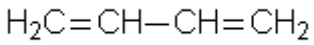
colourless
aromatic odour

CHEMICAL CHARACTERISATION

Extremely flammable gas. Forms explosive mixtures with air.
It may form peroxides already with trace amounts of oxygen, which may cause explosion-like reactions.
Only slightly soluble in water.
Gas is heavier than air.
Chemically unstable at increased temperature.
A sufficient amount of stabilizer has to be added.
When stabilized insufficiently, peroxides are formed and above 80 degree C spontaneous exothermal poymerization may occur.
Acute or chronic health hazards result from the substance.
The substance is hazardous to the aquatic environment.
(see: chapter REGULATIONS).

FORMULA

C4H6



Molar mass: 54,09 g/mol
Conversion factor (gaseous phase) at 1013 mbar and 20 °C:
1 ml/m³ = 2,25 mg/m³

TOXICOLOGY / ECOTOXICOLOGY

TOXICOLOGICAL DATA

LD50 oral rat
Value: 5480 mg/kg
Prehled Prumyslove Toxikologie; Organicke Latky, Marhold, J.Prague, Czechoslovakia, Avicenum, 1986Vol. -, Pg. 14, 1986

LC50 inhalation rat
Value: 285 mg/l/4 h
Russian Pharmacology and Toxicology Vol. 31, Pg. 162, 1968.

Reference: 02071

PHYSICAL AND CHEMICAL PROPERTIES

TRIPLE POINT

Temperature: -108,9 °C
Pressure: 0,693 hPa

MELTING POINT

Melting point: -108,92 °C

BOILING POINT

Boiling Point: -4,5 °C

CRITICAL DATA

Crit. temperature: 152,0 °C
Crit. pressure: 43,2 bar
Crit. density: 0,245 g/cm³

DENSITY

VAPOUR DENSITY
under standard conditions (0 °C, 1013 mbar)
Value: 2,4982 kg/m³

DENSITY OF LIQUID PHASE AT BOILING POINT
Value: 0,65045 kg/l

RELATIVE VAPOUR DENSITY
Ratio of the density to dry air at the same temperature and pressure
Value: 1,92

VAPOUR DENSITY
Value: 2,324 kg/m³
Temperature: 15 °C
at 1 bar

VAPOUR PRESSURE

Vapour pressure: 2,398 bar
Temperature: 20 °C

Vapour pressure: 3,2 bar
Temperature: 30 °C

Vapour pressure: 5,7 bar
Temperature: 50 °C

FLASH POINT

Flash point: -85 °C

IGNITION TEMPERATURE

Ignition temperature: 415 °C
Temperature class: T2
Minimum ignition energy: 0,13 mJ
Max. exper. safe gap (MESG): 0,79 mm
Explosion group: IIB

EXPLOSION LIMITS

Lower explosion limit:
1,4 vol. %
31 g/m³
Upper explosion limit:
16,3 vol. %
365 g/m³
Maximum explosion pressure:
7,9 bar

SOLUBILITY IN WATER

Concentration: 1025 mg/l
Temperature: 20 °C

PARTITION COEFFICIENT (octanol/water)

log Kow: 1,99
Recommended value of LOG KOW Databank.

HAZARDOUS REACTIONS

Thermal decomposition:
Polymerizes explosion-like on heating or in the presence of oxygen.

Hazardous chemical reactions:
Tends to polymerize spontaneously.
Risk of explosion in contact with:
oxygen
aluminium boronhydride
aluminium chloride
butene-3-yne (rare)
crotonaldehyde (heat, autoclave)
iron chloride
peroxides
rust (iron oxide/iron hydroxide)
nitrogen oxides
vinylacetylene (heat)

The substance can react dangerously with:
chlorine
air --> formation of peroxides
antimony chloride
boron trichloride
boron trifluoride
hydrogen chloride
sulphur dioxide
heat

OCCUPATIONAL HEALTH AND FIRST AID

ROUTES OF EXPOSURE

Main Routes of exposure:
The main intake pathway for 1,3-butadiene (1,3-B.) is via the respiratory tract. [7985]

Respiratory tract:
1,3-B. is rapidly absorbed via the respiratory tract and in part exhaled. Equilibrium was already reached prior to the end of a 20 minute exposure to 2 ppm 1,3-B. (4.42 mg/m³) in a test on volunteers. The concentration in the air exhaled was between 1 and 1.9 ppm. The exposure led to an uptake from 0.6 to 4.6 µg/kg bw by the test persons, corresponding to 18 – 74% of the dose inhaled (average of 45.6% for women and 43.4% for men). [7980, 99996]
In animal experiments, the uptake from concentrations up to 1500 ppm occurred according to a first order kinetics. There are indications that the kinetics become saturated at higher concentrations. [2050]

Skin:
Absorption via the skin cannot be excluded in principle but it is not considered to be of any relevance in comparison with the respiratory tract. This assumption is supported by the results of animal experiments (comparable results from studies with exposure of the whole body and exposure nose-only). [2050]

Gastrointestinal tract:
The absorption of 1,3-B. via the gastrointestinal tract is possible in principle. [2050]
However, oral intake either of gases or of the sub-cooled liquid is not considered relevant to the workplace. [419]

TOXIC EFFECTS

Main toxic effects:
Acute:
At high concentrations weak irritation to the eyes and respiratory tract, neurotropic effect (depression of the CNS); [2050]
frostbite following contact with the liquid gas [419]
Chronic:
Carcinogenic effect to the lympho-hemopoietic system (induction of leukemia) [2050]

Acute toxicity:
Liquefied gas or cold gas escaping from pressure vessels and coming into contact with the mucous membranes or skin can cause frostbite and its typical symptoms. [419]
Gaseous 1,3-B. only has the potential to irritate at high concentrations and the acute toxicity is very low. [7619]
In laboratory experiments, concentrations of 1,3-B. under 1 ppm did not irritate the eyes. Earlier studies reported that volunteers exposed to 2000 ppm and 4000 ppm for 6 – 7 hours suffered irritation to the eyes and blurred vision but that the intensity of these symptoms was lower during repeated exposure.
6700 ppm 1,3-B. was tolerated without causing any irritation to the eyes in tests on rabbits and dogs. In tests on rodents tears and inflammation of the conjunctiva were only seen at still higher concentrations (from about 90,000 ppm).
Many years of occupational experience indicate that 1,3-B. does not have any significant potential to cause irritation to the skin and no potential to set off allergies on the skin or in the airways. [2050]
1,3-B. has a weak aromatic gasoline type odor which is already noticeable at very low exposure. The odor threshold values given vary widely (0.099 – 76 ppm). Acceptable values are about 0.45 ppm (1 mg/m³) for odor detection and around 1.1 ppm (2.4 mg/m³) for odor recognition. [419]
The results of earlier studies on volunteers showed that even very high concentrations of 1,3-B. hardly cause any acute effects. Volunteers exposed to 10,000 ppm for 5 minutes noticed slight irritation and dryness in the mouth and nose. There was a slight increase in the pulse rate while the blood pressure and respiration were not affected. When the volunteers were exposed to 8000 ppm for 8 hours, they did not notice any effect on their attentiveness but a “tapping test” at an exposure to 4000 ppm revealed irregularities in their psychomotor reactions.
The IDLH (immediately dangerous to life or health) value was set at 2000 ppm. [7930]
In test on rats, inhalation of 129,000 ppm for 1 hour led to narcosis and there were signs of irritation to the airways. The 4 h-LC50 for rats was determined to be 129,000 ppm. For mice (the most sensitive species for effects caused by 1,3-B.), a 2 h-LC50 of 121,000 ppm was determined.
The oral toxicity data determined for 1,3-B. (LD50 for rats: 5480 mg/kg bw, LD50 for mice: 3210 mg/kg bw) confirm the exceptionally low acute toxicity. However, no information was provided on which form of application was used for these high doses. [2050]

Chronic toxicity:
Earlier studies on employees exposed to 1,3-B. during the production of synthetic rubber (no details provided) reported irritation to the eyes, nose, throat and deeper airways (sometimes also coughing and dizziness). The symptoms disappeared after the exposure ceased. There were no changes to the lung function and nothing was found in x-rays of the lung. There may have been mixed exposure in these studies and therefore these symptoms cannot safely be attributed to 1,3-B.
In a recent, well documented study, the effects on employees exposed during the production of butadiene monomer were investigated. They were subjected to an average concentration of 3.5 ppm 1,3-B. for 8 hours per day (within a range of 0.1 to 143 ppm but mostly under 1 ppm). No increase in morbidity or changes in

hematological parameters was found [2050].
The potential to cause cancer has been investigated in several large epidemiological studies (see under “Carcinogenicity”). [7980].
Long-term animal studies revealed large differences in the sensitivity to chronic effects caused by 1,3-B.
Effects on the blood and bone marrow were found in a 13-week study on mice using concentrations of 1000 or 1250 ppm: megaloblastic anemia, damage to the bone marrow, including influence on the maturation of the stem cells. [7985] In a 2-year study on mice, neoplastic and non-neoplastic changes appeared in various organs. The life span was shortened from 20 ppm upwards. [7742, 7985]
By comparison, a 13-week exposure of rats to 8000 ppm revealed no changes to clinical-chemical parameters or hematological parameters and there were no histopathological effects to organs. In a 2-year study, rats tolerated concentrations up to 8000 ppm with only minimal effects.
The results of an earlier long-term study on rabbits, guinea pigs and dogs indicated that the toxicity is similarly low for these species, i.e as for rats. [2050]

Reproductive toxicity, Mutagenicity, Carcinogenicity:
For classifying the reproductive toxicity and mutagenic and carcinogenic potential see list in Annex VI of the CLP regulation or TRGS 905 or List of MAK values.
(see section REGULATIONS).
Reproductive toxicity:
Delayed development of the fetus was only found at maternally toxic concentrations in developmental toxicity tests on rodents. This was considered to be hardly relevant in assessing the danger to humans. Dominant-Lethal-Tests on mice revealed no influence on male fertility. The damage to the reproductive organs observed in long-term studies on mice are more likely to be a consequence of the high general toxicity for this species than the result of any direct effect on the reproductive organs. Overall, the information on disturbances to fertility is insufficient. [2050]
Mutagenicity:
There are sufficient indications to conclude that the exposure of humans to the substance can lead to hereditary disorders.
1,3-B. has been proven to be genotoxic to somatic and germ cells in tests on mice.
Metabolites of 1,3-B. were genotoxic to somatic and germ cells in mice and rats.
The results of studies on persons occupationally exposed were contradictory. Amongst negative results, signs of genotoxicity were found in 2 studies (increase mutation frequency at the hprt locus, a marginal increase in chromosome aberrations and evidence for an impairment of DNA repair efficiency. [2050]
Carcinogenicity:
A carcinogenic effect on humans has been demonstrated.
[2050]
A clear connection between exposure to 1,3-B. and an increased incidence of leukemia was found in large epidemiological studies on workers in the styrene-butadiene rubber industry. In addition, studies on workers engaged in the production of butadiene monomer indicated further induction of tumors of the lympho-hemopoietic system, particularly non-Hodgkin lymphoma.
A carcinogenic effect was definitely proven for 1,3-B. in long term studies on mice and

rats. Mice were particularly sensitive and for them 1,3-B. proved to be a multi-organ carcinogen, even at very low concentrations. [7980]

Biotransformation and Excretion:
The metabolism of 1,3-B. has been intensively investigated in animal experiments. The first step in the metabolism is the oxidation to 1,2-Epoxy-3-butene (catalyzed by cytochrome P450-dependent monooxygenases). The reactive epoxide can be hydrolytically transformed to 3-butene-1,2-diol or (alternatively) oxidized to the diepoxide 1:2,3:4-diepoxybutane. Both metabolites can be further react to form 3,4-epoxy-1,2-butandiol. The hydrolysis of this epoxide leads to the formation of erythrite. Alternatively, the epoxides and 3-butene-1,2-diol can participate in conjugation reactions with glutathione and in further reactions form mercapturic acids which can be excreted via the bladder. In the body, the epoxide can also bind to proteins and DNA. [7985,7620]
The elimination of 1,3-B. and its metabolites takes place mainly with the urine or the exhaled air and a very small part is excreted with the feces. The elimination in the urine of rodents took place in two phases: 77 - 99% of the dose was eliminated with a half-life of a few hours and the rest with a half-life of a few days.
Although the metabolism in many different species of laboratory animals took place via similar pathways, mice showed significant quantitative deviations in comparison with rats and monkeys. For mice, significantly higher proportions of 1,3-B. were retained in the body and a higher proportion transformed to epoxides, particularly to the diepoxide. The particularly high sensitivity of mice to the effects of 1,3-B. is considered to be mainly caused by these differences in the kinetics.
The metabolism in humans has not been completely investigated. Knowledge available to date indicates that it is more similar to the metabolism in rats than to that in mice. However, in-vitro studies revealed interindividual differences in the oxidative metabolism, so the sensitivity is also expected to differ from one human to another. [2050]
The determination of 1,3-B. in the exhaled air and of mercapturic acid derivatives in the urine were recommended as methods to determine the exposure of persons occupationally exposed. The determination of the mercapturic acid derivative of 3-butene-1,2-diol was particularly recommended because it is the main metabolite in the urine, making up 97% of the mercapturic acid excreted via this pathway.
Hemoglobin adducts are also suitable for determining exposure. They result from the reaction of epoxides with hemoglobin. The determination of DNA adducts seems to be a possibility for monitoring the biological effects. [7620]

Annotation:
This occupational health information was compiled on 13.04.2010.
It will be actualised if necessary.

FIRST AID

Eyes:
If there is irritation following the impact of high concentrations:
Rinse the affected eye with widely spread lids for 10 minutes under running water whilst protecting the unimpaired eye.

[7985]
Following the impact of cold gas resulting from vaporization or impact of the liquefied gas: Immediate rinsing of the eye only for a short time with water at normal temperature or lukewarm water. Do not spread the lids and leave contact lenses in place. Do not warm the eyes. Apply a sterile covering.
Arrange medical treatment.
[419, 99996]

Skin:
Whilst protecting yourself, relocate the casualty away from the source of danger.
Remove contaminated clothing while protecting yourself.
Following contact with liquefied 1,3-butadiene or the depressurized gas, defrost clothes which have frozen onto the skin by initially rinsing with large quantities of cold or lukewarm water, then remove clothing very carefully. [80149]
Also rinse skin areas with cold or lukewarm water wherever there are frost burns resulting from sub-cooled 1,3-butadiene or where frostbites are suspected. Do not rub affected parts of the body or subject the casualty to any dry warmth, instead cover affected areas with sterile material.
Lay the casualty down in a quiet place to rest and protect him against hypothermia.
Arrange for medical treatment.
[419]

Respiratory tract:
Whilst protecting yourself remove the casualty from the hazardous area and take him to the fresh air.
Lay the casualty down in a quiet place and protect him against hypothermia.
In the case of breathing difficulties have the casualty inhale oxygen.
Arrange medical treatment.
[80149]
Following very massive inhalation, the following can become necessary:
If the casualty has stopped breathing give mouth to nose resuscitation. If this is not possible use mouth to mouth resuscitation. Keep his respiratory tract clear.
In the case of cardiac arrest (lack of heart beat or pulse) immediately apply heart lung resuscitation. The protection of the vital functions (heartbeat and respiration without assistance) takes priority over every other activity.
[419]

Swallowing:
Swallowing of the sub-cooled liquid is hardly conceivable. [419]
If this has nevertheless happened: have the casualty drink 1 – 2 glasses of water.
For further measures, see “Respiratory tract”.
Arrange medical treatment.
[99999]

Information for physicians:
As a gas, 1,3-butadiene is only weakly irritating and the acute toxicity is very low, so acute poisoning is hardly conceivable. If 1,3-butadiene is let down from pressure vessels or the liquefied gas is vaporized it can displace oxygen. The first aid operator and the emergency doctor need to be aware that 1,3-butadiene has the potential to

cause cancer. [419]

- Symptoms of acute poisoning:
Eyes: at concentrations from 2000 – 8000 ppm, slight stinging pain, blurred vision, [2050] frostbites caused by vaporized liquid or depressurized gas
Skin: frostbites caused by liquid or depressurized gas (feeling of deafness, tingling of the skin, itching, burning, stiffness of affected areas)
Inhalation: at very high concentrations (above about 8000 ppm), irritation of the nose, throat and deeper airways, at still higher concentrations systemic effects (see below) and/or anoxic effects due to the displacement of oxygen; [419] following direct inhalation of very cold gas, reflex respiratory/cardiac arrest (stimulation of the nervus vagus) [99996]
Ingestion: no information available
Absorption: following very massive inhalative exposure depression of the CNS with symptoms such as headache, vertigo, dizziness, confusion, possibly loss of consciousness. [419]

- Medical advice:
Following contact of the eyes with liquefied or expanded gas, rinse the eyes. Then consultation of an ophthalmologist is indicated.
Frostbites or sub-cooling of the body can be treated in the usual way. [419]
Following massive inhalative exposure, generously administer fresh air or better have the casualty inhale oxygen. Carry out further treatment symptomatically. [80149]
Following extremely high exposure to the expanded gas or in rooms with limited ventilation (displacement of the oxygen) measures for cardiopulmonary and cerebral reanimation may be necessary.
Following massive exposure, even if there are no poisoning symptoms, a check of the heart-circulatory and lung functions as also of the hematological and biochemical parameters is recommended. [419]

Recommendations:
Provide the physician information about the substance/product and treatment already administered.
[99999]
Exposure to 1,3-butadiene can be determined immediately after the accident by determination of the poison in the air exhaled (noting that the concentration diminishes very rapidly) or by determination of mercapturic acids in the urine.
Using the determination of hemoglobin adducts, exposure to 1,3-butadiene can still be verified some time later.
The determination of DNA adducts is a suitable parameter for monitoring the effects. [7620]

Annotation:
This first aid information was compiled on 13.04.2010.
It will be updated if necessary.

OCCUPATIONAL HEALTH CHECK

Prophylaxis offer: Occupational medical prevention has to be offered when, conducting activities with this substance, repeated exposure cannot be excluded.
Subsequent prophylaxis: After termination of activities with exposure to this substance subsequent occupational medical prophylaxis has to be offered.

Deadlines: Prophylaxis offer has to be made prior to taking up work. Deadlines for the proposal of regularly recurrent occupational medical prevention and subsequent prophylaxis are to gather from the Occupational Health Rule (Arbeitsmedizinische Regel) "AMR Nummer 2.1".

SAFE HANDLING

TECHNICAL MEASURES - HANDLING

Workplace:
Provision of very good ventilation in the working area.
The gas is heavier than air. Adequate ventilation of the floor area must be ensured as well.
The expelled air must not be returned to the working areas.
Devices for detecting and reporting the presence of hazardous gases should be present.
Protect ducts and sewers against penetration by the gas.
Eye bath required. These locations must be signposted
clearly.

Equipment:
Carcinogenic and mutagenic substances should only be used in closed apparatus. If release of the substance cannot be prevented, then it should be suctioned off at the point of exit.
Use small cylinders and place them away from working area or in an exhausting hood.
If dangerous pressure can arise from contact with heat, suitable safety measures and equipment should be provided.
Provide sunblind for compressed gas containers when indicated.
Consider emission limit values, a purification of waste gases if necessary.
Label containers and pipelines clearly.
There should be a shutoff for the lines at a safe distance.
Suitable materials:
For cylinders and valves:
All usual materials.
For seals:
Polychloro trifluoro ethylene PCTFE
Polyvinylidene fluoride
Polyamide PA
Polyethylene PE
Polypropylene PP
Fluoro rubber FKM
Graphite flat gaskets manufactured with perforated metal reinforcements or

comb-shaped gaskets with a graphite layer are normally used for the handling with 1,3-Butadien
When using component parts made from unalloyed steel,
appropriate measures should be adopted e.g.
- sufficient stabilisation of the 1,3-butadiene
- thoroughly cleaning of the component parts
- rinsing the component parts with a 2-3 % sodium nitrite
solution.
When it is possible that butadiene contains acetylene, metals that form explosiv acetylides, especially copper and alloys containing more than 65 % copper, must not be used.
.
There is contradictory information in the literature to the stability of teflon.

Advice on safer handling:
Do not store cylinders at the working area.
Do not force open valve.
When changing bottles, always inspect the leak-proof closure of the filled and empty bottles.
Prevent cylinders from falling over.
Suck back of water into the container must be prevented. Do not allow backfeed into the container.
Use leak-proof equipment with exhaust for refilling or transfer.
Refilling or transfer in storage rooms is prohibited.
Purge air from equipment before introducing the gas.
Usually transport occurs in containers with high pressure. Use suitable equipment for the transport.
Tightly screw on the protective caps and blind nuts when transporting. Secure cylinders against falling over, do not throw.

Cleaning and maintenance:
Regular inspection of leak test required!
Only conduct maintenance and other work on or in the vessel or closed spaces after obtaining written permission.
Only work with vessels and lines after they have been thoroughly rinsed.

TECHNICAL MEASURES - STORAGE

Storage:
Keep in locked storage or only make accessible to specialists or their authorised assistants.
Containers have to be labelled clearly and permanently.
Keep container in a well-ventilated place.
Keep upright, protect against falling over.
Any gases that escape from storage rooms for toxic gases must be capable of being safely drawn off or collected and then disposed of. The facilities must be capable of being operated from a safe location.
Protect from exposure to sunlight.

Do not store in escape routes, work rooms, or in direct proximity to them.
For transporting, storing, preparing, emptying, and maintaining pressurized gas bottles, the detailed rules in TRG 280 must be absolutely adhered to. For pressurised gas packaging, observe the applicable TRG 300.
Butadiene must be stored stabilized for the reduction of the polymerization propensaty and the peroxide formation, preferably at low temperatures (not over 35 degree C).
Storage vessels must be regularly rechecked on polymer deposit.

Conditions of collocated storage:
Storage class 2 A (Gases)
Only substances of the same storage class should be stored together.
Collocated storage with the following substances is prohibited:
- Pharmaceuticals, foods, and animal feeds including additives.
- Infectious, radioactive und explosive materials.
- Flammable liquids of storage class 3.
- Other explosive substances of storage class 4.1A.
- Flammable solid substances or desensitized substances of storage class 4.1B.
- Pyrophoric substances.
- Substances liberating flammable gases in contact with water.
- Strongly oxidizing substances of storage class 5.1A.
- Oxidizing substances of storage class 5.1B.
- Organic peroxides and self reactive substances.
- Combustible and non combustible acutely toxic substances of stora-ge classes 6.1A and 6.1B.
- Combustible toxic or chronically acting substances of storage class 6.1C.
- Noncombustible toxic or chronically acting substances of storage class 6.1D.
- Combustible liquids of storage class 10.

Under certain conditions the collocated storage with the following sub-stances is permitted (For more details see TRGS 510):
- Aerosols (spray bottles).
- Ammonium nitrate and preparations containing ammonium nitrate.
- Combustible corrosive substances of storage class 8A.
- Combustible solids of storage class 11.

Consider the regulations of TRG 280 at collocated storage of different compressed gases.
The substance should not be stored with substances with which ha-zardous chemical reactions are possible.

TECHNICAL MEASURES - FIRE AND EXPLOSION PROTECTION

Technical, constructive measures:
Substance is combustible.
Fire fighting equipment must be available.
Measures required by the "Explosionsschutz-Richtlinie":
- Preventing the formation of an explosive atmosphere (limiting and monitoring the concentration, making inert, sealing, ventilation, warning systems, etc.)
- Preventing the ignition of an explosive atmosphere (separation into zones, removal of sources of ignition, explosion-proof electrical installation, grounding, etc.)

- Architectural measures to limit the effects of an explosion (explosive-force-proof construction, release of explosive pressure, explosion suppression, etc.)
Take precautionary measures against static discharges.
Earth all parts which can be electrically charged.
Protect parts of the system from any warming; if necessary, provide cooling with sprayed water.
Suitable measures must be applied to seal off waste-water systems, cable and pipe access ways, etc. (e.g.: immersing and sand beds).

Precaution on handling:
The gas-air mixture is explosive.
Area with explosion risk.
Keep at a distance from sources of ignition (e.g. electrical devices, open flames, heat sources, sparks).
Observe the smoking prohibition!
Absolutely no welding in the working area.
Only work with vessels and lines after these have been thoroughly rinsed.
Do not displace with air.
Work done with fire or open flame should only be carried out with written permission if the risk of fire or explosion cannot be completely eliminated.
Do not use any tools that cause sparks.
It must be avoided that gases or vapours can escape into other rooms where sources of ignition are present.
Creeping gases from afar may cause ignition.

ORGANISATIONAL MEASURES

Instruction on the hazards and the protective measures using instruction manual (TRGS 555) are required with signature if just more than one minor hazard was detected.
Instruction must be provided before employment and then at a minimum of once per annum thereafter.
An escape and rescue plan must be prepared when the location, scale, and use of the work-site so demand.
The concentration of the substance in the air must be
minimized.
The number of employees who work with the hazardous substance must be kept to a minimum.
Observe the restrictions on juvenile employment as defined in the "Jugendarbeitsschutzgesetz".
Observe the restrictions on the employment of expectant and nursing mothers as defined in the "Mutterschutzverordnung".
Only employees are permitted to enter the work areas. Signposting to this effect must be displayed.

PERSONAL PROTECTION

Body protection:

Depending on the risk, wear gas-tight protective clothing.
Wear flameproof, antistatic protective clothing.
Use protective boots while handling gas cylinders.

Respiratory protection:
In an emergency (e.g.: unintentional release of the substance) respiratory protection must be worn. Consider the maximum period for wear.
This is a low-boiling-point substance of group 1 of the BGR 190.
Respiratory protection: Gas filter AX, colour code brown.
Max. concentration for use:
100 ml/m³ for max. 40 min.
500 ml/m³ for max. 20 min.
Filters may only be used in their original condition. Repeated use is permissible for the appropriate maximum period within a single shift (max. 8 hours). Do not use AX filters against mixtures of low-boiling-point substances and other organic compounds.
Use insulating device for concentrations above the usage limits for filter devices, for oxygen concentrations below 17% volume, or in circumstances which are unclear.

Eye protection:
Sufficient eye protection should be worn.
When handling compressed gas, at least glasses with side protection should be worn.
When handling liquid gas, chemical safety goggles must be used as well as a protective shield.

Hand protection:
Wear leather gloves to prevent frostbite injuries from rapidly expanding gas when handling pressurised gas bottles.

Occupational hygiene:
Avoid skin contact with the liquid phase: risk of frostbite.
Avoid inhalation of gas.
Change clothing that has been in contact with or taken up any of the gas and air the clothing far from any sources of ignition.

DISPOSAL CONSIDERATIONS

Hazardous waste according to Waste Catalogue Ordinance (AVV).
Compressed gas cylinders can normally be returned to the supplier. Pressurised cans are non-returnable and must be disposed of.
Do not empty pressure vessels to the point of pressure compensation. Mark empty vessels to avoid confusion with full ones.

ACCIDENTAL RELEASE MEASURES

Shut off all sources of ignition.
Provide adequate ventilation.
Evacuate area. Warn affected surroundings.
The hazardous area may only be entered once suitable protective measures are implemented. Only then can the hazardous situation be removed.
Wear respiratory protection, eye protection, hand protection and body protection (see

chapter Personal Protection).
Attempt to stop the gas from escaping. Otherwise place leaky bottles under a suctioning device or put them outdoors.
Gas is moving on the ground.
Contain escaping gases/vapours with water.
Use non-sparking tools.
Afterwards ventilate area.

Endangerment of watert:
Severe hazard to waters. Avoid penetration into water, drainage, sewer, or the ground.
Inform the responsible authorities about penetration of even small quantities.

FIRE FIGHTING MEASURES

Classes of fires:
C gaseous, also compressed substances

Suitable extinguishing media:
Dry extinguishing powder
Carbon dioxide extinguisher with gas nozzle
Foam
Fight large fire with water spray.

Instructions:
In the case of fire advise fire fighters on the presence of gas cylinders.
Cool surrounding containers with water spray.
If possible, take container out of dangerous zone.
Heating causes a rise in pressure, risk of bursting and explosion.
Shut off sources of ignition.
Only put out fire if the gas flow can be interrupted.
Risk of explosion from gas accumulation and backfire.
Be watchful for frostbite in case of contact with fluid.
Use only explosion proved equipment.
Explosion danger by penetration into sewerage.
Do not allow runoff to get into the sewage system.

Special protective equipment:
In the case of a fire hazardous substances can be released.
Carbon monoxide and carbon dioxide
Wear self-contained breathing apparatus.

REGULATIONS

Classification:
Flammable gases, Category 1; H220
Gases under pressure, liquefied gas; H280
Germ cell mutagenicity, Category 1B; H340

Carcinogenicity, Category 1A; H350

Signal Word: "Danger"

Hazard Statement - H-phrases:
H220: Extremely flammable gas.
H350: May cause cancer.
H340: May cause genetic defects.
H280: Contains gas under pressure; may explode if heated.

Precautionary Statement - P-phrases:
P210: Keep away from heat, hot surfaces, sparks, open flames and other sources of ignition. No smoking.
P202: Do not handle until all safety precautions have been read and understood.
P308+P313: IF exposed or concerned: Get medical advice/attention.
P377: Leaking gas fire: Do not extinguish, unless leak can be stopped safely.
P381: Eliminate all ignition sources if safe to do so.
P405: Store locked up.
P403: Store in a well-ventilated place.

Manufacturer's specification by Air Liquide

Reference: 01401

The substance is listed in appendix VI, table 3.1 of CLP regulation.
The given classification can deviate from the listed classification, since this classification is to be complemented concerning missing or divergent danger classes and categories for the respective substance.

Reference: 99999

GHS-CLASSIFICATION OF MIXTURES

The classification of mixtures containing this substance results from Annex 1 of Regulation (EC) 1272/2008.

Reference: 07500

COLOUR CODING OF GAS CYLINDERS

Shoulder colour: Red
(flammable gases)

WORKPLACE LABELLING ACCORDING TO GERMAN ASR A1.3

Prohibition label:

No open flame; fire, open ignition sources and smoking prohibited

No admittance for unauthorized persons

No eating and drinking

Warning label:

Caution - gas cylinder

Caution - explosive atmosphere

Precept label:

Use safety goggles

Wear safety shoes

Wear safety gloves

GERMAN WATER HAZARD CLASS

Substance No: 218

WGK 2 - hazard to waters

Classification according to the Administrative Regulation of Substances Hazardous to Water (VwVwS)

Substance No: 218

WGK 3 - severe hazard to waters

Classification of the Commission for the Evaluation of Substances Hazardous to Water (KBwS)

TECHNICAL INSTRUCTIONS ON AIR QUALITY CONTROL (TA LUFT)

Kapitel 5.2.7.1.1 Krebserzeugende Stoffe
Klasse III
Als Mindestanforderung dürfen die folgende Werte im Abgas insgesamt nicht überschritten werden.

Mass flow: 2,5 g/hr

or

Mass conc.: 1 mg/m³

TRANSPORT REGULATIONS

UN Number: 1010
Shipping name: Butadienes, stabilized
Hazard Identification Number: 239
Class: 2.1 (Flammable Gases)
Packing Group: -
Danger Label: 2.1

Tunnel restrictions:
Transports in tanks: passage forbidden through tunnels of category B, C, D and E.
Other transports: passage forbidden through tunnels of category D and E.

RECOMMENDATIONS OF MAK-COMMISSION

This data is recommended by scientific experience and is not established law.

Carcinogenic: Category 1
Substances which cause cancer and make a considerable contribution to the risk of cancer

Germ cells mutagenic: Category 2
Germ cell mutagenic materials whose effect has been proved at a increased mutagenic rate under the descendents of exposed mammals.

TRGS 910

Substance-specific acceptance and tolerance concentrations

Acceptance concentration

Conc. (vol):	0,2 ppm
Conc. (weight):	0,5 mg/m³

Acceptance concentration associated with risk 4:10000

Tolerance concentration

Conc. (vol):	2 ppm
Conc. (weight):	5 mg/m³
Excursion factor:	8

Reference: 05326

Substance-specific equivalent values ??in biological materials for acceptance and tolerance concentration

Parameter:	3,4- Dihydroxybutylmercapturic acid (DHBMA)
Assay material:	Urine
Sampling time:	end of exposure/end of shift for long-term exposure: after several shifts

Equivalent value to the tolerance concentration
2900 µg/g creatinine

Equivalent value to the acceptance concentration (at 4:10000)
600 µg/g creatinine

Reference: 05326

Parameter:	2-Hydroxy-3-butenylmercapturic acid (MHBMA)
Assay material:	Urine
Sampling time:	end of exposure/end of shift for long-term exposure: after several shifts

Equivalent value to the tolerance concentration
80 µg/g creatinine

Equivalent value to the acceptance concentration (at 4:10000)
10 µg/g creatinine

Reference: 05326

SEVESO III - Directive

Annex I Part 2 Number:	18
Liquefied flammable gases, Category 1 or 2	
Qualifying Quantity Column 2:	50 t
Qualifying Quantity Column 3:	200 t

RESTRICTIONS OF USE / BANS OF USE

REACH Regulation (EC) No 1907/2006 Annex XVII
Annex XVII, Point 28 and Point 29 and Point 30
Substances and formulations which are put in circulation and are intended for sale to the general public must not contain the substance in the individual concentration given in the directive 67/548/EEC or directive 88/379/EEC.
Further information on the prohibition and exceptions can be taken from the regulation.
Carcinogens, mutagens or substances toxic to reproduction of the categories 1 and 2 are subject to the same restrictions and are therefore combined at this point.

Directives on Safety in School (BGR/GUV-SR 2003)
General ban for activities in schools.
Substance list to GUV-SR 2004 (as of 11.2010)

FURTHER REGULATIONS

TRGS 200
Einstufung und Kennzeichnung von Stoffen, Zubereitungen und Erzeugnissen; Ausgabe Oktober 2011

TRGS 201
Einstufung und Kennzeichnung bei Tätigkeiten mit Gefahrstoffen; Ausgabe Oktober 2011

TRGS 400
Gefährdungsbeurteilung für Tätigkeiten mit Gefahrstoffen; Ausgabe Dezember 2010;

geändert und ergänzt September 2012

TRGS 555
Betriebsanweisung und Information der Beschäftigten; Ausgabe Januar 2013

TRGS 600
Substitution; Ausgabe August 2008

TRGS 407
Tätigkeiten mit Gasen - Gefährdungsbeurteilung; Ausgabe Juni 2013, berichtigt Dezember 2013

TRGS 725/TRBS 3145
Ortsbewegliche Druckgasbehälter - Füllen, Bereithalten, innerbetriebliche Beförderung, Entleeren; Ausgabe Juni 2013

TRGS 726/TRBS 3146
Ortsfeste Druckanlagen für Gase; Ausgabe April 2014

TRGS 510
Lagerung von Gefahrstoffen in ortsbeweglichen Behältern; Ausgabe Januar 2013, geändert und ergänzt November 2014

TRGS 500
Schutzmaßnahmen; Ausgabe Januar 2008, ergänzt Mai 2008

TRGS 800
Brandschutzmaßnahmen; Ausgabe Dezember 2010

DGUV Grundsatz 350-001 (BGG 904): DGUV Grundsätze für arbeitsmedizinische Untersuchungen
G 40 : Krebserzeugende und erbgutverändernde Gefahrstoffe - allgemein

LINKS

Exposure-risk relationship documentations
International Limit Values
Risk Assessment Report
The MAK Collection for Occupational Health and Safety
DGUV information on Exposure-risk relationships (in german only)
Publications of EIGA (European Industrial Gases Association) Documents Download
Publications of the IGV (Industriegaseverband e.V.) (in german only)

REFERENCES

Reference: 00001
IFA: Erfassungs- und Pflegehandbuch der GESTIS-Stoffdatenbank (nicht öffentlich)

Data acquisition and maintenance manual of the GESTIS substance database (not publicly)

Reference: 00106
Sorbe "Sicherheitstechnische Kenndaten chemischer Stoffe" ("Safety-related characteristics of chemical substances"), sicherheitsNet.de, Landsberg, 07/2011

Reference: 00240
E. Brandes, W. Möller "Sicherheitstechnische Kenngrößen" Band 1 "Brennbare Flüssigkeiten und Gase" ("Safety-related characteristics" Vol. 1 "Combustible liquids and gases"), Wirtschaftsverlag NW, Verlag für neue Wissenschaft GmbH, Bremerhaven, 2003

Reference: 00260
1x1 der Gase. Physikalische Daten für Wissenschaft und Praxis. Herausgeber: AIR LIQUIDE Deutschland GmbH, Düsseldorf, 1. Auflage 2005

Reference: 00304
G. Hommel "Handbuch der gefährlichen Güter" ("Handbook of Dangerous Goods"), CD-ROM "Hommel interaktiv" ab Version 14.0 Springer-Verlag, Heidelberg, 2015

Reference: 00419
CHEMINFO-Datenbankrecherche (CHEMpendium) ab 2001

Reference: 00440
Datenbank CHEMSAFE, Version 2.10 (2014), DECHEMA-PTB-BAM

Reference: 01401
GHS-Sicherheitsdatenblatt (GHS Material Safety Data Sheet), Air Liquide

Reference: 02050
European Union "Risk Assessment Report" European Chemicals Bureau

Reference: 02070
LOG KOW Databank, compiled by Dr. James Sangster, Sangster Research Laboratories, Montreal, Canada, distributed by Technical Database Services (TDS), New York

Reference: 02071
Toxicological Data, compiled by the National Institute of Health (NIH), USA, selected and distributed by Technical Database Services (TDS), New York, 2009

Reference: 05200
Kühn-Birett "Merkblätter Gefährliche Arbeitsstoffe" Loseblattsammlung mit Ergänzungslieferungen, ecomed Sicherheit, Landsberg

Reference: 05240
TRGS 407 "Tätigkeiten mit Gasen - Gefährdungsbeurteilung" Ausgabe Juni 2013, berichtigt Dezember 2013

Reference: 05300
TRGS 510 "Lagerung von Gefahrstoffen in ortsbeweglichen Behältern" Ausgabe Januar 2013, geändert und ergänzt November 2014

Reference: 05326
TRGS 910 "Risikowerte und Exposition-Risiko-Beziehungen für Tätigkeiten mit krebserzeugenden Gefahrstoffen " Ausgabe Februar 2014,zuletzt geändert und ergänzt November 2015

Reference: 06002
L. Roth, U. Weller "Gefährliche Chemische Reaktionen" Loseblattsammlung mit Ergänzungslieferungen ("Dangerous chemical reactions" loose-leaf collection with supplement deliveries), ecomed-Verlag

Reference: 07500
Verordnung (EG) Nr. 1272/2008 des Europäischen Parlaments und des Rates vom 16. Dezember 2008 über die Einstufung, Kennzeichnung und Verpackung von Stoffen und Gemischen, zur Änderung und Aufhebung der Richtlinien 67/548/EWG und 1999/45/EG und zur Änderung der Verordnung (EG) Nr.1907/2006 (EG-GHS-Verordnung)

Reference: 07584
Allgemeine Verwaltungsvorschrift zur Änderung der Verwaltungsvorschrift wassergefährdende Stoffe - VwVwS vom 27. Juli 2005; Bundesanzeiger Jahrgang 57, Nr. 142a, vom 30. Juli 2005

Reference: 07590
Katalog wassergefährdender Stoffe: Einstufungen nach KBwS-Beschluss; Stand 02.12.2015

Reference: 07619
DFG: Toxikologisch-arbeitsmedizinische Begründungen von MAK-Werten; Verlag Chemie

Reference: 07620
DFG: Arbeitsmedizinisch-toxikologische Begründungen von BAT-Werten; Verlag Chemie

Reference: 07635
AUERDATA 98 und BGR/GUV-R 190 "Einsatz von Atemschutzgeräten" Ausgabe 11/2009

Reference: 07742
British Industrial Biological Research Association "Toxicity Profiles" BIBRA Information Department, Carshalton

Reference: 07902
ADR 2015 - Europäisches Übereinkommen über die internationale Beförderung gefährlicher Güter auf der Straße (ADR)

Reference: 07930
NIOSH IDLHs "Dokumentation for Immediately Dangerous to Life or Health Concentrations (IDLHs)" U.S. Department of Health and Human Service, Cincinnati Mai 1994

Reference: 07980
IARC - International Agency for research on cancer: Monographs on the evaluation of carcinogenic risks to humans WHO, Lyon; Serie

Reference: 07985
IPCS: CICADs - Concise International Chemical Assessment Documents. WHO, Genf, Serie ab 1998

Reference: 08102
DFG Deutsche Forschungsgemeinschaft: MAK- und BAT-Werte-Liste 2015, Senatskommission zur Prüfung gesundheitsschädlicher Arbeitsstoffe, Mitteilung 51; VCH

Reference: 80149
BG-Chemie-Merkblatt M 049 Ausgabe 01/98 (BGI 558) 1,3-Butadien

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Reference: 99999
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