BF₃: Boron Trifluoride
Product and Packaging information

INTRODUCTION

ARKEMA is a worldwide supplier fully integrated in Fluorinated Business.

Boron trifluoride (BF₃), part of the FORANEXT® range of specialty fluoro-compounds is manufactured at Pierre-Benite Plant in the Rhône region of France (near Lyon), since the 50’s.

An Integrated Management System has been implemented according to the applicable standards: the BF₃ unit is certified ISO 9001 (Quality), ISO 14001 (Environment) and OHSAS 18001 (Occupational Health and Safety).

BF₃ is produced by means of a continuous process which yields very high purity product.

APPLICATIONS

BF₃ is a gas which is used mainly as a catalyst in a large number of reactions: polymerization, esterification, alkylation, acylation, isomerization, sulfonation, nitration, addition, decyclisation...

The applications of which are related to sectors of activity such as petrochemicals, pharmaceuticals, organic synthesis

Pharmaceutical
Antibiotics(Cephalosporins), Synthesis

Petroleum resins
PolyAlphaOlefins, Lubricant additives, Engine synthetic oils

Resins
Varnishes, paints, glues, adhesives

Miscellaneous
Electronic circuits, antistatic plastics, latex, chewing-gum
PRODUCT CHARACTERISTICS

CHEMICAL PROPERTIES

The acidic nature (Lewis’ type acid) of boron trifluoride, which is due to a missing electron on the boron atom, brings high reactivity towards electron donating compounds, with which it forms very stable complexes.

\[
\begin{array}{c}
\text{H} \\
\text{N} \\
\text{H}
\end{array}
\quad \begin{array}{c}
\text{B} \\
\text{F}
\end{array}
\]

In heterogeneous catalysis processes, combined with a catalyst support, or in homogeneous catalysis processes, complexed in the reaction mixture, BF\textsubscript{3}:

- is more effective than other catalysts:
- provides a higher degree of selectivity

It has also the advantage of forming no tar by-products and in some applications, of being recyclable at the end of the reaction.

Boron trifluoride can be used either directly as a gas or in the form of complexes.

Complexes

BF\textsubscript{3} can react with common solvents containing atoms of oxygen, sulfur, nitrogen, phosphorus, etc... to form complexes in which the BF\textsubscript{3} content is usually between 20 and 65% w/w, depending of the solvent, such as phenol, dihydrate, diethylether, acetic acid, methanol, dioxane...

In addition, BF\textsubscript{3} may react with inorganic acid solvents, with which it undergoes highly exothermic hydrogen exchange reactions (ex. HCl, H\textsubscript{2}SO\textsubscript{4}).
PHYSICAL PROPERTIES

BF₃ is a colorless suffocating gas. The table 1 shows some physical and thermodynamic data.

Thermodynamic properties

<table>
<thead>
<tr>
<th>Table 1: thermodynamic properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight g/mol</td>
</tr>
<tr>
<td>Boiling point (at 1.013 bar) °C</td>
</tr>
<tr>
<td>Melting point °C</td>
</tr>
<tr>
<td>Gas specific gravity (at 1.013 bar) at 20°C kg/m³</td>
</tr>
<tr>
<td>at 65°C kg/m³</td>
</tr>
<tr>
<td>Critical temperature (Tc) °C</td>
</tr>
<tr>
<td>Critical pressure (Pc) bar</td>
</tr>
<tr>
<td>Critical density kg/dm³</td>
</tr>
<tr>
<td>Heat conductivity at 65°C mW/m.K</td>
</tr>
<tr>
<td>Vaporisation latent heat at -119°C kJ/mol</td>
</tr>
<tr>
<td>Formation enthalpy at 25°C kJ/mol</td>
</tr>
<tr>
<td>Formation entropy at 25°C J/mol.K</td>
</tr>
<tr>
<td>Specific heat Cp at 25°C J/kg.K</td>
</tr>
<tr>
<td>Dissolution heat in water kJ/kg</td>
</tr>
</tbody>
</table>

Mollier diagram

**Critical Point**: Transition point between the liquid and gaseous state.

Tc = temperature above which a gas cannot be liquefied, no matter how high the pressure is.

**Vapour pressure** of BF₃ at -50°C

1 bar = 100 kPa = 0.986923 atm = 14.5038 psia

1 Btu/Lb = 2.32444 kJ/kg

Solubility

BF₃ is soluble in most liquid hydrocarbons. Some solubilities at 20°C are given herebelow:

- 0.4% in benzene
- 1% in toluene
- 0.3% in n-pentane
Specific gravity

BF$_3$ is a gas that is heavier than air and so accumulates in low-lying regions. Its density increases as the temperature decreases (fig. 2) under atmospheric pressure.

Compressibility factor

Away from liquid-vapour equilibrium (which is the case under usual condition of use), BF$_3$ does not follow the ideal gas law. A good approximation of the specific gravity of this gas is given by the equation:

$$\rho = \frac{P}{ZRT}$$

Where Z is the compressibility factor of the gas.

As shown by the curves in fig. 3, which give the values of Z for various values of temperature and pressure, the deviation from theory increases at the lower temperature. Figures 4 and 5 give the mass of BF$_3$ contained in a 600 L sphere as a function of pressure at various temperatures.

COMMERCIAL SPECIFICATIONS

BF$_3$ being used as a catalyst, there is a strong necessity for very severe specifications, notably with regard to sulfur-containing compounds which often inhibit catalytic reactions.

The high purity of the BF$_3$ supplied by ARKEMA guarantees a level of quality adequate for all catalytic uses.

The commercial specifications of ARKEMA boron trifluoride can be given by your commercial contact.
PRODUCT SAFETY

REGULATORY INFORMATION

SDS (Safety Data Sheet)

For the latest version of the SDS, please visit Arkema website: https://www.arkema.com/en/products/product-safety/sds/arkema. SDS can also be downloaded from the website http://www.quickfds.com using the SDS supplier name of ARKEMA.

REACH Registration

BF₃ has been REACH registered by Arkema France under the registration name BORON TRIFLUORIDE (CAS 7637-07-02) and under the registration number: 01-2119534579-27-0000.

Classification

Classification (REGULATION (EC) No 1272/2008):

Gases under pressure, LG, H280
Inhalation: Acute toxicity, 2, H330
Skin corrosion, 1A, H314
Serious eye damage, 1, H318
Specific target organ toxicity - single exposure, 3, Respiratory Tract, H335
Inhalation: Specific target organ toxicity - repeated exposure, 2, Kidney, H373

Labelling

Hazard pictograms

Signal word: Danger

Hazard statements:

H280: Contains gas under pressure; may explode if heated.
H330: Fatal if inhaled.
H314: Causes severe skin burns and eye damage.
H335: May cause respiratory irritation.
H373: May cause damage to organs through prolonged or repeated exposure if inhaled.

Supplemental information: EUH014 Reacts violently with water.

EMERGENCY RESPONSE

For emergency response to accident with ARKEMA’s Boron Trifluoride during shipment or in customer facilities in Europe

DIAL: +33. 1. 49. 00. 80. 80

ARKEMA
420 rue d’Estienne d’Orves
92705 COLOMBES CEDEX
FRANCE
PROTECTION

Please refer to the SDS.

- **General protective measures:**
  - Provide sufficient air exchange and/or exhaust in work rooms.
  - Ventilation with later treatment of fumes by water scrubbing of gases.
  - Frequently monitor and control the working atmosphere.

- **Personal protective equipment:**
  - **Respiratory protection:**
    - Low concentrations or short activity: Full mask. Recommended Filter type: A2B2
    - High concentrations or prolonged activity: Self-contained Breathing Apparatus
  - Hand protection: PVC gloves. According to permeation index EN 374: 6 (time elapsed > 480 mins)
  - Eye/face protection: Safety glasses with side-shields
  - Skin and body protection:
    - Acid resistant clothing, Meraclon suit, Safety shoes
  - Intervention at incident: anti-acid diving suit

PREVENTION

The best means of protection lies in the design of the installation and the safety procedure equipment. It is recommended that the following should be available:

- A system for extracting any fumes which may escape when the packaging are connected or disconnected
- Fast and effective isolation systems in the work area
- Safety shower, eyebaths and independent respirators in the work area and storage facilities

Please refer to the SDS for more information.

FIRST AID MEASURES

In case of accident, inform the medical personnel immediately, take off immediately, and under a shower, all contaminated clothing, including shoes. It is recommended that in all cases, the patient should be kept under medical surveillance for 48 hours.

- If BF₃ fumes have been inhaled, the subject must be taken out of the contaminated zone, moved to fresh air and allowed to rest for few hours.
- If the subject shows marked respiratory distress, oxygen should be given, on medical advice.
- In case of skin contact, wash immediately and abundantly the affected parts with plenty of cold or lukewarm water for at least 5 minutes. If the subject has sustained burns, proceed the same way and apply calcium gluconate gel by prolonged massage or injection. In case of extended burns, hospitalize.
- If eyes are affected, rinse immediately with plenty of fresh water for 15 minutes. Consult an ophthalmologist rapidly.

Please refer to the SDS for more information.
COMPATIBILITY OF BF₃ WITH MATERIALS

METALS AND ALLOYS

- Incandescent reaction when heated with: alkaline metals, alkaline earth metals (excepting magnesium)
- At temperature < 200°C and in absence of humidity, common metals (Cu, Fe, Bronze...) undergo little or no corrosion
- In the presence of water, the use of non-alloyed metals should be avoided. Pipes and reactors made of alloys (Inconel, Monel, Stainless steel, Hastelloy...) or with an inner coating of plastic are therefore used (PP, PTFE...).

PLASTICS

The behaviour of plastics in presence of BF₃ varies widely:

- In particular, polymerisable substances must be avoided
- Good resistance of polytetrafluoroethylene (PTFE), polytrifluorochloroethylene (PTFCE) and polyvinylidene fluoride (PVDF)

However, the behaviour of these materials should be tested before any decision is taken, in order to take into account the real mechanical and chemical conditions under which the BF₃ is to be used.

OTHERS

Violent reaction with: alkyl nitrate.

BEHAVIOUR OF BF₃ IN PRESENCE OF WATER

Boron trifluoride combines with water very readily:

- 1 g (1 ml) water at 0°C and 762 mm Hg absorbs 3.22 g BF₃ (1 ml H₂O absorbs 1057 ml of gaseous BF₃)
- At 20°C, solubility in water is 3700 g/kg
- Heat from dissolution in water: 1482 kJ/kg

Different coordination and chemical compounds are formed depending on the amount of water:

### Hydrates of BF₃

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>BF₃ + H₂O</td>
<td>BF₃·H₂O</td>
</tr>
<tr>
<td>BF₃ + 2 H₂O</td>
<td>BF₃·2 H₂O (TDH* – acidic and corrosive)</td>
</tr>
</tbody>
</table>

### Boric and fluoroboric acids

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 BF₃ + 3 H₂O</td>
<td>3 HBF₄ + B(OH)₃</td>
</tr>
</tbody>
</table>

- If [BF₃] is in large excess, the product formed tends to be TDH (>55% BF₃)
- In diluted solution, hydrolysis to boric acid and HBF₄

* TDH: Boron Trifluoride Dihydrate
ARKEMA ships BF$_3$ in 600 liters-spheres containing compressed supercritical gas. The pressure inside the container varies from 100 to 150 bar.

<table>
<thead>
<tr>
<th>Category</th>
<th>Test pressure (bar)</th>
<th>Max weight (kg)</th>
<th>Lifting ears colour</th>
<th>Valve cover colour</th>
<th>Technical information</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>247.5</td>
<td>420</td>
<td>Grey</td>
<td>Blue</td>
<td>Volume : 600 L</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Diameter : 1040 to 1150 mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Height : 1500 to 1700 mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Working pressure : 165 bars*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Test pressure 300 or 247.5 bars</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Reference temperature : 65°C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Thickness : &gt; 33.5 mm</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Filling rate : 0.7 kg/dm3*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Support : palletising frame</td>
</tr>
<tr>
<td>D</td>
<td>300</td>
<td>516</td>
<td>Red</td>
<td>Blue</td>
<td>Visit aperture diameter : Ø 6&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Connections : male on left (diam M35)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Tare weight : 1000 to 1600 kg</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Load capacity : 420 kg*</td>
</tr>
</tbody>
</table>

*Higher filling capacity is available on demand.

The spheres are equipped with an internal safety valve. If the extraction valve is accidentally separated from the sphere, this device will stop the leak. This device is located under the body flange.
PRESSURE VS TEMPERATURE IN THE PACKAGING

Fig. 6 gives the pressure of BF$_3$ versus the temperature related to the fitting ratio inside a sphere

![Graph showing pressure vs. temperature for BF$_3$](image)

*Figure 6: pressure of BF$_3$ vs. temperature for different filling ratios*

HANDLING AND STORAGE

STORAGE

Boron trifluoride is treated as a compressed gas. It will be stored in its original packing according to the following prescriptions:

- In a well-ventilated place
- Under a shelter, in the shadow
- Keep in a dry place at temperature below 50°C
- Away from the workplace so that, if an accident occurs, it is possible to gain easy access
- It may be in a specific room which allows to master possible leakage (column, spraying...)
- Provide an exhaustion of possible vapours
- Storage equipment must comply with the technical requirements specified by the regulations and by local authorities.
DISPENSING INSTALLATION IMPLEMENTATION

Each installation has to be adapted by taking into account all local regulations, requirements and constraints. ARKEMA technical teams are available to assist and advice BF$_3$ users.

Control expansion of gas:

- Transfer is assured by the gas pressure hold in the packaging. A compressor may be used, but will be of dry-type. A residual pressure superior or equal to 5 bar should be maintained in the packaging.
- It is recommended, depending on the flow rate and pressure used, to reduce the pressure of the gas in two stages and to ensure a non-return of product in the packaging.
- Since considerable freezing can occur due to expansion of the gas (see table below), it may also be necessary to provide reheating (electrical tracing) and heat dissipation along the expansion line.

Inert the installation:

- The presence of moisture in the air in an installation using BF$_3$ results in the formation of hydrate of BF$_3$ which may corrode and block the feed lines and pressure-regulation systems. Any installation in which BF$_3$ is used must, therefore, contain a completely dry atmosphere, which is achieved industrially by vacuum pumping and then nitrogen flushing.
- It is also recommended to install a block valve close to the connection sphere/line nut to prevent moisture inflow during changes of empty/full packaging.

Ease intervention:

- It must be possible to isolate each part of the installation and the pressure regulator quickly and efficiently in order to limit emission into the atmosphere if any problem arises and to be able to treat any gaseous effluent.

The tables below present the values for the isenthalpic (P1 à P2) expansion of BF$_3$ at an initial temperature of 25°C.

<table>
<thead>
<tr>
<th>Temperature of BF$_3$ gas (°C) after reducing pressure from P1 to P2 (bar)</th>
<th>Quantity of heat (kJ/kg) exchanged during pressure reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>P2</strong></td>
<td><strong>P1</strong></td>
</tr>
<tr>
<td>200 b</td>
<td>25</td>
</tr>
<tr>
<td>100 b</td>
<td>-13</td>
</tr>
<tr>
<td>50 b</td>
<td>-73</td>
</tr>
<tr>
<td>5 b</td>
<td>-109</td>
</tr>
</tbody>
</table>
## CONNECTION BEST PRACTICES

This table gives explanation of drawbacks that can be encountered when connecting BF₃ packaging onto an installation.

<table>
<thead>
<tr>
<th>What</th>
<th>Why</th>
<th>Prevention</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Corrosion in pipings and valves</td>
<td>Reaction between BF₃ and water (moisture) giving off acidic and corrosive products.</td>
<td>➔ During connecting and disconnecting BF₃ vessels, it is necessary to purge the lines with dry nitrogen or vacuum pump, in order to avoid moisture inlet that creates corrosion of pipings and valves.</td>
</tr>
</tbody>
</table>
| 2 Encrusting / plugging of pipings and valves | Reaction between BF₃ and water (moisture) leading to the formation of a white crystalline solid (Boric acid). Or reaction between BF₃ and piping materials and/or external impurities giving corrosion products. | ➔ Flush lines with dry nitrogen, or vacuum pump (see § 1)  
 ➔ Beware of ambient humidity and external impurities |
| 3 Damaged connection threading     | The thread at connection valve is a gas inverse thread (screwing anti-clockwise) : ∅ 35 mm internal, 45 mm external  
When using a stainless steel nut for connection, a stainless steel thread does not resist if tightening torque is too high, or if connection has been made askew. If the connection is not made properly, the thread can be damaged, leading to potential leakage at connection. | ➔ Well position the packaging towards connecting system. Start connecting to the packaging by hand, then finish by using a dynamometric key  
 ➔ Do not tighten too strong the connecting system : tightening torque = 22 mkg |
| 4 Leakage at connection           | Damaged threading (see § 3)  
Gasket is not working properly  
Presence of various impurities (boric acid, others...) | ➔ Leakage at valve  
 ➔ Use only annealed copper gasket for connection with sphere (supplied with each sphere – to use only once)  
 ➔ Use only PTFE gasket for connection with bottle/cylinder (to use only once)  
 ➔ See § 2  
 ➔ Always clean the connection valve (packaging and connecting system) before any connection. |
| 5 Leakage at valve                 | The internal gasket (gland) has been damaged, either because of direct expansion of BF₃ on valve followed by extensive freezing, or because the command valve has been tighten too strong. | ➔ See prescription § Dispensing installation implementation  
 ➔ Manual sphere : Do not tighten too strong the command valve; tightening torque = 22 mkg |
PROCESSING OF EFFLUENTS

Gaseous effluents can be reabsorbed through a water column, with protection from BF$_3$ return upstream.

In the case of liquid effluents, the emissions of fluoride ions can be limited by neutralization with lime (see under).

Other processing methods can be envisaged according to the constraints and specific nature of the user processes. ARKEMA technical teams are available to assist users in finding specific solutions to each case.

DETECTION OF LEAK

In contact with moisture, BF$_3$ generates a compact and suffocating white mist. This allows the emergency responders to identify any tiny leak of BF$_3$, even traces. This is also a good indication to determine the safety perimeter required around the leak. No specific BF$_3$ leak detecting or analysis devices are yet available, however opacimeters can be used for industrial detection.

ACCIDENTAL LEAK TREATMENT

Recommendations

- In case of leak from the packaging, switch off immediately the dispensing valve. Check if the problem cannot be overcome by following "Connection best practices – Recommendation of use" advices.
- If the leak cannot be overcome, contact our technical teams.
- In case of emergency, dispense the packaging in another packaging or in a large amount of water (see figure with sphere example).
- Proceed to the neutralization of the aqueous solution (therefore obtain after decomposition of BF$_3$ in water) by using caustic soda or lime.

Neutralization

Neutralization can be carried out only after transfer of BF$_3$ in water.

If BF$_3$ is diluted directly in an alkali solution (NaOH), some NaF may precipitate. pH has to be controlled (pH 8). Neutralization of the acidic mixture is performed by slowly adding caustic soda 25% w/w, while stirring and cooling the neutralization tank (Neutralization is releasing more heat than dilution, maybe 2 times higher).

When using lime, the excess of fluoride ions are precipitated in the form of calcium fluoride (the solubility of CaF$_2$ in water is about 16 mg/l at 20°C).
TRANSPORT AND REGULATION

TRANSPORTATION REGULATIONS

Boron trifluoride is subject to the regulations for dangerous substances.

<table>
<thead>
<tr>
<th>BF₃ gas</th>
<th>Class</th>
<th>Labels</th>
<th>UN Number</th>
<th>Hazard number</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADR / RID</td>
<td>2</td>
<td>2.3 + 8</td>
<td>1008</td>
<td>268</td>
</tr>
<tr>
<td>IMDG</td>
<td>2.3</td>
<td>2.3 + 8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DOT</td>
<td>Agreement</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>IATA</td>
<td>Prohibited</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

BF₃ DELIVERY

ARKEMA can deliver BF₃ in spheres anywhere around the world.

10 spheres per FCL

REGULATION

The industrial effluents resulting from the use of BF₃ are subjected to the general regulation in force.

The use, application and handling, of the products referred to, must always comply with regulations resulting from current legislation in force in the concerned country and no liability whatsoever can be accepted by ARKEMA.
As a Boron Trifluoride manufacturer, ARKEMA can provide both chemical and technical assistance world-wide.

ARKEMA can bring support in various fields:

- R&D
- Analysis
- Handling and safety guidelines
- Logistics (piping, connexions...)
- Effluent treatment

ARKEMA is willing to:

- Develop partnership with its customers
- Train operating people (best practices and safety)

Commercial and technical service people are available at any time to answer your questions and give you informations about storage, handling and equipment required for BF3.

For more information, please contact us at: info.foranext@arkema.com

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