SF6 – a gas with unusual properties

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Bibliography
Solvay's sulphur hexafluoride is a non-toxic, inert, insulating and cooling gas of high dielectric strength and thermal stability.

It is particularly suitable for application in both high-voltage and medium-high voltage power circuit breakers as well as in high-voltage cables, transformers, transducers, particle accelerators, X-ray and UHF equipment.

The construction of new equipment with higher capacity and improved performance has been made possible by the excellent electrical, thermal and chemical properties of SF₆. Changing from conventional dielectrics to sulphur hexafluoride—a non-flammable, chemically-inactive and non-toxic heavy gas—results in considerable space and weight savings and improves the operational safety of converted equipment.

The low acoustic velocity is a feature which makes sulphur hexafluoride an excellent filling for insulating-glass units.

SF₆ gas mixtures improve sound-absorption. In this way they contribute to the requirements of energy conservation and improved living conditions.

On account of their high reactivity, magnesium and magnesium alloys must be protected against reaction with atmospheric oxygen during casting. Even small quantities of sulphur hexafluoride added to the atmosphere above the melt provide the necessary protective layer, making this method a very economical one.

A further new area of application in foundry practice is the purification of aluminium melts. Introducing SF₆/inert gas mixtures into the liquid aluminium not only considerably reduces the hydrogen content but also removes oxides and solid inclusions.

Even in the very lowest concentrations, sulphur hexafluoride can be detected by halogen leak detectors. SF₆ is therefore useful as an additive to other gases as a tracer for the purposes of leak detection, or it can be used as a constituent of air for meteorological measurements.

SF₆ is also widely used in medical technology. For example as a contrast agent in ultrasonic examinations as well as in ophthalmology, pneumonectomy and diseases of the middle ear, e.g. treating loss of hearing in middle ear infections [1].
Areas of application for sulphur hexafluoride

Electrical engineering

The use of sulphur hexafluoride in place of solid and liquid insulators offers a number of important advantages:

- **High dielectric strength at lower cost**

  When pressurized, sulphur hexafluoride can exhibit the same dielectric strength as liquid insulators. However, the per-unit-volume cost of SF$_6$ is only a fraction of that of liquid dielectrics.

- **Regeneration capacity**

  Following a breakdown, sulphur hexafluoride regenerates itself. Its original strength is spontaneously restored and, in most cases, is even slightly enhanced.

- **Low pressure-increase in the case of breakdown**

  Due to the very low adiabatic coefficient of sulphur hexafluoride, the pressure rise as a result of thermal expansion following dielectric breakdowns is less than that with other gases and very considerably less than is the case with liquid dielectrics.

![Enclosed, SF$_6$-insulated, high-voltage plant (ABB, Switzerland)](image1)
High-voltage switchgear and switching stations

The excellent quenching and insulating properties of sulphur hexafluoride have permitted the construction of completely new types of high-voltage circuit breakers and switching stations with outstanding features: compact and space-saving design, low noise-levels, protection against accidental contact of live parts, against intrusion of foreign matter through the metal cladding and elimination of the fire hazard.

Substations using sulphur hexafluoride for insulation purposes are particularly in demand where, on account of limited space, a compact design is required. These substations occupy only 10-15% of the space required by conventional units. New SF₆-filled equipment can thus be installed at distribution points in densely-populated areas where site costs would prohibit the use of traditional methods.

Thanks to their insensitivity to polluted air, enclosed outdoor versions of SF₆-insulated substations are installed in the chemical industry, in desert regions and in coastal areas.

SF₆ is used as a quenching agent both in power circuit breakers for enclosed substations and in circuit breakers for open outdoor substations.

fig. 2 SF₆-insulated high-voltage switching station type L-SEP, 145 kV (VA Tech Elin Holec High Voltage, Netherlands)

fig. 3 Gas insulated, high-voltage switching station for 145 kV operating voltage (Siemens, Germany)
fig. 4  Enclosed switching station, 500 kV
       (Alstom, France)

fig. 5  Gas insulated
       High-voltage switching station,
       550 kV
       (Siemens, Germany)
fig. 6  Outdoor transforming station with SF₆ equipment, 420 kV  (Siemens, Germany)

fig. 7  SF₆ switching station, 245 kV  (Schneider Electric High Voltage, France)

fig. 8  High-voltage switching station, 170 – 245 kV  (Alstom, Switzerland)
Solvay Fluor und Derivate GmbH supplied the SF₆ for the world’s largest hydroelectric power station at Itaipú in Brazil. The output at Itaipú is particularly impressive: 18 turbines supply 12.6 billion watts, equivalent to the output of 10 nuclear power stations. The largest SF₆-insulated high-voltage switching station in the world was installed at Itaipú, and contains more than 100 tons of sulphur hexafluoride.

**SF₆ for the Itaipú hydroelectric station**

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**fig. 9a** Hydroelectric power station
Itaipú, Brazil

**fig. 9b** 550 kV SF₆-insulated high-voltage switching station for the Itaipú hydroelectric power station in Brazil (ABB, Switzerland)
**Gas insulated transmission line (GIL)**

Gas insulated transmission lines are particularly well suited for high power transmission. Conventional designs are filled with pure SF₆, and have been operating safely and reliably in all parts of the world for more than 20 years.

The advantage of this technology is the higher capacity compared with cables. GIL’s are either buried or laid in tunnels. They are a viable alternative for energy supply where overhead power lines are either not possible or where the capacity of cables is insufficient.

For long distances the replacement of pure SF₆ with more economical SF₆/N₂ mixtures has been researched because the arc extinguishing properties of SF₆ are not relevant in insulating applications.

Today the overall optimisation of gas mixtures, gas pressure and dimensions of GIL mean this technology is a highly competitive transmission medium in a broad range of applications.

Solvay Fluor und Derivate GmbH Technical Service supports this new application with a spectrum of services ranging from the initial production of mixtures through to the separation of mixtures at end of service life or whenever required. By offering this technical support Solvay enables a closed product loop for SF₆/N₂ mixtures.

*fig. 10* SF₆/N₂ mixture in transmission lines, in tunnel (Siemens, Germany)
Medium-voltage switchgear

The advantages of SF₆ technology, in particular its excellent arc-quenching capacity, are also put to good use in circuit breakers for the 10-40 kV range. They replace conventional, low-oil-volume circuit breakers and also satisfy heavy-duty requirements such as those occurring under short-circuit conditions and repeated switch-off under load.

Like the high-voltage circuit breakers, they require little maintenance and are particularly suitable for locations where oil-filled equipment is undesirable.
High-voltage cables and tubular transmission lines

In recent times, increasing interest has been shown in the application of sulphur hexafluoride in the manufacture of gas-insulated high-voltage cables and tubular transmission lines used for high-power distribution in heavily concentrated industrial areas.

Tubular transmission lines are also used to connect power stations with transformers or switching stations, as for example in the case of underground power stations. Appropriately-dimensioned tubular transmission lines filled with pressurized SF₆ permit unusually high current levels. Compared to those values achieved with conventional types of cables, figures for charging-current and dielectric loss are insignificant.

In high-frequency carrier systems, output has been increased almost tenfold through the use of SF₆-filled tubular transmission lines. An advantage from the constructional point of view is the ability to build high-performance UHF transmission stations with greatly reduced dimensions.

Transformers

Its excellent heat-transfer capacity, non-flammability and non-toxicity have also promoted the use of sulphur hexafluoride in the construction of transformers.

On account of their high operational safety, SF₆-gas transformers are installed in mines and department stores. Their relatively light weight, compact design and low noise levels are decisive advantages.

**fig. 13** SF₆-insulated transformer, 23-107 kV (Fuji, Japan)

**fig. 14** SF₆-insulated high-voltage cable in the JET nuclear-fusion plant (kabelmetal electro, Germany)
Other high-voltage applications

The use of sulphur hexafluoride has also established itself in the insulation of super-voltage generators in particle-accelerating machines, such as in Van de Graaf accelerators, betatrons, neutron generators and other such plant used for radiation applications in scientific institutions, medicine and industry.

By virtue of the high dielectric strength of the gas, pressure vessels can be constructed in considerably lighter fashion. The use of SF$_6$ in older units, previously insulated with mixtures of air and carbon dioxide, has resulted in a marked increase in efficiency.

SF$_6$ fulfills a similar function in voltage stabilizers for electron microscopes and in X-ray equipment used in production control and the non-destructive testing of materials.

Parallel to the development of SF$_6$ plant technology in the high-voltage sector, SF$_6$-insulated, high-voltage measuring instruments and calibrated power sources have also been produced. SF$_6$-fillings are also used in instrument transformers, pressurized gas capacitors and surge arresters for super voltages.
**SF₆ for the Vivitron accelerator**

The largest electrostatic accelerator in the world is already in operation in Strasbourg. Using new technology, the Tandem Van de Graaf Vivitron accelerator is designed to achieve an accelerating potential of 35 million volts. It is 51 m long, has a maximum diameter of 8.5 m and a volume of 1200 m³. The SF₆-gas supply is contained in two storage tanks whose total SF₆-capacity is 60 tonnes. Solvay Fluor und Derivate GmbH was responsible for both the supply of SF₆ and the associated logistics for this project.

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**fig. 16** Perspective view of the Vivitron accelerator and the SF₆-gas supply system with its two SF₆ storage tanks (Centre de recherches nucléaires, France)
Manufacture of insulating glass

Sulphur hexafluoride is being used in increasing quantities in the construction of insulating-glass building components. The requirements of energy conservation and emission protection have greatly increased the demands made on such units. In window manufacture, substantial progress has been made in the field of thermal insulation by using three-pane units and by coating two-pane units with metals or metal oxides. Filling the spaces between panes with SF₆ results in yet further improvements.

The improvement of sound insulation by enlarging the spaces between the window panes and the use of thicker glass usually calls for a change in window-frame design. In the case of conventional two-pane glass, infilling with SF₆ produces improvements of up to 8 dB, depending upon shapes and materials used.

Since sulphur hexafluoride is chemically inert, there is no risk of its reacting with glass, metal or sealing compounds. Its coefficient of permeability is extremely low.

Solvay SF₆ has a very high purity, and its dew-point, which is guaranteed to be below −40 °C, is usually around −50 °C. In order to keep the dew-point as low as possible, molecular sieves, preferably size 3A but not greater than 4A, must be used.

To fill an insulating-glass unit, the air is displaced slowly from the bottom upwards by the much heavier SF₆-gas (whose density is approximately 5 times greater). The gas is dosed with the aid of either simple flow meters or using automatic filling devices, depending on the production quantities involved.

fig. 17  SF₆-filled insulating-glass panes
Foundry practice: magnesium

Magnesium is a highly reactive metal. It must therefore be protected during the casting process, when temperatures of up to 800 °C can occur, against ignition, oxidation and the formation of nitrides. Up to now, only molten salts and SO₂ or powdered sulphur were known as protective materials for this purpose. Although they provide adequate protection, such materials have detrimental secondary effects, such as corrosion, generation of bad smells and the contamination of the cast components by salt. The use of SF₆ as a protective gas eliminates these disadvantages.

In contrast to pure argon, for instance, SF₆ prevents the evaporation of magnesium by forming a thin protective layer. Only very low concentrations of SF₆ are necessary above the melt to achieve this effect, assuming that the melting pot is tightly sealed and that the opening for topping up is kept as small as possible and closed by means of a sliding gate. Accordingly, opening periods should be kept as short as is practicable.

Sulphur hexafluoride is always used in conjunction with a carrier gas, as this achieves a faster and more effective distribution across the melt on account of the larger total quantity of gas. Air, carbon dioxide, argon and nitrogen are all suitable for use as carrier gases. In foundry practice, the residual nitrogen from empty refill cylinders from die-casting machines is used for this purpose.

fig. 18 Schematic representation of a protective-gas supply system for a magnesium melting furnace
Optimum dosage and concentration of the protective gas depend upon such factors as furnace design and levels of pig feeding and molten-charge removal, and must be determined by trial and error. As a rule a suitable mixture consists of 0.04 – 0.3 vol. % SF₆ and more than 99 vol. % of an air/CO₂ mixture and is distributed evenly over the surface of the melt [2].

As only a very thin protective film should be formed and waste metal should be kept to a minimum, an initial value of 100 l of gas mixture per hour is generally used. The dosage can be decreased or increased in steps, as required.

Once metal has ignited, the resulting fire cannot be extinguished even with high concentrations of SF₆. Flow meters are used for both mixing and dosing the gases (manufacturers will be named on request).

Since only small amounts of SF₆ are used, no problems arise with decomposition products. Measurements taken in the immediate vicinity of the melting plant show readings well below the TL value of HF = 3 ppm (2 mg/m³). SF₆ is therefore an ideal protective gas for magnesium melts from the point of view of both operational safety and environmental considerations [3].

fig. 19 Furnace magnesium-moulding plant, using SF₆-CO₂-air as a protective gas. Made by Huskvarna AB, Sweden (Norsk Hydro, Norway)
Foundry practice: aluminium

A fundamental problem in the production of aluminium cast components is porosity caused by the hydrogen content of the aluminium melt. The porosity induced by the presence of hydrogen leads to a reduction in strength of the components. Such an effect can only be avoided by pre-treating the aluminium melt.

Until now, the treatment carried out for purifying the aluminium melt had several disadvantages. The most widely used purifying method is the introduction of chlorine or mixtures of chlorine and inert gas. However, the aggressivity of elemental chlorine means that special safety precautions are necessary in handling. And the introduction of pure inert gases such as argon reduces the hydrogen content but leads to other difficulties on account of the removal of the alkaline and alkaline-earth metals and solids.

The use of hexachloroethane in powder or tablet form also leads to problems, since, when it is used, chlorine is released. The use of fluorohydrocarbon purification methods will be terminated entirely in the future on account of their potential influence on the ozone layer.

The product sulphur hexafluoride opens up a completely new purification technique to the aluminium industry for aluminium melts. The introduction of SF₆/inert-gas mixtures into the liquid aluminium significantly decreases the hydrogen content and at the same time leads to the removal of oxides and solid contaminants. Handling SF₆ gas mixtures presents no problems and SF₆ is generally recognized as physiologically safe. The introduction of SF₆ therefore not only enhances product quality but also improves working conditions.
Other areas of application

Even at the lowest concentration levels, sulphur hexafluoride is detected by modern halogen leak detectors.

For this reason it is used increasingly as a test gas for detecting leaks in boilers, fuel tanks, pneumatic devices, pipeline systems, plastic tubing, containers for carrying radioactive materials and many other vessels. By carrying out a calibrated leak, quantitative measurements are also possible. With the increasing demands imposed by ever stricter standards of environmental protection, work safety and energy saving, this technique is gaining steadily in significance.

Residence-time distributions in high-velocity-flow assemblies can be determined using SF₆. This method is primarily applied in those cases where a radiometric method cannot be employed [4].

On account of its very low detection limit, SF₆ is used as a tracer gas for meteorological measurements. When added in measured quantities at an emission source, the distribution of the emitted substances can be determined even at relatively long distances. Its high stability and the low solubility of SF₆ in water are of particular advantage in this respect.

SF₆ is also widely used in medical technology. For example as a contrast agent in ultrasonic examinations as well as in ophthalmology, pneumonectomy and diseases of the middle ear, e.g. treating loss of hearing in middle ear infections [1].

fig. 21 Ophthalmology
Electron affinity

The excellent insulating properties of sulphur hexafluoride are attributable to the strong electron affinity (electronegativity) of the SF₆ molecule. This is based mainly on two mechanisms, resonance capture and dissociative attachment of electrons, in accordance with the equations:

\[
\begin{align*}
\text{SF}_6 + e^- &\rightarrow \text{SF}_6^- \quad (1) \\
\text{SF}_6 + e^- &\rightarrow \text{SF}_5^- + \text{F} \quad (2)
\end{align*}
\]

The process represented by equation (1) applies to electron energies of 0.1 eV with an energy range of 0.05 eV, and that represented by equation (2) applies to an energy range of 0.1 eV [5].

Dielectric constants

The dielectric constant has a value of 1.0021 at 20°C, 1.0133 bar and 23.340 MHz; a rise in pressure to 20 bar leads to an increase of about 6 % in this value.

At -50 °C, the dielectric constant of liquid sulphur hexafluoride throughout the range from 10 to 500 kHz remains unchanged at 1.81 ± 0.02 [6].

fig. 22 50 Hz breakdown voltage of SF₆ in a homogeneous field as a function of the distance between electrodes at various gas pressures (ETZ Supplement 3 [1966]).
**Dielectric strength**

The strong interaction of high-energy electrons with the polyatomic SF₆ molecule causes their rapid deceleration to the lower energy of electron capture and dissociative attachment. SF₆-breakdown is therefore only possible at relatively high field strengths.

The breakdown voltages at 50 Hz and 1 bar in a homogenous field are thus 2.5 to 3 times higher than the corresponding values for air or nitrogen (fig. 22).

Figure 23 shows the relationship of breakdown voltage to pressure in a non-homogeneous field in comparison with that of a N₂/CO₂ mixture.

The breakdown strength of air is dramatically increased by the addition of small quantities of SF₆. In contrast, air has only a limited influence on the breakdown strength of sulphur hexafluoride. The addition of 10 % of air by volume reduces the breakdown voltage of SF₆ by about 3 %, the addition of 30 % air by about 10 %.

The breakdown voltage of SF₆ reaches that of transformer oil at a pressure of only 3 bar (fig. 24).

The behaviour of sulphur hexafluoride conforms over a wide range of pressures to Pašchen's Law: at higher pressures, however, deviations have been observed under certain conditions [7, 8, 9].

The breakdown strength of SF₆ is independent of frequency: it is therefore an ideal insulating gas for UHF equipment [10].

The Corona-onset voltage using SF₆ in non-homogeneous fields is also considerably higher than that using air. Figures 25 and 26 show the respective dependence on pressure and radius of curvature of the electrodes in the case of SF₆ and air in a point-to-plane electrode system.
**fig. 24** Breakdown strength of transformer oil, air and SF₆ as a function of gas pressure (Kali und Steinsalz, 3, issue 10 [1963] 319)

![Breakdown strength graph](image)

**fig. 25** Dependence on pressure of the Corona-onset voltage in SF₆ and air (ETZ, Supplement 3 [1966])

![Corona-onset voltage graph](image)
**Arc-quenching capacity**

On account of its thermal properties and low ionisation temperature, sulphur hexafluoride exhibits outstanding characteristics for the extinguishing of electric arcs (fig. 27).

All other conditions being equal, the arc-quenching time using SF$_6$ is about 100 times less than that using air [11].

The superior arc-quenching performance of SF$_6$ compared with other gases is impressively illustrated in figure 28.

**Loss factor**

The loss factor, tan $\partial$ of sulphur hexafluoride is extremely low (less than $2.0 \times 10^{-7}$).

A value of tan $\partial < 10^{-3}$ was determined for liquid SF$_6$ at $-50 \, ^\circ$C [6].

Diagrams and data pertinent to the electrical properties of sulphur hexafluoride may be found in the Milek *Sulphur hexafluoride data sheets* [12].

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**fig. 26** Corona-onset voltages for SF$_6$ and air as a function of the radius of curvature $r_K$ at atmospheric pressure (ETZ, Supplement 3, [1966]).
fig. 27  Radial temperature profile in SF\(_6\) and N\(_2\) electric arcs (schematic representation: from Z. Angew. Physik 12, [1960] 5, pp 231 to 237)

fig. 28  Quenching capacity of SF\(_6\), air and a mixture of both gases (Insulating Materials for Design and Engineering Practice, N.Y. [1962], p. 116)
Other physical properties

Sulphur hexafluoride is a colourless, odourless, non-toxic and non-flammable gas. With a molecular weight of 146.05, SF₆ is about 5 times heavier than air and one of the heaviest known gases.

### Mechanical and caloric data

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sublimation point (1.0133 bar)</td>
<td>-63.9 °C</td>
</tr>
<tr>
<td>Melting point (2.26 bar)</td>
<td>-50.8 °C</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>see page 27</td>
</tr>
<tr>
<td>Heat of sublimation</td>
<td>153.2 kJ/kg</td>
</tr>
<tr>
<td>Heat of fusion</td>
<td>34.37 kJ/kg</td>
</tr>
<tr>
<td>Heat of vaporization [13]:</td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>-20 0 +20 +40</td>
</tr>
<tr>
<td>Heat of vaporization (kJ/kg)</td>
<td>91.71 78.96 62.54 34.08</td>
</tr>
<tr>
<td>Critical data [13]:</td>
<td></td>
</tr>
<tr>
<td>Critical temperature</td>
<td>45.58°C</td>
</tr>
<tr>
<td>Critical pressure</td>
<td>37.59 bar</td>
</tr>
<tr>
<td>Critical density</td>
<td>0.74 kg/l</td>
</tr>
<tr>
<td>Density: (see figs. 29 and 31)</td>
<td></td>
</tr>
<tr>
<td>Gas density (20 °C, 1 bar)</td>
<td>6.07 g/l</td>
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<tr>
<td>Liquid density (0 °C, 12.65 bar)</td>
<td>1.56 kg/l</td>
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<tr>
<td>Solid density (-100 °C) [14]</td>
<td>2.77 kg/l</td>
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<tr>
<td>Viscosity</td>
<td>(see fig. 32)</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>(see fig. 33)</td>
</tr>
<tr>
<td>Heat transfer capacity</td>
<td>(see fig. 34)</td>
</tr>
<tr>
<td>Acoustic velocity in SF₆ (0 °C, 1.0 bar)</td>
<td>129.06 m/sec.</td>
</tr>
<tr>
<td>Isentropic exponent (K) [13]:</td>
<td></td>
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<tr>
<td>The dynamic compressibility of SF₆ is particularly high on account of the low value of the isentropic exponent: K = 1.08 (30 °C, 1.0 bar)</td>
<td></td>
</tr>
<tr>
<td>Heat of formation (ΔH₂₅°C)*</td>
<td>-1221.58 ± 1.0 kJ/mol</td>
</tr>
<tr>
<td>Entropy of reaction (ΔS₂₅°C)*</td>
<td>-349.01 J/mol k</td>
</tr>
</tbody>
</table>

* for formation from rhombic sulphur and gaseous fluorine [14].
## Solubility

### Solubility in water [15]

Gas volume corrected to 0 °C, 1.0133 bar

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (cm³ SF₆/kg H₂O)</td>
<td>11.39</td>
<td>9.11</td>
<td>7.48</td>
<td>6.31</td>
<td>5.44</td>
<td>4.79</td>
<td>3.96</td>
<td>3.52</td>
</tr>
</tbody>
</table>

### Solubility in transformer oil [16]

(Esso-Univolt 35)

Gas volume under 0 °C, 1.0133 bar

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>27</th>
<th>50</th>
<th>70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solubility (cm³ SF₆/cm³ oil)</td>
<td>0.408</td>
<td>0.344</td>
<td>0.302</td>
</tr>
</tbody>
</table>

## Specific heat (Cp)

### Solid and liquid phase [17]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>200</th>
<th>210</th>
<th>220</th>
<th>225</th>
<th>230</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific heat (J/mol K)</td>
<td>104.17</td>
<td>116.60</td>
<td>184.22</td>
<td>110.95</td>
<td>119.58</td>
</tr>
</tbody>
</table>

### Gas phase (1 bar) [14, 18]

<table>
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<tr>
<th>Temperature (K)</th>
<th>298</th>
<th>373</th>
<th>400</th>
<th>473</th>
<th>500</th>
<th>573</th>
<th>600</th>
<th>673</th>
<th>700</th>
<th>773</th>
<th>1273</th>
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</thead>
<tbody>
<tr>
<td>Specific heat (J/mol K)</td>
<td>97.26</td>
<td>112.45</td>
<td>116.39</td>
<td>125.89</td>
<td>128.54</td>
<td>134.51</td>
<td>136.07</td>
<td>140.21</td>
<td>141.1</td>
<td>144.35</td>
<td>152.62</td>
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</table>

## Vapour pressure

(cf. fig. 29)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>−50</th>
<th>−45</th>
<th>−40</th>
<th>−35</th>
<th>−30</th>
<th>−25</th>
<th>−20</th>
<th>−15</th>
<th>−10</th>
<th>−5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (bar)</td>
<td>2.34</td>
<td>2.87</td>
<td>3.49</td>
<td>4.20</td>
<td>5.02</td>
<td>5.95</td>
<td>7.01</td>
<td>8.19</td>
<td>9.52</td>
<td>11.01</td>
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</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>0</th>
<th>+5</th>
<th>+10</th>
<th>+15</th>
<th>+20</th>
<th>+25</th>
<th>+30</th>
<th>+35</th>
<th>+40</th>
<th>+45</th>
</tr>
</thead>
</table>
fig. 29  Vapour pressure curve:
lines of equivalent gas
density of SF₆
fig. 30  Mollier-h, lgp diagram
for sulphur hexafluoride

Mollier-h, log p-diagramme
for sulphur hexafluoride
$\text{SF}_6$

Established by Dr.-Ing. R. Döring

Units: $p$ in bar, $h$ in kJ/kg, $s$ in kJ/kg K,
$v$ in m$^3$/kg, $s=1$ kJ K, $h=200$ kJ/kg
at 0° C for the boiling liquid
## Internal pressure in SF₆ tank

as a function of temperature and density (kg SF₆/l tank volume)

Calculated from experimental values [13]

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</table>
fig. 31  Pressure/temperature curves for SF₆
(1at=0.9800665 bar)

fig. 32  Viscosity of SF₆ as a function of
     temperature at atmospheric pressure
     [14]
fig. 33  Thermal conductivity of SF6 at atmospheric pressure [14]

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>SF6 Conductivity (W/cm·K)</th>
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<tbody>
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<tr>
<td>25 °C</td>
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<td>500 °C</td>
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</table>

fig. 34  Heat-transfer coefficients of air and SF6 (for comparison – transformer oil under natural convection) (Conti-Elektro-Berichte, July/September 1966, p 189)
Optical properties

Refractive index [19] \(n_0\) (0°C) 1.0133 bar 1.000783

fig. 35 Infrared spectrum of \(\text{SF}_6\) recorded for three different concentrations (Leitz M 3, NaCl prism)
Under normal conditions, sulphur hexafluoride is chemically inert and stable; its reactivity is among the lowest of all substances.

**Behaviour at elevated temperatures**

SF₆ can be heated to 500 °C in quartz containers without any decomposition occurring. At temperatures of up to approximately 150 °C, generally used materials such as metals, ceramics, glass, rubber and cast resins are completely stable in the presence of sulphur hexafluoride. Not until the temperature exceeds 200 °C do some metals begin to have a decomposing effect on SF₆; however, the usual working metals and alloys do not have a significant decomposing effect until the temperature reaches 400 to 600 °C.

Since SF₆ reacts with metals at high temperatures, it is used as a protective gas for melts. In particular, it is used in magnesium foundries because it forms a thin and impervious layer on the surface of the molten magnesium. This layer acts very effectively in preventing further reaction with air [20, 3]. In spite of the high temperature of the molten magnesium alloys, there is only a minimal level of decomposition of the SF₆.

The hydrogen fluoride (HF) formed in these reactions vigorously attacks any materials containing silicon dioxide (SiO₂) (e.g. glass and porcelain). The use of these materials in equipment in which SF₆ is to be used for arc-quenching is therefore only suitable under certain special conditions.

**Corrosion characteristics of SF₆ and its decomposition products**

As already indicated, pure SF₆ is chemically inert: it cannot, therefore, cause corrosion.

In the presence of moisture, however, the primary and secondary decomposition products of sulphur hexafluoride form corrosive electrolytes which may cause damage and operational failure, particularly in electrical equipment. If the formation of decomposition products cannot be avoided by the use of appropriate construction methods, corrosion can be largely eliminated by the careful exclusion of moisture and the employment of suitable materials.

Commonly used metals such as aluminium, steel, copper and brass remain virtually free of attack. In contrast, materials such as glass, porcelain, insulating paper and similar materials may be severely damaged, depending on the concentration of the corrosive substances. Insulating materials such as epoxy-resin, PTFE, polyethylene, polyvinyl chloride and polymethylene oxide are either only slightly or undetectably affected [22].
**Measures for the removal of corrosive constituents**

Both moisture and the decomposition products of sulphur hexafluoride can be relatively easily removed by adsorption. Aluminium oxide and molecular sieves or mixtures of these materials are all suitable for this purpose. They very effectively and practically irreversibly adsorb the acidic and gaseous products. At the same time they also ensure maintaining a low dew-point in the gas filling.

Especially suitable are adsorbing agents in the form of filter filings, through which the gas is pumped in a circulation. This method is employed for example in the case of SF$_6$ power circuit breakers, where considerable concentrations of decomposition products can occur in arc quenching. In many cases, however, static filters provide adequate protection.

Figure 36 shows the dew-point as a function of the gas moisture content.

**Fig. 36** Dew-point as a function of the moisture content of SF$_6$

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<th>dew-point in °C</th>
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Toxicity

New SF$_6$

Pure sulphur hexafluoride is absolutely non-toxic. The by-products arising during production of the gas are completely removed during subsequent purification operations.

Solvay sulphur hexafluoride is constantly tested for the presence of toxic constituents using the inhalation test described in IEC Recommendation 376 (corresponds to DIN IEC 376, April 1980 and VDE 0373 Part 1/4.80).

In places where work involving large quantities of sulphur hexafluoride in containers and in enclosed areas is carried out, the safety regulations should take into account the potential asphyxiation hazard arising from oxygen deficiency, as, due to its high density, the gas can displace air from lower-lying regions of enclosed areas (pits, sumps etc). This hazard can, however, be easily countered by the provision of adequate ventilation. Measuring instruments functioning on the principles of thermal conductivity can be installed to check the SF$_6$ content of air.

The existing TLV in the Federal Republic of Germany for sulphur hexafluoride is 6000 mg/m$^3 = 1000$ ppm.

Contaminated SF$_6$

It should be noted that electrical discharges (e.g. switching processes, fault electric arcs) lead to the formation of gaseous decomposition products and dusty metal compounds. Gaseous decomposition products of SF$_6$ exhibit very characteristic warning signs even at low concentrations. These warning signs are for example pungent or unpleasant odours (like “rotten eggs”), or irritation of nose, mouth and eyes. Such irritation occurs within seconds, well in advance of any danger arising from poisoning.

When handling contaminated SF$_6$ care must be taken not to breathe in gaseous or dusty decomposition products. In case this cannot be achieved by technical safety measures, i.e. ventilation, personal protective equipment must be worn. Personal protective equipment consists of items of protection for the eyes, body and breathing. More detailed information on handling SF$_6$ is given in the information leaflet “SF$_6$ plant” (Trade Association for Precision Mechanics and Electrical Engineering) and in the DIN Standard IEC 480 and VDE 0373, Part 2/4.80.
SF₆ can be removed from its pressurized gas containers either in the gaseous or in the liquid phase. During the removal of SF₆ in the gaseous phase, the pressure-regulator can be connected directly to the cylinder valve. If the SF₆ is removed in the liquid phase, then a vaporizer must be installed between the container and the regulator.

Filling an enclosed system

Normally, equipment is first evacuated and then filled with SF₆ under pressure. In this process, the feed line from the gas cylinder to the unit to be filled is provided with a branch line incorporating a shut-off valve. This branch line leads to a vacuum pump. Before filling with SF₆ commences, the complete system up to the cylinder valve is evacuated. After the valve in the branch line has been closed, both the cylinder and the regulator are gradually opened.

It is advisable to observe the progress of the entire filling operation on an appropriate pressure gauge (centre-zero). The final pressure of the gas in the filled unit will depend upon temperature. On account of the fact that the gas undergoes a cooling process on leaving the steel cylinder, the pressure reading immediately following the completion of the filling operation will be less than that shown after the gas temperature has risen to the ambient level. This subsequent rise in pressure must be taken into account.
Temporary storage during service and maintenance

Temporary storage of SF₆ during service and maintenance is highly recommended in regard to SF₆ reuse and as a preventive measure for environmental protection.

For the gas operations occurring during temporary storage so called service equipment should be available.

Handling of SF₆ service equipment

This kind of equipment consists of main components such as SF₆ compressor, vacuum pump, storage tank, evaporator and filter unit, which are piped together with valves and fittings. According to the size of the switchgear the appropriate equipment with sufficient storage capacity and performance is selected. SF₆ gas handling in such equipment is only carried out in closed cycles.

Every component within this cycle (SF₆ compressors and diaphragm compressors) are dry-running and therefore absolutely oil-free without a chance of SF₆ gas contamination. The built-in filters provide for the drying and cleaning of the SF₆ gas during each gas operation. SF₆ valves, couplings and fittings guarantee a high degree of leak-tightness and operational safety.

The connecting couplings should be self-closing in order to avoid air and moisture penetrating into the lines.

When selecting service equipment, handling should be as easy as possible to avoid unnecessary faults. Maintenance equipment with automatic sequences is the state-of-the-art and is preferred because of its high degree of operational safety.

fig. 38a SF₆ measuring devices (DILÖ, Germany)

fig. 38b SF₆ servicing unit (DILÖ, Germany)
Safety instructions

Storage

Sulphur hexafluoride is transported as a pressurized liquified gas. In Germany, safety precautions and handling practice are based upon the Order Governing Pressurized Containers and its subordinate Technical Regulations.

The containers should not be exposed to direct sunlight and must be secured against overturning or rolling.

Storage and work areas must be well ventilated. In particular, ventilation must be effective at ground level on account of the fact that SF₆ vapour is heavier than air. If the gas is stored underground, appropriate forced ventilation must be provided.

Wherever SF₆ is handled, there must be no open flames (e.g. welding flames) or hot metal surfaces (e.g. infrared equipment). Eating, drinking and smoking whilst working with SF₆ is strictly forbidden.

Although SF₆ is recognized as being physiologically safe, certain precautions have to be taken in order to guarantee a safe handling of this substance. An important precondition is a strict adherence to the threshold limit value (TLV).

Wherever this cannot be achieved pertinent safety measures must be selected according to the degree of potential danger.

New SF₆

- SF₆ to DIN IEC 376
- Potential hazard: asphyxiation
- Protective measures: Natural and forced ventilation

Contaminated SF₆

If SF₆ does not contain any hazardous substances its potential hazards are comparable to those of new SF₆.

- SF₆ is contaminated with dangerous substances
- Potential hazard: The SF₆ decomposition products have an irritating or corrosive effect on eyes, skin and respiratory system

The presence of small quantities of gaseous decomposition products is accompanied by clear warning signals in the form of a pungent and unpleasant odour. Irritation occurs within seconds, well in advance of any danger arising from poisoning.

- Protective measures: If health hazards associated with the handling of contaminated SF₆ cannot be totally excluded with the aid of technical safety measures, then personal protective clothing must be worn. Personal safety clothing protects the eyes, the body and includes protective breathing apparatus.

Additional organisational safety measures include the display of operational instructions and an annual seminar on the potential hazards and the safety precautions to be adopted when handling SF₆ which is contaminated with irritating and corrosive substances.
Sulphur Hexafluoride

Figure: Safe Handling of SF₆

1. **START**
   - New SF₆
   - Contaminated SF₆

2. **Handling in enclosed equipment**
   - NO
   - YES: filling, refilling, emptying

3. **Sealing possible**
   - NO
   - YES: test for leak-tightness

4. **Less than TLV**
   - NO
   - YES: improved ventilation

5. **Use of personal protective clothing**
   - Eye protection
   - Body protection
   - Breathing protection

6. **Natural ventilation**
   - YES
   - NO: forced ventilation

7. **Safe handling of SF₆**
The SF₆ produced by Solvay Fluor und Derivate GmbH is manufactured in a plant that ensures consistent quality with a purity of min. 99.9 %.

It corresponds to the following guarantee-analysis which in turn conforms to IEC Recommendation 376, 1st Edition, Section 3 or to DIN IEC 376, Chapter 3 and to VDE 0373, Part 1, Chapter 3 (according to this standard all values apply to the composition of the liquid phase).

In general, the impurities in Solvay sulphur hexafluoride are substantially less than the maximum values specified in the guarantee-analysis.

The table on the right shows a typical Solvay quality standards specification.

Prior to shipment, every batch of SF₆ is tested for physiological safety (cf. Toxicity).

### DIN IEC 376

<table>
<thead>
<tr>
<th></th>
<th>DIN IEC 376</th>
<th>Solvay Fluor standard specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF₆</td>
<td>≥ 99.90 % by weight</td>
<td>≥ 99.98 % by weight</td>
</tr>
<tr>
<td>air</td>
<td>≤ 500 ppm by weight (0.25 Vol.-%)</td>
<td>≤ 150 ppm by weight</td>
</tr>
<tr>
<td>CF₄</td>
<td>≤ 500 ppm by weight (0.1 Vol.-%)</td>
<td>≤ 50 ppm by weight</td>
</tr>
<tr>
<td>H₂O</td>
<td>≤ 15 ppm by weight (0.012 Vol.-%)</td>
<td>≤ 0.65 ppm by weight</td>
</tr>
<tr>
<td>mineral oil</td>
<td>≤ 10 ppm by weight</td>
<td>≤ 10 ppm by weight</td>
</tr>
<tr>
<td>acidity, in terms of HF</td>
<td>≤ 0.3 ppm by weight</td>
<td>≤ 0.3 ppm by weight</td>
</tr>
<tr>
<td>hydrolyzable fluorides, in terms of HF</td>
<td>≤ 1 ppm by weight</td>
<td>≤ 1 ppm by weight</td>
</tr>
</tbody>
</table>
Packaging for SF$_6$ according to IEC 376

**fig. 39** Special high-capacity container for SF$_6$:
- test pressure 70 bar
- capacity 600 l
- tare Ø 465 kg
Solvay sulphur hexafluoride is shipped as a pressure-liquefied gas in steel cylinders of various sizes. The filling level is 1.04 kg (at test pressure 70 bar) and 1.3 kg (at test pressure 250 bar) SF₆ per litre of container volume.

SF₆ is supplied in steel cylinders of 5, 10, 20, 40, 50 and 52 kg capacity. For larger quantities, special high-capacity containers are available on loan. These accommodate 600 kg of SF₆ (see fig. 39). Tube trailers can be used for export overseas.

The pressurized containers are fitted with a special gas-cylinder valve. The valves have an external threaded port mounted on the side with the designation W 21.8 x 1/14” (connection No. 6 to DIN 477). This side-connection piece is protected from contamination and damage by means of a hexagon cap nut. The screw-on safety cap protects the valve from mechanical damage and contamination.

In order to avoid any suck-back of other gases, SF₆ pressure-gas containers should never be emptied to such a degree that a partial vacuum occurs. After the containers have been emptied, the cylinder valves must be closed immediately. Please return empty cylinders in a suitable condition for refilling to us at the following address:

Solvay Fluor und Derivate GmbH
Carl-Ulrich-Straße 34
D-74206 Bad Wimpfen am Neckar
Germany

Railway station:
Bad Friedrichshall-Jagstfeld

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**fig. 40** Steel cylinder for SF₆:
est pressure 250 bar
capacity 40 l
tare Ø 48 kg
**SF₆ – a reusable commodity**

SF₆ is a user-friendly product which besides its many other positive characteristics can be recycled as well. This is increasingly the important, particularly today.

This is why Solvay Fluor und Derivate GmbH together with the producer of SF₆ maintenance equipment DILO Armaturen und Anlagen GmbH developed a common concept for the re-use of SF₆, based on many years of experience. The practical side of this approach is illustrated by the following diagram.

As an additional service, an analysis can be conducted on your used SF₆ gas. Detailed information can be found in the brochure “Analysis of Used SF₆”.

You will find further information in the brochure “Concept of Reuse of Used SF₆ gas”, available upon request.
Transport by Road

40 l steel cylinders and 600 l high-capacity containers (see fig. 38) are available. The pressurized containers are fitted with a special gas-cylinder valve, external threaded port connection No. 8 (to DIN 477). This is necessary because corrosive decomposition products could be present.

In documents, the product has to be declared as follows:

- liquefied gas mixture, toxic, n.o.s. (Sulphur Hexafluoride > 95 wt % and Hydrogen Fluoride < 2 wt %)
- GGVs/ADR – GGVE/RID
- UN Nr. 3308
- Class 2, T, C
- Danger label: 6.1 + 8 (for toxic, corrosive substances)
Life cycle assessment study
"Electricity supply using SF₆ technology"

In view of obligations that may arise from the Kyoto Protocol, switchgear manufacturers, utilities and SF₆ producers felt it to be necessary to take their responsibility for the product still further and quantify the environmental profile of the use of SF₆ as an insulating and arc-quenching gas in high-voltage and medium-voltage switchgears by means of a life-cycle assessment. The main motive was the need to replace the one-sided focus on the substance-based global warming potential of SF₆ by an analysis of all the relevant environmental criteria in the context of the use of SF₆ in the electric power industry.

This study, entitled “Electricity Supply Using SF₆ Technology”, was performed in cooperation of the firms ABB, PreussenElektra Netz, RWE Energie AG, Siemens AG and Solvay Fluor und Derivate GmbH. It relates to the conditions in the Federal Republic of Germany.

The assessment compares conventional and SF₆ technology at the levels of switchgear bays and provides a comparison of a municipal power supply network using either air-insulated or SF₆-gas-insulated switchgears at the same level of supply quality. The criteria for this comparison are the parameters primary energy consumption, space requirements, global warming potential, acidification potential and nutrification potential.

Even at the bay level, the use of SF₆ technology offers advantages for four of the five criteria of the life cycle assessment study: primary energy consumption, area required, acidification potential, and nutrification potential. Switchgear with a high utilization factor and/or the low rates of SF₆ loss achievable today provide an ecological advantage even for the greenhouse potential.
At the level that counts in the end, namely the power supply system considered (city covering 40 square kilometres: 130,000 inhabitants, 120 MW peak load and an annual consumption of 400 GWh), the following results are obtained: designing a power supply network with GIS technology (using SF₆) results in a reduction of about 27 percent in the primary energy consumption, of about 86 percent in the area required, of about 21 percent in the greenhouse potential (GWP), of about 21 percent in the acidification potential (AP), and of about 29 percent in the nutrification potential (NP), compared to designing the same network with AIS technology (without SF₆). The transferability of the results from this sample network has been tested in extensive scenario calculations.

The major reasons for this reduced environmental impact are: since SF₆ has considerably better insulating and quenching properties than air, substations and equipment can be made with less material and energy than in the SF₆-free AIS alternative. Furthermore, due to the compact design of the GIS components, the 110/20-kV transformer substations can be built directly at the (downtown) load centers. So the energy is transmitted at high voltage with low losses to the city centers, and distributed from there to the consumers via short medium-voltage lines.

The use of SF₆ technology leads to considerable environmental advantages over the use of SF₆-free switchgear. Therefore, SF₆ technology makes sense for electric power supplies, even from the environmental viewpoint. This requires the use of GIS installations that ensure appropriately low SF₆ emissions, on the one hand, and rigorous application of the SF₆-ReUse-Concept of a closed SF₆ cycle, on the other.

The life cycle assessment was performed according to the specifications of the international standard DIN EN ISO 14040, and was followed and evaluated by an external independent expert from TÜV NORD.

**fig. 42** The use of GIS switchgear in the power supply system considered reduces all the potential environmental impacts studied. The diagram shows the relative environmental impact potentials during the first year of use of the power system variant (blue bars = AIS version, green bars = GIS/SF₆ version). An increase in the system’s supply capacities by about 50 percent (i.e. increased utilization of the system) results in a further reduction of about 5 percent each in the parameters primary energy consumption, greenhouse potential (GWP), acidification potential (AP), and nutrification potential (NP), due to SF₆ technology.
Product stewardship for $\text{SF}_6$

Solvay – well known as a global supplier of new $\text{SF}_6$ gas according to IEC 376 – cares for the environment. We are your partner for the $\text{SF}_6$ ReUse concept and full technical services.

The $\text{SF}_6$ ReUse concept of Solvay Fluor und Derivate GmbH includes:

- environmental consulting
- analytical services of used $\text{SF}_6$
- packaging and transport of used $\text{SF}_6$
- reclaiming of used $\text{SF}_6$

Solvay Fluor und Derivate GmbH is the only company worldwide delivering such a complete range, to fulfill the requirements of the responsible care programme.

For further information, please refer to our $\text{SF}_6$ ReUse Folder.
We produce world-wide in our works in Catoosa (USA), Frankfurt (Germany), Tarragona (Spain) and Tavaux (France). The production of fluorine compounds is concentrated at our Bad Wimpfen (Germany) plant.

The product range includes both organic and inorganic compounds:

**Fluorocompounds**
- Fluor (F₂)
- Solkane® hydrofluoroalkanes
  - Solkane 22
  - Solkane 23
  - Solkane 123
  - Solkane 141b
  - Solkane 142b
  - Solkane 22/142b mixtures
  - Solkane 134a/152a mixtures
  - Solkane 134a
  - Solkane 143a
  - Solkane 152a
  - Solkane 404a
  - Solkane 407C
  - Solkane 410A
  - Solkane 507
- Solkane 227pharma
- Polyetherpolyole: IXOL®
- Flame retardant: KaCeFlam®
- Sulphur hexafluoride (SF₆)
- Iodine pentafluoride (IF₅)
- Hydrogen Fluoride
- Hydrofluoric acid

**Inorganic fluorides**
- Aluminium fluoride hydrate
- Ammonium fluoride
- Ammonium hydrogen fluoride
- Barium fluoride
- Calcium fluoride
- Fluoroboric acid
- Potassium fluoroaluminate
- Potassium hydrogen fluoride
- Potassium fluoroborate
- Potassium fluorotitanate
- Potassium cryolithe
- Synthetic cryolithe
- Lithium cryolithe
- Sodium fluoride
- Sodium hydrogen fluoride
- Nocolok® Flux
  (Registered Trademark of Alcan Inter. Ltd.)

**Fine Chemicals**

**CF₃-Aliphatics:**
- Trifluoroacetic acid
- Trifluoroacetic acid anhydride
- Trifluoroacetyl chloride
- Trifluoroacetic acid esters
  - Trifluoroacetic acid methyl ester
  - Trifluoroacetic acid ethyl ester
- 2,2,2-Trifluoroacetamide
- Alcohols and ketones
  - 2,2,2-Trifluoroethanol
  - 1,1,1-Trifluoroacetone
- Trifluoroacetophenone
- Trifluoromethyl components
  - 1,1,1-Trichloro-2,2,2-trifluoroethan

**CF₂-Aliphatics:**
- Chlorodifluoroacetic acid
- Chlorodifluoroacetyl chloride
- Difluoroacetic acid esters
- Difluoroacetic acid methyl ester
- Difluoroacetic acid ethyl ester

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**Your Solvay Contact**

**Sales SF₆**
- Telephone: +49-(0)511/857-2949
- Fax: +49-(0)511/857-2146
- eMail: sf6@solvay.com
- Internet: www.solvay-fluor.de

**Technical Service SF₆**
- Telephone: +49-(0)511/857-2441
- Fax: +49-(0)511/857-2166
- eMail: sf6@solvay.com
- Internet: www.solvay-fluor.de
Bibliography


Further publications about SF6 by Solvay Fluor

- SF6 ReUse Folder
- Life cycle assessment study “Electricity supply using SF6 technology”
- “Separation of SF6/N2 Mixtures”; Pittroff, 2nd European Conference of Industrial Electrical Equipment and Environment; 24 – 25.01.00

Please note that all users of SF6 are responsible for adherence to applicable instructions and regulations and for the observance of current laws.

The information given in this brochure has been compiled to the best of our knowledge; no liability can be accepted in matters arising therefrom.