Report on potential of CF$_3$I gas for application in high voltage insulation and its prospects for replacing SF$_6$ gas in GIS applications

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1 Introduction

In electric power system, the preferred gaseous insulating medium is air, and for specific applications such as circuit breaker and very compact substations, sulphur hexafluoride (SF₆) is successfully adopted. However many studies show the high environmental impact of SF₆ for its green-house effect. In particular in, the environmental impact of SF₆ is well recognised and is being addressed in [1]:

“Because of its long life span and high GWP potency, even a relatively small amount of SF₆ can have a significant impact on our climate...

Hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), and sulfur hexafluoride (SF₆) are potent greenhouse gases, and some persist in the environment for thousands of years. These gases, referred to as high global warming potential gases (high GWPs) are from 140 to 23,900 times more potent than CO₂ in terms of their capabilities to trap heat in the atmosphere over a 100-year period...

The SF₆ Emission Reduction Partnership for Electric Power Systems is a collaborative effort between EPA and the electricity power industry to identify and implement cost-effective solutions to reduce sulfur hexafluoride (SF₆) emissions. SF₆ is a highly potent greenhouse gas used in the industry for insulation and current interruption in electric transmission and distribution equipment. Currently 81 utilities participate in this voluntary program.”

In this report, the characteristics of trifluoromethyl iodine have been investigated as a replacement for SF₆ in high-voltage applications from literature on various topics. In fact, in the 90s, the characteristics of CF₃I gas were investigated in order to find a replacement for halon as fire extinguisher. Later, further studies were then extended as promising gas insulating media.

1.1 Earlier studies on CF₃I as fire suppressor

In 1994 Moore et al. [24] prepared a report to illustrate the conclusions of several studies in order to replace halon with CF₃I as fire extinguisher. The report was based on a wide number of publications focused on the following key areas:

- fire suppression characteristics,
- global environmental characteristics,
- toxicological information,
- compatibility with other materials
- stability

It was found that CF₃I gas is a good fire suppressor having a concentration of 5-7% with global environmental characteristics much lower than the adopted gas, halon:

- Atmospheric lifetime < 1 day
- Ozone-depletion potential (ODP) < 0.008
- Global warming potential (GWP) <5 times than CO₂ GWP

The toxicological review showed low order of acute toxicity, but significant cardiac sensitization level (no observable adverse effect level - NOAL = 0.2%, lowest observable adverse effect level - LOAEL = 0.4%). The gas presents a cardio-toxicity effect at concentrations required to be fire suppressor. Therefore, the use in normally occupied areas was excluded; the only applications are in streaming and unoccupied areas. However, studies on carcinogenic effects were not completed at the publication date of the report (October 1994).

Extended studies on the compatibility of CF₃I with other materials were also reviewed and analyzed. The gas appeared to be compatible for temperatures below 77° C with normal construction materials (stainless steel, carbon steel, brass, and aluminium) and ethylene-propylene diene monomer (EPDM), nitrile, and neoprene rubbers.

The stability of the gas during the storage was another important characteristic. The studies showed good stability performance for temperatures below 116° C in absence of light, oxygen, and water.
Further interesting properties of CF$_3$I, exhibiting high dielectric strength and its good electronegative attachment characteristics suggested to extend its use as insulating media in power system applications.

1.2 Properties required for power system applications

In this section, general characteristics for SF$_6$ replacement are given according to the possible final use of the insulating gas, circuit breakers, gas-insulated transmission lines, and power transformers [2].

1.2.1 Circuit breaker applications

The most important physical characteristics of the insulating gas in circuit breakers (CBs) are related to the electric arc. The characteristic required for arc interruption are:

- high dielectric strength
- high thermal conductivity

The operational temperatures can vary from ambient conditions (250 K) to arc plasma condition (over 10000 K). As thermodynamic properties, the gas needs to be able to transfer the heat produced by the arc. Therefore, it is required that the gas has a high thermal conductivity.

Another important characteristic is the ability to capture free electrons despite the high gas temperature and the high energy of electrons. The fulfilment of these properties permits to offer to build a device with a high interruption capability. In addition, the exposure of the gas to high temperatures leads to its dissociation into its constituent atoms. Therefore, the gas should be able to reform itself in order to maintain the high dielectric strength.

1.2.2 Gas-insulated transmission line applications

Some properties required for gas-insulated transmission line applications are different from the applications in circuit breakers. Important properties that the adopted gas needs to fulfil are:

- high dielectric strength
- long-range stability
- inertness
- good thermal conductivity at a lower range than for circuit breaker applications (lower than 110 °C)

In particular, the gas needs to show a high dielectric strength under different conditions:

- uniform fields,
- non uniform fields,
- electrode roughness and possible presence of conducting particles,
- various geometric configurations.

An important characteristic is the vapour pressure at the operating temperature range. The gas should have a high vapour pressure to avoid any state change in the operational temperature range. The possibility of chemical reactions with the materials of electrodes, the metallic structure and the sealing-materials should not occur during long-term use (40 years or more). Other contaminations due to deposits, such as carbon deposits or polymerization and decomposition should also avoided.

With regards to maintenance, the following are essential:

- easily removable
- non-harmful by-products
- no hazards for personnel and structure, no risk of fire, explosion, toxicity and corrosion.
1.2.3 Gas-insulated transformer applications

High rate power transformers use oil as dielectric and as cooling medium. However, there are several problems related to the use of oil, e.g. risk of ignition in presence of air, breakdown due contamination particles and ion accumulations.

The adoption of a gas instead of oil can offer several advantages:

- lower risk of ignition and explosion
- reduced weight of equipment
- reduced noise emission (gas transmits less vibration than oil)

The properties that a gas should offer to be adopted successfully in power transformers are:

- high dielectric strength at high pressure (e.g. 500 kPa)
- low boiling point
- low toxicity
- inertness
- good thermal stability
- no risk of fire, fire suppressor
- high cooling capability
- no reaction with several solid materials
- good partial discharges characteristic
- wide operative temperature range
- easy to handle
- large amount available on the market
- low price

2 Physical and thermal properties of CF$_3$I

Iodotrifluoromethane (CF$_3$I) has the following synonyms:

- Trifluoriodomethane,
- Trifluoromethyl Iodide,
- FIC-1311 $^1$,
- Triiodide $^2$,
- Iodoguard® $^3$,
- Halon 13001.

The 3D molecular drawing of CF$_3$I is shown in Figure 1.

![3D molecular drawing of CF$_3$I](image)

**Figure 1:** 3D molecular drawing of CF$_3$I, showing the three fluorine atoms (green) and the iodine atom (purple) connected to the carbon atom (grey).

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$^1$ Halocarbon Numbering system
$^2$ Registered Trademark of Pacific Scientific, 1800 Highland Ave., Duarte, CA, 91010
$^3$ Registered Trademark of West Florida Ordnance, Inc, 441 N. Jefferson St. Suite 111, Pensacola, FL 35201
The iodotrifluoromethane can be identified in the international databases using the following numbers:
- Chemical Abstracts Service (CAS) No. 2314-97-8
- European Chemical (EC) Number 219-014-5

In order to replace successfully SF₆ with the CF₃I, several physical characteristics need to be investigated. The first important property to fulfil is a high dielectric strength. The dielectric strength of the selected gas needs to offer a higher value than air and the same order of SF₆ in order to use the same design applied nowadays in GIS systems. A comparative list with dielectric strength of various gases expressed as relative value to SF₆ is shown in Table 1:

Table 1: Relative DC uniform-field breakdown strengths [2 and 3]

<table>
<thead>
<tr>
<th>Gas</th>
<th>Vₛ relative to SF₆</th>
<th>Vₛ (E/N)ₘₘ</th>
<th>Electron attaching</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C₆F₁₂</td>
<td>≈2.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₄F₆</td>
<td>≈2.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-C₄F₆</td>
<td>≈1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C-C₄F₈</td>
<td>1.3</td>
<td></td>
<td>strongly attaching</td>
</tr>
<tr>
<td>CF₃I</td>
<td>1.21</td>
<td>4.37E-15</td>
<td>strongly attaching</td>
</tr>
<tr>
<td>SF₆</td>
<td>1</td>
<td>3.61E-15</td>
<td>strongly attaching</td>
</tr>
<tr>
<td>C₃F₈</td>
<td>0.9</td>
<td>3.25E-15</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N₂O</td>
<td>0.44</td>
<td>1.59E-15</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>0.3</td>
<td>1.08E-15</td>
<td>weakly attaching</td>
</tr>
<tr>
<td>Air</td>
<td>0.3</td>
<td>1.08E-15</td>
<td></td>
</tr>
<tr>
<td>N₂</td>
<td>0.36</td>
<td>1.3E-15</td>
<td></td>
</tr>
<tr>
<td>H₂</td>
<td>0.18</td>
<td>6.5E-16</td>
<td>non attaching</td>
</tr>
</tbody>
</table>

As it can be seen on Table 1, several gases offer higher dielectric strength than SF₆. In addition, it is needed to consider the gas at different pressure condition for its strength estimation. In fact, at 6 bars, SF₆ shows a very high dielectric strength, comparable with transformer oil. [3]

The good dielectric strength of CF₃I and its mixture are better understood with the examination of its electron interaction properties.

2.1 Electron Interaction Properties

In order to present good dielectric strength, the gas should present the ability to reduce the number of free electrons [2]. Therefore, the following properties need to be considered:
- **electron attachment**: to be electronegative, removing free electrons by attachment
- **ionization cross section**: should present a low value in order to offer a reduced number of free electrons
- **electron slowing-down properties**: to be able to slow down electrons in order to facilitate their capture at lower energy
- **electron impact ionization**: with a high value, it prevents the ionization by electron impact

In 2007, de Urquijo et al. [4, 5] determined many physical properties of CF₃I and CF₃I-N₂ mixture using a pulse Townsend experiment. In particular, the **electron drift velocity** vₑ, the **density-
normalized longitudinal coefficient \( N_{DL} \) and the density-normalized effective ionization coefficient \( (\alpha - \eta) / N \) for CF\(_3\)I and its mixture with N\(_2\) at different percentage were published.

- electron drift velocity \( v_e \)
- density-normalized longitudinal coefficient \( N_{DL} \)
- density-normalized effective ionization coefficient \( (\alpha - \eta) / N \)

2.1.1 Electro attachment

The strongly electronegative attachment in CF\(_3\)I is due to the formation of I\(^-\), F\(^-\) and CF\(_3\)\(^-\) and F\(_2\) via two dissociating negative ion states at 0eV and 3.8eV [6]. The dissociation reaction by the 0 eV process with the formation of ion I is given by

\[
e + CF_3I \rightarrow I^- + CF_3
\]  

(2.1)

The formation of the ions F\(^-\) and CF\(_3\)\(^-\) by the 3.8eV process are expressed by the two following reactions:

\[
e + CF_3I \rightarrow F^- + CF_3\]

(2.2)

and

\[
e + CF_3I \rightarrow CF_3^- + I
\]

(2.3)

The dissociation of F\(^-\) by electron attachment is shown to increase with increasing temperatures. However, the relative cross-section for the formation of F\(^-\) is much lower than the value for the I\(^-\) formation that present insensitivity with temperature. For this reason, the total attachment cross-section is not affected significantly by the temperature. The total electron attachment cross section \( \sigma_{at}(\varepsilon) \) as a function of electron energy is shown in Figure 2.

![Figure 2: Total electron attachment cross section \( \sigma_{at}(\varepsilon) \) as a function of electron energy [6].](image)

In [7], the authors reported that the absolute attachment cross-section in CF\(_3\)I to be \( 2.7 \times 10^{-14} \) cm\(^2\) for thermal electrons.

The thermal electron attachment rate constant \( k_{at,th} \) presents higher values in the temperature range 250-500K and restarts to decline for temperature over 600 K [6], as shown in Figure 3.
2.1.2 Ionization cross section

The graph of the total ionization cross section versus the electron energy is presented by Christophorou in [6] and shown in Figure 4.

2.1.3 Electron drift velocity \( v_e \)

For the pure gas, the values of \( v_e \) showed a linear increase with the ratio \( E/N \) [4], as shown in Figure 5. The CF\(_3\)I-N\(_2\) mixtures with a percentage with 10% and 20% showed a similar trend as pure N\(_2\). For 70% of CF\(_3\)I or more the trend is close to that of SF\(_6\). It was noted that the electron drift velocity for CF\(_3\)I is lower than of SF\(_6\) for the E/N values lower 700 Td.
Longitudinal diffusion coefficients for electrons

A comparison of the density-normalized longitudinal diffusion coefficients \( ND_L \) for electrons in pure CF\(_3\)I, in CF\(_3\)I-N\(_2\) mixtures and in SF\(_6\) [4] is shown in Figure 6. The \( ND_L \) values for pure CF\(_3\)I and CF\(_3\)I-N\(_2\) mixtures with 50% or 70% CF\(_3\)I showed smaller values than SF\(_6\).

![Figure 6: The density-normalized longitudinal diffusion coefficients \( ND_L \) for electrons in pure CF\(_3\)I, in CF\(_3\)I-N\(_2\) mixtures and in SF\(_6\) [4].](image)

2.1.4 Effective ionization coefficients

For the pure gas, the density-normalized effective ionization coefficients \((\alpha - \eta) / N\) showed a linear increase with the ratio \( E/N \) [4]. It is worth to note that the values of the density-normalized effective ionization coefficient \((\alpha - \eta) / N\) of CF\(_3\)I-N\(_2\) mixture (30%-70%) correspond with SF\(_6\) values, shown in Figure 7.

![Figure 7: The density-normalized effective ionization coefficients \((\alpha - \eta) / N\) for CF\(_3\)I and in the CF\(_3\)I-N\(_2\) mixtures with 5%, 10%, 20%, 50% and 70% CF\(_3\)I as a function of \( E/N \) [4].](image)

According to [4], the characteristics of CF\(_3\)I-N\(_2\) mixture suggest the same efficiency or even superior than SF\(_6\) as insulating media.

The limiting field strength \( E / N_{lim} \) is given when ionisations is equal to attachments, \( \alpha = \eta \), and so when \((\alpha - \eta) / N = 0\). The critical field strength of pure CF\(_3\)I is 437Td, higher that of SF\(_6\) which is equal to 361Td. The same plot shows that the trend of the CF\(_3\)I-N\(_2\) mixture (70%-30%) almost overlaps the SF\(_6\) trend.

The comparison of the CF\(_3\)I-N\(_2\) mixtures with SF\(_6\)-N\(_2\) mixtures critical field strengths as function of the percentage of N\(_2\) is shown in Figure 8.
Figure 8: Critical field strength for CF₃I-N₂ mixtures and SF₆-N₂ mixtures [4].

Figure 9 shows the effective ionisation coefficients in air and in SF₆.

2.1.5 Scattering cross sections

In [6], the authors reviewed previous measurements on total electron scattering cross sections, and they presented a curve derived by these two available data sets, as shown in Figure 10.

Figure 10: Total electron scattering cross section $\sigma_{\text{tot}}(E)$ versus electron energy [6].
In addition, it could be interesting to extend the investigation to other properties for a better knowledge of CF₃I such as:

- photodetachment
- collisional detachment
- clustering and ion-molecule reactions [see Appendix A-9.1]
- electron emission from surfaces by ion and photon impact
- photoprocesses
- absorption of photoionizing radiation (discharge development in non-uniform fields)
- dissociation under electron impact decomposition
- reactions with trace of impurities
- reactions with surfaces

2.2 Thermal properties

A good insulating medium for power equipment should show good characteristics under high vapour pressure and high specific heat. A high vapour pressure avoids the possibility of phase change from gas form into liquid state for the temperature range of the device. The second property, the high thermal conductivity, permits to offers good cooling characteristic.

In order to evaluate the phase state of CF₃I for the required temperature range, it is necessary to analyze the saturation vapour pressure curve.

2.2.1 Phase change gas-liquid data

Duan et al. [8] measured the saturated densities of the gas from which the critical point parameters were calculated:

- critical density  $\rho_c$  868 [kg m⁻³]
- critical temperature  $T_c$  396.44 [K] (123 °C)
- critical pressure  $P_c$  3.953 [Mpa]

In two further papers [9, 10], they measured several vapour pressure data points for CF₃I and an analytical correlation of pressure and densities were given. The pressure-temperature conditions of phase change are given by:

$$\ln\left(\frac{P}{P_c}\right) = (A_1 \tau + A_2 \tau^{1.25} + A_3 \tau^3 + A_4 \tau^7) \frac{T_c}{T}$$  

(2.4)

where:

$\tau$: 1-T/Tc
$T_c$: critical temperature 396.44 [K]
$P_c$: critical pressure 3.953 [MPa]
$A_i$: coefficients, shown in Table 2.

Table 2: Coefficients for eq. (2.4).

<table>
<thead>
<tr>
<th></th>
<th>A₁</th>
<th>A₂</th>
<th>A₃</th>
<th>A₄</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-7.19045</td>
<td>1.34829</td>
<td>-1.58035</td>
<td>-5.46680</td>
</tr>
</tbody>
</table>

The saturated densities values can be estimates using:

$$\frac{\rho_r}{\rho_c} = 1 + b_1 \tau^b + b_2 \tau^{2b} + b_3 \tau + b_4 \tau^{1.25}$$  

(2.5)

where:

$\rho_c$: critical density
$\beta$: critical exponent, 0.325
b_j: coefficients determined using the least-squares method, as show in Table 3.

Table 3: Coefficients for eq. (2.5).

<table>
<thead>
<tr>
<th>saturated conditions for</th>
<th>b_1</th>
<th>b_2</th>
<th>b_3</th>
<th>b_4</th>
</tr>
</thead>
<tbody>
<tr>
<td>liquid</td>
<td>1.401532</td>
<td>0.8092603</td>
<td>0.5946375</td>
<td>-0.3991380</td>
</tr>
<tr>
<td>vapour</td>
<td>-1.542282</td>
<td>-1.149425</td>
<td>2.020176</td>
<td>-0.3776717</td>
</tr>
</tbody>
</table>

The experimental measurements of CF_3I densities obtained along the vapour-liquid coexistence curve are reported in Error! Reference source not found., Appendix Error! Reference source not found.

The saturation vapour pressure curve in CF_3I, SF_6, CO_2 and N_2 gas are presented in Figure 11.

![Figure 11: Saturation vapour pressure curve in SF_6, CO_2, N_2 and CF_3I gas.](image)

In [11], the authors highlighted an important limitation of CF_3I in comparison to SF_6, which is the boiling point at higher temperature. At atmospheric pressure, the boiling point of CF_3I is -22.5 °C [12], as show in Table 4.

Table 4: Boiling point of CF_3I at atmospheric pressure.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tboil</td>
<td>250.6</td>
<td>K</td>
<td>-22.5</td>
<td>°C</td>
<td>N/A</td>
<td>Farchan Laboratories, 1990 [13]</td>
</tr>
</tbody>
</table>

At 0.2 MPa pressure, the gas becomes liquid at -3 °C. For this reason it can be difficult the use of compressed CF_3I in HV switchgears at temperatures that are common in winter. The addition of other gases as N_2 or CO_2 helps in reducing the boiling point, and it is absolutely required for outdoor applications. According to the Dalton’s law, the total pressure of a mixture of ideal gases is equal to the sum of the partial pressures of the individual gases present in the mixture. The partial pressure in a CF_3I-N_2 gas mixture can be expresses as:

\[
P_{gas \ mixture} = P_{CF_3I} + P_{N_2}
\]  

where  
\[P_{gas \ mixture}\] total pressure of the gas mixture
\[ P_{CF_3I} \] partial pressure of CF$_3$I gas
\[ P_{N_2} \] partial pressure of N$_2$ gas

Table 5 shows the boiling points of CF$_3$I, SF$_6$, CF$_3$I–N$_2$, CF$_3$I–CO$_2$ and CO$_2$ at three different pressure values 0.1, 0.2 and 0.5 MPa. The latter pressure value is commonly used in GIS applications. Therefore, it is an important pressure level to consider.

Table 5: Boiling point of different gases.

<table>
<thead>
<tr>
<th>Pressure [MPa]</th>
<th>Note</th>
<th>Boiling point of Gas composition [°C]</th>
<th>CF$_3$I</th>
<th>SF$_6$</th>
<th>N$_2$</th>
<th>CO$_2$</th>
<th>50% CF$_3$I – 50% N$_2$</th>
<th>30% CF$_3$I – 70% CO$_2$</th>
<th>70% CF$_3$I – 30% CO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>(atmospheric pressure)</td>
<td></td>
<td>-22.5</td>
<td>-63.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2</td>
<td></td>
<td></td>
<td>-3</td>
<td>-50</td>
<td></td>
<td></td>
<td></td>
<td>-22</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>(GIS application)</td>
<td></td>
<td>+25</td>
<td>-28</td>
<td></td>
<td></td>
<td>2.3( est. )</td>
<td>-12.5</td>
<td>12.9( est. )</td>
</tr>
</tbody>
</table>

Figure 11 shows the saturation vapour pressure curve in CF$_3$I and SF$_6$ gases.

Figure 12: Saturation vapour pressure curve in SF$_6$, CO$_2$, N$_2$ and CF$_3$I gas under the pressure range 0.5 to 10 bar (0.05 to 1 MPa).

2.2.2 Thermal conductivity

Duan et al. [14] determined the CF$_3$I thermal conductivity for saturation vapour and for gas at low pressure. Using a least squares method on several experimental measurements, the thermal conductivity for saturated vapour were expressed by:

\[ \bar{\lambda} = c_0 + c_1 \cdot t + c_2 \cdot t^2 + c_3 \cdot t^3 \] [ mW/m K] (2.7)

and the thermal conductivity for dilute gas by:

\[ \lambda_0 = d_0 + d_1 \cdot t \] [ mW/m K] (2.8)
where
\[ t \] temperature expressed in °C
\[ c_i \text{ and } d_i \text{ coefficients according to Table 6} \]

Table 6: Coefficients for equations eq. (2.7) and (2.8).

<table>
<thead>
<tr>
<th>( c_0 )</th>
<th>( c_1 )</th>
<th>( c_2 )</th>
<th>( c_3 )</th>
<th>( d_0 )</th>
<th>( d_1 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.96539</td>
<td>4.95212 \times 10^{-2}</td>
<td>5.91157 \times 10^{-6}</td>
<td>3.83578 \times 10^{-6}</td>
<td>6.661404</td>
<td>3.0818743 \times 10^{-2}</td>
</tr>
</tbody>
</table>

The thermal conductivity as function of temperature in the range of -10 ± 70 °C is shown in Figure 13.

![Figure 13: CF₃I thermal conductivity as function of temperature in the range of -10 ± 70 °C, continuous line for CF₃I gas under saturation conditions and dotted line for dilute gas conditions.](image)

According to the graph, the thermal conductivity of CF₃I at 0 °C is equal to 6.65 mW/(m K). At the same temperature, the thermal conductivity of SF₆, CO₂ and N₂ are 12.05, 14.65 mW/(m K) and 24 mW/(m K) respectively. Therefore, CF₃I gas presents a lower value of thermal conductivity and further investigations on its impact in the CB applications are needed. The combination of CF₃I and N₂ may provide useful application in CB apparatus due to the increased thermal conductivity of the mixture. However more data is required on the high temperature range.

The thermal conductivity curve of SF₆ and N₂ is shown in Figure 14. For both gases, the curves show qualities which allows to be used for extinguishing arcs by thermal transport. The peak of the thermal conductivity of SF₆ corresponds to the dissociation temperature of SF₆ molecules at 2100 to 2500 K.
Figure 14: Thermal conductivity of SF₆ and N₂\cite{15}.

2.2.3 Gas Phase Thermochemistry Data

The gas phase thermochemistry data available is given in \cite{16}, and consists of the following types of data:

- Enthalpy of formation at standard conditions ($\Delta_f H^\circ_{\text{gas}}$), shown in Table 7
- Molar entropy at standard conditions, 1 bar standard pressure ($S^\circ_{\text{gas, 1 bar}}$).
- Shomate equation parameters for thermochemical functions
- Ideal gas heat capacity ($C_p,_{\text{gas}}$)

Table 7: Enthalpy of formation at standard conditions \cite{16}.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_f H^\circ_{\text{gas}}$</td>
<td>-589.11</td>
<td>kJ/mol</td>
<td>Review</td>
<td>Chase, 1998 \cite{17}</td>
<td>Data last reviewed in June, 1969</td>
</tr>
<tr>
<td>$\Delta_f H^\circ_{\text{gas}}$</td>
<td>-587.8 ± 3.2</td>
<td>kJ/mol</td>
<td>Heat of equilibrium</td>
<td>Goy, Lord, et al., 1967 \cite{18}</td>
<td>Reanalyzed by Cox and Pilcher, 1970 \cite{19}; Original value = -583.2 kJ/mol; ALS</td>
</tr>
</tbody>
</table>

Table 8: Enthalpy of combustion data \cite{16}.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta_c H^\circ_{\text{gas}}$</td>
<td>-71.55 ± 0.71</td>
<td>kJ/mol</td>
<td>Heat of equilibrium</td>
<td>Goy, Lord, et al., 1967 \cite{18}</td>
<td></td>
</tr>
</tbody>
</table>

Table 9: Molar entropy at standard conditions, 1 bar standard pressure \cite{16}.

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Value</th>
<th>Units</th>
<th>Method</th>
<th>Reference</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$S^\circ_{\text{gas, 1 bar}}$</td>
<td>307.62</td>
<td>J/mol K</td>
<td>Review</td>
<td>Chase, 1998 \cite{17}</td>
<td>Data last reviewed in June, 1969</td>
</tr>
</tbody>
</table>
2.2.4  Heat capacity, standard enthalpy and standard entropy

The Shomate equation parameters in Table 6 can be used to calculate the heat capacity, molar enthalpy, and molar entropy using the equations (2.9), (2.10) and (2.11).

The heat capacity ($C_p$) can be calculated by the equation:

$$C_p = A + B \cdot t + C \cdot t^2 + D \cdot t^3 + \frac{E}{t^4}$$  \hspace{1cm} [J/mol K] \hspace{1cm} (2.9)

Standard enthalpy $H^\circ$ can be calculated by the equation:

$$H^\circ - H^\circ_{298.15} = A \cdot t + B \cdot \frac{t^2}{2} + C \cdot \frac{t^3}{3} + D \cdot \frac{t^4}{4} \cdot \frac{E}{t^5} + F - H$$  \hspace{1cm} [kJ/mol] \hspace{1cm} (2.10)

Standard entropy $S^\circ$ can be calculated by the equation:

$$S^\circ = A \cdot \ln(t) + B \cdot t + C \cdot \frac{t^2}{2} + D \cdot \frac{t^3}{3} + \frac{E}{(2 \cdot t^4)} + G$$  \hspace{1cm} [J/mol K] \hspace{1cm} (2.11)

where

\[ t = \text{temperature (K) / 1000.} \]

A, B, C, D, E, F, G and H coefficients given in Table 10.

Table 10:  Shomate equation parameters (2.7) [16].

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Temperature range [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298. - 1200.</td>
</tr>
<tr>
<td>A</td>
<td>44.50353</td>
</tr>
<tr>
<td>B</td>
<td>138.4527</td>
</tr>
<tr>
<td>C</td>
<td>-115.8533</td>
</tr>
<tr>
<td>D</td>
<td>34.58407</td>
</tr>
<tr>
<td>E</td>
<td>-0.488716</td>
</tr>
<tr>
<td>F</td>
<td>-609.2155</td>
</tr>
<tr>
<td>G</td>
<td>322.2914</td>
</tr>
<tr>
<td>H</td>
<td>-589.1072</td>
</tr>
</tbody>
</table>

Numerical values of heat capacity $C_p$, standard entropy $S^\circ$, standard enthalpy ($H^\circ - H^\circ_{298.15}$) of CF$_3$I for the temperature range 298 – 1200 K and for temperature the range 1200 – 6000 K are plotted in Figure 15, Figure 16 and Figure 17 and presented in Error! Reference source not found. and Error! Reference source not found. in Appendix Error! Reference source not found..
Figure 15: Calculation of heat capacity $C_p$ of CF$_3$I according to eq. (2.9).

Figure 16: Calculation of standard entropy $S$ of CF$_3$I according to eq.(2.10).

Figure 17: Calculation of standard enthalpy ($H^\circ - H^\circ_{298.15}$) of CF$_3$I.

For gas evaluation, it may be more convenient to use the specific heat at constant volume. The specific heat at constant volume can be derived from the specific heat at constant pressure using the Mayer's relation for an ideal gas, given by [20]:

15
\[ C_p - C_V = R \]  \hspace{1cm} [J/K\text{ mol}] \tag{2.12} \]

where

- \( C_p \) the specific heat at constant pressure
- \( C_V \) the specific heat at constant volume
- \( R \) the universal gas constant, 8.314472.

3 CO\textsubscript{2}-CF\textsubscript{3}I mixture

In [21], the authors investigated the equilibrium compositions of the CO\textsubscript{2}-CF\textsubscript{3}I gas mixture at different temperatures and at different CF\textsubscript{3}I concentrations at 0.1 MPa pressure. The particle composition of the gas mixture was calculated in the 300-30000 K temperature range.

The investigation was focused on 61 particle species in the gas mixture at the different conditions and on dissociation reactions and ionisation reactions, shown respectively in Table 11, Table 12 and Table 13.

Table 11: 61 particle species in the gas mixture

<table>
<thead>
<tr>
<th>37 neutral molecules</th>
<th>CO\textsubscript{2}</th>
<th>CO</th>
<th>C\textsubscript{2}O</th>
<th>C\textsubscript{3}O\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>C\textsubscript{2}</td>
<td>C\textsubscript{3}</td>
<td>C\textsubscript{4}</td>
<td>C\textsubscript{5}</td>
<td></td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>O\textsubscript{3}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF\textsubscript{3}I</td>
<td>CF</td>
<td>CF\textsubscript{2}</td>
<td>CF\textsubscript{3}</td>
<td>CF\textsubscript{4}</td>
</tr>
<tr>
<td>IF</td>
<td>IF\textsubscript{3}</td>
<td>IF\textsubscript{2}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F\textsubscript{2}</td>
<td>I\textsubscript{2}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>COF</td>
<td>COF\textsubscript{2}</td>
<td>CF\textsubscript{2}OF</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FOOF</td>
<td>FOOF</td>
<td>FOOF</td>
<td>OFO</td>
<td></td>
</tr>
<tr>
<td>IO\textsubscript{3}</td>
<td>IOIO</td>
<td>IOI</td>
<td>IOO</td>
<td>IO</td>
</tr>
<tr>
<td>atoms 4</td>
<td>C</td>
<td>O</td>
<td>F</td>
<td>I</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>19 ions</th>
<th>CO\textsubscript{2}</th>
<th>C\textsubscript{2}</th>
<th>C\textsuperscript{+}</th>
<th>C\textsuperscript{2+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>O\textsubscript{2}</td>
<td>O\textsuperscript{+}</td>
<td>O\textsuperscript{2+}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CF\textsuperscript{3}I</td>
<td>CF\textsuperscript{2}</td>
<td>CF\textsuperscript{+}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>F\textsuperscript{2}</td>
<td>F\textsuperscript{+}</td>
<td>F\textsuperscript{2+}</td>
<td></td>
<td></td>
</tr>
<tr>
<td>I\textsuperscript{+}</td>
<td>I</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 12: Extract from the table dissociation reaction in high temperature CO\textsubscript{2}-CF\textsubscript{3}I mixture.

| 1 | CO\textsubscript{2} | ⇌ | CO | + | O |
| 2 | CO | ⇌ | C | + | O |
| 3 | C\textsubscript{2}O | ⇌ | C | + | CO |
| 4 | C\textsubscript{2}O\textsubscript{2} | ⇌ | CO | + | C\textsubscript{2} |
| ... | |
| 11 | CF\textsubscript{3}I | ⇌ | CF\textsubscript{3} | + | I |
| 12 | CF | ⇌ | C | + | F |
| 19 | IF | ⇌ | I | + | F |
| 35 | IOI | ⇌ | IO | + | I |
| 36 | IOI | ⇌ | IO | + | I |
| 37 | IO | ⇌ | I | + | O |
Table 13: Extract from ionisation reaction in high temperature CO₂-CF₃I mixture.

<table>
<thead>
<tr>
<th>38</th>
<th>CO₂ ⇌ CO₂ + e⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>...</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>I ⇌ I + e⁻</td>
</tr>
<tr>
<td>56</td>
<td>I ⇌ I + e⁻</td>
</tr>
</tbody>
</table>

The following observations were made [21]:
- The number density of each molecule in the temperature range of 300-5000K change significantly according to the CF₃I concentration in the mixture.
- Under the temperature of 15000K, the electron density presents an increase for higher CF₃I concentrations.

The numerical data obtained by the authors are very useful for the characterization of CO₂-CF₃I mixtures for arc interruption.

### 3.1 Arc extinction properties of CO₂-CF₃I mixture

The thermodynamic properties at high temperatures in CO₂-CF₃I mixture have been investigated by Yokomizu et al. [22]. This study aims to analyze various concentrations of CF₃I in CO₂ mixture in the temperature range of 300-30000K and to identify possible improvements in current interrupting capability for circuit breaker application compared with the use of CO₂ only.

The enthalpy and the specific heat at constant pressure (Cₚ) of CO₂-CF₃I mixture for different CF₃I concentrations are shown in Figure 18 and Figure 19. It is interesting to note the different magnitudes of the specific heat according to the different concentration of CF₃I in the temperature range 7000-8000K. According to the authors, the peak for concentration of 0.9 or less of CF₃I is due to dissociation reaction of CO.

![Figure 18: Specific heat at constant pressure (Cₚ) of CO₂-CF₃I mixture for different CF₃I concentrations [22].](image1)

![Figure 19: Enthalpy of CO₂-CF₃I mixture for different CF₃I concentrations [22].](image2)
In addition, the authors evaluated the performance of the mixture as arc extinguisher using their proposed temperature-reduction factor. Larger values of this factor indicate fast decay in the arc temperature due to convection loss. The magnitude of this factor is shown in Figure 20. The most interesting temperature range is from 6000 to 15000K, since it is the temperature range estimated for an interrupting arc around a current zero. From the curves in Figure 20, it is possible to make the following observation; in case of concentration above 0.9 of CF₃I, the thermal performance of the mixture are better than the use of pure CO₂.

Figure 20: Magnitude of the temperature-reduction factor for CO₂-CF₃I mixture [22].

Investigation on the presence of iodine after arc extinction, a gas chromatograph-mass spectometre (GS-MS) and a CO detector tube were used. Table 14 shows the particles detected at various concentrations of CF₃I, in particular, the presence of iodine (I) in solid state is specified.

Table 14: By-products after arc extinction in CO₂-CF₃I mixture (arbitrary unit) [22].

<table>
<thead>
<tr>
<th>particle</th>
<th>CF₃I concentration X₃3CF₃I</th>
<th>0.33</th>
<th>0.71</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>CF₃I</td>
<td></td>
<td></td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>CO₂</td>
<td>0.11</td>
<td>0.39</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>CO</td>
<td>above 0.22</td>
<td>above 0.22</td>
<td>0.26</td>
<td></td>
</tr>
<tr>
<td>C₂F₆</td>
<td>0</td>
<td>0.070</td>
<td></td>
<td>0.26</td>
</tr>
<tr>
<td>CF₄</td>
<td>0</td>
<td>0</td>
<td>0.084</td>
<td></td>
</tr>
<tr>
<td>CF₃I</td>
<td>0</td>
<td>0.01</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td>I₂(s)</td>
<td>confirmed</td>
<td>confirmed</td>
<td>confirmed</td>
<td></td>
</tr>
</tbody>
</table>

The saturation vapour curve of iodine is shown in Figure 21. The molecule presents a melting point at 386.85 K (113.7 °C), a boiling point at 457.4 K (184.3 °C); the triple point is at 386.65 K (113°C) and 12.1 kPa, the critical point 819 K, 11.7 MPa. From the saturation curve, it is possible to predict that the iodine, initially in gas form due to the high temperature of the arc, will change into solid or liquid as the temperature of 300K is re-established. Therefore, the iodine molecule in solid state will be deposited on contacts and on moving parts. This deposit can lead to degradation of electrical insulation characteristic of the gas and be corrosive for the materials. A possible solution is to trap the iodine in gas phase using adsorbing techniques before the cooling of the insulating gas.

Figure 21: The saturation vapour curve of iodine molecule [22].
In a further paper, Yokomizu [23] extended the investigation on CO\textsubscript{2}-CF\textsubscript{3}I mixtures at high temperatures identifying electrical and thermal conductivities.

### 3.1.1 Electrical conductivity of CO\textsubscript{2}-CF\textsubscript{3}I mixture

The electrical conductivity of CF\textsubscript{3}I, SF\textsubscript{6} and CO\textsubscript{2} is shown in Figure 22 for a wide range of temperature. From the plot, can be deducted that the curve of CF\textsubscript{3}I is very close to that of SF\textsubscript{6} than to that of CO\textsubscript{2}.

The dependence of the concentration of CF\textsubscript{3}I in CO\textsubscript{2}-CF\textsubscript{3}I mixture on the electrical conductivity plot at 0.1 and 0.5 MPa pressure is very similar as can be seen on Figure 23.

The curves on the Figure 24 show that the use of CO\textsubscript{2}-CF\textsubscript{3}I mixture with CF\textsubscript{3}I concentration above 0.5 permits to achieve similar electrical conductivity as SF\textsubscript{6} gas.

![Figure 22: Electrical conductivity of CF\textsubscript{3}I, SF\textsubscript{6} and CO\textsubscript{2} in a wide range of temperature (0.3-30kK) and at 0.5 MPa pressure [18].](image)

![Figure 23: Electrical conductivity of CO\textsubscript{2}-CF\textsubscript{3}I mixture for various concentration of CF\textsubscript{3}I at 0.1 MPa [18].](image)
3.1.2 Thermal conductivity of CO$_2$-CF$_3$I mixture

The thermal conductivity of CF$_3$I, SF$_6$ and CO$_2$, over a wide range of temperature, is shown in Figure 25. The thermal conductivity of CO$_2$-CF$_3$I mixture for various concentrations of CF$_3$I in the temperature range 300 to 30·10$^3$ K at 0.1 MPa and 0.5 MPa are very similar. The curves reported in Figure 26 were obtained at 0.5 MPa pressure.

The thermal conductivity exhibits different values according to the concentration of CF$_3$I in the mixture below 12000K. This behaviour can be explained by the reactional thermal conductivity at two different concentrations of CF$_3$I, 0.3 and 1, shown in Figure 27 and Figure 28 respectively.
For CF₃I concentration of 0.3, the reactional thermal conductivity around 7000K is due to the dissociation reaction CO ⇌ C +O, while at concentration of 1, the principal dissociation reactions are C₃ ⇌ 3C and CF₅C+2F around 5000K. Therefore, below 10000K, the dissociation reactions are affected by the presence of CO₂.

These data are very useful for calculation of the performance of the gas mixture in CB applications. In order to identify the arc extinguishing capability of the mixture, theoretical calculation were performed on the transient behaviour of the arc burning in CO₂-CF₃I mixture using the previous data [23].

The following assumptions were used in their calculations:

- CO₂-CF₃I mixture flows along the axis direction of the arc, therefore, the arc energy is dissipated through convection mechanism
- this study was focused on circuit breaker closing around zero current, therefore, the instantaneous arc current is less than 100A
- Local Thermodynamic Equilibrium (LTE) is established in the arc
- the distribution of temperature along the arc presents a symmetry along the axis

Using the previous assumptions, the following expression represents a transient arc burning in axial gas flow:
\[ \rho C_p \left( \frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} \right) = \frac{i^2}{g} + \frac{1}{r} \frac{\partial}{\partial r} \left( r k \frac{\partial T}{\partial r} \right) - \frac{1}{l_{arc}} \rho (h - h_{300}) \left[ V_0 \left( 1 - \frac{r}{R} \right)^{\frac{1}{2}} \right] \] (3.1)

where

- \( i \) current
- \( g \) arc conductance
- \( T \) temperature
- \( r \) radial position
- \( \rho \) mass density
- \( h \) enthalpy
- \( h_{300} \) enthalpy at 300K
- \( C_p \) specific heat at constant pressure
- \( l_{arc} \) arc length
- \( v_r \) radial flow velocity
- \( V_0 \) flow velocity at the centre of the arc cross-section
- \( R \) radius of the wall, at constant temperature of 300K

The authors calculated the time variation in the conductance of the residual arc under an axial gas flow under two conditions:

**A) No transient recovery voltage applied after the current is zero**

Under the hypothesis of current to be interrupted with a slope of 0.3 A/\( \mu \)s and no electrical field within the electrodes after the interruption, as show in Figure 29 a) and b). The conductance of the mixture for different CF\(_3\)I concentration values at 0.1 and 0.5 MPa are shown in c) and d) respectively. The two pressure values appear not to affect the conductance curves, therefore, it is suggested to examine only the 0.1 MPa pressure condition. The best performance of interrupting current are achieved for concentrations of CF\(_3\)I above 0.9, otherwise for the values below 0.9 CF\(_3\)I, the performance are slower than the CO\(_2\) curve.

**Figure 29:** Decay in arc conductance in the hypothesis of no electric field applied after the current is zero (free TRV) for different CF\(_3\)I concentrations [18].
B. Electrical field strength is applied after the current is zero

Under the hypothesis of current to be interrupted with a slope of 0.3 A/µs and an electrical field imposed to simulate the transient recovery voltage (TRV) within the electrodes after the interruption, as shown in Figure 30 a) and b). In Figure 30 c), the conductance is plotted under the following conditions, pressure of 0.1 MPa and for 0.3 CF₃I concentration. The current magnitude that is generated by the imposed electrical field is shown in d).

Under an imposed electric field variation in time of 17 V m⁻¹ µs⁻¹ the gas mixture fails to achieve the interruption. For a $dE_{trv}/dt$ equal to 16 V m⁻¹ µs⁻¹ or lower, a successful interruption is achieved.

Further calculations investigated the interruption under 0.1 and 1.0 A/µs slope of interrupting current. Figure 31 shows the critical rate of rise of recovery voltage for 0.1, 0.3 and 1.0 A/µs slope of interrupting current and for various CF₃I concentrations at 0.1 and 0.5 MPa pressure.

As suggested before, the plots at two different pressure conditions are similar, therefore, it was confirmed that thermodynamic and transport properties investigations can be successfully applied only at 0.1 MPa conditions.

With only CF₃I concentration above 0.9, the arc extinguishing capability in CF₃I-CO₂ mixture increases.

![Figure 30: Decay in arc conductance in the hypothesis of applying electric field after the current is zero (trv) for CF₃I concentrations of 0.3 [18].](image)
Figure 31: Critical rate of rise of recovery voltage for different rate of interrupting current and for various CF$_3$I concentrations [18].

Figure 32: Critical rate of rise transient recovery voltage (trv) in the thermal re-ignition region, pressure 0.5 MPa [18].
Global environmental characteristics - Potential green-house effects

The global environmental characteristics of CF$_3$I were investigated for several decades, initially for its use in fire extinguishers [24], and then for plasma etching in the electronic manufacturing process and as a medical sterilizer, as a possible substitute for CFCs and HCFCs and now as an electrical insulating medium.

The most important environmental characteristics that were considered in the literature are:

- Atmospheric lifetime
- Ozone-depletion potential (ODP)
- Global warming potential (GWP)

In the following paragraphs, these environmental characteristics are briefly described.

4.1.1 Atmospheric lifetime

The atmospheric lifetime of a species represents the time required to restore equilibrium following an increase in its concentration in the atmosphere. The substance concentration in the atmosphere may change due to deposition such as to the soil or to the oceans or rivers or to biological systems, and to degradation into other chemicals. A mathematical definition is given by:

$$\tau = \frac{\text{mass}}{\text{removal rate}} = \frac{m}{F_{\text{out}} + L + D} \quad \text{[yr]} \quad (4.1)$$

where:

- $m$ mass [kg]
- $F_{\text{out}}$ flow of substance x out of the box [kg/yr]
- $L$ loss of substance x [kg/yr]
- $D$ deposition of substance x [kg/yr]

In [25] the atmospheric lifetime of CF$_3$I is reported to be extremely short, order of hours to days. This short lifetime is due to easy degradation by solar radiation. In [29] the atmospheric lifetime of CF$_3$I is reported to be 0.005 days.

4.1.2 Ozone-depletion potential (ODP)

Ozone is present naturally in the atmosphere; the peak of its concentration in the atmosphere is in the stratospheric region, 10-16km to 50km of altitude, as shown in Figure 33 [26]. In the stratosphere, the ozone performs a very important role in the absorption of harmful ultraviolet radiation generated by the Sun (UV-B, 280 to 315 nanometre wavelength). Since high exposure to UV-B radiation can lead to an increased risk of skin cancer, cataracts and immune system suppression in humans, the ozone layer in the stratosphere is very important.

![Figure 33: Ozone concentration as function of altitude](image-url)
However, the concentration of several gases has increased in this region due to human activities, in particular halogen source gases. All the gases that can reduce the ozone concentrations in the stratospheric region are called “ozone-depleting substance” (ODS). The halogen gases can be converted to reactive gases containing chlorine and bromine that reacts with ozone and reduce it significantly. Other ODS are fluorine (F) and iodine (I), that are also halogen atoms. Further gases, such as methane (CH4) and nitrous oxide (N2O), can affect the ozone concentration in the stratospheric region. However, the ozone reduction effect is less significant than the reduction due to halogen gases.

The Ozone Depletion Potential is a relative index that expresses the potential to destroy ozone over its lifetime in the atmosphere compared to the effect of CFC-11. Therefore, the ODP of CFC-11 is set to be 1. The ODP of a compound is the ratio of the impact on ozone of a chemical compared to the impact of a similar mass of CFC-11, and it is given by:

\[
ODP_i = \frac{Global \Delta O_3 \text{ due to substance } i}{Global \Delta O_3 \text{ due to CFC-11}}
\] (4.2)

The fluorine and iodine have a small effect in ozone depletion.

**Fluorine**

The gases that contain fluorine undergo conversion in the stratosphere and release fluorine atoms. However, the fluorine content of these gases is left in chemical forms that do not cause ozone depletion [26].

**Iodine**

Iodine can react with ozone and can participate to ozone destruction. However, the gases, that contain iodine, have a very short atmospheric lifetime. Most of iodine gases are destroyed in the troposphere, lower area of the atmosphere than stratosphere and, therefore, do not reach the ozone area.

For this reason, CF3I gas present a small ODP value (from 0.011 to 0.018 dependent on where emissions take place), and this value may lead to control CF3I gas under the Montreal Protocol in the future.

### 4.1.3 Global Warming Potential (GWP)

In [27], “GWP index, based on the time-integrated global mean RF of a pulse emission of 1 kg of some compound (i) relative to that of 1 kg of the reference gas CO2, was developed (IPCC, 1990) and adopted for use in the Kyoto Protocol.” The GWP of component i is defined by:

\[
GWP_i = \frac{\int_0^{TH} RF_i(t) \, dt}{\int_0^{TH} [a_i \cdot C_i(t)] \, dt}
\] (4.3)

where

- \( RF_i \): Radiative forcing (RF) of the element i
- \( RF_r \): Radiative forcing of the reference gas (CO2)
- \( TH \): the time horizon
- \( C_i \): the time-dependent abundance of the element i
- \( C_r \): the time-dependent abundance of the reference element
- \( a_i \): the RF per unit mass increase in atmospheric abundance of component i (radiative efficiency)
- \( a_r \): the RF per unit mass increase in atmospheric abundance of reference component (CO2)
The exact definition of Radiative Forcing is given by IPCC [28] as:

"The radiative forcing of the surface-troposphere system due to the perturbation in or the introduction of an agent (say, a change in greenhouse gas concentrations) is the change in net (down minus up) irradiance (solar plus long-wave; in Wm\(^{-2}\)) at the tropopause AFTER allowing for stratospheric temperatures to readjust to radiative equilibrium, but with surface and tropospheric temperatures and state held fixed at the unperturbed values".

The IPCC explain the definition of radiative force RF in [27].

“Radiative forcing is a measure of how the energy balance of the Earth-atmosphere system is influenced when factors that affect climate are altered. The word radiative arises because these factors change the balance between incoming solar radiation and outgoing infrared radiation within the Earth’s atmosphere. This radiative balance controls the Earth’s surface temperature. The term forcing is used to indicate that Earth’s radiative balance is being pushed away from its normal state.”

The GWP depends on the following factors:
- the absorption of infrared radiation by a given species
- the spectral location of its absorbing wavelengths
- the atmospheric lifetime of the species

The global warming potential for given time horizon, 20, 100 and 500 years, are given in Table 15 for trifluoroiodomethane, sulphur hexafluoride and methane. The carbon dioxide is used as the reference gas.

Table 15: Global Warming Potential for trifluoroiodomethane, sulphur hexafluoride and methane [29].

<table>
<thead>
<tr>
<th>Industrial designation or Common Name</th>
<th>Chemical Formula</th>
<th>Life time [years]</th>
<th>Radiative Efficiency [W m(^{-2}) ppb(^{-1})]</th>
<th>Global Warming Potential for Given Time Horizon [years]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SAR(^4) (100)</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>CO(_2)</td>
<td></td>
<td>1.4x10(^{-5})</td>
<td>1</td>
</tr>
<tr>
<td>Methane</td>
<td>CH(_4)</td>
<td>12</td>
<td>3.7x10(^{-4})</td>
<td>21</td>
</tr>
<tr>
<td>Sulphur hexafluoride</td>
<td>SF(_6)</td>
<td>3200</td>
<td>0.52</td>
<td>23900</td>
</tr>
<tr>
<td>Trifluoroiodomethane</td>
<td>CF(_3)I</td>
<td>0.005</td>
<td>0.23</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

5 Extrinsic properties of the CF$_3$I gas

GIS system design is based on the behaviour of the insulating gas under uniform field and quasi-uniform field conditions. In low divergent fields, important breakdown mechanisms are the streamer formation and the effect of surface roughness. In addition, the non-uniform field needs to be taken into account to determine breakdown levels under particular conditions such as particulate contamination or other defects. In fact, in GIS systems a severe problem is the presence of free conducting particles (FCPs) especially needle-like that can lead to failure in AC conditions. For this reason, it is important to extend the investigation of the CF$_3$I behaviour under contaminated conditions, such as in presence of FCPs, and under non-uniform field conditions.

In [30] Donohoe reviewed the physical breakdown mechanisms and he compared various breakdown criteria with measured breakdown voltages. These equations are referred in many papers that deal with CF$_3$I physical characteristics.

5.1 Electrical breakdown under uniform field

Toyota et al. [31, 32] studied electrical discharge physics in SF$_6$-N$_2$ gas mixture and in CF$_3$I-N$_2$ gas mixture using a steep-front square voltage of 20ns and a peak value of 200kV. The authors used a hemisphere-to-plane electrode, made of stainless steel with a surface mirror finished. The gaps adopted are 10 and 20 mm, with a field utilization factor of 0.89 and 0.78 respectively. The V-t characteristics for the SF$_6$-N$_2$ mixture showed similar performances in the ratio of 100-40% of SF$_6$. The mixture of 60 CF$_3$I and 40% of N$_2$ showed equivalent dielectric strength of pure SF$_6$. Velocities of the discharge developments were calculated from the data recorded, as shown in Table 16.

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
<th>SF$_6$</th>
<th>CF$_3$I</th>
</tr>
</thead>
<tbody>
<tr>
<td>$v$ Velocity of discharge development</td>
<td>[cm/s]</td>
<td>3.9 - 10$^8$</td>
<td>6.5 - 10$^8$</td>
</tr>
<tr>
<td>$p$ pressure</td>
<td>[MPa]</td>
<td>0.1</td>
<td>0.05</td>
</tr>
<tr>
<td>$a = v/pE$ (factor)</td>
<td>[MPa cm$^2$ /s/ kV]</td>
<td>4.1 - 10$^3$</td>
<td>3.5 - 10$^3$</td>
</tr>
<tr>
<td>$d$ gap length</td>
<td>[cm]</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>$V$ peak value of the impulse</td>
<td>[kV]</td>
<td>188</td>
<td>188</td>
</tr>
</tbody>
</table>

The estimates boundaries of V-t characteristics for short time of sparkover are given by

$$t = \frac{d}{v} = \ldots = \frac{pd^2}{aV}$$  \hspace{1cm} (5.1)

The horizontal lowest boundaries are estimated by Schumann’s breakdown criterion:

$$\int_0^d \alpha \cdot dx = k = 10$$  \hspace{1cm} (5.2)
Nakauchi et al. [33] investigated the breakdown characteristics of SF₆ and CF₃I gases under uniform field gap. A hemisphere-to-plane electrode was used. The gap length is 10 mm, with a field utilization factor of 0.89. Under this set-up, several square pulse voltage with a rise time of 16ns and peak voltage from 40 to 200 kV were applied at four hemisphere electrodes presenting different surface roughness: mirror finishing, cast metal, turning machine, cast metal with a hole.

![Figure 34: Estimates boundaries of V-t characteristics and measured values in SF₆ and CF₃I gas at 0.1MPa [31].](image1)

Figure 34: Estimates boundaries of V-t characteristics and measured values in SF₆ and CF₃I gas at 0.1MPa [31].

![Figure 35: Voltage-time characteristics in SF₆ gas (Positive Steep-front square pulse voltage) [33].](image2)

Figure 35: Voltage-time characteristics in SF₆ gas (Positive Steep-front square pulse voltage) [33].

![Figure 36: Voltage-time characteristics in SF₆ gas (Negative Steep-front square pulse voltage) [33].](image3)

Figure 36: Voltage-time characteristics in SF₆ gas (Negative Steep-front square pulse voltage) [33].
The voltage-time characteristics in SF$_6$ gas under positive and negative steep-front square pulse voltages, for four kinds of surfaces, mirror finishing, cast metal, turning machine, and cast metal with a hole hemisphere-to-plane electrodes and at 0.1 MPa of absolute pressure, are similar as shown in Figure 35 and Figure 36.

Further tests using CF$_3$I gas showed the dependence of voltage polarity, since they presented different trends under negative impulse. As shown in Figure 37 and Figure 38 the spark over voltages using cast metal and turning machine electrodes are lower than the other two surface finishing.

The authors identified 1.2 times higher sparkover voltages in CF$_3$I gas than in SF$_6$ gas under uniform field.

![Figure 37](image1.png)  
**Figure 37:** Voltage-time characteristics in CF$_3$I gas (Positive Steep-front square pulse voltage) [33].

![Figure 38](image2.png)  
**Figure 38:** Voltage-time characteristics in CF$_3$I gas (Negative Steep-front square pulse voltage) [33].

### 5.2 Electrical breakdown under non-uniform field

**Steep-Front impulse voltage**

In paper [33], the voltage time characteristics under non-uniform electric field, using a needle-to-plane electrode configuration are presented. The voltage-time characteristics of SF$_6$ and CF$_3$I gases showed that sparkover voltage on SF$_6$ is 1.4 times larger than in CF$_3$I. It is worth highlight that this ratio under uniform field is 1.2.

The results of a second series of tests applying 1.8/450 µs lightning impulse voltages are very close to the results obtained under steep-front impulse voltage, and they are shown in Figure 39.
50 Hz AC voltage

A further study under non-uniform field was analyzed using needle-to-plane gap configuration under AC voltage at power frequency. The $U_{50}$ breakdown voltage investigation was extended to CF$_3$I/CO$_2$ gas mixture plus SF$_6$/N$_2$, CF$_3$I/N$_2$ and gas mixtures.

Figure 39: Voltage breakdown in SF$_6$/N$_2$ and CF$_3$I/N$_2$ mixture gases under steep-front square voltage [33].

Figure 40: Voltage breakdown and corona starting voltage (csv) under AC voltage at power frequency (50 Hz, needle-to-plane gap) for SF$_6$/N$_2$ mixture gas [33].

Figure 41: Voltage breakdown and corona starting voltage (csv) under AC voltage at power frequency (50 Hz, needle-to-plane gap) for CF$_3$I/N$_2$ mixture gas [33].

Figure 42: Voltage breakdown and corona starting voltage (csv) under AC voltage at power frequency (50 Hz, needle-to-plane gap) for CF$_3$I/CO$_2$ mixture gas [33].
Figure 40, Figure 41 and Figure 42 show the voltage breakdown and corona starting voltage (CSV) under AC voltage at power frequency (50 Hz) in needle-to-plane gap configuration for the different mixture gases.

The voltage breakdown in CF$_3$I/N$_2$ and CF$_3$I/CO$_2$ mixture gases show similar values, mainly due to CF$_3$I characteristics; both values are lower than values for SF$_6$/N$_2$ mixture gas. The authors highlighted that the behaviour of the two mixture gases under steep impulse and AC voltage are different. The SF$_6$/N$_2$ mixture gas show similar values under the two conditions, in contrast to the CF$_3$I/N$_2$ mixture gas, where the U$_{50}$ for impulse voltage is lower than that for power frequency voltage. The authors explained the different behaviour of CF$_3$I mixture noting that the corona discharge seems to initiate more easily under power frequency conditions than under the impulse. The following corona stabilisation effect could explain the higher values of U$_{50}$ under AC voltage.

5.3 **Electrical Breakdown under non-uniform field of Air, N$_2$, CO$_2$**

In 2004, Saitoh et al. [34] investigated the breakdown characteristics of rod-plane gaps in air and N$_2$ gases. Some considerations are extended to carbon dioxide (CO$_2$). The authors stated that CO$_2$ is a good alternative for lower voltages, but the gas discharge property are worst than the ones shown by N$_2$.

![Figure 43](image.png)

**Figure 43:** Positive impulse insulation breakdown voltage with a probability of 50% (BDV$_{50}$) and the partial discharge inception with a probability of 50% (PDV$_{50}$) as a function of gas pressure in SF$_6$, air, and N$_2$ (dia. = 5 mm, d = 40 mm) [34].
Figure 44: Breakdown characteristics of SF₆ under rod-plane gap configuration [3].

In paper [35], the electrical breakdown characteristics of CF₃I and CF₃I-N₂ gas mixture are reported.

6 Summary

The physical and chemical properties of CF₃I and its mixture with CO₂ were investigated in this report using a literature review. The good dielectric strength of CF₃I and the environmental friendly characteristics permit to consider this gas as a good replacement of SF₆. However, the use of pure CF₃I gas is not possible due to its boiling point at higher temperature. For instance at 0.2 MPa pressure, the gas becomes liquid at -3 °C. This is a severe limitation, since the insulating gas can change state at a temperature value within common temperature operational range. This limitation can be addressed by mixing the gas with CO₂ which reduces the boiling point, and permits stability of gas state of the mixture within all the normal operational temperature range. As shown in the report the dielectric performance of the gas mixture are lower than the performance of pure CF₃I gas, but still appreciable.

As high voltage insulating media, the gas mixtures with percentage of 70% of CO₂ and 30% of CF₃I presents the best performance with optimal gas phase stability.

The investigations of the adoption of CO₂ - CF₃I mixture for circuit breaker applications present interesting results. The mixture presents high specific heat and high thermal conductivity, and these two properties are the preliminary characteristics for a gas to be adopted in circuit breakers.

The investigations on arc extinguishing capabilities, representatives of high-voltage circuit breakers, show good performance above concentration of 0.9 of CO₂ in the gas mixture. However, the comparison between SF₆ and CO₂ - CF₃I mixture show the better performance of SF₆, such as higher arc extinguished capability.

Another important issue to investigate is the presence of iodine as by-products on the electrode in the arc chamber during current interruption. Several techniques can be adopted to adsorb the iodine and prevent its deposition on the electrode. An example of the stability of the performance with the introduction of carbon absorber is presented in the report. Possible risk of fire due to the presence of the carbon filter should be investigated and compared with other techniques available on nuclear fuel reprocessing literature.

At the moment, other research group in Japan, China and France are investigating the possibility of CF₃I application as SF₆ substitute. However, from the initial literature survey, it appears that it is not possible to maintain the same design adopted for GIS application, and a new design should be adopted.
7 REFERENCES


