A systematic approach to identify and quantify gases for electrical insulation

Author(s): Rabie, Mohamed

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A systematic approach to identify and quantify gases for electrical insulation

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(Dr. sc. ETH Zurich)

presented by

MOHAMED RABIE

Mag. rer. nat., Universität Innsbruck

born on 18.06.1985

citizen of Austria

accepted on the recommendation of

Prof. Dr. Christian M. Franck,
Prof. Dr. Abderrahmane Beroual

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1. Abstract

Equipment for the transmission and distribution of electric power often contains strongly electron attaching compounds to improve the electrical insulation. The most established and widely-used insulation gas sulfur hexafluoride (SF$_6$) is an extremely long-lived and potent greenhouse gas. The environmental concerns related to the globally increasing SF$_6$ emissions initiated a search for replacements. In the past years, chemical and equipment manufacturers introduced novel and promising replacement gases of lower global warming potential, thereby stimulating research efforts towards an SF$_6$-free transmission and distribution grid.

This thesis presents a series of methods that can support the identification of novel synthetic compounds for gaseous insulation and the quantification of their dielectric properties in carrier gases (also: buffer or background gases). Hereby, the well-known concept of a binary gas mixture, which consists of an electronegative compound in a carrier gas, is adopted. The presented methods are based on publicly available and well documented programs.

Within a statistical analysis of a comprehensive data set clear correlations between certain descriptors and the electric strength or the boiling point of gases is found. These descriptors, which are calculated ab-initio by means of density functional theory, are used to computationally screen a large chemical database (the PubChem database of the National Institute of Health) for compounds suitable for electrical insulation. One electronegative sample compound resulting from this screening is octafluoro-2-butene (2-C$_4$F$_8$).

Together with the well-known greenhouse gases SF$_6$ and C$_3$F$_8$, electron attachment to 2-C$_4$F$_8$ molecules is probed as a function of energy in a swarm experiment. For this purpose, minor propor-
tions ($\lesssim 1\%$) of the sample compounds are added to the well-known carrier gases $\text{N}_2$ and $\text{CO}_2$ and the displacement currents of electron swarms are measured within the Pulsed Townsend method. The electron energy distribution in these carrier gases is calculated with a Monte Carlo collision code that has been developed within this thesis. The measured swarm parameters are unfolded from the electron energy distribution to obtain the total electron attachment cross section of the sample compounds. For this purpose, Tikhonov regularization, which is a well-defined algorithm for discrete linear inversion problems, is proposed and used to directly find robust solutions.

Finally, the electric strength in atmospheric gases ($\text{N}_2$, $\text{CO}_2$, $\text{O}_2$, and technical air) is investigated from low to high proportions of the sample gases by means of Monte Carlos simulations and on the basis of the previously obtained attachment cross sections. The range of application in terms of maximum operating voltage and minimum operating temperature of equipment filled with mixtures of $2$-$\text{C}_4\text{F}_8$ and atmospheric gases is estimated.
2. Kurzfassung


In einer statistischen Analyse wurden starke Korrelationen zwischen empirischen Daten für die elektrische Festigkeit sowie dem Siedepunkt von Gasen und bestimmten Deskriptoren festgestellt. Letztere werden aus der Struktur des jeweiligen Moleküls mittels Dichtefunktionaltheorie berechnet. Mit Hilfe dieser Korrelationen werden aus tausenden Verbindungen (der Pubchem Datenbank des National Institute of Health) potentielle elektrische Isolergase identifiziert. Eine aus dieser Suche resultierende Verbindung ist beispiel-
sweise Oktofluoro-2-Buten (2-C₄F₈).


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3. List of own publications

During the work of this thesis several conference and journal publications have been written.

This thesis is based on the following publications:


6. Rabie M and Franck C M 2017 Basic Concepts for the Comparison of Gases for Electrical Insulation submitted to IEEE Transactions on Dielectrics and Electrical Insulation.

The following publications are closely related to the topic but are not included into this thesis:

1. Rabie M and Franck C M 2013 Predicting the electric strength of proposed SF6 replacement gases by means of density functional theory International Symposium on High Voltage Engineering Seoul (South Korea).


4. Rabie M, Häfliger P and Franck C M 2014 Obtaining electron attachment and ionization rates from simultaneous analysis of electron and ion swarms in a pulsed Townsend setup Symposium on the Physics of Ionized Gases Belgrade (Serbia).


C4F8O in different environments *Journal of Physics D: Applied Physics* 49 375201.


4. Introduction

This chapter is based on the submitted article [Rab17a].

Electrical losses associated with the transmission and distribution of electric power are lower at high voltages for the same transmitted power. The upper limit of the system operating voltage is associated with the electrical insulation in space-saving electric power components. In particular on the distribution level, equipment must be compact to be installed in densely populated areas. Equipment manufacturers address the challenges of both the electric and thermal stress onto the components mainly with sophisticated equipment design and special materials including solid, liquid, gaseous and vacuum insulation. In principle, all types of insulation media can achieve elevated voltage and current ratings of equipment, along with compound-specific trade-offs such as the equipment weight, outer dimensions, durability, flexibility, safety, maintenance effort, production costs, or environmental issues. However, the choice of the actual insulation medium is also influenced by historical developments, political instruments and social factors.

4.1. Liquid, solid and vacuum technology

Solid insulated systems exist up to medium voltage applications. In high voltage equipment, solids often provide mechanical support of electrical devices such as conductors. Solid materials, when used as primary insulation in large equipment, dissipate the heat from high current-densities carrying inner regions less effectively than liquids and gases due to the absence of convective cooling. Partial dis-
charges, as localized discharges resulting from transient gaseous ionization, can irreversibly damage solids, whereas they are less critical in liquids and gases. The likelihood of partial discharges is proportional to the quantity of the installed material and strongly depends on manufacturing standards. Furthermore, solid insulation in the close vicinity of moving parts is technically challenging and there is a longer lead time in the manufacturing process to respond to changes in system dimensions or geometry. Liquids have been used in circuit breakers in the past, and today are mainly used in transformers and partially in medium voltage switchgear. Major disadvantages of oil are flammability hazards, its ecological impact and the deterioration of the insulation performance with increase of moisture. However, synthetic esters can reduce in particular the ecological and flammability risks in comparison to oil. The weight of liquid and solid insulated equipment scales approximately cubically with increasing dimensions, whereas in gas (or vacuum) insulated equipment only a small (or no) fraction of the total weight is due to the insulation medium. Vacuum is solely used in vacuum interrupters for switching loads and breaking fault currents [Mat06, Sla07]. Vacuum circuit breakers hold a dominant market share in distribution systems and solutions up to lower transmission voltage levels exist to date [Yan06, Sme14a]. In contrast to gases, the breakdown voltage in vacuum increases less than linearly with the insulation distance. As a consequence, for elevated voltage ratings the production costs for vacuum breakers might be higher than for SF$_6$ breakers, since larger gaps or multiple vacuum breaks are required. A drawback of vacuum breakers with respect to nominal current ratings is that the one-dimensional heat transfer along the current-carrying conductor is the only efficient cooling process due to the absence of convection [Sme14a].
4.2. Applications of dielectric gases

Most applications of dielectric gases other than air aim to avoid or control discharges in compact apparatuses. The use of dielectric gases as insulator in medium and high voltage equipment has many advantages such as relatively low weight, low costs, simple manufacturing process of equipment, full recovery of insulation performance after partial discharge and the ability of insulating moving parts. In transformers, gas insulated transmission lines (GIL) and bushings the dielectric gas solely serves as an electrical insulator, whereas in high voltage circuit breakers of air-insulated switchgear or substations (AIS), medium and high voltage gas insulated switchgear (GIS) the gas must comply with both electric insulation and - if no vacuum interrupters are used - current interruption. The most important application of dielectric gases are GIS, which can be installed in densely populated areas and therefore support network topologies with lower power losses leading to considerable environmental advantages over the use of open AIS, as shown in several life cycle assessment studies [Pre01, Neu04]. SF$_6$ has been the electrical industry’s favored insulation and arc quenching medium for half a century [Sme14b, See14]. Only in very cold regions, SF$_6$ might be mixed with nitrogen N$_2$ or tetrafluoromethane CF$_4$ to reduce the liquefaction temperature of the gas. GILs, typically filled with 20% of SF$_6$ in nitrogen, can be an alternative to cables, if the installation of overhead transmission lines is challenging due to space limitations or lack of public acceptance [Tru71, Hil00, Koc11]. In radar systems of military reconnaissance planes, including the Airborne Warning And Control System (AWACS), SF$_6$ operates as an electrical insulating medium in the hollow conductors of the antenna [IPC06]. In particle accelerators, e.g. in the waveguide of linear accelerators for medical radiotherapy, SF$_6$ is used to prevent sparking and provide cooling for the dielectric load [Gre97]. In Resistive Plate Chambers (RPC), which are e.g. used as particle detectors in all large experiments of the Large Hadron Collider (LHC) [San81], SF$_6$ is used
very diluted (≤ 1%) due to its strong (desired) quenching effect on streamer discharges [Abb12].

After being classified as one of the greenhouse gases in the Kyoto protocol, regulative measures for the SF₆ usage have been implemented in various industries. The electrical industry, military applications and research have been excluded from any SF₆ ban so far. In the short term, emissions have been reduced by voluntary commitments of the electrical industry by minimizing the use and leakage rates from electrical equipment, improving gas handling and recycling concepts [VDN05, EPA15b]. In the long term, gradually reducing the quantities of greenhouse gases that can be placed on the market has been identified as the most effective way of reducing emissions from refrigerant applications [EU14]. For a phase-out of SF₆ from electrical power equipment, a replacement gas with acceptable environmental impact would be beneficial. Manufacturers have presented apparatuses using gases or gas mixtures with much lower global warming potential (GWP) over the last years [Uch04, Teh15, Hyr15, Kie16b, Pre16a]. The overall performance of these alternatives come very close to the one of SF₆, although some trade-offs such as larger equipment size, higher filling pressures, slightly thicker walls of vessels or higher minimum operating temperatures are necessary [See16].
5. Brief history of gaseous insulation

This chapter is based on the submitted article [Rab17a].

In the very early beginnings of gaseous dielectrics, the focus has been on compounds other than SF$_6$. In pioneering experiments that he reported to the Royal Academy of Sciences of the Austro-Hungarian Empire in 1889, K. Natterer first noticed the high electric strength of some substances, such as CCl$_4$, CHCl$_3$ or SiCl$_4$, relative to that of air or nitrogen [Nat89]. He applied high-voltage pulses generated by an induction coil to the vapor of more than 50 different substances. There is no evidence that Natterer’s discoveries aimed on technological advances by potentially using gases of high electric strength in electrical equipment. Only decades later, the usefulness of these compounds as electrical insulation media were recognized in the United States. In the early 1930s, R.G. Herb noticed that the maximum obtainable voltage of a pressurized-air insulated Van de Graaff generator is significantly increased by using CCl$_4$ [Rod37]. Moreover, he found together with M.T. Rodine that when adding CCl$_4$ to air the electric strength rises more rapidly in the region of low CCl$_4$-concentration than at high concentrations. This effect, known as *synergism*, is generally a quality criteria also for the last generation of insulation gases (see chapter 7).

In the same years, E. E. Charlton and F. S. Cooper found that halocarbons generally have higher electric strength than nitrogen [Cha37], and in particular proposed CCl$_2$F$_2$, also known as the refrigerant CFC-12, which is non-toxic, non-corrosive and chemically stable, for the use in high voltage transformers [Coo37]. Fifty years
Figure 5.1.: Timeline regarding substances used for electrical insulation and crucial events concerning the use and the development of insulation gases.

later the phase-out of CFC-12 was decided within the Montreal Protocol due its role in ozone depletion. Furthermore, E. E. Charlton and F. S. Cooper investigated tetrafluoromethane CF$_4$, which is used until today in admixture with SF$_6$ in polar regions.

Besides highly chlorinated compounds, K. Natterer run into another gas of high electric strength containing the cyano (-CN) functional group, namely cyanogen (C$_2$N$_2$). The electric strength of this toxic inorganic compound, was determined with more accurate experimental methods to be around 2 times the one of nitrogen [McC54]. With some detours over straight-chain nitriles, such as CF$_3$CN, C$_2$F$_5$CN or C$_3$F$_7$CN [Plu62, Dev80], that have toxicities higher than would be considered acceptable for insulation purposes, the (-CN) group recently reappeared in the branched nitrile (CF$_3$)$_2$CFCN (or C$_4$F$_7$N), which is a last generation insulation gas of “acceptable toxicity“ [Owe16].

Shortly after being patented as gaseous fire extinguishing substance [KK28], SF$_6$ was for the first time patented as an insulation medium by F. S. Cooper from the American producer General Elec-
tric [Coo38] and as an arc quenching media by V. Grosse from the German producer AEG in 1938 [Gro38]. In his patent, V. Grosse already explained that its exceptional ability of quenching arcs is due to its high heat capacity and its dissociation during arcing and the subsequent recombination of the dissociation products.

In the 1930-40s dielectric properties of various potential insulation gases including SF$_6$ were experimentally determined [Rod37, Cha37, Coo37, Pol39, Tru41, Ski42, Hoc42]. It has been speculated upon the reasons for their relatively high electric strength that crucial factors are the large molecular weight, complexity and electron affinity, since they affect the interaction between free electrons and gas molecules. More elementary studies by F. M. Penning pointed out that the development of an electron avalanche is suppressed in gases of small first Townsend coefficient (nowadays known as effective ionization coefficient), which quantifies the electron multiplication in an electron avalanche by electron impact [Pen38]. The picture of an electron avalanche as the source of the electric breakdown led H. Raether, J. M. Meek and L. B. Loeb to identify the first Townsend coefficient as the principal controlling factor in the breakdown voltage of a gap in given geometrical conditions and particularly at high pressures [Rae39, Mee40, Loe41]. Small Townsend coefficients should consequently result in relatively high breakdown voltages. Exactly this was experimentally observed in SF$_6$ and other halogenated gases by B. Hochberg and E. Sandberg [Hoc42]. They further speculated that the small Townsend coefficient for halogenated gases resulted from the inefficient production of new electrons by impact ionization or from the higher electron energy losses in inelastic non-ionizing collisions with these rather complex molecules in comparison to oxygen or nitrogen. However, other complex molecules such as hydrocarbons did not show such a high electric strength. It was not until the 1950s, supported by mass spectrometer studies [Kus37, Dib48], that the halogenated molecule’s ability to effectively attach free electrons has become generally recognized to be responsible for the small first Townsend coefficient and the high
electric strength of halogenated gases [War50, War53]. It was found that negative ions are created by the two-body process of dissociative attachment such as in CCl₄, SF₆ [War53, Ahe53] and Trifluoriodomethane CF₃I [McC54], or by the three-body process of electron attachment where a dissociation process does not occur [Blo35], such as in SF₆ [Ahe53].

From all halogenated substances, SF₆ turned out to be the best insulation gas in terms of stability, toxicity and liquefaction temperature, although other gases revealed higher electric strengths. The industrial production of SF₆ began in the 1950s with the first commercial SF₆ circuit breakers in the United States [Mai98]. With the market introduction of GIS in the late 1960s in Europe, companies began the move away from oil towards SF₆, and the use of SF₆ as an arc quenching and insulation medium became widespread. On the transmission level, AIS were more and more replaced by GIS. Also on the distribution level AIS have been gradually replaced by GIS, the latter being more compact, reliable and safe in operation.

In the late 1970s/early 1980s, a search for alternative gases superior to SF₆ was initiated by Westinghouse Electric Corporation [Woo82], General Electric [Dev80] and Oak Ridge National Laboratory [Chr78]. The goal of the systematic investigation was to find a gas or gas mixture that has lower production costs, lower boiling point, and an electric strength that is higher and less sensitive to surface roughness and particles. Ozone-depleting substances such as CFC-12 as well as strong greenhouse gases such as perfluorocarbons (PFCs) [Chr88] or CF₃SF₅ with a GWP (100-year) of 17400 [Sto13] were considered. Even though compounds were not selected with respect to their environmental impact, no gas that would result in technical and economic advantages to the electrical industry could be identified.

In the late 1980s, environmental concerns related to anthropogenetic emissions of halogenated compounds arose for the first time with the discovery of large losses of total ozone in the Antarctic ozone layer [Far85]. This led to the formation of the Montreal Pro-
tocol which resulted in the phase-out of chlorofluorocarbons (CFCs) and later hydrochlorofluorocarbons (HCFCs), which were used at the time as refrigerants, blowing agents and aerosols. The healing of the Antarctic ozone layer due to emission reductions of CFCs has meanwhile been proven [Sol16]. The electrical industry was not affected by political measures or bans since SF$_6$ is not ozone-depleting. However, the classification of SF$_6$ as a greenhouse gas by the United Nations Framework Convention on Climate Change in 1992 and later by the Kyoto Protocol affected also the use of SF$_6$. As a consequence, policy makers and environmental agencies increasingly expressed concern about the climate impact of this extremely strong greenhouse gas. This initiated new attempts to replace SF$_6$ by alternatives with lower global warming potential [Chr97, Nie98a]. In 1999, the United states environmental protection agency (EPA) initiated the “SF$_6$ Emission Reduction Partnership for Electric Power Systems” based on a voluntary partnership with the members of the U.S. electric power industry [EPA15b] and in 2009 classified SF$_6$ as “a threat to the health and welfare of current and future generations due to their effects on world climate” under section 202(a) of the Clean Air Act. In 2006 the EU Regulation No. 842/2006 [EU06] was put into force by the European Parliament and the Council, replaced in 2014 by the EU Regulation No. 517/2014 [EU14]. This regulation makes, among other things, provision to the European commission for an assessment of SF$_6$ replacements in new medium voltage secondary switchgear no later than 2020 and for other applications, including high voltage equipment, no later than 2022. In 2012, the Australian government applied an equivalent carbon tax on synthetic greenhouse gases including SF$_6$, which was repealed in 2014 [Gov14].

In parallel to the increasing number of regulative measures, the resumption of research activities in SF$_6$ replacements resulted in the development of equipment filled with the atmospheric gases CO$_2$, N$_2$ and O$_2$ [Uch04, Pre16a] and mixtures of these gases with synthetic compounds [Teh15, Hyr15, Kie16b]. In particular, the branched flu-
orinated nitrile $\text{C}_4\text{F}_7\text{N}$ [Nov15a] and the fluorinated ketone $\text{C}_5\text{F}_{10}\text{O}$ [Nov15b] are added in relatively small concentrations to atmospheric gases, achieving - at the same filling pressure - dielectric properties close to those of $\text{SF}_6$. These synthetic compounds are characterized by significantly reduced atmospheric lifetimes compared to $\text{SF}_6$. 
6. Climate impact of SF$_6$

This chapter is based on the submitted article [Rab17a].

Anthropogenic emissions of extremely long-lived and potent greenhouse gases might irreversibly change the climate on millennium timescales [Mon11, Sto13]. SF$_6$ has an atmospheric lifetime of 3200 years [Sto13]. Its main removal process is via photo-dissociation by UV radiation in the stratosphere. Ocean invasion, land uptake or other SF$_6$ sinks are at least one order of magnitude smaller [Ko93]. The ability of absorbing the upward atmospheric radiance strongly depends on the spectral positions of a molecule’s infrared bands within the upward atmospheric radiance spectra at the tropopause [Pin95, Wal10]. SF$_6$ has a very pronounced absorption band exactly at an infrared frequency where the earth’s atmosphere is relatively transparent and therefore absorbs upward radiance 42000 times more effectively than CO$_2$. Correspondingly, SF$_6$ has a huge radiative efficiency $RE$ (given in table 8.1), which is defined as the change in net radiation at the tropopause caused by a given change in greenhouse gas concentration or mass and has units of Wm$^{-2}$ppb$^{-1}$ [Sol07]. The GWP of SF$_6$ calculated over a time horizon of 100 years is 23500 [Sto13].

6.1. SF$_6$ abundance and climate response

Pre-industrial atmospheric SF$_6$ abundance has been less than 6.4 ppq (parts per quadrillion) as known from measurements of air trapped in Antarctic firn [Vol02]. Today, SF$_6$ abundance is three orders of magnitude higher. This is known with high precision due to
sampling programs that measure background atmospheric concentrations of SF\textsubscript{6} and other trace species using gas chromatographs, see figure 6.1(a). The NOAA/ESRL (National Oceanic and atmospheric administration/Earth System Research Laboratory) program combines data from an in situ program and a flask system of archived air samples from 13 locations since 1995 [NOA14]. The AGAGE (Advanced Global Atmospheric Gases Experiment) in situ measurement program started in 2001 and collects data at 7 locations at this date [Pri00]. Rigby et al. extended the AGAGE measurements for SF\textsubscript{6} with archived air samples back to 1973 [Rig10]. For the period 1953-1995, before the NOAA/ESRL program started, the CDIAC data [Bul15] are shown in figure 6.1(a), in which the industrial production and release estimates from Maiss et al. [Mai98] are scaled to match the SF\textsubscript{6} abundance measured by the NOAA/ESRL in 1995. Globally, SF\textsubscript{6} concentrations increase equally for all stations over the northern and southern hemisphere. Data from the NOAA/ESRL and AGAGE network generally agree very well with a mean bias of around 0.02 ppt [Rig10].

The equilibrium global mean surface temperature response \( \Delta T = \lambda \cdot RF \) due to the radiative forcing of SF\textsubscript{6} (\( RF = RE \cdot [SF_6] \)) is shown in figure 6.1(b), with the equilibrium climate sensitivity parameter being \( \lambda = (1.5^\circ C - 4.5^\circ C) / 3.7 \text{ Wm}^{-2} \) [Sto13]. The transient temperature rise might be - in comparison to the equilibrium temperature response - time-delayed by the heat capacity of the earth climate system and the timescale for heat transport into the deep ocean [Ko93, Sto13]. The current equilibrium warming due to SF\textsubscript{6} is 0.004°C, with a clear tendency to increase.

6.2. SF\textsubscript{6} emissions: top-down versus bottom-up estimates

The accumulation of SF\textsubscript{6} in the troposphere is a direct measure of its global emissions, since SF\textsubscript{6} is a long-lived compound and uniformly distributed throughout the troposphere with mixing times
Figure 6.1.: (a) Mean global atmospheric SF$_6$ abundance in parts-per-trillion (ppt) derived from indicated locations of the measurement stations from the NOAA/ESRL Global Monitoring Division [NOA14] and the AGAGE [Pri00]. The CDIAC data [Bul15] is also shown. The shading represents 1-sigma uncertainties. (b) Equilibrium warming due to SF$_6$ radiative forcing using the SF$_6$ concentrations from CDIAC and the climate sensitivity parameters 1.5 °C/3.7 Wm$^{-2}$ (lower bound) and 4.5 °C/3.7 Wm$^{-2}$ (upper bound) [Sto13].
in the order of one year [Pat09, Lev10]. Emissions obtained from atmospheric measurements are referred to as top-down emissions. Top-down methods for calculating the SF$_6$ emissions on regional scales, e.g. on the country level, require precise atmospheric measurements and reliable atmospheric transport models [San03, Pat09, Rig10, Rig11, Gan14, Fan14]. In this case, it is possible to geographically resolve the sites of emission sources, such as manufacturing sites of SF$_6$-filled equipment or densely populated regions [San03, Pat09, Rig11, Gan14], as has been shown e.g. for New York City [San03].

Bottom-up emission estimates are either based on reported emissions, e.g. by Annex-1 countries to the United Nations Framework Convention on Climate Change (UNFCCC), or based on inventories such as the Emissions Database for Global Atmospheric Research (EDGAR) [EC10], where emissions are calculated based on production, sales and usage information. At this date, detailed documentation describing the methods of obtaining the SF$_6$ data in EDGARv4.2 [EC10] and its uncertainties are not published. The extent to which top-down estimates are used for EDGAR is not entirely clear, even though EDGAR is supposed to be independent from published top-down data. For EDGARv4.0 emission data, an uncertainty of about 10% for the period 1970-1995, increasing to 15% at 2005 has been estimated by Rigby et al. [Rig10].

Top-down methods provide a way to validate bottom-up emissions estimates. A comprehensive picture of global and regional SF$_6$ emissions should therefore consist of both estimation methods [Hog10]. Figure 6.2(a) shows that top-down global emissions are in agreement with the bottom-up estimates from EDGARv4.2 but significantly exceed reported emissions to UNFCCC. In addition, top-down global emissions have increased over the last decades, whereas reported emissions have decreased. Whereas in the US and the EU total reported emission have decreased over the last years (as shown in figure 6.2(b)), there has been a strong emission increase in China after the year 2000, mainly due to the increasing number of SF$_6$-
filled distribution and transmission equipment for China’s growing energy demand [Fan13]. However, the discrepancy cannot be explained solely by the increasing emissions from non-reporting parties according to various studies and higher emissions than reported by countries are suggested [Har02, Lev10, Rig10].

At this date, reliable top-down data for longer time spans are missing in most national greenhouse gas inventories, except for the United Kingdom [UK13] and Switzerland [BAF15]. Both countries aim to verify their SF$_6$ inventories with continuous measurements at Mace Head (in Ireland) and the high-Alpine site of Jungfraujoch (in Switzerland), respectively. Reported SF$_6$ emissions from these countries show relatively good agreement (within the uncertainties) to the top-down emissions as shown in figure 6.3. Following the model of the UK and Switzerland of tracing down the SF$_6$ emission sources on a country level to find consistency between top-down and bottom-up estimates would be beneficial for climate policy decisions. This could be achieved with a denser network of atmospheric measurement stations in combination with more precise atmospheric transport models [Lev10].

6.3. SF$_6$ emissions from the electrical industry

Since the 1970s to date, the electrical industry is globally the main consumer of SF$_6$ and the largest contributor to (reported) SF$_6$ emissions of all industries [Nie92, Mai98, Oli01, Rig10, Lev10, Sto13], see also figure 6.2(a). The total mass of banked SF$_6$ worldwide in electrical equipment is increasing and is in the order of magnitude of $\sim 10^5$ tons [Nie98b, Rhi10]. The fourth IPCC assessment reported that “approximately 80% of SF$_6$ sales go to power utilities and electrical equipment manufacturers“ [Sim07]. Besides the electrical industry, significant SF$_6$ emissions occur from the magnesium, aluminium or semiconductor production, particle accelerators and military applications. In the EU, SF$_6$ usage in car tires and soundproof windows has been banned and a phase-out for magnesium pro-
Figure 6.2.: Comparison of annual SF$_6$ emissions from top-down and bottom-up estimates. Shading and error bars, representing 1-sigma uncertainties. (a) Global emissions. A: top-down [Rig14]. B and C: EDGARv4.2 for electrical industry and all sectors [EC10]. D and E: total reported for all categories and for electrical equipment (2.F.8) from Annex-1 parties. (b) EU, US and China. A-D: total reported from all sectors as well as for electrical equipment (2.F.8) from EU and US. E-G: China total emissions from EDGARv4.2 [EC10], bottom-up [Fan13] and top-down estimates [Fan14].
Figure 6.3.: SF$_6$ emissions reported to UNFCCC and estimates for Switzerland from measurements at Jungfraujoch [BAF15] and for the United Kingdom from measurements at Mace Head (Ireland) [UK13]. Shading and error bars, representing 1-sigma uncertainties.
duction has been decided by the EU commission [EU14]. Reported global SF₆ emissions from the electrical industry decreased in the recorded period 1990-2012 due to initiated emissions-reducing measures. However, since other industries also implemented emissions-reducing measures, the relative contribution of the electrical industry to SF₆ emissions did not show a clear tendency to decrease and the total emissions from Annex I parties vary between ∼ 40 – 60% in reporting countries within the recorded period.

On the regional level, the relative contribution to SF₆ emissions from the electrical industry can vary strongly between countries. In the period 1990-2012, SF₆ emissions reported from the electrical equipment sector are ∼ 20 – 30% in the EU and ∼ 70 – 80% in the US of total SF₆ emissions, see figure 6.2(b). SF₆ emissions from the US, reported under EPA’s greenhouse gas reporting program, show that in the year (2012) studied by Ottinger et al. [Ott15] consumption based on reports from users accounted for only 59% of the consumption based on reports from suppliers. Ottinger et al. consider particle accelerators and medium-voltage electrical equipment as possible sources for this discrepancy, whereas emissions from military applications were classified as being not responsible since they are included in the US inventory. In those countries that try to verify their national SF₆ inventories with top-down emissions (at this date the UK and Switzerland, see figure 6.3), the relative contribution of the reported emissions from the electrical industry to total reported SF₆ emissions was ∼ 16% (Switzerland) and ∼ 70% (UK) at the last year of the inventory 2012. In China, the electrical equipment sector is estimated to be responsible for ∼ 70% of total SF₆ emissions [Fan13], even though China is the world’s largest magnesium producer and exporter and China’s magnesium production sector is larger than in Europe or in the US.

In open applications SF₆ is emitted directly without delay. For example, SF₆ is used in aluminium and magnesium foundries in the cleaning process as inert gas to fill casting forms. The fraction of SF₆ destroyed or transformed in this process is not well-known, as
can be concluded e.g. from the national inventories of Switzerland and Germany: the Swiss inventory assumes that the total amount of used SF$_6$ quantity is emitted [BAF15], whereas the German inventory assumes (based on confidential measurement records) that in aluminium foundries SF$_6$ predominantly decomposes and only 1.5% of the used SF$_6$ is emitted [UBA16]. Most emissions from AWACS planes occur during the pressure-balancing process. When the plane ascends, SF$_6$ is directly released to the atmosphere to maintain the desired pressure difference between the system and the outside air. When the plane descends, SF$_6$ is filled into the system from an SF$_6$ container on board. Emissions from system leakage can also occur during other phases of flight or during time on the ground. The IPCC provides an annual emission estimate of 740(±100) kg SF$_6$ per plane [IPC06]. With the number of planes worldwide in the order of hundred, this would yield annual SF$_6$ emissions in the order of hundred(s) tonnes. In the United Kingdom, SF$_6$ emissions from AWACS, particle accelerators and tracer testing was estimated to 15% [Ott15].

In contrast to open applications, in electric power equipment SF$_6$ is closed and banked up to \(\sim 40\) years until the end-of-life and only a fraction of the banked SF$_6$ is emitted during this time span. The actual amount of emitted SF$_6$ strongly depends on emission-reducing measures taken during production and testing of equipment, installation, use phase, disposal at the end-of-file and recycling and destruction of the SF$_6$ gas. Reducing SF$_6$ emissions during the equipment’s life cycle has been the strategy adopted by many established manufacturers after the climate impact of SF$_6$ became relevant [Dul15]. Therefore, emissions per GIS unit have decreased in the recent past.

- **SF$_6$ production**: emissions during production of the gas quantity necessary to fill an electrical apparatus are part of its environmental footprint. The IPCC estimates an emission factor of 0.2% (total emissions during the manufacturing process divided by the total quantity of produced SF$_6$) for applications
that do not require highly purified SF$_6$ gas (e.g., electrical equipment) and a factor of 8% for applications that require highly purified SF$_6$ gas (e.g., semiconductor manufacturing) [IPC06]. For Germany, an emission factor of 0.5% has been reported for the production of SF$_6$ that is subsequently used in electrical equipment [Alt07]. For China, emission factors during SF$_6$ production of $1.71 - 3.25\%$ have been estimated [Fan13].

- **Equipment production**: the major manufacturers of electrical equipment are located in Asia and Europe [Mai98]. During the production of equipment, SF$_6$ emissions depend on the production process, in particular whether SF$_6$ or e.g. helium is used for the tightness tests [Dul15], or whether SF$_6$ is used to fill up micro-cavities in the resin insulation of instrument transformers or bushings [IPC06]. The IPCC suggests for the production of medium voltage equipment emission factors (total emissions during the manufacturing process divided by the total quantity of SF$_6$ contained in electrical equipment) of 7% and 29% for Europe and Japan, respectively, and for high voltage equipment emission factors of 8.5% and 29% [IPC06].

- **Use phase**: during the use phase of equipment, SF$_6$ might be emitted due to major failure/arc faults, due to maintenance losses and gas handling mistakes as well as due to natural leakage e.g. through sealings. SF$_6$ leakage rates vary strongly with the equipment’s type, e.g. whether the pressure systems are *closed* or *sealed*. Sealed gas volumes (often medium voltage GIS) do not need to be re-filled, whereas closed gas volumes (mostly high voltage GIS) need to be regularly re-filled during the operating life. The IEC (International Electrotechnical Commission) standard 62271-203 limits the maximum annual leakage rate of SF$_6$ to 0.5% for closed pressure systems, such as high voltage GIS. Most medium voltage GIS are sealed pressure systems with annual leakage rates of $< 0.1\%$. 

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In contrast to the IEC standard, the IPCC suggests in its “Guidelines for National Greenhouse Gas Inventories (2006)“ emission factors (total annual emissions divided by the total quantity of SF\textsubscript{6} contained in electrical equipment including leakage, major failures/arc faults, maintenance losses) of 0.2% and 0.7% for medium voltage GIS for Europe and Japan, respectively, and values of 2.6%, 0.7% and 14% for high voltage GIS in Europe, Japan and in the US, respectively [IPC06]. These values might be outdated, since e.g. in the US, emission factors within EPA’s Emission Reduction Partnership have decreased from 14% in 1999 to 2% in 2013 [EPA15b]. New equipment typically complies with the IEC standard and leakage rates are often far below 0.5% during testing. However, after about 20 years in operation, SF\textsubscript{6} leakage rates from high voltage GIS start increasing drastically with time. The average leakage rates can exceed 2% after 30 years in operation, due to corrosion of flanges and deterioration of sealings [Kaw08, Dul15]. Whether electrical equipment produced today will show a similar increase of emission rates with time cannot yet be answered. Moreover, the measurement of small leakage rates under realistic conditions is challenging [Gra11]. For the installed high voltage equipment in China’s network, a relatively low averaged annual leakage of 0.08% and an annual maintenance/disposal emission factor of 4.3% have been given [Fan13], which result in good agreement of bottom-up with top-down estimates [Fan14], see figure 6.2(b).

- \textit{Disposal phase}: countries where the SF\textsubscript{6} gas-collection infrastructure is well-developed, emissions have been significantly reduced. Currently, in Europe reclaiming and reuse of SF\textsubscript{6} from electrical equipment is widely implemented [Cig03, VDN05], whereas there is almost no recovery of SF\textsubscript{6} in e.g. China [Fan13].

On the one side, the quantity of banked SF\textsubscript{6} in electrical equip-
ment ($M_{\text{banked}}$) is large and the irreversibility of SF$_6$ emissions is well-known. On the other side, leakage rates from electrical equipment are relatively small as discussed above. Therefore, the questions arise: what is the climate impact related to such a quantity of banked SF$_6$ assuming a mean global annual emission rate that is realistic ($\gamma \sim 1\%$), optimistic ($\gamma \sim 0.1\%$) or pessimistic ($\gamma \sim 10\%$)? And how much can a reduction in $\gamma$ decrease the SF$_6$ abundance in the atmosphere on a long-term? In this case, an assessment within typical time horizons (e.g. until 2100, see section 6.4) is incomplete, due to the much larger timescales of the SF$_6$ source and sink terms: firstly, an annual leakage rate of e.g. 1% from equipment corresponds to the entire release of the banked SF$_6$ quantity within 100 years (if equipment is regularly re-filled as it is normally the case). Secondly, the degradation of SF$_6$ in the atmosphere occurs on millennium timescales (the atmospheric lifetime of SF$_6$ is $\tau = 3200$ years). Figure 6.4 illustrates this situation and shows the steady-state quantities for times $t \gg \tau$: total mass of atmospheric SF$_6$ ($M_{\text{atm}}$), SF$_6$ concentration and global mean surface warming due to SF$_6$ (see section 6.1). When the steady-state is reached, the rates of the two competing processes - leakage versus photolysis - are equal: $\gamma M_{\text{banked}} = \tau^{-1} M_{\text{banked}}$. In this simplified mass-balance expression ($M_{\text{banked}} = \text{const.}$, atmospheric transport models are neglected) the total mass of atmospheric SF$_6$ in the steady-state is given by $M_{\text{atm}} = \gamma \tau M_{\text{banked}}$. The resulting concentrations and temperature rises due to SF$_6$ are shown in the figure. Depending on the quantity of banked SF$_6$ and leakage rates, SF$_6$ emissions from electrical equipment increase the temperature of the earth climate system up to $\sim 0.5$°C in the long-term. For comparison, between the early Holocene (5,000 to 10,000 years ago) and the Little Ice Age, about 200 years ago, global temperature decreased by 0.7°C [Mar13].
Figure 6.4.: Estimated global mean surface warming in steady-state (after thousands of years) only due to SF$_6$ emissions from the electrical industry. The details are described in the text.
Table 6.1.: SF$_6$ emissions, abundance and equilibrium temperature rise due to SF$_6$ radiative forcing for the best (RCP2.6) and worst (A2) emission scenario.

<table>
<thead>
<tr>
<th>year</th>
<th>emissions (Gg/yr)</th>
<th>abundance (ppt)</th>
<th>$\Delta T$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2030</td>
<td>2-12</td>
<td>10-15</td>
<td>5-7</td>
</tr>
<tr>
<td>2050</td>
<td>11-26</td>
<td>1-16</td>
<td>5-12</td>
</tr>
<tr>
<td>2100</td>
<td>11-65</td>
<td>0-25</td>
<td>5-30</td>
</tr>
</tbody>
</table>

6.4. SF$_6$ emissions scenarios

The Fifth Assessment Report of the IPCC gives the values of the SF$_6$ abundance (table AII 4.4 in [Sto13]) for the Representative Concentration Pathway (RCP) emission scenarios [Sto13], and the SRES scenarios (Special Report on Emissions Scenarios) A2 and B1 [Nak00]. Figure 6.5(a), (b) and (c) show the SF$_6$ emission, abundance and the equilibrium global mean surface temperature response for these scenarios. Table 6.1 summarizes the projections to 2030, 2050 and 2100 for the RCP and SRES scenarios. In 2100 the projected SF$_6$ abundance will be 11.4 ppt (RCP2.6), 22.3 ppt (RCP4.5), 41.0 ppt (RCP6.0), 50.5 ppt (RCP8.5), 35 ppt (B1) and 65 ppt (A2). The A2 scenario assumes a continuously increasing population and regionally oriented economic development, and would yield a global mean surface warming of $\sim 0.03$ °C due to SF$_6$ in 2100. In view of the Paris Agreement within the UNFCCC of keeping the increase in global average temperature to well below 2 °C, under the A2 scenario a SF$_6$ emission cut today could contribute 1.5% of this goal.

6.5. Climate policy regarding SF$_6$

Some important regulative measures concerning SF$_6$ usage have been mentioned already in chapter 5. The relatively small con-
Figure 6.5.: Scenarios given in the Fifth Assessment Report of the IPCC [Sto13] for (a) emissions and (b) abundances of SF₆. (c) Calculated equilibrium temperature response due to radiative forcing of SF₆ for the same scenarios. Shading, representing the climate sensitivity parameters 1.5°C/3.7 Wm⁻² and 4.5°C/3.7 Wm⁻² [Sto13] for the best and worst case respectively.
tribution of SF$_6$ emissions to global warming or the disproportionate high abatement costs are often emphasized, predominantly by manufacturers and system operators and investment into reducing CO$_2$ emissions should be of primary interest [O’c02, Sol03, ZVE13]. Even though substantial cuts in CO$_2$ emissions are essential to reduce global warming, cuts in non-CO$_2$ greenhouse gas emissions would be a relatively quick way of contributing to this goal according to e.g. Montzka et al. [Mon11] and the IPCC [Sto13]. The IPCC states in Chapter 10 of [Sto13] that while the largest mitigation potential in industry lies in reducing CO$_2$ emissions from fossil fuel use, there are also significant mitigation opportunities for non-CO$_2$ gases ...“ and that “... projects abating waste gases with a high GWP can generate large volumes of emission reductions at low abatement costs“. Such emission reductions could be achieved by replacing SF$_6$ from electrical equipment. Furthermore, the report states that “... the reduction of non-CO$_2$ greenhouse gases also faces numerous barriers. Lack of awareness, lack of economic incentives, and lack of commercially available technologies are typical examples ...“. At this date, the majority of manufacturers and utilities are aware of the climate impact of SF$_6$. On the medium voltage level, various SF$_6$-free switchgear (using vacuum circuit breaker and air, solid or liquid insulation) are commercially available since many years. However, as SF$_6$ insulated switchgear is a mass product, it is generally cheaper than other technologies and there are no economic incentives for utilities to purchase SF$_6$-free switchgear. On the high voltage level, operational experience with SF$_6$-free apparatuses is limited since SF$_6$-free apparatuses are commercially available only since a few years.

In comparison to direct CO$_2$ emissions, SF$_6$ emissions cannot be directly reduced by a household or individual by adapting the lifestyle or behavior. For electric power equipment, the levels of decision-making range from industries or firms to local, regional or national governments and interest groups up to international agreements. Policy makers who are confronted with the climate impact of
SF₆ might ask: how serious is the climate impact of this greenhouse gas? Is immediate action required? What is the expected benefit and the costs of alternatives? A review on decision-making and climate response policy is given by the IPCC [Ede14]. According to this report, the design of climate change risk reduction policies are made by decision-makers, who often have “insufficient or imperfect knowledge about climate risks” or “constraints on time and attention and processing capacity” [Ede14]. In addition, decisions are not solely made on the basis of the costs and benefits of alternatives but also on intuitive thinking that is conditioned by personal past experience, social context, and cultural factors. Indeed, utilities exist that avoid for example vacuum circuit breakers or solid insulation because of bad experience in the past, when these technologies were more prone to failure. Decision-makers might be biased towards the status quo and “give more weight to the negative impacts of undertaking change than the equivalent positive impacts” [Ede14]. For the electrical industry the tendency towards the status quo might be particularly strong: system operators prefer conservative technologies to novel non-approved alternatives because they invest in new equipment of up to 40 years lifetime with extremely low tolerance for failure with possibly huge expenses. The IPCC generally recommends iterative decision-making strategies, allowing to adjust the pathway during implementation according to new information. Therefore, it might be appropriate to encourage pilot installations of alternative technologies to gain long-term experience of alternative technologies under operating conditions.

A comprehensive review on the development of renewable energy technologies has been presented by Negro et al. [Neg12], that deduce specific policy recommendations to avoid hard institutional failures. Since, according to the authors, “one model fits all“ is not likely to work, policy makers need to evaluate the specific circumstances and problems that are related to specific technological fields. The authors recommend long-term policies - possibly changing over time - to stimulate the development of new technologies, rather than ad
hoc policy initiatives that, as observed in many case studies, may increase insecurity for the manufacturers, engineers and other actors. Policy makers should also “listen carefully to new entrants and often small innovative firms . . . since most lobby networks are dominated by large incumbent firms“ [Neg12]. As an example, the “European Association of the Electricity Transmission and Distribution Equipment and Services Industry“, which members are the European national associations, positions itself generally more conservatively towards SF$_6$ alternative technologies than manufacturers of SF$_6$-free equipment. Furthermore, “it is necessary to put pressure on the incumbent locked-in system as otherwise new technologies have to comply with the criteria that are used to measure the performance of incumbent technologies“ [Neg12]. SF$_6$-free solutions for electrical applications are nowadays compared mainly to the corresponding SF$_6$ products and the tolerance for trade-offs (e.g. outer dimensions of equipment) is set very low by the utilities and industrial customers, although the same alternatives would outperform e.g. AIS that have been widely replaced by GIS using SF$_6$ during the last decades.

A problematic role of SF$_6$ within the carbon market was pointed out by the recent study, where instead of achieving cost-effective climate mitigation, all projects abating SF$_6$ (and HFC-23) under the Kyoto Protocol’s Joint Implementation mechanism increased SF$_6$ production in Russia, due to the generation of credits from producing more waste gas [Sch15].

In conclusion, it is likely that, as soon as competitive alternatives enter the market and sufficient user experience has been generated, stricter policies for SF$_6$ usage for electrical equipment will be implemented on the level of national or international governments. A complete climate impact assessment needs an appropriate time horizon in the order of the atmospheric lifetime of SF$_6$, and should consider that SF$_6$ in closed electrical equipment is banked and - in contrast to open applications - not directly emitted. However, abating SF$_6$ has the potential for significant greenhouse gas emission
reductions, considering the net greenhouse gas emissions from alternative technologies over the entire life cycle. Abatement costs of SF₆ should be re-estimated, taking into account that the potential mass production of SF₆-free equipment would further reduce these costs. Future policy decisions should contain technological differentiations between different fields of application, such as medium versus high voltage or insulation versus arc quenching.
7. Basic physics of gas mixtures

This chapter is based on the submitted article [Rab17b].

7.1. Dielectrics

A good insulation gas prevents the undesirable phenomena of electrical discharge and breakdown up to high electric field stress. Above these fields, a single seed electron - created by natural ionizing radiation, field emission or electron detachment from negative ions - may lead to an electron avalanche due to impact-ionization. The electric strength (critical electric field strength), which depends on the gas particle density \(N\) and composition, is the uniform electric field above which an avalanche can develop. The appearance of seed electrons is a statistical process that cannot be avoided in any gas. The electron motion in an avalanche is governed by the applied electric field and the collisions of electrons with gas particles. Thereby, the probability of certain collision processes and thus the amplitude of electron multiplication strongly depends on the particular gas composition. For the relevant conditions of high pressures and large insulation gaps typically encountered in electrical apparatuses, the single most important parameter determining the onset voltage of the discharge is the number of free electrons in the gas, according to the classical avalanche picture and the subsequent streamer mechanism [Rae39, Mee40, Loe41, Fri05]. The growth of an electron avalanche is mainly determined by the kinetics of electrons and short-lived metastable anions that are created in attachment events. Ions have in general little influence on the build-up of the
Table 7.1.: Relevant electron-molecule interactions for modeling electron avalanches. The corresponding cross sections are functions of the electron’s kinetic energy $\varepsilon$.

<table>
<thead>
<tr>
<th>Electron scattering cross section</th>
<th>Keyword used by LXcat [Pit17]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elastic momentum transfer cross section $^a$</td>
<td>elastic</td>
</tr>
<tr>
<td>Rotational excitation cross sections $^b$</td>
<td>excitation</td>
</tr>
<tr>
<td>Vibrational excitation cross sections $^b$</td>
<td>excitation</td>
</tr>
<tr>
<td>Electronic excitation cross sections $^b$</td>
<td>excitation</td>
</tr>
<tr>
<td>Ionization cross sections $^b$</td>
<td>ionization</td>
</tr>
<tr>
<td>Attachment cross sections $^b$</td>
<td>attachment</td>
</tr>
</tbody>
</table>

$^a$ Sometimes the effective momentum transfer cross section (keyword effective) is used, which is the sum of the elastic momentum transfer cross section and all inelastic cross sections (keyword excitation).

$^b$ Can consist of more than one process.

discharge, since even the fastest ions are energetically below the ionization threshold (typically $\sim 10 - 15$ eV). However, ion bombardment onto the surface of equipment might release electrons that initiate additional avalanches. Penning ionization in gas mixtures is another source of free electrons, that is, when highly electronically excited gas species of the discharge ionize upon collision other species that have ionization threshold lower than the internal energy of the excited gas species. Electronically excited gas particles can also de-excite to the ground state by emitting photons that in turn might release additional electrons from gas particles or from surfaces.

When the applied electric field equals the critical electric field strength, the number of ionization and attachment events per unit length in an electron avalanche (given by the ionization and attachment coefficient $\alpha$ and $\eta$, respectively) are equal $\alpha = \eta$. Table 7.1 lists the electron-molecule collision processes that are relevant for
the electric strength of a gas. For many species, the cross sections are known and can be downloaded from various databases. Particular emphasis might be given to the LXCat database, which is a community-based, dynamic, open-access, project for collecting, displaying, and downloading online electron scattering cross sections and swarm parameters [Pit17]. However, for novel species the determination of cross sections in crossed-beam experiments and electron swarm experiments is necessary [Chr84, Bru02, Chr02, Pet07, Rob08]. Ab-initio quantum theoretical calculations provide an option to obtain electron-molecule collision cross sections, but are generally limited to simple molecules with present computing methods and capacities [Huo95, Ten07]. The simulation of electron transport on the basis of all relevant cross sections for the electron-molecule interactions by Boltzmann solvers [Hag05], which are faster, or Monte Carlo methods [Bia99, Rab16a], which are more precise, yields the electron energy distribution function (EEDF) $f(\varepsilon)$ and in particular the density reduced coefficients $\alpha/N$ and $\eta/N$ as a function of the reduced electric field strength $E/N$. In other words, the calculated coefficients $\alpha$ and $\eta$ - and thus the critical electric field strength - linearly increase with the gas particle density $N (\alpha, \eta \propto N)$ at fixed $E/N$. As a consequence, the density reduced critical electric field strength $(E/N)_{\text{crit}}$ is a pressure-independent quantity. However, this is only valid if the processes given in table 7.1 can be represented by two-body collisions between the incident electron and a neutral gas particle. At pressures relevant for electrical equipment ($\sim 0.1 – 1$ MPa) this is generally the case for elastic and inelastic collisions as well as for ionization and dissociative electron attachment. The formation of negative ions by electron attachment where a dissociation process does not occur (unimolecular or parent ion attachment), is enabled by collision with a third body [Bra33, Blo35, Cha59, Ban73, Hun82] as illustrated in figure 7.1. After an electron attaches to a molecule, the excited anion can stabilize only if its vibrational energy is transferred to another molecule before the inverse process (detachment) occurs. In particular, as
long as the electron attaches within a three-body process, the corresponding rate is increasing quadratically with density. Then, the scaling of $\eta \propto N^2$ versus $\alpha \propto N$ has the desirable side-effect of an increased $(E/N)_{\text{crit}}$ towards high pressures. However, above a certain density the three-body process is being replaced by an “effective” two-body process ($\eta \propto N$), that is, when the transfer of vibrational energy occurs during a time, which is short compared to the metastable anion’s lifetime. Due to the relatively long lifetime of the metastable SF$_6^{-*}$, three-body attachment to SF$_6$ is limited up to pressures below $\approx 50$ kPa [Dut70], whereas at higher pressures SF$_6^{-*}$ will always stabilize via collisions and the attachment becomes “effectively” two-body. In the PFCs C$_3$F$_8$, n-C$_4$F$_{10}$ and 1-C$_3$F$_6$, three-body attachment is relevant up to higher pressures in the range of $\sim 0.1 - 1.5$ MPa due to short-lived metastable anions [Asc81, Hun85]. The cyclic PFC c-C$_4$F$_8$O, added in small concentrations to N$_2$ or CO$_2$, the attachment process in the pressure range of $2 - 10$ kPa is in the transition between three-body and “effective” two-body [Cha16a], whereas in the HFO-1234ze three-body attachment occurs up to at least 45 kPa [Cha16b].

Figure 7.2(a) illustrates the spatial evolution of electron numbers $N_e$ in an electron attaching insulation gas under the influence of uniform electric fields. The exponential function for $N_e$ is a probability function, since single ionization/attachment events would yield discrete steps in the evolution of electron numbers and would deviate from $N_e$ particularly when electron numbers are small. The exponential increase/decrease in space of the electron number is given by the exponent $\alpha - \eta$. For weak electric fields - below the critical field $(E/N)_{\text{crit}}$ - it is more likely that free electrons attach than ionize gas molecules and therefore the avalanche build-up is suppressed (case 1, $\alpha < \eta$). If the electric field exactly equals $(E/N)_{\text{crit}}$, attachment and ionization are equally likely (case 2, $\alpha = \eta$). For sufficiently strong electric fields- above $(E/N)_{\text{crit}}$ - electrons tend to ionize gas molecules rather than to be attached (case 3, $\alpha > \eta$), which results in continuous electron multiplication. Figure 7.2(b) shows $\alpha$ and
Figure 7.1.: Qualitative picture of a key process determining the electric strength of a gas over a wide pressures range, namely parent ion (or unimolecular) electron attachment to a molecule. The process is illustrated for two limiting cases: in a sample gas A that forms a long-lived metastable anion and in a gas B that forms a short-lived metastable anion. **Left:** an electron attaches to the gas with a probability of $Nk_{at}$ per unit time. **Middle:** without a third particle being in close vicinity to carry away the extra energy, the electron would detach from the metastable anion within the lifetime $\tau^*$. The probability of a third particle stabilizing the metastable anion is 1 for gas A and less likely for gas B, namely $\tau^*/\tau_s$ ($= Nk_s \tau^*$, stabilization rate coefficient $k_s$). **Right:** as a result, in the considered pressure range, the corresponding attachment rate (or $\eta$) in gas A (effective two-body attachment) scales linearly with pressure. In gas B (three-body attachment) the rate scales quadratically with pressure and therefore will deviate from Paschen’s law at this pressure. In the limits of very low and very high pressures the attachment process will be three-body and “effectively“ two-body, respectively, for both gases.
\( \eta \) as functions of the density reduced electric field \( E/N \). As illustrated in figure 7.2(c) for the three different electric fields around \((E/N)_{\text{crit}}\), \( \alpha \) and \( \eta \) can be calculated from integrals of the form

\[
\alpha, \eta \sim \int_0^\infty \sigma_{i,a}(\varepsilon)f(\varepsilon)d\varepsilon,
\]

\( \sigma_i \) and \( \sigma_a \) being the ionization and attachment cross section, respectively.

Two collisional processes can be identified as being crucial for the insulation performance of gases or gas mixtures. Firstly, electron attaching compounds remove electrons from the avalanche and thus increase \((E/N)_{\text{crit}}\) when added to a gas. For some strongly attaching gases - including SF\(_6\) - \( \sigma_a \) is dominant at low energies (\( 1 \lesssim \text{eV} \)). The physical upper limit of s-wave capture \( \sigma_a = \lambda^2/4\pi \) (\( \lambda \) is the electron de Broglie wavelength), which is typically not exceeded in the low energy range, could be used to designate the “perfectly attaching” compound. Secondly, large cross sections for inelastic processes remove - via vibrational, rotational and electronic excitations - kinetic energy from the system, shifting the electron energy distribution to lower energies. The response to the changing overlap between \( f(\varepsilon) \) and \( \sigma_i \) and \( \sigma_a \) is typically a decrease in \( \alpha \) and an increase in \( \eta \), respectively [Pai79]. In a gas mixture containing a strongly attaching gas, the increase of \((E/N)_{\text{crit}}\) is thereby predominantly due to the increase in \( \eta \) [Pac78]. For both processes, attachment and inelastic collisions, the underlying mechanism is negative ion resonances [Pai79]. For electron attaching molecules (e.g. SF\(_6\)) where the anion is energetically lower than the neutral (in the literature, both terms positive and negative electron affinity are often used interchangeably), negative ion resonances can result in electron capture whereas for molecules where the anion is energetically higher than the neutral (e.g. CO\(_2\)), negative ion resonances can only result in vibrational and rotational excitation or dissociative attachment [Pai79]. In a binary gas mixture where electrons efficiently perform inelastic collisions with a carrier (also buffer or background) gas and are captured by the strongly attaching gas component due to a resonance peak in \( \sigma_a \), already a small admixture of the latter can overproportionately increase the electric strength.
Figure 7.2.: Illustration of an electron avalanche in a uniform electric field (a) in terms of spatial electron number growth, (b) ionization and attachment coefficients $\alpha$ and $\eta$ vs reduced electric field strength $E/N$, and (c) the electron energy distribution function EEDF and ionization and the attachment cross section $\sigma_i$ and $\sigma_a$ respectively. Three values of $E/N$ are indicated: (1) below the critical electric field $(E/N)_{\text{crit}}$, (2) at $(E/N)_{\text{crit}}$ and (3) above $(E/N)_{\text{crit}}$. Ionization and attachment can be represented by the size of the area below the convolution of the EEDF with $\sigma_i$ and $\sigma_a$ respectively. The data shown in this figure are based on the weakly attaching CF$_4$ [LXCc] and a Boltzmann solver [Hag05].
[How57, Mal79, Cha81, Woo82, Chr88, Chr97]. This *synergism*, as already mentioned in chapter 5, can be beneficial for avoiding liquefaction of the less volatile electronegative compound at low ambient temperatures (see section 8.3). Figure 7.3(a) shows the non-linear behaviour of \((E/N)_{crit}\) versus mole fraction for the insulation gas mixtures of last generation for which data are published. In the literature, the terms *synergism* and *positive synergism* are often used interchangeably for the case where \((E/N)_{crit}\) is higher than obtained from the partial pressure weighted sum of the critical fields of the individual gases [Cha81]. However, some authors use the term *positive synergism* solely when the \((E/N)_{crit}\) of the mixture is greater than the critical fields of the individual gases [Hun85]. *Negative synergism* refers to the case where \((E/N)_{crit}\) is lower than obtained from the partial pressure weighted sum of the critical fields of the individual gases. Figure 7.3(b) shows that the electric strength of pure SF\(_6\) could be reached with \(\sim 2 - 6\)% of a “perfectly attaching“ compound with attachment cross sections at the physical limit of s-wave capture in typical background gases: \((E/N)_{crit}\) of SF\(_6\) is reached at \(\sim 2\)% in N\(_2\) (or technical air, 80%N\(_2\)/20%O\(_2\)), \(\sim 4\)% in CO\(_2\) and \(\sim 6\)% in O\(_2\). The results are based on a Boltzmann solver [Hag05] with cross sections from [LXCc] and on the approximation that for low concentrations of the attaching gas, the electron energy distribution is the one of the background gas. This imposes a constraint on the maximum acceptable boiling point of potential insulation gases (see section 8.3).

Besides a favorable combination of inelastic and attachment cross sections of the components, another reason for synergism can be three-body attachment processes. The process of three-body attachment, in which an electron and two gas particles collide inelastically to form a stable anion, can be more effective if involving two different gas species than solely one, and therefore can lead to synergism in gas mixtures [Hun85].
Figure 7.3.: Synergism in binary gas mixtures containing electronegative compounds: (a) electric strength (or $(E/N)_{\text{crit}}$) versus mole fraction of SF$_6$ in N$_2$ [LXCc, Hag05], C$_4$F$_7$N in CO$_2$ [Kie15a], CF$_3$I in N$_2$ [DU07] and HFO-1234ze(E) in N$_2$ (pressure-dependent, presented data at 0.13 MPa) [Kie16a]. The dotted lines are linear interpolants to the data points to guide the eye. (b) $(E/N)_{\text{crit}}$ of a (hypothetical) compound with the physical limit of s-wave capture added in concentrations up to 10% to different background gases. For comparison, the exact (⋄) and approximated values in SF$_6$/N$_2$ are shown.
7.2. Liquefaction

The liquefaction temperature - or dew point - for a gas of one or multiple components must be below the minimum operating temperature of electrical equipment. Liquefaction of a gas fraction has the undesired effect of a density drop in the gas phase and hence a decrease in the breakdown voltage. In gas mixtures, liquefaction can additionally reduce the breakdown voltage, because the electronegative component is typically less volatile than the carrier gas and thus predominantly liquefies. Strong synergism therefore enhances the sensitivity of the breakdown voltage on liquefaction, see figure 7.3. The dew point of a mixture under Dalton’s and Raoult’s law is given by $p^{-1}(T) = \sum_{i(Tc<T_c)} k_i/p_i(T)$ [Sko08], where $p_i(T)$ is the vapor pressure of pure component $i$ at temperature $T$, and $k_i$ is its mole fraction in the gas phase. Compounds above their critical temperature $T_c$ are considered as non-condensable and can be excluded from this formula. This is typically the case for N$_2$ and O$_2$ since their critical temperatures are below minimum operating temperatures of equipment. Figure 7.4 illustrates the dew point estimation of a binary gas mixture (here CF$_3$I/CO$_2$) in an electrical apparatus. Deviations from the ideal gas conditions might occur towards high pressures and low temperatures, when intermolecular interactions increase. The ideal gas law might be replaced by e.g. van der Waals-equation or more accurate Peng-Robinson-equation of state [Pen76]. Furthermore, Dalton’s and Raoult’s law might be imprecise due to the nonideality of the gas and liquid phase and due to the Poynting Effect [Lui99]. Software packages allow the calculation of phase-equilibrium data of (binary) mixtures based on more accurate models such as the activity coefficient model used in the ThermoData Engine from NIST [Dik09]. Direct measurements to detect the dew point of a mixture are typically performed by recording the gas pressure, by the chilled-mirror principle or by infrared spectroscopy. A few dew point measurements in insulation gases exist, e.g. [Min82, Man16], that show strong deviations from idealized
Figure 7.4.: Measured vapor pressure curves for pure CO$_2$ [Spa96], pure CF$_3$I [Dua96] and calculated vapor pressure curve for a 20%/80% CF$_3$I/CO$_2$ mixture on the basis of ideal conditions following Dalton’s and Raoult’s Law (see text). After filling a compartment up to a pressure of 0.8 MPa at 20 °C at the manufacturing site, its pressure linearly decreases when exposed to decreasing ambient temperatures according to the ideal gas law (dashed line) until the gas starts to liquefy at the dew point (here at -7 °C).
8. Current status of insulation gases

This chapter is based on the submitted articles [Rab17a, Rab17b].

8.1. Selection and validation of potential candidate gases

At this date, requirements on insulation gases listed by producers and utilities cover dielectric, thermal, environmental, chemical, thermodynamic and financial aspects. The ideal insulation gas would be a compound with minimum environmental impact that withstands electric fields associated to the highest voltage levels and meets safety, risk and toxicity standards in equipments that operate under all foreseeable conditions from arctic to tropic. It should be low-cost gas of high reliability and long durability, be chemically stable inside equipment, in particular not flammable and compatible with materials in electrical and service equipment. In addition, its degradation products within the troposphere and within the equipment should be harmless to the environment and human health.

Drop-in replacements of SF$_6$ require similar electric strength in order to keep the compact dimensions of SF$_6$-filled electrical equipment. Installed equipment must sustain its functionality and safety under various climate and weather conditions. Avoiding liquefaction of gas components at sub-zero ambient temperatures is of major importance for utilities. IEC 62271-203 (2011) defines the “normal“ minimum operating temperature for indoor high voltage GIS as ei-
ther -5 °C or -25 °C and for outdoor GIS as -25 °C or -40 °C. It also sets the “special“ conditions to -25 °C for indoor and -50 °C for outdoor GIS. As can be seen from figure 8.2, these requirements are a challenge for the shown synthetic compounds, since their vapor pressures are - except for SF₆ - generally below typical filling pressures of 0.1-0.8 Mpa at these low temperatures. Temperature requirements down to -50 °C in cold weather regions are - for pure gases - solely achieved by the atmospheric gases N₂, O₂ and CO₂. The latter is e.g. used as an insulation and quenching gas in circuit breakers. For applications below -40 °C, SF₆ must be mixed with a more volatile carrier gas such as CF₄ or N₂. For example, in the year 2000 more than hundred circuit breakers using a ~ 50/50% CF₄/SF₆ mixture were in operation in the system of an electric utility in Canada [Mid00].

No compound stands out above all the others in being the ideal gas that is superior with respect to all requirements. The desired requirements are often in conflict with each other.  

I. Maximum voltage levels versus minimum ambient temperatures: increasing the molecular size typically leads to a higher electric strength and at the same time decreased vapor pressure [Bra82, Rab15a].  

II. Maximum voltage levels versus minimum environmental impact: the radiative efficiency of a molecule enters linearly into semi-empirical electric strength estimations [Meu04] and into the GWP definition [Sto13].  

III. The advantage of SF₆ being chemically inert inside equipment, is accompanied by the disadvantage of its long atmospheric lifetime: on the one hand, unstable molecules inside equipment accelerate the aging process (and thus increase maintenance costs) due to reactions with materials such as gaskets, by-products formation under partial discharge and undesired decomposition on solid insulators or electrodes. On the other hand, designing fluorinated compounds with short atmospheric lifetimes is the best method to ensure low GWP - rather than searching for compounds with small radiative efficiency- and is the strategy adopted by many industries to screen for the best molecule for an application [Tap00, Wal10]. However,
substances with very short lifetimes (in the order of days or week) might contribute to smog formation and the decomposition products could affect aquatic ecosystems [Pap09, Cal08].

The difficulty of combining two desired characteristics in one compound is represented e.g. by the group of saturated halocarbons: increasing the number of hydrogen atoms in these compounds generally decreases the atmospheric lifetime but increases the flammability and the boiling point. Therefore, low-fluorinated saturated HFCs are often relatively short-lived but flammable in contrast to more volatile PFCs which are typically very long-lived but non-flammable. From these considerations, it seems likely that the ideal gas does not exist and that certain trade-offs between competing criteria are necessary. Besides these general trends with respect to functional groups, there are large variations of properties within one chemical class. Figure 8.1 shows that the lifetimes and radiative efficiencies of halocarbons can spread over several orders of magnitude even within the same chemical class. In many drug or material related industries, so-called virtual screening of chemical libraries is an integral part of finding promising candidates for specific applications [Sho04]. Computationally designing the molecular structure of compounds on the basis of calculated atmospheric lifetime, radiative efficiency, thermodynamic properties, flammability, toxicity and chemical stability has been done for refrigerants [Kaz12], where - except the electric strength - similar properties as for insulation gases are desired. In view of the difficulties in predicting the electric strength by means of ab initio calculations and full kinetic models (see section 7.1), several empirical estimation methods, analyzing the correlation between the electric strength and certain molecular properties, have been developed [Wil50, Hey56, Cro60, Dev80, Bra82, Meu04, Oli07]. Despite suffering from high uncertainties, these methods allow to rapidly screen large databases of chemical compounds for their suitability as high voltage insulation gases.

Neither experimental nor computational systematic searches for direct SF$_6$ replacements in electrical equipment found compounds
Figure 8.1.: Radiative efficiencies and atmospheric lifetimes from halocarbons and related compounds listed in the Fifth Assessment Report of the IPCC [Hod13, Sto13] as well as the compounds CF$_3$I, HFO-1234ze(E), C$_4$F$_7$N and C$_6$F$_{12}$O. The RE of C$_5$F$_{10}$O is currently not published.
than can be used as pure gases [Dev80, Woo82, Nie98a, Rab15a]. This is in particular due to the high vapor pressure (or low boiling point) of SF$_6$ compared to other fluorinated compounds, as shown in figure 8.2. The selection of potential candidate gases must be followed by a validation of the predicted properties [TD 16]. Some properties of novel compounds such as vapor pressure, electric strength or GWP can be determined in a straightforward way in dedicated experiments, whereas other properties such as materials compatibility, long durability and a complete impact assessment on the environment and human health require operational experience and time-consuming studies. It is particularly challenging to quantify the acute toxicity (as translated in e.g. LC50) as well as chronic toxicity (as translated in e.g. exposure levels) of a chemical. Furthermore, a quantity such as the LC50 “is a somewhat imprecise value traditionally used to compare toxicity among chemicals“ and “lethality is only one of many parameters used to characterize acute toxicity“ [Cha04].

8.2. Last generation of insulation gases

Insulation gases that resulted from the historical developments given in chapter 5 and from the design strategies given in section 8.1 are presented below. Table 8.1 lists relevant properties of pure compounds that are already widely-used as insulation in electrical equipment (SF$_6$, CF$_4$, CO$_2$, N$_2$, O$_2$), of gases that are used in products since a few years (C$_5$F$_{10}$O$_3$C$_4$F$_7$N) and gases that have been proposed (HFCs, CF$_3$I, C$_6$F$_{12}$O). The GWPs of the last generation gases (in particular their mixtures) are significantly lower than that of pure SF$_6$. None of the listed gases is ozone-depleting.

Hydrofluorocarbons HFCs in particular replace PFCs as refrigerants. The main atmospheric removal mechanism for the HFCs is through reaction with hydroxyl radicals. The atmospheric lifetime of HFCs depends on their reactivity towards hydroxyl radicals and ranges from 2.1 days for CH$_2$=CHF to 242 years for CF$_2$CH$_2$CF$_3$,
Figure 8.2.: Full lines: vapor pressure curves for various gases, namely (a) \( \text{N}_2 \) [Spa00], \( \text{O}_2 \) [Ste91], \( \text{CO}_2 \) [Spa96], \( \text{SF}_6 \) [Gud09], \( \text{CF}_3 \text{I} \) [Dua96], \( \text{C}_4\text{F}_7\text{N} \) [Kie14], \( \text{C}_6\text{F}_{12}\text{O} \) [McL15] as well as (b) the 3 isomers of \( \text{C}_3\text{H}_2\text{F}_4 \): HFO-1234yf [Tan10], HFO-1234ze(Z) [Fed14] and HFO-1234ze(E) [Aka10]. Dashed lines: for (novel) compounds the approximated vapor pressure curve on the basis of the Clausius-Clapeyron relation and Trouton’s rule \( \ln(p/p_B) = 10.5(1 - T_B/T) \) could be used if solely the boiling point \( T_B \) (at pressure \( p_B = 101.3 \text{ kPa} \)) is known and reliable vapor pressure data are not available.
see figure 8.1. For unsaturated HFCs such as fluorinated alkenes (olefins), alkynes and aromatics this reaction is much more efficient than for saturated HFCs leading to much shorter lifetimes. A subclass of HFCs, the hydrofluoroolefins HFOs, were proposed as refrigerants to replace the HFC-134a and are also considered as insulation gases, in particular HFO-1234ze(E) [Kie16a, Koc15, Cha16b]. Although HFO-1234yf has a higher vapor pressure than HFO-1234ze(E) (see figure 8.2) it is not considered for electrical insulation due to its relatively high flammability.

The class of fluorinated oxiranes have been investigated and generally have high electric strength [Tum12, Pic13]. However, their GWP is in general similar to PFCs.

CF$_3$I was introduced as replacement for the ozone-depleting substance CF$_3$Br as gaseous fire suppression agent and as inert gas in aircraft fuel tanks. It is also used for plasma etching in semiconductor manufacturing. The ODP of CF$_3$I is in the range of 0.006-0.017 [Sol94, Li06, You10], and in Europe it is subject to reporting under the EU Regulation No. 1005/2009 [EU09]. CF$_3$I was found to be a cardiac sensitizer at concentration in air above 0.4% [Dod98], and objections were raised to its use. Its electric strength is slightly higher than of SF$_6$ [DU07, Chr00], however its vapor pressure is significantly lower, see figure 8.2. Therefore, CF$_3$I should be mixed, e.g. with CO$_2$ [DU07, Kat08] or N$_2$ [DU07]. The degradation by UV-radiation in the atmosphere occurs within days. CF$_3$I also decomposes in electrical equipment under electrical arc and discharges, leading to iodine deposition and as a consequence reduced insulation performance [Ngo09, Tak11]. In arcing chambers, where the iodine deposition is particularly strong, iodine might be removed from the gas flow during switching operations by adsorption materials, such as organic liquids, organic solids or carbon filters [Bur04, Kat08].

The branched nitrile, C$_4$F$_7$N (2,3,3,3-tetrafluoro-2-(trifluoromethyl)-2-propanenitrile, known by the trade name Novec-4710) has been introduced as admixture to CO$_2$ with mole fractions from $\sim 4-10\%$ with lower temperature limits from $-5\,^\circ$C- for the 10% mixture-
down to $-30^\circ$C for the 4% mixture [Kie15b, Kie15a, Kie16b]. CO$_2$ is used since it shows good synergism with C$_4$F$_7$N (see figure 7.3(a)) and since CO$_2$ has better arc quenching capabilities than N$_2$. The materials compatibility of C$_4$F$_7$N is different from that observed with SF$_6$ [Nov15a]. A pilot installation exists of 420 kV gas insulated busbars in a substation in UK down to $-25^\circ$C. Furthermore, 145 kV gas insulated substations are planned in several European countries, and several 245 kV current transformers down to $-30^\circ$C are planned in Germany [Kie16b].

The ketones C$_5$F$_{10}$O (1,1,1,3,4,4,4-heptafluoro-3-(trifluoromethyl)-2-butanone, known by the trade name Novec-5110) and C$_6$F$_{12}$O (1,1,1,2,2,4,5,5,5-Nonafluoro-4-(trifluoromethyl)-3-pentanone, known by the trade names Novec-612, Novec-649 and Novec-1230) have been proposed as electrical insulation gases in binary mixtures with technical air or CO$_2$ [Man14a, Man14b, Sim15]. The presence of O$_2$ in the mixture might reduce soot deposits and harmful by-products like CO [Man16]. C$_6$F$_{12}$O is also used as fire protection fluid, as an alternative to SF$_6$ in cover gases for molten magnesium and as the working fluid in Organic Rankine Cycle applications due to its short lifetime and zero ODP [Nov04]. In order to reach lower minimum temperatures, the C$_5$F$_{10}$O has been chosen in preference to C$_6$F$_{12}$O. Similar to C$_4$F$_7$N, the materials compatibility of C$_5$F$_{10}$O is different from that observed with SF$_6$ [Nov15b]. At this date, medium voltage GIS with mixtures of $\sim 7-14\%$ C$_5$F$_{10}$O in air are commercially available with minimum operating temperatures down to $-25^\circ$C. In high voltage GIS, C$_5$F$_{10}$O is admixed in mole fractions of $\sim 6\%$ to O$_2$ and CO$_2$. A pilot installation with a minimum operating temperature of $+5^\circ$C is in operation since 2015 [Teh15, Dig16].
### Table 8.1.: Properties of pure compounds used or considered for electrical insulation

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>GWP (1)</th>
<th>lifetime (2)</th>
<th>RE (3)</th>
<th>Boiling Point (4) (°C)</th>
<th>Critical field strength (5)</th>
<th>Acute toxicity (6)</th>
<th>LC50 (ppm)</th>
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<td>CF₄</td>
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<td>3200</td>
<td>0.575</td>
<td>-64 (7)</td>
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<td>0.50</td>
<td>26.9</td>
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<td>1.5-2.0</td>
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<td>2</td>
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<tr>
<td>HFC-1234ze(E)</td>
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<td>-</td>
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<td></td>
<td>-</td>
<td>400 000</td>
</tr>
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<td>1.2</td>
<td>160 000</td>
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<tr>
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</table>

(1) Global warming potential from references: [Sto13, Sol07, Nov15b, Nov04, SA17]. The GWP calculation assumes that the compound is well-mixed throughout the troposphere. Short lived compounds do not meet this condition and therefore the calculated GWP value is overestimated.

(2) Atmospheric lifetime from references: [Sto13, Nov15b, Nov04, SA17, Sol94]

(3) Radiative efficiency from references: [Sto13, Nov15b, Nov04, SA17, Kie14, Sol94]

(4) Boiling point from references: [NIS16, Hay14, NIS16, Nov15b, Owe02, Nov15a, Aka10, Fed14, Tan10, Dua96]

(5) For the gases lacking data of the critical field strength (C₅F₁₀O, C₆F₁₂O, C₄F₇N and HFC-1234ze(E)) and for N₂ (α − η always positive), the electric strength determined from breakdown experiments is shown. References: [Chr96, Há02, Nov15b, Man14b, Nov15a, Kie16b, Koc15, DU07, Bra82]

(6) 4 hour rodent (rat) LC50 (lethal concentration at 50% mortality) from references [Nov15b, Nov02, Nov15a, Hon08b, Hon08a]

(7) Sublimation point
Environmental and safety assessment

A complete impact assessment of insulation gases should include effects on atmosphere, aquatic systems, farmland, biodiversity and human health. For most industries, the introduction of novel compounds have been driven by the Montreal and Kyoto protocols to reduce stratospheric ozone depletion and global warming of the compound itself.

The full global warming impact of electrical equipment is not entirely reflected by the direct GWP of the gas components including possible by-products. In general, manufacturers calculate the overall CO$_2$ equivalent environmental impact of equipment by means of life cycle assessments including gas leakage, materials, transport, Joule losses, maintenance and recycling. For example, air - a zero-GWP insulation gas - can reach the breakdown voltage of most synthetic gases only at significantly larger gap distances or higher filling pressures. Therefore, larger equipment or thicker walls of vessels are required, resulting in more material use for aluminum or steel. The leakage rate through gaskets varies between different gas species and materials. However, leakage rates from equipment using alternative gases do not significantly differ from SF$_6$ equipment, if compatible gasket materials are used. For example, for equipment using CO$_2$/C$_4$F$_7$N mixtures, EPDM rubber of the SF$_6$ equipment is replaced by halogenated butyl rubber [Poh16]. The European F-Gas Regulation [EU14] calculates the GWP as “a weighted average, derived from the sum of the weight fractions of the individual substances multiplied by their GWP”. A complete comparison of different insulation gases in equipment consists of their carbon dioxide equivalents rather than their GWPs. For example, the average molar mass of the C$_4$F$_7$N/CO$_2$ mixture is lower by a factor of $\sim 2.5 – 2.9$ than the molar mass of SF$_6$. Correspondingly, the same system at the same filling pressure contains a mass of C$_4$F$_7$N/CO$_2$ that is smaller by the same factor.

Highly fluorinated compounds are mainly synthesized by fluorination with elementary fluorine, fluorination with fluorine-active metal
fluorides, or electrochemical fluorination [Ger81]. Elementary fluo-
rine is produced by the energy-intensive electrolysis of hydrogen
fluoride $2 \text{HF} \rightarrow \text{H}_2 + \text{F}_2$, whereas HF in turn is produced from nat-
urally occurring calcium fluoride $\text{CaF}_2$. The electricity consumption
for the electrolysis of HF is 14-17 kWh/kg $\text{F}_2$ [Alt07] and is e.g. re-
ponsible for more than 95% of the power consumption for the $\text{SF}_6$
production [Shi06]. The subsequent fluorination of sulphur to pro-
duce $\text{SF}_6$ is exothermic and therefore a low energy consumption can
be assumed [Alt07]. EPA’s emission factor of 0.7 kg $\text{CO}_2$-equivalents
per kWh electricity [EPA15a] from 2012, yields $\sim 7 - 9$ kg $\text{CO}_2$-
equivalents for the production of 1 kg $\text{SF}_6$ (≪ GWP of $\text{SF}_6$) and
will be in the same order of magnitude for other compounds that
are synthesized by fluorination with elementary fluorine.

For the separation of gas mixtures into their components various
methods exist such as distillation, gas centrifuges, cryogenic meth-
ods, plasma methods, catalytic decomposition and porous materials
used as molecular sieves [Pit01]. To separate $\text{N}_2$ from $\text{SF}_6$ in mix-
tures used e.g. in GIL systems, mainly distillation [Ham98, Nie98b]
and molecular sieves [Yam02, Toy03, MM15], alone or combined,
may be used. However, due to the relatively high vapor pressure of
$\text{SF}_6$, liquefaction procedures might be not economically viable when
applied to mixtures of small percentages of $\text{SF}_6$, since the required
pressures are very high and/or temperatures very low, e.g. for a 10%
content of $\text{SF}_6$ in nitrogen $\approx 20$ MPa are required to liquefy $\text{SF}_6$
at room temperature [Ham98, Toy03]. The decomposition by plasma
methods might produce undesirable waste [Tsa08, Rad09]. In com-
parison to $\text{SF}_6$, the distillation of mixtures containing less volatile
compounds (e.g. $\text{C}_4\text{F}_7\text{N}$ or $\text{C}_5\text{F}_{10}\text{O}$) might be technically easier,
since the required pressures are lower and the cooling temperatures
can be higher.

By-products that are formed during operation of equipment or in
the atmosphere are often neglected in the environmental assessment
since their concentrations are generally much lower than of the com-
pound itself. Most fluorinated compounds, including $\text{C}_5\text{F}_{10}\text{O}$ and
CF$_3$I, form the stable by-product CF$_4$ in electrical equipment under arcing conditions [Man67, Man16, Pre16b]. CF$_4$ is an extremely long-lived greenhouse gas with much higher GWP than the original compounds (see table 8.1). It is also formed in SF$_6$ near to organic materials such as polymeric spacers under partial discharge conditions [Hei97]. Toxic by-products formation under discharge or arcing conditions might involve risks to the health of anyone in the immediate surroundings of electrical equipment filled with SF$_6$ [Sch49, Chu86, Der00, Pow02] or alternative gases [Pre16b, TD 16]. Often the assumption is made that the formation rates of by-product is linearly correlated with the energy input of the partial discharge, sparking or the arc. However, formation rates depend on many parameters such as current, voltage, gas pressure and purity, materials of electrodes and spacers, humidity and the sampling technique used for the analysis [Hei97]. As a consequence, a quantitative comparison of by-product formation rates in different insulation gases for different setups is difficult. Therefore, the prediction of by-product concentrations in a specific setup, based on the values obtained from another setup and different conditions, might strongly deviate from the actual concentrations.

The main atmospheric removal mechanism for organic halogenated compounds from the troposphere are reactions with hydroxyl free radicals, photo-dissociation (or photolysis) and reaction with tropospheric ozone [Tap00]. Reactions with hydroxyl radicals represent the primary removal process e.g. for HCFCs and HFCs and are characteristic for compounds with at least one hydrogen atom as well as unsaturated compounds. For unsaturated compounds the reaction is much more efficient than for saturated compounds. Tropospheric photo-dissociation requires that a compound absorbs radiation in the range of 299-700 nm. For example, CF$_3$I undergoes strong photolysis due to its weak C-I bond that is broken by UV radiation [Sol94]. Similarly, the ketones C$_5$F$_{10}$O and C$_6$F$_{12}$O degenerate via rupture of the bond between the (C=O) functional group and the $\alpha$ carbons [Plu01, Tan03, Nov04]. Photolysis can be generally a strong
removal process for compounds with conjugated multiple bonds, carbonyl, nitrosyl, bromine or iodine [Tap00]. Tropospheric ozone reaction is a significant removal process e.g. for alkenes [Tap00]. For compounds considered for electrical insulation the physical removal processes via rainout, ocean uptake and scavenging by aerosols are negligible due to the typically low water solubility and high vapor pressure. However, aquatic systems could be potentially negatively affected by the rainout of certain atmospheric degradation products. For example, the photo-dissociation products of the ketone C₆F₁₂O are CF₃C(O)F and COF₂ [Tan03]. In contact with rain, clouds or seawater COF₂ will undergo hydrolysis to form hydrogen fluoride, whereas CF₃C(O)F will form trifluoroacetic acid [Tan03, Wal94]. Similarly, the new-generation refrigerant HFC-1234yf forms trifluoroacetic acid that in turn is removed by rainout and potentially accumulates in water bodies as trifluoroacetate. However, a risk evaluation of HFC-1234yf as alternative refrigerant for North America predicted concentrations of trifluoroacetate to remain below levels that could impair water quality [Pap09, Rus12]. This must be seen in relation to the comparatively small quantities needed in the electrical industry.

8.3. Range of application of electronegative compounds in carrier gases

The technical rating of an electrical apparatus, in particular the minimum operating temperature and the maximum operating voltage, are primarily achieved by adjusting the filling pressure and equipment dimensions. Thereby, for a given filling pressure and equipment size, favorable dielectric and liquefication properties of the insulation gas can strongly increase the breakdown voltage and reduce the minimum operating temperature. In particular, an electronegative compound of low boiling point can be added to a carrier gas up to high concentrations without liquefication. Gases with high electric strength and strong synergism with a carrier gas can increase
the breakdown voltage. However, gases with high electric strength typically also have a high boiling point. Therefore, a conclusive comparison of electronegative compounds must include vapor pressure as well as synergism information in carrier gases. A metric is proposed that combines the two properties to find a maximum electric strength that is achievable in mixtures for different filling pressures and desired minimum temperatures. This metric supports the selection process of potential candidate gases.

To quantify synergism, a \textit{synergy coefficient} is defined as the ratio of the critical electric field of the mixture and the critical electric field calculated as the mole fraction weighted sum of the critical electric fields of the individual components. Figure 8.3(a) shows two typical cases for the synergism of gas mixtures that will be used in the following: \textit{no} synergism (linear increase of \((E/N)_{\text{crit}}\) vs mole fraction) as well as \textit{good} synergism (increase of \((E/N)_{\text{crit}}\) as in SF\(_6\)/N\(_2\)).

In figure 8.3(b), properties of pure insulation gases are represented in the 2D-plane of boiling point and electric strength. The curves represent Pareto-efficient frontiers that denote compounds lying on the same curve as equally suited for the specific minimum temperature in case of \textit{no} (dotted lines) or \textit{good} synergism (dashed-dotted lines) in a background gas (here N\(_2\)). The Pareto frontiers are given for two filling pressures (0.13 MPa and 0.6 MP) and minimum operating temperatures of \(-5^\circ\text{C}\) and \(-25^\circ\text{C}\). Vertical lines show the maximal acceptable boiling point given by the compounds of attachment cross sections at the physical limit of s-wave capture. Assuming \textit{no} and \textit{good} synergism in N\(_2\), the curves indicate limits that should be exceeded by a compound to be suitable for the minimum operating temperatures of \(-5^\circ\text{C}\) and \(-25^\circ\text{C}\) at filling pressures of typical medium (0.13 MPa) and high voltage equipment (0.6 MPa). Each curve represents a Pareto-efficient frontier that denotes compounds lying on the same curve as equally suited as insulation gas for the specific filling pressure and minimum operating temperature. These Pareto-efficient frontiers are highly sensitive to
Figure 8.3.: (a) Synergy coefficients for two binary mixtures: synergy coefficient \( s(x) > 1 \) similar to SF\(_6\) in N\(_2\) (*good synergy*) and \( s(x) = 1 \) (*no synergism*). (b) Electric strength versus boiling point of some pure compounds (symbols). See text for more details.
the synergy coefficient and the dew point of a gas mixture, underlining the necessity of exact data concerning these quantities. The curves are obtained by the following steps: for a given boiling point of a compound, its vapor pressure curve is calculated by means of Clausius-Clapeyron relation and Trouton’s rule (see figure 8.2). Dew point calculations are performed on the basis of Dalton’s, Raoult’s and ideal gas law as explained in figure 7.4: for the defined filling pressures, the maximum possible mole fraction of the compound is calculated that can be added to a non-condensable carrier gas such as N₂ or O₂ (for CO₂ there are only slight deviations) without liquefaction at the indicated minimum temperatures. This maximum possible mole fraction yields - using the synergy coefficients for no and good synergism - two values for the electric strength of the mixtures. The no-synergism-curve imposes a very strict constraint on the boiling point and electric strength. For 0.13 MPa filling pressure, solely C₄F₇N and CF₃I can reach temperatures below −5°C, even if they had no synergism. The same compounds could reach temperatures below −25°C if they had good synergism. For 0.6 MPa filling pressure, no compound could reach −5°C, even if it showed good synergism. Due to the low electric strength of compounds like CO₂ or HFO-1234ze(E), their mixtures can obviously not reach the electric strength of pure SF₆. However, a low electric strength could be compensated by increasing the pressure compared to pure SF₆. This is illustrated in figure 8.4, which compares the breakdown voltage of SF₆ to that of the gases of known synergism (see section 7.1) as a function of the minimum operating temperature. Mixtures that liquefy at the given filling pressures at 20°C are excluded. Here, the dew point calculations are based on the methods described in figure 7.4, using the exact vapor pressure curves of the pure compounds shown in figure 8.2. For example, following information can be extracted from figure 8.4 (circle): it is possible to prepare a HFO-1234ze(E)/N₂ mixture at 1 MPa that has the same breakdown voltage and can reach the same minimum temperature as pure SF₆ at around 0.5 MPa. At equal pressure, non
of the mixtures is equivalent to SF$_6$ in terms of breakdown voltage and minimum operating temperature. Solely with over pressures of the mixtures the properties of pure SF$_6$ can be reached.
Figure 8.4.: Breakdown voltage of pure SF$_6$ and various mixtures in homogeneous electric fields versus minimum operating temperature for filling pressures in the range of 0.1 – 1 MPa and mole fractions from 0 to 1. Full lines are contours of equal pressure (in steps of 0.1 MPa), whereas dashed lines are contours of equal mole fraction (the non-equidistant values for mole fractions are not indicated for the sake of clarity). The vertical lines indicate -5°C and -25°C, respectively. See text for more details.
9. Aim of this work

The overall strategy of this thesis is illustrated in figure 9.1:

1. **Computational screening of electronegative compounds:** in other fields of research, as e.g. in medical sciences or economic statistics, it is very common to identify the relationship between numerically calculated predictor variables (independent variables) with phenomenological quantities (dependent variables) by statistical methods. This statistical approach is used in this thesis to estimate the electric strength and the boiling point from descriptors which are calculated ab-initio by means of density functional theory. This estimation method is applied to the PubChem database of the National Institute of Health to rapidly identify electronegative compounds suitable for gaseous insulation (chapter 10). An example compound resulting from this screening is octafluoro-2-butene (2-C₄F₈), which is subsequently investigated.

2. **Simulation of electron transport with METHES:** a publicly available Monte Carlo collision code for the simulation of electron transport in the presence of uniform electric fields is developed. The program uses established Monte Carlo techniques and is compatible with the electron scattering cross section files from the open-access Plasma Data Exchange Project LX-Cat. In this thesis, METHES is used to calculate the electron energy distribution in the pure carrier gases (chapter 11).

3. **Obtaining attachment cross sections from swarm parameters:** electron attachment to strongly attaching molecules is investigated as a function of the electron energy. The total elec-
1. **Screening for candidate compounds**

![Screening Diagram](image1)

2. **Monte Carlo simulations in carrier gases**

![Monte Carlo Diagram](image2)

3. **Obtaining attachment cross section of a compound**

![Attachment Cross Section Diagram](image3)

4. **Calculation of electric strength in mixtures**

![Calculation Diagram](image4)

Figure 9.1.: Overview of the systematic approach applied in this thesis to identify and quantify gases for electrical insulation
tron attachment cross section of a molecule is determined from swarm measurements in the carrier gases $N_2$ and $CO_2$ with minor proportions ($\lesssim 1\%$) of the electronegative compound. The measured attachment rates for varying reduced electric field strengths $E/N$ are unfolded from the nearly undisturbed electron energy distribution of the carrier gases obtained by METHES simulations. Different unfolding routines for so-called ill-posed problems are tested to find robust solutions for the attachment cross section. Finally, Tikhonov regularization, which is a well-defined algorithm for discrete linear inversion problems, is proposed as most efficient. This method gives rise to an approximate and clearly defined solution for the attachment cross section and is applied to three sample compounds: $SF_6$, $C_3F_8$ and $2-C_4F_8$ (chapter 12).

4. Calculation of electric strength of gas mixtures: Using the attachment cross section determined in the previous step, simulations with METHES and BOLSIG+ provide the electric strength of gas mixtures, neglecting collision processes with the strongly attaching compounds. This crude approximation yields accurate results for diluted ($\lesssim 10\%$) $SF_6/N_2$ mixtures, and it is applied to $2-C_4F_8$ admixed to atmospheric gases (chapter 13).

The introduced methods require a considerable amount of measured and calculated data. To eliminate uncertainties due to different data sources and simulation methods, it has been stressed that the methods are robust and transparent. METHES (or BOLSIG+) is well documented and publicly available. In addition, the required input files can be downloaded from LXCat, a platform of collecting, evaluating and sharing cross section and transport data. The toolbox containing the methods needed for the linear inversion (e.g. Tikhonov regularization) are well-documented, publicly available and its use is straightforward.

In this thesis, the well-known concept of a binary gas mixture,
that consists of an electronegative compound in a carrier gas, is adopted due to various advantages over pure gases, which are:

- **Minimum operating temperature**: the liquefaction temperature of most strongly attaching gases is higher than the one from SF$_6$. The use of e.g. atmospheric gases as the main component of the insulation gas allows lower minimum operating temperatures of electrical equipment.

- **Synergism in mixtures**: when adding electronegative compounds to certain carrier gases, the electric strength of the gas mixture rises more rapidly in the region of low concentration than at high concentrations, a beneficial effect known as synergism.

- **Costs and environmental impact**: using smaller quantities of electronegative (mostly fluorinated) compounds in atmospheric gases is typically cheaper and more environmentally friendly than using them in pure form.

- **Experimental aspects**: measuring swarm parameters in a Pulsed-Townsend setup in gas mixtures with high concentrations of fluorinated compounds (or even purely) is often difficult and is limited to a narrow $E/N$-range close to the critical field. These difficulties arise from the very strong electron attachment and the high reactivity of these molecules. Other experiments such as electron beam experiments can extract very detailed attachment information. They typically operate at low pressures, and therefore electron-molecule collisions are dominated by two-body collisions, whereas collisions with a third particle do not occur. However, attachment processes, where three bodies are involved, are crucial for most strongly-attaching gases.

- **An academic aspect**: a small admixture of a novel compound can be regarded as a small perturbation to the "exact solution" of the carrier gas. It might be advisable to add a
novel compound of unknown physical properties only in small concentrations to well-known carrier gases and to investigate the corresponding response rather than to investigate the pure compound. Electron transport in gases such as $\text{N}_2$ and $\text{CO}_2$ have been investigated extensively in the past and are therefore relatively well understood. For novel gases, most electron-molecule collision processes are completely unknown and thus the Boltzmann equation is not easily solvable.
10. Computational screening of electronegative molecules

10.1. Predictors for compounds of high electrical strength

This section is based on the published article [Rab13].

In this section results from density functional theory (DFT) calculations are related to the electric strength (ES) and the boiling point ($T_B$) determined by experiments for a set of 75 test molecules. The correlation analysis seeks the predictor variables with maximum correlation to the ES and $T_B$, and it includes no expectations based on theoretical models.

10.1.1. Literature overview

Previous studies have analyzed the correlation between molecular properties (descriptors) and the phenomenological quantities electric strength (ES) and boiling point ($T_B$) of a gas [Dev80, Wil50, Dev56, Cro60, Hey56, Bra82]: Molecular quantities such as the weight or the chemical structure clearly show correlations with the ES [Wil50]. It was empirically demonstrated that for saturated hydrocarbons only the number of C-H bonds, and not the number of C-C bonds, influences the ES [Dev56], whereas [Cro60] points out the importance of the carbon double bonds for unsaturated hydrocarbons. General rules for the molecular structure of gases of high ES are given in [Dev80]. The possible correlation of the ES with the Ultra-violet spectra and Ramsauer cross section is discussed for the first time.
Another physically motivated attempt is to correlate measured values of the polarizability and the ionization energy with the ES [Bra82].

So far, all correlation analyses were carried out with measured molecular quantities or quantities that can be determined by means of simple chemical rules. The first attempt to correlate the ES to a quantity that can be solely calculated with the computer, and is thus in principle suitable to be used for all gases, was presented in [Meu04]. A correlation coefficient of $R^2 = 0.726$ between the ES and the integrated optical absorption spectrum was found, with a data set of 43 gases. In another work, semi-empirical quantum chemistry calculations were performed for the same set of molecules: for the calculated ionization energies no trend with respect to the ES was found, whereas for the electron affinity the analysis results in a correlation coefficient of $R^2 = 0.37$ [Oli07].

**10.1.2. Methods**

**Descriptors**

The attempt is to calculate only those physical properties, which reflect the physics of electron-molecule interactions, and therefore could affect the electron transport and thus the ES of a gas. Promising descriptors are:

- average static electronic polarizability $\alpha$
- electric dipole moment $\mu$
- vertical ionization energy $\varepsilon_i^v$
- adiabatic ionization energy $\varepsilon_i^a$
- vertical electron affinity $\varepsilon_a^v$
- adiabatic electron affinity $\varepsilon_a^a$
- molecular mass $m$
- electron number \( N_e \)
- HOLUM: lowest unoccupied minus highest occupied molecular orbital energy.

The averaged static electronic polarizability \( \alpha \) is 1/3 of the trace of the static electronic polarizability tensor. The latter quantifies the electronic response of a molecule when applying a static electric field. In the case of molecules in the field of approaching electrons, the possible anisotropy of the polarizability tensor is averaged out by the random orientation of the thermal gas molecules. Contributions to the static polarizability due to the modification of the interatomic equilibrium geometry (relaxation polarizability) are usually small compared to the electronic polarizability. Nevertheless, some molecules, especially those having roughly spherical shape and containing halogen atoms, can reach significant values of relaxation polarizabilities [Gus98]. However, within the short period of electron-molecule collisions the fast electronic response dominates over changes of interatomic distances.

The vertical ionization energy \( \varepsilon_v^i \) is the difference in total electronic energy between the neutral molecule and the cation with the equilibrium geometry of the neutral species. The adiabatic ionization energy \( \varepsilon_a^i \) corresponds to the difference in total electronic energy between the neutral molecule and the cation with their respective equilibrium geometries. The same picture holds for the vertical electron affinity \( \varepsilon_v^a \) and the adiabatic electron affinity \( \varepsilon_a^a \) by considering the anion instead of the cation.

**Density functional calculations**

The molecular properties are calculated for isolated gas molecules whose structure has been optimized in the electronic ground state. Vibrational and temperature corrections have been neglected. These Kohn-Sham DFT calculations were performed with the Turbomole program package [Ahl89] employing the BP86 density functional
[Bec88, Per86] in combination with density fitting techniques. Ahlrichs’ polarized valence triple-zeta basis def-TZVP [Sch94] was applied in the calculations of $\varepsilon^v_i$, $\varepsilon^a_i$, $\varepsilon^v_a$ and $\varepsilon^a_a$ while the larger def2-QZVPP basis set [Wei03] was used for the calculation of $\alpha$ and $\mu$. DFT calculations are performed for the neutral, the positively as well as the negatively charged molecules to calculate ionization energies and electron affinities. Energy differences between potential curves of neutral and cation and of neutral and anion are evaluated, neglecting the discrete structure of the vibrational energy levels. The quantities $\alpha$ and $\mu$ are then calculated for the geometry-optimized neutral molecule.

**Experimental data**

The experimental values of the molecular properties were taken from literature (see tables A.1 and A.2). The listed values of ionization energies and electron affinities have been mainly measured by techniques of photoelectron spectroscopy [Car75] or photoionization mass spectrometry [Dib65, Ber87]. The averaged static electronic polarizabilities have been obtained by means of dielectric measurements of a gas by the Lorentz-Lorenz equation [Fro56]. Electrical dipole moments of molecular gases have been determined via molecular beam electric resonance methods, microwave spectroscopy or via measurements of the dielectric constant of the gas. The listed values of the ES were taken from [Bia85, Bra82, NIS11, Woo82, Chr00] and were measured under quasi-uniform AC field. The values of the boiling point are taken from [Bra82, NIS11]. All sources are compilations of data, where the authors evaluated original literature, or where the authors themselves performed experiments with a variety of gases. The ES scale of the data is converted to the ES relative to SF$_6$, which subsequently is written as $E_r$. Using gases that appear in more than one source it was verified that the values of $E_r$ from different sources are commensurable. Precedence was given to the most recent data.
Regression analysis

If variables have approximately normal distributed values they can be treated by correlation and regression analyses. In general, the simple linear regression produces coefficients \((p_0, p_1)\) of the response \(y = (y(1), \ldots, y(n))\) on the predictor \(x_1 = (x_1(1), \ldots, x_1(n))\), where \(n\) is the number of elements of both, the predictor variable and the response variable. The simple linear regression is of the form

\[
y(x_1) = p_0 + p_1 x_1,
\]

where \(x_1\) is a continuous variable and \(y(x_1)\) is a function of \(x_1\). The values of \((p_0, p_1)\) depend on the regression method. Either least-squares regression or robust regression will be used. In the case of least-squares linear regression the vector \((p_0, p_1)\) is the unique solution of a two-dimensional linear system of equations, which is obtained by minimizing the residual sum \(\Sigma_i |y(i) - y(x_1(i))|^2\), whereas robust regression produces \((p_0, p_1)\) using iteratively reweighted least squares with a bisquare weighting function [Hol77].

For the correlation analyses of \(E_r\) or \(T_B\) generalized predictor \(A^u B^\nu\) are introduced as the product of two descriptors \(A\) and \(B\) to the power of the arbitrary exponents \(u\) and \(\nu\). Correlations between the predictor \(A^u B^\nu\) and \(E_r\) or between the predictor \(A^u B^\nu\) and \(T_B\) is analyzed by the least-squares method. The predictor that minimizes the residual sum at the same time maximizes the \(R^2\)-value, and it is identified as the one with the strongest correlation with \(E_r\) or \(T_B\). The special case that \(x_1\) directly is one of the descriptors, is included in the present analysis by setting \(u = 1\) and \(\nu = 0\).

The analytical expression for the multiple regression is

\[
y(x_1, x_2) = p_0 + p_1 x_1 + p_2 x_2.
\]

Within the multiple regression the vector \(x_1\) (but not \(p_1\)) obtained by the simple regression is fixed and the second vector \(x_2\) is sought that minimizes the residual sum. The vector of coefficients \((p_0, p_1, p_2)\) is the solution of a three-dimensional linear system of equations.
The significance of the multiple regression compared to the single regression is verified by the F-statistic [NIS12]. The additional second predictor significantly improves the regression, if the F-value of the multiple regression exceeds the upper critical value of the F-distribution at the 5% significance level.

10.1.3. Results

Histograms and correlations

First histograms from the values of the descriptors, $E_r$ and $T_B$ are produced. The values of all these variables are nearly normally distributed, except the dipole moment $\mu$, which shows a prominent peak around $\mu = 0$. The $\mu$-histogram reflects the either symmetric or asymmetric nature of molecular structures. Therefore, the data is analyzed separately for polar ($\mu \neq 0$) and for nonpolar molecules ($\mu = 0$). The values of of the polar molecules are again nearly normally distributed and were included in the subsequent analysis, whereas for the nonpolar molecules $\mu$ is excluded from the statistical analysis.

The analysis is continued with a robust linear regression of the experimental data to the DFT-calculated values of the descriptors, as described in Section 10.1.2. Figure 10.1 shows the linear regression between calculated and measured values for the descriptors $\mu$, $\varepsilon_{iv}$ and $\alpha$. For the $N = 33$ polar molecules with known experimental dipole moments $\mu$ the linear regression yields $y = 0.06 + 0.96x$, with a standard deviation around this regression line of $\sigma = 0.11$ D (1 Debye $\approx 3.33564 \cdot 10^{30}$ Cm). Thus, good agreement is found between the measured and calculated values of $\mu$. Only for a small number of molecules around $\mu \approx 0.5$ D the DFT calculations systematically result in smaller values compared to the experimental ones. Furthermore, Figure 10.1(b) displays the regression between measured and calculated values of $\varepsilon_{iv}$ for the $N = 44$ molecules, for which the experimental values are known. The solution is $y = 0.14 + 1.02x$. The standard deviation of the data is $\sigma = 0.43$ eV, which is slightly
Figure 10.1.: Measured values vs calculated values of the (a) electric dipole moment $\mu$, (b) the vertical ionization energy $\varepsilon_v$ and (c) the polarizability $\alpha$ for the molecules of tables A.1 and A.2 (circles). The solid line is the regression of the calculated values to the experiment values. The dashed line corresponds to perfect agreement between experimental and DFT data. $N$ is the number of molecules, $\sigma$ is the standard deviation.
larger than in the case of $\mu$. Hence, the data show a small offset but strong correlation. The result of the regression for $\alpha$ for the $N = 43$ molecules is $y = 0.13 + 0.98x$, showing a standard deviation of $\sigma = 0.28 \cdot 10^{-30} \text{m}^3$. The outlier in the upper right corner of figure 10.1(c) corresponds to Hexafluorobenzene c-C$_6$F$_6$.

For $\alpha$, $\mu$, $\varepsilon_i^v$ and $\varepsilon_i^a$ the slopes of the regression lines are within 4% of the ideal value of 1 and the offset $\leq 0.14$. In general, good agreement is found between the experimental and theoretical results, establishing the present DFT descriptor calculations as a reliable basis for the subsequent regression analyses.

**Regression on Electric strength**

The single as well as multiple least-squares regressions of $E_r$ according to equations (10.1) and (10.2) were performed for all possible predictors $x_1$ and $x_2$. For selected predictors the results of the regression in terms of $R^2$-values are shown in table 10.1. For polar molecules the predictor $x_1$ with maximum $R^2$-value and minimum residual sum is given by the expression (1), whereas for nonpolar molecules the predictor with the highest correlation is given by (6). The second predictor $x_2$ that maximizes the $R^2$-value in combination with $x_1$ is given for polar (2) and for nonpolar molecules (7). Furthermore the sensitivity of the $R^2$-value with respect to small deviations in the exponents $u$ and $\nu$ is illustrated for some selected cases. For polar molecules the predictor (3) is compared to (1), and (4) is compared to (2), whereas for nonpolar molecules the predictor (8) is compared to (6) and (9) is compared to (7). The relative electric strength $E_r$ seems to be more robust against small deviations of the exponents than $T_B$ (see table 10.2). Hence, the exponents $u$ and $\nu$ are sufficiently described by one decimal digit in the case of $E_r$, whereas for $T_B$ two digits are necessary. Table 10.1 also contains the $R^2$-values of the predictor $\varepsilon_i^v \alpha^{3/2}$ suggested by [Bra82] for polar (5), nonpolar (10) and all molecules (11), as well as the $R^2$-values of the simple predictors $m$ (12) and $N_e$ (13).

The best regression for $E_r$, using equation (2), is presented in
Table 10.1.: $R^2$-values for single and multiple regression of $E_r$ with various predictor variables.

<table>
<thead>
<tr>
<th>No.</th>
<th>Predictor variables</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polar</td>
<td>$x_1 = \mu^{0.3} N_e^{1.3}$</td>
<td>0.58</td>
</tr>
<tr>
<td>(1)</td>
<td>$x_1 = \mu^{0.3} N_e^{1.3}, x_2 = \alpha^{0.6} \varepsilon_i^{2.8}$</td>
<td>0.71</td>
</tr>
<tr>
<td>(2)</td>
<td>$x_1 = \mu^{1/2} N_e^{3/2}$</td>
<td>0.56</td>
</tr>
<tr>
<td>(3)</td>
<td>$x_1 = \mu^{1/2} N_e^{3/2}, x_2 = \alpha^{1/2} \varepsilon_i^3$</td>
<td>0.70</td>
</tr>
<tr>
<td>(4)</td>
<td>$x_1 = \varepsilon_i^3 \alpha^{3/2}$</td>
<td>0.34</td>
</tr>
<tr>
<td>Nonpolar</td>
<td>$x_1 = \alpha^{1.5} \varepsilon_i^{1.7}$</td>
<td>0.85</td>
</tr>
<tr>
<td>(6)</td>
<td>$x_1 = \alpha^{1.5} \varepsilon_i^{1.7}, x_2 = \alpha^{6.5}</td>
<td>\varepsilon_a^v - \varepsilon_a^a</td>
</tr>
<tr>
<td>(7)</td>
<td>$x_1 = \alpha^{3/2} \varepsilon_i^{a3/2}$</td>
<td>0.85</td>
</tr>
<tr>
<td>(8)</td>
<td>$x_1 = \alpha^{3/2} \varepsilon_i^{a3/2}, x_2 = \alpha^{13/2}</td>
<td>\varepsilon_a^v - \varepsilon_a^a</td>
</tr>
<tr>
<td>(9)</td>
<td>$x_1 = \varepsilon_i^v \alpha^{3/2}$</td>
<td>0.83</td>
</tr>
<tr>
<td>All molecules</td>
<td>$x_1 = \varepsilon_i^v \alpha^{3/2}$</td>
<td>0.48</td>
</tr>
<tr>
<td>(11)</td>
<td>$x_1 = m$</td>
<td>0.48</td>
</tr>
<tr>
<td>(12)</td>
<td>$x_1 = N_e$</td>
<td>0.50</td>
</tr>
</tbody>
</table>
Figure 10.2 for (a) 48 polar and (b) 19 nonpolar molecules. The predicted $E_r$ of the polar molecules with the predictors (4) of table 10.1 and vector of coefficients $(p_0, p_1, p_2) = (-1.05, 3.8 \cdot 10^{-3}, 5.6 \cdot 10^{-4})$ resulted in $R^2 = 0.71$ and a standard deviation $\sigma = 0.35$ with respect to the measured values. Outliers were identified outside the $2\sigma$-region, and $\text{S}_2\text{Cl}_2$ was the only one. For the nonpolar molecules the predictors (9) and the vector of coefficients $(q_0, q_1, q_2) = (1.73 \cdot 10^{-2}, 1.2 \cdot 10^{-3}, -6.51 \cdot 10^{-8})$ yields $R^2 = 0.92$ and $\sigma = 0.18$. Here, the outliers are $\text{c-C}_6\text{F}_6$ and $\text{CCl}_4$. The predicted $E_r$ of SF$_6$ is in good agreement with its measure value.

**Regression on Boiling point**

Exactly the same method as for $E_r$ was applied to the boiling point $T_B$. The results for various predictor variables are presented in table 10.2. The predictors with maximum $R^2$-value are given by (1) for polar and by (6) for nonpolar molecules, whereas the multiple regression results in (2) for polar and (7) for nonpolar molecules. The vector of coefficients is $(p_0, p_1, p_2) = (3.37, 0.27, -2.83) \cdot 10^3$ for polar and $(q_0, q_1, q_2) = (-174.73, 232.15, -12.22)$ for nonpolar molecules. In Figure 10.3 the results of the multiple regressions of $T_B$ for (a) 48 polar and (b) 17 nonpolar molecules are shown. The measured values of $T_B$ show correlation of $R^2 = 0.69$ and $\sigma = 28$ K for polar molecules. Outliers are: CO, CHClF$_2$ and CH$_3$CN. Nonpolar molecules show $R^2 = 0.95$ and $\sigma = 20$ K, with the single outlier CO$_2$.

**10.1.4. Discussion**

The detailed discussion of the deviations between measured and calculated descriptors for individual molecules is not within the scope of this thesis. However, it should be pointed out, that calculations of the electronic ground state of the molecules were performed without rotational or vibrational excitations, whereas most of the experiments deal with thermal gas samples. The temperature may affect
Figure 10.2.: Measured electric strength $E_r$ relative to SF$_6$ vs predicted $E_r$ for (a) 48 polar and (b) 19 nonpolar molecules (circles). Outlier molecules are A: S$_2$Cl$_2$, B: c-C$_6$F$_6$ and C: CCl$_4$. D: SF$_6$ is no outlier. For polar molecules the coefficients for the regression with maximum $R^2$ are $p_0 = -1.05, p_1 = 3.8 \cdot 10^{-3}$ and $p_2 = 5.6 \cdot 10^{-4}$ with the predictor variables (2) of table 10.1. For nonpolar molecules the coefficients are $q_0 = 1.73 \cdot 10^{-2}, q_1 = 1.2 \cdot 10^{-3}$ and $q_2 = -6.51 \cdot 10^{-8}$ with the predictor variables (5) of table 10.1. The solid line ($y = x$) corresponds to perfect correlation.
Table 10.2.: $R^2$-values for single and multiple regression of $T_B$ with various predictor variables.

<table>
<thead>
<tr>
<th>No.</th>
<th>Predictor variables</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Polar</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1)</td>
<td>$x_1 = \alpha^{0.23} \mu^{0.04}$</td>
<td>0.53</td>
</tr>
<tr>
<td>(2)</td>
<td>$x_1 = \alpha^{0.23} \mu^{0.04}$, $x_2 = \varepsilon^{a 0.07} m^{0.01}$</td>
<td>0.69</td>
</tr>
<tr>
<td>(3)</td>
<td>$x_1 = \alpha^{1.4}$</td>
<td>0.45</td>
</tr>
<tr>
<td>(4)</td>
<td>$x_1 = \alpha^{1.4}$, $x_2 = \varepsilon^{a 0.1}$</td>
<td>0.54</td>
</tr>
<tr>
<td>(5)</td>
<td>$x_1 = \varepsilon^{y} \alpha$</td>
<td>0.34</td>
</tr>
<tr>
<td><strong>Nonpolar</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(6)</td>
<td>$x_1 = \alpha^{0.36}</td>
<td>\varepsilon^{y}_i</td>
</tr>
<tr>
<td>(7)</td>
<td>$x_1 = \alpha^{0.36}</td>
<td>\varepsilon^{y}_i</td>
</tr>
<tr>
<td>(8)</td>
<td>$x_1 = \alpha^{1/3}$</td>
<td>0.92</td>
</tr>
<tr>
<td>(9)</td>
<td>$x_1 = \alpha^{1/3}$, $x_2 = \alpha^{3/4}</td>
<td>\varepsilon^{y}_i - \varepsilon^{a}_i</td>
</tr>
<tr>
<td>(10)</td>
<td>$x_1 = \varepsilon^{y}_i \alpha$</td>
<td>0.86</td>
</tr>
<tr>
<td><strong>All molecules</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(11)</td>
<td>$x_1 = \varepsilon^{y}_i \alpha$</td>
<td>0.52</td>
</tr>
<tr>
<td>(12)</td>
<td>$x_1 = m$</td>
<td>0.31</td>
</tr>
<tr>
<td>(13)</td>
<td>$x_1 = N_e$</td>
<td>0.32</td>
</tr>
</tbody>
</table>
Figure 10.3.: Measured boiling point $T_B$ vs predicted $T_B$ for (a) 48 polar and (b) 17 nonpolar molecules (circles). Outlier molecules are A: CO, B: CHClF$_2$, C: CH$_3$CN and D: CO$_2$. For polar molecules the coefficients for the regression with maximum $R^2$ are $(p_0, p_1, p_2) = (3.37, 0.27, -2.83) \cdot 10^3$ with the predictor variables (2) of Table 10.2. For nonpolar molecules the coefficients are $(q_0, q_1, q_2) = (-174.73, 232.15, -12.22)$ with the predictor variables (7) of Table 10.2. The solid line ($y = x$) corresponds to perfect correlation.
the measured ionization energy of the molecule, which is sensitive to the population of excited vibrational states. Quantities as $\mu$ or $\alpha$ are not strongly affected by the temperature [Kon07], mainly because the oscillatory deviation of $\mu$ or $\alpha$ during the vibration is averaged out. Therefore, the standard deviation $\sigma$ of the calculated $\varepsilon_i^V$ with respect to the measured $\varepsilon_i^V$ is larger than in the case of $\mu$ or $\alpha$, as shown in Section 10.1.3. Qualitatively, the static properties $\mu$ and $\alpha$ show better agreement with experimental data than $\varepsilon_i^V$ or $\varepsilon_a^V$ (see tables A.1 and A.2). The latter are determined experimentally from dynamical processes (e.g. photoionization) which are often accompanied by different types of excitations or even dissociation processes of the molecule. Hence, the measured value of $\varepsilon_i^V$ is often higher than the calculated value, as shown in Figure 10.1(b).

The predictors present a distinct improvement to those of previous works, as shown in table 10.2. The splitting of the species into the two groups of polar and nonpolar molecules is an important step towards predictors that show high correlations with the ES. Especially for nonpolar gases strong correlations are observed of certain predictors to $E_r$ and $T_B$, as illustrated in table 10.1 and table 10.2. Without the distinction between polar and nonpolar species the predictor of [Bra82] yields the unsatisfying correlation with $R^2 = 0.48$, whereas the simple quantities $N_e$ and $m$ achieve nearly the same $R^2$-value. Reference [Meu04] suggests the integrated optical absorption spectrum as a predictor for the ES. It yields $R^2 = 0.726$ for their set of 43 dielectric gases, which is a very good correlation for a single descriptor.

Qualitatively the dependency of the ES on certain descriptors can be related to the scattering potential of electrons on a target molecule. The attractive part of the scattering potential is proportional to $\alpha$ and $\mu$. In the first-order Born approximation the elastic cross section is proportional to the squared Fourier transform of the scattering potential. Therefore, high values of $\alpha$ and $\mu$ increase the rate of elastic collisions, and thus increase the ES. At the same time the correlation between $\alpha$ and $N_e$ or between $\alpha$ and $m$ is strong, since
$\alpha$ increases with the number of electrons of the molecule. Quantum mechanically $\alpha$ is the second-rank molecular property tensor in the second order energy correction (quadratic Stark shift) to the ground state of a molecule in an external static electric field. In this picture $\alpha$ is given as a sum over all possible dipole transitions normalized by the energy differences between the corresponding electronic states [Lan03]. Here the ionization energy and the HOLUM explicitly determine the lower and upper bound of $\alpha$, and therefore may affect the scattering potential and thus the ES. The second predictor (4) for polar molecules indeed depends on $\varepsilon_1^a$, which also determines the energy loss of a highly energetic electron by a single ionizing collision event. For small electron-molecule distances the scattering potential is dominated by the strongly repulsive Coulomb interaction between incident electron and target electrons of the molecule. Thus, the exchange interaction will increase with the number of electrons in a molecule. The increase of the ES with $\alpha$, $\mu$ and $N_e$ is confirmed by the regression analysis (see table 10.1).

In gases with high ES electron attachment plays an important role. In general, the total attachment rate corresponds to the sum of different non-dissociative and dissociative attachment processes. All these processes are mainly affected by the scattering potential of electrons on a target molecule. Thus, attachment can be related to the same descriptors as for elastic collisions, namely $\alpha$, $\mu$ and $N_e$. In addition, the wave functions of all transient and product species determine the transition rates for attachment processes. Therefore, one may expect a dependence of the ES on energy differences between transient and product states, e.g. electron affinities or molecular dissociation energies. Direct correlation between $\varepsilon_{a}^y$ or $\varepsilon_{a}^a$ and the ES are not observed. However, for increasing differences between vertical and adiabatic electron affinities $|\varepsilon_{a}^y - \varepsilon_{a}^a|$, a decrease of the ES is found, as can be seen from expression (9) in Table 10.1 (note the negative coefficient $q_2$). For high values of $|\varepsilon_{a}^y - \varepsilon_{a}^a|$, the attachment rate might suffer from decreasing Franck-Condon factors for the vertical transition from the neutral ground state to the
excited vibrational state of the anion. In addition, in the case of an attachment event the produced anion will be highly excited and will then probably de-excite by the release of the attached electron after a short time period, resulting in a low ES.

10.2. Screening of compounds with low global warming potential

This section is based on the published articles [Rab15a].

Kazakov et al. identified a set of 1234 candidate refrigerant fluids by means of virtual screening from the PubChem database of the National Institute of Health [Kaz12, Bol08]. The environmental and safety criteria applied by the authors to this large number of molecules were: low GWP, low LFL (lower flammability limit), and filters for toxicity and chemical stability. In this section, the remaining 1234 molecules are investigated by the methods introduced in section 10.1.2 to estimate the electric strength (ES) and the boiling point ($T_B$) of these compounds.

10.2.1. Filtering methods based on environmental characteristics

It is attempted to calculate the ES of only environmentally friendly and safe molecules. To avoid unnecessary computation of molecules that may reveal good insulation properties but are harmful to health or environment, the starting point of the present gas screening is, instead of the entire library of the PubChem database, only the set of molecules that are the filtering results from Kazakov et al. [Kaz12]: The authors limit the molecular size to maximum 15 atoms and allow only compositions of the elements: C, H, F, Cl, Br, N and S. Further, filters for toxicity and stability were based on functional groups. The critical temperature $T_c$ of chemicals used as refrigerant fluids should be in the range of $300 \text{ K} < T_c < 550 \text{ K}$, due to technical
aspects described in [Kaz12]. The lower flammability was limited to LFL > 0.1 kgm$^{-3}$. The chosen LFL is the boundary value of Class 2 flammability in the ASHRAE refrigerant classification standard [ANS10], which corresponds to a moderate [Kaz12] flammable compound. For the estimation of the GWP the authors calculated two properties of a compound, the atmospheric lifetime ($\tau$) and the radiative efficiency (RE) [Kaz12]. The authors selected the PM6 [Ste07] semiempirical method for computing vibrational frequencies and IR intensities, providing in comparison to other semiempirical methods more consistent results for the RE. Even though the computationally more expensive DFT methods are in better agreement with experimental RE data, the accuracy of the PM6 method is still reasonable for screening purposes. To obtain RE, the authors calibrated the semiempirical calculations by a uniform vibrational frequency factor, based on a comparison between the predicted data and a given experimental data set. The GWP was evaluated over a time horizon of 100 years assuming an exponential decay for the time evolution of the gas in the atmosphere with a rate of $1/\tau$. Here, the decay mechanism accounts for compound removal via reactions with OH only. The rate coefficient for this reaction was calculated by means of group-contribution method [Kwo95]. Subsequently, the lifetimes were estimated as the inverse reaction rate coefficient times an empirical parameter which was determined by comparison with reported lifetime data. Chemical reactions with atmospheric compounds other than OH as well as loss mechanisms such as ultraviolet photolysis, rainout or wet deposition were not considered by the authors. The calculations for the lifetimes and RE were performed with the Gaussian 09 package [14][Fri10].

The constraint for the GWP was set to GWP < 200. This value is based on the current policy outlook for refrigerants [Mas10]. For the remaining set of molecules the GWP is mainly controlled by atmospheric lifetimes, which are in the range from 0.02 years to 6 years.
### Table 10.3.: Filtering steps for the 1234 molecules with GWP < 200.

<table>
<thead>
<tr>
<th>Filter</th>
<th>constraint</th>
<th># of remaining compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_B$</td>
<td>$T_B &lt; 320 \text{ K}$</td>
<td>408</td>
</tr>
<tr>
<td>$E_r$</td>
<td>$E_r &lt; 0.5$</td>
<td>384</td>
</tr>
<tr>
<td>Pareto front</td>
<td>$\sigma = 0.35$ for $E_r$</td>
<td>141</td>
</tr>
</tbody>
</table>
| with $\sigma$-area | $\sigma = 28 \text{ K for } T_B$ | |}

#### 10.2.2. Filtering methods based on electric strength and boiling point

In a next step towards gases that are suitable for high voltage insulation constraints for the ES and $T_B$ are applied. The remaining compounds are subsequently investigated by means of Pareto efficiency in the design space with $E_r$ and $T_B$ as parameters. The reduction of the initial number of compounds by the individual steps is illustrated in table 10.3. Constraints of $E_r > 0.5$ and $T_B < 320 \text{ K}$ are chosen in agreement with the considerations given in more detail in chapter 8.3.

The Pareto efficient compounds of the remaining set with the most promising candidates are identified. Here, a Pareto efficient molecule means the “best“ option for the ES and simultaneously $T_B$: it is not possible to find a single molecule with higher ES value and at the same time lower $T_B$. The set of all Pareto efficient compounds are determined. Again, to not exclude interesting candidates all molecules in the $\sigma$-region around the Pareto frontier are incorporated. This region will be called in the following Pareto-area.

In the context of high voltage insulation a molecules GWP is commonly compared to one of the two prominent greenhouse gases: SF$_6$ or CO$_2$. On the one hand, all compounds would represent a drastic improvement to SF$_6$ in terms of environmental impact. On the other hand, in comparison to CO$_2$, there is still a high variation between 0 and 200. Hence, to have an overview of the different environmental impacts of the remaining compounds they are sub-
divided into four different groups according to their GWP: \( \text{GWP} < 1, 1 < \text{GWP} < 10, 10 < \text{GWP} < 100 \) and \( 100 < \text{GWP} < 200 \).

### 10.2.3. Results

Figure 10.4(a) shows the results for ES and \( T_B \) for the investigated compounds. The filtering methods described in section 10.2.1 and 10.2.2 result in 384 compounds. The constraints for the ES and \( T_B \) given in table 10.3 result in 384 compounds. In figure 10.4(b) the Pareto frontier of the remaining data is identified, created by a set of 15 molecules. Including all molecules in the \( \sigma \)-region there are 141 Pareto-compounds, which are identified as superior candidates.

These Pareto-compounds were split into four groups with respect to the GWP as described above. The results for the estimated \( T_B \) and \( E_r \) are listed in the appendix A. In addition, when available, values for \( T_B \) from the literature were given.

- **GWP < 1** (table A.3): the list contains only Fluoro-alkenes containing one or two hydrogen atoms. However, there is one exception: the Fluoroethanethiol \( \text{C}_2\text{HF}_5\text{S} \). For the latter, an ES clearly higher than \( \text{SF}_6 \) is estimated. At the same time it has a high reaction rate with OH resulting in an estimated lifetime below one day [Kaz12]. The ES of each of the four isomers of \( \text{C}_4\text{H}_2\text{F}_6 \) is around two times larger than for \( \text{SF}_6 \). The atmospheric lifetimes of the same compounds are of around two days [Kaz12]. The compound 91450 has a vapor pressure of 1.2 bar at 20°C [Syn13], whereas 52991879 has a vapor pressure of 0.6 bar at 20°C [Syn13]. Agreement is found between the calculated \( T_B \) values and values from the literature within the 1σ-uncertainty. Furthermore, table A.3 contains seven Fluoro-alkenes of the form \( \text{C}_5\text{HF}_9 \) and two isomers of \( \text{C}_5\text{H}_2\text{F}_8 \). The list contains a single Perfluoro-alkene which is the cyclic alkene \( \text{C}_5\text{F}_8 \).
Figure 10.4.: (a) estimated electric strength $E_r$ relative to SF$_6$ vs estimated boiling point $T_B$ for 1234 molecules (dots). (b) inset of upper panel: 384 remaining compounds (dots) after filtering with $T_B < 320$ K and $E_r > 0.5$. The Pareto frontier (upper dashed line) and its standard deviation (lower dashed line) confine the ideal candidate compounds, one of them being 2-C$_4$F$_8$. 
• $1 < \text{GWP} < 10$ (table A.4): the Fluoro-alkenes represent again the dominant group. Other compounds are Fluoroalkyl-sulfides $C_2F_6S$, $C_3F_8S$ and $C_4F_{10}S$, as well as the Fluoro-alcohols $C_4H_3F_7O$ and $C_4H_4F_6O$. The $T_B$ values for the compounds found in the literature agree all with the calculated values within the accuracy.

• $10 < \text{GWP} < 100$ (tables A.5 and A.6): in addition to certain Fluoro-alkenes and Fluoro-alcohols, the group of Fluoroalkyl-amines such as $C_3H_2F_7N$ or $C_3H_3F_6N$. For the compounds 2776724, 13529, 9872 and 12223 the estimated values of $T_B$ are clearly outside the $1\sigma$-uncertainty.

• $100 < \text{GWP} < 200$ (table A.7): these are the Pareto compounds with the highest GWP values. Basically, the same chemical classes as before represent the most important candidates.

For all compounds, certain trends for the ES and $T_B$ were clearly observed. The values of these quantities strongly vary with the elemental composition and the molecular structure. Certainly, for increasing number of F-atoms in a molecule the ES increases due to the higher rate of electron attachment. Furthermore, increasing number of C-atoms in a molecule increases the rate of elastic collisions, and thus the ES. The increased value of $T_B$ for larger molecules is the result of increasing van der Waals interaction. Substances of the same molecular formula but different chemical structures may reveal very different values for ES.

The initial set of 1234 compounds does not contain any perfluoro- or hydrofluoro- carbonyl compounds. The ketones and aldehydes with more than 4 carbon atoms (such as $C_5F_{10}O$ and $C_6F_{12}O$) were already filtered out by the constraint that the molecular size is limited to 15 atoms, as described in section 10.2.1.

The estimation method for $E_r$ and $T_B$, as well as the estimation methods [Kaz12] for the GWP, flammability and toxicity are subject to significant uncertainties, and outliers may exist. In general,
Table 10.4.: Safety and Risk phrases for the Pareto efficient compounds that are commercially available [Syn13].

<table>
<thead>
<tr>
<th>CID</th>
<th>Risk phrases</th>
<th>Safety phrases</th>
</tr>
</thead>
<tbody>
<tr>
<td>53395686</td>
<td></td>
<td>36/37/39-41</td>
</tr>
<tr>
<td></td>
<td>36/37/38</td>
<td>26-36</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>9.16</td>
</tr>
<tr>
<td>15914919</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2736596</td>
<td>20/22-34</td>
<td>3/7-23-24/25-26-36/37/39-45</td>
</tr>
<tr>
<td>164598</td>
<td>18</td>
<td>9-15-16-33</td>
</tr>
<tr>
<td>10154032</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
good agreement is found between the calculated $T_B$ values and values from the literature. Furthermore, not all identified substitutes meet the desired toxicity- and flammability- criteria, as shown in table 10.4. For example one identified compound is the fluorocarbon alkene perfluoroisobutene (CID = 61109), which is very toxic as mentioned in section 10.2.3. The commercially available compounds in table 10.4, which, according to safety data sheets, might fulfill basic requirements for a substitute gas are: 5708528, 91450, 11053485, 2775851, 5708514, 164598 and 13529. The latter is harmful by inhalation and if swallowed [Syn13]. For the compound 53395686 no safety data sheet was available.

**Octafluoro-2-butene $2\text{-C}_4\text{F}_8$**

One of the ideal candidates is $2\text{-C}_4\text{F}_8$ (CID=2775851). It has an estimated electric strength of 1.7 relative to $\text{SF}_6$ and an estimated boiling point of $-15^\circ\text{C}$. A reference value for the boiling point is $-1^\circ\text{C}$ [Syn13]. Its estimated atmospheric lifetime is 24 days and its radiative efficiency is 0.2477 Wm$^{-2}$ppb$^{-1}$, yielding an estimated GWP of $\sim 5$ [Kaz12]. The strong electron attachment to $2\text{-C}_4\text{F}_8$ has been already investigated previously, e.g. in [Chr79, Jia08]. For the rest of the thesis, $2\text{-C}_4\text{F}_8$ serves as an example gas. Its attachment properties will be probed and its electric strength in atmospheric gases will be calculated.
11. Monte Carlo simulation of electron transport in carrier gases

This chapter is based on the published article [Rab16a].

The code METHES for the simulation of electron transport in arbitrary gas mixtures in the presence of uniform electric fields is developed and presented. For steady-state electron transport, the publicly available program provides the transport coefficients, reaction rates and the electron energy distribution function. The program uses established Monte Carlo techniques and is compatible with the electron scattering cross section files from the open-access Plasma Data Exchange Project LXCat. The code is written in object-oriented design, allowing the tracing and visualization of the spatiotemporal evolution of electron swarms and the temporal development of the mean energy and the electron number due to attachment and/or ionization processes. The code was used to investigate space-charge effects on an avalanche and the avalanche-to-streamer transition [Rab16b] (which will not be described in this thesis). The code is tested with well-known model gases as well as the real gases argon, N$_2$, O$_2$, CF$_4$, SF$_6$ and mixtures of N$_2$ and O$_2$. The simulations in this chapter are solely performed to present and benchmark the code. In the subsequent chapters METHES is used, but partially for other carrier gases and other cross section sets.
11.1. Introduction

Electron transport in a gas subject to electric fields is crucial for various applications such as gas based radiation detectors [Bia99, Boš14], plasma processing [Chr02] and high-voltage insulation [Chr88]. Simulations support the understanding of the fundamental processes but are also technologically relevant for the design of equipment. The kinetic modeling on the basis of microscopic collision cross sections is possible either by numerically solving the Boltzmann equation for the electron distribution [Kum84, Rob86, Hag05], or by tracking the stochastic motion of the individual electrons by means of Monte Carlo simulation [Bia99, Sku68, Fra86, You94, Vah95, Duj08]. For steady-state conditions kinetic modeling can provide transport parameters and reaction rates that are the necessary input parameters for macroscopic fluid models used in low-temperature plasmas and gas discharges [Rob05].

Both Boltzmann solvers and Monte Carlo methods require the knowledge of all relevant types of electron-neutral collisions that are possible in a gas or gas mixture. The most common methods to obtain the corresponding cross sections for individual processes are ab-initio quantum theoretical calculations [Huo95], electron beam measurements [Chr84] and electron swarm experiments [Hux74]. The latter provide cross sections indirectly from transport parameters and reaction rates. The main challenge is to collect, compare and share the cross section data and decide which data set to use for a certain species. This procedure has been greatly simplified by the open-access Plasma Data Exchange Project LXCat [Pit17], which provides in addition to cross section data also transport parameters and reaction rates as a function of the reduced electric field \( E/N \), which is the ratio of the electric field strength to the gas particle number density.

Several Boltzmann solvers and Monte Carlo programs are only commercially available or are inconvenient in sense of data handling or are suffering from limited source information. The freely avail-
able Boltzmann solver BOLSIG+ [Hag05] provides a user-friendly and fast option to calculate transport parameters and reaction rates and is compatible with the cross section data from LXCat. However, BOLSIG+ is based on the two-term approximation, whose applicability has been discussed in the literature [Whi03, Pet09]. The precision of Monte Carlo methods depends, when no numerical integrations are used, mainly on the precision of the used cross sections. The disadvantage of Monte Carlo methods is the long run-time compared to Boltzmann solvers when reasonable precision is needed. A freely available Monte Carlo program is MAGBOLTZ [Bia99]. The cross sections for this program are embedded in the code and straightforward comparison with other programs such as BOLSIG+ is thus not possible. Therefore, it is often unclear whether the source of possible discrepancies between the results of BOLSIG+ and MAGBOLTZ arise from different cross section sets or from numerical approximations such as the two-term approximation. Furthermore, BOLSIG+ and MAGBOLTZ do not provide bulk transport data, whereas the distinction between flux and bulk transport parameters might be important for plasma modeling and the derivation of cross sections from measured transport data [Pet09, Bor99, Rob91].

In the following, a user-friendly Monte Carlo program is presented that calculates flux and bulk transport parameters, reaction rates and electron energy distribution functions (EEDF) for arbitrary gas mixtures. Cross section sets complying with the format of LXCat are needed as an input. Thus, cross-checking the results of e.g. BOLSIG+ and the present program is possible and confusion about different cross section inputs as a possible source of discrepancies between the results of both programs can be eliminated. The code is written object-orientated in MATLAB, allowing a single-core simulation (@ 2.5 GHz CPU) of up to $10^6$ electrons simultaneously. Furthermore, all functions are well documented so that modification or extension of the code by the user is possible. For non-steady state processes the temporal development of an electron avalanche
can be investigated in-situ and visualized in terms of electron trajectories, electron densities, electron number, mean energy and mean position.

The program is tested using the Maxwell model [Cha70] and Reid’s ramp model [Rei79]. An extensive test of the code is performed in argon over a wide $E/N$-range using various numerical settings. In order to directly compare the present results with those of BOLSIG+ and MAGBOLTZ, the mean energy, transport data and reaction rates are calculated for argon, N$_2$ and O$_2$. In addition, the code is applied for different N$_2$/O$_2$ mixtures as well as to the electron attaching gases CF$_4$ and SF$_6$.

11.2. Methods

In this chapter the methods are described for modeling electron trajectories in the presence of collisions with a background gas in a uniform electric field. Figure 11.1 gives an overview of the structure of METHES. The input data of electron-molecule collision cross sections has the form provided by the LXCat database. The class "ImportLXCat" imports the cross sections and the corresponding threshold energies for ionization and excitation processes. The details are described in section 11.2.1. Subsequently, the class "MonteCarlo" contains all methods and properties that are necessary for the Monte Carlo simulation. In section 11.2.2, the principles of determining the collision times and the collision types are briefly summarized in case of a single electron. The matrix formalism that is needed for following the trajectories of an electron ensemble is described in section 11.2.3. The treatment of the collision processes in sections 11.2.4 and 11.2.5 is followed by the description of the sample techniques that allow to extract the energy data, transport parameters and reaction rates. MATLAB has a built-in feature for documentation of classes, methods and properties. Typing e.g. "doc MonteCarlo" into the MATLAB command window gives a description of the class MonteCarlo and information on the methods and
the properties.

11.2.1. Cross sections

The relevant types of electron-neutral collisions for the Monte carlo simulation are elastic, inelastic, ionization and attachment collisions. The collision data for a specific species can be either downloaded from the LXCat database, or be constructed by the user conserving the format of LXCat. "LXCat uses the key words "elastic" and "momentum" to refer to "elastic momentum transfer" and "effective momentum transfer" cross sections, respectively. A better choice of keywords would be "elastic" and "effective", and we (comment: Pancheshnyi et al.) intend to phase in this change" [Pan12]. If the
"effective momentum transfer" cross section is given, then the code calculates the "elastic momentum transfer" cross section by subtracting all inelastic cross sections (keyword "excitation"), including ionization. This "elastic momentum transfer" cross section is then used together with the inelastic, ionization and attachment cross sections (keywords "ionization" and "attachment", respectively) for the simulation. A linear interpolation is used between the points in a table of cross section versus energy. Below the first data point and beyond the last data point, METHES assumes that the cross section is constant at the values of these data points. No differential cross sections are used by the present method.

11.2.2. Null-collision technique

The times between collisions can be determined either by the integration technique [Ito60] or the null-collision technique [Sku68]. In the present code the latter is used, which allows to choose times between collisions, without any approximation or numerical integration by the use of a constant trial collision frequency $\nu'$ that for all times must be larger than the total collision frequency

$$\nu' > \max(n\sigmaTv).$$

(11.1)

Here, $n$ is the space- and time-independent total gas number density, $v(t)$ is the electron velocity and $\sigma_T(\varepsilon)$ is the total collision cross section. For a gas mixture of $K$ components with partial fraction $k_i$ of the $i^{th}$ gas species, the total cross section is given by

$$\sigma_T = \sum_{i=1}^{K} \sum_{j=1}^{S_i} k_i \sigma_{i,j}. \tag{11.2}$$

The $i^{th}$ gas species has $S_i$ different types of collisions with the cross section $\sigma_{i,j}$ for the $j^{th}$ type, where $1 \leq j \leq S_i$.

The time between collisions depends on $\nu'$ and on the random numbers $p_c$ in the interval $[0, 1]$ and is given by

$$\Delta t = -\frac{1}{\nu'} \ln(p_c).$$

(11.3)
The time of collision events are assumed to be much smaller than the time between collisions and therefore are set to zero. The thermal energy of the background gas is neglected at this point, which is a good approximation at moderate and high $E/N$ values but is known to affect the electron transport parameters at low $E/N$ values when the kinetic energy of electron and gas molecules are of the same order of magnitude [You94].

### 11.2.3. The null-collision technique for an electron ensemble

During the time $\Delta t$ the $N_e$ electrons gain energy in the electric field $E$. The positions $\mathbf{r}$ and velocities $\mathbf{v}$ at each time are followed. In cartesian coordinates $\mathbf{r}$ and $\mathbf{v}$ are of the form

$$\begin{align*}
\mathbf{r} &= \begin{pmatrix}
    r_x^{(1)} & r_y^{(1)} & r_z^{(1)} \\
    r_x^{(2)} & r_y^{(2)} & r_z^{(2)} \\
    \vdots & \vdots & \vdots \\
    r_x^{(N_e)} & r_y^{(N_e)} & r_z^{(N_e)} 
\end{pmatrix}, \\
\mathbf{v} &= \begin{pmatrix}
    v_x^{(1)} & v_y^{(1)} & v_z^{(1)} \\
    v_x^{(2)} & v_y^{(2)} & v_z^{(2)} \\
    \vdots & \vdots & \vdots \\
    v_x^{(N_e)} & v_y^{(N_e)} & v_z^{(N_e)} 
\end{pmatrix}.
\end{align*}$$

(11.4)

For the derivation of the transport parameters, a uniform field in $z$-direction of amplitude $E_z$ is considered

$$\mathbf{E} = \begin{pmatrix}
    0 & 0 & E_z \\
    0 & 0 & E_z \\
    \vdots & \vdots & \vdots \\
    0 & 0 & E_z 
\end{pmatrix}.$$  

(11.5)

During the time $\Delta t$, the electron position $\mathbf{r}$ and velocity $\mathbf{v}$ undergo the transformation

$$\begin{align*}
\mathbf{r} &\longrightarrow \mathbf{r} + \mathbf{v} \Delta t - 0.5 e E / m_e \Delta t^2, \\
\mathbf{v} &\longrightarrow \mathbf{v} - e E / m_e \Delta t.
\end{align*}$$

(11.6)  

(11.7)
Here \( e \) and \( m_e \) are the electron charge and the electron mass.

After a period \( \Delta t \) of free motion, the decision has to be made which electron undergoes which type of collision. For the \( k^{th} \) electron the collision frequency for each process is recorded. Since the cross section for a process depends on the electron energy, the norm of \( \mathbf{v} \) is here defined as a \( N_e \times 1 \) vector \(|\mathbf{v}|\) with the entries

\[
|\mathbf{v}|_k = \sqrt{\sum_{d=x,y,z} \left( v_d^{(k)} \right)^2}.
\]  

The corresponding kinetic energies of the electrons are given in the vector \( \epsilon \) with the entries

\[
\epsilon_k = m_e |\mathbf{v}_k|^2 / 2
\]

A \( N_e \times M \) matrix is constructed, which contains the collision frequencies of all possible processes column-wise, where \( M = \sum_{i=1}^{K} S_i \). Subsequently the matrix is normalized with the collision frequency \( \nu' \), and the rows are summed up cumulatively to obtain the (column-wise) monotonically increasing Matrix \( C \), which can be expressed as

\[
C_{1\ldots N,m} = \frac{n|\mathbf{v}|}{\nu'} \sum_{i=1}^{f(m)} \sum_{j=1}^{g(i,m)} k_i \sigma_{i,j}
\]

\[
f(m) = 1 + \sum_{m'=1}^{m} \sum_{i=1}^{K} \delta_{m', \sum_{i'=1}^{i} S_{i'}}
\]

\[
g(i,m) = m + S_i - \sum_{i'=1}^{i} S_{i'}
\]

with the Kronecker-Delta \( \delta \).

Finally, a \( N_e \times 1 \) vector \( \mathbf{p} \) of random numbers with entries in the interval \([0,1]\) is introduced, which is refreshed at each time step. Each line in \( C \) is compared to the same line in \( \mathbf{p} \): if the random number is the smallest number, then the first collision process occurs. If the random number is larger than the \((m-1)^{th}\) and smaller
than the $m^{\text{th}}$ entry in the line of C, then the collision process $m$ happens. In case of the random number being the largest number no collision occurs. This is called a null-collision.

11.2.4. Conservative collisions

From the previous section it is known which electron will undergo which type of collision after the time step $\Delta t$. Here, the details are given of how conservative collisions are treated within the code. These are the collisions in which the number of electrons does not change, namely elastic and inelastic collisions. In case of a null-collision the electron velocity after the collision remains unchanged, whereas for elastic or inelastic collisions the electron is isotropically scattered. The change of direction is given by the azimuthal $\phi$ and polar angle $\theta$, which are determined by the random numbers $p_1$ and $p_2$ in the interval $[0, 1]$ via the relations

$$\phi = 2\pi p_1, \quad (11.13)$$
$$\cos(\theta) = 1 - 2p_2. \quad (11.14)$$

The energy loss due to an elastic collision with a gas particle of mass $M$ is given by

$$\Delta \varepsilon = \varepsilon \frac{2m_e}{M} (1 - \cos \theta), \quad (11.15)$$

whereas for an inelastic collision the energy-loss corresponds to the threshold energy $\varepsilon^*$ of a certain electronic, vibrational or rotational excitation

$$\Delta \varepsilon = \varepsilon^*. \quad (11.16)$$

11.2.5. Non-conservative collisions

In the present code ionization and attachment are considered as non-conservative processes, but no other electron number changing processes such as detachment or recombination. Two different ways to model non-conservative collisions are provided by the code:
• Non-fixed electron number $N_e(t)$: the electrons that are created in ionization events and annihilated during attachment events are taken into account during the simulation. In an ionization event an additional electron is created at the same position and the remaining energy is shared with a factor $0 \leq W \leq 1$, where e.g. $W = 0.5$ would correspond to equal energy sharing between the electrons. Similar to the case of conservative collisions, the direction of the velocity vector for both electrons are given by the random scattering angles from equations (11.13)-(11.14). In an attachment process the electron is simply removed from the electron ensemble. The uncertainty of the results strongly increase in case of strong attachment or ionization: for strong ionization the exponential increase of the electron number will reach the limit set by the memory resource before enough collisions are performed to extract accurate transport parameters. Similar, in the limit of strong attachment, most electrons might be attached before the steady state is reached, precluding the extraction of transport data due to a too small ensemble size.

• Fixed electron number $N_e(t) = N_e$: the number of electrons is fixed to a constant value even in case of strong ionization or attachment. The present code uses a technique that does not affect the average properties of the electron ensemble, see e.g. [Duj10]: in case of an ionization event, an electron is created and energy is shared between electrons with the factor $W$. Subsequently a random electron is removed from the ensemble in order to keep the electron number constant. Similarly, for an attachment event the electron is removed and then a random electron from the remaining ensemble is cloned in terms of position and energy. In contrast to the non-fixed method, within the fixed method the transport data can be obtained even for strong attachment or ionization.
11.2.6. Data sampling

The mean energy, electron energy distribution, transport coefficients and reaction rates are determined from the electron’s kinetic energies $\varepsilon$, positions $\mathbf{r}$, velocities $\mathbf{v}$ and the numbers of reaction events, after the electrons reached the steady-state. This time $t_0$ strongly depends on the gas species and on $E/N$ and is automatically determined for each simulation from the evolution of the electron ensemble’s mean energy, as illustrated in figure 11.2, 11.3 and 11.4: as soon as the mean energy remains beside statistical noise temporally constant, the system is considered to be in the steady-state. The most relevant parameters such as the electron energy probability function, mean energy, position and width of the electron ensemble are plotted during the simulation. The user can monitor those parameters to check if the steady-state has been reached.

**Mean energy and electron energy distribution**

The mean energy $\langle \varepsilon \rangle$ is derived by time-averaging the energies of all electron trajectories

$$\langle \varepsilon \rangle = \frac{1}{T} \frac{m_e}{2} \sum_{k=1}^{N_e} \int_{t_0}^{t_f} |\mathbf{v}_k(t)|^2 dt,$$

(11.17)

whereas the time $T$ is the sum of the travel times of all electrons between $t_0$ and the time at the end of the simulation $t_f$. The integral in equation (11.17) is analytically calculated between collisions using the right hand side of equation (11.7).

The electron energy probability function (EEPF) $p(\varepsilon)$ is derived from counting the number of electron energies within energy increments $d\varepsilon$. The code ensures no cutoff of high-energy electrons and automatically determines an upper bound for the energy until which the EEPF is sampled. The number of energy intervals, and thus indirectly the size of $d\varepsilon$, can be specified by the user. Before steady-state is reached, the program extracts the EEPF for each
Figure 11.2.: A screenshot during the METHES simulation showing selected swarm properties vs time. Settings: argon, electric field into z-direction, $E/N = 100$ Td, $p = 10^5$ Pa, energy sharing $W = 0.5$ and electron number fixed to $N_e = 10^4$. The energy and position of the initial electrons has been set to zero. Left: mean energy $\langle \varepsilon(t) \rangle$ at current point in time. After the indicated point of time $T_{sst} = t_0$ the swarm is considered to be in steady-state and the swarm data is being collected. Right: number of ionization events $N_i$ - number of attachment events $N_a$. The slope of the curve is proportional to $\nu_{eff}$, as describe by equation (11.26).
Figure 11.3.: A screenshot during the METHES simulation showing selected swarm properties vs time. Settings: argon, electric field into z-direction, $E/N = 100$ Td, $p = 10^5$ Pa, energy sharing $W = 0.5$ and electron number fixed to $N_e = 10^4$. Left: $\langle r \rangle$ in x-, y- and z- direction. The slopes of the curves are equal to $w$. Right: $\langle (r - \langle r \rangle)^2 \rangle$ in x-, y- and z- direction. The slopes of the curves are equal to $2 \cdot D$, according to equation (11.21).
<\varepsilon> = 6.7071 \text{ eV}

Figure 11.4.: A screenshot during the METHES simulation showing selected swarm properties vs time. Settings: argon, electric field into z-direction, $E/N = 100$ Td, $p = 10^5$ Pa, energy sharing $W = 0.5$ and electron number fixed to $N_e = 10^4$. The energy and position of the initial electrons has been set to zero. Left: EEPF collected from $t_0$ until current point in time. Right: electron distribution in space at current point in time.
point in time. For these "snap-shots", the noise is relatively high
due to the small number of sampling data, which corresponds to the
used electron number for the simulation. As soon as the electrons
are in steady-state, the EEPF is averaged over the interval $[t_0, t_f]$ and
the accuracy of the EEPF increases with time.

The probability function EEPF is normalized

$$\int_0^\infty p(\varepsilon) d\varepsilon = 1,$$

(11.18)

whereas the electron energy distribution function (EEDF) $f(\varepsilon)$ is
calculated by

$$f(\varepsilon) = \varepsilon^{-1/2} p(\varepsilon).$$

(11.19)

**Transport coefficients**

The bulk drift velocity $w$ and diffusion constant $D$ [Tan77]

$$w = \frac{1}{dt} \langle \mathbf{r} \rangle,$$

(11.20)

$$D = \frac{1}{2} \frac{d}{dt} \langle (\mathbf{r} - \langle \mathbf{r} \rangle)^2 \rangle,$$

(11.21)

are obtained as the coefficient estimates for a linear regression of the
swarm’s center of mass $\langle \mathbf{r} \rangle$, and of the squared width $\langle (\mathbf{r} - \langle \mathbf{r} \rangle)^2 \rangle$
respectively, versus time $t - t_0$.

The flux drift velocity $\tilde{w}$ and diffusion constant $\tilde{D}$ [Pet02]

$$\tilde{w} = \left\langle \frac{dr}{dt} \right\rangle,$$

(11.22)

$$\tilde{D} = \langle rv \rangle - \langle r \rangle \langle v \rangle.$$

(11.23)

are determined, similar as for the derivation of $\langle \varepsilon \rangle$, as average over
all electron trajectories

\[ \tilde{w} = \frac{1}{T} \sum_{k=1}^{N_e} \int_{t_0}^{t_f} v_k(t) dt, \]

\[ \tilde{D} = \sum_{k=1}^{N_e} \frac{1}{T} \int_{t_0}^{t_f} r_k(t) v_k(t) dt - \frac{1}{T} \int_{t_0}^{t_f} r_k(t) dt \cdot \frac{1}{T} \int_{t_0}^{t_f} v_k(t) dt. \] (11.24)

These equations are analytically integrated using the right hand side of equations (11.6) and (11.7).

**Reaction rates**

Reaction rates are derived by two different methods. The first one is to calculate a rate \( \nu_{i,j} \) for a process \( j \) of the species \( i \) with cross section \( \sigma_{i,j} \) by the convolution

\[ \nu_{i,j} = k_i \sqrt{\frac{2}{m_e}} \int_0^\infty \sigma_j(\varepsilon) \varepsilon f(\varepsilon) d\varepsilon. \] (11.25)

For such a numerical integration a precise EEDF is necessary with low statistical noise.

Another method to obtain a certain reaction rate is to count the events for the corresponding process. In section 11.2.5, two methods were introduced of computationally keeping the electron number \( N_e(t) \) fixed or not. If the number of electrons is fixed, \( N_e(t) = N_e(t_0) \), then the number of counts \( N_j \) of a process increases linearly in time, and the rate \( \nu_{i,j} \) can be obtained from \( N_j \) between times \( t \) and \( t_0 \) by

\[ \nu_{i,j}^{t_0,t} = \frac{N_j(t) - N_j(t_0)}{N_e(t_0)(t - t_0)}. \] (11.26)
In case of non-fixed electron number $N_e(t)$ increases exponentially and the effective ionization rate is given by

$$\nu_{t_0,t} = \frac{\log N_e(t) - \log N(t_0)}{t - t_0}. \quad (11.27)$$

The rates of the individual processes such as attachment, ionization or excitation are calculated by

$$\nu_{t_0,t}^{i,j} = \frac{N_j(t) - N_j(t_0)}{N_j(t_0)} \frac{\nu_{\text{eff}}}{e^{\nu_{\text{eff}} t} - 1}. \quad (11.28)$$

The final results for the reaction rates are the averaged rates from equations (11.26-11.28) over the time interval $[t_0, t_f]$

$$\nu_{i,j} = \langle \nu_{i,j}^{t_0,t_f} \rangle_{t_0}, \nu_{\text{eff}} = \langle \nu_{\text{eff}}^{t_0,t_f} \rangle_{t_0}. \quad (11.29)$$

### 11.3. Testing and comparison with other programs

#### 11.3.1. Model gases: Maxwell and Reid’s Ramp model

The Maxwell model [Cha70] is given by an elastic cross section $\sigma_{\text{el}}(\varepsilon)$ of the form $\sigma_{\text{el}}(\varepsilon) = 6 \cdot 10^{-20} \varepsilon^{-1/2} \text{m}^2$ ($\varepsilon$ in eV), whereas Reid’s Ramp model [Rei79] is given by a constant elastic cross section $\sigma_{\text{el}}(\varepsilon) = 6 \cdot 10^{-20} \text{m}^2$ and a linearly increasing excitation cross section $\sigma_{\text{ex}}(\varepsilon) = 10 \cdot \text{Heaviside}(\varepsilon - 0.2) \cdot 10^{-20} \text{m}^2$, with a threshold energy of 0.2 eV. The mass $M$ of the background gas is 4 atomic units and the temperature is equal to zero. The results for the mean energy $\langle \varepsilon \rangle$, drift velocity in z-direction $w_z$ and density reduced diffusion constants $ND_x$, $ND_y$ and $ND_z$ are compared, see table 11.1. The latter is always within the $3\sigma$ error of the present simulation data and the agreement is $\lesssim 0.1\%$ for the mean energy and the drift velocity, and $\lesssim 1\%$ for the diffusion constant.
Table 11.1.: A comparison of the transport parameters for the Maxwell ($E/N = 1$ Td) and Ramp model ($E/N = 12$ Td) using the present code with the results from [Nes94]. The simulations stopped after $\sim 2 \cdot 10^9$ and $\sim 2 \cdot 10^8$ real collisions for the Maxwell and the Ramp model, respectively.

<table>
<thead>
<tr>
<th></th>
<th>$\langle \varepsilon \rangle$ (eV)</th>
<th>$w_z$ ($10^3$ ms$^{-1}$)</th>
<th>$ND_{x,y}$ ($10^{24}$ m$^{-1}$ s$^{-1}$)</th>
<th>$ND_z$ ($10^{24}$ m$^{-1}$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maxwell</td>
<td>0.5058</td>
<td>4.946</td>
<td>1.663</td>
<td>1.685</td>
</tr>
<tr>
<td></td>
<td>0.5064$^a$</td>
<td>4.943$^a$</td>
<td>1.668$^a$</td>
<td>1.668$^a$</td>
</tr>
<tr>
<td>Reid</td>
<td>0.270</td>
<td>6.851</td>
<td>1.133</td>
<td>0.566</td>
</tr>
<tr>
<td></td>
<td>0.269$^b$</td>
<td>6.838$^b$</td>
<td>1.135$^b$</td>
<td>0.569$^b$</td>
</tr>
</tbody>
</table>

$^a$ Calculated values at zero temperature using the analytical expressions in [Nes94]; $^b$ Values taken from table 3 in [Nes94].

11.3.2. Benchmark data

The calculations of benchmark data were done with BOLSIG+ (version 08.2012, default settings: Number of energy intervals: 100, Grid type: Automatic, Precision $10^{-9}$, Convergence $10^{-3}$, Iterations 100). Monte Carlo simulations were done with MAGBOLTZ (version 10.0.2, setting $4 \cdot 10^8$ real collisions). Both programs provide the flux drift velocity and the flux diffusion constant for isotropic electron scattering.

For the real gases argon Ar, nitrogen N$_2$ and oxygen O$_2$ Biagi’s cross sections were chosen [LXCa]. According to the documentation of the MAGBOLTZ code the cross sections of N$_2$ and O$_2$ are equal in MAGOLBTZ-versions 10.0.2 and 8.9 and therefore direct comparison of the present results with those of BOLSIG+ and MAGBOLTZ is possible. However, for the argon cross sections used in MAGBOLTZ-version 10.0.2 the documentation states: ”update with small increase in excitation cross sections in resonance region
for s-levels and compensating increase in elastic momentum transfer cross section at the maximum (11 eV”).

Furthermore, to show the applicability of the present program for the case of gas mixtures as well as for strong attachment, simulations in N$_2$/O$_2$-mixtures with the cross section sets from before, CF$_4$ [LXCb] and SF$_6$ [LXCc] are performed. No MAGBOLTZ simulations are performed for CF$_4$ and SF$_6$, since direct comparison with the same cross section input is not possible.

### 11.3.3. Simulation settings

Different simulation settings are tested in argon, namely the treatment of non-conservative collisions in terms of fixed and non-fixed electron numbers, different electron numbers $N_e$, pressures $p$ and energy sharings $W$. The gas particle number density $N$ is deduced from the pressure $p$ and the temperature $T = 300$ K via the ideal gas law. The results for $\langle \varepsilon \rangle$, $\tilde{w}$, $N\tilde{D}_z$ and $\nu_{eff}/N$ in argon are presented in figure 11.5. For all parameters, the difference between the results of the fixed and non-fixed method are equal beside statistical noise. The standard deviation $\sigma$ of all parameters derived from the non-fixed method increases with increasing $E/N$ due to the limited statistics as mentioned in section 11.2.5. Thus, using the method of a fixed electron number seems to be valid up to high electron multiplication. This method was also verified for the case of strong attachment in CF$_4$, which is not shown here. There is no significant influence of $p$ and $N_e$ on the results, whereas the energy sharing $W$ has an significant influence on $\tilde{w}$ and $N\tilde{D}$ towards high $E/N$-values.

For the remaining simulations, the following settings were used: fixed $N_e(t) = 10^4$, $p = 10^5$ Pa, $W = 0.5$. For the calculation of rates from the EEDF according to equation (11.25) the number of energy intervals was set to 2000. For these settings, figure 11.6 displays the EEPF in argon for a low and a high $E/N$ value in comparison to the EEPF from BOLSIG+. 

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Figure 11.5.: Results in argon as a function of the reduced field $E/N$ for (a) mean electron energy $\langle \varepsilon \rangle$, (b) flux drift velocity $\tilde{w}$, (c) reduced longitudinal flux diffusion constant $N \tilde{D}_z$ and (d) effective ionization rate constant $\nu_{\text{eff}}/N$ obtained by counting. Shown are the results for 8 different numerical settings for electron number, pressure and energy sharing ($N_e, p, W$): 1 (nonfixed, $10^5, 0.5$), 2 ($10^4, 10^5, 0.5$), 3 ($10^3, 10^5, 0.5$), 4 ($10^4, 10^5, 0.5$), 5 ($10^4, 1, 0.5$), 6 ($10^4, 10^3, 0.5$), 7 ($10^4, 10^5, 0$) and 8 ($10^4, 10^5, 1$)
Figure 11.6.: Present results in pure argon for the electron energy probability function (EEPF) for $E/N = 1 \text{Td}$ and $E/N = 1000 \text{Td}$ (dashed line). Settings: fixed $N_e(t) = 10^4$, $p = 10^5 \text{ Pa}$, $W = 0.5$. BOLSIG+ (full line).

11.3.4. Accuracy

The accuracy of the simulation results increases with the number of real collisions and thus with the computation time. Figure 11.7 shows the relative error of $\langle \varepsilon \rangle$, $w$, $\tilde{w}$, $N \tilde{D}_z$, $N \tilde{D}_z$ and $\nu_{\text{eff}}$ as a function of the number of real collisions. The relative errors of $\tilde{w}$ and $N \tilde{D}_z$ are limited to $\gtrsim 0.1\%$ and $\gtrsim 1\%$ respectively, whereas bulk data, rates and mean energy become more accurate as the number of collisions increases. The accuracy of the EEDF can be cross-checked by comparing the effective ionization rates calculated by the two independent methods described in section 11.2.6.

11.3.5. Real gases: Ar, N$_2$, O$_2$ and N$_2$/O$_2$ mixtures

In this section, the results of the present simulation code are compared with those of BOLSIG+ and MAGBOLTZ for pure argon, N$_2$ and O$_2$ and N$_2$/O$_2$ mixtures with the cross section data given in section 11.3.2.

For the pure gases, the present results for the mean energy, drift velocity and effective ionization rate constant as a function of $E/N$
are presented in figure 11.8 and the results for the reduced diffusion constant are shown in figure 11.9. The energy data and transport coefficients are derived following section 11.2.6 and section 11.2.6. The effective ionization rate constant $\nu_{\text{eff}}/N$ is calculated by numerical integration of the EEDF using equation (11.25), as well as by counting ionization/attachment events and using equation (11.26). In general, good agreement was found between the present results for $\langle \varepsilon \rangle$, $\tilde{w}$ and $\nu_{\text{eff}}/N$ and the results from BOLSIG+ and MAGBOLTZ for the considered $E/N$-range, see table 11.2. The agreement for $N_2$ and $O_2$ with MAGBOLTZ is better than with BOLSIG+. The slight deviations from MAGBOLTZ results for argon might be related to the update in the cross section set as described in section 11.3.2. For the diffusion constant the agreement with BOLSIG+ is poor, whereas good agreement was found with MAGBOLTZ. The present results for $D_{x,y}$ and $D_z$ are in general smaller than the BOLSIG+ results. The inaccuracy of $D_{x,y}$ and $D_z$ calculated by means of two-term approximation is well-known [Nes86, Pet09]. Figure 11.10 shows $\tilde{w}$ and $\nu_{\text{eff}}/N$ for the $N_2/O_2$ mixtures 100/0%, 80/20%,
Figure 11.8.: Present results in pure Ar, N$_2$ and O$_2$ as a function of the reduced field $E/N$ for (a) mean electron energy $\langle \varepsilon \rangle$ (□), (b) flux drift velocity $\tilde{w}$ (△) and (c) effective ionization rate constant $\nu_{\text{eff}}/N$ obtained by counting (□) and convolution (△). BOLSIG+ results (solid line), MAGBOLTZ results (dashed line).
Figure 11.9.: Reduced flux diffusion constant $\tilde{N} \tilde{D}$ (longitudinal:$\triangleright$, transversal:+) vs reduced field $E/N$ in (a) Ar, (b) N\textsubscript{2} and (c) O\textsubscript{2}. BOLSIG+ results (solid line), MAGBOLTZ results (dashed line).
Figure 11.10.: Present results in N$_2$/O$_2$ mixtures in the ratios of 100/0%, 80/20%, 60/40%, 40/60%, 20/80% and 0/100% vs reduced field E/N for (a) flux drift velocity $\tilde{w}$ ($\triangle$) and (b) effective reaction rate constant $\nu_{\text{eff}}/N$ obtained by counting (□) and convolution ($\bigtriangleup$). BOLSIG+ results (solid line), MAGBOLTZ results (dashed line).

60/40%, 40/60%, 20/80% and 0/100%. The discrepancy between the present results and those from BOLSIG+ and MAGBOLTZ are of the same order as for the pure gases.

### 11.3.6. Strongly attaching gases: CF$_4$ and SF$_6$

For the gases CF$_4$ and SF$_6$ the mean energy, transport coefficients, effective $\nu_{\text{eff}}/N$, ionization $\nu_i/N$ and attachment rate constants $\nu_a/N$ are calculated. The cross section set used for SF$_6$ contains the effective momentum transfer cross section from which the elastic momentum transfer cross section is calculated as described in section 11.2.1.

Figure 11.11 displays METHES and BOLSIG+ results for CF$_4$. The agreement with the BOLSIG+ results is good for $\langle \varepsilon \rangle$, $\nu_{\text{eff}}/N$, $\nu_i/N$, $\nu_a/N$ and $\tilde{w}$, see also table 11.2. For the lowest $E/N$-value the present results for $\tilde{w}$ are significantly smaller than BOLSIG+.
Table 11.2.: Relative difference in \% between results from MEHTES and BOLSIG+/MAGBOLTZ for selected quantities. The listed values are associated with those data points from figure 11.8, 11.9, 11.11 and 11.12 that reveal the largest discrepancies between MEHTES and BOLSIG+ and between MEHTES and MAGBOLTZ. The numbers for SF\textsubscript{6} exclude the noisy data points from BOLSIG+ simulations.

<table>
<thead>
<tr>
<th></th>
<th>$\langle \varepsilon \rangle$</th>
<th>$\tilde{\nu}$</th>
<th>$N\tilde{D}$</th>
<th>$\nu_{\text{eff}}/N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar</td>
<td>0.4/2</td>
<td>0.1/3</td>
<td>30/5</td>
<td>0.4/7</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>5/0.5</td>
<td>1/1</td>
<td>15/3</td>
<td>7/1.5</td>
</tr>
<tr>
<td>O\textsubscript{2}</td>
<td>1/0.5</td>
<td>1/0.3</td>
<td>30/7</td>
<td>8/0.1</td>
</tr>
<tr>
<td>CF\textsubscript{4}</td>
<td>0.8/-</td>
<td>15/-</td>
<td>$&gt;100/-$</td>
<td>3/-</td>
</tr>
<tr>
<td>SF\textsubscript{6}</td>
<td>30/-</td>
<td>20/-</td>
<td>75/-</td>
<td>20/-</td>
</tr>
</tbody>
</table>

results. The present results for $N\tilde{D}$ are in general smaller compared to the BOLSIG+ results. This discrepancy is due to the limited applicability of the two-term approximation in case of a pronounced Ramsauer Townsend minimum of the elastic cross section compared to the inelastic cross sections, see e.g. [Bor99, Pet09].

Figure 11.12 shows MEHTES and BOLSIG+ results for SF\textsubscript{6}. For $E/N > 20$ Td, the results for $\langle \varepsilon \rangle$, $\tilde{\nu}$, $N\tilde{D}$ and the reaction rates agree with BOLSIG+ within the numbers given in table 11.2. For $E/N < 10$ Td, the present results for $\nu/N$ and $N\tilde{D}$ show large ($>100\%$) deviations from BOLSIG+. In addition, the ”jump” of the mean energy, transport data and $\nu_a/N$ at $E/N \approx 10$ Td is shifted to higher $E/N$-values compared to the BOLSIG+ data. For this regime, the reliability of the BOLSIG+ is questionable due to numerical noise of $\langle \varepsilon \rangle$, $N\tilde{D}$ and the reaction rates over several orders of magnitude.

For both attaching gases, flux and bulk transport data are equal in the absence of non-conservative collisions. However, when attachment becomes dominant, flux and bulk data differ strongly. This is significant for the drift velocities in CF\textsubscript{4} and SF\textsubscript{6} over the whole
Figure 11.11.: Present results in CF$_4$ as a function of the reduced field $E/N$ for (a) mean electron energy $\langle \varepsilon \rangle$ (□), (b) bulk $w$ (□) and flux $\tilde{w}$ (△) drift velocity, (c) reduced flux diffusion constant $N\tilde{D}$ (longitudinal:◁, transversal:+) and (d) effective $\nu_{\text{eff}}/N$, ionization $\nu_i/N$ and attachment rate constant $\nu_a/N$ obtained by counting (□) and convolution (△). BOLSIG+ results (solid line).
Figure 11.12.: Present results in SF$_6$ as a function of the reduced field $E/N$ for (a) mean electron energy $\langle \varepsilon \rangle$ (□), (b) bulk $w$ (□) and flux $\tilde{w}$ (△) drift velocity, (c) reduced flux diffusion constant $N\tilde{D}$ (longitudinal:◁, transversal:+) and (d) ionization $\nu_i/N$ and attachment rate constant $\nu_a/N$ obtained by convolution (△). BOLSIG+ results (solid line).
11.3.7. METHES download

METHES is available for download from the CPC (Computer Physics Communication) database (http://dx.doi.org/10.1016/j.cpc.2016.02.022) as well as from the LXCat database (lxcat.net/download/METHES/). The download statistics obtained via Google Analytics from the LXCat data exchange site is shown in 11.13.
Figure 11.13.: Screenshot from Google Analytics of the LXCat data exchange site. The METHES page has been viewed over 6000 times in the period between January 2015 and March 2017.
12. Obtaining attachment cross sections from swarm parameters

This chapter is partially based on the published article [Rab15b].

Electron attachment to strongly attaching gases as a function of the electron energy is investigated. The total electron attachment cross section of this electronegative sample gas is determined from the effective ionization rate constant $\nu_{\text{eff}}/N$ measured in a swarm experiment using the buffer gases $\text{N}_2$ and $\text{CO}_2$ with minor proportions ($\lesssim 0.8\%$) of the sample gas $\text{SF}_6$, $\text{C}_3\text{F}_8$ and $\text{2-C}_4\text{F}_8$. The measured rate constants $\nu_{\text{eff}}/N$ for varying reduced electric field strengths $E/N$ are unfolded from the electron energy distribution (derived by both BOLSIG$+$ and METHES) of the buffer gases. Different unfolding routines for so-called ill-posed problems are tested to find robust solutions for the attachment cross section. Finally, Tikhonov regularization, which is a well defined algorithm for discrete linear inversion problems, is proposed as most efficient. The method gives rise to an approximate and clearly defined solution for the attachment cross section, and it is described in detail.

12.1. Introduction

Electron collision cross sections are required for modeling processes in low temperature plasmas on the basis of the kinetic gas theory [Rob08]. The ability of electronegative gases to attach free electrons is crucial for various industrial applications such as semiconductor
manufacturing or high voltage gas insulation [Chr02]. Thus, it is particularly instructive to monitor a molecule’s attachment cross section as a function of the incident electron energy. Several methods have been introduced to obtain attachment cross sections and also other types of electron collision cross sections. The most common methods to obtain elastic, excitation or ionization cross sections are ab-initio quantum theoretical calculations [Huo95], electron beam measurements [Chr84] and electron swarm experiments [Hux74].

In the context of swarm experiments, with exquisite control over electrical field strength, density, temperature and mixing ratio of a gas mixture, assessing cross sections is enabled by measuring the swarm parameters [Pet09]. The extraction of a full cross section set derived from swarm measurements requires numerical methods for solving the Boltzmann equation or Monte Carlo techniques to simulate the motion of electrons. Furthermore, numerical optimization techniques are necessary to adapt an initial guess of cross sections over a wide energy range. In general, these iterative procedures have to deal with the non-uniqueness problem of the obtained cross section sets [Hux74, Pet09].

The attachment cross section $\sigma_a$ of a strongly attaching gas can be probed by mixing it in small proportions to a buffer gas, such as Ar, N$_2$ or CO$_2$, with well known collision cross sections. Then the derivation of $\sigma_a$ is decoupled from the entire cross section set of the sample gas, assuming that the mixture is undisturbed by the present sample gas in terms of electron energy distribution. Some methods derive $\sigma_a$ by means of algorithms, which minimize the sum of the least squares between calculated and measured effective ionization rate constants $\nu_{\text{eff}}/N$ by iteratively adapting $\sigma_a$ towards a positive solution. Such a method “requires a considerable degree of experience and discernment” [Chr71]. Typically, the solution for $\sigma_a$ depends on its initial guess as well as on the exact form of the iteration algorithm. Furthermore, the statistical uncertainty of the experimental data affects the outcome.
Extracting cross sections from swarm parameters could be based on a transparent method which gives rise to an approximated and well-defined solution for $\sigma_a$. Besides, before trying to unfold the cross section, the actual existence of a usable solution should be checked. Subsequently, if necessary the problem must be modified either experimentally, by e.g. extending the range of measurements, or mathematically by introducing constraints on the solution for the cross section. The latter may also be independent of an initial guess, iteration procedures and measurement noise to make comparison between different data sources possible. Similar to the problem of determining $\sigma_a$ from observed rate constants $\nu_\text{eff}/N$, in other fields of science and engineering, such as e.g. medical imaging or geophysical prospecting, so called “ill-posed” problems arise when computing a source that gives rise to some observed data [Par77, Gon87, Nat86, Col13, Cra86].

In the following sections, the well known linear inversion methods for ill-posed problems is adapted to the problem of determining the source $\sigma_a$ from the experimentally observed data $\nu_\text{eff}/N$. The linear inversion technique is applied to measurements with SF$_6$ as well as C$_3$F$_8$ in the buffer gases N$_2$ and CO$_2$, and the results for $\sigma_a$ are compared with literature data. The limits of this method for unfolding the attachment cross section $\sigma_a$ from the rate constants $\nu_\text{eff}/N$ will be discussed. Furthermore, the linear inversion method is generally proposed as a simple tool for determining initial guess cross sections for numerical optimization techniques that determine cross section sets from swarm data.

12.2. Theory

For an equilibrated electron swarm in a binary gas mixture with mixing ratio $k$, the effective ionization rate constant $\nu_\text{eff}/N$ is described by [Hag05]:
\[ \nu_{\text{eff}}/N = (1 - k)\nu_{\text{eff}}^B/N + k\sqrt{\frac{2}{m_e}} \int_0^\infty (\sigma_i - \sigma_a)\varepsilon f d\varepsilon. \] (12.1)

Here \( m_e \) is the electron mass, \( N \) is the number density of the gas. The effective ionization rate constant of the pure buffer gas is \( \nu_{\text{eff}}^B/N \), whereas \( \sigma_i(\varepsilon) \) and \( \sigma_a(\varepsilon) \) are the ionization and attachment cross sections of the sample gas. The electron energy distribution function (EEDF) of the gas mixture is a function of the reduced electric field \( E/N \), where \( E \) is the electrical field strength. The EEDF \( f(E/N, \varepsilon) \) is normalized to

\[ \int_0^\infty \sqrt{\varepsilon} f d\varepsilon = 1. \] (12.2)

Equation (12.1) can be written in the form of a Fredholm integral equation of the first kind:

\[ \int_0^\infty K(E/N, \varepsilon)\sigma_a(\varepsilon)d\varepsilon = g(E/N), \] (12.3)

where the Kernel \( K \) is given by the EEDF of the mixture

\[ K(E/N, \varepsilon) = \varepsilon f(E/N, \varepsilon). \] (12.4)

The right-hand side additionally depends on the measured values of \( \nu_{\text{eff}}/N \) and \( \nu_{\text{eff}}^B/N \) as well as the ionization cross section \( \sigma_i \):

\[ g(E/N) = \int_0^\infty \sigma_i\varepsilon f d\varepsilon + \frac{1}{k} \sqrt{\frac{m_e}{2}} \{(1 - k)\nu_{\text{eff}}^B/N - \nu_{\text{eff}}/N\} \] (12.5)

The Kernel \( K \) linearly relates the cross section \( \sigma_a \) with the right-hand side \( g \). Furthermore, it is a square integrable function, according to equation (12.2) and \( f(\varepsilon \to \infty) = 0 \). This is an important requirement for the linear inversion methods described in section
12.3.5. If $\nu_{\text{eff}}/N$ and $\nu_{\text{eff}}^B/N$ are measured in the experiment, and the EEDF as well as the cross section $\sigma_i$ are given, then the functions $K$ and $g$ are known. Then, the integral equation (12.3) corresponds to the classical example of an ill-posed problem [Gro84]. Its discretization into a matrix problem leads to a system of linear algebraic equations, for which standard routines for the analysis of discrete ill-posed problems can be applied [Han10, Han94].

12.3. Methods

12.3.1. Pulsed Townsend method

The experimental method and evaluation procedure applied in this chapter have been described elsewhere [Dah12, Dah13, Cha16b]. A short laser pulse of 1.5 ns FWHM releases approximately $10^6 - 10^7$ start electrons from a photo cathode into the gas volume. The electron swarm drifts in a uniform electric field through a gap between two Rogowski type electrodes. The gap distance is controlled and in the range of 9 to 18 mm and the applied voltage is up to 40 kV. The base pressure is $< 10^{-8}$ mbar and the measurements are typically taken between 20-100 mbar and at room temperature. The resulting reduced electrical field strength is typically in the range of 20 - 200 Td, where the upper value is determined by the critical electric field strength that only can be exceeded by a few percent to avoid a breakdown. The displacement current of the electron swarm drifting in the gas gap is recorded and evaluated. From an exponential fit to this current the effective ionization rate $\nu_{\text{eff}}$ is determined, corresponding to the exponential growth/decrease of the electron number in the swarm. Electron attachment to SF$_6$, C$_3$F$_8$ and 2-C$_4$F$_8$ in terms of reaction rates was already investigated previously [Dah13, Cha15]. The rate constant $\nu_{\text{eff}}/N$ is measured for different reduced field strengths $E/N$, given in Townsend (1 Td = $10^{-21}$Vm$^2$).
12.3.2. Obtaining the kernel \( K(E/N, \varepsilon) \)

For solving equation (12.3), the Kernel \( K \) and thus the EEDFs of the gas mixtures are needed, which is in general not known due to non-existing cross section data of the sample gas. Nevertheless, for a buffer gas the change in the electron energy distribution due to a small amount of the sample gas is supposed to be small [Ble85, Bor96]. This assumption was tested by means of the Boltzmann solver BOLSIG+ (version 08.2012) using the two-term approximation [Hag05]. Therefore, \( \nu_{\text{eff}}/N \) was calculated for a gas mixture (0.6% of \( \text{C}_3\text{F}_8 \) in \( \text{Ar} \), \( \text{N}_2 \) and \( \text{CO}_2 \)) according to equation (12.1) using both, the exact EEDF of the mixture and an approximated one (given by the EEDF of the pure buffer gas). The cross section sets from SIGLO database (www.lxcat.net, retrieved on December 9, 2013) for \( \text{N}_2 \) and Phelps database (www.lxcat.net, retrieved on July 5, 2014) for \( \text{CO}_2 \) were used. For the buffer gases \( \text{N}_2 \) and \( \text{CO}_2 \), both results yield the same values for \( \nu_{\text{eff}}/N \). However, for \( \text{Ar} \) strong influence of the sample gas on the electron energy distribution and thus on \( \nu_{\text{eff}}/N \) is detected. For high \( E/N \)-values, the change of \( \nu_{\text{eff}}/N \) due to adding a sample gas might be even dominated by the change of the EEDF and not by the attachment and ionization cross sections of the sample gas. Finally, the EEDF of the carrier gases, and thus \( K(E/N, \varepsilon) \), are calculated using METHES and BOLSIG+.

12.3.3. Obtaining the right-hand side \( g(E/N) \)

In order to obtain the first term of equation (12.5), the EEDF’s \( f(E/N, \varepsilon) \) from section 12.3.2 and reference data for the ionization cross section \( \sigma_i \) for \( \text{SF}_6 \) [Phe88], \( \text{C}_3\text{F}_8 \) [Chr98] and \( 2-\text{C}_4\text{F}_8 \) [Jia08] are used. The second term is calculated from the measured \( \nu_{\text{eff}}/N \)- and \( \nu_{\text{eff}}^B/N \)-data (see section 12.3.1), which is fitted with smoothing spline to evaluate the fit in 1 Td steps.
12.3.4. Discretization

The discretization of equation (12.3) into a linear system of equations is necessary to numerically unfold $\sigma_a$ on a computer. Two different discretization methods, namely quadrature and expansion methods, are generally used to find approximated solutions for the continuous function $\sigma_a$. Expansion methods approximate $\sigma_a$ with a set of basis functions, which should be chosen in such a way that they provide a good solution. The subsequent linear inversion would then return the corresponding expansion coefficients. In this thesis the quadrature method is chosen, which evaluates approximated function values at selected abscissas. After the discretization, the linear system of equations is given by $n$ equations and $m$ unknowns, where $n$ is the number of all used EEDF’s and $m$ is the length of the solution vector $\sigma_a$, which is given by the number of selected abscissas introduced by the quadrature method.

Increasing the number of linear independent algebraic equations for the inversion procedure reduces the noise of the solution for $\sigma_a$. Thus, to increase the rank of this Matrix problem, it is instructive to use as many different EEDF’s as possible. In the experiment, this would correspond to measuring $\nu_{\text{eff}}/N$ over a wide $E/N$-range for a high variety of buffer gas species.

12.3.5. Linear inversion

The matrix inversion of the discretized form of equation (12.3) yields a "naive" solution that is very sensitive to perturbation of the right-hand side, which is in the present case determined by the measurement error of $\nu_{\text{eff}}/N$ as well as uncertainties in the EEDF. Therefore, to deal with such noise problem, regularization methods that provide stable solution are needed. This fact is mathematically well defined by the so-called discrete Picard condition [Han94].

The superior tool for linear inversion is the singular value decomposition (SVD), which is needed for all regularization methods. Common methods are truncated SVD (TSVD), damped SVD
Figure 12.1.: The L-curve for Tikhonov regularization in case of SF₆: logarithmic plot of the solution norm $\|\sigma_a\|_2$ vs. the residual norm $\|g - \int K\sigma_a\|_2$ (full line). The regularization parameter $\lambda$ is tuned from low (upper left) to high (lower right) values, with the regularized $\lambda$-parameter at the corner (dashed line).
(DSVD), compact generalized SVD (CGSVD), Tikhonov regularization or Maximum Entropy regularization, which are all implemented in Matlab Regularization Tools (Version 4.1) [Han94].

These methods are applied to different measurements involving different kinds of gas compounds, and the Tikhonov regularization is identified as the most convenient method for obtaining attachment cross sections. This method introduces a regularization parameter \( \lambda \) that controls the large noise components of the solution by minimizing the functional

\[
\left\| g(E/N) - \int_0^\infty K(E/N, \varepsilon) \sigma_a(\varepsilon) d\varepsilon \right\|_2^2 + \lambda^2 \left\| \sigma_a(\varepsilon) \right\|_2^2 \longrightarrow 0. \tag{12.6}
\]

Depending on the value of \( \lambda \), the solution will either be dominated, for small \( \lambda \)-values, by the perturbations or will be oversmoothed for large \( \lambda \)-values. To obtain the regularized solution \( \sigma_a \) for a well defined parameter \( \lambda \), the L-curve method is used [Han94]. It finds a balance between the two norms \( \| \sigma_a \|_2 \) and \( \| g - \int_0^\infty K \sigma_a \|_2 \), which occur in equation (12.6). Graphically, the L-curve identifies the corner when plotting these norms, as shown in figure 12.1 for the case of cross section unfolding in SF\(_6\), see section 12.4.1.

If the solution has negative components, \( \lambda \) is increased until the absolute value of the minimum is below 5% of the peak value of the solution. All positive and negative values of \( \sigma_a \) within this 5% tolerance are identified as noise and are set to zero.

### 12.4. Results

The attachment cross sections of the two sample gases SF\(_6\), C\(_3\)F\(_8\) and 2-C\(_4\)F\(_8\) were unfolded from the measurements summarized in table 12.1. The electron current evaluation procedures are given in section 12.3.1. For C\(_3\)F\(_8\), the final values for \( \nu_{\text{eff}}/N \) and \( \nu_{\text{eff}}^B/N \) are obtained by linear regression over the gas number density \( N \). For SF\(_6\) and 2-C\(_4\)F\(_8\), \( \nu_{\text{eff}}/N \) was calculated as the mean value of the rates measured at the pressures given in table 12.1. The sources of
Table 12.1.: Overview of the measurements that were used to determine the attachment cross sections $\sigma_a$.

<table>
<thead>
<tr>
<th></th>
<th>% in $\text{N}_2$</th>
<th>$E/N$ (Td)</th>
<th>% in $\text{CO}_2$</th>
<th>$E/N$ (Td)</th>
<th>pressures (kPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SF}_6$</td>
<td>0.25</td>
<td>63-172</td>
<td>0.01</td>
<td>11-94</td>
<td>$\sim 2 - 8$</td>
</tr>
<tr>
<td></td>
<td>0.62</td>
<td>127-178</td>
<td>0.05</td>
<td>30-99</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_3\text{F}_8$</td>
<td>0.81</td>
<td>32-150</td>
<td>0.27</td>
<td>25-104</td>
<td>$\sim 2 - 10$</td>
</tr>
<tr>
<td></td>
<td>0.03</td>
<td>50-127</td>
<td>0.02</td>
<td>11-94</td>
<td>$\sim 10$</td>
</tr>
</tbody>
</table>

The EEDF’s and the ionization cross sections of the sample gases are given in sections 12.3.2 and 12.3.3. Following section 12.3.4 and section 12.3.5, the linear inversion was applied to the measurement data to find the attachment cross sections $\sigma_a$.

### 12.4.1. Attachment to $\text{SF}_6$, $\text{C}_3\text{F}_8$ and $2-\text{C}_4\text{F}_8$

The mixing ratios were chosen in such a way that the measured waveforms could still be evaluated over a wide $E/N$-range, especially towards low $E/N$-values. Figures 12.2, 12.3 and 12.4 show the measured rate constants $\nu_{\text{eff}}/N$ for both, $\text{N}_2$ and $\text{CO}_2$ mixtures with the sample gases $\text{SF}_6$, $\text{C}_3\text{F}_8$ and $2-\text{C}_4\text{F}_8$. With increasing sample gas content, $\nu_{\text{eff}}/N$ decreases. The results for the unfolded attachment cross section $\sigma_a$ are shown and compared with the reference data [Phe88, Hum84, Jia08]. The rate constants by equation (12.1) is calculated with the attachment cross section from linear inversion as well as from the same reference data.
Figure 12.2.: Measured and calculated effective ionization rate constants $\nu_{\text{eff}}/N$ vs. $E/N$ for SF$_6$ in buffer gases N$_2$ and CO$_2$. Calculated $\nu_{\text{eff}}/N$ with cross section derived from linear inversion using METHES (full line) and BOLSIG+ (dashed line) and from Ref. [Phe88] (dashed-dotted line).
Figure 12.3.: Measured and calculated effective ionization rate constants $\nu_{\text{eff}}/N$ vs. $E/N$ for $C_3F_8$ in buffer gases $N_2$ and $CO_2$. Calculated $\nu_{\text{eff}}/N$ with cross section derived from linear inversion using METHES (full line) and BOLSIG+ (dashed line) and from Ref. [Hun84] (dashed-dotted line).
Figure 12.4.: Measured and calculated effective ionization rate constants $\nu_{\text{eff}}/N$ vs. $E/N$ for 2-C$_4$F$_8$ in buffer gases N$_2$ and CO$_2$. Calculated $\nu_{\text{eff}}/N$ with cross section derived from linear inversion using METHES (full line) and BOLSIG+ (dashed line) and from Ref. [Jia08] (dashed-dotted line).
12.5. Discussion and Conclusion

12.5.1. Thermal electron attachment to SF$_6$ and 2-C$_4$F$_8$

In general, the cross section derived by the linear inversion method is in good agreement with the reference data, see figure 12.2 and 12.4. The calculated rate constants fit the measurement $\nu_{\text{eff}}/N$-values well for $\sigma_a$ derived by the linear inversion.

In both gases, the linear inversion solution for $\sigma_a$ tends to converge to zero for energies below 0.01 eV, whereas electron attachment to SF$_6$ is known to be high near zero energy predominantly due to parent ion attachment [Phe88, Jia08]. The linear inversion method is tested with different discretization methods as well as with a higher number of abscissas in order to improve energy resolution. However, the zero-energy peak of $\sigma_a$ could not be unfolded perfectly from the swarm data. The limiting resolution of swarm derived cross section is generally known and therefore the uncertainty of the swarm-derived attachment cross section for SF$_6$ near zero energy accepted to be large, see e.g. [Chr00]. From a more mathematical perspective, the resolution limit of $\sigma_a$ obtained by the linear inversion method, applied to the present $\nu_{\text{eff}}/N$-data, is due to the relatively large $\lambda$-parameter in order to regularization the solution, see section 12.3.5.

12.5.2. Parent ion attachment to C$_3$F$_8$

Electron attachment to C$_3$F$_8$ has been investigated in beam experiments [Spy83], which cannot detect the parent ion C$_3$F$_8^-$ due to its reported lifetime of $5 \cdot 10^{-11} - 1 \cdot 10^{-8}$ s [Hun84]. In swarm studies, pressure dependency due to three body stabilization of short-lived parent anions has been observed for high gas pressures larger than 500 kPa [Hun84].

In contrast to that, in the present data a purely linear increase of the rate constant $\nu_{\text{eff}}$ with the gas number density is measured without second order contributions $\propto N^2$ due to three-body processes.
Thus, no significant pressure dependence could be detected over the present (see table 12.1) pressure range, where the three-body stabilization might not play a role.

Both unfolding methods, linear inversion as well as gauss expansion, yield a peak around 3 eV corresponding to dissociative attachment, which is qualitatively in agreement with the reference data [Hun84], see figure 12.3. Interestingly, in contrast to the same reference, both unfolding methods detect a low-energy contribution to the attachment cross section. The reported lifetimes of $C_3F_8$ are small compared to the electron transit times of $(1 - 10) \cdot 10^{-7}$ s in the present experiment. From this finding, together with the fact of no observed three body stabilization, it can be concluded that the reported lifetimes for $C_3F_8$ must be at least one order of magnitude larger than reported.

12.5.3. Comments on the linear inversion method

The measurements give important insights into advantages and problems of the linear inversion method applied to swarm studies. The present results underline the usefulness of the linear inversion method for the investigation of attachment cross sections from $\nu_{\text{eff}}/N$. Nevertheless, several steps in the present method have to be questioned carefully. First of all, the method relies on an undisturbed electron energy distribution in the buffer gas when adding a sample gas in small proportion. For the buffer gases $N_2$ and $CO_2$, this assumption seems to be valid as was tested by means of simulations using BOLSIG+, whereas in Argon the energy balance of the electrons is affected by collision with the molecules of the sample gas. In general, for the linear inversion, too strong attachment rates should be avoided due to the effect of attachment heating [Rob86]. Performing measurements with even lower partial pressures of the sample gas can circumvent the problem of a disturbed energy balance.

Secondly, the fact that the inversion problem typically is ill conditioned and needs regularization might give solutions for $\sigma_a$ that are over-smoothed in energy. Often, the regularization parameter has
to be increased even more than given by the corner of the L-curve in order to obtain positive solutions for $\sigma_a$. In addition, any contribution to $\sigma_a$ below a certain threshold, typically 5% of the peak value, has to be neglected. In case of one dominant attachment channel that exceeds all other weaker channels by at least 1 order of magnitude, only the dominant attachment channel can be detected in the solution of $\sigma_a$. SF$_6$ is such an example where due to very large parent ion attachment, the other channels are not visible within the linear inversion method.

From a more general point of view, the need of regularization might be undesirable since the original inversion problem has to be modified. At the same time, it acts as an indicator for the cross section unfolding method not being accurate without extending the range of the experimental data or any additional information on the shape of the cross section. Therefore, any solution for $\sigma_a$ derived from a certain data set by means of an unfolding method that does not regularize the problem is highly questionable being well-defined and robust with regard to uncertainties in the data.
13. Calculation of electric strength of gas mixtures

Synergism of the critical electric field strength \((E/N)_{\text{crit}}\) is a key property when adding a compound to a carrier gas, as described in section 7.1. In this chapter, \((E/N)_{\text{crit}}\) of the carrier gases \(N_2\) and \(CO_2\) versus mole fraction of the sample gases \(SF_6\), \(C_3F_8\) and \(2-C_4F_8\) are estimated. \((E/N)_{\text{crit}}\) of a gas mixture containing a novel sample compound and a (mostly well-known) carrier gas can typically not be directly calculated since not all relevant cross sections (see table 7.1) are known. Elastic and inelastic cross sections of the sample gas are in particular important if they differ strongly from those of the carrier gas and they gain importance for increasing mole fraction of the sample gas. However, when adding strongly attaching compounds to carrier gases such as \(N_2\) or \(CO_2\), the most crucial parameter that affects \((E/N)_{\text{crit}}\) is the attachment cross section of the sample compound.

13.1. Linear response of \((E/N)_{\text{crit}}\) of a carrier gas to a strongly attaching admixture

This section describes the response of the critical electric field strength \((E/N)_{\text{crit}}\) when adding a strongly attaching compound in very low concentrations \(k \ll 1\). It gives a qualitative picture on the relevant properties of the sample and carrier gases and should support the basic understanding of how to maximize \((E/N)_{\text{crit}}\) in a diluted gas mixture.

A first-order Taylor series expansion of \((E/N)_{\text{crit}}\) in \(k\) can be
written as (see appendix A.2 for details)

\[(E/N)_{\text{crit}} \approx (E/N)_{\text{crit}}^{(0)} + \frac{A}{B} k - \ldots, \quad (13.1)\]

with the coefficients

\[A = \sqrt{\frac{2}{m_e}} \int_0^\infty \sigma_a \varepsilon f((E/N)_{\text{crit}}^{(0)}, \varepsilon) \, d\varepsilon, \quad (13.2)\]
\[B = \left. \frac{\partial (\nu_{\text{eff}}/N)}{\partial (E/N)} \right|_{(E/N)_{\text{crit}}^{(0)}}. \quad (13.3)\]

Here, \(\nu_{\text{eff}}^B/N\) and \((E/N)_{\text{crit}}^{(0)}\) are the effective ionization rate coefficient and the critical electric field strength of the pure carrier gas \((k = 0)\). The ratio \(A/B\) gives the initial linear response of \((E/N)_{\text{crit}}\) versus \(k\) as shown in figure 13.1 for technical air and CO\(_2\). The corresponding coefficients \(A\) and \(B\) are given in table 13.1. In this section, \(N_2\) is not treated, since for \(N_2\) \(B = 0\) \((A/B \to \infty)\) due to no attachment. In general, the following conclusions can be made:

- \(A\) is a property related to both the carrier and the sample gas, and is proportional to the overlap between the EEDF of the carrier gas with the attachment cross section of the sample gas. In other words, it quantifies the ability of the sample gas to attach electrons in the carrier gas. The quantity \(A\) should be maximized to increase \((E/N)_{\text{crit}}\). In this sense, 2-C\(_4\)F\(_8\) is superior to SF\(_6\) in both carrier gases, technical air and CO\(_2\).

- \(B\) corresponds to the slope of the effective ionization rate coefficient of the carrier gas versus \(E/N\) at its critical field. A carrier gas with a flat slope of \(\nu_{\text{eff}}/N\) at its zero-crossing should be chosen to maximize \((E/N)_{\text{crit}}\). Technical air and CO\(_2\) have similar values for \(B\).

However, the linear regime in the expansion is typically limited to very small values of \(k\). The second-order term in this expansion is responsible for the flattening of the synergy curve, and it depends in particular on the change of the electron energy distribution function.
Figure 13.1.: Critical electric field strength versus mole fraction of the electronegative compounds SF$_6$ and 2-C$_4$F$_8$ in technical air (80%N$_2$/20%O$_2$) and CO$_2$ using BOLSIG+ with Phelps cross sections. The dashed lines are the linear response of $(E/N)_{\text{crit}}$ (for $k \ll 1$) according to equation (13.1) with the response parameters given in table 13.1.
Table 13.1.: Response parameters A (in $m^3 s^{-1}$) and B (in $m^3 s^{-1} Td^{-1}$) for different gases (using BOLSIG+ with Phelps cross sections).

<table>
<thead>
<tr>
<th></th>
<th>in CO₂</th>
<th>in air</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>$2.07 \cdot 10^{-19}$</td>
<td>$2.09 \cdot 10^{-19}$</td>
</tr>
<tr>
<td>A (SF₆)</td>
<td>$1.73 \cdot 10^{-15}$</td>
<td>$2.07 \cdot 10^{-15}$</td>
</tr>
<tr>
<td>A (2-C₄F₈)</td>
<td>$2.62 \cdot 10^{-15}$</td>
<td>$3.67 \cdot 10^{-15}$</td>
</tr>
</tbody>
</table>

of the carrier gas with increasing $E/N$ (see appendix A.2). Therefore, the presented concept of maximizing $(E/N)_{crit}$ represents a crude simplification.

13.2. Comparison of two different approximations to calculate the critical field in a gas mixture

If the attachment and ionization cross section of the sample compound is known, following approximations are possible to solve the Boltzmann equation and thus to estimate $(E/N)_{crit}$ of the mixture:

1. **Approximation 1**: the added sample compound is not disturbing the electron energy distribution function of the carrier gas. This approximation assumes for the calculation of the EEDF that all cross sections (elastic, excitation, ionization and attachment) of the sample compound are equal to the ones of the carrier gas.

2. **Approximation 2**: attachment and ionization cross sections (not elastic and excitation) of the sample compound are taken into account for the calculation of the energy distribution function. This approximation assumes that elastic and excitation cross sections of the sample compound are equal to the ones of the carrier gas.
Figure 13.2 shows the results following from these approximations for the case of $0 - 100\% \text{SF}_6$ in $\text{N}_2$ and compares it with the BOLSIG+ simulations based on the full cross section sets of both gases. The two approximations nearly give nearly identical results and are in fair agreement with BOLSIG+ up to 10%. For increasing concentrations, the discrepancy between BOLSIG+ and the approximations increases. This is as a result of the increasing deviation of the mixture’s EEDF due to the presence of SF$_6$. For both approximations, the error is reduced for low concentrations of the sample gas and if carrier and sample gas have similar cross sections.

As a conclusion, both approximation give accurate results in the regime of low mole fraction and they do not significantly differ from each other. Therefore, subsequently approximation 1 will be used, due to the much lower computational effort compared to approximation 2 (only simulation in carrier gases are necessary).

### 13.3. Estimation of the critical field in gas mixtures containing electronegative compounds

In the following, the electric strength of mixture of SF$_6$ and 2-C$_4$F$_8$ in the atmospheric gases $\text{N}_2$, $\text{CO}_2$, $\text{O}_2$ and technical air (80%$\text{N}_2$/20%$\text{O}_2$) is estimated using the method from the previous section. Those carrier gases are used because they are chemically stable, not flammable, cheap and have low/no environmental impact. Furthermore, they have a very high vapor pressure and relatively large inelastic cross sections in comparison to noble gases. CO$_2$ is also used due to its favorable arc quenching properties (in case the gas should be used for switching applications).

Figure 13.3 shows that both SF$_6$ and 2-C$_4$F$_8$ have strong synergism in the present carrier gases. Both compounds show a particularly strong increase of $(E/N)_{\text{crit}}$ versus mole fraction (at low concentrations) in $\text{N}_2$. The discrepancy between BOLSIG+ and
Figure 13.2.: Critical electric field strength versus mole fraction of SF$_6$ in N$_2$ for two different approximations (see text). Approximation 1 (full line), approximation 2 (□). The results are based on the cross sections obtained from the linear inversion (see 12.2, 12.3 and 12.4) using METHES with cross sections from Phelps and Siglo database (see 12.3.2). For comparison, BOLSIG+ results in SF$_6$/N$_2$ (◦) are shown (same cross section set for N$_2$, Siglo database for SF$_6$).
METHES results are relatively small for low concentrations. Uncertainties in \((E/N)_{\text{crit}}\) resulting from the linear inversion method are supposed to be larger.

**13.4. Validation of 2-C\(_4\)F\(_8\)**

This section is following section 8.3 to estimate the minimum operating temperature and the maximum operating voltage of 2-C\(_4\)F\(_8\) in mixtures. In the previous section it was shown that among the investigated carrier gases 2-C\(_4\)F\(_8\) shows the best synergism in N\(_2\). Therefore, solely 2-C\(_4\)F\(_8\)/N\(_2\) mixtures are considered in the following. Figure 13.4 compares the breakdown voltage of SF\(_6\) to that of 2-C\(_4\)F\(_8\)/N\(_2\) mixtures as a function of the minimum operating temperature (see section 8.3). At present, a measured vapor pressure curve of 2-C\(_4\)F\(_8\) is not available and therefore its range of application cannot be determined precisely. Therefore, its vapor pressure curve of 2-C\(_4\)F\(_8\) is estimated by means of Clausius-Clapeyron relation and Trouton’s rule (see figure 8.2).

It is apparent from figure 13.4 that SF\(_6\) is superior to 2-C\(_4\)F\(_8\)/N\(_2\) in terms of minimum operating temperature and the maximum operating voltage. For example, an apparatus for an application down to -25 °C must be filled with 0.8-0.9 MPa of 2-C\(_4\)F\(_8\)/N\(_2\) to reach a similar breakdown voltage as the corresponding SF\(_6\)-filled apparatus of 0.5 MPa filling pressure (which additionally could operate down to < -30 °C). For indoor applications, such as underground gas-insulated lines, with a minimum operating temperature requirement of typically -5 °C there exists a 0.9 MPa 2-C\(_4\)F\(_8\)/N\(_2\) mixture with approximately equal breakdown voltage to 0.6 MPa SF\(_6\). Gas-insulated lines are typically filled with 20%SF\(_6\)/80%N\(_2\) mixtures, which reach 70 – 80% of the electric strength of pure SF\(_6\) (see e.g. figure 7.3). Such an electric strength could be also reached with \(\approx\) 0.6 MPa 2-C\(_4\)F\(_8\)/N\(_2\) for the -5 °C requirement, as can be seen from figure 13.4. The extremely low GWP of 2-C\(_4\)F\(_8\)/N\(_2\) in comparison to SF\(_6\), makes this mixture a possible option for gas-insulated lines.
Figure 13.3.: Critical electric field strength versus mole fraction of the electronegative compounds SF$_6$ and 2-C$_4$F$_8$ in the gases N$_2$, CO$_2$, O$_2$ and technical air (80%N$_2$/20%O$_2$). The results are based on the cross sections obtained from the linear inversion (see 12.2, 12.3 and 12.4) using METHES (full line) and BOLSIG+ (dashed line) with cross sections from Phelps and Siglo database (see 12.3.2) and on the approximation that the electron energy distribution is the one of the background gas.
Figure 13.4.: Breakdown voltage of pure SF₆ and 2-C₄F₈/N₂ mixtures in homogeneous electric fields versus minimum operating temperature for filling pressures in the range of 0.1 – 1 MPa and mole fractions from 0 to 0.2. Full lines are contours of equal pressure (in steps of 0.1 MPa), whereas dashed lines are contours of equal mole fraction (the non-equidistant values for mole fractions are not indicated for the sake of clarity). The vertical lines indicate -5°C and -25°C, respectively. For comparison and more explanations see also figure 8.4

since for such applications the banked and thus emitted SF₆ quantities are particularly large. In addition, gas-insulated lines require no switching operations and thus any unfavorable arc quenching properties or stability issues of the gas are of no concern.
A systematic approach to identify gases for electrical insulation has been presented in this thesis. The approach is in particular suited for strongly attaching compounds of - in comparison to SF$_6$ - relatively large molecular size that are added only in low concentrations to carrier gases. The selection of candidate compounds, which is depending on various aspects, has been based mainly on chemical, environmental, thermodynamic and dielectric properties. As carrier gases atmospheric gases N$_2$, O$_2$, CO$_2$ and technical air were chosen due to various advantages over more complex (often synthetic) carrier gases.

A method has been developed that enables the computational screening of electronegative compounds. Using this method, the PubChem Database has been screened and more than 100 compounds have been identified to be potential candidates. Many of these compounds are not commercially available at this date. One of the available compounds was 2-C$_4$F$_8$, and it has been investigated as a sample gas for the rest of the thesis. The present screening method, similar to other methods available in the present literature, presents a statistical approach and therefore the predicted values suffer from large uncertainties. The method has been designed on the basis of a relatively small data set and therefore it does not guarantee that screening will include all - in particular exotic - candidate compounds. The ultimate goal for a more accurate screening of candidate gases should be based on first-principle calculations, such as calculating a full set of cross sections. A simplified screening of candidate compounds could also aim to find the best candidate compound as admixture to defined carrier gases. The corresponding screening could then be solely based on the attach-
ment cross sections of sample gases that yield maximum synergism. However, the quantum-chemical simulation of a crucial process such as three-body attachment seems challenging. A completely different approach to screen large databases could be machine learning, which is increasingly used in various fields such as drug discovery [Bur01, Wit16].

A Monte Carlo code for the simulation of electron transport has been written and made publicity available under the name METHES. It has been used to derive the electron energy distribution in carrier gas. A robust routine has been proposed to unfold measured swarm data in diluted gas mixtures from the calculated electron energy distributions in well-known carrier gases. METHES was subsequently used to calculated the electric strength in gas mixtures up to higher concentrations of 2-C₄F₈ (and SF₆). For higher concentrations of sample gases $\gtrsim 10\%$ the assumption of an undisturbed electron energy distribution is imprecise since collision processes other than attachment play an increasing role. Therefore, this method is particularly suited to compounds that are limited to small concentrations due to their relatively high boiling point and the corresponding undesired liquefaction in installed electrical equipment at low ambient temperatures.

2-C₄F₈ has been investigated as a sample compound in the present work and should represent only one example of a large set of candidate compounds. It showed qualitative and quantitative similar synergism to SF₆ in different atmospheric gases. Therefore, replacing SF₆ by 2-C₄F₈/N₂ might be an option e.g. in underground gas-insulated lines that are typically filled with 20%SF₆/80%N₂ mixtures. However, for outdoor application down to low temperatures 2-C₄F₈/N₂ mixtures might not be possible due the liquefaction.

In the future, further compounds identified in the present screening of the PubChem database or other databases could be efficiently investigated with the methods developed in this thesis. It would be also possible to efficiently evaluate the dielectric properties of mixtures, if more than one electron attaching compound is added to a
carrier gas.
A. Tabulated experimental results

A.1. DFT-calculated and measured values of molecular properties
Table A.1.: DFT-calculated and measured values of molecular properties for \( E_r \) [5,11,26-28], \( T_B \) [11,26], \( \alpha \) [16,32-34], \( \mu \) [33-35], \( \varepsilon_a^i \) and \( \varepsilon_a^a \) [26].

<table>
<thead>
<tr>
<th></th>
<th>( E_r )</th>
<th>( T_B )</th>
<th>( \alpha )</th>
<th>( \mu )</th>
<th>( \varepsilon_a^i )</th>
<th>( \varepsilon_a^a )</th>
</tr>
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<td>2.59</td>
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<td>3.72</td>
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<td>111.0</td>
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<td>2.56</td>
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</tr>
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<td>0.79</td>
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<td>334.3</td>
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<td>8.32</td>
<td>1.04</td>
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<td>6.39</td>
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<td>354.8</td>
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<td>195.0</td>
<td>4.94</td>
<td>5.55</td>
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</tr>
<tr>
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<td>354-58-5</td>
<td>2.49</td>
<td>319.0</td>
<td>10.45</td>
<td>10.45</td>
<td>0.59</td>
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<tr>
<td>( 1,1,1-C_{2}Cl_{3}F_{3} )</td>
<td>76-13-1</td>
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<td>244.8</td>
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<td>189.2</td>
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<td>10.24</td>
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Units: \( T_B \) in K, \( \alpha \) in \( 10^{-3} \), \( \mu \) in \( A^0 \cdot cm \), \( \varepsilon_a^i \) and \( \varepsilon_a^a \) in \( 10^{-6} \).
Table A.2.: DFT-calculated and measured values of molecular properties for $E_r$ [5,11,26-28], $T_B$ [11,26, $\alpha$ [16,32-34], $\mu$ [33-35], $\varepsilon^{a}$ and $\varepsilon^{a}_a$ [26].

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<tr>
<th>Compound</th>
<th>$E_r$ (kcal/mol)</th>
<th>$T_B$ (K)</th>
<th>$\alpha$ (K)</th>
<th>$\mu$ (Debye)</th>
<th>$\varepsilon^{a}$ (N)</th>
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Table A.3.: Compounds in the Pareto-area with GWP < 1. \( T_B \) data from [Syn13].

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Table A.4.: Compounds in the Pareto-area with 1 < GWP < 10. \( T_B \) data from [Syn13, Bol08, Che14].

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Table A.5.: Compounds in the Pareto-area with $10 < \text{GWP} < 100$. $T_B$ data from [Syn13].

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Table A.7.: Compounds in the Pareto-area with $100 < \text{GWP} < 200$. $T_B$ data from [Syn13, Mat14].

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A.2. Details of response of \((E/N)_{\text{crit}}\) to a strongly attaching compound

This section supports section 13.1.

In this section the following notation is used:

- \((E/N)_{\text{crit}}\): critical field strength of the gas mixture (a function of the mole fraction of the sample gas \(k\))
- \((E/N)_{\text{crit}}^0\): critical field strength of the pure carrier gas
- \(R_{\text{eff}} = \nu_{\text{eff}}/N\): effective ionization rate coefficient of the gas mixture (a function of \(E/N\) and \(k\))
- \(R_{\text{eff}}^0 = \nu_{\text{eff}}^B/N\): effective ionization rate coefficient of the pure carrier gas (a function of \(E/N\))
- \(\sigma_a\): total attachment cross section of the strongly attaching compound (a function of electron energy \(\varepsilon\))
- \(\sigma_i\): total ionization cross section of the strongly attaching compound (a function of electron energy \(\varepsilon\))
- \(f\): electron energy distribution function of the pure carrier gas (a function of electron energy \(\varepsilon\) and \(E/N\))

The linear response (initial slope) of \((E/N)_{\text{crit}}\) to \(k\) can be calculated solely from carrier gas properties \(R_{\text{eff}}^0\) and \(f\) as well as the sample gas property \(\sigma_a\). The derivation of this statement follows here.

At \((E/N)_{\text{crit}}\), the effective ionization rate coefficient \(R_{\text{eff}} = \nu_{\text{eff}}/N\) is zero by definition. The total derivative of \(R_{\text{eff}}\) at \((E/N)_{\text{crit}}\) with respect to \(k\) can be written as

\[
\frac{dR_{\text{eff}}}{dk} = \frac{\partial R_{\text{eff}}}{\partial k} + \frac{\partial R_{\text{eff}}}{\partial (E/N)_{\text{crit}}} \frac{\partial (E/N)_{\text{crit}}}{\partial k} = 0. \tag{A.1}
\]
Therefore the response is given by

$$\frac{\partial (E/N)_{\text{crit}}}{\partial k} = -\frac{\partial R_{\text{eff}}/\partial k}{\partial R_{\text{eff}}/\partial (E/N)_{\text{crit}}}.$$  \hfill (A.2)

For small concentrations $k \ll 1$ of a compound in a carrier gas, equation (12.1) can be applied and it follows at $E/N = (E/N)_{\text{crit}}$

$$R_{\text{eff}} \approx (1 - k) R_{\text{eff}}^0 + k \sqrt{\frac{2}{m_e}} \int_0^\infty (\sigma_i - \sigma_a) \epsilon f d\epsilon = 0. \hfill (A.3)$$

Inserting this expression for $R_{\text{eff}}$ into equation (A.2) yields for the response

$$\frac{\partial (E/N)_{\text{crit}}}{\partial k} \approx \frac{R_{\text{eff}}^0 + \sqrt{\frac{2}{m_e}} \int_0^\infty (\sigma_a - \sigma_i) \epsilon f d\epsilon}{(1 - k) \frac{\partial R_{\text{eff}}^0}{\partial (E/N)} + k \sqrt{\frac{2}{m_e}} \int_0^\infty (\sigma_i - \sigma_a) \epsilon \frac{\partial f}{\partial (E/N)} d\epsilon} \bigg|_{(E/N) = (E/N)_{\text{crit}}}.$$  \hfill (A.4)

For strongly attaching gases attachment dominates around the critical field of the carrier gas: $\int_0^\infty \sigma_a \epsilon f d\epsilon \gg \int_0^\infty \sigma_i \epsilon f d\epsilon$. For $k \to 0$, expression (A.4) further simplifies to

$$\frac{\partial (E/N)_{\text{crit}}}{\partial k} \bigg|_{k \to 0} \approx \sqrt{\frac{2}{m_e}} \int_0^\infty \sigma_a \epsilon f d\epsilon \frac{\partial R_{\text{eff}}^0}{\partial (E/N)} \bigg|_{(E/N) = (E/N)_{\text{crit}}}.$$  \hfill (A.5)
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