

Properties of potential eco-friendly gas replacements for particle detectors in high-energy physics

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Properties of potential eco-friendly gas replacements for particle detectors in high-energy physics

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ABSTRACT: Gas detectors for elementary particles require F-based gases for optimal performance. Recent regulations demand the use of environmentally unfriendly F-based gases to be limited or banned. This work studies properties of potential eco-friendly gas replacements by computing the physical and chemical parameters relevant for use as detector media, and suggests candidates to be considered for experimental investigation.

KEYWORDS: Materials for gaseous detectors; Muon spectrometers; Particle tracking detectors (Gaseous detectors); Micropattern gaseous detectors (MSGC, GEM, THGEM, RETHGEM, MHSP, MICROPIC, MICROMEAS, InGrid, etc)

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1 Introduction

Many refrigerant gases currently used have a great impact on the environment since they either contribute largely to the greenhouse effect, or because they tear the ozone layer, or both. In an attempt to protect the environment, regulations preventing the production and use of certain refrigerant gases have been implemented [1].

Gas detectors are widespread for detection, tracking and triggering of charged particles such as muons in Nuclear and High Energy Physics (HEP). They are characterised by simple and reliable use, but utmost care must be taken to issues such as properties of gas interaction with materials, gas purification, gas mixture contaminants, etc. [2]–[8].

A large part of gas muon detectors used in HEP operates with mixtures containing the regulated refrigerants as quenching medium in applications where excellent time resolution and avalanche operation are necessary. Therefore, actions towards finding new mixtures must be undertaken. Gas Electron Multiplier (GEM) [9] detectors operate in experiments such as CMS (Compact Muon Solenoid) at the LHC (Large Hadron Collider) with an Ar/CO₂ mixture [10]. However, for high time resolution applications an Ar/CO₂/CF₄ mixture is used [11], where CF₄ has a Global-Warming Potential (GWP) of 7390 [12]. Resistive Plate Counters (RPC) [13] currently operate with a F-based R134a/Isobutane/SF₆ gas mixture, with typical GWP of 1430. Investigations into new gas mixtures have to be performed in order to keep the mixture properties while complying with the regulations. A few industrial refrigerant replacements were proposed [14] as alternatives to R134a. A study of transport properties of currently used gas mixtures in HEP, and evaluation of transport properties of freon-less gas mixtures, was recently published [15, 16]. Few recent results on candidate ecogases have been published [17].

The aim of this paper is to discuss some of the important properties of gases for particle gas detectors, to list and summarize basic properties of eco-friendly refrigerants from the literature,

to discuss their properties for materials compatibility and safe use, and to make a prediction on selected parameters crucial for the performance of gas detectors considered, by means of parametric formulas. While this study is aimed to GEM and RPC detectors, its findings can be considered for selection of ecogas replacement for other gas detectors.

2 Gas properties

For a gas mixture to be appropriate in an elementary particle gas detector, first of all it has to comply with the regulations. Furthermore, its properties must also be appropriate for the specific type of detectors. For example, a gas that is suitable for the RPC detectors may not be fully optimized for the GEM detectors. To better find the appropriate gas for a detector, an understanding of the influence of different parameters is required. This section aims to clarify the most essential parameters for gases. Parametric formulas used in literature have been used to compute parameter of candidate gas replacements such as stopping power, radiation length, ion pair production. Basic details on the interaction of elementary particles in matter are discussed in textbooks, or reviews such as [18]

The impact of a refrigerant on the environment is characterised in terms of contribution to the greenhouse effect and depletion of the ozone layer. The greenhouse effect is measured in Global-Warming Potential (GWP), the 100-year integrated potential of a chemical, or the weighted average of the GWPs of the chemicals in a blend, relative CO₂ ($\text{GWP}_{\text{CO}_2} \equiv 1$). The effect on the ozone layer is measured in Ozone Depletion Potential [19] (ODP), normalized to the effect of CCl₃F or CFC-11 ($\text{ODP}_{\text{CCl}_3\text{F}} \equiv 1$). Nomenclature, GWP and ODP of selected refrigerant candidates are listed in table 1.

When a particle passes through a medium, energy is transferred from the particle to the surrounding atoms. The energy lost is typically defined as the stopping power expressed as $\frac{1}{\rho} \left\langle \frac{dE}{dx} \right\rangle$, where ρ is the density of the medium, E is the particle energy, and x is length of medium crossed. The minimum mean ionization energies for the refrigerants under consideration are summarized (see section 4) in table 2.

The radiation length X_0 is a characteristic length of a medium which describe the energy loss of electrons and photons in a medium [20]. These quantities are estimated by means of parametric formulas (see section 4) and summarized in table 2.

When an incoming particle passes through a medium, it will eventually interact with the medium and transfer some of its energy to ionize atoms. In this process, a pair consisting of an ionized atom and a free electron is produced. The number of ionizations produced by an incoming particle per unit length is denoted by N_P , in units of cm^{-1} . Each produced ion pair will have an initial kinetic energy and can itself produce an ion pair, called secondary ion pair production. The sum of the primary and secondary ion pairs production per unit length is denoted N_T , and will be mainly depending on the material and the incoming particle energy and mass. This parameter is relevant in particle gas detectors as it determines both the number and the size of avalanches produced by a single incoming particle when the gas is under an amplifying electric field.

When electrons and ions in a gas are subject only to an electric field they move on average along the electric field. Individual electrons, however, deviate from the average due to scattering on the atoms of the gas. Scattering leads to variations in velocity, called longitudinal diffusion, and to lateral displacements, called transverse diffusion.

Table 1. Summary of various refrigerant candidates. Also shown is the Chemical Abstracts Service (CAS) Registry Number.

Molecular name	Chemical formula	CAS	Refrigerant identifier	GWP	ODP
Chloropentafluoroethane	C_2ClF_5	76-15-3	R115 [49]	7370	0.44
Hexafluoroethane	C_2F_6	76-16-4	R116 [47]	-	-
2,2-Dicloro-1,1,1-trifluoroethane	$C_2HCl_2F_3$	306-83-2	R123 [38]	120	0
1-Chloro-3,3,3-Trifluoropropene	$C_3H_2ClF_3$	2730-43-0	R1233zd [45]	4.7-7	0
2,3,3,3-Tetrafluoropropene	$C_3H_2F_4$	754-12-1	R1234yf [46]	4	0
1,3,3,3 Tetrafluoropropene	$C_3H_2F_4$	29118-24-9	R1234ze [43]	6	0
Trifluoroiodomethane	CF_3I	2314-97-8	R131I [44]	0.4	0.01-0.02
1,1,1,2-Tetrafluoroethane	CH_2FCF_3	811-97-2	R134a [35]	1430	0
Tetrafluoromethane	CF_4	75-73-0	R14 [31]	7390	0
1,1,1-trifluoroethane	CH_3CF_3	420-46-2	R143a [30]	4300	-
1,1-Difluoroethane	$C_2H_4F_2$	75-37-6	R152a [51]	124	0
Octafluoropropane	C_3F_8	76-19-7	R218 [40]	-	-
Propane	C_3H_8	74-98-6	R290 [39]	3	0
Difluoromethane	CH_2F_2	75-10-5	R32 [48]	650	0
Isobutane	C_4H_{10}	75-28-5	R600a [42]	3	0
Sulfur Hexafluoride	SF_6	2551-62-4	R7146 [32]	23000	0.04
Carbon Dioxide	CO_2	124-38-9	R744 [37]	1	0
Octafluorocyclobutane	C_4F_8	115-25-3	R318 [41]	-	-
Pentafluoroethane	HF_2CF_3	354-33-6	R125 [28]	3400	0
Trifluoromethane	CHF_3	75-46-7	R23 [29]	0	0
R409:	$CHClF_2$	75-45-6 2837-89-0 75-68-3	R22 (60%), R142b (25%), R124 (15%)	1700-620	0.5/0.065/0.02
R407c:	CH_2F_2 , CF_3CHF_2 , CH_2FCF_3	75-10-5, 354-33-6, 811-97-2	R32 (21-25%), R125 (23-27%), R134a (50-54%)	650 3400 1430	0 0 0

The average distance an electron travels between ionizing collisions is called mean free path and its inverse is the number of ionizing collisions per centimeter α (the first Townsend coefficient). This parameter determines the gas gain. If n_0 is the number of primary electrons without amplification in uniform electric field, and n is the number of electrons after distance x under avalanche condition, then n is given by $n = n_0 e^{\alpha x}$ and the gas gain G is given by $G \equiv n_0/n = e^{\alpha x}$. The first Townsend coefficient depends on the nature of the gas, the electric field and pressure. To take into account the augmented emission of electrons by the cathode caused by impact of positive ions, it is customary to introduce η , Townsend's second ionisation coefficient or attachment parameter, i.e., the average

Table 2. Minimum ionization, radiation length and number of primary ion pair creation for the considered refrigerants, as well as the approximated mean ionization energy used. Values have been computed by means of the parametric formulas described in section 4. Uncertainty on values is determined by numerical propagation of errors on the experimentally known quantities.

Name	I [eV]	$-\langle \frac{dE}{dx} \rangle_{\min}$ [MeV $\frac{g}{cm^2}$]	X_0 [$\frac{g}{cm^2}$]	N_P [cm $^{-1}$]
R32	89.4	1.81	35.46	49.2
R7146	127.4	1.68	28.60	92.0
R600a	47.84	2.24	45.22	81.0
R1234yf	91.9	1.77	35.82	89.5
R152a	78.2	1.89	37.10	67.1
R1234ze	91.97	1.77	35.82	89.5
R115	116.7	1.69	29.22	98.4
R1233zd	106.7	1.74	29.76	105
R290	47.01	2.26	45.37	65.2
R13j1	201.7	1.42	11.54	172
R134a	95.0	1.77	35.15	81.6
R14	107.1	1.70	33.99	63.6
R123	125.3	1.70	25.54	98.4
R143a	87.8	1.81	35.89	74.8
R744	88.7	1.81	36.19	37.2
R23	99.9	1.74	34.52	56.9
R116	105.1	1.71	34.29	93.3
RC318	101.6	1.72	34.84	123
R218	104.1	1.71	34.43	117

number of electrons released from a surface by an incident positive ion, according to the formula

$$G \equiv \frac{e^{\alpha x}}{1 - \eta(e^{\alpha x} - 1)} \quad (2.1)$$

Many refrigerants may constitute danger for the user and its environment. The greatest dangers involved are the flammability and toxicity. In this work, two standards have been used in categorizing the refrigerants in tables 3 and 4. The American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) standard [22] gives each refrigerant a number denoting flammability from 1 (not flammable) to 3 (highly flammable), as well as a letter A (non-toxic) or B (Toxic). The Health Material Hazardous Material Information System (HMIS), rates Health/Flammability/ and Physical hazards from 0 (low) to 4 (high).

Some refrigerants are incompatible with certain materials, and can either react violently, or have long term effect, while others may even produce toxic decomposition and/or polymerisation. Known incompatibilities and toxic byproducts are summarized in tables 3 and 4.

Table 3. Chemical, physical and compatibility information of the refrigerants (Part 1).

Refrigerant	Molecular weight	Density g/L	Boiling point °C	HMIS	Ashrae Safety Group
Material incompatibility					
Hazardous decomposition products and polymerization					
R115 [49]	154.4	6.623	-39.1	1/0/2	A1
Material is stable. However, avoid open flames and high temperatures. Incompatible with alkali or alkaline earth metals-powdered Al, Zn, Be, etc.					
Decomposition product are hazardous."FREON" 115 Fluorocarbon can be decomposed by high temperatures (open flames, glowing metal surfaces, etc.)forming hydrochloric and hydrofluoric acids, and possibly carbonyl halides. Thermal decomposition can yield toxic fumes of fluorides such as Hydrogen Fluoride, Hydrogen Chloride, Carbon Monoxide and Chlorine.					
R116 [47]	138.01	5.734	-79	1/0/0	A1
May react violently with alkaline-earth and alkali metals Thermal decomposition yields toxic products which can be corrosive in the presence of moisture. If involved in a fire the following toxic and/or corrosive fumes may be produced by thermal decomposition: Carbonyl fluoride, Hydrogen fluoride, Carbon monoxide					
Thermal decomposition products: halogenated compounds, oxides of carbon					
R1233zd [45]	130.5	6.10	-19	-	-
Incompatible with polyacrylate, Viton, natural rubber, silicon rubber and other elastomers.					
Is considered non-toxic at less than 800 ppm. Hazardous polymerization can occur. If involved in a fire, production under thermal decompose into pyrolysis products containing Hydrogen Fluoride, Carbon Monoxide, Carbonyl halides, and Hydrogen Chloride can occur.					
R1234yf [46]	114.0	4.82	-29	0/2/2	-
Incompatible with alkali metals, Zn, Mg and other light metals.					
If involved in a fire, production under thermal decompose into pyrolysis products containing Fluorine, Carbon Monoxide, Carbonyl halides, and Hydrogen halides can occur. No toxic decomposition should happen under normal conditions.					
R1234ze [43]	114.0	4.82	-29	1/0/0	-
Incompatible with strongly oxidizing materials and finely divided Mg and Al.					
If involved in a fire, production under thermal decompose into pyrolysis products containing Fluorine, Carbon Monoxide, Carbonyl halides, and Hydrogen halides can occur. Polymerization may also occur.					
R131I [44]	195.9	-	-22.5	-	-
Incompatible with active metals, fires of hydrides, and materials containing oxygen.					
Can decompose to Iodine, Hydrogen Fluoride, and Hydrogen Iodide.					
R134a [35]	102.0	4.320	-26.5	1/1/0	A1
Chemically reactive with K, Ca, powdered Al, Mg, Zn. Under high temperature/ high pressure, may react with Al surfaces.					
Under special circumstances (e.g. high temperature) Carbon monoxide, Carbonyl fluoride, Hydrogen fluoride can be produced. Under normal storage and use, no hazardous decomposition should be produced					
R14 [31]	88.0	3.65	-128	0/0/0	A1
Not compatible with aluminium, alloys containing more than 2% magnesium, alkali metals in powdered form and carbon dioxide above 1000 °C.					
If involved in a fire, production under thermal decompose into pyrolysis products containing hydrogen fluorid and carbonyl fluoride.					

Table 4. Chemical, physical and compatibility information of the refrigerants (Part 2).

Refrigerant	Molecular weight	Density g/L	Boiling point °C	HMIS	Ashrae Safety Group
Material incompatibility					
Hazardous decomposition products and polymerization					
R143a [30]	84.0	-	-47.6	-	A2
Can form explosive mixture with air. May react violently with oxidants. Air, Oxidiser. Non recommended: Hydrocarbon based lubricant, significant loss of mass by extraction or chemical reaction and Fluorocarbon based lubricant, significant loss of mass by extraction or chemical reaction.					
Thermal decomposition yields toxic products which can be corrosive in the presence of moisture.					
R125 [28]	120	1.24g/cm ³	-48.5	1/1/0	A1
Under very high temperature and/or appropriate pressures freshly abraded aluminum surfaces may cause strongly exothermic reaction. Chemical reactive metals: potassium calcium powdered aluminum, magnesium and zinc.					
The product is stable. Do not mix with oxygen or air above atmospheric pressure. Any source of high temperatures, such as lighted cigarettes, flames, hot spots or welding may yield toxic and/or corrosive decomposition products.					
R22 [50]	86.45	3	-40.1	1/0/0	-
Chemically reactive metals: potassium, calcium, powdered aluminum, magnesium, and zinc, powdered metals, powdered metal salts					
Hazardous decomposition products: Halogens, halogen acids and possibly carbonyl halides. Carbon monoxide, Phosgene, Hydrogen chloride, Hydrogen fluoride, Carbonyl fluoride.					
R744 [37]	44	1.52	-78.5	1/0/0	A1
The product is stable under regular conditions					
Materials to avoid: strong oxidising agents, strong acids. Hazardous decomposition products: In combustion emits toxic fumes.					
R142b [34]	100.5	4.18	-10	2/4/0	-
Materials to avoid: Light and/or alkaline metals, Alkaline earth metals, Powdered metals, Oxidizing agents, Chlorine, Powdered aluminum, magnesium, zinc, beryllium and their alloys.					
Hazardous decomposition products: Gaseous hydrogen fluoride (HF), Gaseous hydrogen chloride (HCl), Fluorophosgene, Phosgene					
R152a [51]	66.1	2.738	-25	1/4/2	A2
Extremely reactive with oxidizing materials, such as alkaline, alkaline earth metals, and other reactive chemicals, (i.e. Na, K, Ca, Mg, powdered Al, Zn), brass, and steel. Incompatible with amines, bases, and halogens.					
Under normal condition, hazardous decomposition and/or polymerization products should not be produced. If exposed to fire, hazardous products may be produced.					
R218 [40]	188.0	8.17 g/l gas	-36.7	-	A1
Stable under normal conditions materials with which gas mixture is incompatible: oxidizing materials and alkali and alkali earth metals. May react violently with chemical active metals as sodium, potassium and barium powdered magnesium, powdered aluminum and organometallics					
Thermal decomposition yields toxic products which can be corrosive in presence of moisture hazardous decomposition products: acid halides					
R23 [29]	70.0	-2.946 kg /m ³	-84.4	-	A1
Incompatible materials: metals, polystyrene, natural rubber, alloys of more than 2% magnesium in the presence of water, nitrosyl fluoride, N ₂ O ₃ , lime at dull red heat, and metals at elevated temperature					
Decomposition products: halogenated compounds, oxides of carbon, hydrogen fluoride, thermal decomposition may produce toxic fumes of fluorides. Decomposition products may include the following materials: carbon dioxide carbon monoxide halogenated compounds carbonyl halides.					

Table 5. Chemical, physical and compatibility information of the refrigerants (Part 3).

Refrigerant	Molecular weight	Density g/L	Boiling point °C	HMIS	Ashrae Safety Group
Material incompatibility					
Hazardous decomposition products and polymerization					
R290 [39]	44.1	1.86	-42	1/4/0	A3
Incompatible with acids, oxygen, oxidizing materials, copper, some plastics, Chlorine Dioxide.					
Under normal condition, hazardous decomposition and/or polymerization products should not be produced . May produce carbon monoxide and other toxic gasses under thermal decomposition.					
R32 [48]	52.0	11.4	-51.7	1/4/1	A2
incompatible with acids and oxidizing materials as Na, K, Ca, Zn, Mg, powdered Al, and other active metals. Incompatible with air and moisture.					
No hazardous decomposition/polymerization should be produced under normal conditions.					
R600a [42]	58.1	8.93	-11.7	1/4/0	A3
Incompatible with oxidizing materials, halogenated hydrocarbons, halogens, and metal catalysts.					
No hazardous decomposition/polymerization should be produced under normal conditions. May produce carbon monoxide and other toxic gasses under thermal decomposition.					
R7146 [32]	146.1	6.17	-63.7	1/0/0	-
Stable with most chemical, except metals other than aluminium, stainless steel, copper brass, silver, at elevated temperatures (> 204°C). Also reacts violently with disilane.					
Decomposes into Sulfur oxides and hydrogen fluorine.					

Aging is defined (following [23]) as the general deterioration of the detectors during their operation. The aging phenomenon is very complex and depends on several parameters. The commonly used variables include the cross-sections, electron/photon energies, electrostatic forces, dipole moments, chemical reactivity of atoms and molecules, etc. For a comprehensive (although non recent) collection see [24–26]. A more recent review of ageing effects in GEM detectors can be found in [27].

3 Organofluorine gas compounds for particle physics detectors

F-based compounds used by gaseous particle detectors for experiments at high interaction rates belong to the family of organofluorines, and their use is motivated by high drift velocities and excellent quenching power. The carbon-fluorine bond is one of the strongest in organic chemistry, thus resulting in high chemical and thermal stability. Fluorine has the highest electronegativity of all elements.

Fluorocarbons (FC) such as CF_4 have been used originally, and replaced in the 1990's by more ecofriendly hydrofluorocarbons (HFC) such as 1,1,1,2-Tetrafluoroethane or R134a. Hydrofluoro olefins (HFO) differ from HFC by being derivatives of alkenes rather than alkanes. A perfluorinated compound (PFC) is an organofluorine compound containing only carbon-fluorine bonds (no C-H bonds) and carbon-carbon bonds but also other etheroatoms, with an example being CF_3I , which

was proposed recently [14] as candidate substitute of 1,1,1,2-Tetrafluoroethane. CF_3I is a new substance neither restricted nor controlled, but subject to reporting, without limitations of use [19].

Hydrofluoro ethers (HFEs) are liquid at room temperature. The insertion of an ether oxygen atom into the molecule is exploited to modify the thermo-physical properties of a compound for specific end users. HFEs have significantly shorter atmospheric lifetime when compared to HFCs and PFCs, with their lifetime decreasing when the number of hydrogens in the molecule increases. The lifetime can be dramatically affected by the location of the hydrogen atoms relative to the ether oxygen [70–72]. HFEs show generally a boiling point higher than environmental temperature, thus making their application as gases rather problematic (table 6). For HEP detectors, namely, the use of high boiling point HFEs will require the design of a gas system which avoids the vapour condensation. Therefore, only a few HFEs have been taken in account which are characterised by low boiling point and acceptable GWP, while still showing high vapour pressure at STP conditions. Experimental use of HFE is still critical, and attention should be paid to both high vapour pressure values, and to avoid condensation of mixtures in order to guarantee availability of mixture in gaseous phase. The two HFEs candidates (HFE-143m and HFE-245mc) considered as substitutes of gas mixtures presently in use in gaseous particle detector at CERN belong to the family of segregated HFEs. Segregated HFEs are those in which all hydrogen atoms reside on carbons with no fluorine substitution and are separated from the fluorinated carbons by the etheric oxygen bridge (R-O-R). This segregated structure maximizes the effect of the ether oxygen in reducing the atmospheric lifetimes. The shorter lifetimes of these HFEs lead to lower GWPs. The two commercially available segregated HFEs have lifetimes and GWPs lower than any nonflammable, commercial HFC; they are nonflammable, low in toxicity and have both physical and chemical properties suitable to replace PFCs and HFCs in a number of applications [74, 75]. The wide range of structures and boiling points available from this class of compounds creates opportunities for replacement of HFCs and PFCs in solvent, cleaning, heat transfer and other applications [72, 76, 77]. Table 7 shows the comparison between some HFEs and HFCs with similar composition, lifetime and GWP values. In this family of molecules, two have been identified as candidate for high energy gas detectors: HFE-143m and HFE-245mc (table 8). Both have a low boiling point along with an acceptable GWP, even if they show an high vapor pressure at 25°C. Furthermore, these two compounds show a good compatibility (avoiding humidity and in normal operational conditions) with materials expected to be in contact during the experiment. The vapour pressures properties of HFC-143a and HFE-245mc have been measured in a wide range of temperatures and pressures [72, 76, 77].

Finally, fluorinated ketones (F-ketons) are a new class of materials that have been shown to be useful in substitution of non eco-friendly gases in some industrial applications. F-ketons are liquid at room temperature, but they are easily evaporated into a carrier gas stream by a number of methods [73]. F-ketons are an attractive potential replacements for SF_6 in many applications. F-ketons with short chain are expected to show lower boiling points and have been considered in this study; in fact, F-ketons with a longer chain are expected to have a higher boiling point, not suitable for the application in gas detectors. Table 9 shows some properties of F-ketons with a chain made by three carbon atoms. Compounds showed in table are all flammable and in particular the Hexafluoroacetone, the only one available as gas in the operational conditions for gas detectors is highly reactive and corrosive. $\text{CF}_3\text{CF}_2\text{C}(\text{O})\text{CF}(\text{CF}_3)_2$ (CF_6 -ketone), commercialized as 3M Novec 1230 [78, 81] and easily available on market, has high environmental compatibility but a boiling

Table 6. Physical properties of some HFEs actually available on market. The useful low temperature was defined as the higher of the freezing temperature and the temperature at which the fluid kinematic viscosity reached a 30 cSt viscosity.

	HFE-7000 [52, 53] C ₃ F ₇ OCH ₃	HFE-7100 [52, 54] C ₄ F ₉ OCH ₃	HFE-7200 [52, 55] C ₄ F ₉ OC ₂ H ₅	HFE-7500 [52, 56] C ₇ F ₁₅ OC ₂ H ₅
Atmospheric Lifetime [yrs]	4.7	4.1	0.8	2.5
GWP (100 year ITH)	400	320	55	210
Boiling Point [°C]	34	61	76	128
Pour Point [°C]	-122.5	-138	-135	-100
Useful low Temperature [°C]	-122.5	-106	-106	-75
Density [kg/m ³]	1400	1420	1510	1614
Coefficient of Expansion [1/°C]	0.00219	0.0016	0.0018	0.00129
Specific Heat [J/kg-K]	1300	1220	1180	1128
Thermal Conductivity [W/m-K]	0.075	0.068	0.069	0.065
Viscosity [cSt] at 25°C	0.32	0.37	0.44	0.77
Viscosity [cSt] at -40°C	0.78	1.1	1.26	3.55
Dielectric Strength [kV, 0.1 inch gap]	≈ 40	≈ 40	≈ 40	≈ 40
Dielectric Constant	7.4	7.3	7.4	5.8
Electrical Resistivity Ω m	1.00E+08	1.00E+08	1.00E+08	1.00E+08

Table 7. Comparison of selected HFEs and HFCs.

Compound	Halocarbon Number	Atm. Lifetime (yrs)	GWP (100 yr ITH)
CH ₃ CF ₃	HFC-143a [57]	53.5	5400
CH ₃ OCF ₃	HFE-143a [52]	5.7	970
CF ₂ HCF ₃	HFC-125 [58]	32.6	3800
CF ₂ HO CF ₃	HFE-125 [52]	165	15300
CF ₃ CFHCF ₃	HFC-227ea [59]	36.5	3800
CF ₃ CFHO CF ₃	HFE-227ea [60]	11	1500
CF ₃ CH ₂ CF ₃	HFC-236fa [61]	226	9400
CF ₃ CH ₂ OCF ₃	HFE-236fa [62]	3.7	470
CF ₃ CH ₂ CHF ₂	HFC-245fa [64]	7.4	820
CF ₃ CH ₂ OCHF ₂	HFE-245fa [63]	4.4	570
CF ₃ CF ₂ OCH ₃	HFE-245cb2 [52]	1.2	160
C ₄ F ₉ OCH ₃	HFE-449s1 (HFE7100) [54]	4	320
C ₄ F ₉ OC ₂ H ₅	HFE-569sf2 (HFE7200) [55]	1	55

Table 8. Comparison of HFE143m and HFE125mc properties.

Compound	Halocarbon Number	Boiling point [°C]	Vapour pressure (Bar at 25°C)	GWP
CF ₃ OCH ₃	HFE-143m [52]	-24	5.8	750
CF ₃ CF ₂ OCH ₃	HFE-245mc [52]	5.51	2.6	622

Table 9. Properties of fluorinated ketons with a chain made by three carbon atoms.

Molecular formula	Compound	Boiling point [°C at 1 atm]	Vapour pressure (atm at 20°C)	Notes
CH ₃ COCH ₂ F	Fluoroacetone [65]	75		Highly toxic Flammable Corrosive
CH ₃ COCHF ₂	1,1-Difluoroacetone [66]	47		Flammable
CH ₃ COCF ₃	1,1,1-Trifluoroacetone [67]	21-24	1	Flammable
CF ₃ COCH ₂ F	1,1,1,3-Tetrafluoroacetone [68]	35.0.67		Flammable
F ₃ COCF ₃	Hexafluoroacetone [69]	-28	5.8	Highly reactive Corrosive

Table 10. Properties of Novec 1230 and more recent 4710 [79] and 5150 [78].

	1230 [78]	4710 [79]	5110 [80]
Ozone Depletion Potential (ODP)	0	0	0
Global Warming Potential IPCC2	1	2100	<1
Atmospheric Lifetime (Years)	0.014 (5 days)	30	0.04 (14 days)

point of 49°C at 1 atm. Table 10 shows properties of Novec 1230, along with more recent Novec 5110 [80] and Novec 4710.

4 Estimation of gas parameters

This section reviews the parametric formulas for the physics quantities of interest for elementary particle detectors with the aim of evaluating them for new candidate ecogases. Details of how the formulas are derived are omitted for brevity, the interested reader can find them in any elementary particle physics textbook, or reviews such as [18].

4.1 Stopping power

Quantities such as the minimum ionization energy can be computed if the stopping power is known. An approximate expression for moderately relativistic particles in the momentum region $0.1 \leq \beta\gamma = p/Mc \leq 1000$ can be found using the Bethe-Bloch equation, given by [18]

$$\frac{1}{\rho} \left\langle -\frac{dE}{dx} \right\rangle = K z^2 \frac{Z}{A} \frac{1}{\beta^2} \left[\frac{1}{2} \ln \frac{2m_e c^2 \beta^2 \gamma^2 T_{\max}}{I^2} - \beta^2 - \frac{\delta(\beta\gamma)}{2} \right] \quad (4.1)$$

where $\langle -\frac{dE}{dx} \rangle$ is the mean energy loss per length, ρ is the density of the medium, I is the mean excitation energy, and $\delta(\beta\gamma)$ is the density effect correction function to ionization energy loss. K is a constant given by $4\pi N_A r_e^2 m_e c^2$, and T_{\max} is the maximum energy transfer in a single collision, given by

$$T_{\max} = \frac{2m_e c^2 \beta^2 \gamma^2}{1 + 2\gamma m_e/M + (m_e/M)^2}, \quad (4.2)$$

where M is the mass of the incoming particle.

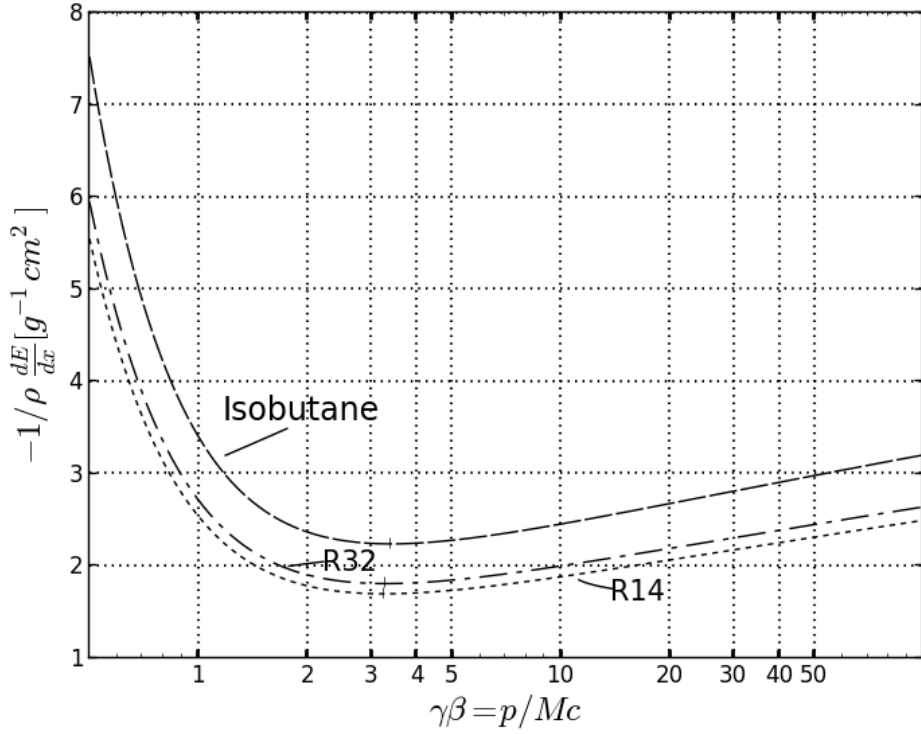


Figure 1. Energy loss as a function of the relativistic time dilation factor $\gamma\beta$ as computed via eq. (4.1) for various refrigerants.

The mean excitation energy I for a composite medium can be approximated from the composite atoms by the relation [83].

$$I = \exp \left\{ \left[\sum_j w_j (Z_j/A_j) \ln I_j \right] / \langle Z/A \rangle \right\} \quad (4.3)$$

where w_j , Z_j , A_j and I_j is the fraction by weight, atomic number, atomic weight and mean ionization energy, respectively, of the j 'th constituent. The shape of the $\delta(\gamma\delta)$ function for non-conducting materials can be approximated by

$$\delta(\gamma\delta) = \begin{cases} 2(\ln 10)X - \bar{C} & \text{if } X \geq X_1; \\ 2(\ln 10)X - \bar{C} & \text{if } X_0 \leq X < X_1; \\ 0 & \text{if } X < X_0; \end{cases} \quad (4.4)$$

where $X = \log_{10}(\gamma\delta)$. To find an approximate expression for the parameters \bar{C} , X_0 and X_1 based on experimental fits, we refer to [84]. For gases with momenta below $\beta\gamma$, the density effect correlation function can be neglected. A plot of the calculated energy loss (eq. (4.1)) for various refrigerants is shown in figure 1.

Table 11. L_1 and L_2 expressions for various atom numbers from [20].

Z	L_1	L_2
1	5.31	6.144
2	4.79	5.621
3	4.74	5.805
4	4.71	5.924
$5 \geq$	$\ln(184.15Z^{-1/3})$	$\ln(1994Z^{-2/3})$

4.2 Radiation length

The radiation length of an atom is determined by [20]

$$X_0 = 716.405(\text{cm}^{-2}\text{mol})A/[Z^2(L_1 - f(z)) + ZL_2] \quad (4.5)$$

$$f(z) = z^2 \sum_{n=1}^{\infty} \frac{1}{n(n^2 + z^2)} \approx 1.202z - 1.0369z^2 + \frac{1.008z^3}{1+z} \quad (4.6)$$

where L_1 and L_2 are given by table 11, $f(z)$ is the one-photon exchange approximation, and $z = \alpha Z$, α being the fine-structure constant and Z is the atomic number. This formula, however, only holds for free atoms. The stopping power for a molecule is determined by taking into account the influence from molecular bindings, crystal structures and polarization of the medium. By neglecting these effects, however, one can find an approximate expression by weighting the radiation length of the single atoms

$$\frac{1}{X_0} = \frac{1}{A_{\text{molecule}}} \sum_j \frac{A_j}{X_{0j}}, \quad (4.7)$$

where j refers to the j 'th constituent of the atom.

4.3 Estimation of ionization pair production

In order to model the number of primary ionizations caused by a single particle, the cross section for all the particle-atom interactions should be calculated. The number of primary electrons per unit length would then be the integral over energy across all the energy transfer cross sections. This is problematic, since all electron orbital transfers have to be considered. An easier, but approximate, correlation between primary ionization and atom number has been found based on experimental data by [85]

$$N_P = 3.996 \frac{Z_m}{\bar{Z}^{0.4}} - 0.025 \left(\frac{Z_m}{\bar{Z}^{0.4}} \right) \text{cm}^{-1}, \quad (4.8)$$

which holds for normal pressure and temperature (NPT). For different pressure and temperature, the number scales with the density. This value should only be taken as a rough estimation though. This formula, whose result should be taken as an approximate estimate, has proven to work best for hydrocarbons and only partially for molecules consisting mainly of fluorine, differing as much as 30% from the experimental value for CF_4 .

The total number of ionizations has proven to be more difficult to estimate. Whereas no general formula has been derived, the most straightforward method will be to use the cross sections used to

calculate the primary ionization electrons, and use Monte Carlo simulations to track the production of secondary electrons from primary electrons. The total number of pair ionization turns out to be dependent on the incoming particle energy and mass, and a general expression can therefore be difficult to find. For an incoming particle, $W = \frac{\Delta E}{N}$ defines the average energy necessary to produce an ion pair. The energy W is a slowly varying function of the particle energy [86], and can therefore be taken to be a constant in an energy interval. The total ionization per unit length can then be found by

$$N_T = \rho \frac{dE}{dx} \frac{1}{W} \quad (4.9)$$

If the W values for specific gases are known, the average W value for a gas mixture can be found by [85]

$$\bar{W} = \frac{\sum_m [f(n_m)Z(n_m)W(n_m)]}{\sum_m [f(n_m)Z(n_m)]}, \quad (4.10)$$

where n_m denotes the index of the molecule, and $f(n_m)$ denotes the relative number of molecules of the given sort in the mixture.

The value of W is difficult to predict, and there is not a direct way to give a proper estimate based on experimental data alone. A Monte Carlo simulation is in preparation which uses the photoabsorption ionization and relaxation (PAIR) model [85] and it will be the subject of a forthcoming paper.

5 Conclusions

Fluorine-based gases today used in HEP gas detectors are being phased out by industry and replaced by eco-friendly substitute gases. This study has reported on a general survey of industrially available replacements for HEP gases, discussed their physical properties, materials compatibility and safety issues. Parameters of interest for their use in HEP detectors have been computed by means of parameterizations: ionisation energy, electronegativity, number of primary pairs. Promising candidates with lower GWP are identified for further experimental studies.

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