

CHEMICAL AND ELECTRON INTERACTION PROPERTIES OF POTENTIAL GASEOUS INSULATION AND ARC-QUENCHING MEDIA

LILI ZHU, DONXIAN TANAND, SU ZHAO, DENGMING XIAO*

Department of Electrical Engineering, Shanghai Jiao Tong University, No.1954 Huashan Rd., 200030, Shanghai, People's Republic of China

* dmxiao@sjtu.edu.cn

Abstract. The global warming effects of sulphur hexafluoride (SF_6) lead researchers to look for new environmentally-friendly gas media in high-voltage electrical apparatus. The present paper discusses basic chemical and electron interaction properties that brings high insulation strength and good arc interruption capability for a gas. The conclusion shows that gaseous compounds composed of elements in the upright area of periodic table of elements generally have stronger electronegative ability and good electrical properties. And double bond or triple bond in gas molecule can effectively improve the dielectric strength. For gas mixtures, good cooperation of gases will generate synergetic effect, which makes its dielectric strength higher than the weighted average value of each gas. Some aspects in searching for new arc interruption media are also discussed.

Keywords: chemical property, electron interaction, insulation, arc interruption.

1. Introduction

With increasing concern on the potential effects of global warming, sulphur hexafluoride (SF_6), a common insulation and arc interruption gas medium, has been stipulated to be banned in the year 2020 according to the Kyoto protocol at COP3 (the 3rd Conference of Parties) in 1997 [1]. The WMO (World Meteorological Organization) has recently published Greenhouse Gas Bulletin which shows that the current mole fraction of SF_6 is about twice the level observed in the mid-1990s in the atmosphere [2]. To deal with the issue, studies to search for new environmentally friendly gas to substitute SF_6 in electrical equipment become an urgent problem [3–5]. However, it is too complicated and even impossible to make overall experiments and research for each possible gas. One solution is to refer to general properties of gas with high insulation strength to narrow down the searching scope and make preliminary judgment of insulation property for a certain gas beforehand.

This paper summarized basic chemical and electron interaction properties that will lead to high insulation characteristics for a gas. As the electron attachment ability could reduce the number of free electrons and thus inhibit discharge process, Section 2 lists the values of electronegativity for common elements in period table of elements. The effect of molecule structure on the insulation property is analysed in Section 3, such as the effect of atomic configuration and double bond. For gas mixtures, the cooperation of different gases is introduced in Section 4. Some considerations of SF_6 substitute used for arc interruption are discussed in Section 5.

2. Electronegativity

In chemical molecules, electron pairs are subject to tug competition between adjacent atoms that share it. If one atom has a greater pulling power than the other, the covalent bond owns some ionic characteristics. Then the electron pair tends to be closer to one atom than to the other. The electron pulling force of an atom as part of a bond is called electronegativity.

A simplest analogy is to regard electronegativity as the ability of an atom competing for electrons. It is related to the ionization energy (I) ($\text{kJ}\cdot\text{mol}^{-1}$) and electron affinity energy (EA) ($\text{kJ}\cdot\text{mol}^{-1}$) of the element. The EA represents the energy released in the formation of negative ion when an atom in ground state obtains an electron. With high ionization energy, electrons are given up reluctantly. While with high electron affinity, no more energy is needed to attach electrons to an atom. Thus, elements with high values of both the two properties are hard to lose electrons and easy to gain them. Halogen elements will develop into a stable electron distribution configuration like inert gases when obtain an extra electron in the outer orbit of electrons, and tend to own strong electron affinity. Additionally, considering the function of covalent bond for atom in molecules, electronegativity is identified as the affinity of atom to the electron in covalent bond in a molecule. By contraries, if the values of ionization energy and the electron affinity are both low, it takes little energy to give up electrons and its inclination to gain other electrons is weak. The electronegativity of such element is low [6].

In the chemical periodic table based on the definite scale derived from Linus Pauling, the ionization energies and electron attachments reach the maximum value at the upper right of the periodic table close to fluorine element. It is obvious that fluorine F, oxygen

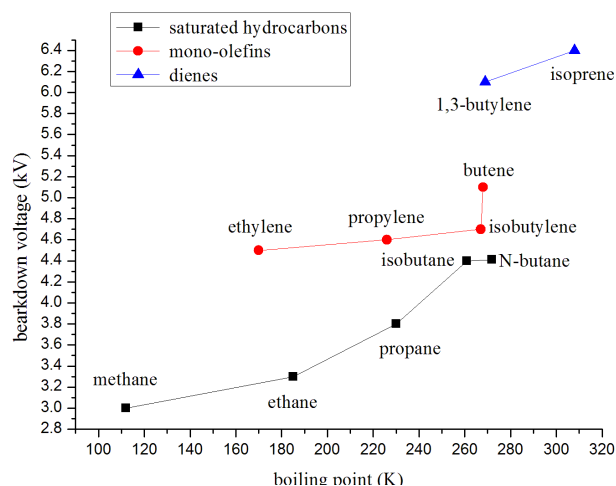


Figure 1. The relationship between the breakdown voltages ($pd=50$) and the boiling points.

O, chlorine Cl, nitrogen N, and bromine Br are the elements with the highest electronegativity. Whenever such elements are presented in compound molecules, their atoms are expected to tug strongly on electron pairs shared with their neighbor atom. Electron clouds are still shared with the less electronegative atom, which, however, is unequal. And the electron cloud at the side of the more electronegative element will be denser [7]. As fluorine F has the highest value of electronegativity among all the elements, the expected gases with high insulation strength all contain F element, such as SF_6 , CF_3I and $c-C_4F_8$.

3. The impact of double bond

A.E.D Heylen has compared the electrical insulation strengths of several kinds of hydrocarbons [8, 9]. For alkene, the addition of methyl to mono-olefin will only obtain limited improvement of the dielectric strengths, but raise the boiling points, which limit the utilization as the gaseous media. However, butadiene and isoprene has a much higher dielectric strength than mono-olefins, which show an obvious effect of carbon-carbon double-bond on the improvement of the dielectric strength. This conclusion is also confirmed by the excellent electrical characteristic of butadiene C_4F_6 by comparing to 1-butane through the experiment of J. C. Devins [10, 11].

To further verify the function of the carbon-carbon double bond in the promotion of the electrical property, we compare saturated hydrocarbon, mono-olefin and di-olefin gases. Fig. 1 and 2 show the relationship of the boiling temperature with breakdown voltages under $pd=50$ (cm·mmHg) and the ratio (U/pd) between the breakdown voltages U and the pd values respectively. And Fig. 3 shows the relationship between the ratio (U/pd) and the molecular weights.

Seen from the above Figures, for a particular gas structure, with larger number of methyl, the boiling point will increase with the molecular weight. For gaseous molecules with similar chemical structure, the

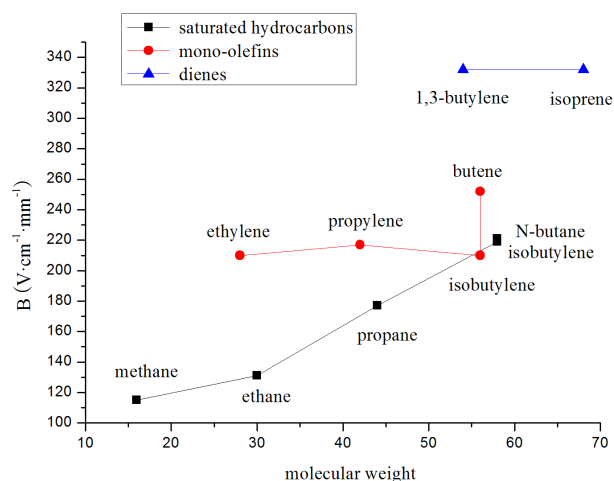


Figure 2. The relationship between the ratio (U/pd) between the breakdown voltages and the pd and the molecular weights.

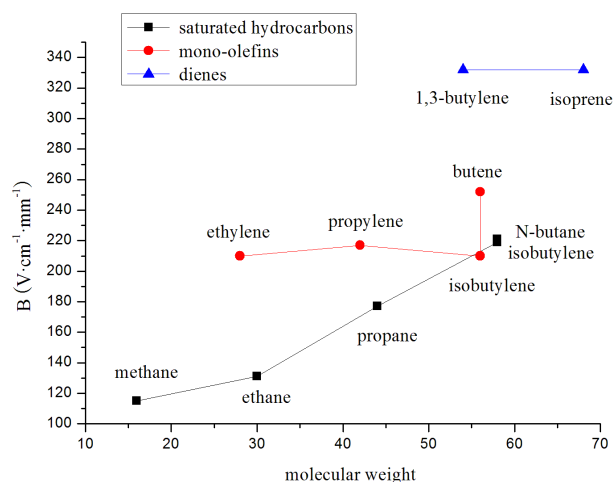


Figure 3. The relationship of the ratio (U/pd) between the breakdown voltages and pd with the boiling points.

containing of more carbon atoms brings better dielectric strength, though with small improving extent, which relates to the growing molecular volumes.

The variation of dielectric strength is significant for gases with similar molecular weights and boiling points but different structures. By the comparisons between ethylene and ethane, as well as butadiene and 1-butene, carbon-carbon double bond substantially improves the electrical performances of a gas. Research shows that the dielectric strength of hydrocarbon compounds largely depends on the integrated cross sections at low electron energy below 4 eV. For hydrocarbon gases, the double bonds or even triple bonds greatly improve the values of electron collision cross sections. The spectroscopy experiment shows that at low electron energy, such as 2 eV, the total collision cross section of ethylene is much higher than that of ethane, both of which reach an extremum at 2 eV. Study of ethylene and acetylene shows that double bond can effectively improve the insulation charac-

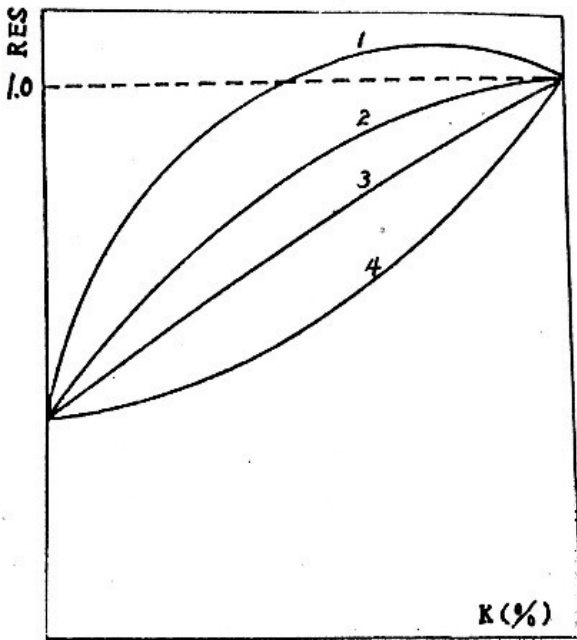


Figure 4. Four kinds of RES for binary gas mixtures.

teristics of the hydrocarbon gases, while the further improvement of dielectric strength brought by triple bond is limited compared to bi-bond hydrocarbon.

4. Synergistic effect

For gas mixtures, the affective factors are more complicated. The dielectric strength is not only related to the electric properties of gas components themselves, but also the synergistic effect between gas components. Fig. 4 represents the relative electric strength (RES) of binary gas mixtures in four different types [11]. Curve 1 refers to a positive synergistic effect, Curve 2 a synergistic effect, Curve 3 a linear effect which can be considered no interaction, and Curve 4 a negative synergistic effect. The mixing ratio k refers to the mole fraction of the gas component with higher dielectric strength in the binary mixtures, and the dielectric strength of this gas is set to be the reference of RES. For example, among SF_6 binary gas mixtures, $\text{SF}_6/\text{CF}_2\text{Cl}_2$ and $\text{SF}_6/\text{C}_3\text{F}_8$ belongs to positive synergistic effect, SF_6/N_2 and SF_6/CO_2 synergistic effect, SF_6/He linear effect, and $\text{SF}_6/\text{C}_2\text{F}_3\text{Cl}_3$ negative synergistic effect [10].

Gas mixtures utilized as insulation media in electric apparatus will bring many advantages including gas cost reduction, less environmental impact and wider application range. So taking good use of synergistic effect is significant when searching for new environmentally friendly gas in high voltage engineering. For example, SF_6/N_2 is typical gas mixtures with a synergistic effect, whose electrical strength is much higher than its linear value. When the SF_6 ratio is 50%, the uniform electrical strength of SF_6/N_2 gas mixtures is over 85% of that of pure SF_6 gas.

Additionally, the electron-attachment energy of different electronegative gases is best to cover the entire low energy range and thus free electrons with various energies in the range can be captured.

For example, the synergistic effect in electrical insulation characteristics is made good use of in the gas mixtures composed of electronegative gases N_2O , CO_2 and O_2 gases, which have electron affinity at different electron energy levels. The gases N_2O , CO_2 and O_2 have the electron attachment cross section respectively at 0.5–4.0 eV, 4.5–8 eV and 6–10 eV [12]. In other words, such gas mixtures will attach electrons over wide-range of energy level, and effectively suppress the discharging inception and propagation.

5. Interruption capability

Besides dielectric strength, a good arc-extinguishing gas medium should own good thermodynamic properties to satisfy more complicated and serious requirements in a high-pressure and high-temperature environment. The temperature of arcs in SF_6 or air circuit breaker can reach as high as over 30,000 K. Despite of insulation in room temperature, most gases become good conductor of electricity with temperature over 4000 K. The thermal recovery process after current zero largely relies on the thermodynamic and transport properties of high-temperature plasma. Researchers have long been searching for a certain property that has direct relationship with arc quenching capability, but have not reach a universal agreement yet. Recently, J Liu et al. have concluded a decisive influence of the product between density and specific heat ρC_p on the thermal interruption capability of a gas, based on the comparison between ρC_p for air and SF_6 . This discovery provides guidance for the search of SF_6 switching gas substitute [13]. Another literature [14] emphasizes the strong influence from the material properties ρ , ρC_p and ρh of a gas on the interrupting capability of a gas blast arc.

As a widely-used arc quenching medium, SF_6 will also partly decompose after arc. Literature [15] compared the density of fluorine arising from SF_6 and CF_3I which has been broadly proposed as a potential replacement for SF_6 . While the fluorine density from SF_6 increased exponentially with the current, that generated from CF_3I was small. For $\text{CF}_3\text{I}-\text{CO}_2$ gas mixtures, the fluorine could not even be detected. This result corresponds to the computational result in literature [16]. But the iodine generated from CF_3I gas brings bad effect on the arc interruption performance, which calls for effective removal of iodine by a gas flow [15]. Through a series of tests and experiments on a nozzle arc model, disconnecting switches and other arc models, it is concluded that the application of $\text{CF}_3\text{I}-\text{CO}_2$ mixtures to circuit breaker and switchgear that interrupt large fault currents is difficult, but suitable for small current interruption lower than 4000 A [17], taking into the consideration of its low damaging influence on the atmosphere and global

warming. However, its arc interruption mechanism and thus improvement on the switchgear design needs further investigation.

Besides newly gas media, some traditional gases in high voltage engineering including air and CO₂ come to the horizon of the researchers again as they are environmentally friendly. So the substitute of SF₆ in electric and arc extinguishing still has a long way to go.

6. Toxicity and effect on environment

With growing demand and concerning about environmental protection, the development of high voltage, high capacity and compact high-voltage electrical equipment become increasingly urgent, and therefore researchers are seeking for non-flammable, anti-aging excellent insulation. The max temperature using SF₆ is 180 °C, recommended by the International Electrotechnical Commission (IEC). Low fluoride in high temperature converts into acidic substances with water, and the products have an adverse effect on the human body. Then the recombination of F and S atoms (ions) ($S+6F \rightarrow SF_6$) is blocked, which will affect the interruption performance. The decomposition products in the process of SF₆ discharge or arc have highly toxic and corrosive compounds (for example, S₂F₁₀, SOF₂), non-polar pollutants (for example, air, CF₄). SF₆ breakdown voltage are sensitive to water vapor, conductive particles and surface roughness. The non-ideal gas properties of SF₆ appear at low ambient temperatures. For example, in cold climates (about at -50 °C), under normal working pressure (0.4 MPa ~ 0.5 MPa), the portion of the SF₆ gas will be liquefied. Infrared absorption of SF₆ is also effective, due to its chemical inactivity, which is difficult to be removed in the atmosphere. All these undesirable characteristics of SF₆ are called for potential greenhouse gases. One alternative is PFC (perfluorinated hydrocarbons), whose global warming potential GWP is about 1/3-1/4 of SF₆. But their GWP (6000-9200) are still relatively high and their life expectancy in the environment are also long (2600-10000). What is really expected is an environmentally friendly low-GWP value alternative to SF₆ gas. In recent years, researchers have broadly proposed a new environmentally friendly insulating gas, trifluoriodomethane (CF₃I). GWP values of this gas and CO₂ gas are rather similar, whose lifetime in the environment is only 1-2 days. Since 2007, international researchers continue to publish research reports about CF₃I insulating properties and arc performance on high-level international journals. Theoretical simulation results and experimental data have shown that, the dielectric strength of CF₃I is approximately 1.23 times more than that of SF₆. Considering environmental factors, CF₃I is regarded as an alternative to SF₆ gas in practical applications in the future.

7. Conclusion

Research on SF₆ and other potential insulation gas media applied in high voltage electric apparatus shows that

1. Gaseous compounds composed of elements in the upright area of periodic table of elements generally have stronger electronegative ability and good electrical properties. These elements with high values of both the ionization and electron affinity energy are hard to lose electrons and easy to gain them, and thus own good insulation features.
2. Double bond or triple bond in gas molecule can effectively improve the dielectric strength.
3. For gas mixtures, good cooperation of gases will generate synergetic effect, which makes its dielectric strength higher than the weighted average value of each gas.
4. Both decomposed gas and raising rate of recovery voltage affect the arc interruption capability.
5. The toxicity and environmental friendliness of alternative gas, as well as its decomposed products, also should be taken into consideration.

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References

- [1] Z. S. Zhang, D. M. Xiao, X. L. Liu, W. J. Wang, and Y. A. Wang. Analysis of the insulation characteristics of c-C₄F₈/CO₂ gas mixtures by the monte carlo method. *Journal of Physics D: Applied Physics*, 41(1):015206, 2008. doi:10.1088/0022-3727/41/1/015206.
- [2] WMO Greenhouse Gas Bulletin. The state of greenhouse gases in the atmosphere based on global observations through 2014. [2015-11-09].
- [3] L. L. Zhu, X. G. Li, and D. M. Xiao. Electron transport coefficients in SF₆ and xenon gas mixtures. *Journal of Physics D: Applied Physics*, 33(23):L145, 2000. doi:10.1088/0022-3727/33/23/102.
- [4] L. L. Zhu, Y. Z. Chen, and D. M. Xiao. Electron swarm parameters in and helium gas mixtures. *Journal of Physics D: Applied Physics*, 32(5):L18, 1999. doi:10.1088/0022-3727/32/5/004.
- [5] A. R. Ravishankara, R. R. Garcia, S. Solomon, and J. B. Burkholder. Ozone depletion and global warming potentials of CF₃I. *Journal of Geophysical Research*, 99(D10):20929, 1994. doi:10.1029/94JD01833.
- [6] W. S. Harwood, R. H. Petrucci, and F. G. Herring. *General Chemistry Principles and Modern Applications*. 8th printing, Eighth Edition. Upper Saddle River, New Jersey, New Jersey: Prentice-Hall Inc., 2002.
- [7] P. Atkins and L. Jones. *Chemistry Molecules, Matter, and Change*. 3rd printing. New York: W. H. Freeman and Company, 1997.

- [8] A. Heylen. Electric strength, molecular structure, and ultraviolet spectra of hydrocarbon gases. *The Journal of Chemical Physics.*, 29(4):813–819, 1958. doi:10.1063/1.1744595.
- [9] A. Heylen and T. Lewis. The electric strength and molecular structure of hydrocarbon gases. *Canadian Journal of Physics*, 36(6):721–739, 1958. doi:10.1139/p58-079.
- [10] J. Devins and R. Crowe. Electric strength of saturated hydrocarbon gases. *The Journal of Chemical Physics.*, 25(5):1053–1058, 1956. doi:10.1063/1.1743096.
- [11] J. Devins. Replacement gases for sf6. *IEEE Transactions on Electrical Insulation.*, EI-15(2):81–86, 1980. doi:10.1109/TEI.1980.298243.
- [12] M. Yoshida, T. Ogawa, H. Kojima, O. Kinoshita, N. Hayakawa, F. Endo, and H. Okubo. Breakdown characteristics of N₂O gas mixtures for quasiumiform electric field under lightning impulse voltage. *IEEE Transactions on Dielectrics and Electrical Insulation.*, 14(6):1492–1497, 2007. doi:10.1109/TDEI.2007.4401233.
- [13] J. Zhong, M. Fang, J. Liu, Q. Zhang, and J. Yan. Analysis of the characteristics of dc nozzle arcs in air and guidance for the search of SF₆ replacement gas. *Journal of Physics D: Applied Physics*, 49(43):435201, 2016. doi:10.1088/0022-3727/49/43/435201.
- [14] D.T. Tuma. A comparison of the behavior of SF₆ and N₂ blast arcs around current zero. *IEEE Transactions on Power Apparatus and Systems.*, PAS-99(6):2129–2137, 1980. doi:10.1109/TPAS.1980.319791.
- [15] H. Katagiri, H. Kasuya, H. Mizoguchi, and S. Yanabu. Investigation of the performance of CF₃I gas as a possible substitute for SF₆. *IEEE Transactions on Dielectrics and Electrical Insulation.*, 15(5):1424–1429, 2008. doi:10.1109/TDEI.2008.4656252.
- [16] Y. Cressault, V. Connord, H. Hingana, P. Teulet, and A. Gleizes. Transport properties of CF₃I thermal plasmas mixed with CO₂, air or N₂ as an alternative to SF₆ plasmas in high-voltage circuit breakers. *Journal of Physics D: Applied Physics.*, 44(49):495202, 2011. doi:10.1088/0022-3727/44/49/495202.
- [17] H. Kasuya, Y. Kawamura, H. Mizoguchi, Y. Nakamura, S. Yanabu, and N. Nagasaki. Interruption capability and decomposed gas density of CF₃I as a substitute for SF₆ gas. *IEEE Transactions on Dielectrics and Electrical Insulation.*, 17(4):1196–1203, 2010. doi:10.1109/TDEI.2010.5539690.