ON CALCULATION OF BREAKDOWN VOLTAGES OF MIXTURES OF ELECTRON ATTACHING GASES

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Abstract

In this paper we report the analysis of dc breakdown tests on mixtures of CCl2F2, SF6, c-C4F8, 2-C4F8, N2, CO2, CF4, CHF3, and 1,1,1-CH3CF3 gases on the basis of the NKH formula \( V_{\text{mix}} = k(pd)\alpha N^\beta U^\sigma \) developed by us earlier for the binary mixtures of SF6 with air, N2, N2O, and CO2. It is shown that while \( \alpha \) and \( \sigma \) have the values 0.915 and 0.850 respectively as earlier, \( k \) and \( \beta \) depend on the component gases. There is a good agreement between the calculated values on the basis of the formula and measured values reported in the literature.

Introduction

Heavy gases such as fluorine, chlorine, etc., belonging to the seventh group of the Periodic Table, are known to have considerably higher breakdown strengths compared to air, N2, and CO2 under similar experimental conditions because of the electron-attaching property of these gases. Due to the high cost of SF6, there is a considerable amount of experimental work in progress [1] to find alternative gases and gas mixtures which may have comparable breakdown strengths at reduced cost. It has also been shown [2] that CHF3, CF4, and 1,1,1-CH3CF3 have electron-moderating qualities resulting in improved properties when mixed with SF6 or any other electron-attaching gases. Quite a few studies [2,3] are available reporting the static breakdown voltages of these gases and gas mixtures in uniform and non-uniform filed conditions for different mixture ratios tested at different pressures. As before, we have analyzed the data of [1-3,6] and shown that the NKH formula developed by us earlier [4] can be applied to these gases and their mixtures to predict the breakdown voltages and thus putting the measured data in a handy form so that it is useful to practicing engineers.

Analysis and Results

The breakdown voltage of the gases under consideration relative to SF6 are shown in Table 1. The measurements [1-3,6] indicate that the breakdown voltage of a mixture containing an electronegative gas is related to its breakdown voltage. The available data also show that any correlation between the mixture proportion and breakdown voltage obtained from measurements at a particular \( pd \) (pressure times electrode gap) is also true for other \( pd \) values. Earlier [4] it has been shown by us that a simple mathematical expression fits such data for computing the breakdown voltages. The expression is given as

\[
V_{\text{mix}} = k(pd)^\alpha N^\beta U^\sigma
\]

which gives \( V_{\text{mix}} \) in V, when \( pd \) is in kPa-cm. \( N \) is the percentage of the electronegative gas in the mixture and \( U \) is the field utilization factor. The values of constants \( \alpha \) and \( \sigma \) are 0.915 and 0.850 respectively, whereas \( k \) and \( \beta \) depend on the component gases.

<table>
<thead>
<tr>
<th>Gas</th>
<th>RBDV</th>
<th>Gas</th>
<th>RBDV</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF6</td>
<td>1</td>
<td>CF4</td>
<td>0.39</td>
</tr>
<tr>
<td>CCl2F2</td>
<td>1.05</td>
<td>CO2</td>
<td>0.36</td>
</tr>
<tr>
<td>c-C4F8</td>
<td>1.22</td>
<td>N2</td>
<td>0.39</td>
</tr>
<tr>
<td>2-C4F8</td>
<td>1.54</td>
<td>N2</td>
<td>0.4</td>
</tr>
<tr>
<td>1,1,1-CH3CF3</td>
<td>0.41</td>
<td>Air</td>
<td>0.39</td>
</tr>
<tr>
<td>CHF3</td>
<td>0.27</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

RBDV = Relative Breakdown Voltage
above formula can be used to a minimum pd value of 1.0 kPa-cm and a minimum N of 5%. Eq. (1) is valid in uniform fields when \( \mu = 1 \) and in non-uniform fields when the non-uniformity is obtained by calculating a field utilization factor \( U \) in case of hemispherical point-plane or coaxial cylindrical geometries [4,7]. In the present case the measurements are available in coaxial cylinders only; \( U \) is therefore calculated from

\[
U = \frac{R_t}{R_o} \frac{R_o - R_t}{R_o - R_i} \ln \frac{R_o}{R_t}
\]  

(2)

where \( R_t \) and \( R_o \) are the radii of inner and outer cylinders respectively.

**METHOD OF ANALYSIS**

We have used the breakdown voltages of \( \text{CCl}_2\text{F}_2 \) in uniform fields from the measurements of Malik and Qureshi [1] to formulate the Paschen's curve in the pd range of 100 to 500 kPa-cm. A simple mathematical expression has been found to fit the data (Appendix 1) to compute the breakdown voltage of \( \text{CCl}_2\text{F}_2 \) and it is written as

\[
V_{\text{CCl}_2\text{F}_2} = 1841(pd)^{0.15}
\]  

(3)

Equation (3) gives \( V_{\text{CCl}_2\text{F}_2} \) in volts when the product \( pd \) is in kPa-cm. A comparison of the calculated values from Eq. (3) and the measured data [1] show a reasonable agreement with the error not exceeding \( \pm 8\% \).

Measurements [1] show that the breakdown voltage of a mixture containing \( \text{CCl}_2\text{F}_2 \) is a certain fixed percentage of the breakdown voltage of \( \text{CCl}_2\text{F}_2 \) itself. It can also be seen that any correlation between the mixture proportion and the breakdown voltage obtained from measurements at a particular \( pd \) is also true for other \( pd \) values. On the basis of this information, the breakdown voltage of mixtures of \( \text{CCl}_2\text{F}_2 \) with \( \text{N}_2 \) can be put into a formula (Appendix 1) such as:

\[
M = 38.03 (N)^{0.21}
\]  

(4)

where \( M \) gives the breakdown voltage of \( \text{CCl}_2\text{F}_2+N_2 \) mixture as a percentage of the breakdown voltage of \( \text{CCl}_2\text{F}_2 \) under similar conditions and \( N \) is the percentage of \( \text{CCl}_2\text{F}_2 \) in the mixture by volume. Thus if the relation is to be used for 400 kPa-cm, the breakdown voltage for \( \text{CCl}_2\text{F}_2 \) from Eq. (3) is obtained as 322.5 kV. In order to find the breakdown voltage of \( \text{CCl}_2\text{F}_2+N_2 \) mixture in which \( \text{CCl}_2\text{F}_2 \) is 40%, \( N \) is substituted as 40 in Eq. (4) and \( M \) is obtained as 82.52. Again 82.52% of the breakdown voltage 322.5 kV of \( \text{CCl}_2\text{F}_2 \) is found to be 266.13 kV as the breakdown voltage of the mixture which agrees very well with that published in the literature [1]. Calculated and measured [1] values of breakdown voltages of \( \text{CCl}_2\text{F}_2+N_2 \) mixtures are compared in Fig. 1(a) and the agreement between them is good.

Eqs. (3) and (4) can be combined into a simple expression to give the breakdown voltage of the mixture \( V \) as

\[
V_{\text{mix}} = 510(pd)^{0.15} N^{0.21}
\]  

(5)

which gives \( V_{\text{mix}} \) in \( V \) when the product \( pd \) is in kPa-cm. Thus from the above, it can be seen that the values of

\[
k, a, \text{ and } b \text{ in Eq. (1) are } 510, 0.915, \text{ and } 0.21 \text{ respectively.}
\]

Similar computations can be made for any other electronegative gas and its mixtures with other gases and the values of constants \( k, a, \text{ and } b \) can be obtained as shown in Table 2.
TABLE 2

<table>
<thead>
<tr>
<th>GAS</th>
<th>$k$</th>
<th>$b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SF$_6$+mix</td>
<td>502.4</td>
<td>0.210</td>
</tr>
<tr>
<td>SF$_6$+N$_2$</td>
<td>502.4</td>
<td>0.210</td>
</tr>
<tr>
<td>SF$_6$+CO$_2$</td>
<td>330.0</td>
<td>0.300</td>
</tr>
<tr>
<td>SF$_6$+H$_2$</td>
<td>527.7</td>
<td>0.210</td>
</tr>
<tr>
<td>SF$_6$+CHF$_3$</td>
<td>250.0</td>
<td>0.338</td>
</tr>
<tr>
<td>SF$_6$+CF$_4$</td>
<td>250.0</td>
<td>0.338</td>
</tr>
<tr>
<td>SF$_6$+1,1,1-CH$_3$CF$_3$</td>
<td>566.0</td>
<td>0.160</td>
</tr>
<tr>
<td>CCl$_2$F$_2$+N$_2$</td>
<td>510.0</td>
<td>0.210</td>
</tr>
<tr>
<td>CCl$_2$F$_2$+CO$_2$</td>
<td>335.0</td>
<td>0.300</td>
</tr>
<tr>
<td>2-C$_4$F$_8$+N$_2$</td>
<td>370.0</td>
<td>0.370</td>
</tr>
<tr>
<td>2-C$_4$F$_8$+1,1,1-CH$_3$CF$_3$</td>
<td>640.0</td>
<td>0.250</td>
</tr>
<tr>
<td>c-C$_4$F$_8$+CF$_4$</td>
<td>250.0</td>
<td>0.598</td>
</tr>
<tr>
<td>c-C$_4$F$_8$+N$_2$</td>
<td>310.0</td>
<td>0.370</td>
</tr>
<tr>
<td>c-C$_4$F$_8$+CHF$_3$</td>
<td>310.0</td>
<td>0.370</td>
</tr>
<tr>
<td>c-C$_4$F$_8$+1,1,1-CH$_3$CF$_3$</td>
<td>540.0</td>
<td>0.250</td>
</tr>
</tbody>
</table>

(1) Always $a=0.915$ and $c=0.850$
(2) Equation (1) is applicable when $pd > 1$
(3) $N=100$ gives breakdown voltage of the first gas.
(4) $U=1$ for uniform fields.
(5) In non-uniform fields
  (1) For co-axial cylinders [6] - eqn(2)
  (2) For a hemispherical point (radius $R$ and plane [7] having a gap $d$)

$$U = \left[0.6162 \frac{d}{R}\right]^{0.9716} + 1.1377$$
when $0.8 \leq \frac{d}{R} \leq 4.0$.

MIXTURES OF ELECTRON MODERATING GASES

Studies on mixtures of electron attaching gases indicate that the contribution of electron attachment towards inhibiting breakdown has been nearly optimized. Recently [2,3] it has been shown that mixtures of electronegative gases like SF$_6$ with one or more electron moderating or thermalizing gases serve to slow down free electrons for more efficient capture, thus improving the breakdown voltage of mixtures. The gases used for this purpose are polar gases like 1,1,1-CH$_3$F$_3$, CF$_4$, and CHF$_3$. We have analyzed the breakdown data [2,3] on mixtures of SF$_6$, C-C$_4$F$_8$, and 2-C$_4$F$_8$ with N$_2$, 1,1,1-CH$_3$F$_3$, CF$_4$, and CHF$_3$. These measurements have been made at $pd$ values from 8.454 to 65.437 kPa·cm in uniform field and at 126.65 kPa·cm and 556.73 kPa·cm in case of non-uniform fields using co-axial cylinders of inner and outer radius of 0.75 and 2.0 cm respectively.

**Fig. 2:** Measured [6] and calculated values of static breakdown voltages in mixtures of SF$_6$+CO$_2$ in uniform field

**Fig. 3:** Measured [2] and calculated values of static breakdown voltages in mixtures of SF$_6$+CF$_4$ in uniform field
Mixtures with \( \text{SF}_6 \)

The breakdown voltage of \( \text{SF}_6 \) at different \( pd \) can be obtained from Eq. (1) in uniform field conditions when \( \mu=1 \) and \( N=100 \) with \( k \) and \( b \) values shown in Table 2. Analysis of the relative breakdown voltage ratios in \( \text{SF}_6+\text{CF}_4 \), \( \text{SF}_6+\text{CHF}_3 \), and \( \text{SF}_6+1,1,1-\text{CH}_3\text{CF}_3 \) shows that Eq. (1) yields breakdown voltages of these mixtures in uniform and non-uniform fields with the values of \( k \) and \( b \) also shown in Table 2. It is to be noted that the values of \( a \) and \( c \) remain constant in all cases. The calculated and measured [3] values have been plotted in Figs. 3, 4 and 5 and are in good agreement.

Mixtures with \( \text{C}_2\text{H}_4\text{F}_8 \) and \( 2-\text{C}_4\text{F}_8 \)

\( \text{C}_2\text{H}_4\text{F}_8 \) and \( 2-\text{C}_4\text{F}_8 \) have higher dielectric strengths than \( \text{SF}_6 \) and their breakdown voltage is related to \( pd \) by Eq. (1) with appropriate values of \( k \) and \( b \) from Table 2; \( a \) and \( c \) remaining constant. The mixtures of these gases show relatively a higher breakdown voltage compared to the mixtures of \( \text{SF}_6 \) under similar conditions. Breakdown in 2-\( \text{C}_4\text{F}_8+\text{N}_2 \), 2-\( \text{C}_4\text{F}_8+1,1,1-\text{CH}_3\text{CF}_3 \), c-\( \text{C}_4\text{F}_8+\text{CF}_4 \), c-\( \text{C}_4\text{F}_8+\text{CHF}_3 \), c-\( \text{C}_4\text{F}_8+\text{N}_2 \), and c-\( \text{C}_4\text{F}_8+1,1,1-\text{CH}_3\text{CF}_3 \) shows that Eq. (1) gives reasonably accurate values of breakdown voltages as shown in Figs. 6-9.

Fig. 4: Measured [2,3] and calculated values of static breakdown voltages in mixtures of \( \text{SF}_6+\text{CHF}_3 \) (a) in uniform field and (b) in non-uniform field (coaxial cylinders, \( R_0=0.76 \) cm and \( R=5.0 \) cm)

Fig. 5: Measured [2,3] and calculated values of static breakdown voltages in mixtures of \( \text{SF}_6+1,1,1-\text{CH}_3\text{CF}_3 \) in uniform and non-uniform field (coaxial cylinders, \( R_0=0.76 \) cm and \( R=5.0 \) cm)

Fig. 6: Measured [3] and calculated values of static breakdown voltages in mixtures of 2-\( \text{C}_4\text{F}_8+\text{N}_2 \) and 2-\( \text{C}_4\text{F}_8+1,1,1-\text{CH}_3\text{CF}_3 \) in coaxial electrode systems (\( R_0=0.76 \) cm and \( R=5.0 \) cm)
DISCUSSION

It is important to note that Eq. (1) synthesizes three factors which can be separated by appropriately splitting \( k \) into \( k_1 \) and \( k_2 \) \((k=k_1k_2)\) and writing

\[ V_{mix} = k_1(pd)^\alpha \cdot k_2 \cdot \beta \cdot d^\beta \]

(7)

The first part \( k_1(pd)^\alpha \) gives breakdown of the main gases illustrated by Eq. (3) in the case of CCl\(_2\)F\(_2\). Secondly, it incorporates in itself an expression \( k_2d^\beta \) such as Eq. (4) which tells what percent of the breakdown voltage of the main gas can be realized for a particular mixture and thirdly it includes \( U \) as the effect of non-uniformity of the electrode system. The first part of the equation can be correlated to the ionization property of the gas leading to breakdown as shown in Appendix 2 [5]. It is thus possible to replace this part of the empirical Eq. (1) with an equation which is based on fundamental properties of a gas. The second part of the equation will have to be based on the effective electron attachment property of the gas and its relative efficiency in a mixture. Quantitative data on attachment is not yet available in electron-negative gases over the full \( pd \) range discussed here. The third part of Eq. (1) is analytical in nature and is based at present on considerations of maximum and average electric field \((E_{max} \text{ and } E_{av})\) in different electrode systems and their effect on the breakdown voltage.

With some limitations Eq. (1) has however been applied earlier quite successfully in dc and power frequency ac breakdowns [4] over a wide range of \( pd \). Studies reported here are available in a limited \( pd \) range and only in dc voltage. On the basis of earlier comparison it may be said that power frequency ac breakdown voltages in the mixtures reported in this paper will not be much different than dc voltages, thus Eq. (1) will be valid with small modifications in numerical values of \( k \) and \( b \) in most of these cases.

SUMMARY

Table 2 summarizes the full analysis of the breakdown in electron attaching gases and their mixtures for all the measurements discussed in this and the earlier [4] paper. Calculated and measured values of breakdown voltages are found to be in good agreement in all these cases. This analysis illustrates that the breakdown voltage data on gas-mixtures can be formulated and similar measurements in gas mixtures not analyzed here can easily be understood by using this analysis. It should, however, be noted that there is a need of devising a standard test cell and procedure to ascertain variability in experimental measurements and make this analysis more accurate.
APPENDIX - I

BREAKDOWN VOLTAGE OF CCl₂F₂

The breakdown voltage of a uniform field gap in CCl₂F₂ for pd values of 100, 200, 300, and 400 kPa cm from the data of Malik and Qureshi [1] is shown in Fig. 10. On a log-log scale the data follows a straight line showing an equation of the form

$$\ln V_{CCl_2F_2} = m \ln(pd) + n$$

(8)

can be fitted to these data. Numerical values of slope m and constant n are determined by considering any two points on the line. The values determined by us are \(m=0.915\) and \(n=13.31\) which therefore yields Eq. (3).

BREAKDOWN OF MIXTURE OF CCl₂F₂+N₂

As stated in the text, the breakdown voltage of a mixture containing CCl₂F₂ is a certain fixed percentage of the breakdown voltage of CCl₂F₂ itself. Also any correlation between the mixture proportion and the breakdown voltage obtained from measurements at a particular pd also holds for other pd values. Average values of percentage breakdown voltages of a mixture relative to CCl₂F₂ from measurements at 100, 200, 300, 400, and 500 kPa cm are obtained from the published data [1] and are shown in Fig. 11 against percentage (5 to 100) of CCl₂F₂ in the mixture.

These average values follow an approximate straight line on a log-log scale indicating that Eq. (8) can be applied in this case also. The numerical values of \(m\) and \(n\) determined by us here are 0.21 and 38.03 respectively, yielding Eq. (4).
APPENDIX - 2

On the basis of Townsend breakdown criteria for electron attaching gases

\[ \gamma \frac{a}{(a-n)} \left[ \exp(a-n)d - 1 \right] = I, \]

the breakdown voltage is given as

\[ V_b = \frac{Bpd}{\ln[\frac{Apd}{\ln(1+\frac{a-n}{\alpha})}]} \]

(9)

where \( p \) is pressure, \( d \) is gap distance, \( a, \gamma, n \) are primary ionization, secondary ionization, and attachment coefficients respectively, and \( A \) and \( B \) are constants related to molecular properties of the gas. Eq. (9) may be rewritten as

\[ V_b = \frac{Bpd}{\ln pd + K} \]

(10)

where

\[ K = \ln[\frac{A}{\ln(1+\frac{a-n}{\alpha})}] \]

(11)

Eq. (10) may be used for evaluating the breakdown voltage \( V_b \) if \( B \) is known and if it is possible to evaluate \( K \) for all \( pd \) values. It has been made possible by us in the case of SF6 by obtaining \( B \) from published literature and computing \( K \) from

\[ K = \ln[6.4541(pd)^{-0.3174}] \quad \text{for } 3.0 \leq pd \leq 1200 \text{ kPa·cm} \]

and

\[ K = \ln[4.2827(pd)^{-0.3131}] \quad \text{for } 0.3 \leq pd \leq 3.0 \text{ kPa·cm} \]

(12)

Using Eqs. (10) and (11), it is possible to evaluate \( V_b \) in \( V \) at any \( pd \) for SF6 in the \( pd \) range of 0.3 to 1200 kPa·cm.

It is thus possible to replace the first part of Eq. (7) with a fundamental equation of the form as given by Eq. (10) and the same can be written as

\[ V_{mix} = \frac{Bpd}{\ln pd + K} k_2 \mu^2 \rho \]

(12)

REFERENCES


