Theoretical Study of Energy Distribution Function and Other Parameters for CF$_4$-He Gas Mixtures Discharge

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Abstract: In this research, the electron energy distribution function of electrons in plasma discharge is studied for CF$_4$-He gas mixtures. The Boltzmann equation was solved by using Fortran computer program. The Boltzmann transport equation was solved by using two-terms approximation for pure gases and mixtures. This method of solution is used to calculate the electron energy distribution function and electric transport parameters were evaluated in the range of E/N varying from $1 \times 10^{-17} \leq E/N \leq 5 \times 10^{-15}$ V.cm^2. The electron energy distribution function of CF$_4$-He gas mixture is nearly of Maxwellian distribution at 1, 2 Td and when E/N $\geq$ 5 Td the distribution function is non Maxwellian. Also, the mixtures are have different energy values depended on transport energy between electron and molecule through the collisions.

Key words: Electric discharge, collisions, gas mixtures, Boltzmann equation, CF$_4$-He, Maxwellian distribution

INTRODUCTION

The Electron Energy Distribution Function (EEDF) and transport parameters of gas mixtures have been studied for a wide range of applied electric field.These parameters such as the drift velocity, mobility, diffusion coefficient, ionization coefficient and mean electron energy which are defined in collision cross section and EEDF is represented the backbone of the electron swarm behavior of pure gas and gas mixtures in discharge of plasma (Date *et al.*, 1989).

Solution of transport Boltzmann equation for the electron-velocity distribution function $f(\vec{r}, \vec{v}, t)$ in spherical harmonics is given by Smith and Thomson (1978):

$$f(\vec{r}, \vec{v}, t) = \sum_{\ell=0}^{\infty} f_\ell(\vec{r}, \vec{v}, t) p_\ell \cos\theta \qquad (1)$$

where, $f_\ell(\vec{r}, \vec{v}, t)$ represent coefficient of expansion and $P_\ell \cos\theta$ is Legendre polynomials. By using two-terms approximation, the equation form become:

$$f(\vec{r}, \vec{v}, t) = f_0(\vec{r}, \vec{v}, t) + f_1(\vec{r}, \vec{v}, t) \cos\theta \qquad (2)$$

$$f(\vec{v}) = f_0(\vec{v}) + \frac{\vec{v}}{v} f_1(\vec{v}) \qquad (3)$$

The first term $f_0(\vec{v})$ is isotropic distribution in velocity space. This occurs in elastic collisions where the electrons could be expected to suffer large directional changes of velocity but relatively small energy losses because of mass deference between electrons and molecules. The second term $\frac{\vec{v}}{v} f_1(\vec{v})$ the distribution is anisotropic because of large energy losses of electron in in elastic collisions, f_1, f_0.

Theory: The fundamental equation governing the electron distribution function is the Boltzmann equation. For spatially uniform gas in the presence of steady electric field. The Boltzmann equation for electrons in collisions state is given by Holstein (1946):

$$\frac{\partial f}{\partial t} + v \frac{\partial f}{\partial r} - \frac{e\vec{E}}{m} \frac{\partial f}{\partial v} = \left(\frac{df}{dt}\right)_c \qquad (4)$$

where $(df/dt)_c$ represents the rate of change of $f(\vec{r}, \vec{v}, t)$ due to collision, thus, when collisions are considered. The total derivative df/dt represents all particles moving in the phase space where the partial derivative $\partial f/\partial t$ represents the change in the number of electrons at a given point in the phase space.

Now one considers the case of spatially uniform gas, also, $f(\vec{r}, \vec{v}, t)$ function of velocity only where $\nabla_r f = 0$ and thus, Eq. 4 becomes:

$$\frac{\partial f}{\partial t} - \frac{e\vec{E}}{m} \nabla_v f = \left(\frac{df}{dt}\right)_c \qquad (5)$$

Consider now only electron-neutral atoms collisions. The contribution of collision of each kind to the change the distribution function can be quite simply added together. One will divide collisions into elastic and inelastic collisions:

$$\left(\frac{df}{dt}\right)_c = \left(\frac{df}{dt}\right)_{elastic} + \left(\frac{df}{dt}\right)_{inelastic} \tag{6}$$

The first part of Eq. 6 represents the change of function due to elastic collisions and the second part of equation represents the change of function because the inelastic collisions. The class of inelastic collisions do not include excitation process o f atoms or molecules but also, the creation of new electrons as a result of ionization. After the compensation (two-terms approximation), we obtain two equations:

$$\frac{\partial f_0}{\partial t} - \frac{e\vec{E}}{m}\frac{1}{3v^2}\frac{\partial}{\partial v}\left(v^2 f_1\right) = \left(\frac{df_0}{dt}\right)_c \tag{7}$$

$$\frac{\partial f_1}{\partial t} - \frac{e\vec{E}}{m}\frac{\partial f_0}{\partial v} = \left(\frac{df_1}{dt}\right)_c \tag{8}$$

When the electron collision frequency for momentum-transfer is much larger than the electron collision frequency for excitation, the necessary condition for the two terms expansion for distribution function to be valid , the momentum-transfer collisions play the major role in reducing the asymmetry in the distribution function. The function change in elastic collisions state is given by Hussein (2007):

$$\left(\frac{df_1}{dt}\right)_c = -\upsilon_e(v) f_1(\vec{v}) \tag{9}$$

υ_e is the electron momentum-transfer collision frequency where, $\upsilon_e(v) = NQ_m(v)v$:

$$\left(\frac{df_1}{dt}\right)_c = -NQ_m(v) v f_1(\vec{v}) \tag{10}$$

Where:
V = Electron velocity
Q_m = Momentum transfer cross section

From the solution of Eq. 8, we will find $f_1(v)$ value where all quantities are assumed to independent of time is given by:

$$f_1(\vec{v}) = \frac{e\vec{E}}{mvNQ_m(v)}\frac{\partial f_0}{\partial v} \tag{11}$$

The change of function in elastic collisions is given by:

$$\frac{\partial f_0}{\partial t} - \frac{2e}{mv}\frac{\partial}{\partial \varepsilon}\left[\begin{array}{c}\dfrac{\vec{E}^2 \varepsilon}{3NQ_m}\dfrac{\partial f_0}{\partial \varepsilon} + \dfrac{2m}{M}NQ_m \varepsilon^2 f_0 + \\[2mm] \dfrac{2mK_BT}{Me}NQ_m \varepsilon^2 \dfrac{\partial f_0}{\partial \varepsilon}\end{array}\right] = \left(\frac{df_0}{dt}\right)_c \tag{12}$$

Now , the change of the function $(df/dt)_c$ for inelastic collisions is given by equations:

$$\left(\frac{df}{dt}\right)_{LOSS} = \sum_j N_0[f_0\left(\varepsilon+\varepsilon_j\right)Q_j\left(\varepsilon+\varepsilon_j\right) \tag{13}$$
$$\left(\varepsilon+\varepsilon_j\right) - f_0\left(\varepsilon\right)Q_j\left(\varepsilon\right)\varepsilon]2e/mv$$

The energy gain from electric field in superelastic collisions is given by Holstein (1946):

$$\left(\frac{df}{dt}\right)_{GAIN} = \sum_j N_j\left[f_0\left(\varepsilon-\varepsilon_j\right)Q_j\left(\varepsilon-\varepsilon_j\right) - \tag{14}$$
$$f_0\left(\varepsilon\right)Q_j\left(\varepsilon\right)\varepsilon\right]2e/mv$$

Now, the sum of function change in two state (ground state and excitated state), after the equations compensation (Eq. 12-14), we obtain on work equation (Hussein, 2007):

$$\left(\frac{m\varepsilon}{2e}\right)^{1/2}\frac{\partial f_0}{\partial t} = \frac{E^2}{3}\frac{\partial}{\partial \varepsilon}\left(\frac{\varepsilon}{NQ_m}\frac{\partial f_0}{\partial \varepsilon}\right) + \frac{2m}{M}\frac{\partial}{\partial \varepsilon}\left(\varepsilon^2 NQ_m f_0\right) +$$
$$\frac{2mk_BT}{Me}\frac{\partial}{\partial \varepsilon}\left(\varepsilon^2 NQ_m \frac{\partial f_0}{\partial \varepsilon}\right) +$$
$$\sum_j\left[\left(\varepsilon+\varepsilon_j\right)f_0\left(\varepsilon+\varepsilon_j\right)N_0Q_j\left(\varepsilon+\varepsilon_j\right) - \varepsilon f_0\left(\varepsilon\right)N_0Q_j\left(\varepsilon\right)\right] +$$
$$\sum_j\left[\left(\varepsilon-\varepsilon_j\right)f_0\left(\varepsilon-\varepsilon_j\right)N_jQ_{-j}\left(\varepsilon-\varepsilon_j\right) - \varepsilon f_0\left(\varepsilon\right)N_jQ_{-j}\left(\varepsilon\right)\right] \tag{15}$$

In right hand side of Eq. 15, the first part accounts for the gain of energy result from electric field. The second part of equation accounts for gain in energy (KT) and elastic losses by 2 m/M. Also, in third part of the equation, few energy losses occur because of elastic scattering of electron due to electron collision with molecule. These, processes all occurs in ground state of molecules. The first term of excitation state, accounts energy losses of electrons result the inelastic collisions. The last part of Eq. 15 is the energy gain of electrons given by the electric field electrons to compensatethe energy loss of electrons because the collisions.

When the left hand side of Eq. 15 = 0, the function f (ε) species becomes isotropic. Equation 15 is used in pure gasious state if the gas is mixture of different species. The momentum transfer cross section, excitation cross section and super elastic for molecules of species (k) in inelastic processes are represented by Q_m^k, Q_j^k, Q_{-j}^k, respectively. Also, the electron collision frequency in elastic collisions state for molecules of k (mixtures) become:

$$\upsilon_e^k(v) = N_K Q_m^K(v) v \qquad (16)$$

where, N_k is the number of molecules of species k, Eq. 15 becomes to have different new form for molecules of species k and is given by Holstein (1946):

$$\left(\frac{m\varepsilon}{2e}\right)^{1/2}\frac{\partial f_0}{\partial t} = \frac{E^2}{3}\frac{\partial}{\partial\varepsilon}\left(\varepsilon\left(\sum_j N_K Q_m^k\right)^{-1}\frac{\partial f_0}{\partial\varepsilon}\right)+$$

$$2m\frac{\partial}{\partial\varepsilon}\left(\varepsilon^2\left(\sum_K \frac{NQ_m^k}{M_K}\right)f_0\right)+$$

$$\frac{2mk_BT}{e}\frac{\partial}{\partial\varepsilon}\left(\varepsilon^2\left(\sum_j \frac{N_K Q_m^k}{M_k}\right)\frac{\partial f_0}{\partial\varepsilon}\right)+ \qquad (17)$$

$$\sum_j\sum_k\left[\left(\varepsilon+\varepsilon_{jk}\right)f_0\left(\varepsilon+\varepsilon_{jk}\right)N_K Q_j^K\left(\varepsilon+\varepsilon_j\right)-\varepsilon f_0(\varepsilon)N_K Q_j^K(\varepsilon)\right]+$$

$$\sum_j\sum_k\left[\left(\varepsilon-\varepsilon_{jk}\right)f_0\left(\varepsilon-\varepsilon_{jk}\right)N_{kj}Q_{-j}^k\left(\varepsilon-\varepsilon_{jk}\right)-\varepsilon f_0(\varepsilon)N_{kj}Q_{-j}^k(\varepsilon)\right]$$

where, ε_{jk} represent energy of excitation in j excited state of species k.

MATERIALS AND METHODS

Transport coefficients: The transport coefficients were calculated in this research and represent processes related to the transport of mass, momentum, energy and charges in plasma are generally called transport phenomena.

The drift velocity is nonlinear function with electric field and the mobility depends on strengthfield. at sufficiently low E/N where an electron loses all equal to the gain from the electric field at one elastic collision , the drift velocity is proportional to E/N.

The relation between drift velocity and distribution function of electron energy is given by Nighan, (1970):

$$v_d = -\frac{E}{3}\left(\frac{2e}{m}\right)^{1/2}\int_0^\infty \frac{u}{NQ_m(u)}\frac{df_0}{du}du \qquad (18)$$

The mobility is defined as the proportionally coefficient between the drift velocity of a charged particle and electric field. The mobility of electrons is:

$$\mu_e = \frac{e}{m\upsilon_m} = \frac{v_d}{E} \qquad (19)$$

where, υ_m represent the electron momentum-transfer collision frequency. The electron mobility decreased as E/N increase, this occur energy loss result of electron through the collisions between electrons and neutral molecules.

From the relation between the drift velocity and mobility with EEDF, we can be calculating electron mobility equation (Truesdell, 1962):

$$\mu_e = -\frac{1}{3}\left(\frac{2e}{m}\right)^{1/2}\int_0^\infty \frac{u}{\sum \delta_s Q_m(u)}\frac{df_0}{du}du \qquad (20)$$

where, δ_s represents fractional concentration of the s species ($\delta_s = N_s^j/N_s$) and N_s^j is the number of molecules of species s in the excited state j.

When the density of charged particles is very low, the charges of opposite signs diffuse independently of each other. This is known as free diffusion.

In a weakly ionized gas discharge, the ambipolar diffusion coefficient is simplified by noting that μ_e, μ_i usually, the relation between diffusion coefficient and electron energy distribution function is given by Makabe and Petrovic (2006):

$$D_T = \frac{1}{3}\left(\frac{2}{m}\right)^{1/2}\int \frac{u^{1/2}}{NQ_m(u)}f(u)du\frac{1}{n} \qquad (21)$$

An electron colliding with a neutral atom can produce a negative ion in a process termed electron attachment. Dissociative and non dissociative electron attachment reactions depend strongly on the electron energy. The rate electron attachment R_a is define by relation (Raizer, 1991):

$$R_a = \left(\frac{2}{m}\right)^{1/2}\int_\varepsilon NQ_a(\varepsilon)f(\varepsilon)d\varepsilon \qquad (22)$$

Where:
$Q_a(\varepsilon)$ = Attachment cross section
$f(\varepsilon)$ = The energy distribution function of electrons is normalized to unity

The rate electron attachment describes directly the loss of electrons and the increase of negative ion density in plasma kinetics.

The attachment coefficient of electron η/N is given by the relation:

$$\frac{\eta}{N} = \frac{1}{v_d}\left(\frac{2}{m}\right)^{1/2} \sum_k \int_{ik} \frac{N_K}{N} Q_{ak}(u)uf_0(u)du \quad (23)$$

RESULTS AND DISCUSSION

Pure helium gas: The momentum transfer cross-section of electrons in helium gas is almost constant up to electron energies of about 2 eV (Raizer, 1991) for energies higher than that the momentum transfer cross-section of electrons decreases for entire inelastic collision regime.

At low E/N the electrons in thermal equilibrium with the gas and thus Te = Tg. As E/N increases, the average value of Te rises well above this value. In the simple case where only a constant elastic cross-section is involved, Te increases linearly with E/N values above Tg, however, the elastic collision cross-section changes with electron energy.

Figure 1 represents ship between distribution function and electron energy. At the value (1 Td) of E/N, the distribution function apparently is approximately Maxwellian (less losses in energy) and this means that the system is in thermal equilibrium (isotropic distribution). For E/N >5 Td, the electron energy distribution is modified by inelastic collisions and excitation of the helium gas limits the mean energy of the electrons and the distribution is non Maxwellian (eD/μ, 2/3⟨ε⟩).

Figure 2 shows the mean electron energy for helium gas in range (0.59-3.15) eV, for E/N values 1×10^{-17} V. cm^2-1×10^{-15} $V.cm^2$. At low E/N the electron energy distribution is defined by elastic collisions and the mean electronic energy significantly exceeds the gas temperature.

We notice that the drift velocitydepends linearly on the ratio E/N as shown in Fig. 3 and can be explained by the kinetic theory. These results are in good agreement with results of Makabe and Petrovic (2006). As an electron swarm drifts with a velocity V_d under the influence of an electric field E, it also, diffuses due to the thermal motion of the electrons.

The characteristic energy of electron is a widely measured parameter of electron swarms and represented in Fig. 4. It is approximately equal to the average electron energy at (1-2Td) (the elastic collision region). At low E/N electrons are in thermal equilibrium with the gas and thus, $T_e = T_g$. When E/N increases, the average value of thermal energy of electron isrises as result of collisions.

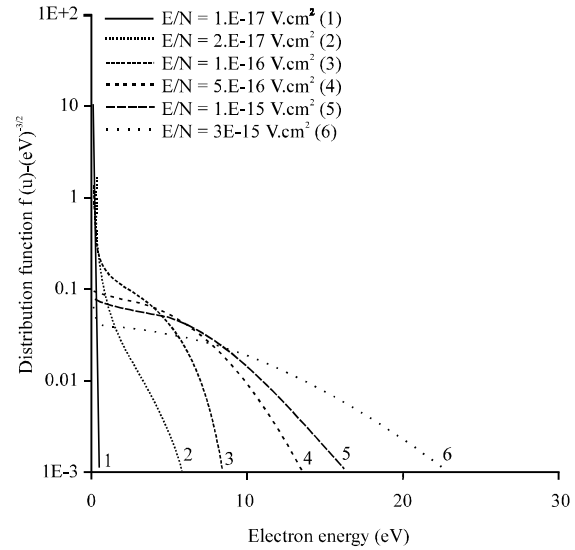Fig. 1: The EEDF as a function of electron energy for several values of E/N in pure helium gas
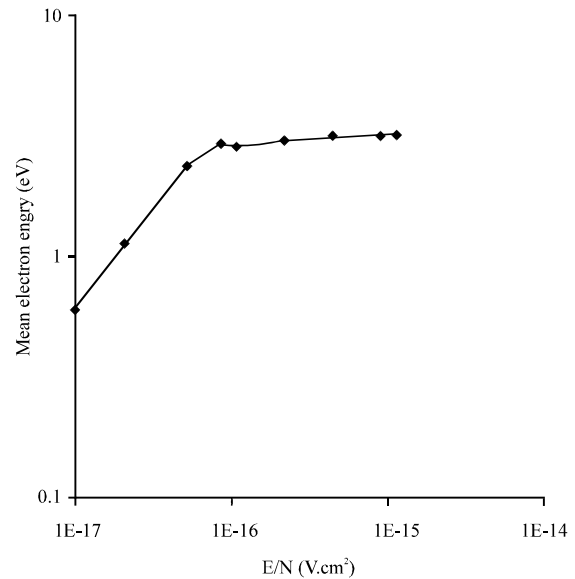

Fig. 2: The mean electron energy as a function of E/N in pure helium

Figure 5 shows the mobility of electron as a function of E/N, it decreases with E/N increase from 1-5Td, thereafter, the electrons get energy gain from the electric field and result in momentum transfer of atoms through inelastic collisions, also, number of collisions with neutral atoms expected decreases, therefore, the electron mobility increases.

We see that at very low electric field strength the diffusion is isotropic in elastic collisions. The diffusion coefficient when E/N $\leq 5\times10^{-17}$ $V.cm^2$ is increased due to elastic collisions in this region Fig. 6.
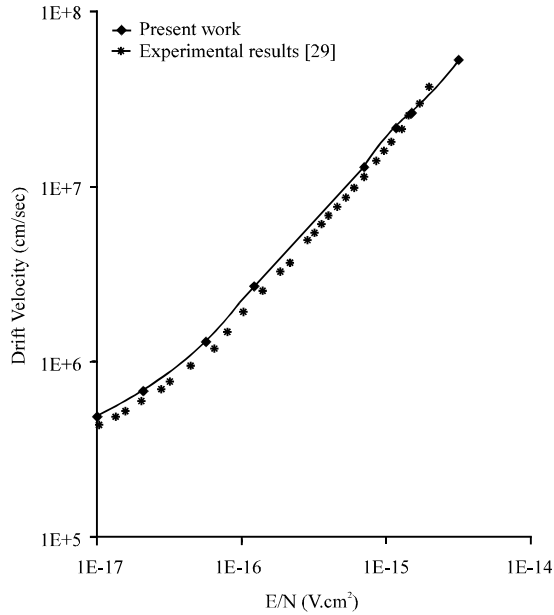
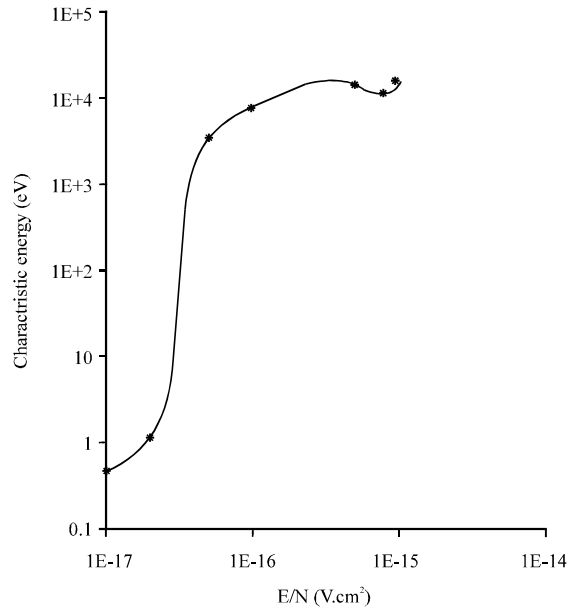Fig. 3: The drift velocity of electron

Fig. 5: The mobility of electron as a function of E/N in pure helium gas

Fig. 4: The characteristic energy of as a function of E/N in pure helium gas. Electron as a function of E/N in pure helium
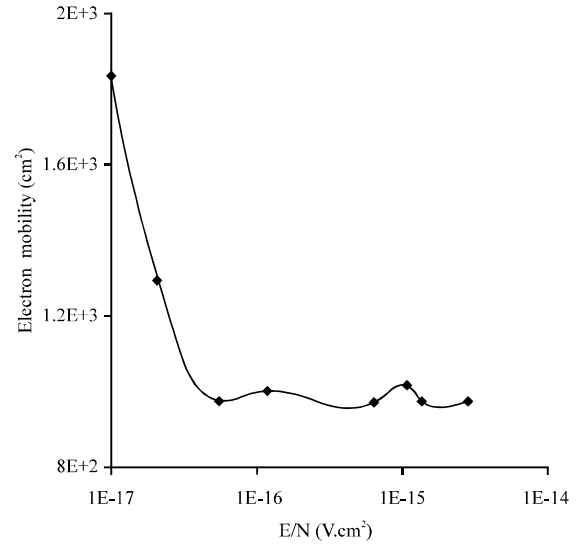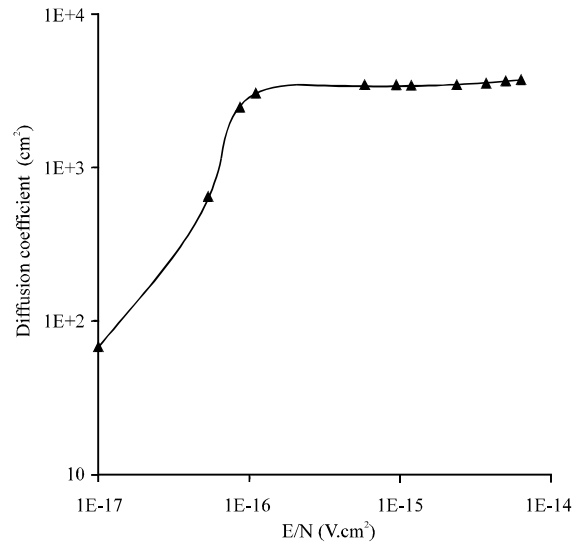

Fig. 6: The diffusion coefficient of electron as a function of E/N in pure helium gas

Carbon tetrafluoride-helium mixtures: The transport Boltzmann equation was solved for CF_4-He mixtures of different ratios. The electron swarm parameters for different mixtures have been analyzed for the range of E/N values $(1\times10^{-17}$ V.cm$^2 \leq$ E/N $\leq 5\times10^{-15}$ V.cm$^2)$. The different mixing ratios of CF_4-He gases are illustrated in Table 1.

The electron energy distribution functions are represented in Fig. 7-10. The electron energy distribution

Table 1: The gas mixtures of different ratios of CF_4-He gases

Mixtures	CF_4 (%)	He (%)
1	90	10
2	75	25
3	50	50
4	25	75
5	10	90

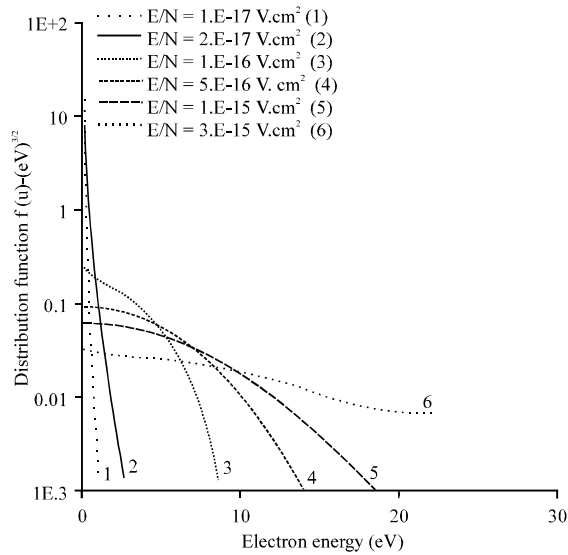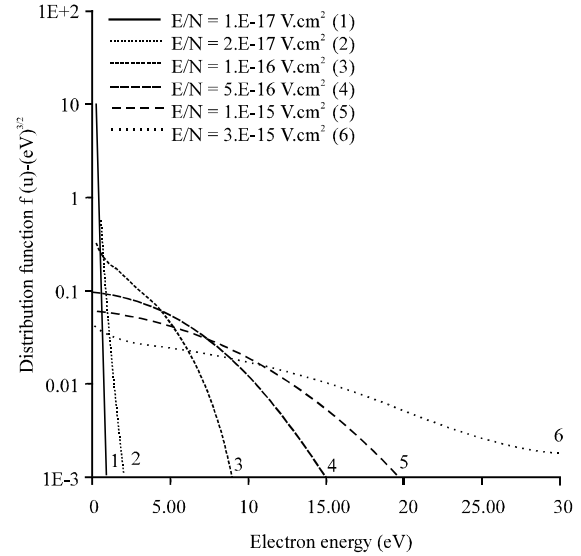Fig. 7: The EEDF as a function of electron energy for several values 0f E/N in 90% CF_4+10% Ar gases mixture

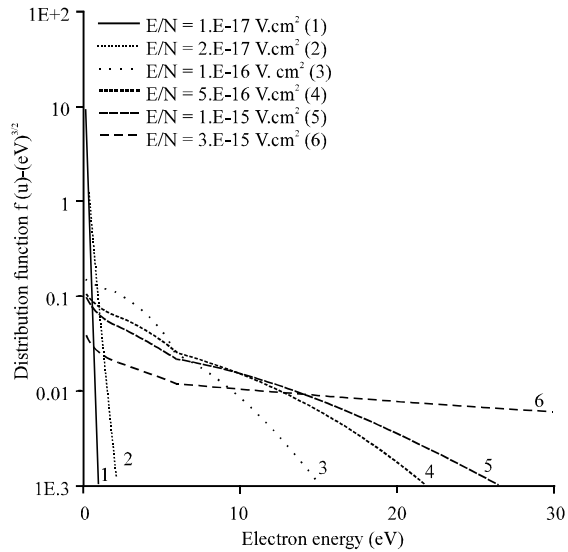Fig. 9: The EEDF as a function of electron energy for several values of E/N in 50% CF_4+50% He gases mixture

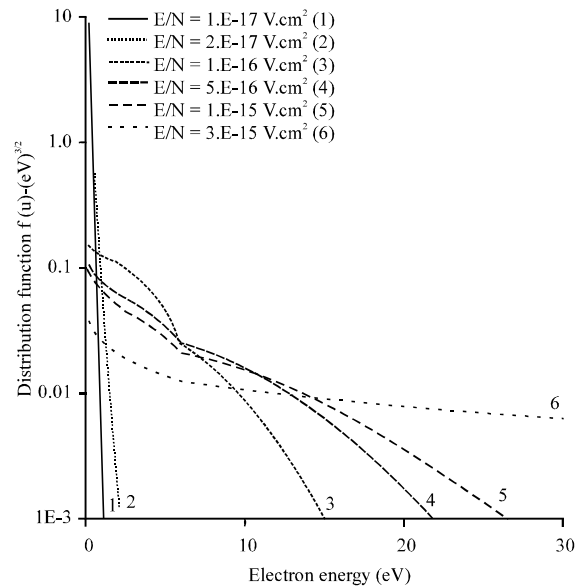Fig. 8: The EEDF as a function of electron energy for several values of E/N in 25% CF_4+75% He

Fig. 10: The EEDF as a function of electron for values of E/N in 10% CF_4+90% He mixture

function in most mixtures has very nearly on isotropic distribution at 1, 2 Td with energy losses of electrons is very small compared with the equilibrium state. The distribution is non Maxwellian when the values of E/N is larger than 2Td.

Figure 11 shows the values of mean electron energy of different mixtures. The electron energy in mixture (10% CF_4, 90% He) is higher than other gas mixtures in energy range (0.24-17.65) eV for electric field

density between 1×10^{-17} V.$cm^2 \leq E/N \leq 5 \times 10^{-15}$ V.cm^2 and this occurs at minimum ratio of CF_4 gas because the probability of collisions between the electrons and neutral atoms of gas is very small, therefore, the energy loses of electrons during collisions decrease and vice versa in gas mixture (90% CF_4, 10% He), the number collisions increase (lose of electron energy is larger).
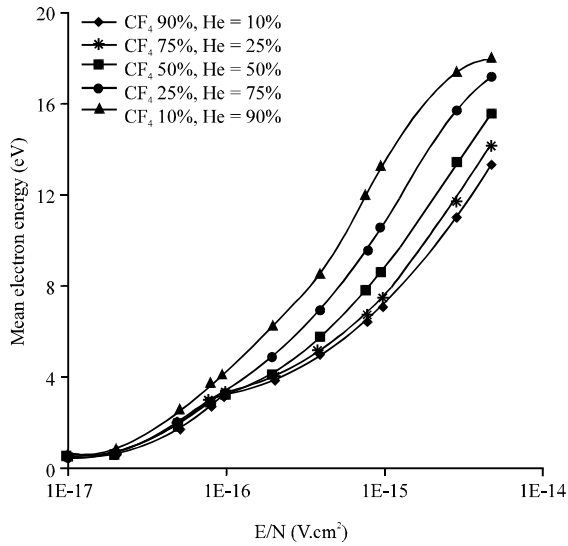
Fig. 11: The EEDF as a function of E/N ratios of gas mixtures (CF$_4$-He)
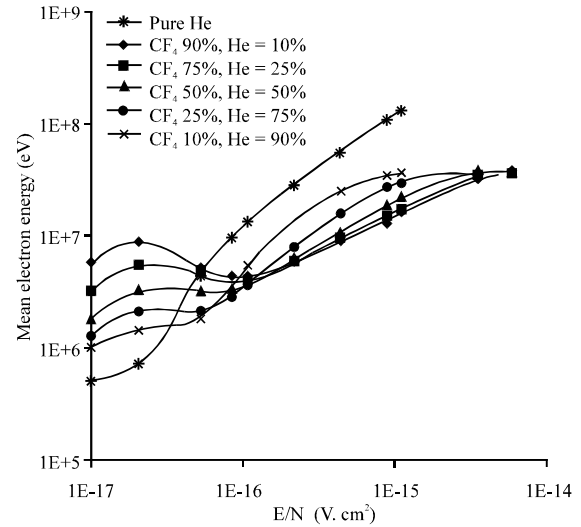

Fig. 13: The drift velocity of electron as a function of E/N in different ratios of gas mixtures (CF$_4$-He)
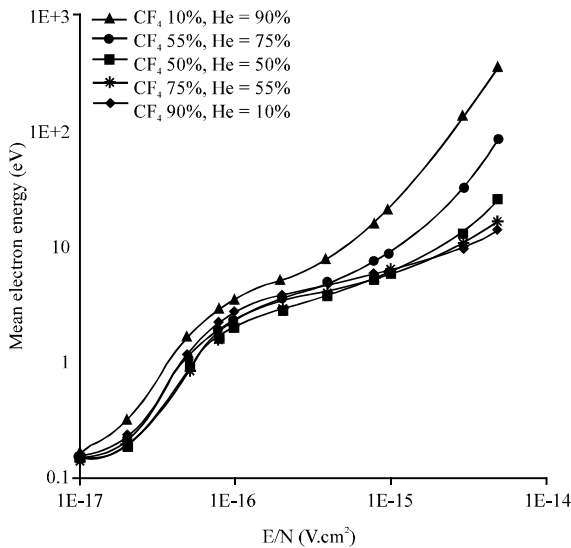

Fig. 12: The characteristic energy of different in electron as a function of E/N in different of mixtures (CF$_4$-He)
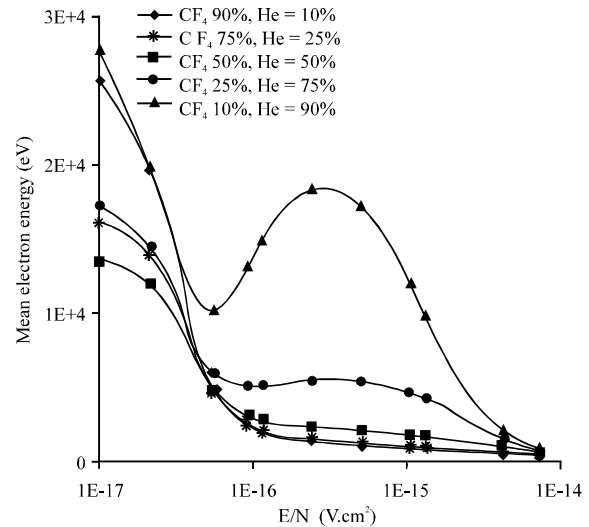

Fig. 14: The mobility of electron as a function of E/N in different ratios of gas mixtures (CF$_4$-He)

The characteristic energy (thermal electron energy) is represented in Fig. 12. The characteristic energy increase with E/N for minimum ratio of CF$_4$ gas because the thermal energy is transformed due to collisions between the electrons and neutral atoms.

The drift velocity of different mixtures as a function of E/N is shown in Fig. 13. The drift velocity increases when the electric field increases and become larger at maximum ratio of CF$_4$. In this ratio the electrons is gained large momentum transfed from molecule or atoms during collision.

Figure 14 shows the electron mobility as a function of E/N for different mixtures. The mobility is nonlinear and decreases as E/N increase, the behavior is change to mixture (10% CF$_4$, 90% He) at $5Td \leq E/N \leq 20Td$ where the mobility increases. This means that in this region number of collisions very small and energy gain from electric field is larger than energy losses due to collision, also, it is expected that the electron momentum has high value after collision.

CONCLUSION

The characteristic of energy in helium gas is large compared with mixtures. The mean electron energy to mixture is increasing at helium ratios increased. The higher of mean electron energy in 10% CF_4+90% He gas mixture and the behavior variation in electron mobility at this ratio.

REFERENCES

Date, H., Y. Sakai and H. Tagashira, 1989. Boltzmann equation analysis of electron collision cross sections and swarm parameters for Krypton. J. D. Appl. Phys., 22: 1478-1481.

Holstein, T., 1946. Energy distribution of electrons in high frequency gas discharges. Phys. Rev., 70: 367-384.

Hussein, S.R., 2007. Solution of Boltzmann equation using two terms approximation for several SF6 and other gases mixture. Ph.D Thesis, Salahaddin University-Erbil, Erbil, Iraqi Kurdistan.

Makabe, T. and Z. Petrovic, 2006. Plasma Electronics: Application in Microelectronics Device Fabrication. Taylor & Francis, Milton Park, Didcot, USA., Pages: 339.

Nighan, W.L., 1970. Electron energy distributions and collision rates in electrically excited N2/sub>, CO and CO2. Phys. Rev. A., 2: 1989-2000.

Raizer, Y.P., 1991. Gas Discharge Physics. Springer, Berlin, Germany, ISBN:9783540194620, Pages: 449.

Smith, K. and R.W. Thomson, 1978. Computer Modeling of GasLasers. Plenum Press, New York, USA.,ISBN:9780306310997, Pages: 416.

Truesdell, C., 1962. Mechanical basis of diffusion. J. Chem. Phys., 37: 2336-2344.