DEVELOPMENT OF EQUATION-OF-STATE AND TRANSPORT PROPERTIES FOR MOLECULAR PLASMAS IN PULSED PLASMA THRUSTERS PART I: A TWO-TEMPERATURE EQUATION OF STATE FOR TEFLON

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ABSTRACT

The chemical composition of tetrafluoroethylene (C_2F_4) is calculated with a two-temperature LTE formulation. Twenty-five chemical species are included in the analysis. The equilibrium constants are calculated using the most recent spectroscopic data available. Calculations are performed for pressures from 0.001 atm to 1.0 atm and for temperature ranges of 0.05 ev to 10 ev for both heavy particle and electron temperatures.

INTRODUCTION

Knowledge of the chemical, thermodynamic, and transport properties of a gas is required in almost any gasdynamic analysis. Accurate thermochemical and transport properties become particularly important in high-temperature applications such as the pulsed plasma thruster. In this paper, we shall concentrate on calculating the equilibrium composition of a gas mixture. This is the necessary first step for determining the thermodynamic and transport properties of a gas.
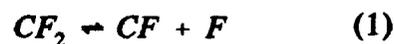
There are three primary thermochemical states possible for a gas. A calorically perfect gas has specific heats that are constant, and the enthalpy and internal energy are only functions of temperature. A thermally-perfect gas, in which variable vibrational and electronic excitation are taken into account, has specific heats, enthalpy, and internal energy that are all functions of temperature. If the conditions are right for chemical reactions to occur, then we can treat the gas as an equilibrium chemically-reacting gas
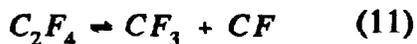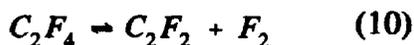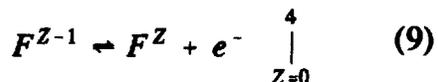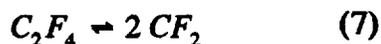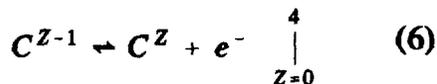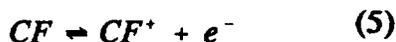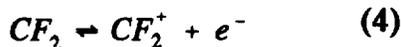
for which properties area all functions of temperature and pressure. Even this can be generalized by stating that the reacting gas is in local thermodynamic equilibrium (LTE). This means that a local Boltzmann distribution exists at each point in the flow at the local temperature. We will extend this statement further for the case of a two temperature LTE gas modeled here. In this paper we calculate the chemical composition of the gaseous Teflon monomer (C_2F_4).

POSSIBLE SPECIES, REACTIONS, AND EQUILIBRIUM EQUATIONS

In this paper, we calculate the chemical composition of tetrafluoroethylene (C_2F_4). The analysis will include vibrational and electronic excitation, dissociation, first molecular ionization, and first through fourth monatomic ionization. Throughout of the analysis, we shall assume a perfect gas, where intermolecular forces are non-existent or negligible. This might seem a strange assumption when the gas is in the plasma state due to the presence of Coulomb collisions, but it is a widely used and accepted approximation.[1]

For a polyatomic base gas, C_2F_4 in our case, with the possibility of undergoing full dissociation, singular molecular ionization, and up to fourth monatomic ionization, we first assume there are twenty-five possible chemical species, which are C_2F_4, C_2F_2, CF_2, CF_2^+, CF_3, CF_3^+, CF_4, C_2, CF, CF^+, F_2, F_2^+, C^Z (Z=-1,4), F^Z (Z=-1,4), and e^-'s. For a gas containing twenty-five chemical species, which is composed of three elements (C, F, e^-), we are required to have twenty-two (25-3=22) independent chemical reaction equations (laws of mass action). The reactions considered here are

$$CF_2 \rightleftharpoons CF + F \qquad (1)$$

$$CF \rightleftharpoons C + F \qquad (2)$$

$$F_2 \rightleftharpoons 2F \qquad (3)$$

$$CF_2 \rightleftharpoons CF_2^+ + e^- \qquad (4)$$

$$CF \rightleftharpoons CF^+ + e^- \qquad (5)$$

$$C^{Z-1} \rightleftharpoons C^Z + e^- \quad \Big|_{Z=0}^{4} \qquad (6)$$

$$C_2F_4 \rightleftharpoons 2\,CF_2 \qquad (7)$$

$$F_2 \rightleftharpoons F_2^+ + e^- \qquad (8)$$

$$F^{Z-1} \rightleftharpoons F^Z + e^- \quad \Big|_{Z=0}^{4} \qquad (9)$$

$$C_2F_4 \rightleftharpoons C_2F_2 + F_2 \qquad (10)$$

$$C_2F_4 \rightleftharpoons CF_3 + CF \qquad (11)$$

$$C_2F_4 \rightleftharpoons CF_4 + C \qquad (12)$$

$$C_2 \rightleftharpoons 2C \qquad (13)$$

In actuality, there are other possible reactions that could yield the same chemical species. But, for an equilibrium calculation, the reactions chosen are arbitrary as long as they are linearly independent and account for all possible species.

Writing these reactions in terms of equilibrium relations for the partial pressures, we have

$$K_{p,j}(T) = \prod_i p_i^{v_i} \qquad (14)$$

where the $K_{p,j}$ are the equilibrium constants for the reaction (j) at the equilibrium temperature T, in terms of the partial pressures. Using the appropriate

formulations, they may also be put in terms of concentrations, K_c, or number densities, K_n. It is important to note in the above equations that the equilibrium constants are written as functions of temperature only, as most authors point out. However, they may be functions of two or more state variables depending on whether such things as thermal non-equilibrium assumptions or electronic partition function cutoff is taken into account.[2]

In addition to twelve independent equations relating the twenty-five unknown partial pressures, we need three more equations to solve for the gas composition. The three chosen are; conservation of nuclei, Dalton's Law, and charge neutrality. The ideal thermal gas law for each species is written in the form

$$p_i = n_i k T_i \qquad (15)$$

where

$$p = \sum p_i \qquad (16)$$

For charge neutrality, we have

$$\sum_{i=1}^{25} Z\, n_{i^Z} = 0 \qquad (17)$$

In terms of partial pressures, this becomes (for ideal gases)

$$\sum_{i=1}^{25} Z\left(\frac{1}{T_i}\right) p_{i^Z} = 0 \qquad (18)$$

For conservation of nuclei, we write

$$\left(n_{C_2F_4}\right)_0 = \frac{1}{2}\left(n_C\right)_0 = \frac{1}{4}\left(n_F\right)_0 \qquad (19)$$

where

$$\left(n_C\right)_0 = \sum_{i=1}^{25} N n_{i_{C_N}} \qquad (20)$$

and

$$\left(n_F\right)_0 = \sum_{i=1}^{25} Nn_{i_{F_N}} \qquad (21)$$

where $(n_{C2F4})_0$ is the total number of tetrafluoroethylene molecules available for dissociation and ionization (ie. the number of C_2F_4 molecules present if the gas was non-reacting at some initially low temperature). Dividing Eq. (20) by Eq. (21) and utilizing Eq. (19) gives us the nuclei conservation statement, where the number densities are related to the partial pressures by Eq. (15).

CALCULATION OF THE EQUILIBRIUM CONSTANT - PARTITION FUNCTIONS

To solve the system of equations, we only need values for the equilibrium constants which may be calculated from equilibrium statistical mechanics. In terms of partition functions Q_i, the law of mass action for a general system is

$$K_N(T) = \prod N_i^{v_i} = e^{\frac{-\Delta\epsilon_0}{kT}} \prod Q_i^{v_i} \qquad (22)$$

or alternatively, substituting $n_i = N_i/V$ we have

$$K_n(T) = \prod n_i^{v_i} = \left(\frac{1}{V}\right)^{\Sigma v_i} e^{\frac{-\Delta\epsilon_0}{kT}} \prod Q_i^{v_i} \qquad (23)$$

where v_i is the stoichiometric mole number for species (i), that is, the coefficients in the balanced chemical equation, $\Delta\epsilon_0$ is the reaction energy (change in zero-point energy) and Q_i is the total partition function for species (i). Thus, for a given reaction and thermodynamic state, the only unknowns in Eq. (23) are the Q_i's.

For a system in thermodynamic equilibrium, we have

$$N_j^* = N\frac{g_j e^{-\frac{\epsilon_j}{kT}}}{\sum g_j e^{-\frac{\epsilon_j}{kT}}} \qquad (24)$$

which gives the number of particles N_j^* in energy level ϵ_j with g_j degenerate states. We define the partition function, Q, as the sum in the denominator of Eq. (24) which is, in general, a function of T and

$$Q \equiv \sum g_j e^{-\frac{\epsilon_j}{kT}} \qquad (25)$$

V. It is typical to express the total energy as the sum of translational and internal energies. Note that Eqs. (23) and (24) contain only one temperature. For the two temperature case considered in this research we make the assumption that the heavy-particle gas composed of neutrals and ions, has a Maxwellian distribution in velocities and a Boltzman distribution in energies at a heavy-particle temperature , T. The electron gas, composed of both free and bound electrons is in equilibrium with an electron temperature T_e defined by their Maxwellian velocity distribution. Note that, in this analysis, we are ignoring the interaction between electronic and vibrational states. Thus, we have defined a two-temperature LTE situation. For a molecule we have

$$\epsilon = \epsilon_{trans} + \epsilon_{rot} + \epsilon_{vib} + \epsilon_{el} \qquad (26)$$

and for an atom

$$\epsilon = \epsilon_{trans} + \epsilon_{el} \qquad (27)$$

where ϵ is the sensible energy, measured above the zero-point energy ϵ_0. Quantum mechanics gives us theoretical values for the quantized energies of a particle, at least for the translational, rotational, and vibrational modes.[3] Along with the assertion that particle energy is simply the sum of the modal energies, that is, the internal energies are uncoupled, which is a consequence of the more fundamental assumption of a separable Hamiltonian, the partition function is expressed as the product of the modal partitions Q_j, where

$$Q = \prod Q_j \qquad (28)$$

with j extending over all modes. Armed with the quantized values for the modal energies, and the associated degeneracies we can calculate the modal partition functions which are given here in reduced form, without proof as[4]

$$Q_{trans} = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}} \times V \quad (29)$$

$$Q_{rot} = \frac{8\pi^2 IkT}{\sigma h^2} \quad (30)$$

$$Q_{vib} = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} \quad (31)$$

where σ is a factor which arises from the symmetry requirements of the wave function in the exchange of an identical particle. It is equal to 1 for heteronuclear molecules (ex. CF), and equal to 2 for homonuclear molecules (ex. F_2). For electronic energy there is no closed form general expression for the quantized energy levels. Thus the electronic partition function must be left as an infinite series in the form

$$Q_{el} = \sum_{j=0}^{\infty} g_j e^{-\frac{\epsilon_j}{kT}} \quad (32)$$

Equation (32) is the true theoretical representation of the electronic partition function for an *isolated* particle. In theory there are in infinite number of electronic levels extending from the ground state energy ($\epsilon_0 = 0$) to the ionization potential, which is the amount of energy needed to remove an electron from its ground state to infinity (bound-free transition). The electronic partition function is a diverging series because although the energy approaches a finite limit, the degeneracy increases as the square of the principal quantum number, so the series diverges.[5] For any general polyatomic molecule of N atoms, if we still assume a separable Hamiltonian then we can factor the partition function as in Eq. (28) with the product extending not only over all fundamental modes but also over all modal degrees of freedom.[6]

In actuality, the electronic series in not infinite because a particle in the real world is never truly isolated. Due to various interparticle interactions that arise in any finite density medium, the series will actually terminate at some principal quantum number, n^{cutoff}. The evaluation of n^{cutoff} and its associated effect

of ionization potential lowering is the subject of some controversy and was explored in detail in a previous work.[2] Results from that work give the correct cutoff criterion as

$$n^{cutoff} = \sqrt{\frac{1 - \frac{1}{2}(\alpha_i)^{\frac{1}{2}}}{\tilde{a}}} \times n_p^{-\frac{1}{6}} \quad (33)$$

where $\tilde{a} = Z_{eff}*e^2/2*IP$. The lowered ionization potential is given by

$$\overline{IP} = IP\left(1 - \frac{1}{n_{cutoff}^2}\right) \quad (34)$$

The K_n's are converted to K_p's using the relation

$$K_{p,j}(T) = (k)^{\Sigma \nu_i}\left(\prod_i T_i^{\nu_i}\right)K_{n,j}(T) \quad (35)$$

The required molecular and atomic data, which are too numerous to give here, are taken from the works of Chase,[7] Moore,[8,9] Rosenstock,[10] Herzberg,[11] Buckely,[12] and Paulino and Squires.[13]

SOLUTION OF THE EQUILIBRIUM EQUATIONS

The equations given in the previous section to calculate the equilibrium composition in terms of partial pressures, given T, T_e and P, provide a closed set of twenty-five coupled nonlinear algebraic equations for which there is no analytic solution and numerical methods must be used. The numerical solution of systems of nonlinear equations is universally very difficult and is a topic of current research. As of yet, there are no appropriate numerical methods for solving coupled nonlinear systems of algebraic equations from arbitrary starting vectors.[14] One of the most commonly used methods and the one used previously for nitrogen research,[2] is the Newton-Raphson method. The Newton-Raphson method usually exhibits excellent convergence qualities when the starting vector (initial guesses for the roots) is near the actual root. For a homonuclear diatomic gas a good initial guess can usually be obtained through Saha-type statistical arguments using

weighted averages due to limited reactive simultaneity. In this case though, since we are dealing with a polyatomic heteronuclear gas, it was initially assumed that we could not get close enough to the root for Newton-Raphson to work properly. Many hybrid techniques have been proposed but most fail when the Jacobian becomes singular, or at stationary point.[15,16] The solution procedure initially chosen for this research is the one proposed by Powell.[17] Powell's technique exhibits almost guaranteed convergence even for poor initial guesses. It also has the ability to correctly handle stationary points. The price of this behavior is that the convergence is linear until very close to the root then it converges quadratically like the standard Newton-Raphson. Thus, the total number of iterations required is greatly increased resulting in much longer runtimes, up to 200 minutes per isobar on a Sun Supersparc . Thus, it was decided that the Newton-Raphson method would be used combined with a raster processing iteration procedure.

Given T, T_e, and P, an initial equilibrium composition is approximated using simple Saha-type arguments assuming totally uncoupled physical process, then partial pressures are backed out using weighted approximations or the initial guess was set equal to the previous converged root at the last temperature and pressure and stepped up in temperature on each isobar in small increments of from 0.1 to 10 K for heavy particle temperatures and 1 K to 100 K for electron temperatures. The completely closed system is solved at each point using the Newton-Raphson procedure, which iterates until the sum of the absolute values of the corrections is less than the chosen tolerance of

$$\frac{\epsilon\,P}{\left(\dfrac{T_e}{T} + \dfrac{T}{T_e}\right)} \qquad (36)$$

where $\epsilon = 10^{-4}$ or until 20,000 iterations are performed. Convergence to the tolerance is usually obtained quickly. An additional convergence check is performed after each completed iteration so that the total isobaric deviation is not allowed to exceed 5%. The correct composition is now known to within desired accuracy. The mixture molecular is was computed using the expression

$$MMG = \sum_{i=1}^{25} X_i MM_i \qquad (37)$$

where X_i is the mole fraction of species i, obtained using

$$X_i \equiv \frac{\eta_i}{\eta} = \frac{n_i}{n_{tot}} \qquad (38)$$

where n_{tot} is, of course, just the total number of particles.

RESULTS AND DISCUSSION

The chemical composition in terms of the mole fractions at 1 atm. and $T_e/T = 1.0$ from 300 to 30,000 K is shown in Fig. 1. We see the same rapid dissociation of C_2F_4 as observed by Paulino and Squires[13] due to the inherent weakness of the carbon double bond in this molecule. The results are consistent with those obtained by Kovitya.[18] Figure 2 shows a better view of the composition in the low temperature region where molecules dominate. In our case we see that at about 800 K C_2F_4 partially dissociates into C_2F_2 and CF_4, almost completely recombines as temperature increases, then dissociates into CF_2. Dissociation of CF_2 begins to at about 4,000 K and is almost completely dissociated by 7,500 K. The primary dissociation products are C and F which reach their maxima at about 7,500 K. Past this temperature ionization begins to occur and singly ionized C and F and electrons dominate the composition. Second ionization begins to occur between 22,500 and 25,000 K. Figures 3 through 8 show representative species compositions of C, C^+, F, F^+, e^- and CF_2 at two different pressures, 1 atm and .1 atm, for the case of thermal nonequilibrium. They are given for four heavy isotherms of .05, .1, 1, and 10 ev. Here we see drastically different behavior due to the highly energetic electrons at their elevated temperature. Dissociation of CF_2 happens rapidly, other molecules exhibited similar behavior. Single and multiple ionization of C and F follows the expected pattern of following the electron temperature, consistent with our original formulation. Figure 7, the electron partial pressure, shows we reach regions where dP_e/dT_e goes to zero. The composition is constant after this for we had assumed that the maximum ionic charge state was four. This suggests that for a correct chemical model at elevated electron temperatures we may need to extend the possible ionic species to a greater charge value. The molecular ionic and electronegative species were found to exist in only

very small amounts at all T_e/T values. In future work it is planned to include multi-phase species in like amorphous carbon. Molecular effects that are being evaluated for inclusion in future models include anharmonic vibrations and internal energy mode coupling. Also research is being performed to develop the complete reactive thermodynamic and transport models.

ACKNOWLEDGMENTS
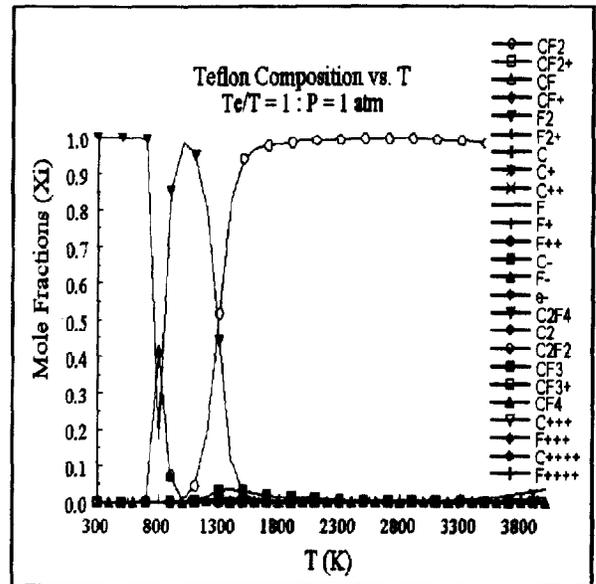
Figure 2. Composition of Teflon for Te/T = 1.0 at 1 atm. Lower temperature range.
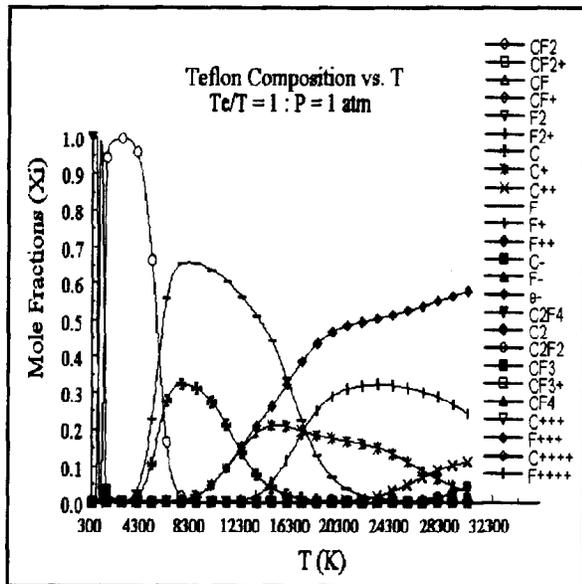
Figure 1. Composition of Teflon for Te/T = 1.0 at 1 atm.
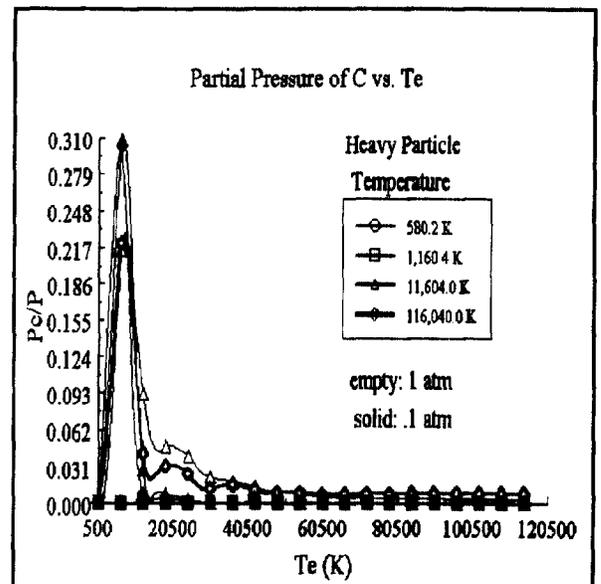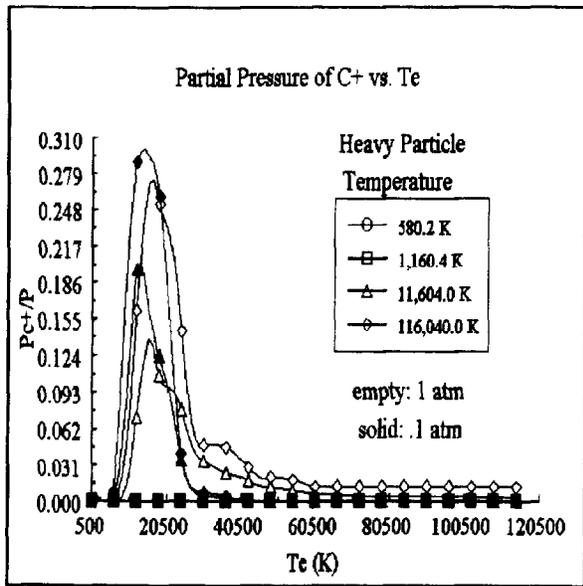

Figure 3. Partial Pressure of C vs. Te.

Figure 4. Partial Pressure of C$^+$ vs. Te.
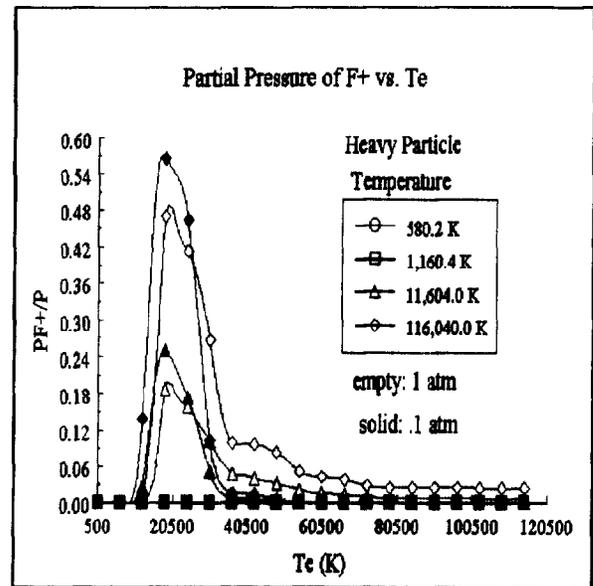

Figure 6. Partial Pressure of F$^+$ vs. Te.
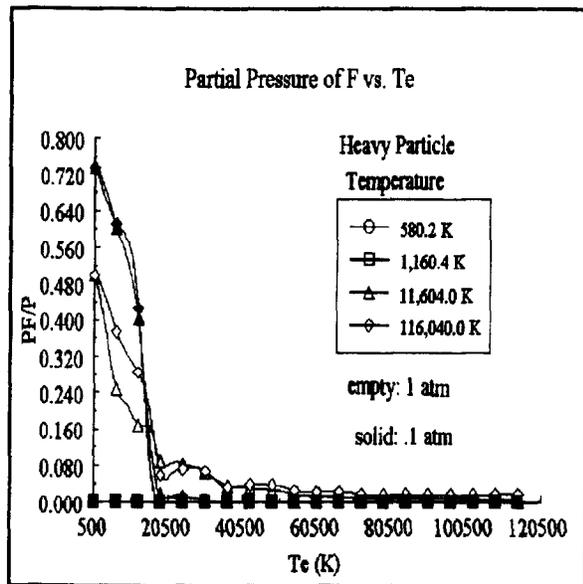

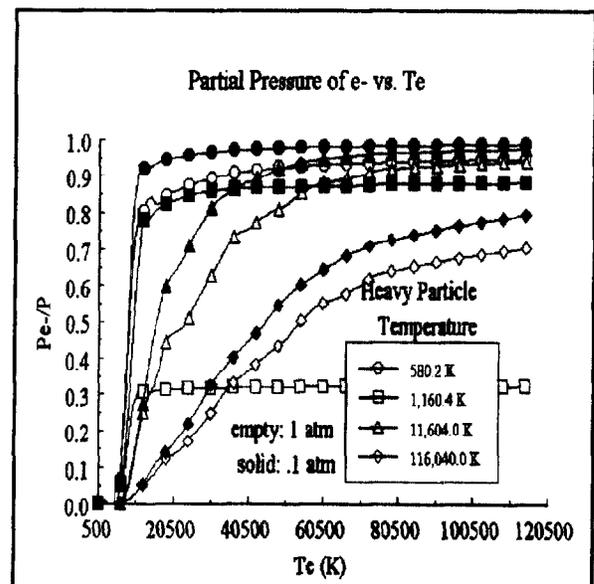**Figure 5.** Partial Pressure of F vs. Te.

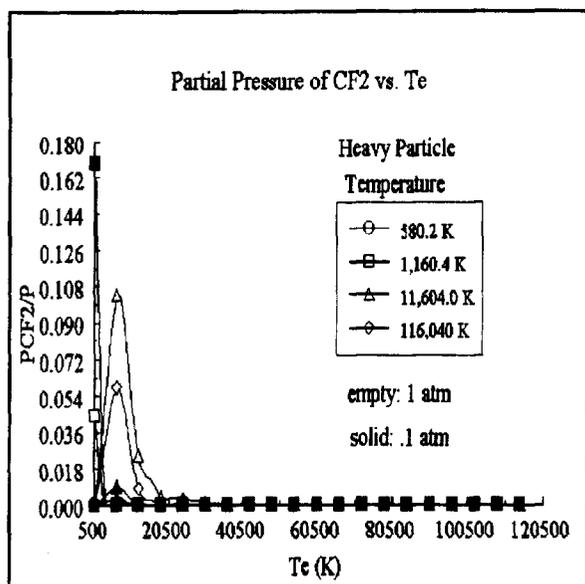**Figure 7.** Partial Pressure of electrons vs. Te.

Figure 8. Partial Pressure of CF_2 vs. Te.

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