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Space Sciences, Inc.
301 Bear Hill Road
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Contract No. AF19(628)-5097 7

Project No. 4642    Task No. 464202

SCIENTIFIC REPORT NO. 1

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AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
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UNITED STATES AIR FORCE
BEDFORD, MASSACHUSETTS 01730

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# FOREWORD

This report was prepared by Space Sciences Incorporated, of Waltham, Massachusetts, for the Office of Aerospace Research, Air Force Cambridge Research Laboratories, Hanscom Field, Bedford, Massachusetts, under Contract AF19(628)-5097. The work was monitored by Mr. John F. Lennon.

The principle investigator for this program was Dr. Sol Aisenberg.

# ABSTRACT

This report is part of an analytical and experimental program to investigate the enhancement of microwave communication by employing small quantities of chemical additives introduced into the plasma sheath of a re-entry vehicle and to deduce the optimum types and forms of additives to be used. An analytical investigation has shown that electron attachment to electrophylic molecules is one of the more important mechanisms in reducing the plasma free electron concentration and thereby in alleviating the re-entry sheath black-out problem. The attachment cross section data necessary for the theoretical selection of the more effective additives is not always available in the literature. An analysis is presented here, where attachment cross sections are correlated with more readily available fundamental thermodynamic data so that attachment data can be predicted. Qualitative reasoning based upon the potential energy diagram concept is employed to describe the physics of electron attachment and to derive graphical correlations between the more readily obtained thermodynamic values and the attachment cross-section parameters. Average attachment rate constants are also calculated for molecules from data in the literature. The attachment rate constant can be employed as a figure of merit to determine the most efficient additive, for the limiting case of negligible dissociation. The results show that carbon tetrachloride is the most efficient of the compounds investigated and is potentially at least two orders of magnitude better than water for moderate plasma temperatures.

# CONTENTS

# ILLUSTRATIONS

# 1. INTRODUCTION

This report describes one phase of an analytical and experimental research program dealing with the enhancement of microwave transmission through the re-entry plasma sheath. The results of this program should help in the alleviation of the re-entry black-out problem. The purpose of this program is to determine the optimum type, forms and quantity of additive material (gas, liquid, and solids) that will enhance the microwave transmission through the re-entry sheath.

Among the suggested techniques to alleviate the black-out problem is the addition of small quantities of material to reduce the free electron concentration of the re-entry plasma sheath. For example, re-entry experiments with water that have been reported for the Gemini vehicle(1), show an improvement due to seeding. The analytical portion of the program has therefore studied the relative importance of various mechanisms for the reduction of free electron density and has shown that with the use of electrophylic additives, electron attachment is an important process compared to other mechanism such as recombination, and diffusion. Since data on attachment cross sections are somewhat limited, this present report is concerned in part with various correlations between attachment properties and the more readily obtained thermodynamic data. In addition, this report compares the relative theoretical effectiveness (on a specific mass basis) of various additives. The effect of additives on the high power breakdown of the re-entry plasma sheath is also being investigated and will be discussed separately.

For the experimental part of the study, an arc tunnel facility has been constructed to simulate the plasma sheath at various altitudes. The additives are injected into the simulated plasma sheath, and various diagnostic techniques are used to compare the relative effectiveness. The effects of the additives are being studied using various diagnostic techniques, including microwave transmission, radiation measurements, and special plasma conductivity probes. The final results of these experiments will be described in separate reports.

## 2. ELECTRON ATTACHMENT RATES

This section describes the relationship between attachment cross sections and the electron removal rates. The result of the attachment process is the loss of free electrons and subsequent formation of negative ions. The rate of electron attachment however, depends on the molecular cross section for attachment. Attachment cross sections have been measured only for a limited number of atoms and molecules and theoretical calculations have been performed only for simple molecules and theoretical calculations have been performed only for simple molecules such as hydrogen(2). It would thus be useful to be able to predict the attachment cross section for molecules where experimental data has not been obtained. This paper presents a correlation to predict attachment cross sections, as a function of the energy of a single impacting electron, and also calculates the average electron attachment rate constants for an aggregate of impacting electrons for a number of interesting additives.

The rate that free electrons are removed by attachment to an additive molecule for the limiting case of negligible thermal dissociation can be expressed as;

$$\frac{dn_e}{dt} = - K_D n_e C \qquad (1)$$

where;

$K_D$ = rate constant for attachment, (cm$^2$/g-mole sec.)

$n_e$ = electron concentration, (cm$^{-3}$)

t = time (sec.)

C = additive concentration (g-mole/$cm^3$).

The rate constant for attachment is the product of the electron random velocity, v, and the attachment cross section depends very strongly upon the kinetic energy of the impacting electron, since all electrons are not impacting with the same energy. Experimentally, a resonance behaviour (with respect to electron energy) has often been observed. As an example, the reported(3) data for $CCl_4$ and $SF_6$ are shown in Figure 1. Thus the true attachment cross section must be an averaged quantity over the velocity spectrum described by a velocity distribution law, such as the Maxwell-Boltzmann distribution for a plasma in thermodynamic equilibrium. The average attachment rate constant is the weighted average of the product of attachment cross section and the electron velocity. Thus,

$$K_D(E') = \frac{\overline{v\,\sigma(E')}}{N_o} = \frac{1}{N_o} \int_0^\infty v\,\sigma(E)\, f(v,E')\, dv \qquad (2)$$

where;

$N_o$ = Avogadro's constant (6.025 x $10^{23}$ molecules/g-mole) and is used to convert the rate constant from a per molecule to a per g-mole basis,

$\sigma(E)$ = attachment cross section at mono-electron energy, E, ($cm^2$),

f(v,E') dv = normalized velocity distribution function,

v = electron velocity (cm/sec.),

E = electron energy (electron volts),

E' = characteristic energy specifying the electron velocity distribution function.

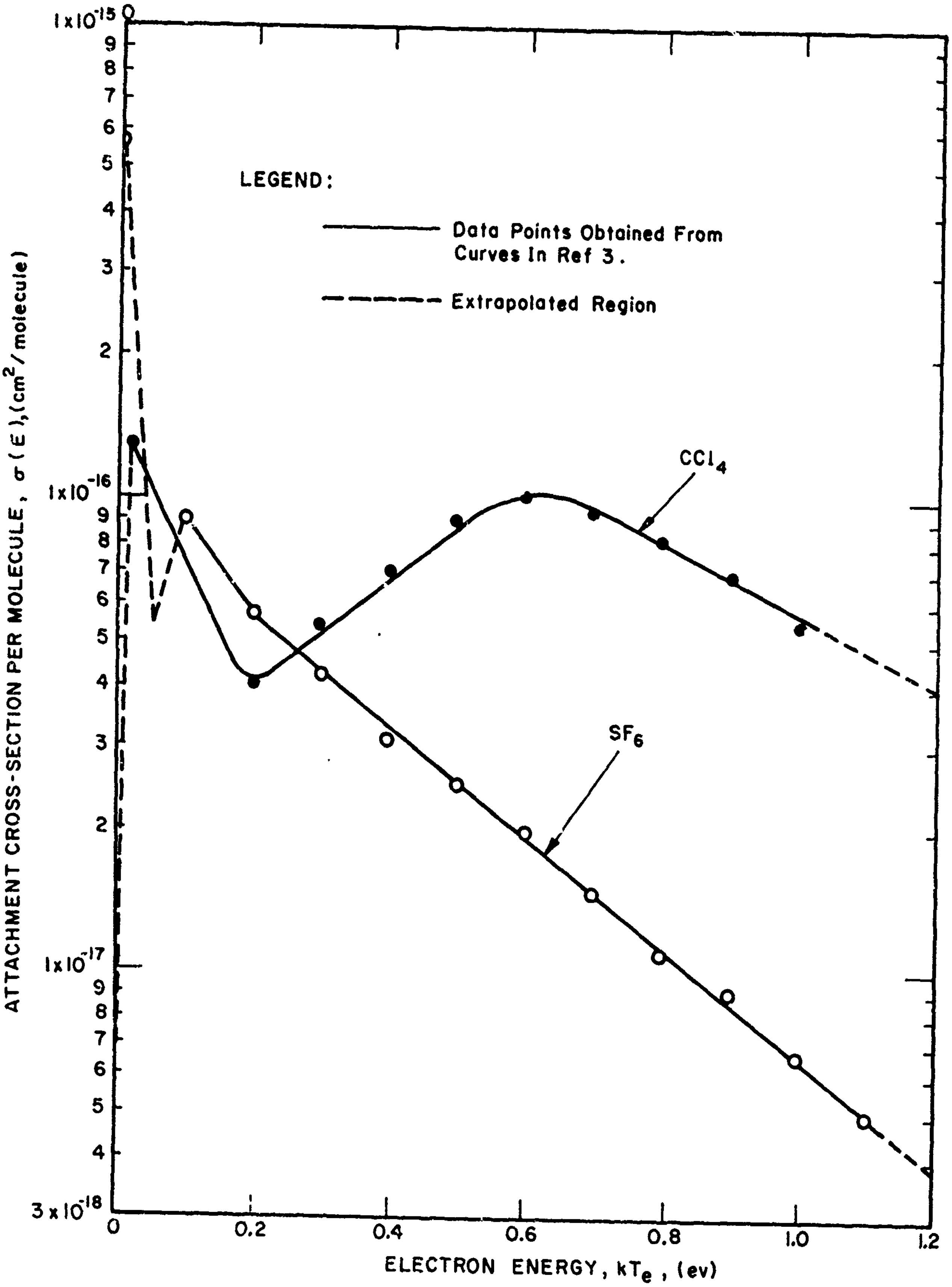

FIGURE 1.
TYPICAL VARIATIONS OF ATTACHMENT CROSS-SECTION WITH ELECTRON ENERGIES.

To calculate the rate of electron removal from a plasma by electron attachment, values of attachment cross section as a function of the mono-electron energy, E, must be known numerically or analytically to perform the required integration in Equation (2). Neglecting the effects of thermal dissociation, the average attachment rate constant, evaluated from Equation (2), becomes the figure of merit for determining the most effective additive.

## 3. EMPIRICAL CORRELATION OF ATTACHMENT CROSS SECTION

The attachment cross section for a molecule is a difficult quantity to obtain experimentally or to calculate (requiring a detailed quantum mechanical calculation). Experimental results for many molecules have been reported(3,4,5,6,7). However, there still remain many potentially attractive complex additive compounds for which values of attachment cross section are unknown. Therefore, a correlation against a basic molecular or thermodynamic quantity, more easily obtainable, would be very helpful. To obtain such a correlation it is first necessary to qualitatively understand the electron attachment process.

Massey(5) suggests that capture of an electron by a neutral molecule is governed by the potential energy diagram (based upon nuclear separation, i.e., vibrational spectrum) for the neutral molecule and for the negative vibrationally excited resultant ion and is described in terms of the Frank-Condon principle. The Frank-Condon principle states that transitions are most probable when the nuclear separation, position, and velocity are unaltered. The two potential energy curves (for neutral and negative vibrationally excited molecule) are separated by the electron affinity of the negative ions at large nuclear distances. Since electron attachment involves evolution of energy, the potential energy of the negatively excited molecules lies below that of the neutral molecule at large nuclear distances.

Massey(5) presents the picture reproduced as Figure 2 to describe attachment processes. If the initial energy state of the neutral molecule can be represented by state ab , the energy necessary for electron capture is between $E_1$ and $E_2$ and the final energy state of the negative

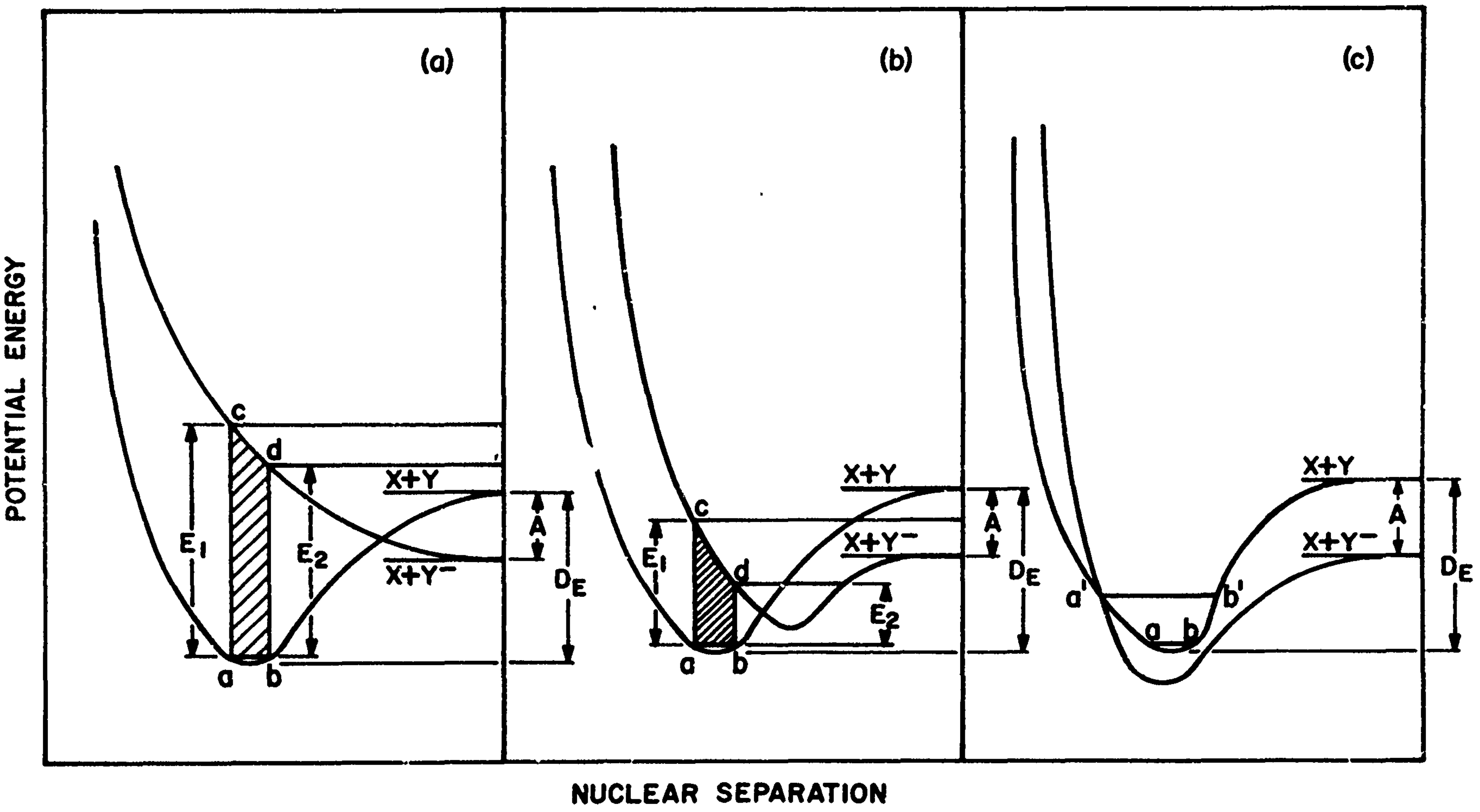

FIGURE 2.

POTENTIAL ENERGY CURVES ILLUSTRATING THREE POSSIBLE WAYS IN WHICH NEGATIVE IONS MAY BE FORMED FROM A MOLECULE BY ELECTRON CAPTURE.

molecule is between c and d. Energies $E_1$ and $E_2$ result from collisions with energetic electrons, and therefore the peak attachment cross sections occurs for electrons with these energies. Notice that dissociation (into $X+Y^-$) is always part of the electron capture process for case (a). For case (b) the products of the transitions may be a negative, vibrationally excited ion ($XY^-$) or dissociation of the ion specie. In case (c) the neutral molecule is first excited to state a' b' by an impacting electron which is then captured forming a vibrationally excited ion ($XY^-$). For some molecules it is only necessary that an electron be present (that is have very little energy) for excitation and subsequent capture to occur. Thus, it is possible to have a large attachment cross section at low energy levels (i.e., for collision with very slow electrons). In fact, this behaviour has been observed for sulfur hexafluoride ($SF_6$). The above qualitative explanation also explains the peaks observed at different electron energies. For example, in Figure 2b, a collision with an electron having an energy less than the minimum of the $X+Y^-$ potential curve will result only in a vibrationally excited neutral molecule. If the electron energy is very large, the potential energy curve of a higher electronic state (greater than $X+Y^-$) may be reached and another maximum should appear. For a complex molecule such as $SF_6$, this means a different negative vibrationally excited ion or different dissociation products will result. Thus, observed multiple peaks in the attachment cross section are the result of the relative location of the potential energy diagrams for different negative, vibrationally excited negative ions.

From the qualitative picture of electron attachment pictured above, it is evident that the dissociation energy, $D_E$ (difference between the potential energy at large nuclear distances and the minimum value) and as well as the electron affinity, A, influence the cross section. It would be expected that the electron energy at which the peak attachment cross section ($E_{max}$) occurs increases with the difference between dissociation energy and electron affinity ($D_E$ - A in Figure 2). The term $D_E$ - A, represents the total heat of formation for a dissociative attachment process. Figure 3, obtained from published data of experimental attachment cross sections(3,4,5,6,7), of thermochemical dissociation energies(8) and of electron affinities(4) show this predicted increase of $E_{max}$ with the total heat of formation, $D_E$ - A. The minor deviations for $Cl_2$ and $Br_2$, are probably related to the measurement technique and are discussed subsequently.

The heat of formation, $D_E$ - A (plotted in Figure 3 and 4) for the dissociative attachment process can be calculated from knowledge of the dissociation products and the heats of formation of the reactants and products. For example, the dissociative reaction for carbon tetrachloride corresponding to the first peak is(3);

$$CCl_4 + e \rightarrow CCl_3 + Cl^-. \qquad (3)$$

Thermochemically, this reaction can be thought of as the sum of the following four reactions with the corresponding heats of formation:

$CCl_4 \rightarrow C + 2Cl_2 \qquad \Delta H = 1.125$ ev. (3a)*

$C + 3/2\ Cl_2 \rightarrow CCl_3 \qquad \Delta H = 1.525$ ev. (3b)*

$1/2\ Cl_2 \rightarrow Cl \qquad \Delta H = 1.260$ ev. (3c)*

$Cl + e \rightarrow Cl^- \qquad A = 3.1$ to $3.83$ ev. (3d)*

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* Equations (3a) through (3d) are not descriptions for the <u>kinetics</u> of the chemical reaction described by Equation (3).

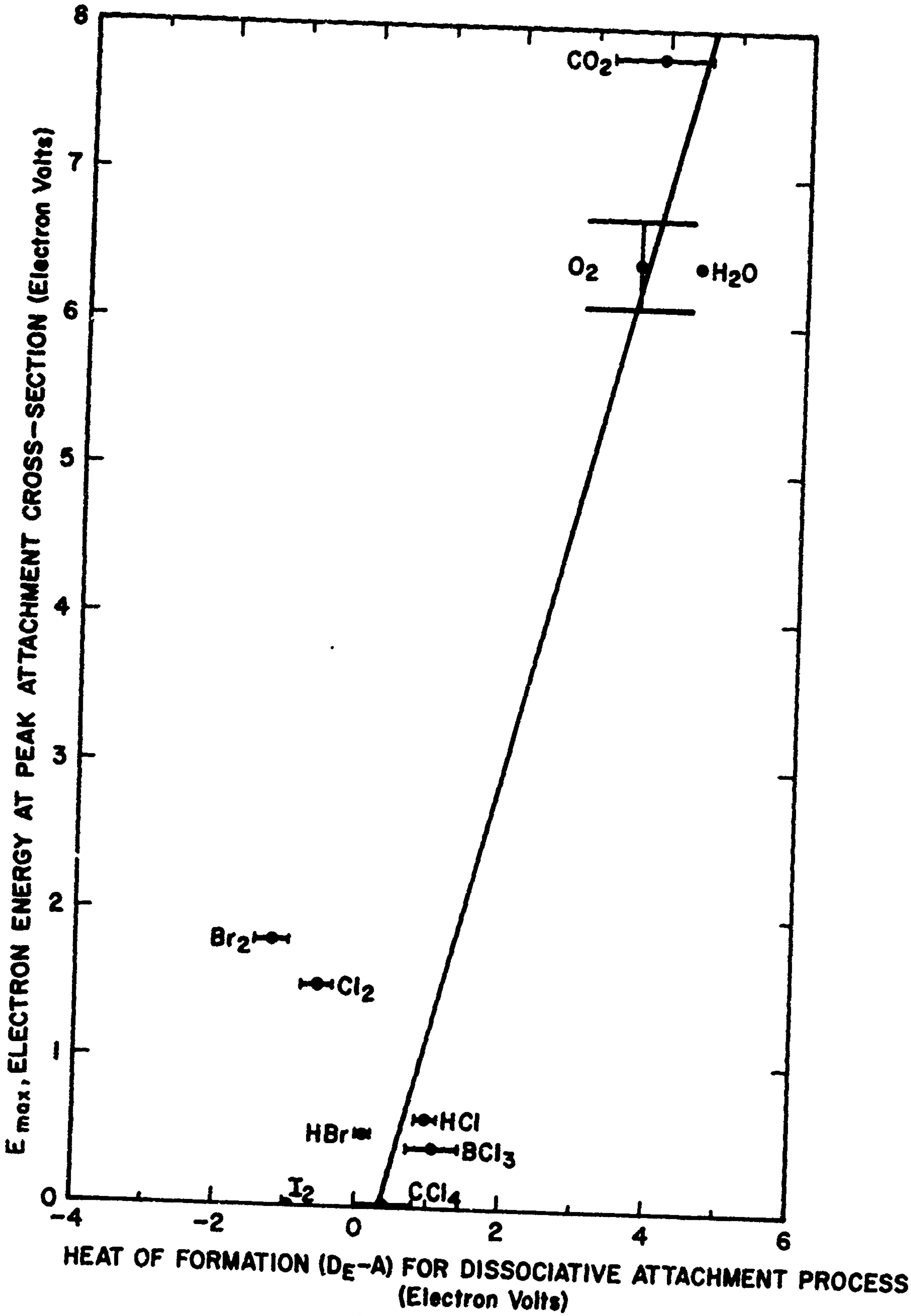

FIGURE 3.

ELECTRON ENERGY AT PEAK ATTACHMENT CROSS-SECTION AS A FUNCTION OF HEAT OF FORMATION FOR DISSOCIATIVE REACTION.

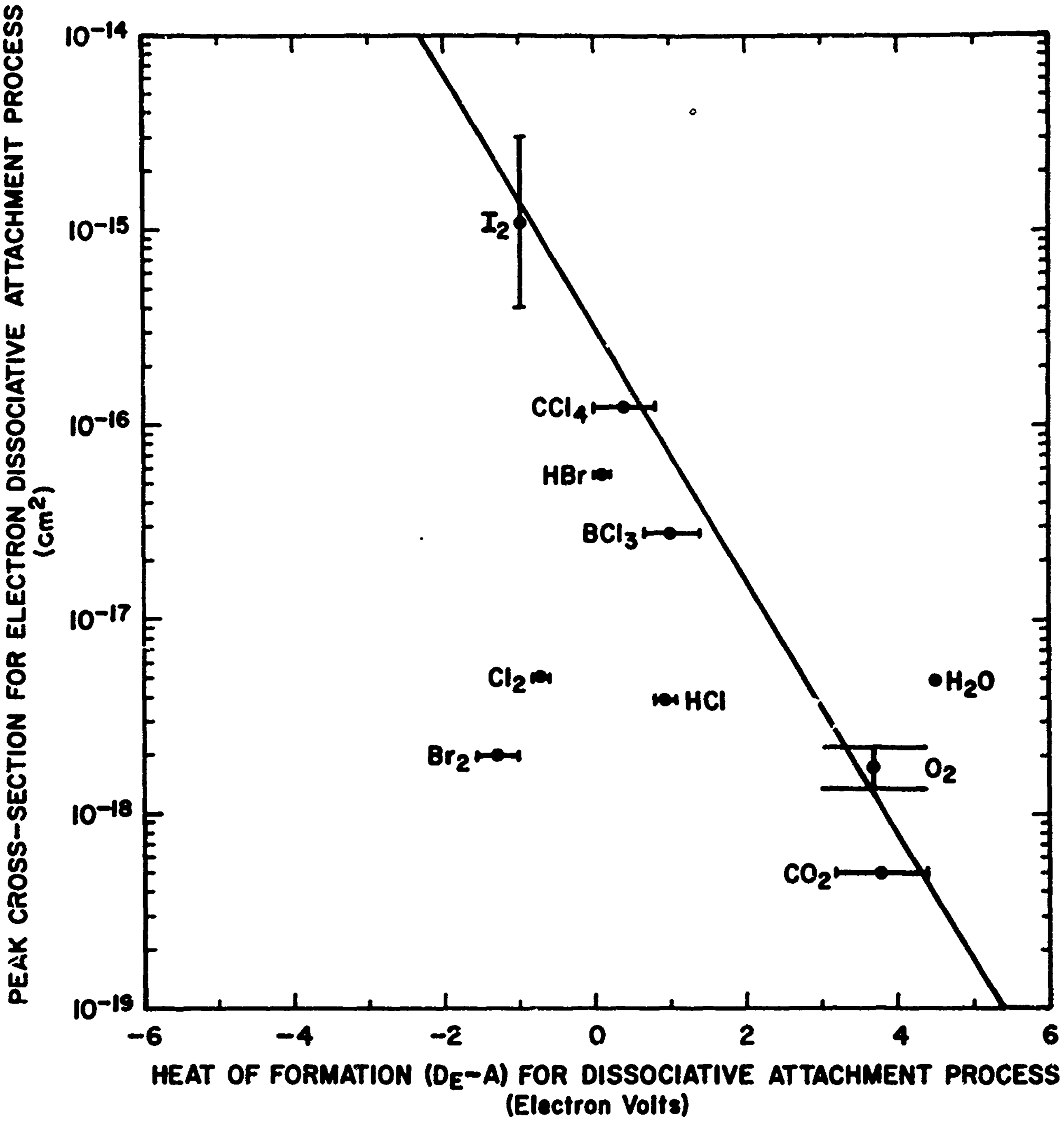

FIGURE 4.

PEAK ATTACHMENT CROSS-SECTION AS A FUNCTION OF HEAT OF FORMATION FOR DISSOCIATIVE REACTION.

The total heat of formation,for chemical dissociation described by Equation (3), is obtained by adding the heats of formation for Equations (3a) through (3d). Therefore, $\Delta H_{attachment} = 0.11 \pm 0.81$ ev. (Note the uncertainty range due to the uncertainty in the electron affinity). This is the method employed to obtain the correlations shown in Figures 3 and 4. The dissociative reactions corresponding to the resonant conditions (attachment cross-section peaks) and the total heat of formations are listed in Table 1 for reference.

The peak attachment cross section has also been plotted in Figure 4 as a function of the total heat of formation for the corresponding dissociative attachment reaction. The peak attachment cross sections generally decrease with increasing heat of formation. This can be explained in two ways. First, it is reasonable to expect that electrons with low energies will have a higher probability for attachment since the transit time of the electron in the vicinity of the attaching molecule is longer. Secondly, energy is released in the attachment process (since the electron affinity is negative) and thus the net energy required for the reaction is less than in a standard chemical dissociation. Thus, the potential energy curve for the negative, vibrationally excited molecule is below the potential energy curve for the neutral molecule and less total energy is required for the attachment process. The two curves in the region of the transition will in fact be closer together and Hirschfelder(9) shows that the probability for transitions becomes greater as the potential energy curves come together. Data for $SF_6$ are not presented in Figures 3 and 4,because the electron affinity for $SF_6^-$* (corresponding to first peak) has not been found in the literature. It should be noted that the transition for the first peak exhibited

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* The electron affinity for $SF_6^-$ will in general be different than for $F^-$.

## Table I

## Attachment Cross Section, Attachment Reactions, and Associated Heats of Formation for Various Molecules

| Molecule | Cross Section at First Peak ($cm^2$) | Electron Energy at First Peak (ev.) | Attachment Reaction for First Peak | Heat of Formation for Attachment Reaction, (ev.) |
|---|---|---|---|---|
| $SF_6$ | $5.7x10^{-16}$ | 0.00 [a,b] | $SF_6+e \rightarrow SF_6^-$ [a] | ——— |
| $CCl_4$ | $1.3x10^{-16}$ | 0.02 [a,b] | $CCl_4+e \rightarrow CCl_3+Cl^-$ [a] | 0.08 to 0.81 |
| $CCl_2F_2$ | $5.4x10^{-17}$ | 0.15 [a,b] | ——— | ——— |
| $BCl_3$ | $2.8x10^{-17}$ | 0.4 [a,b] | $BCl_3+e \rightarrow BCl_2+Cl^-$ [a] | 0.74 to 1.47 |
| HBr | $5.8x10^{-17}$ | 0.5 [a,b] | $HBr+e \rightarrow H+Br^-$ [a] | -0.02 to 0.26 |
| HCl | $3.9x10^{-17}$ | 0.5 [a,b] | $HCl+e \rightarrow H+Cl^-$ [a] | 0.8 to 1.1 |
| $H_2O$ | $4.8x10^{-18}$ | 6.4 [a,b] | $H_2O+e \rightarrow H^-+OH$ [a] | 7.3 to 8.6 |
| $O_2$ | $1.3x10^{-18}$ to $2.2x10^{-18}$ | 6.2 [a,b,d] | $O_2+e \rightarrow O^-+O$ [b,d] | 2.9 to 4.2 |
| $I_2$ | $4x10^{-16}$ to $3x10^{-15}$ | 0.01 [a,e] | $I_2+e \rightarrow I+I^-$ [b,e] | -0.9 to -1.0 |
| $Br_2$ | $2x10^{-18}$ | 1.8 [c] | $Br_2+e \rightarrow Br+Br^-$ [c] | -1.22 to -1.50 |
| $Cl_2$ | $5x10^{-18}$ | 1.5 [c] | $Cl_2+e \rightarrow Cl+Cl^-$ [c] | -0.6 to -0.7 |
| $CO_2$ | $5.0x10^{-19}$ | 8.0 [b] | $CO_2+e \rightarrow CO+O^-$ [b] | 3.2 to 4.5 |

[a] Ref. 2.

[b] Ref. 3.

[c] Ref. 4.

[d] Ref. 6.

[e] Ref. 7.

by $SF_6$ is of the variety shown in Figure 2c. The relative closeness of the two potential energy curves might explain the high peak attachment cross section.

With the exception of bromine and chlorine, all the data in Figure 4 have a mean deviation of about a factor of 4 from a least square curve. The experimental data for bromine and chlorine is about 2 and 3 orders of magnitude lower than the least square curve. It should be noted however, that the data for chlorine and bormine are from swarm (i.e.,electrons with a Maxwellian distribution of energy) measurements while the remaining data are for single collision mono-energetic electron beams. As noted by Massey(5), it is reasonable to expect a deviation between the results obtained from swarm and single collision mono-energetic electron experiments.

In fact the swarm experiments have not been conducted below about 0.4 ev. on chlorine and bromine. Massey(10) also points out that it is reasonable to expect that these two halogens act like iodine ($I_2$). Iodine's first attachment cross-section peak is extremely high and occurs at a very low energy level (almost 0 ev.). A lower peak does occur at about 2 ev. Therefore, if chlorine and bromine exhibited the same behaviour, the attachment cross sections for their first peak would lie approximately on the least square fit of Figure 4. The electron energy corresponding to this peak would also correlate better in Figure 3.

It shoulded be noted that the correlations presented in Figure 3 and Figure 4 require that the products of the attachment process be known. It should be pointed out that the correlations presented in this section are based upon experimental and theoretical data at 300°K.

## 4. CALCULATION OF AVERAGE ATTACHMENT RATE CONSTANTS

The effective rate constants for high temperature plasmas will be calculated for comparison of the effectiveness of various additives. In a previous section, the average attachment rate constant has been shown to be;

$$K_D\,(E') = \int_0^{\infty} v\sigma\,(E)\, f(v,E')\, dv \qquad (4)$$

where;

$E = 1/2\, mv^2$,

m = electron mass.

Assuming that the electron velocity spectrum can be described by the Maxwell-Boltzmann (M-B) distribution, Equation (4) becomes;

$$K_D(E') = \int_0^{\infty} v\sigma\,(E)\, 4\pi \left(\frac{m}{2\pi kT_e}\right)^{3/2} \exp\left(\frac{-mv^2}{2kT_e}\right) v^2\, dv \qquad (5)$$

where the normalized M-B distribution in velocity space is;

$$f\,(v,E')\, dv = 4\pi \left(\frac{m}{2\pi kT_e}\right)^{3/2} \exp\left(\frac{-mv^2}{2kT_e}\right) v^2\, dv. \qquad (6)$$

It should be noted that $kT_e$ in Equation (5) and Equation (6) is related to the characteristic energy, E', by;

$$E' = kT_e \qquad (7)$$

where;

$k$ = Boltzmann's constant,

$T_e$ = electron temperature.

(To convert the temperature $T_e$ in degrees Kelvin to $E'$ in electron volts, the conversion factor $q/k$ = 11,606 degrees Kelvin/electron volt is used. The factor $q/k$ is the ratio of the electron charge to Boltzmann's constant.)

Actually, the distribution function is not exactly M-B because of the energy loss mechanisms from the electrons (such as continuum radiation and electron diffusion) and the necessary replenishment of this energy from the gas atoms and ions. However, the electron-electron interactions are very frequent and strong and are effective in driving the distribution function towards the M-B. The electrons (because of their mass equality, and greater velocity) will come to equilibrium among themselves more rapidly than will the other particles$^{(11)}$. In addition, the deviations of the electrons from a M-B distribution is expected to be small because the energy is fed to the electrons from the rest of the plasma which itself is very close to a Maxwell-Boltzmann distribution.

Upon converting from the velocity domain to an energy domain, Equation (5) becomes;

$$K_D = 2\left(\frac{2}{\pi m}\right)^{1/2}\left(\frac{1}{E'}\right)^{3/2}\int_0^{\infty}\sigma(E)\,E\,\exp\left(\frac{E}{E'}\right)dE \qquad (8)$$

To simplify the integration process, Equation (8) can be expressed as the sum of segments;

$$K_D = 2\left(\frac{2}{\pi m}\right)^{1/2}\left(\frac{1}{E'}\right)^{3/2}\sum_{1}^{n}\int_{E_{n-1}}^{E_n}\sigma(E)\,E\exp\left(\frac{E}{E'}\right)dE. \qquad (9)$$

This form eases the integration, since (over limited energy ranges between $E_n$ and $E_{n-1}$) the attachment cross section, $\sigma(E)$, can typically be approximated by simple exponential functions of energy;

$$\sigma(E) = \exp\left(A_n E + B_n\right) \qquad (10)$$

where;

$A_n$ and $B_n$ are constants determined from the data for the electron energy interval between $E_n$ and $E_{n-1}$.

Expressing $\sigma(E)$ as a series of exponential functions between $E_n$ and $E_{n-1}$ can be justified by examining a typical plot of attachment cross sections, $\sigma(E)$, versus the mono-electron energy, E, shown in Figure 1. With the substitution of Equation (10), Equation (9) can be integrated in closed form as;

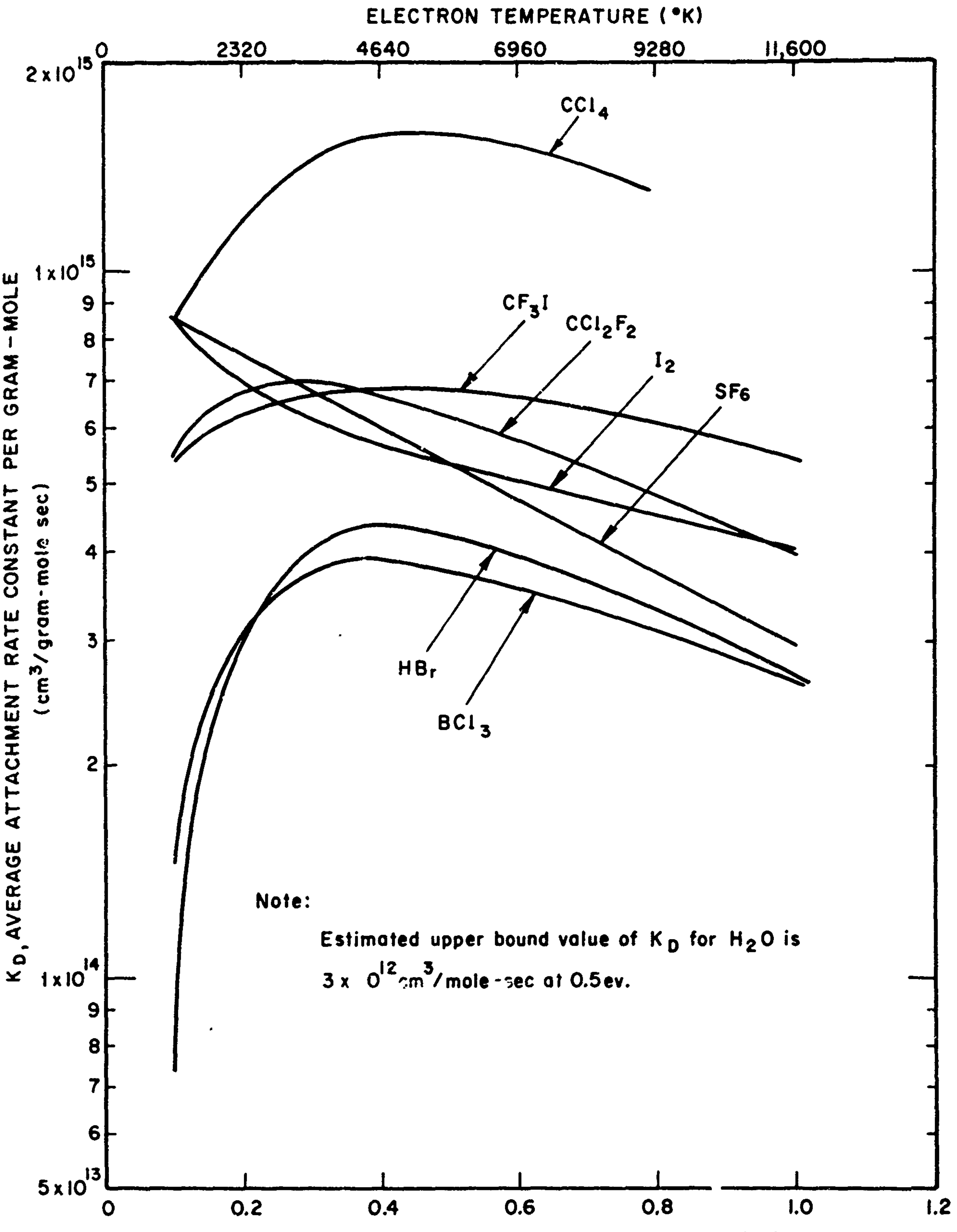
$$K_D = 2\left(\frac{2}{\pi m}\right)^{1/2}\left(\frac{1}{E'}\right)^{3/2}\sum_{1}^{n}\frac{\exp(B_n)}{(A_n-1/E')^2}\left\{\exp\left[\left(A_n-\frac{1}{E'}\right)E_n\right]\left[\left(A_n-\frac{1}{E'}\right)E_n-1\right]\right.$$

$$\left.-\exp\left[\left(A_n-\frac{1}{E'}\right)E_{n-1}\right]\left[\left(A_n-\frac{1}{E'}\right)E_{n-1}-1\right]\right\} \qquad (11)$$

The summation in Equation (11) was extended up to an electron energy value of 9 ev., thus including greater than 99.5% of the electron energy spectrum. Data was generally available to about 1.0 ev. Beyond 1 ev., the attachment cross section was extrapolated as an exponential function of energy. For several compounds, extrapolation was also necessary in the very low energy region. (See Figure 1 for examples of extrapolation regions.) For most characteristic electron energies, the accuracy of the calculation should not be significantly affected by the extrapolation, since, in general, the values of the attachment cross section decreased very rapidly in the extrapolated regions or else the range (i.e., the electron energy band) of the extrapolated regions are very small. The peak cross section for $SF_6$, occurring at about 0.0 ev., has been reported to be $2.6 \times 10^{-14}$ $cm^2$/molecule(12). This value for room temperature thermal electrons is about 200 times greater than the value ($5.7 \times 10^{-16}$ $cm^2$/molecule)(3) employed in the present calculation. However, because the peak is narrow (about 0.03 ev.) and occurs at the low end of the distribution function (i.e., few electrons exist at these low energies), the results are not significantly affected.

Any minor deviations from the M-B distribution are expected to result in minor errors in the integrals also, because the integration process itself tends to reduce the effect of fluctuations and deviations. In addition, if a modified distribution function is assumed, then the average attachment cross sections that are computed will still have, essentially, the same relative effectiveness.

The results of these calculations are shown in Figure 5 and Figure 6. Values of $K_D$ are plotted on a mole basis in Figure 5 and on a mass basis in Figure 6. On both a g-mole and a mass basis, carbon tetrachloride ($CCl_4$) is the most efficient electron attacher. At the higher

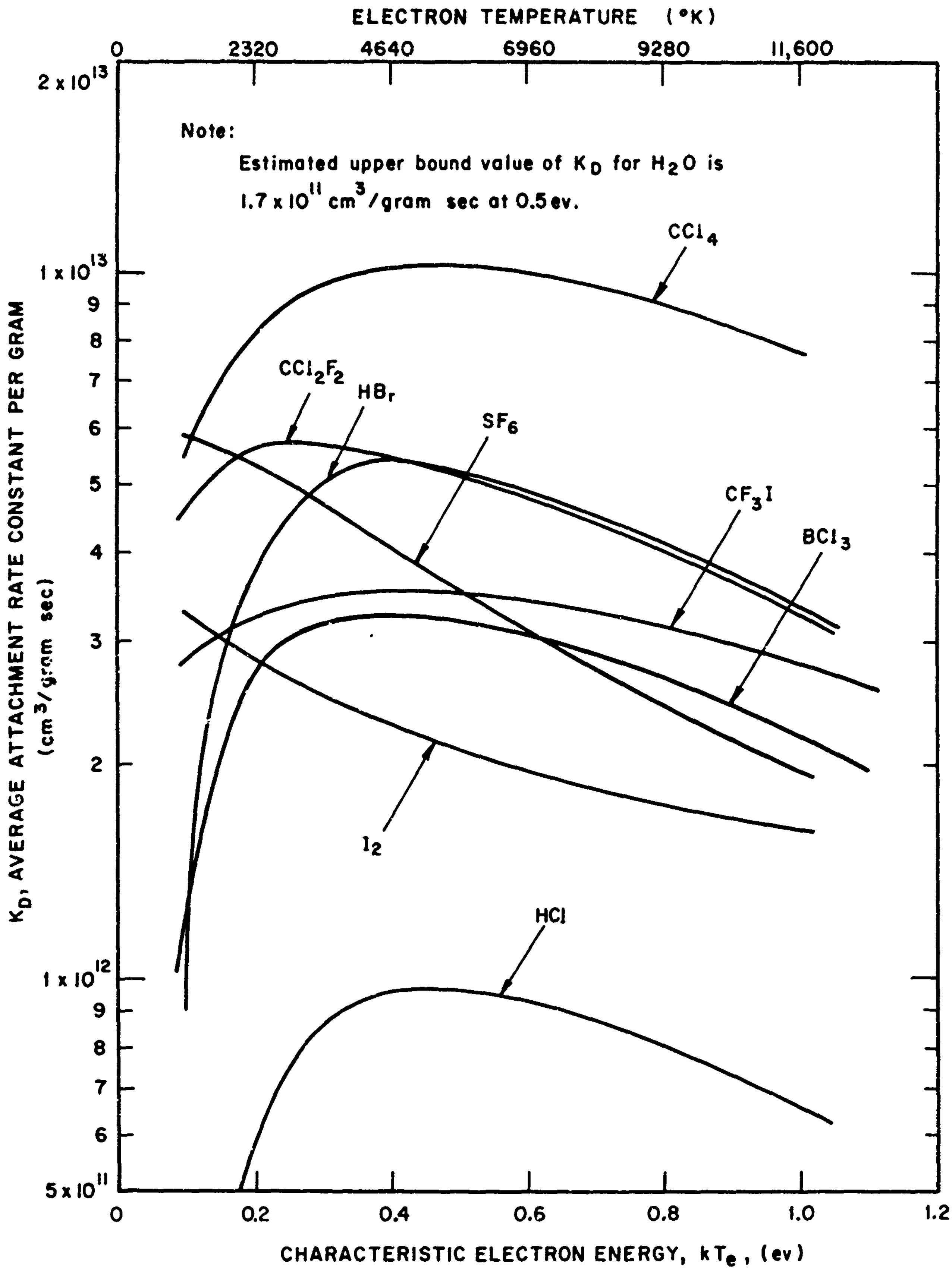


**Note:**

Estimated upper bound value of $K_D$ for $H_2O$ is 3 x $0^{12}$ $cm^3$/mole-sec at 0.5ev.

FIGURE 5.

AVERAGE ATTACHMENT RATE CONSTANT PER MOLE VS. CHARACTERISTIC ELECTRON ENERGY.



Note:
Estimated upper bound value of $K_D$ for $H_2O$ is $1.7 \times 10^{11}$ cm$^3$/gram sec at 0.5 ev.

FIGURE 6.
AVERAGE ATTACHMENT RATE CONSTANT PER GRAM
vs.
CHARACTERISTIC ELECTRON ENERGY.

plasma characteristic energies (> .4 ev., or about 4,600°K) the difference between $CCl_4$ and the other electrophylic compounds increases. $K_D$ for $CCl_4$ is as much as three times greater than for the next higher compound (at 1 ev.). At the lower electron energies (around 0.1), $CCl_4$, $SF_6$ and $CCl_2F_2$, have comparable values of $K_D$ (on a mass basis).

Evaluation of Equation (11),though simple in principle, is somewhat cumbersome and is best done by computer calculation. Values of K were calculated for this analysis by programming* Equation (11) on Telecomp**. The approximate values of $K_D$, can be readily evaluated for preliminary screening by the following approximation;

$$K_D(E') = \frac{\overline{v\sigma(E')}}{N_o} \approx \frac{\bar{v}\,\overline{\sigma(E)}}{N_o} \tag{12}$$

where the average of the product $\overline{v\,\sigma(E)}$ is replaced by the product of averages. The average, v, for a Maxwell-Boltzmann distribution is;

$$\bar{v} = \left(\frac{8kT_e}{\pi m}\right)^{1/2} = \left(\frac{8E'}{\pi m}\right)^{1/2} \tag{13}$$

The average value of $\sigma(E)$ is determined by a delta-function technique corresponding to a weighting by a Maxwell-Boltzmann distribution. Thus,

$$\overline{\sigma(E)} = \sigma(E') \tag{14}$$

---

[*] Copies of the program are available from the authors upon request.

[**] Telecomp is a time-shared computer service developed by Bolt Beranek and Newman, Inc., Cambridge, Massachusetts.

(For an equilibrium plasma, the electron temperature equals the gas temperature.)

Comparisons of the two methods for calculating $K_D$ are shown in Figure 7. It is evident that, in general, only order of magnitude results can be obtained from the delta-function approximation of Equation (12). (This approximation calculation however is much more rapid than the numerical integration.) It is of interest to note that calculation of $K_D$ from Equation (11) tends to smooth out the resonances in the attachment cross sections (see Figure 1), while calculation by means of Equation (12) does not. This occurs because Equation (12) is essentially a delta-function calculation. The peaks in the values calculated from Equation (12) occur at the same characteristic energy level as the resonances in the attachment cross sections.

It is of interest to compare the above materials to water, since flight experiments have been reported for water. There are no available data attachment cross section below electron energies of about 5.3 ev(well below $1 \times 10^{-19}$ cm$^2$)(3). The first resonant peak occurs at 6.4 ev with a maximum value of $4.8 \times 15^{-18}$ cm$^2$/molecule. An estimated upper bound for $K_D$ for water can be obtained by assuming that the value of the cross section at 5.3 ev. is valid also for lower electron energies. Or this basis $K_D$ is estimated to be $1.5 \times 10^{11}$ cm$^3$/gm sec. at 0.5 ev. It is again emphasized that this is at best an upper bound and most probably the actual value is significantly lower. Therefore the most electrophylic additives are potentially more than two orders of magnitude better than water vapor as attachers of electrons for limiting cases of negligible additives of a low degree of dissociation.

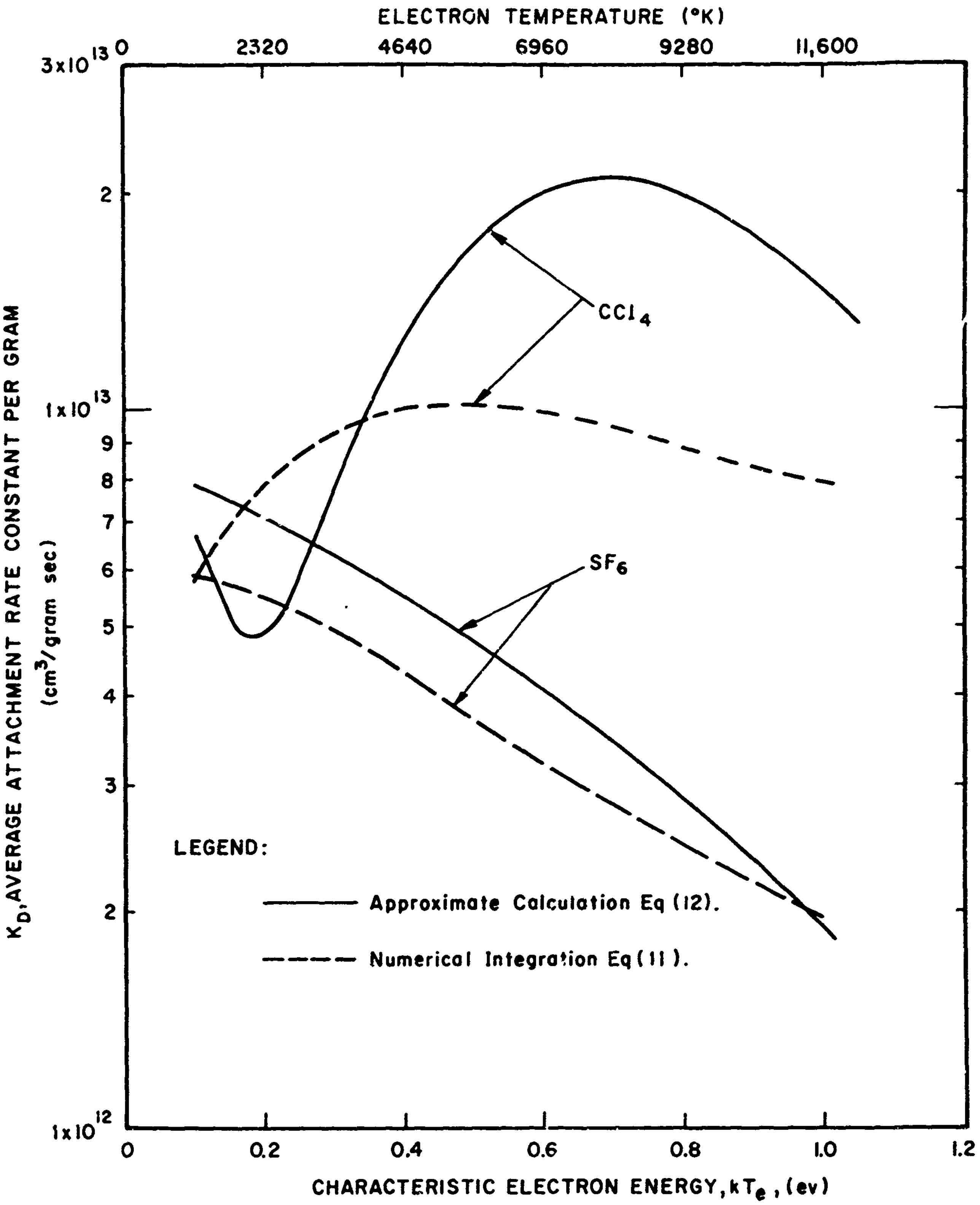


FIGURE 7.

COMPARISON OF METHODS EMPLOYED TO CALCULATE THE AVERAGE ATTACHMENT RATE CONSTANT.

It should be noted that comparison of potential compounds as electron attachers on the basis of the average attachment rate constant, $K_D$, neglects the effect of dissociation, which can be appreciable at the high gas temperatures of interest. The data employed in the calculation of $K_D$ also, was in general, obtained in cold plasmas (300°K).

## 5. SUMMARY

1) The process of electron attachment to an electrophylic molecule can be explained qualitatively in terms of the potential energy diagrams of the resulting excited and/or ion species.

2) The resonant behaviour of the attachment cross section with electron energy can be explained also by reference to the potential energy diagrams of the resultant species and to the Frank-Condon transition principle.

3) Multiple peaks in attachment cross section are the result of the relative location of the potential energy diagram for different resultant species.

4) The location and value of the resonant peak can be correlated with the effective heat of formation for the ion reaction corresponding to the resonant peak.

5) In general, and in the absence of dissociation, carbon tetrachloride ($CCl_4$) is an extremely effective electron attacher and its average attachment rate constant is approximately two orders of magnitude greater than for water. At lower characteristic (average) electron energies (about .1 ev.), $SF_6$ and $CCl_2F_2$ are comparable to $CCl_4$ as an electron attacher. At higher characteristic electron energies (> 0.4 ev.) and of the compounds investigated, $CCl_4$ is more than twice as effective as the next best compound.

6) Order of magnitude values of the average electron attachment rate constant can be obtained by multiplying the electron random velocity, $\bar{v}$ (E') and the attachment cross section evaluated at the characteristic electron energy, E'.

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13 ABSTRACT

This report is part of an analytical and experimental program to investigate the enhancement of microwave communication by employing small quantities of chemical additives introduced into the plasma sheath of a re-entry vehicle and to deduce the optimum types and forms of additives to be used. An analytical investigation has shown that electron attachment to electrophylic molecules is one of the more important mechanisms in reducing the plasma free electron concentration and thereby in alleviating the re-entry sheath black-out problem. The attachment cross section data necessary for the theoretical selection of the more effective additives is not always available in the literature. An analysis is presented here, where attachment cross sections are correlated with more readily available fundamental thermodynamic data so that attachment data can be predicted. Qualitative reasoning based upon the potential energy diagram concept is employed to describe the physics of electron attachment and to derive graphical correlations between the more readily obtained thermodynamic values and the attachment cross-section parameters. Average attachment rate constants are also calculated for molecules from data in the literature. The attachment rate constant can be employed as a figure of merit to determine the most efficient additive, for the limiting case of negligible dissociation. The results show that carbon tetrachloride is the most efficient of the compounds investigated and is potentially at least two orders of magnitude better then water for moderate plasma temperatures.

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