AD-767 709

NEGATIVE ION DETACHMENT

A. Mandl

Avco Everett Research Laboratory,
Incorporated

Prepared for:

Office of Naval Research
Advanced Research Projects Agency

June 1973

NEGATIVE ION DETACHMENT

FINAL TECHNICAL REPORT

Contract # N00014-71-C-0386

June 1973

Sponsored by

ADVANCED RESEARCH PROJECTS AGENCY

ARPA ORDER NO. 1479

AVCO EVERETT RESEARCH LABORATORY, INC.

A SUBSIDIARY OF AVCO CORPORATION

38

FINAL TECHNICAL REPORT

CONTRACT N00014-71-C-0386

NEGATIVE ION DETACHMENT

Sponsored by
ADVANCED RESEARCH PROJECTS AGENCY
ARPA ORDER NO. 1479

PROJECT CODE 421

PRINCIPAL INVESTIGATOR:

Dr. A. Mandl
Avco Everett Research Laboratory, Inc.
Everett, Massachusetts 02149
Telephone - A/C 617, 389-3000, Extension 648

SCIENTIFIC OFFICER:

Director, Physics Program
Division of Physical Sciences
Office of Naval Research
800 North Quincy Street
Arlington, Virginia 22217

EFFECTIVE DATE OF CONTRACT: 1 June 1971

CONTRACT EXPIRATION DATE: 30 June 1973

AMOUNT OF CONTRACT: $108,913

ABSTRACT

A series of detachment rates of electrons from both F^- and I^- have been measured at high temperatures. The F^- was produced by shock heating CsF and the I^- was produced by shock heating CsI. The following reactions and reaction rates have been measured:

$$F^- + F \xrightarrow{k_F} F_2 + e - 1.9\ eV \qquad 3500^\circ K < T < 5500^\circ K$$

$$k_F = 1.4 \times 10^{-10}\ e^{-22,000/T}\ cm^3/sec$$

$$F^- + O_2 \xrightarrow{k_{O_2}} O_2F + e - 2.8\ eV \qquad 4000^\circ K < T < 5500^\circ K$$

$$k_{O_2} = 2.5 \times 10^{-9}\ e^{-27,600/T}\ cm^3/sec$$

$$F^- + O \xrightarrow{k_O} OF + e - 0.5\ eV \qquad 3500^\circ K < T < 5000^\circ K$$

$$k_O = 2.0 \times 10^{-10}\ e^{-8,700/T}\ cm^3/sec$$

$$F^- + CF_2 \rightarrow CF_3 + e + 0.5\ eV \qquad 4000^\circ K < T < 5500^\circ K$$

$$k_{CF_2} \sim 10^{-12}\ cm^3/sec$$

$$I^- + Ar \rightarrow I + Ar + e - 3.5\ eV \qquad 3800^\circ K < T < 5800^\circ K$$

$$k_{Ar} = 7 \times 10^{-11}\ e^{-35,000/T}\ cm^3/sec$$

$$I^- + N_2 \rightarrow N_2 + e - 3.5\ eV \qquad 3500^\circ K < T < 5000^\circ K$$

$$k_{N_2} = 1.2 \times 10^{-10}\ e^{-35,000/T}\ cm^3/sec$$

$$I^- + H_2 \rightarrow \text{Detachment} \qquad 3100^\circ K < T < 4800^\circ K$$

TABLE OF CONTENTS

I. Technical Problem

1. Introduction

Electron attachment and detachment processes have received considerable study in recent years. The rates of these processes are necessary for estimating the free electron density in the ionosphere, combustion processes, gas discharges and reentry physics. Because of their high electron affinity the attachment of electrons to halogens to form negative ions and the competing process of collisional detachment of the electron from the negative ion are of particular interest.

We have measured the collisional detachment rate of the negative ion of atomic fluorine with a large number of collision partners. The reactions measured together with the measured rate constants are given in Table I. Reactions (a-e) have already been reported in the literature.[1-3] Reaction (a) has also been measured by another group[4] and the rate constant measurements are in reasonably good agreement. Under this contract additional F^- detachment rates listed in Table I (i. e., rates f-i) have been measured. In addition, detachment rate measurements have also been made on the I^- system. The reactions measured are also listed in Table I (j-l).

2. Applications

a. F^- Detachment

A major interest in F^- detachment was created by the development of the AERL Teflon boundary layer model since certain key assumptions depended on some of these rates.

In the new AERL model only those species were included whose production in the boundary layer could be justified by kinetic arguments.[5] This led to much more simplified computer calculations as compared

with the initial partial equilibrium model.[6] Comparison with the on-board optical data gave as good agreement between the calculated and measured neutral chemistry as the original partial equilibrium model.

In the proposed chemical model of the boundary layer on Teflon vehicles, 14 species are assumed to be in equilibrium. At the high boundary layer temperature this implies that all the F^- in the boundary layer is detached and, in fact, that all the negative charge is being carried by the free electrons. This model is consistent with a minimum set of eight chemical reactions which are sufficiently fast to provide for an equilibrium situation. Because of the large electron affinity of F, ~ 3.5 eV, there are fast exothermic reactions involving fluorine compounds that can attach electrons. Therefore, in order to provide for free electrons in the boundary layer, fast detachment processes are necessary. Under Contract F04701-70-C-0128 "Reentry Physics Program (REP)," AERL measured the rates of collisional detachment of electrons from F^- for a number of species (i.e., Ar, N_2, CO and H_2). However, none of the rates measured under this program gave rates fast enough to give complete detachment in the boundary layer. It was therefore one of the purposes of this program to see if there were any additional species in the boundary layer which would cause detachment in the given flow time in agreement with a major assumption of the AERL model.

These experimentally measured rates evaluated at 2500°K are shown in Fig. 1 as the dashed horizontal lines. Also shown in Fig. 1 are curves (solid lines) that indicate the kinetic rates necessary to make the chemical time for detachment equal the flow time in the boundary layer as a function of altitude for a number of species important in TFE boundary

layers. Conditions typical for boundary layers on slender vehicles were used for these calculations.

As can be seen from Fig. 1, atomic oxygen is fast enough to detach electrons from F^- in typical boundary layer flow time. This crucial experiment thus showed that a central assumption of the AERL limited partial equilibrium model of the Teflon boundary layer was valid.

b. I^- Detachment

Many high temperature ablators contain phenolic resins and therefore will produce large amounts of hydrogen in the boundary layer and wake. In these cases experimental evidence indicates that SF_6 is not a good electron quench material since the highly exothermic process

$$H + F^- \rightarrow HF + e + \Delta E;\ \Delta E = 2.3\ eV \qquad (1)$$

has a fast rate of about 10^{-9} cm^3/sec [7] at room temperature. Even the comparable reaction with molecular hydrogen, H_2, measured under our REP program has a very fast rate (see Table I). The use of e.g. CF_3I, which has a very large electron attachment cross section, [8] as a quenchant to produce I^- as the negative ion might be far superior to SF_6 since the reaction

$$H + I^- \rightleftarrows HI + e + \Delta E;\ \Delta E \sim 0 \qquad (2)$$

will be slower than Reaction (1) in the forward direction due to its decreased exothermicity. Reaction (2) is the only hydrogen-halogen ion reaction which is not exothermic.

Thus for ablators containing phenolic resins, iodine containing quenchants could well be more effective. For example, Fehsenfeld[8] has recently measured the associative attachment cross section for the molecule CF_3I. He finds a very rapid rate of 1.1×10^{-7} cm^3/sec at $T = 300^oK$ which is almost as fast as attachment to SF_6. For CF_3I the negative ion formed is I^-.

Other iodine containing quenchants, e. g. HI which also has a large attachment cross section[9] or I_2 directly could also be quite effective for wake quench in the presence of hydrogen.

c. Detachment (General)

Even though there is great interest in the general problem of detachment/attachment, there is no theory which can be used to calculate these rates. It is one of the aims of this program to provide at least the beginnings of a data base on which such a theory may be built. Some work has already begun using this data and the results will be discussed later.

II. Experiment and Apparatus

The measurements were performed in a CsF* seeded shock tube. A detailed description of the shock tube construction and operation has appeared earlier.[1] A schematic diagram of the apparatus is shown in Fig. 2. A mixture of diluent gas and CsF particles (~ 0.3% CsF) is flowed into a 6 inch shock tube. The CsF particles (~ .07μ in diam.) are produced by passing the diluent gas over a CsF melt (~ 1000°K) which causes the particles to self-nucleate. The mixture is subjected to both incident and reflected shock heating. The incident shock temperature is chosen to be high enough to ablate but not dissociate the CsF. Thus, the incident shock reaction can be represented schematically as $CsF_{(s)} + M \rightarrow CsF_{(g)} + M$. The ablation time of the CsF particles is typically a few microseconds (laboratory time)[10] while the incident shock heating lasts for about 40μsec. The mixture of CsF and diluent gases at about 2000°K is then subjected to a reflected shock which almost doubles the temperature and causes the CsF to completely dissociate. This reflected shock heating lasts for the rest of the test time (~ 150μsec). The dissociation of the CsF is almost entirely into the ionic branch[11] $CsF + M \rightarrow Cs^+ + F^- + M$ although equilibrium at these high temperatures (3000-6000°K) favors neutral fluorine. We measure the decay of the F^- concentration toward equilibrium. The F^- decays via detachment collisions by both Cs^+ and diluent gases.

*In this section F^- detachment experiments are being described. The same description holds equally well for the I^- detachment work with the F replaced by I. For example in the I^- work CsI is the salt used instead of CsF.

To find the rate of collisional detachment of F^- by M, we write the overall rate equation

$$(1/[F^-])\,(d[F^-]/dt) = -k_{Cs^+}[Cs^+] - k_M[M] \equiv k_{tot}[M] \qquad (3)$$

where

$$k_M = k_{tot} - k_{Cs^+}([Cs^+]/[M]) \qquad (4)$$

and [ ] means particle density.

We have previously measured[1] the rate constant for collisional detachment of F^- by Cs^+ as $k_{Cs^+} = 2.8 \times 10^{-9}\, e^{-40,000/T}$ cm^3/sec. Thus, we can solve Eq. (2) for k_M by measuring the overall rate constant, k_{tot} from the rate of decay of the F^- signal, $[Cs^+]$ from the free-bound radiation signal and [M] from the initial pressure and calculated shock conditions.

III. Technical Results

1. Detachment of F^- by F

The source of the atomic fluorine in these detachment measurements was F_2 which was mixed with argon. Fluorine concentrations of about 1% were used. With such low concentrations of fluorine the risks associated with using fluorine gas were reduced but certain precautions must be taken. In order to insure that fluorine is not lost to the walls of the shock tube, the walls had to be passivated initially with fluorine. This process requires that the shock tube be filled at a few p. s. i. a. of F_2 for several minutes. During this process the metal oxide surfaces of the tube are

replaced by fluorides. After passivation, the shock tube could be filled with fluorine to a specified pressure which then remained constant whereas before passivation the pressure would rapidly decrease due to fluorine absorption at the walls.

In order to insure that there was indeed no loss of fluorine to the walls, a mixture of argon and fluorine was admitted into the shock tube and a sample of the gas was removed at the other end. The sample was analyzed on a commercial gas analyzer.[12] Once the shock tube was passivated it was found to remain inert to fluorine as long as it was not opened to air.

The measurements of F^- detachment by fluorine were made in incident shock using mixtures of about 1% F_2 and 0.3% CsF in argon. Both the CsF (as described above) and the F_2[13] dissociate at the shock front. The CsF dissociates into Cs^+ and F^- while the F_2 dissociates into atomic fluorines. The detachment rate measurements are shown in Fig. 3. The solid line drawn through the data points is for an activation energy of 1.9 eV. This gives a reasonably good fit to the data and implies that this is an associative detachment reaction which can be written as

$$F^- + F \underset{}{\overset{k_F}{\rightleftharpoons}} F_2 + e - 1.9\ \text{eV} \qquad (5)$$

The rate described by the solid line in Fig. 3 is

$$k_F = 1.4 \times 10^{-10}\ e^{-22,000/T}\ \text{cm}^3/\text{sec.} \qquad (6)$$

Using the equilibrium constant one could also calculate the dissociative attachment rate of F_2 by electrons, k'_F, i.e., the reverse of reaction (5). In the temperature range of these measurements, we find

$$k'_F = 4.6 \times 10^{-6} \left(\frac{300}{T}\right)^{3/2} \text{ cm}^3/\text{sec} \qquad (7)$$

Such rates have been observed[14] for other dissociative attachment reactions at room temperature.

2. Detachment of F^- by O_2

The measurement of the detachment of F^- by O_2 is straightforward. Mixtures of oxygen with N_2 and with Ar were used. A typical mix contained about 1% O_2 and 0.3% CsF. In cases where N_2 was used as the diluent, measurements were made in reflected shock and in those cases where Ar was the diluent, incident shock measurements were performed. The measured detachment rates are shown in Fig. 4. The solid line is a fit to the data and gives a rate constant

$$k_{O_2} = 2.5 \times 10^{-9} e^{-27,000/T} \text{ cm}^3/\text{sec} \qquad (8)$$

The measured activation energy is thus less than the electron affinity of F^- (E.A. = 39,500°K) and so this is clearly an associative detachment process. It is however very difficult to deduce a reaction from just energy considerations. The reaction given in Table I is

$$F^- + O_2 \rightarrow O_2F + e \qquad (9)$$

Using the measured energy dependence and the electron affinity of F^-, reaction (9) implies about 1 eV binding energy for O_2F which is in reasonable agreement with the JANAF value of 3/4 eV.

A second possible reaction is

$$F^- + O_2 \rightarrow OF^- + O \qquad (10)$$

followed by

$$OF^- + M \rightarrow OF + M + e.$$

The OF bond and electron affinity have been calculated by O'Hare and Wahl[15] as 3 eV and 1.2 eV respectively. If one uses these values one would expect an activation energy of at least 4.1 eV for reaction (10) whereas we measure an activation energy of 2.4 eV. Such a large energy discrepancy has led to the assignment of reaction (9) for the detachment mechanism of F^- by O_2.

3. Detachment of F^- by O

The source of atomic oxygen was ozone. The use of ozone in a dusty shock tube presents certain difficulties. One has to first insure that the shock tube can hold ozone for reasonable periods of time without significant decomposition to O_2. In order to insure this the shock tube must be passivated with O_3 in a process similar to the F_2 passivation described above. In this process the stainless steen walls of the tube are allowed to be oxidized by the highly active ozone until

sufficient oxides built up on the surface making it nonreactive to ozone. In order to check the degree of passivation in the tube a one meter glass cell with quartz end windows was attached to the shock tube and after the tube was filled with a mixture of O_3 and Ar the cell was periodically filled and the ozone density measured. The ozone was monitored using the 2537 $\mathring{A}$ line of a mercury lamp which is just about at the peak of the O_3 absorption. A one meter absorption cell was necessary because of the relatively small absorption cross section of O_3 and the fairly low concentrations of O_3 in the mix.

A second test which had to be made was the survival of O_3 in the presence of CsF particles in the shock tube. Gas mixtures were made with O_3 and CsF particles (particle size ~ .07μ). The ozone density was monitored using the one meter cell. Again the O_3 was found to survive. These observations could have some important implications for atmospheric physics, where ozone-particulate interactions are known to occur in the upper atmosphere.

Once we had convinced ourselves that O_3 survives in the dusty shock tube environment, mixes of O_3, CsF and Ar were made. The O_3 density was checked in the one meter cell just before the run. Measurements were made in the incident shock. In these experiments the CsF and O_3 dissociate at the shock front. The observed F^- detachment is then due to Cs^+, Ar, O_2 and O. The only unknown rate is the detachment of F^- by O. The measured rates are shown in Fig. 5. The solid line drawn through the data gives a rate of

$$k_O = 2 \times 10^{-10} e^{-8,700/T} \text{ cm}^3/\text{sec.} \qquad (11)$$

This is consistent energetically with the reaction

$$F^- + O \rightarrow OF + e. \qquad (12)$$

4. I^- Photodetachment Cross Section

Before measuring electron detachment in I^-, measurements of the I^- photodetachment cross section were made in order to insure that the system is well understood. Similar preliminary measurements were made on the F^- system[16] when that work was initially begun. The measured I^- photodetachment cross section together with the calculated values of this cross section[17] are presented in Figure 6. It will be noted that for wavelengths greater than 2800Å the agreement between experiment and theory is excellent. Below 2800 Å the agreement is not as good and, in fact, an unexpected resonance was observed in the cross section at about 2200 Å. These measurements are discussed in some detail in a paper which we recently published.[18] It should be pointed out that this is the first direct spectroscopic observation of an excited (autodetaching) state of a negative ion.

In our earlier [1] work on F^- we had postulated the existence of such a state in F^-. This was used as a possible explanation of the rather rapid detachment of F^-.

5. I^- Detachment by Argon

Measurements of the collisional detachment rate of I^- by Ar have been made in a manner conceptually similar to the F^- detachment by Ar measurements described in an earlier publication.[1] The source of I^- in this work was CsI salt which as in the case for CsF dissociates entirely into the ionic branch,[11] i.e.,

$$CsI + M \rightarrow Cs^+ + I^- + M \qquad (13)$$

Our major diagnostic is the absorption signal from the I^- photodetachment absorption continuum. Since the I^- photodetachment cross section is significantly larger than the F^- photoabsorption cross section our signal-to-noise ratio is generally better in the I^- work.

The measured detachment rates of I^- by Ar as a function of temperature shown in Figure 7. The solid line through the data points is for an activation energy of 3.06 eV which is the electron affinity of I^-. This is the temperature dependence that one might expect. The rate derived from the data for the reaction

$$I^- + Ar \xrightarrow{k(Ar)} I + Ar + e - 3.06\ eV \qquad (14)$$

is

$$K_{Ar}(I^-) = 7 \times 10^{-11}\ e^{-35,500/T}\ cm^3/sec \qquad (15)$$

6. I^- Detachment by N_2

The collisional detachment measurements of I^- by N_2 were similar to the I^- by Ar measurements except that N_2 is used as a diluent gas instead of Ar. A plot of the detachment rate as is function of temperature is shown in Figure 8. The solid line again is for 3.06 eV activation energy and the rate constant for the reaction

$$N_2 + I^- \rightarrow N_2 + I + e - 3.06\ eV \qquad (16)$$

is found to be

$$K_{N_2}(I^-) = 1.2 \times 10^{-10} e^{-35,500/T} \text{ cm}^3/\text{sec} \quad (17)$$

7. I^- Detachment by H_2

Finally, a series of rate measurements have been made of the detachment of I^- by H_2. These measurements were made using Ar and N_2 as diluent gases with 0.5% H_2 in each case. The measured total rate constant is shown in Figure 9. The solid line is for detachment by N_2. The data does seem to fall off with an activation energy less than the electron affinity below ~ 4,000°K and seems to fall with an activation energy of about the election affinity above 4,000°K. These measurements are still somewhat preliminary. For calculational purposes we have arbitraily assumed that the data does fall with an activation energy of exactly the election affinity, i.e., 3.06 eV and we have used an average fit to the data (dashed line).

Thus, we are assuming the reaction

$$H_2 + I^- \rightarrow H_2 + I + e \quad (18)$$

It will be noticed that this arbitrary fit gives a rate of about 2 x the nitrogen value. This is for 0.5% H_2. This would put an upper limit on the hydrogen detachment rate of about 200 x the nitrogen rate. However, since the data seens to have an uncertainty of about $\pm$ 2, all we can say is that within our error bars H_2 and N_2 seem to have about the same rate for detachment. Future experiments using different mole fractionsof H_2 will help to tie down these detachment rates.

IV. IMPLICATIONS OF RESEARCH

The work performed in the negative ion shock tube facility to date together with the resulting publications is summarized in Table II. The overall effect of this research has been to markedly increase our understanding of detachment. We have measured all the important detachment processes in the Teflon boundary layer. This work has confirmed a central assumption of the AERL limited partial equilibrium model of the Teflon boundary layer. This gives a certain measure of confidence to those using this model.

Secondly, we have pointed out that in a wake containing large mole fractions of hydrogen, fluorine would be a poor quenchant. Iodine was proposed as a better quenchant in such cases. It has been shown during the past year that iodine would not be readily detached by nitrogen in the atmosphere and the question of the effect of hydrogen on I^- detachment was also addressed. While these results are still preliminary, it seems that the molecular hydrogen collisionally detaches the I^- with a cross section of between 1 to 200 times the molecular nitrogen cross section. Whether or not there is a change in the activation energy below 4000°K is a question which will have to be resolved by future research. Certainly, around 5000°K where a small fraction of the H_2 is dissociated one does not see a marked increase in the detachment rate (see Fig. 9). This implies that the reaction

$$H + I^- \rightarrow HI + e$$

is not remarkably fast, i. e., much slower than the $\sim 10^{-9}$ rate which Fehsenfeld found for the reaction

$$H + F \rightarrow HF + e$$

However, questions like this will have to be settled more definitiyely by future experiments.

Finally, the data on detachment obtained so far will serve as the start of a data base against which detachment theories can be checked in the future. Not only have collisional detachment processes been measured in these experiments but we have also been the first to measure associative detachment processes.

Theoretical calculations have already been made using the F^- detachment rates from this experiment.[19] The agreement between experiment and theory is remarkably good. A comparison between our data and the calculation of Ven Shui is shown in Fig. 10. The solid lines are his calculated values of the detachment rates and the points are our data. The cases shown are for F^- detachment by Ar, N_2 and CO.

V. IMPLICATIONS FOR FUTURE EXPERIMENTS

There are several future experiments which are suggested by this research. The I^- detachment by H_2 should be continued with the mole fraction of H_2 varied. By taking measurements at several other hydrogen densities the uncertainties in the measurement could be reduced. Also since this work was done, a Bremsstrahlung I. R. detection system has been added to our diagnostics. This system will directly measure the electron densities which will be of further help in reducing the data.

An experiment which would also be of importance in accessing the value of iodine as a wake quenchant would be a flowing afterglow measurement of the type done by Fehsenfeld for the reaction

$$I^- + H \rightarrow HI + e$$

Even though this measurement would be at room temperature, it would be of value in measuring the relative efficacy of I^- vs. F^- as a quenchant in the presence of atomic hydrogen.

Finally, there is a real need to provide a broad data base for general electron detachment calculations. We are now in a unique position of having developed a reliable system to perform these measurements. Thus, the electron detachment rates of Cl^- and Br^- would give a complete set of detachment data for the halogens. The halogens are themselves of interest as potential wake quenchants. Also, this data could be used as the basis for a more general theory of detachment which could eventually be extrapolated to other systems of interest.

TABLE I

MEASURED RATE CONSTANTS

Reaction	$k(cm^3/sec)$
a. $F^- + Ar \rightarrow F + e + Ar$	$1.2 \times 10^{-11}\ e^{-40,000/T}$
b. $F^- + Cs^+ \rightarrow F + e + Cs^+$	$2.8 \times 10^{-9}\ e^{-40,000/T}$
c. $F^- + N_2 \rightarrow F + e + N_2$	$6.0 \times 10^{-11}\ e^{-40,000/T}$
d. $F^- + CO \rightarrow F + e + CO$	$1.7 \times 10^{-10}\ e^{-40,000/T}$
e. $F^- + H_2 \rightarrow HF + H^-$	$2.8 \times 10^{-11}\ e^{-9,400/T}$
f. $F^- + F \rightarrow F_2 + e$	$1.4 \times 10^{-10}\ e^{-22,000/T}$
g. $F^- + O_2 \rightarrow O_2F + e$	$2.5 \times 10^{-9}\ e^{-27,600/T}$
h. $F^- + O \rightarrow OF + e$	$2.0 \times 10^{-10}\ e^{-8,700/T}$
i. $F^- + CF_2 \rightarrow CF_3 + e$	$\sim 10^{-12}$
j. $I^- + Ar \rightarrow I + e + Ar$	$7 \times 10^{-11}\ e^{-35,500/T}$
k. $I^- + N_2 \rightarrow I + e + N_2$	$1.2 \times 10^{-10}\ e^{-35,500/T}$
l. $I^- + H_2 \rightarrow$ detachment	

TABLE II

MEASUREMENTS OBTAINED ON NEGATIVE ION SHOCK TUBE FACILITY

Detachment of Electrons from F^-	References
1) $F^- + Cs^+$	Results published in Chem. Phys. Letters 5, 307 (1970), AERL Amp 301; J. Chem. Phys. 53, (1970), AERL RR 351.
2) $F^- + Ar$	
3) $F^- + N_2$	Published J. Chem. Phys. 54, 4129 (1970), AERL Amp 329.
4) $F^- + CO$	Published in J. Chem. Phys. 57, 5617 (1972). AERL Amp 378.
5) $F^- + H_2$	
6) $F^- + O_2$	Results presented at the Ninth International Shock Tube Symposium, July 1973, to be published in J. Chem. Phys. (Oct. 1973).
7) $F^- + F$	
8) $F^- + O$	
9) $F^- + CF_2$	To be published.
Photodetachment of F^-	
$F^- + h\nu \rightarrow F + e$	Published in Phys. Rev. A, 3, 251 (1971) AERL Amp 311.
Photodetachment of I^-	
$I^- + h\nu \rightarrow I + e$	Published in Phys. Rev. Letters 31, 417 (1973).
Photodissociation of CsF	
$CsF + h\nu \rightarrow Cs + F$	Published in J. Quant. Spectrosc. Radiat. Transfer 11, 1197 (1971). AERL Amp 320.
Dissociation rate of CsF	
$CsF + M \rightarrow Cs^+ + F^- + M$	Published in J. Chem. Phys. 55, 2918 (1971), AERL Amp 336.

TABLE II, CONTINUED

Ablation rate of CsF	
$CsF_{(solid)} \rightarrow CsF_{(gas)}$	Published in J. Appl. Phys. 42, 4936 (1971), AERL Amp 332.
Detachment of Electrons for I^-	
$I^- + Ar$, $I^- + N_2$	To be published.
$I^- + H_2$	Measurements in progress.

Acknowledgment

The author wishes to gratefully acknowledge the technical assistance recieved from C. Deradourian in the operation of the shock tube and other experimental apparatus. I am also indebted to G. E. Caledonia for some helpful discussions on detachment processes.

This research was supported by the Advanced Research Projects Agency of the Department of Defense and was monitored by ONR under Contract No. N00014-71-C-0386.

REFERENCES

1. A. Mandl, B. Kivel and E. W. Evans, J. Chem. Phys. 53, 2363 (1970).

2. A. Mandl, J. Chem. Phys. 54, 4129 (1971).

3. A. Mandl, J. Chem. Phys. 57, 5618 (1972).

4. K. Luther, J. Troe and H. G. Wagner, Ber. Bunsenges. Physik. Chem. 76, 53 (1972).

5. L. A. Young and D. O. Ham, A Simplified Teflon-Air Boundary Layer Model (U), .RN 867, November 1970.

6. L. A. Young, R. A. Greenberg, and K. L. Wray, J. Quant. Spectrosc. Radiat. Transfer 10, 189 (1970).

7. F. C. Fehsenfeld and A. Mandl, REP Final Technical Progress Report, Contract F04701-70-C-0128, December 1970, p. 65.

8. REP Final Report, November 197[illegible].

9. L. G. Christophorou and J. A. D. Stockdale, J. Chem. Phys. 48, 1956 (1968).

10. A. Mandl . J. Appl. Phys. 42, 4932 (1971).

11. R. S. Berry, T. Cernoch, M. Coplan and J. J. Ewing, J. Chem. Phys. 49, 127 (1968); J. J. Ewing, R. Milstein and R. S. Berry, 7th Shock Tube Symposium, Toronto, Canda (1969).

12. In order to measure the ratio of fluorine to argon in the gas analyzer, a separate measurement of the electron impact cross section of fluorine had to be made. This measurement is described in a paper by R. E. Center and A. Mandl, J. Chem. Phys. 57, 4104 (1972).

13. C. D. Johnson and D. J. Britton, J. Phys. Chem. 68, 3032 (1964); V. H. Shui, J. P. Appleton and J. C. Keck, "The Three Body Recombination and Dissociation of Diatomic Molecules: Comparison Between Theory and Experiment," Fluid Mech. Lab. Pub. No. 70-3, M.I.T. (1970).

14. L. G. Christophorou and R. P. Blanstein, Chem. Phys. Letters 12, 173 (1971).

15. P. A. G. O'Hare and A. C. Wahl, J. Chem. Phys. 53, 2469 (1970).

16. A. Mandl, Phys. Rev. 3, 251 (1971).

17. E. J. Robinson and S. Geltman, Phys. Rev. 153, 4 (1967).

18. A. Mandl and H. A. Hyman, Phys. Rev. Letters 31, 417 (1973).

19. V. H. Shui and J. C. Keck, "Phase Space Theory of Electron Detachment in Slow Atomic Collisions," Fluid Mech. Lab. Pub. No. 73-4, May 1973. To be published in J. Chem. Phys.

FIGURE CAPTIONS

Fig. 1 — Solid lines give minimum values of the rate constant necessary for complete detachment of F^- in the boundary layer of a Teflon ablating vehicle at various altitudes. The density, n, used is the maximum value of density, n_{max}, in the region of the boundary layer above 2500°K as given by the AERL model in which 14 species are in equilibrium. The dashed curves are our measured values of rate constants. Complete detachment will occur below the intersection of a dashed and solid curve of the same species.

Fig. 2 — Schematic diagram of apparatus.

Fig. 3 — Measured detachment rate of F^- by F as a function of temperature.

Fig. 4 — Measured detachment rate of F^- by O_2 as a function of temperature.

Fig. 5 — Measured detachment rate of F^- by O as a function of temperature.

Fig. 6 — Measured photodetachment cross section of I^- (open circles) and comparison with calculated values of Robinson and Geltman (closed circles).

Fig. 7 — Measured detachment rate of I^- by Ar as a function of temperature.

Fig. 8 — Measured detachment rate of I by N_2 as a function of temperature.

Fig. 9 Measured detachment rate of I^- by a mixture of N_2 and 1/2% H_2.

Fig. 10 Detachment rate coefficient k_d vs. temperature O: F^- + Ar, F^- + N_2, Δ: F^- + CO. Solid lines are theoretical results.[19]

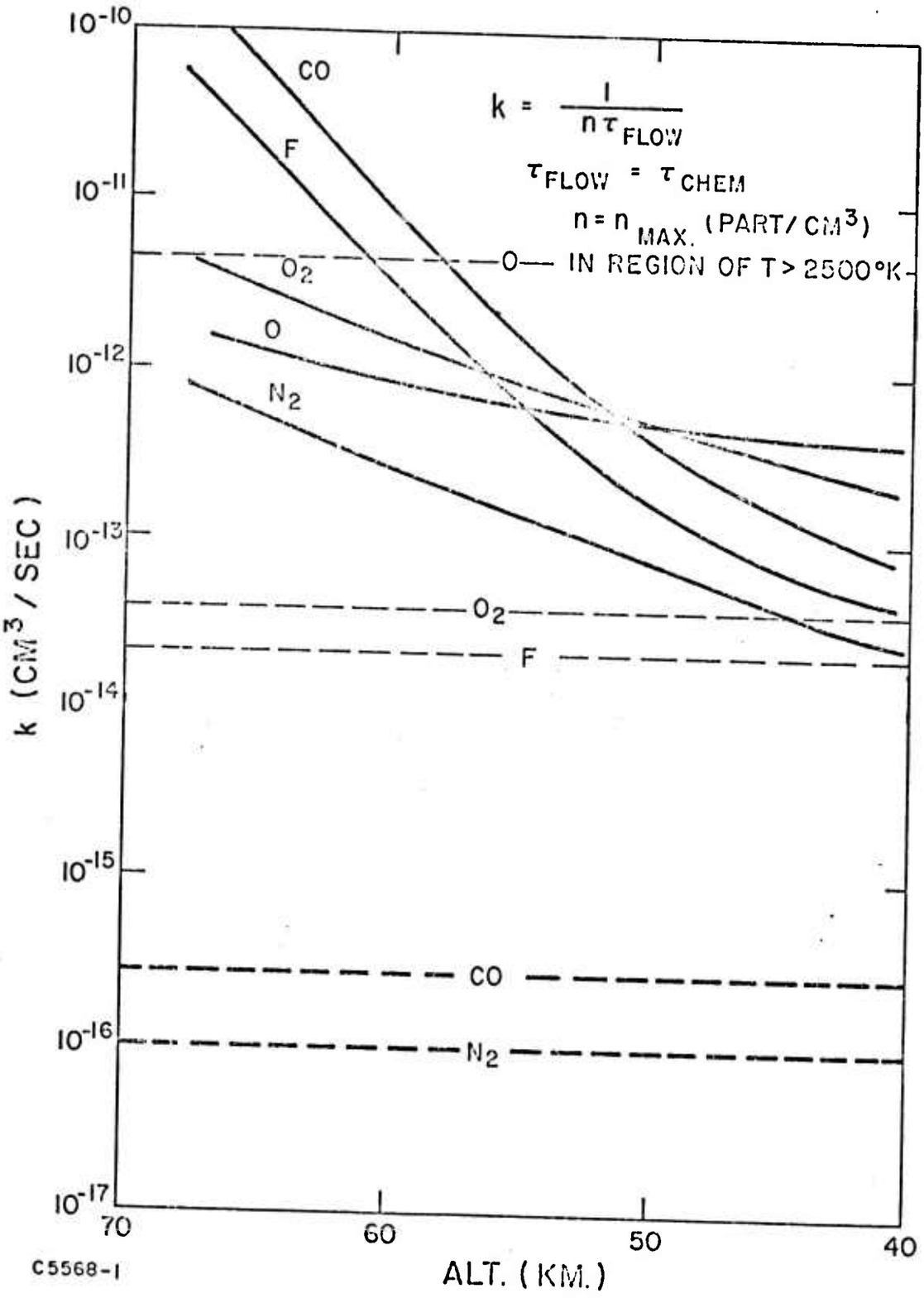
10^{-10}
10^{-11}
10^{-12}
10^{-13}
10^{-14}
10^{-15}
10^{-16}
10^{-17}
k (CM³ / SEC)
CO
F
O_2
O
N_2
$k = \frac{1}{n\tau_{FLOW}}$
$\tau_{FLOW} = \tau_{CHEM}$
$n = n_{MAX.}$ (PART/ CM³)
O — IN REGION OF T > 2500°K
O_2
F
CO
N_2
70
60
50
40
ALT. (KM.)
C5568-1

Fig. 1

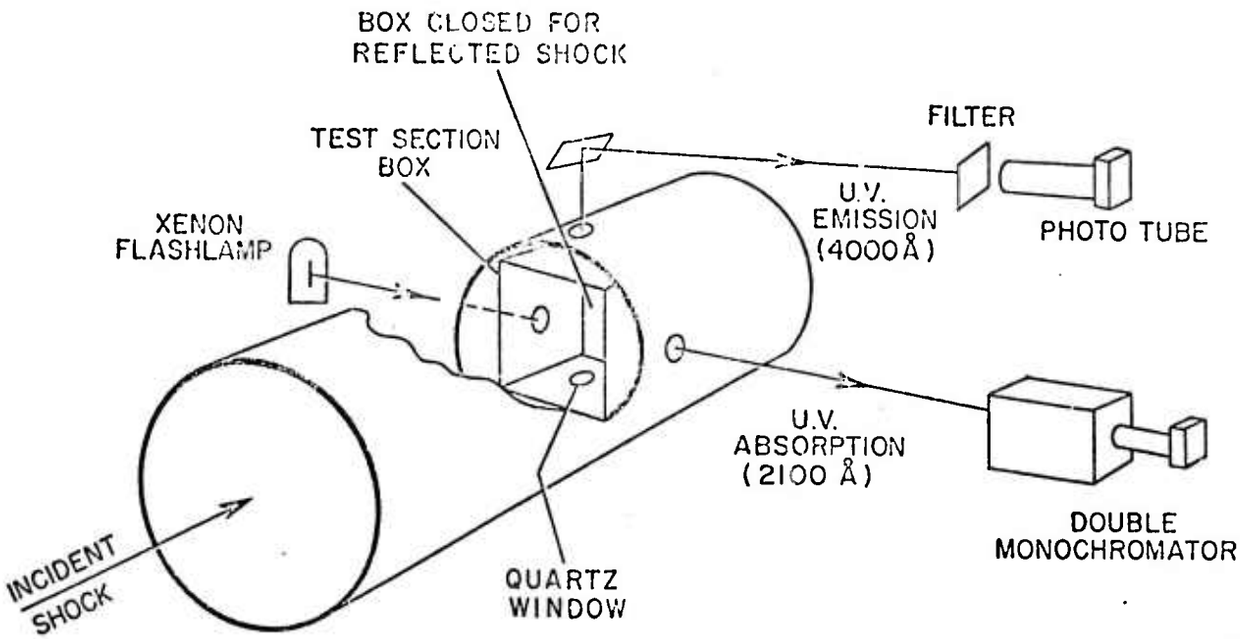
BOX CLOSED FOR
REFLECTED SHOCK
TEST SECTION
BOX
FILTER
U.V.
EMISSION
(4000Å)
PHOTO TUBE
XENON
FLASHLAMP
U.V.
ABSORPTION
(2100 Å)
DOUBLE
MONOCHROMATOR
INCIDENT
SHOCK
QUARTZ
WINDOW

Fig. 2

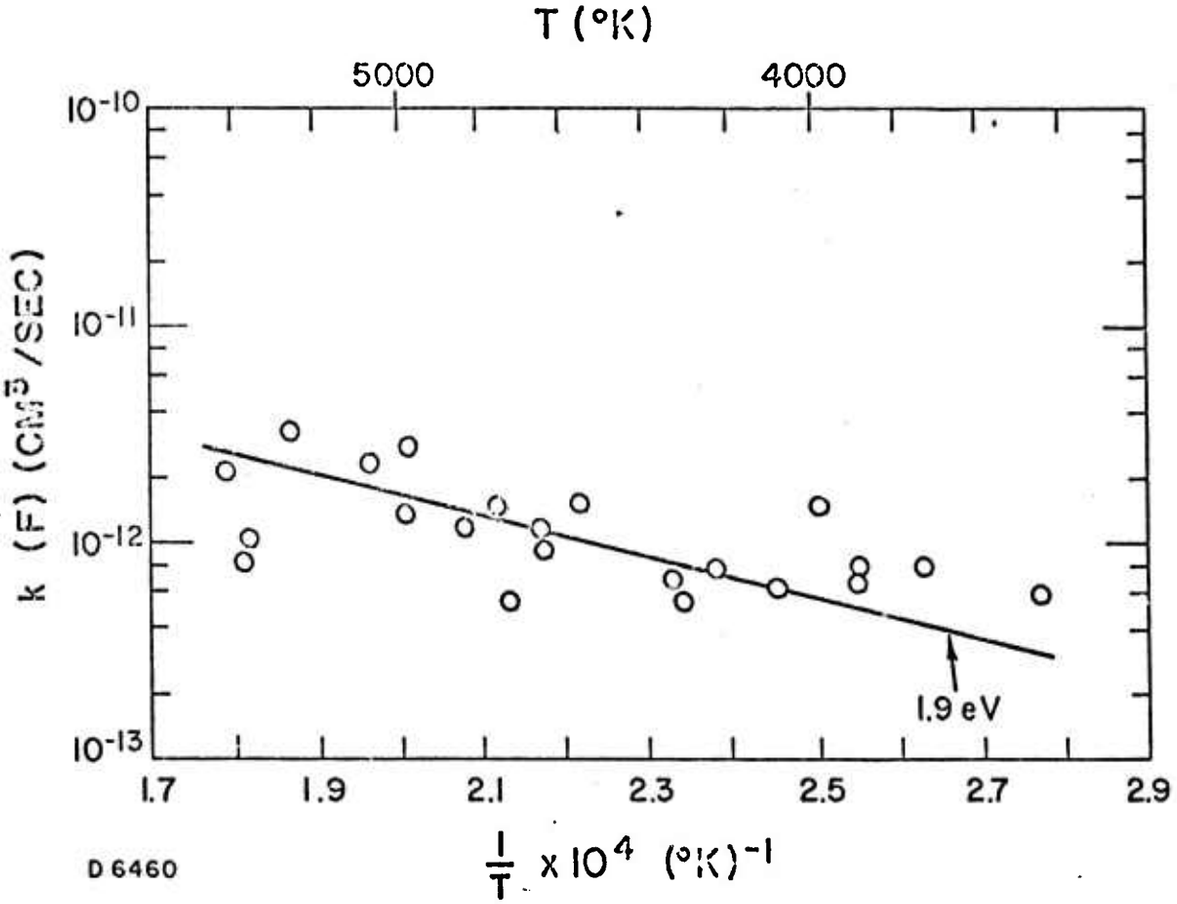
T (°K)
5000
4000
10-10
10-11
10-12
10-13
k (F) (CM3 /SEC)
1.9 eV
1.7
1.9
2.1
2.3
2.5
2.7
2.9
D 6460
1/T x 10^4 (°K)-1

Fig. 3

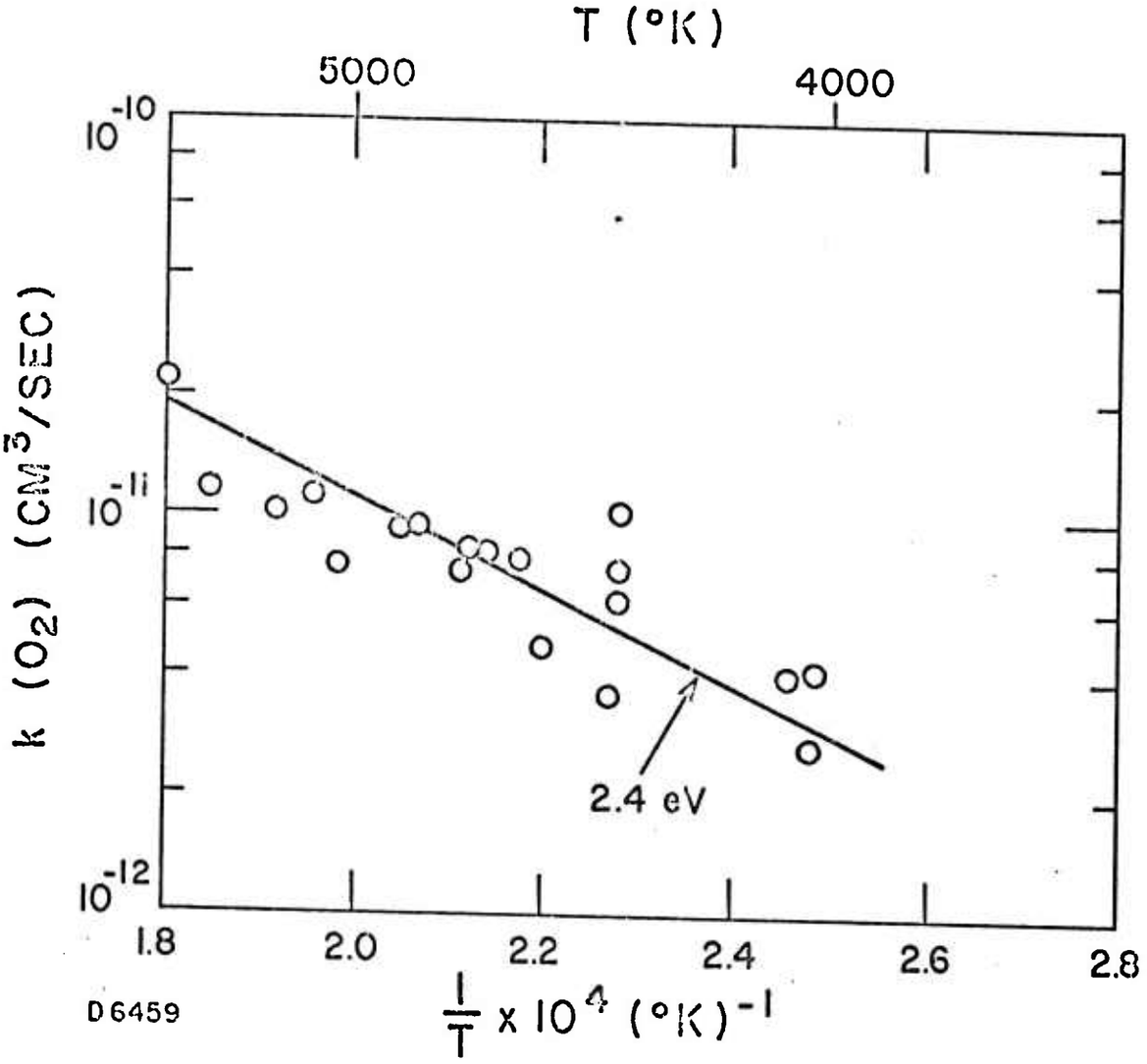
T (°K)
5000
4000
10^{-10}
10^{-11}
10^{-12}
k (O_2) (CM^3/SEC)
2.4 eV
1.8
2.0
2.2
2.4
2.6
2.8
D6459
$\frac{1}{T} \times 10^4$ (°K)$^{-1}$

Fig. 4

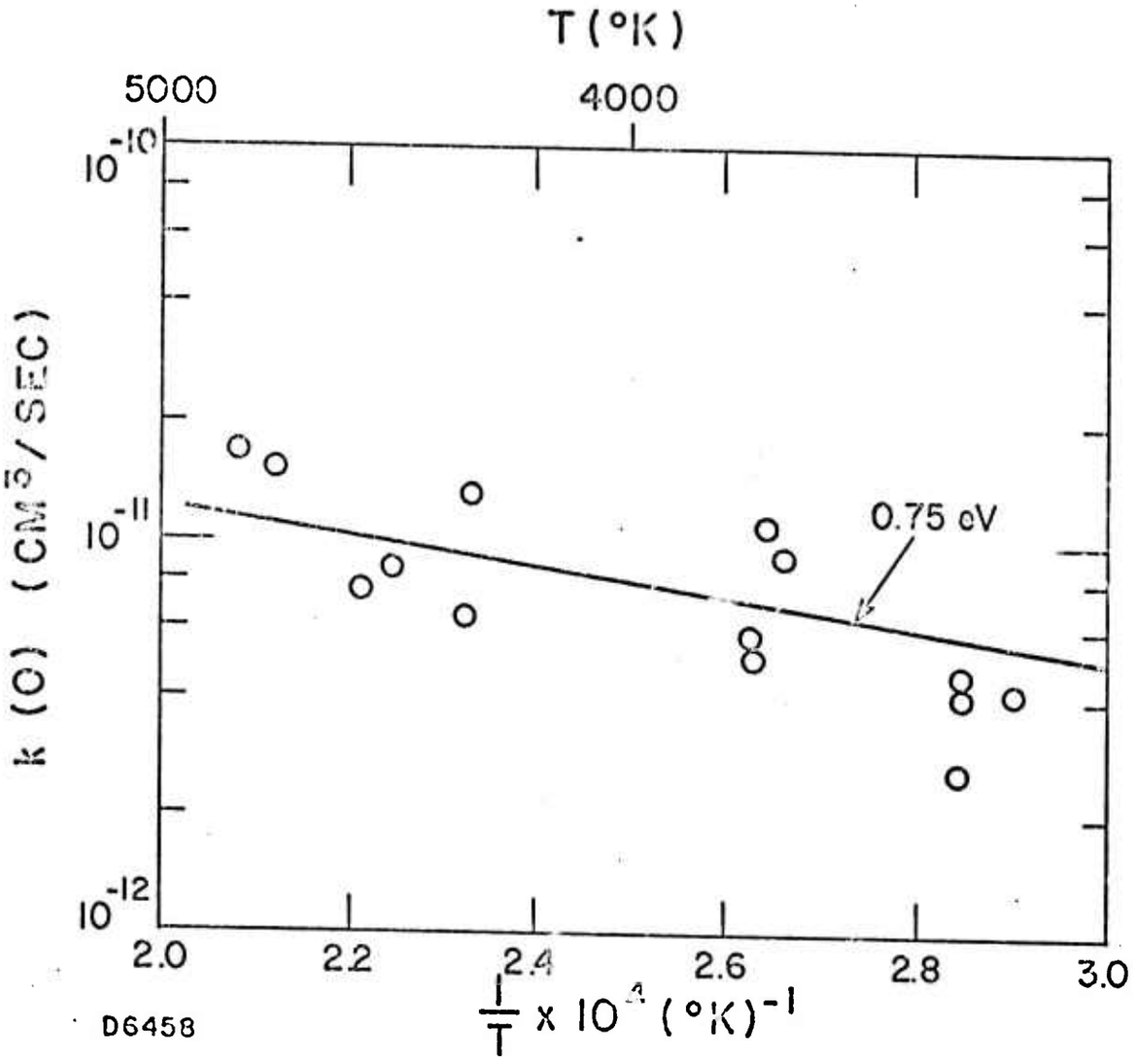
T (°K)
5000
4000
10^-10
10^-11
10^-12
k (C) (CM³/SEC)
0.75 eV
2.0
2.2
2.4
2.6
2.8
3.0
1/T x 10^4 (°K)^-1
D6458

Fig. 5

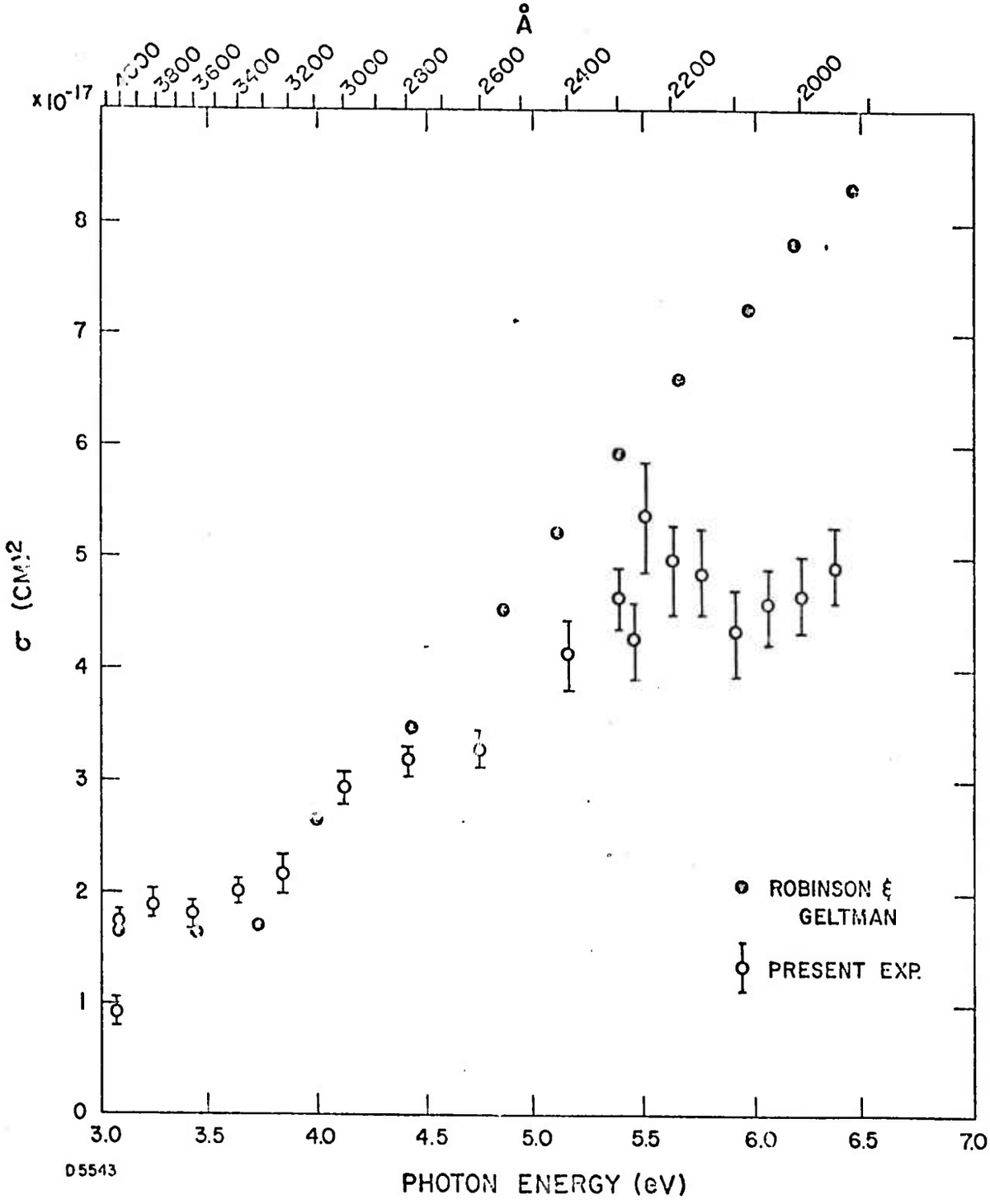

Photo detachment cross section of I^-.

Fig. 6

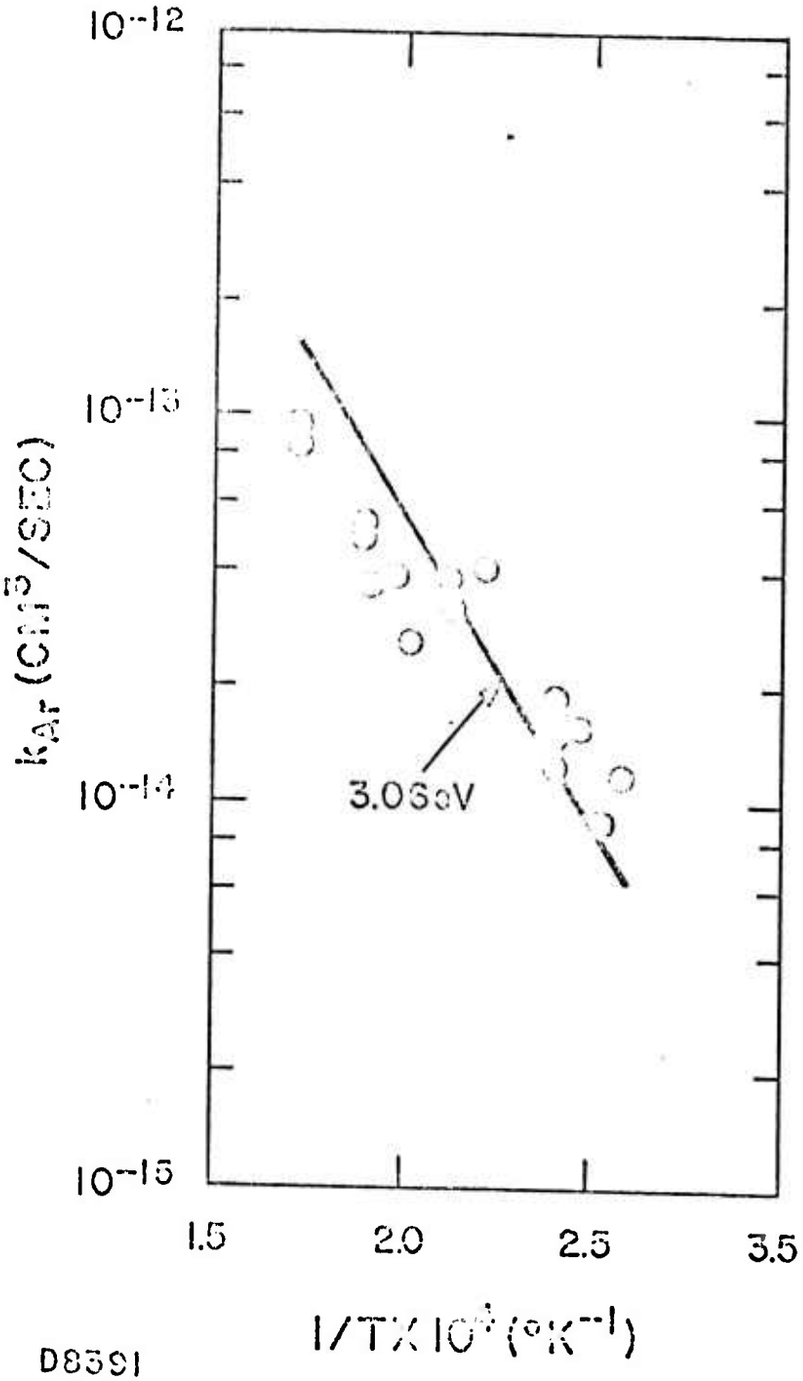
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
k_Ar (cm³/sec)
3.06eV
1.5
2.0
2.5
3.5
1/TX 10³ (°K⁻¹)
D8391

Fig. 7

3/

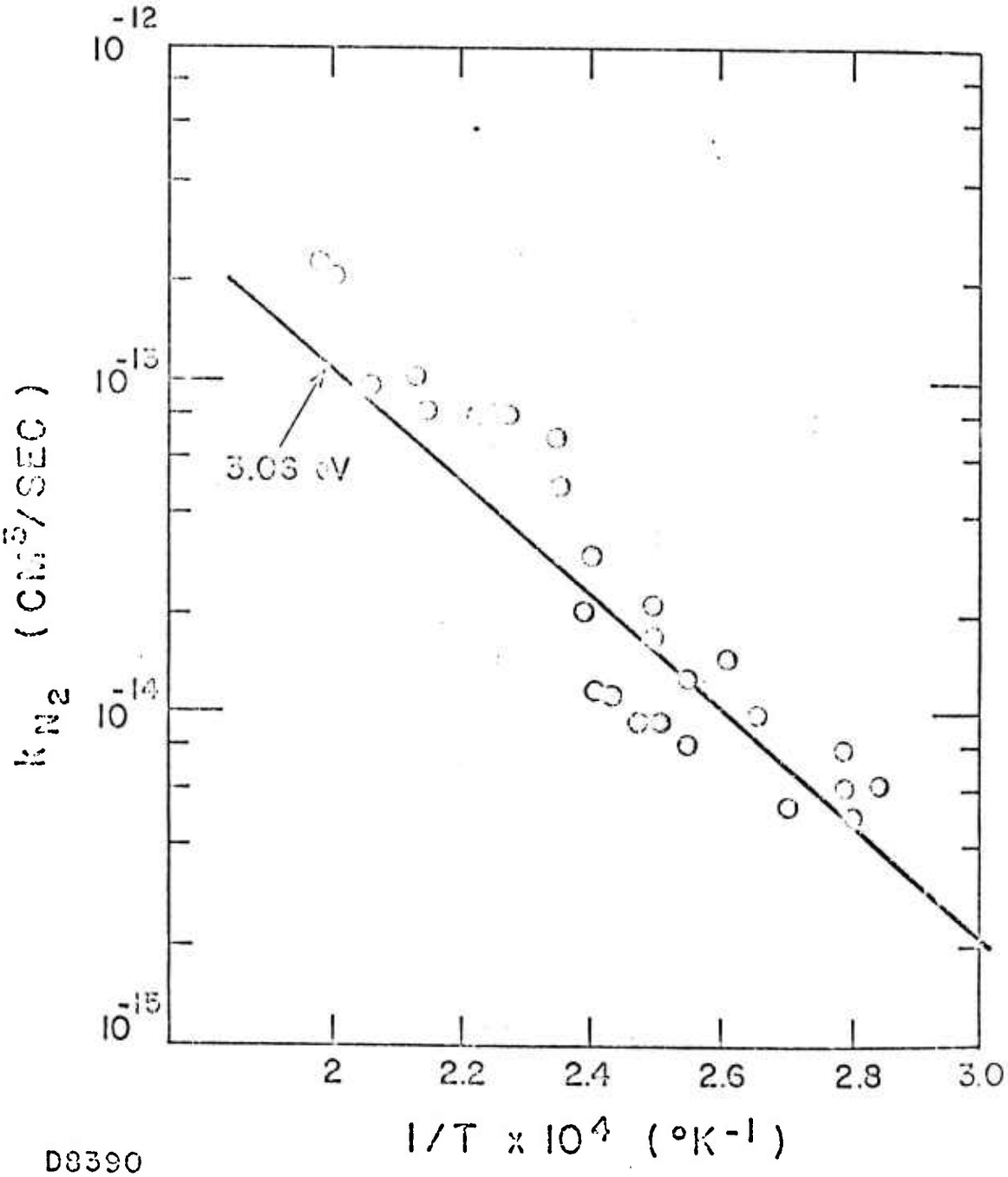
10^{-12}
10^{-13}
10^{-14}
10^{-15}
k_{N_2} (CM^3/SEC)
3.03 eV
2
2.2
2.4
2.6
2.8
3.0
1/T x 10^4 ($°K^{-1}$)
D8390

Fig. 8

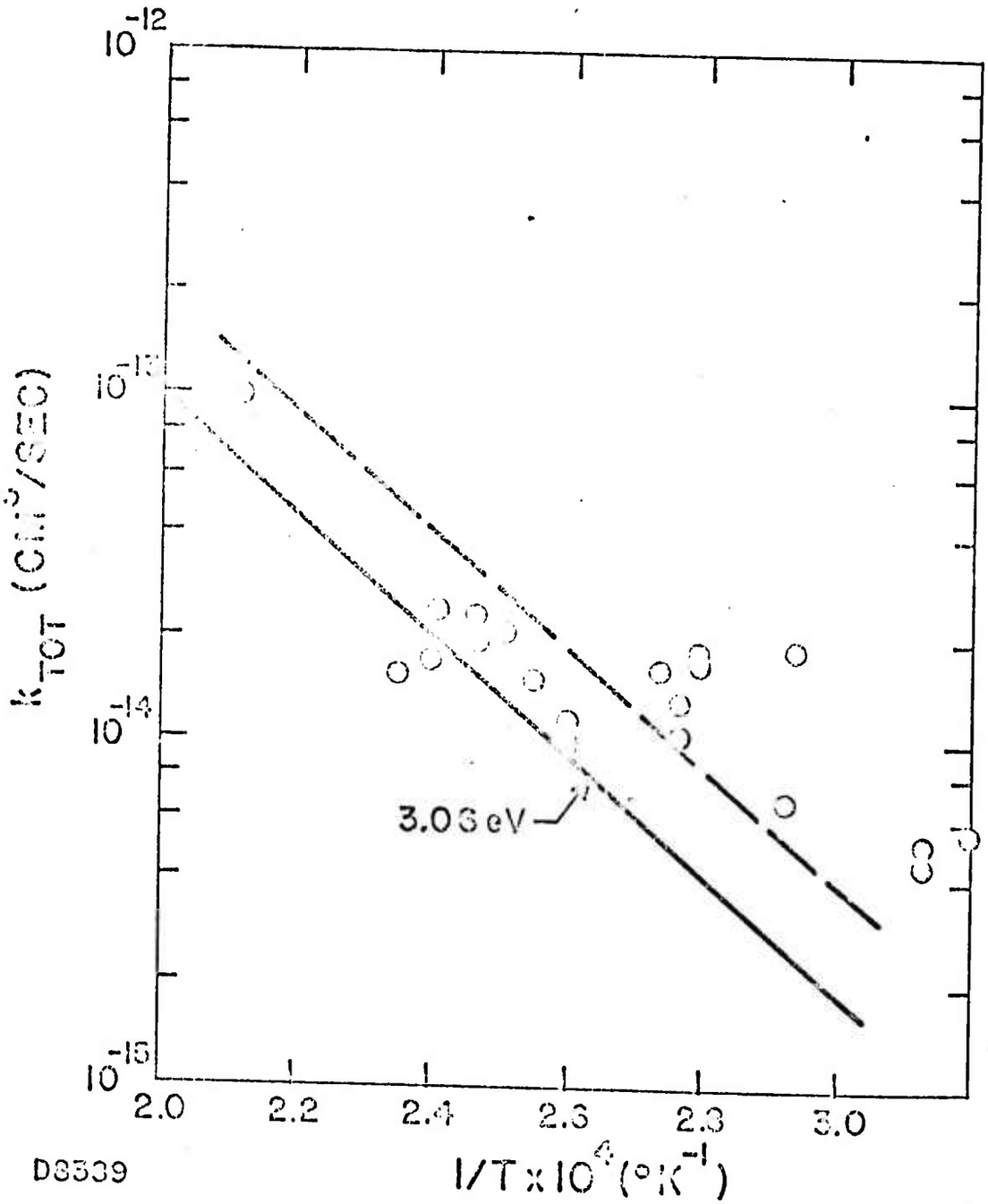
10^{-12}
10^{-13}
10^{-14}
10^{-15}
K_{TOT} (CM.^{3}/SEC)
3.03 eV
2.0
2.2
2.4
2.6
2.8
3.0
$1/T \times 10^4$ (°K^{-1})
D8339

Fig. 9

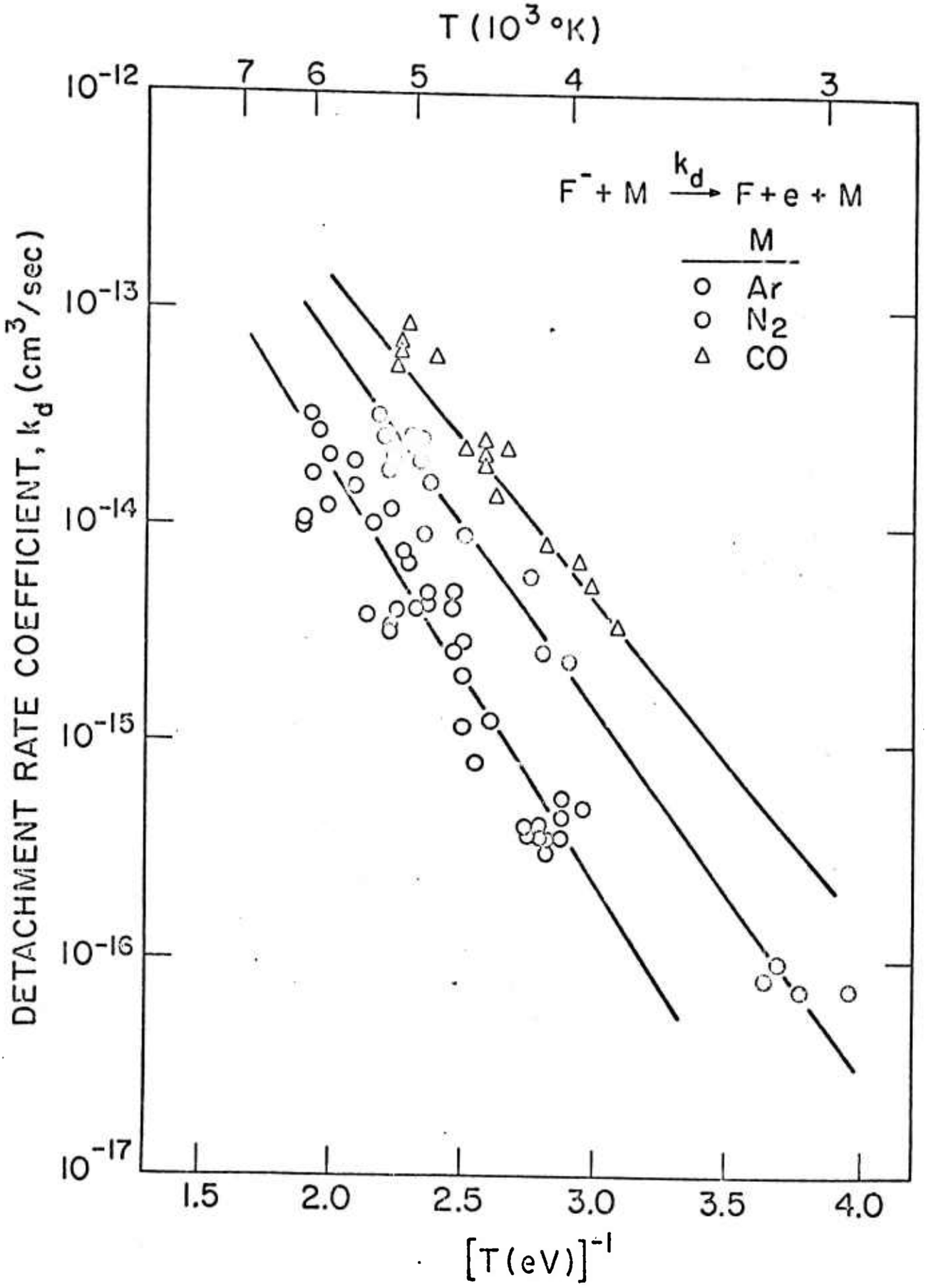
T (10³ °K)
7
6
5
4
3
10⁻¹²
10⁻¹³
10⁻¹⁴
10⁻¹⁵
10⁻¹⁶
10⁻¹⁷
F⁻ + M → F + e + M
k_d
M
Ar
N₂
CO
DETACHMENT RATE COEFFICIENT, k_d (cm³/sec)
1.5
2.0
2.5
3.0
3.5
4.0
[T(eV)]⁻¹

Fig. 10