*

**,   ,   ,

(,   100080)

:   .   , 10^6 K/s

,   . Langmuir

,   ,   .   1200   2200 K

F   ,   .

:   ;   ; Langmuir   ;

: O643. 16, O613. 41   : A

Shock Tube Studies on the Nonequilibrium Electron Affinity Kinetics

of Fluorine Atom at High Temperatures*

Wang Su** ,   Cui Jiping,   Fan Bincheng,   He Yuzhong

(Key Laboratory of High Temperature Gas Dynamics, Institute of Mechanics, Chinese Academy of Sciences, Beijing   100080)

Abstract   To study electron affinity kinetics, a shock tube method was applied, in which the test gas was ionized by a reflected shock wave and subsequently quenched by a strong rarefaction wave. As the quenching speed of 10^6 K/s was reached, a nonequilibrium ionization-recombination process occurred, which was dominated by ion recombination with electrons. A Langmuir electrostatic probe was used to monitor variation in the ion number density at the reflection shock region. The working state of the probe was analyzed, and a correction was introduced for reduction of the probe current due to elastic scattering in the probe sheath. The three-body electron affinity rate coefficient of the fluorine atom over the temperature range 1200 to 2200 K in an ambiance of argon gas was directly determined. The temperature dependence of electron affinity rate coefficient was discussed.

Key words   Electron affinity, Fluorine atom, Langmuir probe, Shock tube

1   Introduction

The fluorine-containing polymer on the hypersonic space vehicle surface will be ablated and pyrolyzed by the shock heating. The fluorine atoms as one of the principal pyrolysis products will recombine with electrons, and the electron density in the plasma sheath around the vehicle will be change as a result.

Thus the ionization degree, Radar scatter section and infrared irradiation properties of the flowfield around the vehicle will be affected. Experimental research on electron affinity at the temperatures above 4000 K was carried out with both shock tube and arc discharge techniques. Mandel et al [1] determined the electron detachment rate coefficient from negative fluorine ions in mixtures of cesium fluoride and argon, shock heated

to 5000 K. They also deduced the electron affinity rate coefficient of fluorine atoms using the detailed balance principle. Their result is still used in engineering calculations. However, research on the vehicle wake at temperature of 1000 to 2000 K is lacking. The difficulty in this temperature range is that the ionization degree is not high enough to meet the observation need in the electron affinity experiments because of the relatively low temperatures.

In this article, the electron affinity rate coefficient of the fluorine atom was directly determined in a shock tube. Considering the lower ionization potential of sodium atom, sodium amide was chosen as the source substance for introducing ions and electrons into the experiments. A shock tube method was developed[2, 3], in which the test gas was heated and ionized by a reflected shock wave and subsequently quenched by a strong rarefaction wave reflected on the end wall of the driver section in the shock tube. As the quenching speed of the strong rarefaction wave reached 10^6 K/s, the temperature in the region of reflection shock wave could decrease from 3000 to 600 K within about 3 ms. A nonequilibrium ionization-recombination state was attained at the later stage of the process, during which the recombination with electrons dominated.

On the basis of the experimental recombination of sodium ions with electrons, fluorine gas was added. In the cooling process of the rarefaction wave, fluorine atoms competed against sodium ions in recombining with electrons, which underlies the present experiments. The decay rates of sodium ions with and without the presence of fluorine atoms were compared. The electron affinity rate coefficient of fluorine atoms was determined through analysis of the different aforementioned decay rates.

2 Experimental

2. 1 Setup

The experiments were carried out in a single pulse shock tube. The driver section has a length of 1. 2 m and the driven section is 1. 8 m in length. Both have circular cross sections with an inner diameter of 44 mm. A 20 L dump tank is connected to the driven section through a branch tube just ahead of the diaphragm, which is utilized for absorbing the reflected shock wave and enhancing the cooling speed. Hydrogen was used as the driver gas. The shock tube was preheated and maintained at 343 K throughout the experiments to avoid the adsorption of any material on the tube wall. A adjustable piston was installed in the driver section in order to determine the optimum reflection time of the rarefaction wave. A spiral coil (70 mm in length and 28 mm in circle distance), of steel wire, 2. 7 mm in diameter, was mounted on the side wall at the rear of the driven section in order to promote production of vortexes. The incident shock speeds were measured by two pressure transducers mounted on the shock tube wall. The conditions behind the reflected shock were calculated from the incident shock speed using the shock relations.

Solid sodium amide was ground into powders under the protection of benzene, which was volatilized in the shock tube and excluded out by evacuation before every experimental run. The driven section was filled with the test gases. Two series of experiments were run using nearly identical experimental conditions, except that the test gas was the pure argon and a mixture of 1. 72% fluorine and 98. 28% argon by volume, respectively. Because the property is between those of ionic and molecular crystals, sodium amide is easily molten, vaporized and decomposed at relatively low temperatures. After the bursting of the diaphragm and under the successive action of the incident and reflected shock waves, grains of sodium amide firstly hiked up from the wall and subsequently underwent solid heating, melting, liquid heating and vaporization processes, afterwards vapor sodium amide molecules were decomposed into Na atoms and NH_2 radicals, finally Na atoms were ionized into sodium ions and electrons. Sodium amide in solid state was first ground into powders, the particle diameters of which were verfied to be less than 20 μ m.

In order to ensure that the whole process, from the hiking of grains from the wall to the ionization, took place within the stationary time of the reflected shock wave (about 1 ms), the characteristic times of

the above physical and chemical processes were estimated. It was concluded that the heat transfer, phase change and decomposition processes could take place within the lifetime of the reflected wave. However, the complete ionization equilibrium could not be achieved, in accordance with the experimental measurements.

The aim of installing a spiral coil was to leave the grains of sodium amide on the tube wall to hike fully up through producing vortexes. The interaction of the reflected wave with vortexes caused the pressure, density, and temperature behind the reflected wave to continue increasing and fluctuate. This was in addition to the abrupt rise in temperature caused by compression from the reflected wave. Correspondingly, enhancement of the probe signal was observed in the experiments.

The shock tube was run at the fixed initial temperature $T_1 = 343$ K and pressure $P_1 = 4.0$ kPa, with a shock Mach number ranging from $M_S = 3.11$ to 3.85. A piezo-electric transducer mounted on the end wall of the driven section was used to monitor the pressure changes during the whole process. The rarefaction wave cooling stage was treated as an adiabatic process. The inert gas Ar was used as diluent in the experiments so that the density and temperature of the test gas could easily be calculated from the pressure by use of the adiabatic relations

$$\frac{\rho}{\rho_{50}} = \left(\frac{P}{P_{50}}\right)^{1/\gamma}, \qquad \frac{T}{T_{50}} = \left(\frac{P}{P_{50}}\right)^{\frac{\gamma-1}{\gamma}} \qquad (1)$$

where $\gamma = 5/3$ is the adiabatic index of argon and the subscript 50 refers to the corresponding initial state just behind the reflected shock wave.

2.2 Langmuir probe

A cylindrical Langmuir electrostatic probe mounted on the end wall of the driven section was used to monitor the variation of sodium ion number density at the reflection shock region. The probe, with a radius $r_P = 0.01$ cm and a length $l_p = 1.3$ cm, was biased negatively at $V_P = -9$ V. The Debye length of the ionized gas in our typical case was approximately $\lambda_D \approx 10^{-3}$ cm, and the mean free path of sodium ion in the ambiance of argon gas was estimated as $\lambda_i \approx 10^{-4}$ cm.

Since $\lambda_D > \lambda_i$, the influence of the collision of the falling ion with neutral atoms in the probe sheath on the probe collecting current must be taken into account. According to the theories given by Schulz & Brown and Jakubowski[4,5], the correction factor for reduction of the probe current due to elastic scattering is expressed as

$$\psi = \begin{cases} \dfrac{3 - 2\exp(-\lambda_D/\lambda_i)}{1 + 2(\lambda_D/\lambda_i)}, & \lambda_D/\lambda_i < 1 \\[3mm] \dfrac{3 - \exp(-\lambda_D/\lambda_i)}{2(1 + \lambda_D/\lambda_i)}, & \lambda_D/\lambda_i \geq 1 \end{cases} \qquad (2)$$

$$\lambda_D = \left(\frac{kT}{4\pi e^2 N_{Na^+}}\right)^{1/2}, \quad \lambda_i = (N_{Ar}\sigma_c)^{-1} \qquad (3)$$

where ψ is the correction factor, λ_D/λ_i is the average collision number in the sheath, N_{Na^+} and N_{Ar} are the number density of sodium ions and argon atoms, respectively. As $r_P/\lambda_D \approx 10$ in the present experiments, only the collisions that lead to large deflection angles should be considered. The so-called close collision cross-section for the elastic scattering between sodium ion and ambient argon atoms σ_c, which leads to deflection angles greater than $\pi/2$, was obtained as the effective collision cross-section through integrating over the collision trajectory[6].

The cold boundary layer of the probe may grow unsteadily as a result of interaction of the probe with a sequence of vortices whose length scale is of the order of r_P. Using Lin's boundary layer theory of oscillating flow[7], the maximum thickness of the boundary layer growing unsteadily was estimated as $\delta_{max} \approx 10^{-4}$ cm. For $\delta_{max} << \lambda_D$, the effect of the cold boundary layer is negligible.

3 Results

By analyzing the thermochemical equilibration dissociating into atoms of fluorine molecule, it was found known that the full dissociation (i.e. the degree of dissociation greater than 95%) is assured when the temperature behind the reflected shock wave is higher than 1200 K. With the aforementioned experimental conditions, the characteristic time of dissociation reaction of the fluorine molecule is approximately 10 μs, which is much smaller than the stationary time of

the reflected shock wave (i. e. about 1 ms). Therefore, the full dissociation of fluorine molecule is also kinetically assured, and the recombination of fluorine atom with electrons will occur in the cooling process of the rarefaction wave.

On the basis of the experiment recombining sodium ions with electrons[6], the result of which was found to be k_{i2} ($\text{Na}^+ + e + \text{Ar} \rightarrow \text{Na} + \text{Ar}$) = 3. 43 × $10^{-14} T^{-3.77}$ cm^6/s, fluorine gas was added into the test gas. In the cooling process of the rarefaction wave, fluorine atoms compete against sodium ions for recombining with electrons. The kinetic equation for the electron affinity of fluorine atom in the cooling process is derived, thus the variation of the number density of negative fluorine ions is expressed as:

$$N_{F^-} = \frac{1}{k_{i2} N_{Ar}} \left[\frac{d \ln N_{Na^+}^-}{dt} - \frac{d \ln N_{Na^+}^+}{dt} + k_{i2} (N_{Na^+}^- - N_{Na^+}^+) N_{Ar} \right] \quad (4)$$

where k_{i2} is the recombination rate coefficient of sodium ion with electrons, and the superscripts - and + refer to the test gas with and without the fluorine gas, respectively. Because k_{i2} has been determined, and $N_{Na^+}^-$, $N_{Na^+}^+$ and N_{Ar} are the quantities measured in the present experiments, N_{F^-} can be determined according to Eq. (4).

Using the kinetic equation of the electron affinity process, the affinity rate coefficient of fluorine atom is derived as

$$k_r = k_{i2} \frac{\dfrac{dN_{F^-}}{dt} - N_{F^-} \dfrac{d \ln}{dt}}{(N_F^0 - N_{F^-}) \left(\dfrac{d \ln}{dt} - \dfrac{d \ln N_{Na^+}^-}{dt} \right)} \quad (5)$$

where N_F^0 is the initial number density of fluorine atom in the reflected shock region. Because the number density of negative fluorine ion is far below the equilibrium value, the collision detachment process of negative fluorine ions is negligible in the kinetic equation.

After correcting for reduction of the probe current due to elastic scattering at the probe sheath, the variation of sodium ion number density with temperature in the presence of fluorine is obtained, as

shown in Fig 1a. The variation of sodium ion number density without fluorine is shown in Fig 1b. The
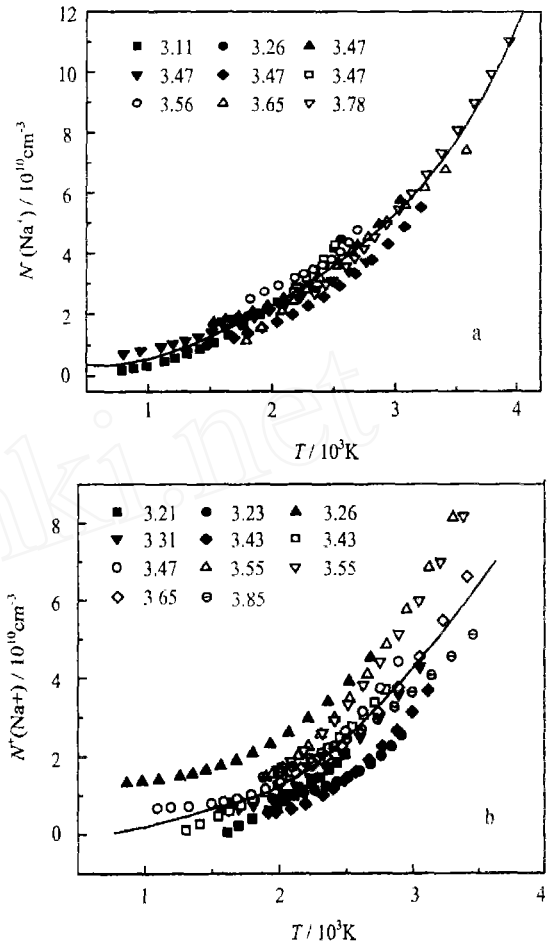

Fig 1   Variation of the number density of the sodium ion with
temperature, the different symbols correspond to different
Mach numbers

a   in the presence of fluorine atom,

b   without fluorine atom.

different symbols on the graph correspond to different Mach numbers. Using the piezo-electric transducer to monitor the pressure changes of the whole process, the variation of d ln /dt with temperature in the cooling process is derived according to the adiabatic relations. The plot of $\lg \left(\dfrac{d \ln}{dt} \right)$ versus $\lg T$ exhibits a liner property, as shown in Fig 2. Using least square analysis of all the data points in Fig 2 and the adiabatic relations, we obtain $\dfrac{dT}{dt}$ = - (1. 62 ± 0. 42) × $10^6 T^{-0.068}$ K/s. The exponent of temperature
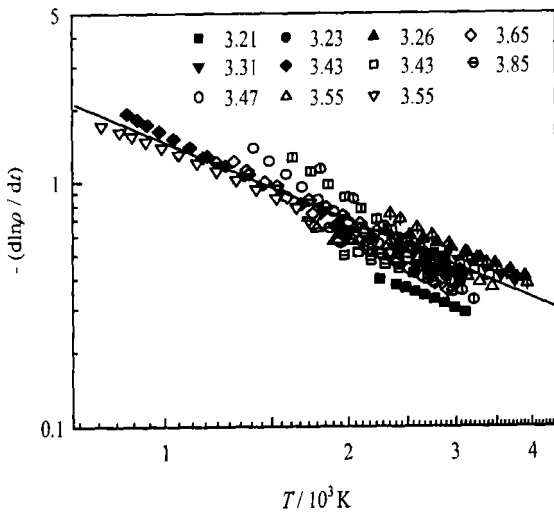
Fig 2   Variation of lg($-\dfrac{d\ln\rho}{dt}$) with lg$T$

indicates that $\dfrac{dT}{dt}$ is nearly independent of temperature and constant in the cooling process of the present experiments. Using this relation, the derivative with respect to temperature can be transformed into the derivative with respect to time.

Substituting the fitting results of $N_{Na^+}^-$, $N_{Na^+}^+$, N_{Ar} and $\dfrac{d\ln}{dt}$ into equations （4） and （5）, the electron affinity rate coefficient of the fluorine atom is determined directly for cases where argon atoms act as the third body in the collision process and the temperature range is 1200 to 2200 K in the form

$$k_r = 1.29 \times 10^{-12} T^{-6.36} \ cm^6/s,$$
$$1200 < T < 2200 \ K \qquad (6)$$
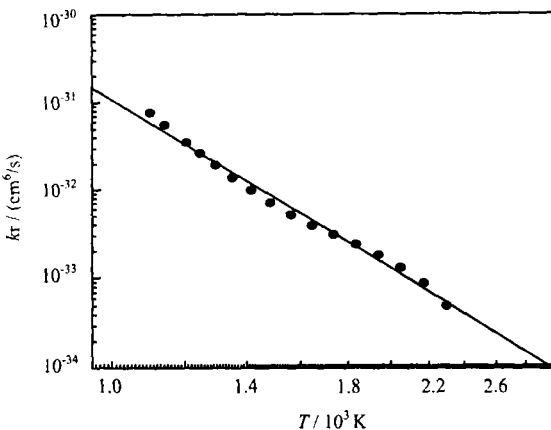
as shown in Fig 3.

Fig 3   Variation of the electron affinity rate coefficient of
fluorine atom with temperature

4   Discussion

In order to compare the present result with those of Mandel *et al*, the three-body electron affinity rate coefficient of fluorine atom is deduced from the electron detachment rate coefficient of negative fluorine ion given by Mandel *et al*, at 5000 K by using the detailed balance principle $k_r = k_f/K_c$. The equilibrium constant K_c is obtained by fitting the data of Ref [8] over the temperature range of 4000 to 6000 K. Finally, we get

$$k_r(F + e + Ar \quad F^- + Ar)$$
$$= 4.22 \times 10^{-29} T^{1.24} \ cm^6/s,$$
$$4000 < T < 6000 \ K \qquad (7)$$

The temperature dependence of the affinity rate coefficient of the present work is at odds with Mandel s result for Eq （7）. We belive this discrepancy originates, in part, in the indirect determination of Eq （7） from the electron detachment coefficient by using the detailed balance principle. As the temperature dependence of the rate coefficient of endothermic electron detachment is due mainly to the exponential factor of activation, it is difficult to observe and analyze accurately the temperature dependence of the pre-exponential factor experimentally. However the temperature dependence of the pre-exponential factor contributes greatly to deriving the temperature dependence of the affinity coefficient by using the detailed balance principle. In addition, the temperature dependence of the affinity coefficient in direct determination is expressed in terms of power function and is more sensitive to change of temperature, so direct determination would yield a more reliable result. On the other hand, the detailed balance principle can be applied only when the internal states of the reactant species are populated according to the so-called quasi-steady-state distribution. Unfortunetly, for the most cases, the quasi-steady-state condition does not exist behind a shock wave[9].

In summary, applying a shock tube method in combination with the electrostatic probe technique, employing argon atoms as the third body in the collision process, the three-body electron affinity rate coefficient

of fluorine atom is directly determined over the temperature range of 1200 to 2200 K: $k_r = 1.29 \times 10^{-12} T^{-6.36}$ cm^6/s. The correction for reduction of the probe current due to elastic scattering at the probe sheath is introduced. This present experimental temperature range is important for the engineering application and is the extension, at low temperatures, of the experiment conducted by Mandel *et al*

References

[1] Mandel A, Kivel B, Evans E W. *J. Chem. Phys*, 1970, **53**: 2363

[2] Cui J P, Fan B C, He Y Z, Wan S X. *Chin J. Chem. Phys*, 1999, **12**: 13

[3] Cui J P, He Y Z, Wang S, Fan B C, Wang J. *Chin J. Chem. Phys*, 2002, **15**: 337

[4] Schulz G J, Brown S C. *Phys Rev*, 1955, **98**: 1964

[5] Jakubowski A K. *AIAA J.*, 1972, **8**: 988

[6] Wang S, Cui J P, He Y Z, Fan B C, Wang J. *Chin Phys Lett*, 2001, **18**: 289

[7] Lin C C. Proc. 9th Intern. Congress Appl Mech., Brussels, 1957. Vol 4, 155

[8] Glushko V P. Thermodynamic Properties of Identical Matters, Vol 2, Part 2, Science, in Russian, 1978.

[9] Park C. AIAA-Paper, 1989, 89 - 1740