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DIFFUSION COEFFICIENTS OF ATOMIC HALOGEN

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Diffusion coefficients of atomic halogen with noble gases were calculated from the potential curves reported in the literature from the crossed-molecular-beam scattering experiments. The deviations of the diffusion constants between the atomic halogen-noble gas systems and the neighboring noble gas-noble gas systems were obtained over the temperature range of 200 K to 1100 K . The parameters of Lennard-Jones 6-12 potentials were also obtained for the chlorine and iodine atoms . The internal consistency of the diffusion constants calculated from the 6-12 potential parameters among the halogen atom-noble gas systems is very good . However, the agreement was found to be only fair for the inert molecular systems with the chlorine atoms . The extent of the similarity of the diffusion constants between the atomic halogen-noble gas and the noble gas-noble gas systems is discussed.

INTRODUCTION

In the past decade, the noble gas-halide systems, RgX (Rg: Ar, Kr, Xe; X: F, Cl, Br, I), have generated much research interest because of their applications as active media for ultraviolet lasers.[1] Laser action has been achieved from the relevant electronic transition which originates from excited ion-pair states and terminates on a unbound or weakly bound lower state correlated with atoms in their ground states.[2] The observed emission wavelength is in the near or vacuum ultraviolet, a region of great importance for many photochemical and photophysical applications. The lasing excited states are rather well described by an ionic model[3] and the effect of the spin-orbital interaction has been elucidated in detail in *ab initio* molecular calculations.[4,5] In the molecular-beam- scattering experiments,[6-10] much attention has been given to the lower electronic configurations ($^2P_{3/2,1/2}$ + $^1S_0$) in obtaining the interaction potentials .

For a thorough understanding of the laser action coming from these noble gas-halide molecular systems, a good knowledge of the transport properties of the halogen atoms is important. These transport properties are also of importance for many applications such as combustion,[11] plasma physics,[12] gaseous discharges,[13] etc. Through the first-order approximation of Chapman & Enskog's gas-kinetic theory,[14] one can calculate accurately the diffusion coefficients from the potential curves.

Recently, we reported a novel method to measure the diffusion coefficients of Br- noble gas,[15] Cl-noble gas,[16] and Cl-inert gas systems[17] through the radiative recombination process of the reactive atomic halogen. In those reports, some conclusions of the general properties of the diffusion coefficients of Cl and Br atoms were drawn. The diffusion constants of the Br-noble gas systems calculated from the interaction curves were shown to be consistent with our experimental results.

To complete the study of these atomic halogen-noble gas systems, in this paper we extend the calculations to other atomic halogen-noble gas systems. The parameters of Lennard-Jones 6-12 potentials of chlorine and iodine atoms have also been obtaind about ambient temperature. The internal consistency of the diffusion constants calculated from the Lennard-Jones parameters among the atomic

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+ Dedicated to Professor Wei-chuwn Lin on the occasion of his retirement from National Taiwan University.

halogen-noble gas systems is described. We also discuss the similarity of the diffusion constants between the atomic halogen- noble gas systems and the neighboring noble gas-noble gas systems over the temperature range 200 K-1100 K.

CALCULATION PROCEDURE AND RESULTS

In the first-order approximation of Chapman and Enskog's theory, the diffusion coefficient of a binary mixture can be expressed as[14]

$$D_{12} = 0.002628\,\frac{\left[T^3\cdot(M_1+M_2)/(2\cdot M_1\cdot M_2)\right]^{1/2}}{P\cdot\sigma_{12}^2\cdot\Omega_{12}^{(1,1)*}(T^*)}, \qquad (1)$$

in which the symbols denote T: temperature (K); P: pressure (atm); T* : $k\cdot T/\varepsilon_{12}$; ε_{12}/k and σ_{12}: well depth (K) and equilibrium distance (Å) of potential curve; and M_1, M_2: molecular masses (amu) of species 1 and 2.

The reduced collision integrals $\Omega^{(1,1)*}$ (T*) were calculated numerically from the collision cross sections $S^{(1)}$ (E):

$$\Omega_{12}^{(1,1)*}(T^*) = (2\pi\mu/\kappa)^{1/2}\,\Omega_{12}^{(1,1)}(T)/\pi\sigma_{12}^2\,, \qquad (2)$$

$$\Omega_{12}^{(1,1)}(T) = (\kappa T/2\pi\mu)^{1/2}\int \exp(-x^2)\,x^5 S^{(1)}(\kappa T x)\,dx\,, \qquad (3)$$

where μ is the reduced mass of M_1 and M_2 and k is the Boltzmann constant. The classical collision cross section, being a function of E (the initial kinetic energy), was expressed as

$$S^{(1)}(E) = 2\pi\int_0^\infty b(1-\cos^1\chi)\,db\,, \qquad (4)$$

where b is the impact parameter and χ is the classical angle of deflection of the relative velocity vector. The deflection angle can be calculated according to

$$\chi = \pi - 2b\int_{r_m}^\infty \frac{dr/r^2}{F(r)}\,, \qquad (5)$$

where r_m, the classical turning point, is the outermost zero of

$$F(r) = (1-\varphi(r)/E - b^2/r^2)^{1/2}\,, \qquad (6)$$

and $\varphi(r)$ is the interaction potential. The general numerical procedure for the above integrations is found in Ref. 18. The higher-order corrections of the gas-kinetic theory, which in most situations would contribute much less than the experimental error, were neglected in the present calculations.

Similarly for the crossed-molecular beam experiments, there are four interaction potential forms adopted here: Morse-Morse-switch function-van der Waals[6,7,9,10] (MMSV), Morse-Morse-Hermite spline-van der Waals[8] (MMHV), exponential- spline-Morse-spline-van der Waals[19] (ESMSV), and Morse-spline-van der Waals[20] (MSV).

It is well known that dissociation of halogen molecules X_2 produces both X ($^2P_{1/2}$) and X ($^2P_{3/2}$) states. Using Hund's case c notation, the X ($^2P_{3/2}$) + Rg ($^1S_0$) fourfold degenerate asymptote splits into two doubly degenerate states at smaller internuclear distances: the $X_{1/2}$ (or $I_{1/2}$) and $I_{3/2}$. The asymptote for the doubly degenerate spinorbital excited X ($^2P_{1/2}$) + Rg ($^1S_0$) gives rise to the $II_{1/2}$ state.

Assuming that $II_{1/2}$ and $I_{3/2}$ have the same interaction potential forms, a condition also assumed in the molecular beam experiments,[6-10] one can calculate the diffusion coefficients of RgX by properly taking into account the individual statistical weight of each potential

$$\frac{1}{D_{RgX}} = \frac{0.5(1-\alpha)}{D_{X_{1/2}}} + \frac{0.5(1-\alpha)}{D_{I_{3/2}}} + \frac{\alpha}{D_{II_{1/2}}} \qquad (7)$$

where $D_{I_{3/2}}$ and $D_{II_{1/2}}$ are approximately the same; the population $\alpha = \exp(-\nabla\varepsilon/kT)/(1+\exp(-\nabla\varepsilon/kT))$; $\nabla\varepsilon$ is the energy gap between X ($^2P_{1/2}$) and X ($^2P_{3/2}$). The results of the diffusion coefficients of the atomic halogen-noble gas systems over the temperature of 200-1100 K are shown in Figs. 1-3. Their numerical values are listed in Appendixes

A, B, and C.

The diffusion coefficients of the noble gas-noble gas systems have been well reported in the literature.[21-29] To test the program procedure and to compare with the halogen atom-noble gas systems, these diffusion coefficients were also calculated from the available interaction potentials and shown in Figs. 4-6. The agreement between the calculated values and the experimental results is excellent. This agreement also supports the accuracy of the interaction potentials.

According to Eq. (1), the uncertainties for the calculated diffusion coefficients originate mainly from the uncertainties of ε_{12} and σ_{12}. According to their reported uncertainties, the maximum uncertainties for the present results are estimated to be ±55% for F-Ne,[6] ± 43% for F-(Ar, Kr),[6] ± 35% for F-Xe,[7] ± 21% for Cl-Xe,[8] ± 25.5 % for Br-(Ar, Kr),[9] ± 18 % for Br-Xe,[9] and ± 30% for I-(Kr, Xe).[10] Because of the difficulties in carrying out the scattering experiments of reactive species, the interaction potentials of the atomic halogen-noble gas systems have consistently much greater uncertainties than those of the noble gas-noble gas systems.

DISCUSSION

With the Lennard-Jones 6-12 model and the combination laws $\sigma^{LJ}_{12} = 1/2 (\sigma^{LJ}_1 + \sigma^{LJ}_2)$ and $\varepsilon^{LJ}_{12} = (\varepsilon^{LJ}_1 \varepsilon^{LJ}_2)^{1/2}$, $\sigma^{LJ}(\mathrm{Br}) = 3.616$ Å and $\varepsilon^{LJ}(\mathrm{Br})/k = 150$ K have been reported previously for the Br-noble gas systems.[15] The results of the theoretical calculation (MMSV and 6-12 models) are in agreement with the experimental values.[15]

In the halogen group, the iodine atom has a comparatively larger atomic size and yet has a weaker ionic character than the bromine atom. One obtains $\sigma^{LJ}(\mathrm{I}) = 3.9$ Å and $\varepsilon^{LJ}(\mathrm{I})/k = 215.0$ K by fitting the diffusion coefficients of

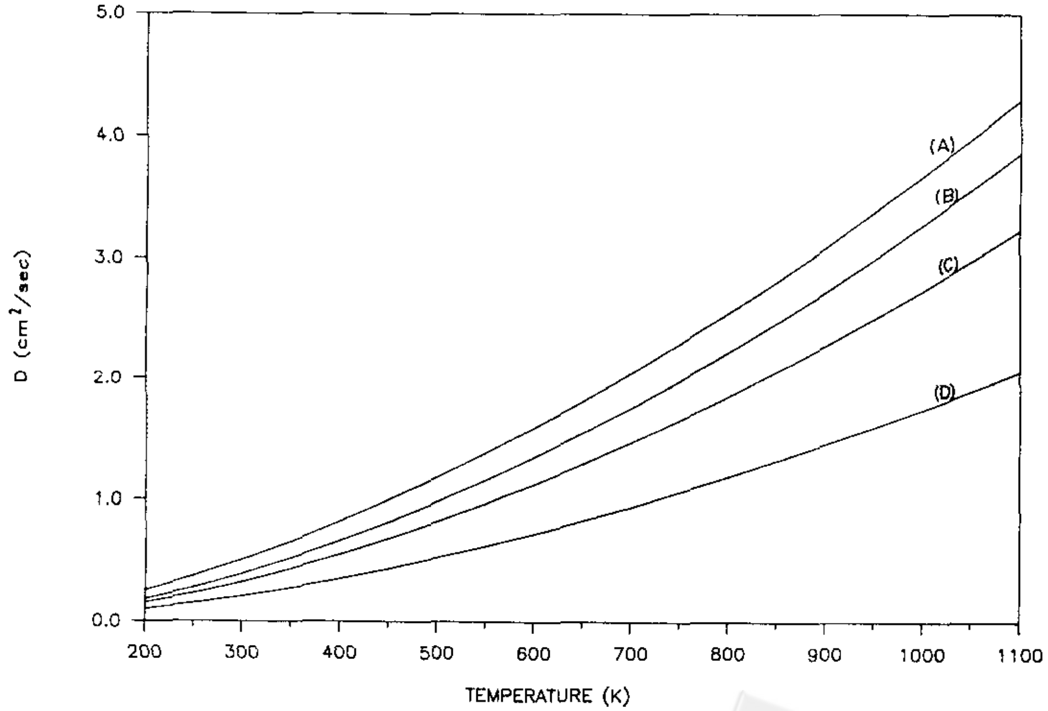

Fig. 1. Diffusion coefficients of F-noble gases as a function of temperature calculated from the potential curves determined by the crossed-molecular-beam experiments. Curve A: Ne; curve B: Ar; curve C: Kr; curve D: Xe.

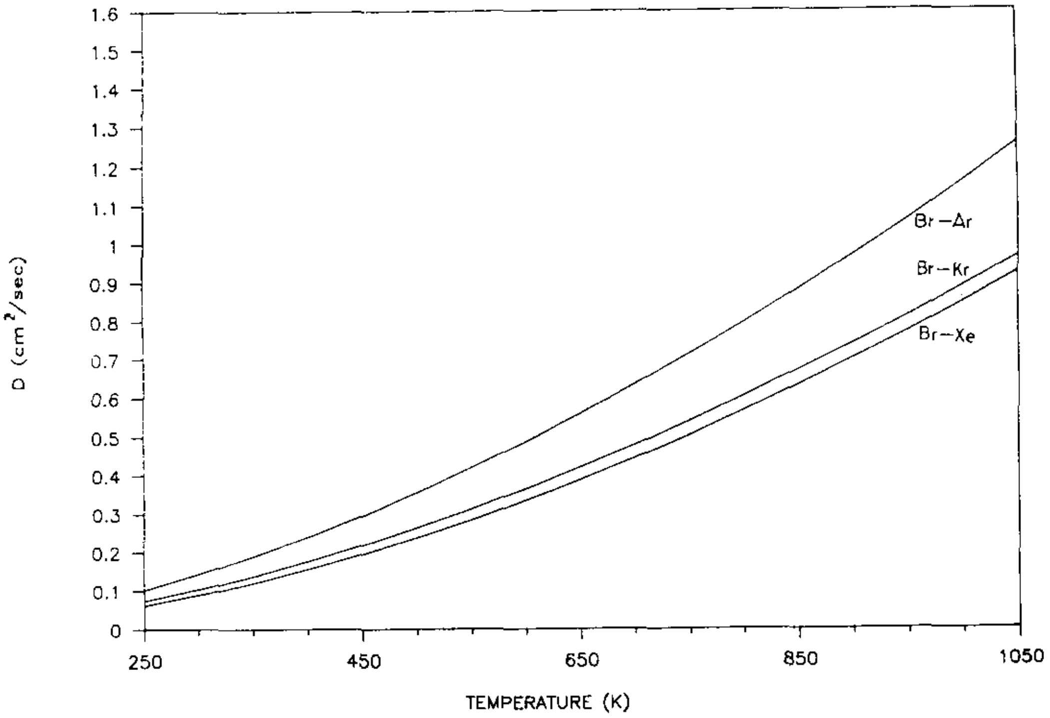

Fig. 2. Diffusion coefficients of Br-Xe, Br-Kr, Br-Xe as a function of temperature (adapted from Ref. 15).

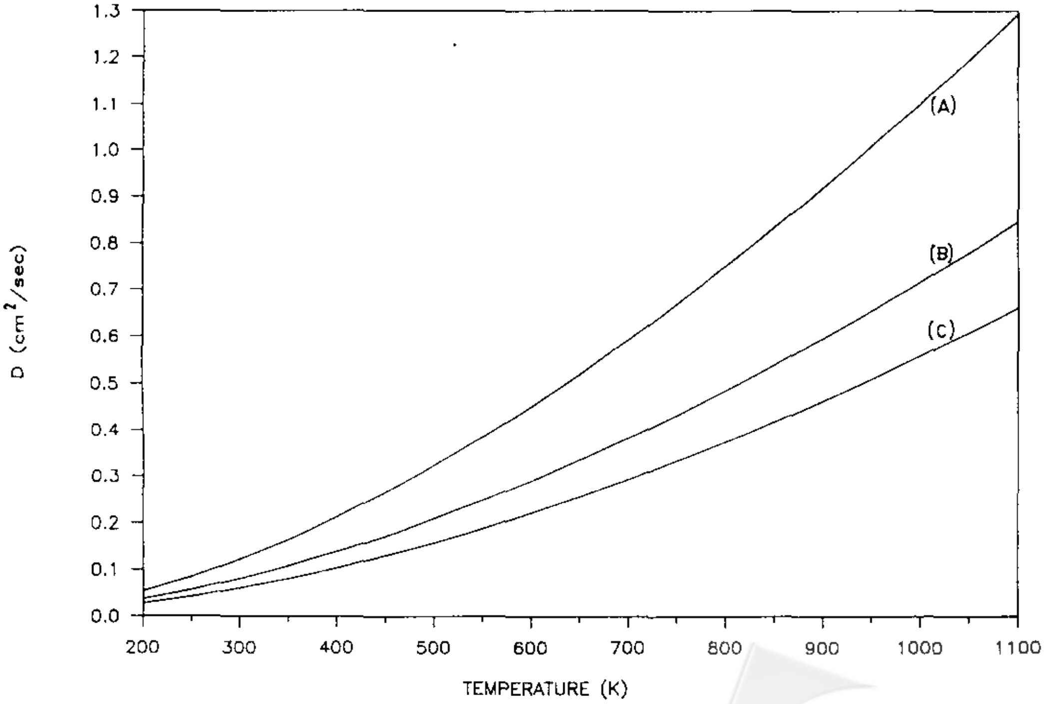

Fig. 3. Diffusion coefficients of Cl-Xe, I-Kr, I-Xe as a function of temperature calculated from the potential curves determined by the crossed-molecular-beam experiments. Curve A: Cl-Xe; curve B: I-Kr; curve C: I-Xe.

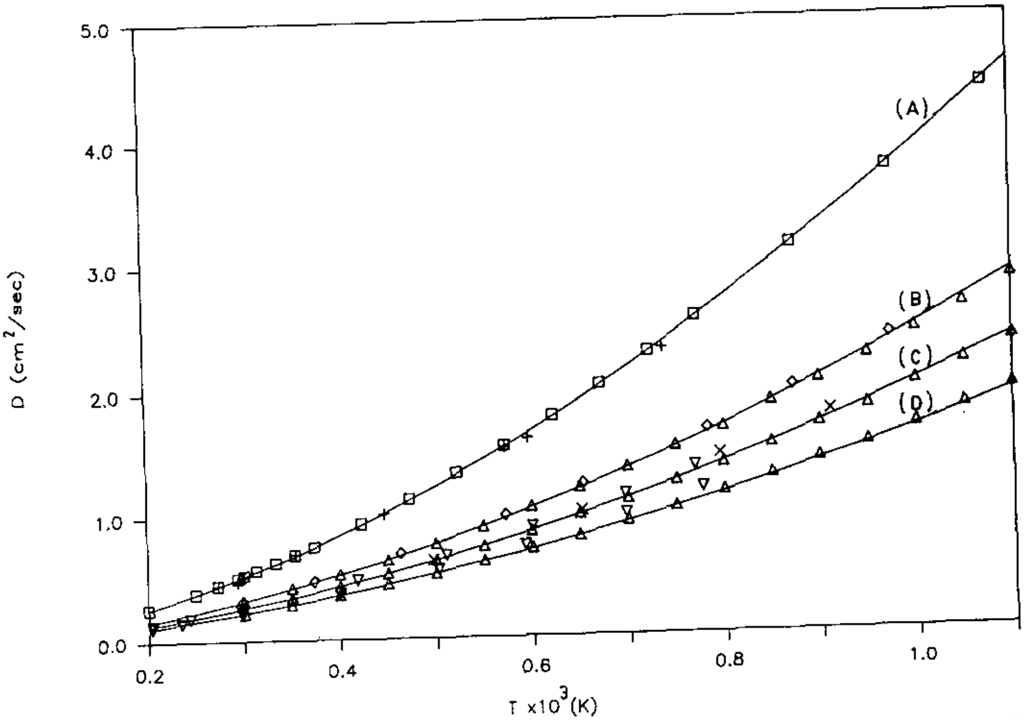

Fig. 4. Diffusion coefficients of Ne-noble gases as a function of temperature calculated from the potential curves determined by the crossed-molecular-beam experiments. Curve A: Ne; curve B: Ar; curve C: Kr; curve D: Xe. +: Ref. 21; □ : Ref. 22; x: Ref. 23; ◇: Ref. 24; Δ: Ref. 25; ∇: Ref. 26.

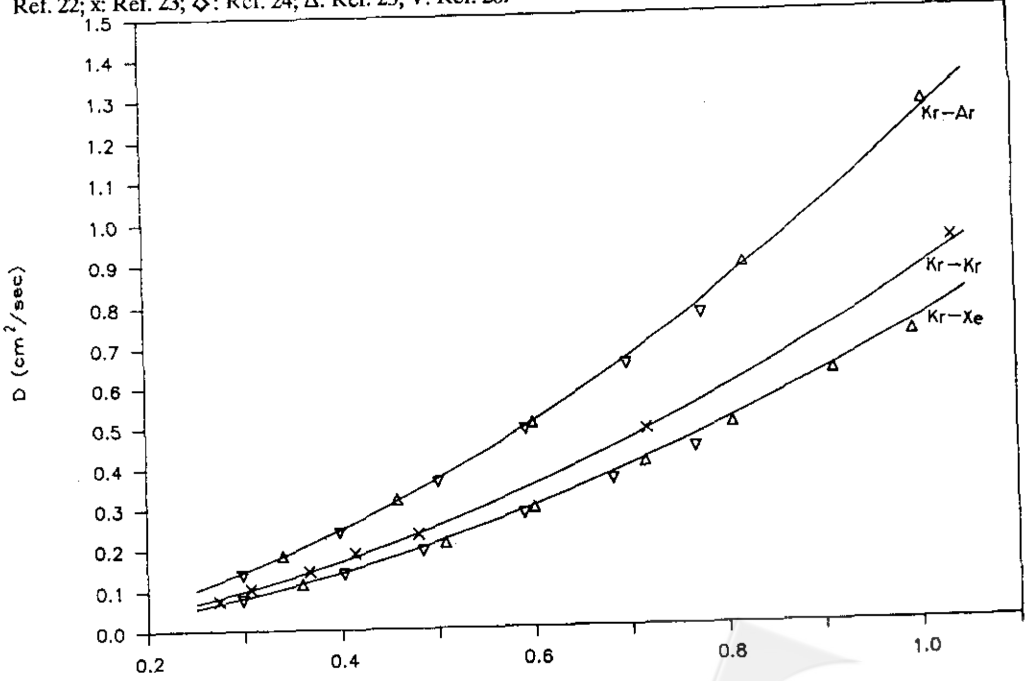

Fig. 5. Diffusion coefficients of Kr-noble gases as a function of temperature (adapted from Ref. 15). Δ : Ref. 23; ∇: Refs. 26,27; x: Ref. 28.

I-Kr around room temperature. By the same process one obtains $\sigma^{LJ}(I(^2P_{1/2})) = 3.95$ Å and $\varepsilon^{LJ}(I(^2P_{1/2}))/k = 205.0$ K. The Lennard-Jones parameters of the gases listed in the tables are adopted from Ref. 14. The diffusion coefficients of I and $I(^2P_{1/2})$ in various gases calculated from these parameters are listed in Table I. Comparing with the MMSV model of the I-Xe systems, the internal consistency is very good. There have been several measurements of the diffusion coefficients of the first excited state of the iodine atom, I ($^2P_{1/2}$), by Abrahamson *et al.*[31] Their results are listed in Table I. The experimental values of $I(^2P_{1/2})$-noble gases are generally much larger than our calculated values. For comparison, the diffusion constants of Xe - inert gases were also calculated and are shown in Table I. It has been generally accepted that the interaction potentials of the atomic halogen-noble gases and the neighboring noble gas - noble gases resemble each other. The transport properties of these two systems should also be similar to each other. In this report we take the accuracy of the measured diffusion constants of I ($^2P_{1/2}$) with some reservation. Apparently more experiments are needed for the clarification of these systems.

For the Cl-noble gas systems, only the interaction potentials of Cl-Xe have been determined by the crossed-molecular-beam experiments. Because Cl-Xe has 5.8 % fractional ionic character[33] according to the theoretical calculation, a property which could invalidate the combination laws, we decided not to use the diffusion constants of Cl- Xe to determine the parameters of Lennard-Jones 6-12 model of chlorine atom. Instead, the previous experimental diffusion coefficients of the Cl-Ne and Cl-Ar systems[16] were used and $\sigma^{LJ}(Cl) = 3.548$ Å and $\varepsilon^{LJ}(Cl) = 75$ K were obtained. Using these parameters, one can predict the diffusion coefficients of Cl-various gases. They are shown in table II. The agreement is quite good between our previous experimental results[16] and the predicted data.

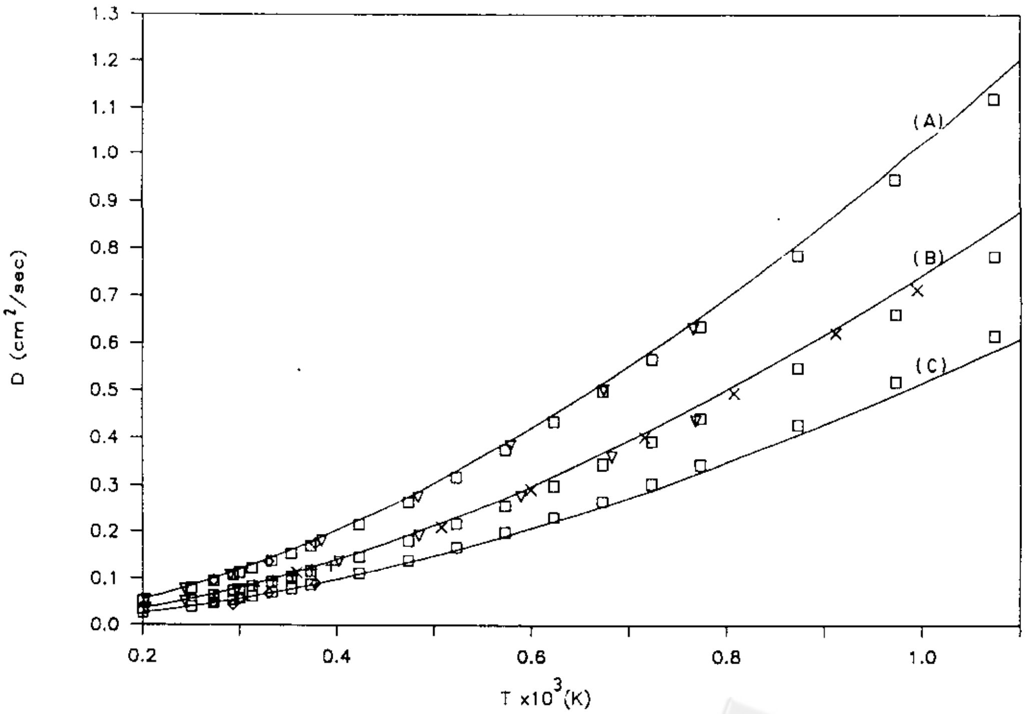

Fig. 6. Diffusion coefficients of Ar-Xe, Xe-Kr, Xe-Xe as a function of temperature calculated from the potential curves determined by the crossed-molecular-beam experiments. Curve A: Ar-Xe; curve B: Xe-Kr; curve C: Xe-Xe. □ : Ref. 22; x: Ref. 23; ∇: Ref. 27; + : Ref. 29; ◊ : Ref. 30.

Table I Diffusion coefficients of iodine atoms in various gases
Temperature: 300 K; Pressure: 1 atm

Media [M]	Calculated diffusion coefficients of I in M (cm^2/sec) MMSV model[a]	6–12 model[b,c]	Experimental diffusion coefficients of I in M (cm^2/sec) Other works	Diffusion coefficients of Xe in M (cm^2/sec) 6–12 model
He		0.58	$0.95 \pm 0.09_0$[d]	0.55
Ne		0.23	$0.40 \pm 0.03_5$[d]	0.21
Ar		0.12	$0.36 \pm 0.06_7$[d]	0.11
Kr	0.080	0.080	$0.11 \pm 0.02_7$[d]	0.075
Xe	0.060	0.061	0.25[e]	0.057
N_2		0.13		0.13
CO_2		0.090		0.085
CF_4		0.063		0.060
SF_6		0.043		0.041
I_2		0.035		0.032

[a] Potential curves determined by Lee and coworkers, Ref. 10.

[b] The parameters of the Lennard-Jones 6–12 potential of I were determined from the diffusion coefficients of I-Kr calculated from the MMSV model: $\sigma^{LJ}(I) = 3.9$ Å, $\epsilon^{LJ}(I)/\kappa = 215.0$ K. See text for the details.

[c] The diffusion coefficients of $I(^2P_{1/2})$ are the same with those of I in the same media.

[d] Diffusion coefficients of $I(^2P_{1/2})$ measured by Abrahamson, Andrews, Husain, and Wiesenfeld, Ref. 31.

[e] *Adapted from Ref. 32.*

Table II Diffusion coefficients of chlorine atoms in various gases
Temperature: 300 K; Pressure : 1 atm

Media [M]	Calculated diffusion coefficients of Cl in M (cm^2/sec) MMHV model[a]	6–12 model[b]	Experimental diffusion coefficients of Cl in M (cm^2/sec) Our works[c]	Other works
He		0.725	0.75± 0.12	0.43± 0.01[d]
Ne		0.321	0.32± 0.05	
Ar		0.191	0.19± 0.03	0.26± 0.05[e](295 K)
Kr		0.148	0.14± 0.02	
Xe	0.121	0.120	0.12± 0.02	
N_2		0.202	0.230± 0.035	
CO_2		0.150	0.190± 0.029	
CF_4		0.114	0.132± 0.020	
SF_6		0.0855	0.098± 0.015	
Cl_2		0.119	0.149± 0.025	

[a] Potential curves determined by Lee and coworkers, Ref. 8.

[b] The parameters of the Lennard-Jones 6–12 potential of Cl were determined from the diffusion coefficients of Cl-Ne and Cl-Ar obtained by our previous works: $\sigma^{LJ}(Cl) = 3.548$ Å, $\epsilon^{LJ}(Cl) = 3.548$ Å, $\epsilon^{LJ}(Cl)/\kappa = 75$ K.

[c] Our previous works, Refs. 16, 17.

[d] Measurement of Andre, Jezequel, Clark, and Husain, Ref. 34.

[e] Measurement of Judeikis and Wun, Ref. 35.

For a comparison of the diffusion coefficients of the atomic halogen-noble gas systems and the neighboring noble gas-noble gas systems, the percentage deviations of the diffusion coefficients between these two gas systems were calculated as a function of temperature and are shown in Figs. 7-9. The extent of the deviations is a reflection of the degree of the similarity of the interaction potentials between these two gas systems.

Fig. 7 shows the F-noble gas cases. Comparing the potential curves of F-Ar ($I_{3/2}$) versus Ne-Ar and F-Kr ($I_{3/2}$) versus Ne-Kr, one finds that the parameters (ϵ,σ) are similar but the parameter β which determines the slope of the repulsive wall is different. For this reason, the deviation values of lines B and C of Fig. 7 are quite large, especially at high temperature. For the F - Ne case, as the radius of Ne

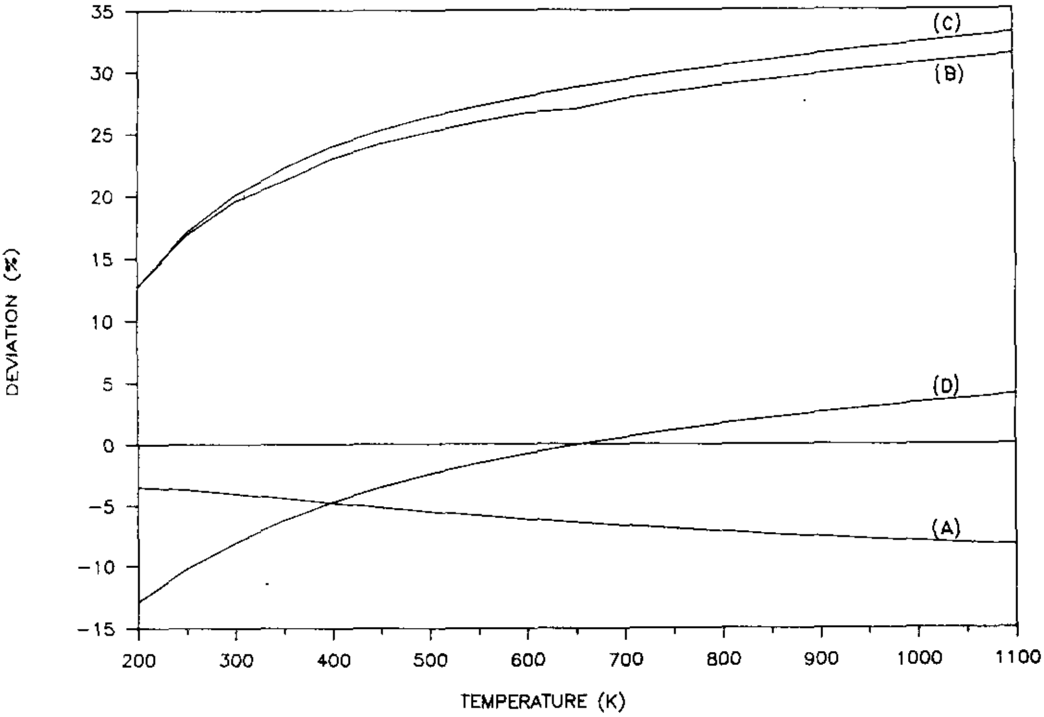

Fig. 7. Percentage deviations of the diffusion coefficients between F-noble gases and Ne-noble gases as a function of temperature : (D(F-M)-D(Ne-M))x100/D(Ne-M). The F mass has been adjusted to the mass of Ne for comparison. Curve A: Ne; curve B: Ar; curve C: Kr; curve D: Xe.

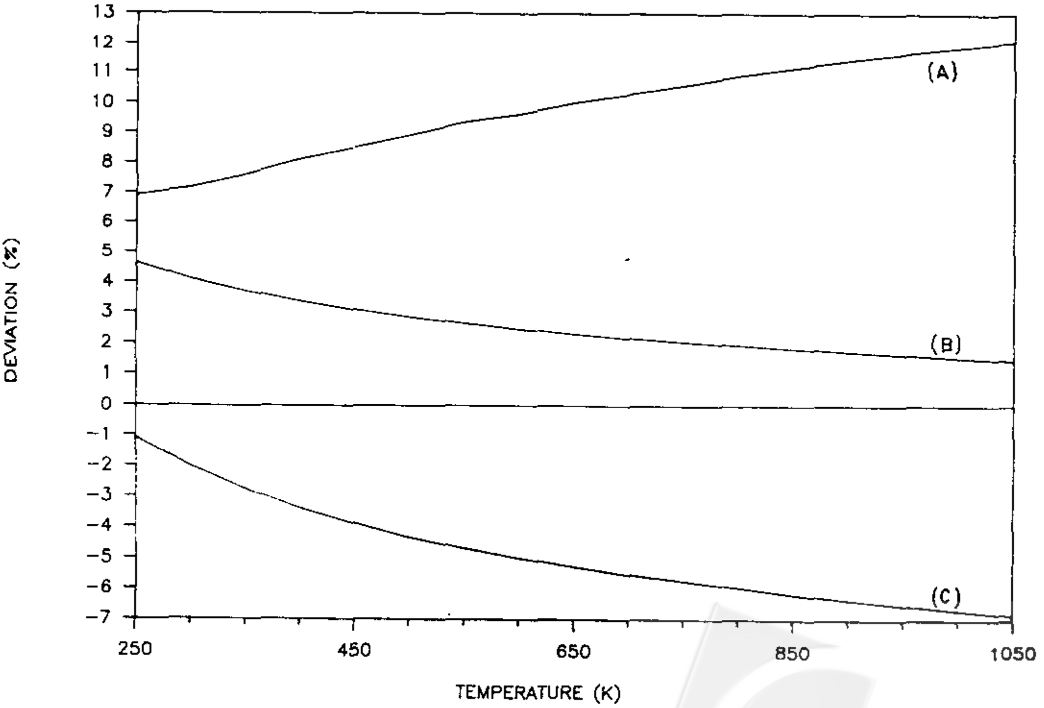

Fig. 8. Percentage deviations of the diffusion coefficients between Br-noble gases and Kr-noble gases as a function of temperature (adapted from Ref. 15). Curve A: Xe; curve B: Kr; curve C: Ar.

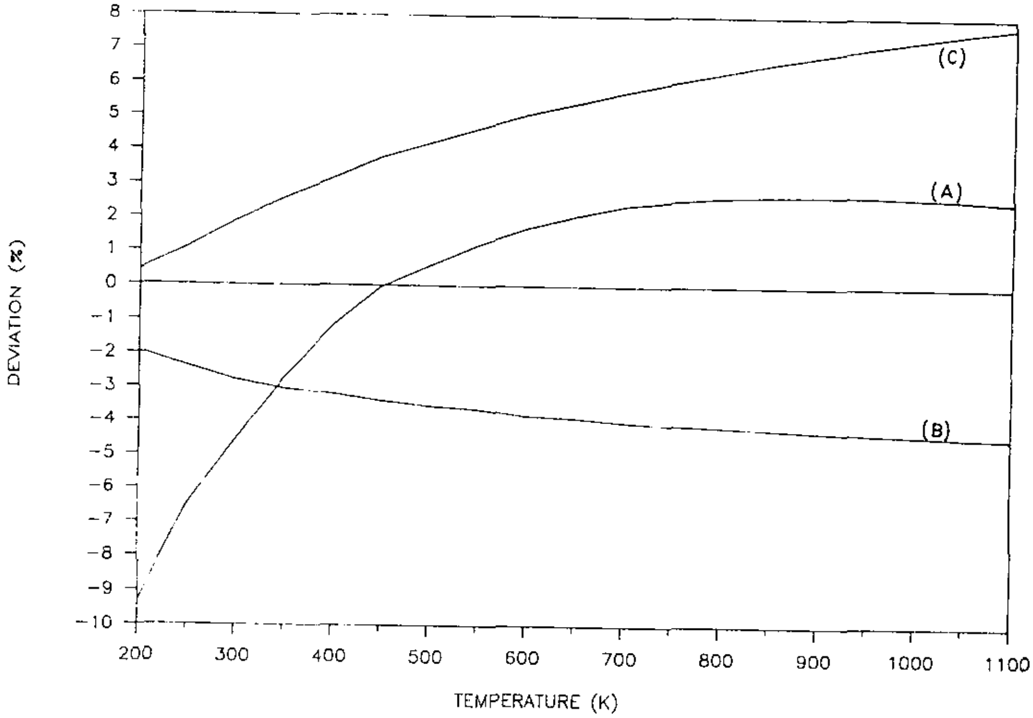

Fig. 9. Percentage deviations of the diffusion coefficients between (Cl,I)-noble gases and the neighboring noble gas-noble gases as a function of temperature: The halogen mass has been adjusted to the mass of the neighboring noble gas for comparison Curve A: Cl-Xe and Ar-Xe; curve B: I-Kr and Xe-Kr; curve C: I-Xe and Xe-Xe.

is comparatively small, its ionic character in the interaction potentials is expected to be relatively small. The extent of similarity is quite good over the temperature range considered. As for the F - Xe case, we considered the individual diffusion coefficients of the interaction potentials $X_{1/2}$ and $I_{3/2}$ separately. For the potential curves of F-Xe ($I_{3/2}$) and Ne-Xe ($^1S_0$), because the parameters of the potentials are similar, one obtained similar diffusion coefficients . The potential well of F - Xe ($X_{1/2}$) is deeper than that of Ne-Xe. However, that effect also made the equilibrium distance of F-Xe ($X_{1/2}$) shorter. Due to the compensation of the two parameters, the diffusion behaviors of F-Xe ($X_{1/2}$) and Ne-Xe resemble each other. Combining the diffusion constants of F-Xe ($X_{1/2}$) and F-Xe ($I_{3/2}$), one would expect to obtain similar diffusion constants of F-Xe and Ne-Xe as the calculation results indicate.

Recently, the potentials of F-Xe have also been determined with the crossed-molecular-beam experimental technique by Aquilanti[36,37] and coworkers. The potential forms are different to those used by Lee and coworkers[6-10]. Comparing the present results with the diffusion coefficients they obtained,[37,38] both calculated diffusion coefficients agree with each other within 4.5 per cent over the temperature range we considered. These recent molecular-beam experiments have yielded improved potentials and have a maximum uncertainty of 14 % in the diffusion constants of F-Xe. Apparently , the potentials of F-Xe obtained by Lee and coworkers are actually very good in predicting consistent diffusion constants despite these potentials having a comparatively large uncertainty. This result implies that at least the repulsive part of the potentials agree with each other very well, as the diffusion process is mainly sampling the repulsive part of the interaction potentials.

However, for the other F-noble gas systems, there are disagreements between the interaction potentials in these two molecular - beam studies. This difference has been pointed out cautiously by Aquilanti *et al.*,[36-38] especially in the case of the F-Kr system .[38] To know the effect of this disagreement on the diffusion coefficients of these F-noble gas systems for these two sets of interaction potentials, further work is needed.

As shown in Fig. 9, the deviation of diffusion constants between Cl-Xe and Ar - Xe behaves the same as that between F-Xe and Ne-Xe. The deviation is large at low temperature but is quite small at high temperature. As for the Br and I cases, due to their large radii and slight ionic character, the deviations are comparatively small as shown in Figs. 8 and 9. Thus one can use the neighboring rare gases of Br and I to predict the transport properties of Br and I.

APPENDIX A: Diffusion coefficients of F-(Ne, Ar, Kr, Xe) at 1 atm (cm^2/sec)

Temperature	Diffusion Coefficients			
(K)	F-Ne	F-Ar	F-Kr	F-Xe
200	0.255	0.182	0.151	0.0988
250	0.372	0.278	0.231	0.150
300	0.505	0.390	0.325	0.209
350	0.653	0.516	0.430	0.277
400	0.814	0.656	0.548	0.352
450	0.988	0.809	0.676	0.434
500	1.175	0.975	0.814	0.523
550	1.375	1.152	0.963	0.618
600	1.586	1.342	1.122	0.720
650	1.809	1.544	1.290	0.828
700	2.043	1.757	1.469	0.942
750	2.288	1.981	1.656	1.062
800	2.544	2.217	1.853	1.187
850	2.810	2.464	2.060	1.319
900	3.086	2.722	2.275	1.456
950	3.374	2.991	2.499	1.598
1000	3.671	3.270	2.733	1.746
1050	3.978	3.560	2.975	1.899
1100	4.295	3.861	3.226	2.058

In conclusion, the parameters of Lennard-Jones 6-12 potentials for Cl, Br, and I atoms are similar to their neighboring noble gases: Ar, Kr, and Xe . Their diffusion behaviors therefore resemble each other. However, a consistent set of Lennard-Jones parameters of the fluorine atom could not be found. This effect may originate from the unique chemical properties of the fluorine atoms. In another respect, one should also bear in mind that there are also relatively large uncertainties in the interaction potentials of F- noble gas systems which would cause the calculation of the diffusion constants to be less accurate than one would wish. Further experimental work on the fluorine atoms is needed to clarify these points.

APPENDIX B: Diffusion coefficients of Br-(Ne, Ar, Kr, Xe) at 1 atm (cm^2/sec)

Temperature	Diffusion Coefficients		
(K)	Br-Ar	Br-Kr	Br-Xe
200	0.0678	0.0487	0.0403
250	0.102	0.0740	0.0624
300	0.143	0.104	0.0891
350	0.189	0.138	0.120
400	0.239	0.176	0.155
450	0.294	0.218	0.194
500	0.354	0.263	0.237
550	0.418	0.312	0.283
600	0.485	0.364	0.333
650	0.557	0.419	0.386
700	0.632	0.477	0.442
750	0.711	0.538	0.502
800	0.793	0.602	0.564
850	0.879	0.669	0.630
900	0.968	0.738	0.698
950	1.061	0.810	0.770
1000	1.156	0.885	0.844
1050	1.255	0.962	0.921
1100	1.358	1.042	1.000

APPENDIX C: Diffusion coefficients of Cl-Xe, I-Kr, and I-Xe at 1 atm (cm^2/sec)

Temperature (K)	*Diffusion Coefficients* Cl-Xe	I-Kr	I-Xe
200	0.0535	0.0368	0.0273
250	0.0842	0.0566	0.0420
300	0.121	0.0802	0.0596
350	0.163	0.107	0.0800
400	0.211	0.138	0.103
450	0.265	0.172	0.129
500	0.322	0.208	0.157
550	0.384	0.248	0.188
600	0.450	0.290	0.221
650	0.519	0.335	0.256
700	0.593	0.382	0.293
750	0.669	0.432	0.332
800	0.749	0.484	0.373
850	0.832	0.539	0.417
900	0.918	0.595	0.462
950	1.008	0.654	0.509
1000	1.100	0.716	0.558
1050	1.195	0.779	0.608
1100	1.293	0.845	0.661

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Key Word Index-

Diffusion coefficient; crossed-molecular-beam scattering experiments; Chapman & Enskog's theory; Lennard-Jones (6-12) potentials.

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