MEASUREMENTS OF THE DIFFUSION COEFFICIENTS OF ATOMIC BROMINE IN INERT GASES

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The laser-photolysis–recombination-luminescence detection method was employed to measure the diffusion coefficients of atomic bromine in inert gaseous media. The measured values are 0.191, 0.102, 0.208, 0.0719, 0.196 and 0.122 cm^2/s for N_2, CF_4, O_2, SF_6, CO and CO_2, respectively, at 1 atm and 300 K. The diffusion coefficient of $Br–Br_2$ was 0.0623 cm^2/s which is close to the value reported previously. The diffusion coefficients of Br–inert gas systems were also calculated from the Lennard-Jones (6–12) parameters of $\epsilon^{LJ}(Br) = 150$ K and $\sigma^{LJ}(Br) = 3.616$ Å determined previously from Br–rare gas systems. The similarity of the diffusion constants at 300 K between Br–inert gas and Kr–inert gas systems is discussed.

1. Introduction

In the past decade, the interaction potentials between open-shell atoms and rare gas atoms or other nonreactive molecules have been obtained by the molecular beam scattering technique [1–14]. Usually for a set of known interaction potentials one can calculate the macroscopic properties of gases, such as their binary diffusion coefficients, from gas kinetics theory [15].

For closed-shell atom–atom systems calculation of their transport properties is well established [15–17]. In the case of open-shell atom–atom systems, because of the electronic fine structure, all the electronic interaction potentials should be taken into account when calculating the transport properties. Several possible coupling schemes between these interaction potentials need to be considered. For internal consistency the coupling scheme used to calculate the transport properties should be consistent with the coupling scheme used to obtain the interaction potentials from the molecular beam scattering experiments. Fine structure effects on transport properties have been elaborated recently by Aquilanti and Vecchiocattivi [10].

In open-shell atom–molecule systems, accurate potentials are more difficult to obtain. Up to now, only a few molecular systems have been reported in the literature [11–14]. Even if the interaction potentials were known, a full calculation of the transport properties of these systems is a time-consuming task [18]. Direct measurements of the diffusion coefficients of these binary systems are necessary as experimental observations and also as a macroscopic check for the interaction potentials obtained by molecular beam scattering experiments. Besides, these quantities are also important in understanding macroscopic chemical reactions, such as combustion, heterogeneous chemical reactions, atmospheric chemistry [19] and plasma etching processes [20].

Diffusion coefficients of several open-shell atomic species in inert media have been reported. They include H [21,22], O [23], N [24], Na [25], Cs [26], Rb [27], Cl [23,28] and Br [29]. Varieties tech-

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niques for their measurements were developed. Recently we employed the newly developed laser-photolysis–recombination-luminescence detection method to measure the diffusion coefficients of chlorine and bromine atoms in rare gases [30,31]. The measured diffusion constants are in good agreement with theoretical values calculated from the interaction potentials obtained via molecular beam experiments. A consistent set of Lennard-Jones (6–12) parameters for Cl and Br were also obtained for the rare gas systems around room temperature [31,32]. In this paper, we report measurements of the diffusion coefficients of Br–inert molecule systems and compare them with the corresponding theoretical values predicted from the Lennard-Jones parameters determined previously. We also discuss the similarity of the diffusion behavior between Br–inert molecule systems and Kr–inert molecule systems at 300 K.

2. Experimental method and results

The mechanism for the photodissociation and recombination of Br_2 molecules and the detailed experimental procedure have been discussed elsewhere [31]. Briefly, near-Gaussian 532 nm laser radiation was used to generate bromine atoms in a cell containing various concentrations of Br_2 and inert gases. The chemiluminescence which radiates from the recombination of bromine atoms was collected by a red-enhanced photomultiplier tube. The recombination rate constants (K_r) of Br and the photon emission and quenching rate constants (K_e and K_q) of excited state Br_2 (Br_2^*) in inert gases are similar to their values in rare gases. K_r, K_e and K_q are known to be of the order of 10^{-32} cm^6 molecule^{-2} s^{-1} [33], 10^3–10^5 s^{-1} [34,35] and 10^{-10}–10^{-15} cm^3 molecule^{-1} s^{-1} [36–38], respectively. Under the experimental conditions ($[Br_2] \approx 10^{17}$ molecules cm^{-3}, [inert gases] $\approx 10^{17}$ molecules cm^{-3}, laser beam diameter ≈ 0.5 cm and $[Br] \approx 10^{14}$ molecules cm^{-3}) the decay behavior of the total chemiluminescence intensity of Br_2^* is controlled by the diffusion of bromine atoms. After fitting the detected chemiluminescence signal by a nonlinear least-squares method, one could obtain the diffusion coefficients of trace bromine atoms in inert gases in a series of mole fractions of Br_2, as shown in figs. 1, 2 and 3.

The straight lines in the figures are linear least-squares fitting by Blanc's law

$$\frac{1}{D_{\mathrm{Br}-[\mathrm{M}+\mathrm{Br}_2]}} = \frac{a_{\mathrm{Br}_2}}{D_{\mathrm{Br}-\mathrm{Br}_2}} + \frac{1-a_{\mathrm{Br}_2}}{D_{\mathrm{Br}-\mathrm{M}}}, \qquad (1)$$

where a_{Br_2} is the mole fraction of Br_2 and $D_{Br-[Br_2+M]}$ is the diffusion coefficient of Br in Br_2 and M mixtures. The measured diffusion constants of Br in inert gases and Br_2 are shown in table 1.

Because the intensity of the laser profile fluctuates during the experiments, it contributes a 14% uncertainty to the diffusion coefficients. The uncertainties in the least-squares curve fitting and the extrapolation of the bromine molecule mole fraction to zero contribute another 3% error. Since the volume of the cell is quite large (diameter = 15 cm), the wall effect is negligible. The total uncertainty is estimated to be ±17%.

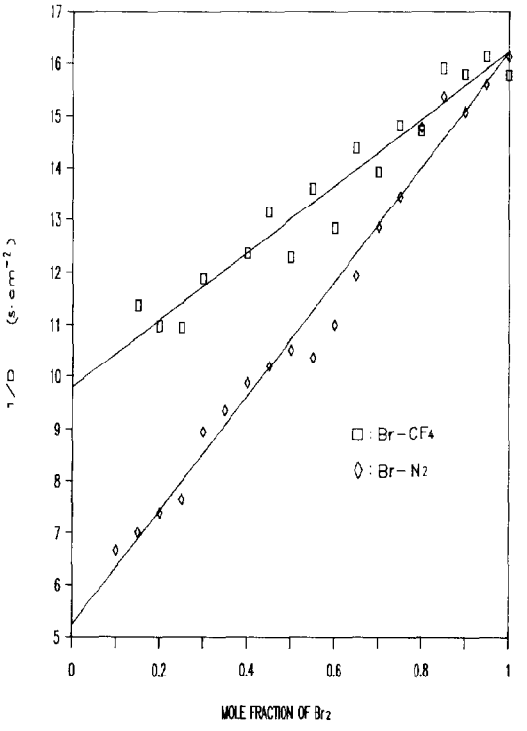

Fig. 1. Reciprocal diffusion coefficients of Br–N_2 and Br–CF_4 as a function of the mole fraction of Br_2. The solid lines are a least-squares fitting of Blanc's law. Temperature is 300 K and total pressure is 1 atm.

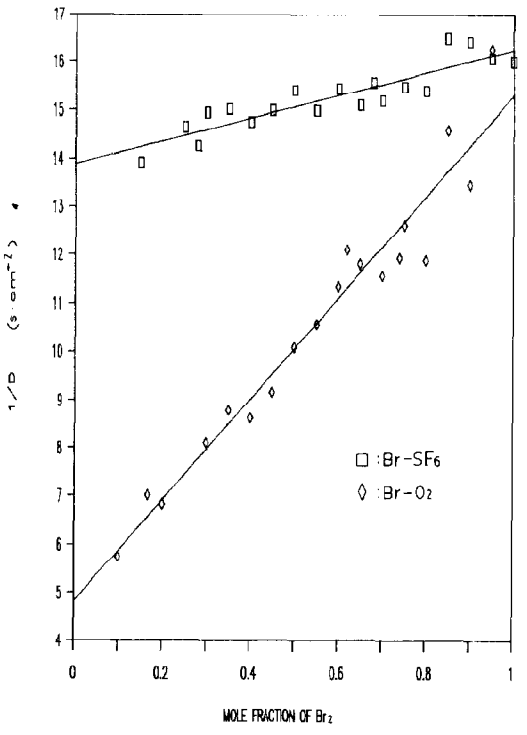

Fig. 2. Reciprocal diffusion coefficients of Br–O_2 and Br–SF_6 as a function of the mole fraction of Br_2. The solid lines are a least-squares fitting of Blanc's law. Temperature is 300 K and total pressure is 1 atm.

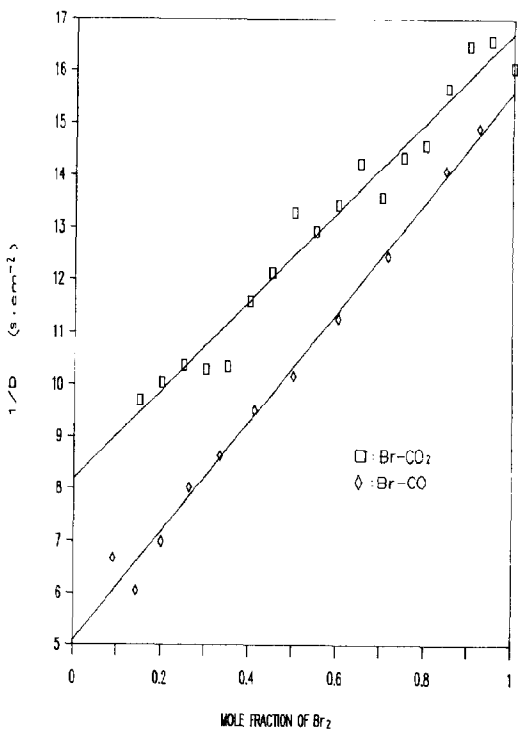

Fig. 3. Reciprocal diffusion coefficients of Br–CO and Br–CO_2 as a function of the mole fraction of Br_2. The solid lines are a least-squares fitting of Blanc's law. Temperature is 300 K and total pressure is 1 atm.

Br_2 (Merck, 99.5%) was used after one vacuum distillation. N_2 (San Fu, 99.9%), CO (Union Carbide, 99.8%), O_2 (San Fu, 99.9%), CO_2 (Matheson, 99.995%), CF_4 (Matheson, 99.9%) and SF_6 (Matheson, 99.99%) were used without further purification.

3. Discussion

The Lennard-Jones (6–12 model) parameters for Br have been determined to be $\epsilon^{LJ}(Br) = 150$ K and $\sigma^{LJ}(Br) = 3.616$ Å [31,32] by fitting the diffusion constants of the Br–Ar system around room temperature. With the combination laws of $\sigma_{12}^{LJ} = \frac{1}{2}(\sigma_1^{LJ} + \sigma_2^{LJ})$ and $\epsilon_{12}^{LJ} = (\epsilon_1^{LJ}\epsilon_2^{LJ})^{1/2}$ the calculated diffusion constants of Br in rare gases are in good agreement with the experimental results. This observation implies that despite the fine structure splitting in the interaction potentials, the overall diffusion behavior of bromine atoms in rare gases is not significantly different from that of the closed-shell atoms. In the same way, one can calculate the diffusion constants of Br in inert molecular gases and Br_2. The theoretical values are shown in table 1. The parameters for the inert molecular gases were obtained from ref. [15]. Comparing these values with the experimental results, the agreement is not so good as in the Br–rare gas systems. The experimental results are consistently appreciably larger. This difference reflects the possibility that extra interaction forces between the unpaired electron of the open-shell atom and molecular valence electrons are involved. In other words, the simple Lennard-Jones parameters and their combination laws in predicting the transport quantities of open-shell atoms have their limitations, especially in molecular systems.

The Lennard-Jones parameters of Kr are

Table 1
Diffusion coefficients of bromine atoms in inert gases. Temperature: 300 K; pressure: 1 atm

Media [M]	Experimental diffusion coefficients of Br in M (cm^2/s)	Calculated diffusion coefficients of Br in M (cm^2/s) [a]	Percentage deviation (%)
N_2	0.191 ± 0.032	0.165	15.8
CO	0.196 ± 0.033	0.160	22.5
O_2	0.208 ± 0.035	0.159	30.8
CO_2	0.122 ± 0.021	0.112	8.9
CF_4	0.102 ± 0.017	0.0801	27.5
SF_6	0.072 ± 0.012	0.0570	26.3
Br_2	0.062 ± 0.016	0.0508	22.0

[a] The parameters of the Lennard-Jones 6–12 potential of Br were determined from the diffusion coefficients of Br–Ar obtained in ref. [31]: $\sigma^{LJ}(Br) = 3.616$ Å, $\epsilon^{LJ}(Br)/k = 150$ K.

Table 2
Comparison of the diffusion coefficients (cm^2/s) between bromine and krypton atoms in inert gases. Temperature: 300 K; pressure: 1 atm

Media [M]	Diffusion coefficients of Kr in M from other work	Diffusion coefficients of Br–M after adjusting Br mass to Kr mass		Deviation of diffusion coefficients between adjusted Br–M and Kr–M (%)	
		6–12 model	exp.	6–12 model	exp.
N_2	0.160 [a]	0.164	0.190	2.5	18.8
CO	0.163 [b]	0.159	0.195	2.5	19.6
O_2	0.148 [c]	0.158	0.207	6.8	39.9
CO_2	0.117 [d]	0.111	0.121	5.1	3.4
CF_4	0.078 [e]	0.079	0.101	1.3	29.5
SF_6	0.060 [f]	0.056	0.071	6.7	
Br_2		0.050	0.061	6.8 [g]	29.9 [g]

[a] Ref. [39]. [b] Ref. [40]. [c] Obtained by interpolating the experimental values of ref. [41].
[d] Adapted from ref. [42]. [e] Calculated from the parameters adapted from ref. [43]. [f] Adapted from ref. [44].
[g] Compared with the value of 0.047 calculated from the parameters of the Lennard-Jones (6–12) potential.

$\epsilon^{LJ}(Kr) = 190$ K, $\sigma^{LJ}(Kr) = 3.6$ Å [15]. Comparing the force constants of Br and Kr, one might expect their diffusion behavior to be similar. Using the relevant parameters the diffusion constants of Kr–inert gas systems were calculated. They are in good agreement with the experimental values [39–44]. For a further examination of the diffusion behavior of bromine atoms in inert molecules, both the theoretical and experimental diffusion constants of Br–M were adjusted by changing the mass of Br to that of Kr and comparing with the experimental values of Kr–M. Note that in adjusting the mass, we only took the relative motion of the molecular center of mass into account and ignored the mass effect on the internal degrees of freedom. The deviations between the diffusion coefficients of Br–inert molecular systems and Kr–inert molecular systems, which are shown in table 2, are quite appreciable. Assuming that the small difference between Br and Kr does not change the transition behavior of the internal degrees of freedom during the collision, one can only attribute the difference to a different interaction force in open-shell atom–molecule systems, a reiteration of the previous statement. For the $Br–Br_2$ system, the chemical exchange reaction between Br and Br_2 may also contribute to a larger measured diffusion constant.

In conclusion, the diffusion coefficients of bromine atoms in some nonreacting gaseous media were measured. The diffusion coefficient is a macroscopic

manifestation of the interaction potentials. The simple combination rules used to predict the binary diffusion coefficients of closed-shell systems are not as good in open-shell atom–molecule systems. This observation implies that the interaction potentials between an open-shell atom and a molecule are unique and should be considered individually.

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