Calculation of Cross Sections for Zero Activation Energy Processes by Simple Collision Models with Emphasis on the Penning Effect*

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Recent cross sections obtained for the destruction of $He(2\,^3S)$ metastable atoms by ionization of Ar, Kr, Xe, H_2, and N_2 are analyzed by a simple collision picture. It is found that the ratio of the experimental to momentum transfer cross sections is the same order as the efficiency of ejection of electrons from metal surfaces by $He(2\,^3S)$ atoms, namely 0.2–0.3. The momentum transfer cross sections agree with the experimental values better than some of the published experimental values agree among themselves and in addition there is a great paucity of data in this area so that an order-of-magnitude estimate is often useful. In addition, it is shown that calculated momentum transfer cross sections for the reactions,

$$He(2\,^3S)+He(2\,^3S) \rightarrow He^+ + He(1\,^1S)+e^-,$$
$$He_2^+ + Ne \rightarrow Ne^+ + 2\,He$$
$$He(1\,^1S)+He(n\,^1P) \rightarrow He(1\,^1S)+He(nf),$$
$$He(2\,^1S)+Ar \rightarrow He(1\,^1S)+Ar^+ + e^-,$$

agree very well with literature values of cross sections for the processes. It appears that for a broad class of atomic reactions requiring zero activation energy, a momentum transfer collision has a high probability of reaction. Momentum transfer cross sections are dominated by the long-range attractive forces and can easily be calculated, thereby providing a useful estimate of the actual reaction cross section.

INTRODUCTION

EXPERIMENTAL cross-section measurements of deactivation of $He(2\,^3S)$ metastable atoms in ionizing collision with several gases, the so-called Penning effect, are reported in the preceding paper.[1] The present paper analyzes these data according to a simple classical momentum transfer collision cross section model. It is a surprising result that these cross sections can be predicted to somewhat better than an order of magnitude by a simple model and it appears that in many cases of reactions involving zero or very little activation energy this is the case. Several examples of this are shown.

DISCUSSION

For attractive potentials of the form $\phi(r) = -ar^{-\delta}$, the momentum transfer cross section is given by[2]

$$Q = 2\pi\left(\frac{\delta a}{\frac{1}{2}\mu g^2}\right)^{2/\delta} A^{(1)}(\delta), \quad A^{(1)}(\delta) = \int_0^\infty (1-\cos\chi)\beta d\beta, \quad (1)$$

where μ is the reduced mass, g the relative velocity, and $A^{(1)}(\delta)$ are collision integrals which have been calculated for $\delta = 2, 3, 6$ by Eliason, Stogryn, and Hirschfelder.[2] The use of such a cross section has been quite successful in the study of ion-molecule reactions which have been carried out in mass spectrometers.[3–6] In this case

$$\phi(r) = -e^2\alpha/2r^4$$

and

$$Q = (4e\pi/g)(\alpha/\mu)^{1/2}[A^{(1)}(4)], \quad (2)$$

with $A^{(1)}(4) = 0.55259$. The reaction cross section can be expressed as $Q_R = fQ$, where f is an efficiency factor or probability, which in the case of the ion-molecule reactions, is very nearly unity. In the case of metastable-neutral molecule collisions, the attractive forces are the van der Waals forces which have an inverse sixth-power potential. The momentum transfer cross section in this case is

$$Q = 2\pi(12a/\mu g^2)^{1/3} A^{(1)}(6), \quad (3)$$

with $A^{(1)}(6) = 0.434$.[2]

RESULTS

Calculated values for Q are shown in Table I along with experimental cross-sections for Penning processes with $He(2\,^3S)$. Experimental r^{-6} coefficients are taken from Table II of Pitzer[7] for the rare gases and H_2 and N_2. There is some uncertainty about the r^{-6} coefficient for $He(2\,^3S)$ interacting with other species (or itself). Buckingham and Dalgarno have discussed this matter in some detail[8] and have made several calculations for the interaction of a ground-state and 2s-state helium atom. They calculate values 20×10^{-60} and 30×10^{-60} erg cm^6 but prefer a value of 10×10^{-60}–20×10^{-60} erg cm^6. We have chosen the value 20×10^{-60} erg cm^6. A later calculation[9] yields a value 58×10^{-60} erg cm^6. The collision cross section is fairly insensitive to this choice because of the cube root involved, a factor 2 in interaction constant giving only a 26% change in cross

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TABLE I. $He(2\,^3S)$ metastable destruction and momentum transfer cross sections.

Reactants		Momentum transfer cross section, Q (10^{-15} cm^2)	Experimental reaction cross section, σ (10^{-15} cm^2)	σ/Q
$He(2\,^3S)$	Ne	2.30	0.028±20%[a]	0.01
	Ar	3.45	0.66 ±20%[a]	0.19
	Kr	3.92	1.03 ±20%[a]	0.26
	Xe	4.55	1.39 ±20%[a]	0.31
	H_2	2.42	0.61 ±35%[a]	0.26
	N_2	3.53	0.64 ±50%[a]	0.19
	He $(2\,^3S)$	7.60	10[b]	1.3
$He(2\,^1S)$	Ar	4	1.2[c]	0.3
	Ne	3.21	0.41 ±20%[a]	0.13
$He(1\,^1S)$	He $(n\,^1P)$	$0.59n^2$	$0.14n^2$ [d]	0.25
$He(2\,^3S)$	Hg	6.2	14 ± 3[e]	~2
$He(2\,^1S)$	Hg	5.6		

[a] Reference 1.
[b] A. V. Phelps and J. P. Molnar, Phys. Rev. **89**, 1202 (1952).
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section. The choice will affect only the relative values of Q for Penning reactions with a particular metastable. The usual combining rule of interaction constants is used, $a_{12}^2=a_{11}a_{22}$.

It is of interest to note that σ/Q, a phenomenological efficiency factor, is of the same order as found for the electron ejection efficiency of $He(2\,^3S)$ metastables bombarding metal surfaces. Stebbings[10] found a value $\gamma_m=0.29\pm0.03$ electron/metastable for a gold surface. Hasted[11] found values 0.11, 0.14, and 0.25 for 1700°C flashed surfaces of Mo, W, Pt and values 0.19, 0.17, and 0.26 for the same surfaces contaminated by air.

The systematic increase in σ/Q with mass could indicate an unaccounted for influence of mass, ionization potential, polarizability, or other property which increases monotonically with mass, however the accuracy of the experimental data does not justify such a conclusion at this time. One value of a $He(2\,^1S)$ metastable Penning cross section is calculated to compare with Phelps value and shows the same kind of agreement (Table I). The tentative singlet $He(2\,^1S)$ Penning cross sections reported in reference 1 for Ar, Kr, and Xe appear to be larger than the triplet $He(2\,^3S)$ cross sections by nearly an order of magnitude. The simple collision theory would predict a ratio $Q(2\,^1S)/Q(2\,^3S)$ of only 1.1 to 1.2, using theoretical van der Waals coefficient ratios from Dalgarno and Kingston.[9] The singlet $He(2\,^1S)$ cross sections are very difficult to measure experimentally because of the shorter lifetimes of the singlets in the parent helium gas and because other processes including superelastic collision $He(2\,^1S)+e^-\rightarrow He(2\,^3S)+e+0.79$ eV are very important which are strongly modified by the addition of Penning gases for study.[1] For this reason, the reported singlet cross sections may be too high and are considered tentative pending further experimental investigation.

In the case of the non-Penning gas neon (the only gas whose ionization potential lies above the helium metastable levels), both singlet and triplet cross sections have been measured and are shown in Table I. In this case one might expect the destruction cross section to be considerably less than the momentum transfer cross section, or the reaction efficiency to be much less than unity. For $He(2\,^3S)$, this is clearly the case and for $He(2\,^1S)$ the ratio σ/Q is less than for Penning gases, although only by a factor ~2. Neon has a number of levels within a few kT of either helium metastable level but the density of such states is greater in the vicinity of the $He(2\,^1S)$ level.

On the same basis cross sections for reactions of the type $A^*+B^*\rightarrow A^++B+e^-$ may be estimated. One such cross section has been measured,[12] namely, for two $He(2\,^3S)$ metastables colliding. The experimental cross section is 10^{-14} cm^2. The calculated Q in this case 0.76×10^{-14} cm^2, is in good agreement. An attempt to calculate this cross section quantum mechanically has been unsuccessful, yielding a value $\sigma=10^{-18}$ cm^2.[13]

A calculation has been made for the reaction $He_2^+ + Ne\rightarrow Ne^+ + 2He$, in this case utilizing the appropriate ion-neutral cross section $Q=(2e\pi/g)(\alpha/\mu)^{1/2}$ and the result, $Q=5.4\times10^{-15}$ cm^2, agrees very well with the experimental value measured by Oskam,[14] $\sigma\sim1.5\times10^{-15}$ cm^2. It should be pointed out that the experimental values are often difficult to obtain and in the few cases where more than one measurement has been made, order-of-magnitude discrepancies sometimes exist.[1] The observation that the reaction cross section is essentially gas kinetic in this process is of interest since it implies that the reaction is not endothermic and that either the dissociation energy of He_2^+ is less than ionization potential (He)–ionization potential (Ne) $=3.0$ eV or that the He_2^+ species have vibrational excitation. The two experimental values of $D_0^0(He_2^+)$ in the literature are 3.1 eV[15] and 2.1 eV.[16]

St. John and Fowler[17] have recently reconsidered reactions of the type

$$He(1\,^1S)+He(n\,^1P)\rightarrow He(1\,^1S)+He(n\,^3D),$$

in which the Wigner spin conservation rule is violated and for which improbably large cross sections have been postulated in order to explain experimental observations. Lees and Skinner,[18] for example, estimated

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$\sigma \sim 4.5\times10^{-14}$ cm^2 for $n=3$. St. John and Fowler[17] and Lin and Fowler[19] consider the reaction to go via nf states which are strongly mixed singlet-triplet states, thence cascading to D states. They calculate cross sections for transfer of excitation from an $n\,^1P$ state to an $n\,^3F$ state, (or better to an nf mixed spin state) and find that cross sections $\sigma=1.4\times10^{-16}\ n^2$ cm^2 or $\sigma=4.7\times10^{-18}\ n^4$ cm^2 are consistent with their data and probably represent upper limits on the transfer cross sections. The simple collision cross section of

$$\mathrm{He}(1\,^1S)+\mathrm{He}(n\,^1P)\rightarrow\mathrm{He}(1\,^1S)+\mathrm{He}(nf), \qquad (6)$$

which may be considered as a near resonance reaction for n as large as 5, where the energy separations are only a few thousandths of a volt, is $Q=5.9\times10^{-16}\ n^2$ cm^2, in reasonable agreement with the first value above. This assumes that polarizability is proportional to n^6. This is perhaps a better approximation for higher n than for the change of n from 1 to 2. The numerical coefficient is obtained with $n=2$. The ratio σ/Q leads to a probability or efficiency factor 0.25, not unlike the factors for ratios of experimental Penning cross sections to collision cross sections for He$(2\,^3S)$. This has also neglected any branching or competing reactions as do all cross sections computed on this model. The collision cross section only measures the statistics of the proper reactants colliding and can say nothing about the further course of events. The philosophy of this simple approach is that if a resonance reaction is possible, the collision cross section is a reasonable first approximation to the reaction cross section. If two resonance reactions were possible, the collision cross section would be even more likely to represent the cross section for reactant loss but could not, of course, predict a branching ratio.

CONCLUSIONS

It appears that simple collision theory yields cross sections of at least order-of-magnitude reliability for a number of investigated reactions between systems of atomic mass which might be characterized as having zero or very small activation energies and which are "resonant" reactions. Such reactions are then dominated by long-range forces, each collision having a large probability for reaction. Among these are Penning reactions whose cross sections show only slight correlation with the ionization potential of the atoms so that it appears that reactions in which electrons are available to carry away excess energy are essentially resonance reactions regardless of the internal energy change of the system. We use resonance in the sense of large probability of reaction per collision or very low activation energy. This may perhaps be confusing since Massey and Burhop[20] show, that for exact resonance, charge or excitation cross sections may greatly exceed gas kinetic cross sections and be as large as 5×10^{-14} cm^2. This is not because of the wave aspect of the collision but because the possibility of resonance transfer introduces a long-range interaction which would otherwise not occur, as for example in atomic charge-transfer reactions such as $\mathrm{He}^++\mathrm{He}\rightarrow\mathrm{He}+\mathrm{He}^+$. The de Broglie wavelengths of the atoms are very small and the collision is otherwise essentially classical according to Massey and Burhop.

For reactions in which electrons are not ejected with kinetic energy it is not possible in all cases to determine *a priori* whether the reaction is resonant and has a reaction cross section approximately equal to the collision cross section. While it appears that ion-molecule reactions almost always satisfy this criterion,[3–5] Bates and Nicolet[21] have recently argued that the reactions $\mathrm{O}^++\mathrm{O}_2\rightarrow\mathrm{O}_2^++\mathrm{O}+1.5$ eV and $\mathrm{O}^++\mathrm{N}_2\rightarrow\mathrm{NO}^++\mathrm{N}+1.1$ eV must either be inhibited by steric hindrance or more probably by an activation energy since the atmospheric composition data are more consistent with a recombination coefficient $\sim10^{-13}$ cm^3/sec than with a coefficient $\sim10^{-9}$ cm^3/sec$=Qg\sim10^{-14}$ cm$^2\times10^5$ cm/sec which would result from collision theory. There is great need for direct laboratory measurements of such cross sections.

Further experimental investigations are being carried out in this laboratory. In particular, it is hoped to check the $T^{-1/3}$ temperature dependence predicted by collision theory for the Penning effect and to investigate a wider range of reactants and parameters in Penning reactions and related processes.

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