Temperature dependence of de-excitation rate constants of He(2^3S) by Ne, Ar, Xe, H$_2$, N$_2$, O$_2$, NH$_3$, and CO$_2$

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Temperature dependence of de-excitation rate constants of He(2³S) by Ne, Ar, Xe, H₂, N₂, O₂, NH₃, and CO₂

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Reaction rate constants for the quenching of the 2^3S state of helium by Ne, Ar, Xe, H₂, N₂, O₂, CO₂, and NH₃ have been measured as a function of temperature between 300 and 900°K in a flowing afterglow. All of these rate constants increased with temperature. This finding offers an explanation for the discrepancies among recently published values for the reaction rate constant of He(2^3S) with these gases obtained in different experiments.

INTRODUCTION

The production and destruction of the long-lived atomic metastables He(2^3S) and He(2^1S) in helium are of fundamental importance to discharge processes in helium and gas mixtures which are predominantly helium. Moreover, owing to their simple nature, these metastables and their interactions have been the subject of considerable theoretical interest.[1-5]

For these reasons, during the past two decades a great deal of experimental data has become available on cross sections and rate constants for the quenching reactions of the metastable He(2^1S) and He(2^3S) states of helium. These data have been taken by various techniques such as beams,[6-17] stationary afterglows[18,20,24-30] and flowing afterglows.[19,21-23,31] Since these values were measured with increasing precision, systematic differences began to appear between the results obtained with the various experimental techniques applied at low (thermal or near thermal) energies. The nature of these discrepancies have been discussed in some detail previously.[6,21,32]

In brief, the present disagreement occurs between the results of pulsed afterglow or flowing afterglow experiments done at thermal (300 °K) energies, which find that the He(2^1S) quenching rate constants are significantly larger than the He(2^3S) quenching rate constant for the same molecules, and those from beam results (done at interaction energies several times thermal), which indicate that the cross sections for the quenching of the two helium excited states by the common atmospheric gases are about equal. When the cross sections obtained by beam measurements are converted to rate constants by using the measured velocity distribution of the interacting particles, rate constants are obtained which agree relatively well with afterglow results for the He(2^1S) reactions but which are considerably larger than the rate constants obtained from afterglows for the He(2^3S) reactions. These differences for all cases investigated are well outside the combined estimated experimental uncertainties.

In order to better understand the nature of the He(2^3S) reactions and to uncover, if possible, the source of the discrepancies in the measurement of these reactions, rate constants for the reactions of He(2^3S) with Ne, Ar, Xe, H₂, N₂, O₂, CO₂, and NH₃ have been measured between 300 and 900 °K in a temperature variable flowing

afterglow. These measurements revealed an unexpectedly large variation in the quenching rate constants with temperature. The finding that these rate constants increase rapidly with increasing temperature offers a possible explanation for the discrepancies in measured He(2^3S) rate constants outlined above.

EXPERIMENTAL

These measurements were made in a variable temperature flowing afterglow. The flowing afterglow technique and its utilization to measure reaction rate constants has been described in the literature.[33] The modification of this system to allow controlled temperature variability was discussed earlier.[34]

The temperature stability of the system was better than ±2% over the entire range of temperature studied. The temperature of the system was determined by a sequency of five thermocouples located at various positions along the tube and embedded in the walls of the tube, or contacting the copper heat exchanger which surrounded the stainless steel tube.

The present method used to measure the He(2^3S) rate constants is quite similar to that used in our earlier measurements[21] of helium metastable reactions carried out at a single temperature (296 °K). Briefly, helium is introduced into the flow tube with a flow rate of about 180 atm · cm³/sec. This gas is excited and ionized by ~100 eV electrons from an electron gun. The ions, metastables, and electrons so produced are carried downstream in the flowing gas. Superelastic collisions between thermal electrons and He(2^1S) quickly convert this metastable to the He(2^3S) state. Under typical operating conditions, the He(2^1S) concentration is much less than 1% of that of He(2^3S).

The remaining metastables are carried downstream past an inlet port, where a reactant gas is added in measured amounts. In the region following this inlet, reaction between the He(2^3S) and the reactant gas takes place. The reaction region is terminated by the He(2^3S) detector. These measurements were performed using the 7033 Å and the 6032 Å lines of neon. The upper levels of the states associated with these radiations were populated by collisions between the remaining He(2^3S) and neon which was added through an inlet port at the end of the reaction region. The neon emissions were monitored using a tandem optical spectrometer

consisting of two 0.8 m Fasti Ebert spectrometers in series. The detector of this spectrometer was a liquid nitrogen cooled S-20 photomultiplier. The output of this photomultiplier was fed into a standard pulse counting system. The characteristic counting rate was of the order of 5×10^4 counts/sec in the absence of reactant gas with a background at room temperature of less than 20 counts/sec. This background increases with temperature until a count rate of 4.4×10^3 counts/sec was measured at 613 °C due to the thermal radiation from the tube at 7033 Å. Under these conditions, the emission from the 6032 Å line of neon, which was as intense as the 7033 Å line, was monitored. With this line, the background was reduced to 1.6 ± 10^3 counts/sec. In either case, the background contribution in any given run was constant and could be subtracted. The rate constants calculated from the decline of either line were the same.

A typical run of data is shown in Fig. 1. These data were taken for the reaction of argon with He(2³S) at 252 °C. The rate constant is calculated from the slope of the decline of the monitoring radiation as a function of the rate of addition of the reactant gas. The rate constant measured is for all the various destruction channels: Penning ionization, quenching, associative ionization, and excitation transfer.

At each temperature, the rate constants were measured for each gas as a function of buffer gas pressure. These binary reactions should be independent of pressure and, indeed, in all of the reactions studied, this was the case.

RESULTS AND COMPARISONS

The results for the measured temperature dependences of the quenching rate constants for He(2³S) with the various gases studied are shown in Fig. 2. In all cases, the measured rate constants increased with temperature. In the case of NH_3, for temperatures above 750 °K, the rate constant for the reaction of He(2³S) with NH_3 fell off sharply with increasing temperature. Since this is probably due to the decomposition of NH_3, the results above 750 °K are not included.
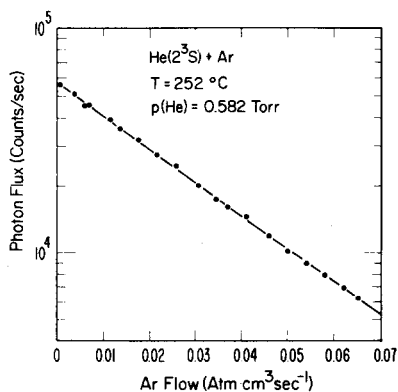
Helium metastables may react as follows:

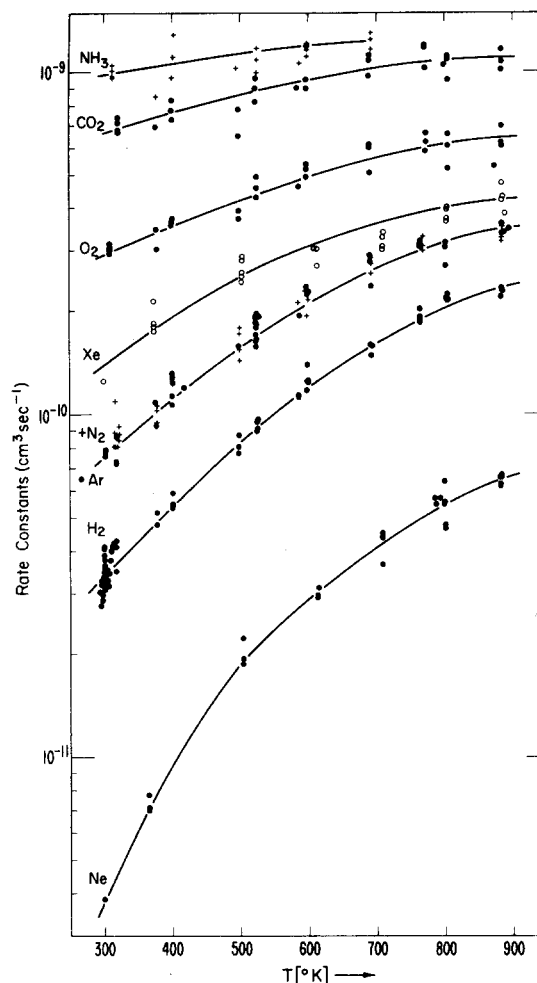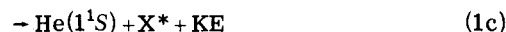FIG. 1. Typical run of data for the reaction of He (2³S) and argon at 252 °C.

FIG. 2. Reaction rate constants for the quenching of the 2³S state of helium by various gases between 300 and 900 °K.

$$H(2^3S) + X \rightarrow He(1^1S) + X^+ + e + KE \qquad (1a)$$

$$\rightarrow HeX^+ + e + KE \qquad (1b)$$

$$\rightarrow He(1^1S) + X^* + KE \qquad (1c)$$

$$\rightarrow He(1^1S) + X_{KE}^{h\nu} , \qquad (1d)$$
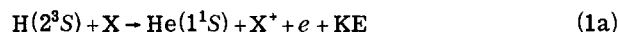
where (1a) is Penning ionization, (1b) is associative ionization, (1c) is excitation transfer not accompanied by ionization, and (1d) is collisional de-excitation in which the excess energy appears as radiation and/or kinetic energy of the products. In each of the processes (1a)–(1d), a certain fraction of the energy of reaction may be carried away in the form of kinetic energy, KE, distributed among the reaction products. In the present experiment, we measured the total destruction of He(2³S) by all processes. All the afterglow experiments monitor the disappearance of He(2³S). The beam experiments obtain cross sections from ion production and measure only the contribution from channels (1a) and (1b). In fact, however, with the exception of neon, in the reaction of He(2³S) with any of the simple atoms and molecules used in these experiments, the contribution to the destruction of He(2³S) by channel (1c) and (1d) is usually considered to be negligible.

Table I shows a comparison between the present results and other afterglow results at 300 °K. These re-

TABLE I. Rate constants for the quenching of He (2³S) with various neutrals at about 300 °K, all in units of 10^{-11} cm³ sec⁻¹.ᵃ

Ne	Ar	Kr	Xe	H_2	D_2	N_2	O_2	NO	CO	HBr	HCl	CO_2	NH_3	CH_4	N_2O	C_2H_6	C_3H_8	C_4H_{10}	References	Year of Publ.	Method	Accuracy
0.36	7.1		12.5	2.9		7.1	24.5					65.5	94.2						this workᵇ		FA	±30%
0.71	9.4																		Arrathoon (18)	1974	SA	±30%
				5.2															Bush et al. (19)	1973	FA	
										100	82								Veatch et al.ᶜ	1973	SA	
						6.3													Märk et al. (20)	1971	SA	±15%
0.385	7.04	9.94	12.4	3.18	2.6	6.96	21	24.2	9.85			57.5	84	13.7	43.3	25	31.7	41.7	Schmeltekopf (21)	1970	FA	±30%
	9.2	10.3	14	4.6		6.7	20	21.3	10.7			56.5	74	17					Bolden et al. (23)	1970	FA	±20%
						10			17			79							Cher et al. (22)	1969	FA	±30%
	10.3																		Jones et al. (24)	1968	SA	±10%
						11	43		29			77							Dunn (31)	1966	FA	±30%
0.39	8.7	13.3	16.5	18.8		8.6													Benton et al. (25)	1962	SA	±20 to 50%
0.52	~13		~13			~14													Javan (26)	1961	SA	
																			Colegrove et al. (30)	1960	SA	
0.31	5.0																		Phelps (27)	1957	SA	
	1.24																		Biondi (28)	1953	SA	

ᵃIn cases where cross sections were reported in the literature, these were converted into rate constants according to the expression $k = \langle\sigma\rangle\langle v\rangle$. $\langle\sigma\rangle$ means the reported cross section, $\langle v\rangle$ is the average relative velocity $(8kT/\pi m)^{1/2}$, and m is the reduced mass of the respective He(2³S) neutral system.

ᵇThe values correspond to the intersection of the Arrhenius plots of 1/300 °K in Fig. 4.

ᶜG. E. Veatch and H. J. Oskam, Phys. Rev. 8, 389 (1973).

sults are similar in that the measurements were made at relatively high pressures so that the reactants could be expected to be in thermal equilibrium (or nearly so) at the given temperature. For the most part, the agreement between these measured values is satisfactory. In particular, the present measurements at 300 °K agree with our earlier results[21] to within the quoted experimental uncertainty of ±30%. (The average deviation of the two sets of measurements is 6.1%.)

There are fewer cases in which we may compare our results as a function of temperature. In Fig. 3, we show the current results for the reactions of He(2³S) with N_2, O_2, and CO_2 compared with those results obtained by Cher and Hollingsworth.[22] In this case, we find the agreement to be relatively good over the entire range of temperatures studied. In their measurements, Cher and Hollingsworth used a flowing afterglow technique with an afterglow tube heated by external furnaces, a technique quite similar to that used in the present measurements. There is very little overlap in temperature between the present results and those of Arrathoon,[18] who used a variable temperature static afterglow. Within the temperature range common to both experiments for the reaction of He(2³S) with Ar, the rate constants agree reasonably well. The rate constants measured for this reaction using a static pulsed afterglow technique in Ref. 18 declined somewhat more slowly at lower temperatures than do the present results at room temperature and above. On the other hand, for the reaction of He(2³S) with neon, the rate constants obtained by Arrathoon are larger by almost a factor of 2 than present results. They do, however, exhibit a strong temperature dependence similar to our results.

Pulsed static afterglow results were also obtained by Jones and Robertson[24] for the reaction of He(2³S) with argon over a temperature range from 80–500 °K. The comparison between these results and the present measurements are somewhat less favorable. In particular, there is almost no temperature variability compared to a strong increase with temperature which we find.

A comparison between the present results and those obtained in beam experiments is much more difficult. For the present purposes, we shall limit this comparison to very recent results obtained by Riola, Howard, Rundel, and Stebbings[7] in a crossed beam apparatus. The quantity experimentally determined in the beam experiment is the ionization reaction cross section of the helium metastables with the crossed neutral beam averaged over the relative velocity distribution of the interacting particles. The velocity distribution of the metastable atoms in this experiment has been discussed in detail.[7,35] The distribution is non-Maxwellian and somewhat above room temperature. For the purpose of comparison, we will relate the beam results to cross sections derived from our data at 300 and 800 °K. We feel that our cross sections at 800 °K would yield a relative velocity of interacting particles which would more nearly correspond to that found in the beam experiment. These cross sections, along with the corresponding values from the crossed beam experiments, are listed in Table II. Our cross sections measured at
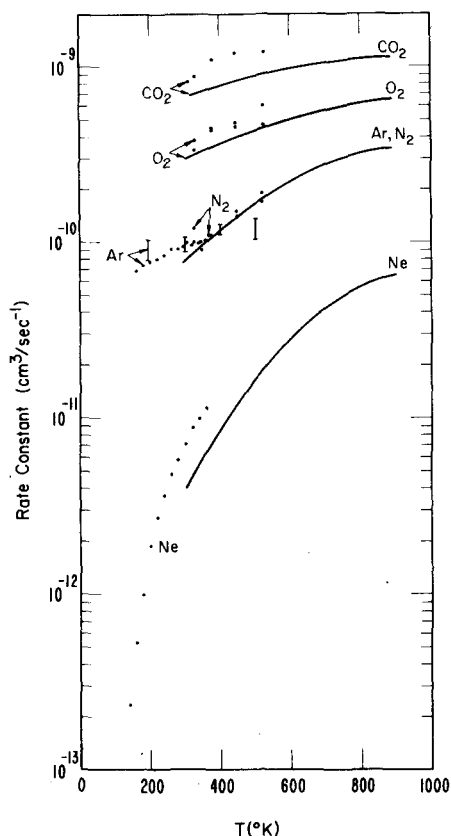
FIG. 3. Comparison of experimental results obtained over a range of temperatures for the quenching of the 2^3S state of helium by various gases. The rate constants obtained from the present measurements are shown as solid lines, the results of Cher and Hollingsworth[22] for N_2, O_2, and CO_2 are shown as closed circles (•), the results of Arrathoon[18] for Ar and Ne are shown as open circles (O), and the results of Jones and Robertson[24] for argon are shown as the vertical bars (I).

800 °K are obviously in much better agreement with the beam results than are the cross sections at 300 °K. In the worst case, He(2^3S) reacting with CO_2, the afterglow results are 24% smaller than the beam cross section while, on the average, the afterglow results are 12% smaller than those obtained from the beams. The present comparison indicates that the most probable source of the systematic differences between beam results and afterglow results for these reactions is associated with differing velocity distributions of the interacting particles in the two experiments.

There are systematic differences which have occurred among beam experiments owing to the technique used to calibrate the concentration of helium metastables in the beam. This is discussed in Ref. 7. For this reason, we will not attempt a systematic comparison of our measurements. It is worth noting, however, that in Ref. 9 the velocity dependence of the total ionization cross section of argon atoms by metastable He atoms was obtained. These results indicated that the cross section increases by perhaps 30% between 0.02 eV and 0.4 eV. The flowing afterglow results indicate a cross section which would increase much more sharply for the He(2^3S) reaction with argon. Since there was no provision for quenching the He(2^1S) state in this beam ex-

periment, it was presumably present in indeterminate quantities. We suggest that in this experiment[9] the He(2^1S) state is present in appreciable quantities and that the cross section increases much more slowly for the reaction of He(2^1S) with argon than does that of He(2^3S). This is, in fact, required if the ratio of singlet to triplet cross sections measured at 300 °K in the flowing afterglow $(\sigma_S/\sigma_T = 3.01)$[21] are to agree with the beam results $(\sigma_S/\sigma_T = 1.34)$.[7]

DISCUSSION

Figure 2 shows that the rate constants increase rapidly with temperature. The rate of increase is largest for the atoms and diatomic molecules of smallest polarizability which have the smallest reaction rate constants for He(2^3S) at 300 °K. To further clarify the nature of this variation, the measurements are plotted as a function of $1/T$ in Fig. 4. All the molecules studied yield reasonably straight lines in this Arrhenius plot. This effect was first observed by Cher and Hollingsworth.[22] Such a behavior is characteristic of a reaction that requires a small activation energy, ΔE_x. We may, in fact, adequately express the entire set of rate constants measured in the present series by

$$k_x(T) = 1.9 \times 10^{-9} \exp\left(-\frac{\Delta E_x}{0.057} - \frac{\Delta E_x}{RT}\right) \text{ cm}^3/\text{sec}, \quad (2)$$

with ΔE_x in eV. The appropriate values of ΔE_x for the various molecules studied are listed in Table III. Equation (2) has the interesting property that a reaction rate constant is determined by only one adjustable parameter, ΔE_x. Thus, from a measurement at a single temperature, ΔE_x is determined and thereby the approximate rate constant over a range of temperatures near thermal (i.e., 273–900 °K). We make use of this property to calculate ΔE_x for a variety of other reactions which were studied in our earlier measurements.[21] These values of ΔE_x are also listed in Table III.

Since the present results were measured over a limited range of temperature and there is some scatter in the data, it should be stressed that the fit to experiment offered by Eq. (2) is by no means unique. These curves may be fit equally well by an expression

$$k_r = A T^m e^{-\Delta E_x/kT}, \quad (3)$$

TABLE II. Comparison of He (2^3S) quenching cross sections σ_{300} and σ_{800} calculated from the measurements at 200 °K and 800 °K from this work with cross sections σ_b measured in a beam experiment by Riola et al.[7] (All values in Å².)

Reactant	σ_{300} (This work)	σ_{800}	σ_b (Ref. 7)
N_2	5.3	13.3	15.5
Ar	5.4	13.6	16.9
Xe	9.8	19	20.0
O_2	19	28	29.4
CO_2	50	48	63
H_2	0.94	3.25	3.34[a]
Error	< 30%	< 30%	20%–25%

[a]See A. Niehaus, Berichte der Bunsen-Gesellschaft, Fortschr. Phys. Chem. 77, 633 (1973).
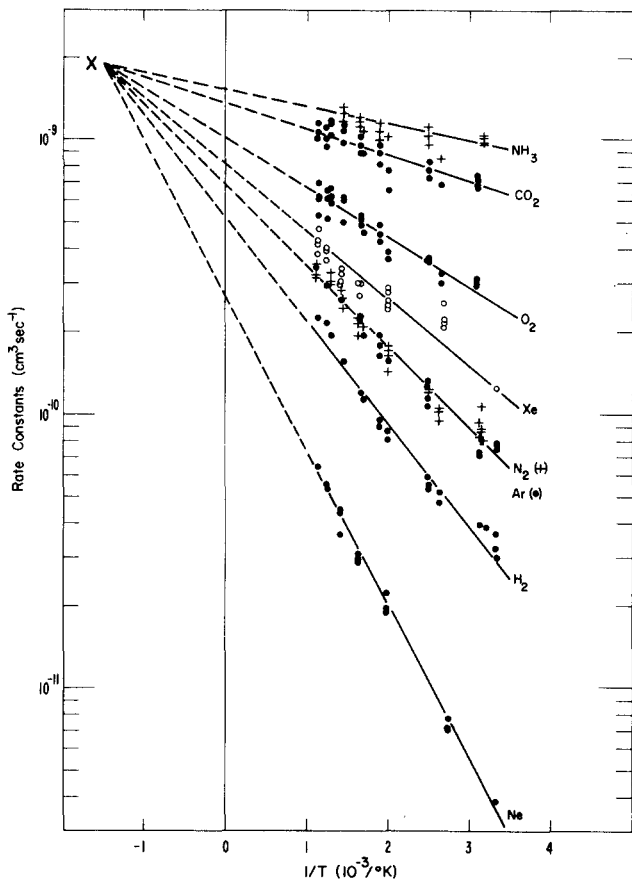
FIG. 4. Arrhenius plot of the de-excitation rate constant for He (2³S) by various gases as a function of $1/T$.

TABLE III. Values of the activation energy ΔE_x for the quenching reactions of He (2³S) with various neutrals X.

(a) Present measurements		(b) Predicted values[a]	
X	ΔE_x (in mV)	X	ΔE_x (in mV)
Ne	112	Kr	53
Ar	59	CO	53
Xe	48	NO	37
H_2	72	D_2	76
N_2	59	CH_4	47
O_2	36	N_2O	28
CO_2	19	C_2H_6	37
NH_3	12	C_3H_8	34
		C_4H_{10}	28

[a]The predicted values were obtained by solving Eq. (2) from the results of Ref. 21.

molecules can only be obtained from scattering data. Very recent measurements using beam techniques have shown that there are cases where each of the above models may be applicable.[36-38]

Figure 5 plots ΔE from Table III vs the diameter of the reactant particle. This graph is shown to illustrate how well, in general, ΔE is correlated with diameter. Of course, the diameter is related to many other molecular properties such as polarizability, and this graph illustrates a correlation for them as well. We attach no particular significance to this graph but include it to stimulate some thought about this problem by others.

CONCLUSIONS

In the present series of measurements, the de-excitation rate constants for the 2³S state of helium by Ne, Ar, Xe, H_2, N_2, O_2, CO_2, and NH_3 have been determined as a function of temperature between 300 and 900 °K. These rate constants are found to increase with temperature with the dependence being the strongest for the simplest, least polarizable atoms and molecules (Ne,
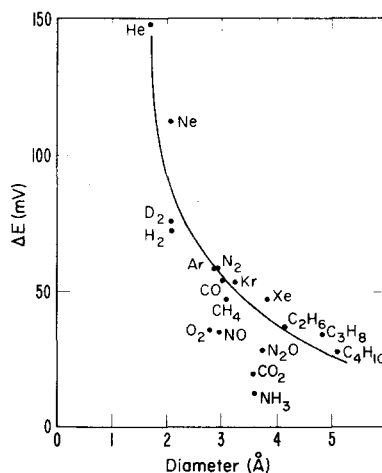
where A is a temperature independent constant and $0 \lesssim m \lesssim 0.2$. As m is increased to obtain the best fit to the data, the value of ΔE_x must be somewhat reduced. It should be noted that $m = 0.5$ (hard sphere collision) would not properly fit the data as shown in Fig. 4.

From the semiclassical theories that have been used to describe metastable reactions, there are two obvious ways to rationalize the behavior exhibited by these reactions in Fig. 4. In one case, it is possible that a barrier exists in the potential surfaces for the interacting particles. Outside this barrier, the probability for reaction is small. For the particles that are able to surmount the barrier, the probability of reaction is large. In this case, the ΔE's given in Table III are associated with the height of the potential barrier.

Alternatively, it is possible that the reaction probability is a strong function of internuclear separation increasing rapidly at small internuclear separation. At small internuclear separations, these potential surfaces become strongly repulsive. With increasing kinetic energy the particles are able to approach more closely against this core repulsion, resulting in increased reactivity.

The data presented in this paper cannot be used to determine which of the two models described briefly above is correct (or if, indeed, either or a combination of the two is correct). The true nature of the model that does describe the de-excitation of He(2³S) with atoms and

FIG. 5. Plot of the activation energy ΔE measured for the reaction of He (2³S) with various molecules vs molecular diameter. The molecular diameters were calculated from the viscosities in the Matheson Gas Data Book.[39]

H_2). It was discovered that within the limited temperature independent pre-exponential factor coupled to a temperature dependent exponential factor which is commonly associated with an activation energy and which decreases with increasing molecular size and polarizability.

The present observations offer a reasonable explanation for the observed difference in measured or inferred rate constants yielded by thermal (300 °K) afterglow experiments and near thermal beam experiments. None of the existing theories proposed *a priori* predict the behavior of the rate constants observed in the present experiment and shown in Figs. 2 and 4. However, by a suitable selection of reasonable hypothetical interaction potentials (and reaction resonant width), the semiclassical theories can generate cross sections that reproduce the present results over the limited range studied.

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