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COMPARISON OF NUMERICAL CAPTURE CROSS SECTIONS WITH EXPERIMENTAL REACTION CROSS SECTIONS FOR $NH_3^+ + NH_3$

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ABSTRACT

Numerically calculated capture cross sections σ_c are compared with Ryan's experimental reaction cross sections for $NH_3^+ + NH_3$ $NH_4^+ + NH_2$. The numerical reaction cross section $\sigma_R = 0.6\ \sigma_c$ is obtained assuming that vibrationally excited NH_3^+ do not react. Theory and experiment agree satisfactorily from thermal energy to nearly 1 eV although their slopes are slightly different and both steeper than Langevin.

INTRODUCTION

Experimental cross sections have been reported by Ryan[1] for the NH_3-parent ion reaction at low ion energies where:

$$NH_3^+ + NH_3 \longrightarrow NH_4^+ + NH_2$$

The purpose of this note is to compare the numerically calculated capture cross sections with Ryan's experimental results. These numerical capture cross sections for ion-dipole collisions have been obtained by solving many randomly generated trajectories,[2,3] These capture cross sections should set upper limits to reaction cross sections in the region where rotational quantum numbers are large so that classical approximations are valid. Chupka[4] has shown that NH_3^+ in higher vibrational states react less efficiently to produce NH_4^+. Ryan reports that the vibrational distribution of NH_3^+ species in his experiment is such that the observed reaction cross section should be only 60% of the capture cross section,[5] (assuming that the reaction efficiency for unexcited ions is unity). In the region of ion energy from thermal to one eV the permanent dipole plays a dominant role in determining the capture cross section.[2,3] Thus, one should not expect the Langevin formula to predict accurate values or slope for the capture cross section.

EXPERIMENTAL REACTION CROSS SECTIONS

In Ryan's studies[1] an applied repeller voltage sets an upper limit to the ion energy at the exit. At exit energies ϵ_m somewhat greater than thermal (0.3 to 4 eV) the reaction cross section is obtained from the measured rate coefficient k by the relation $\sigma = k/\langle v \rangle$ where $\langle v \rangle = (2\bar{\epsilon}_1/ m_r)^{1/2}$; $\bar{\epsilon}_1$ is the average ion energy $= \epsilon_m/4$ and m_r is the reduced mass. Because of the uncertainties about the ion energy distribution in the thermal region[6] the experimental cross section for thermal energy is herein obtained both from the Maxwell averaged results and by extrapolation of the higher energy results to the thermal region.

MONOENERGETIC NUMERICAL CROSS SECTIONS

The numerical capture cross sections σ_c are obtained from the capture ratio C_R which is the fraction of collisions in which the ion and molecule approach within a specified separation (2Å was used for all calculations in this paper).[2] The capture ratios for $NH_3^+ + NH_3$ are plotted against the square of the impact parameter in Fig. 1 for 3 different ion velocities. Fifty trajectories were calculated for each point. The higher ion velocities correspond to ion energies of 0.2 and 0.8 eV; the lower velocity corresponds to relative thermal energy. These C_R values are obtained for the same random number sets; it has been shown that the variation of cross sections with random number sets is within 20%. The simple step function behavior which would be expected for Langevin capture collisions with NH_3 is shown for comparison at $b = b_L$. The corresponding monoenergetic cross section σ_c is simply π times the area under the curve of C_R against b^2. This cross section is plotted against relative translational energy ϵ in Fig. 2. The experimental cross section σ_{exp} and Langevin cross section σ_c (using NH_3 polarizability = 2.26 Å$^{3)}$ are plotted for comparison.

COMPARISON OF RESULTS

The numerical capture cross section σ_c has a slope $\epsilon^{-0.69}$ whereas the experimental cross section has a steeper slope $\sim\epsilon^{-0.78}$. Ryan obtained a reaction rate coefficient of 18.1×10^{-10} cm^3 sec^{-1} at 350 K which corresponds to a cross section $\sigma_{exp} = 181$ Å^2 (1.81×10^{-14} cm^2) for an average velocity of $(8kT/\pi m)^{1/2} = 9.5 \times 10^4$ cm sec^{-1} ($\epsilon = 0.030$ eV). This σ_{exp} value is only slightly lower than the extrapolated value of 185 Å^2. A theoretical value of the thermal collision coefficient $\langle\sigma_c v\rangle$ can be obtained by integrating the monoenergetic σ_c over a Maxwellian distribution at $T = 350$ K. The expression for the capture collision coefficient is

$$\langle\sigma_c v\rangle \approx 10^{-8} \int_0^\infty (\sigma_o)_c \, \epsilon^n \, e^{-\epsilon/kT} \, d\epsilon \qquad (1)$$

where $(\sigma_o)_c = 33 \text{ Å}^2 \, (\mathrm{eV})^{n'}$

$n = 1 - n'$ and n' describes the power dependence of the numerical cross section, i.e., $\sigma_c = (\sigma_o)_c \, \epsilon^{-n'}$. The n' is 0.69 for σ_c and 0.78 for σ_{exp}. The integral of Eq. (1) is

$$\langle\sigma_c v\rangle \approx 10^{-8}(kT)^{1.3} \, (\sigma_o)_c \Gamma(1.3) = 3.3\text{x}10^{-9} \text{ cm}^3 \text{ sec}^{-1}. \qquad (2)$$

where $\Gamma(1.3)$ is the gamma function and $kT = \epsilon = 0.030$ eV. For thermal velocity, $\langle v\rangle = 9.5\times10^4$ cm sec^{-1}, this corresponds to a cross section $\sigma_c \approx 347 \text{ Å}^2$ or a theoretical reaction cross section of 208 Å^2 (using $\sigma_R = 0.6 \, \sigma_c$). This latter value is about 13% larger than the extrapolated experimental cross section which is satisfactory agreement.

The experimental reaction cross section of Fig. 2 is 0.45 to 0.50 of the numerical values over the range of relative energy shown. The ion-dipole interaction is the chief potential term over this range. This cross section ratio is in satisfactory agreement with the reaction efficiency factor of 0.6,[6] although the slope of σ_{exp} is a little steeper than for σ_c.

CONCLUDING REMARKS

The numerically calculated capture cross sections for NH_3^+ on NH_3 are in good agreement with experimental values in the low energy region from thermal to several eV if a constant reaction efficiency is used. The dependence of the cross section on relative translational (or ion) energy is also in satisfactory agreement with the experimentally observed $\epsilon^{-0.78}$. Fortuitous agreement between Langevin theory and experiment suggests that the reaction efficiency masks the role which the permanent dipole plays in the capture mechanism. Better agreement could be obtained if the reaction efficiency were known as a function of relative energy. Earlier experiments suggested that the σ_{exp} values were Langevin-like.[7] Although the dipole term determines the capture cross section the absolute value of this cross section is considerably less than the maximum capture cross section and coincidentally near the Langecin capture cross section. This behavior has been discussed for other polar targets in mass spectrometry.[2,3]

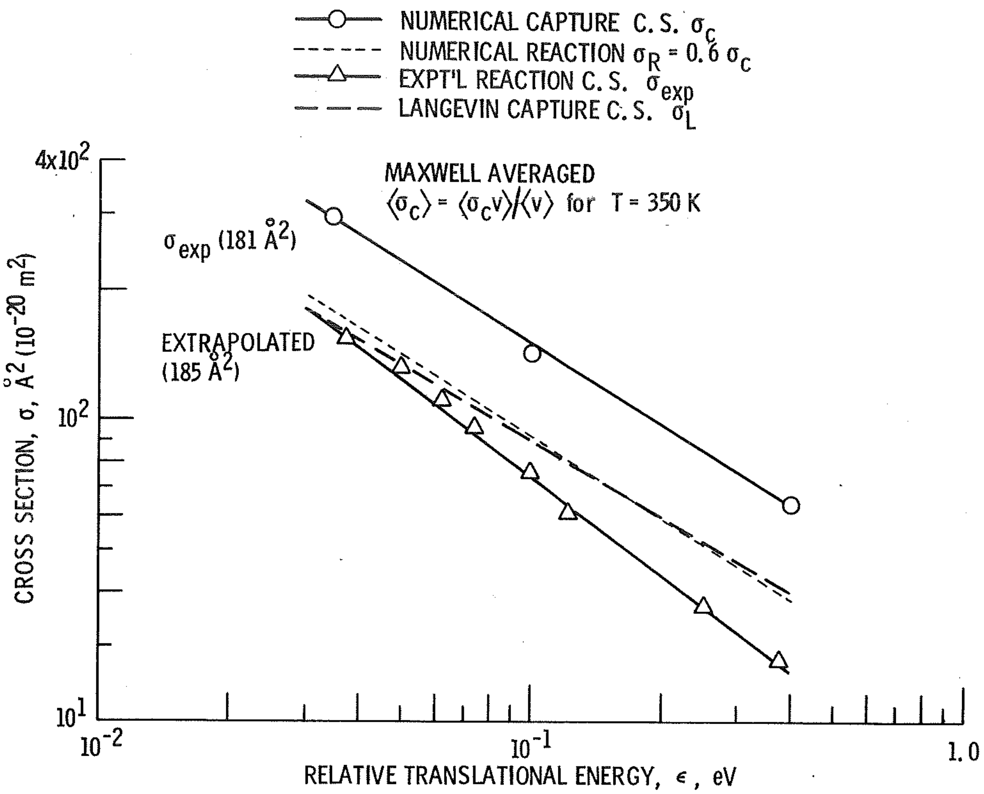

Figure 2. - Variation of numerical, experimental and Langevin capture cross sections with relative (ion-molecule) translational energy for $NH_3^+ + NH_3$ capture and reactive collisions.

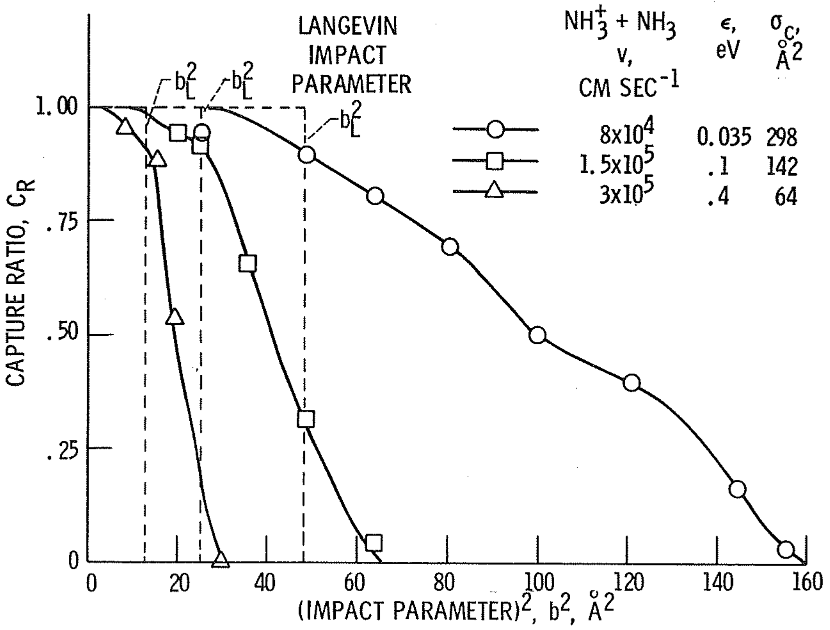

Figure 1. - Variation of capture ratio with impact parameter for $NH_3^+ + NH_3$ capture collision at 3 ion velocities. Target rotators are chosen from a heat bath at 350 K.

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