



Rates of some reactions of N(2 D and 2 P) near 300 K

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where $N_{eq} = \int_a^R dr r^{d-1} P_{eq}(r)$. For example, Weaver⁴ has recently considered the one-dimensional problem j(R, t) = 0, $P(a, t) = [\kappa (R-a)]^{-1} \int_0^t dt' D(\partial P/\partial x)_{x=a}$ with D constant and U=0. One can find $P_{eq} = [(1+\kappa)(R-a)]^{-1}$ and $\tau = [\kappa/(1+\kappa)](R-a)^2/3D$ by direct integration and avoid the need to solve⁴ a second order differential equation with mixed boundary conditions.

Finally we note that this method can also be employed to advantage for other stochastic models where approximate relaxation times are sought for nonequilibrium decay. An example is provided by the discrete Master equation $\mathbf{\hat{P}}(t) = \mathbf{W} \cdot \mathbf{P}(t)$ where $P_n(t)$ is the probability of being in state *n* at time *t* and $N(t) = \sum P_n(t)$. With $\delta \mathbf{P}$ = $\mathbf{P}(0) - \mathbf{P}_{eq}$ where $\mathbf{W} \cdot \mathbf{P}_{eq} = 0$, the result⁵ for the mean passage time, Eq. (11) is

$$\tau = [\mathbf{l}^{\mathrm{T}} \cdot \mathbf{W}^{-1} \cdot \delta \mathbf{P}] [\mathbf{l}^{\mathrm{T}} \cdot \delta \mathbf{P}]^{-1} , \qquad (12)$$

Here I^T is the unit column vector.

This result can be used to advantage to describe ap-

proximate exponential relaxation for discrete or continuous⁶ master equation systems.

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Rates of some reactions of $N(^{2}D \text{ and } ^{2}P)$ near 300 K^{a)}

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Laboratory studies of quenching and reaction processes of the lowest N metastables have been reported since 1969 when Black *et al.*¹ used the vacuum ultraviolet photolysis of N₂O to infer N(²D) quenching rates. Resonance line absorption detection of both N(²D) and N(²P) as well as O(³P) in flow tube experiments allowed us² to establish that reaction rather than quenching was the principal channel for the interaction of N(²D) with O₂, CO₂, and N₂O. Other rate measurements have since been reported.³⁻⁸

These processes are of great importance in the upper atmosphere, because the reaction with O_2 , e.g., $N(^2D)$ $+O_2 \rightarrow NO + O(^3P) + 3.8 \text{ eV}$, is a major source of NO both in the normal and perturbed thermosphere, and also because it leads to substantial vibrational excitation of NO and consequent infrared emission.⁹

The present, brief study was undertaken primarily to reduce the uncertainties in the measurements of the $N(^{2}D, ^{2}P)$ reactions with O_{2} by use of resonance fluorescence detection of the metastables. An attempt was also made to resolve the discrepancy between the single laboratory value of 1.8×10^{-12} cm³ s⁻¹⁸ and the lower range of $(1-6) \times 10^{-13}$ deduced from airglow intensity data¹⁰⁻¹² for the rate constant of $N(^{2}D)$ quenching by $O(^{3}P)$.

The simple flow tube apparatus is similar to that used in our earlier study, 2 the principal differences being (a) a faster pumping line consisting of a Roots blower (Heraeus Model RG-350) backed by a mechanical pump (Stokes, Model 148-H) that allows the use of a larger diameter flow tube (2.5 cm i.d.) and (b) a stainless steel cell at the entrance slit of the vacuum monochromator (Jarrell Ash, 0.5 m, Model 84-110) that allows resonance fluorescence as well as absorption measurements to be made using combinations of microwave discharge lamp and filters as described below. For the $N^* + O_2$ experiments, the excited species were generated 26 cm upstream of the detector in a microwave discharge (Raytheon Microtherm, 2450 MHz) using a stabilized power supply¹³ and Evenson cavity. Ar or He carrier gas at about 3 Torr containing about two percent N_2 was used. O_2 was added through a fixed loop injector 14 cm upstream of the detector at concentrations of 10^{13} to 10^{14} cm⁻³, diluted with approximately 15% of the total carrier gas flow ($\sim 60 \text{ cm}^3 \text{ atm s}^{-1}$) in order to aid rapid mixing. Reaction times ranged from 2.5 to 5 ms.

In the $N(^{2}D) + O(^{3}P)$ experiments, variable amounts of NO were added 68 cm upstream of the fluorescence cell to discharged two percent N₂-Ar mixtures at 3 to 3.5 Torr. 48 cm farther downstream, a similarly discharge Ar-N₂ stream entered the flow tube carrying the $N(^{2}D)$ reactant. Roughly equal flows passed through both branches so that the flow velocity in the upstream length was half that in the reaction zone. N-metastables from the upstream discharge had decayed by wall or gas reac-

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I his article is copyrighted as indicated in the article. Reuse of AIP content is subject to the terms at: http://scitation.aip.org/termsconditions. Downloaded to IP: 130.113.76.26 On: Mon, 24 Nov 2014 17:42:51 tion before the mixing point.

The resonance lamp was a microwave discharge in He at 2 Torr containing a trace of N₂. Its excitation cavity was placed 1.3 cm from its MgF₂ window. A second window or filter was placed between lamp and cell in order to isolate the 149.2 nm (Acton Research band rejection filter) or 174.2 nm (Suprasil-2 Quartz, cutoff filter) excitation wavelength, since both transitions reach a common upper state, $2p^2 3s^2 P$. This allowed detection of the fluorescence signal at a wavelength other than that used in excitation and reduced the scattered light signal. Detection limits were $\sim 5 \times 10^8$ to 1×10^9 cm⁻³.

Three sets of experimental results are reported. The first deals with pseudo-first-order rate constants of $N(^{2}P)$ decays obtained by moving the discharge cavity along the flow tube, thereby varying reaction time from ~4 to 16 ms at Ar pressures from 7.2 to 15.3 Torr. The linear plot of kp vs p^2 (see Ref. 2) gives an intercept that corresponds to a diffusion coefficient of 230 $\text{cm}^2 \text{ s}^{-1}$ for $N(^{2}P)$ in Ar at 1 Torr, in good agreement with measured values for $N(^{4}S)$, ¹⁴ and a slope that corresponds to a rate constant for quenching of $N(^{2}P)$ by Ar of 4×10^{-16} cm³ s⁻¹. This value is lower than that reported earlier, 2 7×10⁻¹⁶, but must still be regarded an upper limit because of possible contributions by fast-quenching impurities whose concentration will increase with increasing pressure, and because the radial flow distribution (see below) will lower the slope of the kp vs p^2 plot.

The principal findings are those of the $N^* + O_2$ rate experiments. These were carried out both in He and in Ar carrier gas in order to shed light on the parabolic flow correction. In fully developed laminar flow, with efficient surface removal of the metastables, the measured plug flow rate constant, $k^* \equiv (\overline{v}/a)d\ln[X]/d[O_2]$, where \overline{v} is the average flow velocity, and a = 14 cm is the length of the reaction zone, must be multiplied by 1.62.¹⁵ The establishment of the parabolic velocity distribution from an initially constant $v = \overline{v}$ is characterized by a calculated transition length, ¹⁶ $l=0.227 r_0 R_e$, where r_0 is the tube radius and R_e the Reynolds number. Under our experimental conditions, l=6 cm for He and 53 cm for Ar. In that length the transition to laminar flow is virtually complete, i.e., $v_0 = 1.98\overline{v}$ whereas $v_0 = 2\overline{v}$ for laminar flow, where v_0 is the velocity at the center of the tube. For experiments with He carrier gas, the parabolic profile should be established very quickly and the full 1.62 correction factor applies. For Ar, however, the reaction zone is only $\sim l/4$, the calculated¹⁶ v_0 equals 1.8 \overline{v} at the detector, and the average value of v_0 along the reaction zone is ~1.6 \overline{v} . With a rough, linear interpolation, the correction factor for the rate constant would be 1 $+0.6 \times 0.62 = 1.37$. In our earlier work,² we had suggested 1.3 ± 0.3 in order to encompass the entire range.

Six experiments for $N(^2D) + O_2$ in He gave $k^* = (3.17 \pm 0.22) \times 10^{-12}$ cm³ s⁻¹ where the uncertainty is 1 σ of the random errors. Reaction times were varied from 2.8 to 4.3 ms, and the pressure was 2.9 to 3.2 Torr. The corrected k is 1.62 $k^* = (5.14 \pm 0.36) \times 10^{-12}$ cm³ s⁻¹. Six experiments in Ar gave $k^* = (4.01 \pm 0.23) \times 10^{-12}$, t = 2.7 to 4.8 ms, p = 2.9 to 3.1 Torr, which is multiplied by 1.37 to give $(5.49 \pm 0.32) \times 10^{-12}$ cm³ s⁻¹, in good agree-

ment with the He value.

Four experiments for $N({}^{2}P) + O_{2}$ in He gave $k^{*} = (2, 16 \pm 0.08) \times 10^{-12}$, corrected to $k = (3, 50 \pm 0.13) \times 10^{-12}$ cm³ s⁻¹. Twelve experiments in Ar gave $k^{*} = (2, 57 \pm 0.12) \times 10^{-12}$, t = 2.5 to 4.8 ms, b = 2.3 to 2.8 Torr, corrected to $(3, 52 \pm 0.12) \times 10^{-12}$ cm³ s⁻¹, in excellent agreement with the He value. It is particularly encouraging to note the improved agreeement when the transition length factor¹⁶ is introduced.

For the $N(^2D) + O_2$ reaction, published values of k are 7, $^1 6 \pm 2$, $^2 7.4$, $^3 9.3 \pm 2.2$, $^4 5.2 \pm 0.4$, 5 and $(5.8 \pm 0.5) \times 10^{-12}$. ⁸ The last two are in excellent agreement with our average $(5.3 \pm 0.5) \times 10^{-12}$ cm³ s⁻¹. For $N(^2P)$, the agreement is poorer; 4.6 ± 2.5 , $^4 2.6 \pm 0.2$, 5 and ≤ 2 , 6 compared to our $(3.5 \pm 0.13) \times 10^{-12}$ cm³ s⁻¹. Inclusion of systematic errors will increase our error limits to about $\pm 15\%$ (1 σ).

The results of three $N(^{2}D) + O$ rate measurements, although consistent, are much more difficult to interpret. Since the maximum attainable O atom concentration was only $\sim 7 \times 10^{13}$ cm⁻³, the corresponding $\ln[N(^2D)]$ vs $\left[\text{NO}\right]_{added}$ plots showed small decreases (~25%-30%) for the required short reaction times. For NO additions past the titration end point, the $N(^{2}D)$ fluorescence signal turned sharply lower due to the much faster N and N* + NO reactions. The early, linear decays gave values of 1.6, 1.8, and 2.1×10^{-12} cm³ s⁻¹ for the desired rate constant. This result is in good agreement with the only published value, $(1.8 \pm 0.6) \times 10^{-12}$, by Davenport *et al.*⁸ It must be emphasized, however, that our measurements cover a very small dynamic range and may only represent an upper limit to the true value of this important rate coefficient.

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