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THREE-BODY REACTIONS (*)

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RÉSUMÉ. — *Le système de décharge est la technique expérimentale qui se révèle la plus utile pour l'étude des réactions aéronomiques par collisions triples. On indique d'abord quelles sont les valeurs numériques des constantes de vitesses des réactions par collisions triples conduisant à la formation de l'azote et de l'oxygène moléculaires, de l'ozone, de l'anhydride carbonique et des oxydes d'azote NO et NO_2. En même temps, on a indiqué quelle est la fraction allant de 0,001 à 0,05 qui se présente sous forme d'émission lumineuse au cours de la réaction globale. Le mécanisme conduisant à une émission est presque toujours lié à l'existence d'un état intermédiaire au cours de la réaction. Les réactions présentant de l'importance dans la haute atmosphère sont celles où interviennent l'oxygène moléculaire et l'ozone car elles fixent les concentrations atmosphériques. La présence des bandes de la molécule NO dans un spectre de la lumière nocturne d'une planète peut servir d'indicateur parfait de la présence d'azote atomique. Les réactions par collisions triples qui se manisfestent dans le spectre du ciel nocturne sont à la fois la recombinaison de l'oxygène atomique en oxygène moléculaire et la recombinaison de l'oxygène atomique et de l'oxyde d'azote.*

L'excitation de la radiation verte à 5577 Å exige une collision entre un atome et une molécule d'oxygène excitée comme processus intermédiaire. Les travaux expérimentaux ont déjà fourni beaucoup d'éléments destinés aux applications aéronomiques, mais ils sont limités dans le cas des réactions lumineuses par suite de l'utilisation des pressions nettement supérieures à celles de la haute atmosphère.

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ABSTRACT. — *The experimental technique most useful in studying upper atmosphere three-body reactions is the discharge flow system. The overall reaction rate coefficients of three-body reactions forming molecular nitrogen, nitric oxide, oxygen, nitrogen dioxide, carbon dioxide, and ozone are tabulated. The rate coefficients of three-body reactions that lead to the emission of light have values between 0.001 and 5 % of the overall rate coefficients. The reaction mechanisms that lead to light emission almost always involve an intermediate state. Recent experimental evidence challenges the necessity of a collision in converting the intermediate state into the light-emitting state. The only three-body reactions that are important in determining the particle density in the earth's upper atmosphere are the reactions that form molecular oxygen and ozone. The presence of nitric oxide bands in the night airglow of a planet is a sensitive test of the atomic nitrogen density. Three-body reactions that contribute to the night airglow of the earth are the recombination of atomic oxygen to form molecular oxygen and the recombination of nitric oxide and atomic oxygen to form nitrogen dioxide.*

The excitation of the 5577 A line requires a collision between an oxygen atom and an excited oxygen molecule as an intermediate step. Laboratory experiments have provided overall rate coefficients that are useful in upper atmosphere calculations, but many of the laboratory measurements of the chemiluminescent reactions are inapplicable because of their having been conducted at pressures that are higher than the upper atmosphere pressures.

Author

Резюме. — Система разряда является экспериментальной техникой проявившейся самой полезной для изучения аэрономических реакций по тройным столкновениям. Сначала показывается какими являются цифровые величины постоянных скоростей реакций по тройным столкновениям приводящим к образованию молекулярных азота и кислорода, озона, углекислоты и окислов азота NO и NO_2. В то-же время приведена фракция простирающаяся от 0,001 да 0,05 которая появляется под видом светового излучения в течении реакции. Реакции представляющие важность в высокой атмосфере являются теми в которых принимают участие молекулярный кислород и озон потому что оне определяют атмосферные концентрации. Присутствие линии молекулы NO в спектре ночного свечения планеты может служить отличным указателем присутствия атомного азота. Реакции по тройному столкновению которые обнаруживаются в спектре ночного свечения являются одновременно рекомбинацией атомного кислорода в молекулярный кислород и рекомбинацией атомного кислорода и окиси азота. Возбуждение зеленого излучения в 5577 Å требует столкновения между атомом и молекулой кислорода возбужденной во время промежуточного процесса. Экспериментальные работы уже дали много элементов предназначенных для аэрономических применений, но они ограничены в случае световых реакций вследствии использования давлений значительно больших чем в высокой атмосфере.

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Introduction

When the atoms in the upper atmosphere recombine, the recombination takes place through a three-body reaction in many cases. The third body is necessary to enable the reactants simultaneously to conserve both energy and momentum. The details of the recombination depend upon the potential energy curves of the individual molecules that are accessible to the recombining atoms. Three-body recombinations that are of interest in the earth's upper atmosphere lead to the formation of molecular oxygen, molecular nitrogen-nitric oxide, ozone, nitrogen dioxide, and carbon dioxide. These reactions will be discussed here. It will turn out that one of the most important aspects of three-body reactions are the two-body reactions that accompany them.

It is the intention of this review initially to discuss laboratory experimental technique, then to review the laboratory results on overall reaction rates, to examine in detail the three-body reactions that lead to the emission of light, and finally to apply the laboratory results to the earth's upper atmosphere and the night airglow. This review takes advantage of there being two reviews on the experimental work on atomic oxygen reactions by Kaufman (1961) and Kaufman and Kelso (1961). In addition, there recently have been published the proceedings of a discussion of the Faraday Society (1962) devoted to inelastic collisions of atoms and simple molecules and a symposium arranged by the Stanford Research Institute (1961) on chemical reactions in the lower and upper atmosphere.

Experimental technique

An experimental technique that is particularly useful in measuring overall reaction rates of three-body recombinations is the discharge flow system. A typical arrangement is depicted in figure 1. A molecular gas is pumped at low pressure through an electrical discharge which in many cases is generated by microwaves. The atoms that are produced in the discharge are pumped down the reaction tube. In some experiments a second gas is added to the atom stream through a titration inlet. For three-body reactions that produce light, the rate of decay of the atoms in the reaction tube may be measured with a combination of photomultiplier tubes and filters that may be moved the length of the tube. The emission of

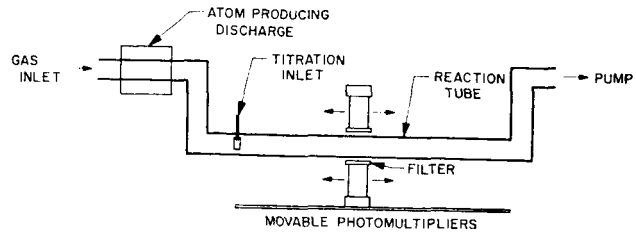

Fig. 1. — Discharge flow system. Atoms are produced in a discharge at low pressures and pumped through the reaction tube. The rate of decay of the light emission from the recombining atoms is measured by the movable photomultipliers.

the first positive bands of molecular nitrogen have been used to measure the recombination rate of atomic nitrogen (Harteck et al., 1958*a*). Since the emission of the nitric oxide beta bands is proportional to the product of the atomic nitrogen density and the atomic oxygen density, while the intensity of the first positive bands is proportional to the square of the nitrogen atom density, the ratio of the beta bands to the first positive bands gives the ratio of the number of oxygen atoms to the number of nitrogen atoms. The simultaneous observation of these two emissions permits the measurement of the three-body recombination of atomic nitrogen to form molecular nitrogen, atomic nitrogen and oxygen to form nitric oxide, and atomic oxygen to form molecular oxygen over a wide range of experimental conditions (Barth, 1961*a*). The reaction between nitric oxide and atomic oxygen which produces a green afterglow has been used to measure both the rate of the nitric oxide-atomic oxygen three-body reaction (Kaufman, 1958) and the three-body atomic oxygen reaction (Morgan and Schiff, 1963). Experimental techniques in which the atom disappearance rates are measured using fixed-position, multiple titration nozzles and isothermal calorimetric detectors are reviewed by Kaufman (1961).

Typical dimensions and physical conditions in the laboratory experiments on atom reactions are given in Table 1. The pressure range lies between 0.1 and 10 mm Hg and the diameter of the reaction tube is usually between 10 and 50 mm. The particle densities and collision frequencies for these conditions are shown in Table 1. In order to enhance three-body reactions and minimize wall collisions, the experiments are usually run at pressures that are as high as possible. This necessity leads the laboratory experimenter away from the pressures and phenomena that are appropriate to the upper atmosphere.

In order to determine reaction rates from the

TABLE I

TYPICAL DIMENSIONS AND PHYSICAL CONDITIONS IN LABORATORY EXPERIMENTS ON ATOM REACTIONS.

Pressure	0.1	— 10 mm Hg
Diameter	10	— 50 mm
Particle Densities	3×10^{15}	— 3×10^{17} cm^{-3}
Collision Frequency	3×10^{5}	— 5×10^{7} sec^{-1}
Wall Collision Frequency	2.5×10^{5}	— 5×10^{1} sec^{-1}

measurements of light intensity along the tube, it is necessary to take into account the flow rate and the pressure of the reacting gases. The proper procedure and the limitations on the technique are discussed by KAUFMAN (1961). Another factor that needs to be correctly taken into account when determining a particular reaction rate coefficient is the consumption of the reacting atoms by competing reactions. The usual procedure is to eliminate the competing reactions by experimentally removing the impurities causing the reactions. In many cases, this is neither necessary nor desirable. In the measurement of the three-body reaction between atomic nitrogen and atomic oxygen, eight other reactions involving these species and their products occur concurrently. In situations such as this, it is convenient to write the differential equations describing all nine reacions and integrate them on a high-speed digital computer (BARTH, 1961*a*). The experimentally-determined decay rates of the atoms may be compared to the computer solutions, and the rate coefficients adjusted until satisfactory agreement is obtained. An example of such a calculation is shown in figure 2. The integration was performed for one second of reaction time for a mixture of 2×10^{15} oxygen atoms cm^{-3}, 1×10^{14} nitrogen atoms cm^{-3}, 2×10^{17} nitrogen molecules cm^{-3}, and 5×10^{10} nitric oxide molecules cm^{-3}. The atoms combine, forming molecular oxygen and ozone which participate in the subsequent reactions. The figure also shows the solutions of two analytic approximations to the rate equations and indicates how, to varying degrees, they differ from the correct solution. The computer solutions make it unnecessary for experimental conditions to be made to fit situations for which there are exact analytic solutions.

Figure 2 also illustrates an experimental situation where atomic oxygen reactions may be studied

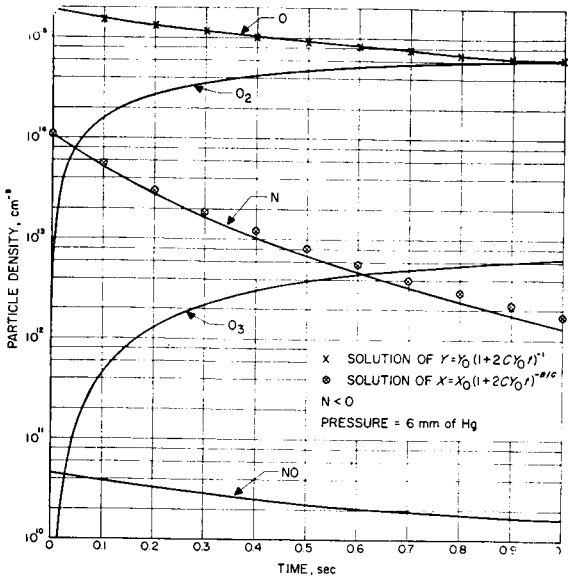

FIG. 2. — Computer solution of reaction rate equations. Six simultaneous differential equations that describe nine reactions were integrated on a high-speed computer. The resulting change of density with time is plotted for each of the atom and molecule species involved. Two approximate analytic solutions are shown for comparison.

without interference from large numbers of oxygen molecules. The 1 % mixture of oxygen atoms in nitrogen molecules are produced by titrating a 1 % mixture of nitrogen atoms in nitrogen molecules with 1 % nitric oxide. The oxygen atoms are formed rapidly while the oxygen molecules and ozone are produced more leisurely. The number of oxygen molecules never exceeds one-half the number of oxygen atoms that were present initially. This technique has been used in the study of the 5577 A line and the molecular oxygen Herzberg bands (BARTH and PATAPOFF, 1962).

An experimental arrangement that is useful in measuring the light emission from three-body reactions is shown in figure 3. The atoms are once again produced in a discharge flow system. They are pumped at low pressure to an observation tube where simultaneous measurements of the

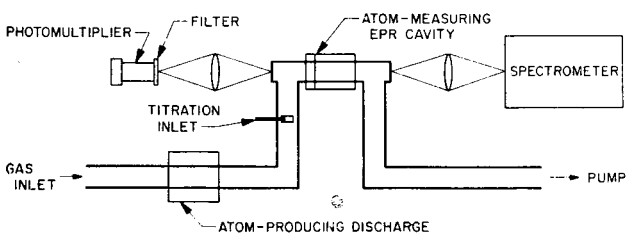

FIG. 3. — Apparatus for the simultaneous measurement of atom density and light emission. The atoms are produced in a microwave discharge and pumped into an observation tube where a simultaneous measurement of the atom density and light emission is made.

atom density and the light emission are made. The optical observations may be made with either a spectrometer or a combination of filters and photomultipliers. In the apparatus shown, the atoms are measured with an electron paramagnetic resonance spectrometer (BARTH et al., 1962). Figure 4 shows the results of the simultaneous

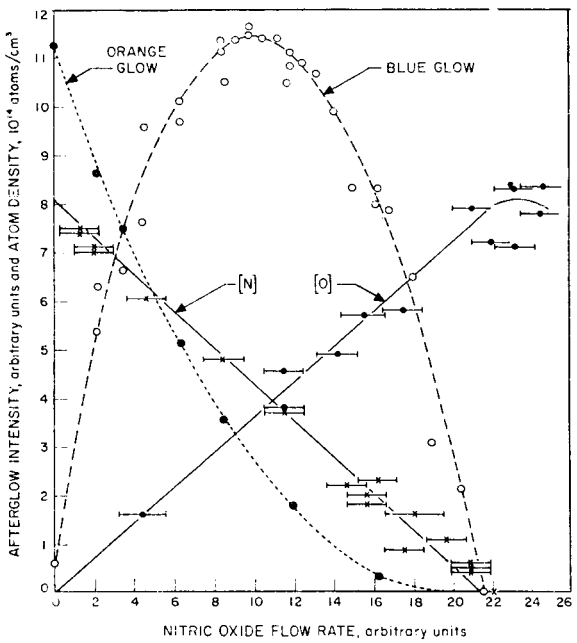

FIG. 4. — Simultaneous observation of atom densities and afterglow emissions. Varying amounts of nitrogen atoms and oxygen atoms were produced by titrating atomic nitrogen with nitric oxide. The atom densities were measured with an electron paramagnetic resonance spectrometer and the nitrogen first positive bands, the orange glow, and the nitric oxide beta bands, the blue glow, were measured with photometers.

observations of the nitrogen first-positive bands, the nitric oxide beta bands, and the density of atomic nitrogen and oxygen when nitric oxide is added to a nitrogen afterglow. The first positive bands are proportional to the square of the atomic nitrogen density and the beta bands are proportional to the product of atomic nitrogen and atomic oxygen (KAPLAN et al., 1960). This technique permits the measurement of intensity vs. atom density over a range of pressures.

Other authors have used titration techniques to measure the atom density while measuring the light output with photomultipliers (see KAUFMAN, 1961).

THREE-BODY REACTION RATES

The rate coefficients of six three-body reactions that are important in aeronomy are tabulated in Table II. The results that are quoted were selected on the basis that, in the view of the reviewer, the experimental technique had the most chance of producing results that would be directly applicable to the upper atmosphere. This has meant experiments that were performed at low temperatures and at pressures that were as low as possible. These criteria have led almost uniformly to experiments using the discharge flow system. The sole exception is the stirred-reactor experiments on carbon monoxide and atomic oxygen by MAHAN and SOLO (1962), where it was thought that because of the temperature range studied the results might be of use in the chemistry of the atmosphere of Venus. Results from experiments using other techniques are reviewed by KAUFMAN (1961).

The table lists several experimental results for each reaction, since each of the reactions has been studied by different workers with a variety of techniques. No attempt is made to evaluate which value is the " best ". All other things being equal, the smallest value may be closest to the value the reaction would have in the upper atmosphere.

The rate coefficients listed are for the rates of atom loss ; thus if,

$$X + X + M \rightarrow X_2 + M, \tag{1}$$

then

$$\frac{d\,[X]}{dt} = -\,2k\,[X]^2\,[M], \tag{2}$$

where k is the rate coefficient in units of cm^6 molecules^{-2} sec^{-1}. The coefficients in Table II are the rate coefficients of the overall reaction that leads to the formation of the molecule, but the coefficient does not specify the electronic, vibrational, or rotational state of the resulting molecule. The pressure range over which the experiment was conducted is listed along with the temperature. The range of these parameters is very limited.

Five three-body reactions that lead to the emission of light are listed in Table III. All of these chemiluminescent reactions are potential contributors to the night airglow of the earth and other planets. The rate coefficients listed in this case are the effective coefficients for light emission. Where the complete interaction proceeds as a three-body reaction, the coefficient is given in units of cm^6 molecules^{-2} sec^{-1} ; and where the interaction is effectively a two-body reaction, the coefficient is given in units of cm^3 molecules^{-1} sec^{-1}. The coefficients are given for

TABLE II

THREE-BODY REACTION RATES. OVERALL RATES AS MEASURED IN THE LABORATORY IN STIRRED REACTOR AND DISCHARGE FLOW EXPERIMENTS. THE PRESSURE AND TEMPERATURE RANGE USED IN THE LABORATORY ARE GIVEN.

	Reaction	Rate coefficient, cm^6 molecules^{-2} sec^{-1}	Pressure, mm Hg range	Temperature, °K	Reference
(1)	$N + N + M \rightarrow N_2 + M$	1.7×10^{-32}	0.5 — 1.3	300	Harteck, et al., 1958*a*
		7.4×10^{-33}	3 — 10	200-450	Herron, et al., 1959.
		1.5×10^{-32}	0.5 — 4	300	Mavroyannis and Winkler, 1961.
		7.0×10^{-33}	5	300	Barth, 1961*a*.
(2)	$N + O + M \rightarrow NO + M$	5.1×10^{-33}	3 — 4	300	Mavroyannis and Winkler, 1961.
		1.6×10^{-32}	5	300	Barth, 1961*a*.
(3)	$O + O + M \rightarrow O_2 + M$	2.7×10^{-33}	0.95 — 1.34	300	Reeves, et al., 1960.
		2.8×10^{-33}	2.3 — 4.8	300	Morgan and Schiff, 1963.
		2.8×10^{-33}	0.4 — 5	300	Kaufman and Kelso, 1961.
		8.2×10^{-33}	5	300	Barth, 1961*a*.
(4)	$NO + O + M \rightarrow NO_2 + M$	6.9×10^{-32}	0.2 — 1.6	300	Kaufman, 1958.
		7.5×10^{-32}	0.62 — 1.11	300	Harteck et al., 1958*b*.
		5.1×10^{-32}	1.21 — 3.05	213-294	Ogryzlo and Schiff, 1959.
		10×10^{-32}	0.5 — 10	300	Broida, Schiff and Sugden, 1961.
		$2.8 \times 10^{-33}\, e^{+\frac{1800 \pm 400}{RT}}$	1 — 2	212-315	Clyne and Thrush, 1962.
		7.5×10^{-32}	1 — 2	293	
(5)	$CO + O + M \rightarrow CO_2 + M$	1.4×10^{-34}	0.86 — 2.69	293	Clyne and Thrush, 1962.
	two-body reaction	1.6×10^{-17} cm^3 molecule^{-1} sec^{-1}	0.2 — 1.5	338-532	Mahan and Solo, 1962
(6)	$O + O_2 + M \rightarrow O_3 + M$	2.8×10^{-34}	0.5 — 5	300	Elias et al., 1959.
		1.1×10^{-34}	0.4 — 5	300	Kaufman and Kelso, 1961.

each of the band systems or continua that were measured. In addition, the fraction of the reactions that result in the emission of light out of the total number of reactions is given. The value varies between 5 % and 0.001 % for the cases listed at an effective pressure of 3 mm Hg. The pressure at which the measurements were made is also listed. In all cases, the absolute intensity calibration was performed by comparing the emission being studied to that of the green continuum from the nitric oxide-atomic oxygen reaction. This reaction has been measured quantitatively by three groups of workers by both chemical and photometric techniques. It should be realized, however, that the fundamental standards for measuring the number of light quanta emitted and for measuring the number of atoms reacting are quite different. Thus, any comparison between the rate for photons emitted to the rate of atoms removed is subject to large systematic errors.

TABLE III

CHEMILUMINESCENT REACTION RATES

	Reaction	Rate coefficient	Pressure range	Fraction of overall rate (3 mm Hg)	Reference
(1)	$N + N + (M) =$ First Positive Bands	1.9×10^{-18} cm^3 sec^{-1}	1 — 12 mm Hg	2.5×10^{-3}	Young and Sharpless, 1963.
(2)	$N + O + M =$ Beta Bands	2.4×10^{-31} cm^6 sec^{-1}	4 mm Hg	5×10^{-2}	Young and Sharpless, 1963.
	$+ M =$ Gamma Bands	2.4×10^{-35} cm^6 sec^{-1}	4 mm Hg	2×10^{-2}	
	$+ (M) =$ Gamma Bands	8.2×10^{-18} cm^3 sec^{-1}	4 mm Hg	2×10^{-2}	
	$+ (M) =$ Delta Bands	1.1×10^{-17} cm^3 sec^{-1}	4 mm Hg	2×10^{-2}	
(3)	$O + O + (M) =$ Herzb rg Bands	3×10^{-21} cm^3 sec^{-1}	.8 — 65 mm Hg	10^{-5}	Young and Sharpless, 1963.
	$O + O + M =$ Atmospheric Bands	1×10^{-37} cm^6 sec^{-1}	.24 — 12 mm Hg	10^{-4}	
(4)	$NO + O + (M) =$ Nitrogen Dioxide Bands and Continuum 3875 — 6200 A	2×10^{-17} cm^3 sec^{-1}	0.2 — 1.6 mm Hg	2.5×10^{-3}	Kaufman, 1958.
		1.7×10^{-17} cm^3 sec^{-1}	1.0 — 4.3 mm Hg	2.5×10^{-3}	Fontijn and Schiff, 1961.
		6.7×10^{-17} cm^3 sec^{-1}	.8 mm Hg	1×10^{-2}	
		$5 \times 10^{-18}\, e^{\frac{+1500}{RT} \pm 400}$			Clyne and Thrush, 1962.
(5)	$CO + O + (M) =$ Flame Bands and	$2.3 \times 10^{-13}\, e^{\frac{-9500}{RT}}$ cm^{3}sec^{-1}	0.2 — 1.5 mm Hg	2.8×10^{-3}	Mahan and Solo, 1962.
	Continuum	$1 \times 10^{-17}\, e^{\frac{-3700}{RT} \pm 500}$	.86 — 2.69 mm Hg		Clyne and Thrush, 1962.

THREE-BODY RECOMBINATION MECHANISMS

All of the reactions listed in Table III require several steps to lead to the final emission of light. These intermediate reactions include collision-induced transitions and deactivations. These are the important two-body processes involved in a three-body chemiluminescent reaction.

The classic reaction of this type is the nitrogen afterglow. The emission of the nitrogen first-positive bands from the recombination of nitrogen atoms owes its modern interpretation to the work of Kistiakowsky and his students (BERKOWITZ et al., 1956 ; BAYES and KISTIAKOWSKY, 1958 ; KISTIAKOWSKY and WARNECK, 1957). The nitrogen atoms recombine in a three-body reaction to form a nitrogen molecule in a $^5\Sigma$ state. This excited nitrogen molecule then collides with another body and undergoes a transition into the $B^3\Pi$ state or, alternately, it is simply deactivated. The nitrogen molecule in the $B^3\Pi$ state then either radiates the firstpositive bands or is deactivated by another collision. These reactions may be expressed by the following equations, where the chemical symbol M stands for any molecule,

(3) $N + N + M \rightarrow N_2\,(^5\Sigma) + M$ $\quad k_{1a}$.

(4) $N_2\,(^5\Sigma) + M \rightarrow N_2\,(B^3\,\Pi) + M$ $\quad k_{1b}$

(5) $N_2\,(^5\Sigma) + M \rightarrow N_2 + M$ $\quad k_{1c}$

(6) $N_2\,(B^3\,\Pi) \rightarrow N_2 + h\nu$ $\quad A_1$

(7) $N_2\,(B^3\,\Pi) + M \rightarrow N_2 + M$ $\quad k_{1d}$.

$h\nu$ represents photons of the first positive bands, the k_1 s are the various rate coefficients, and A_1 is the transition probability of the first positive bands. An energy-level diagram of molecular nitrogen is given in figure 5. The intensity of the firstpositive bands in terms of the rate coefficients and particle densities is given in the following expression :

$$(8)\quad I = \frac{k_{1a}\,k_{1b}}{(k_{1b} + k_{1c})}\,[N]^2\,[M]\,\frac{1}{\left(1 + \frac{k_{1d}}{A_1}\,[M]\right)},$$

where I is the intensity in photons $cm^{-3}\,sec^{-1}$ and the symbols in square brackets represent particle densities in atoms or molecules cm^{-3}.

In some unpublished work by the author and M. PATAPOFF using the apparatus shown in figure 3 the intensity of the first positive bands was found to be independent of pressure between 1 and 5 mm Hg. YOUNG and SHARPLESS (1963) have reported

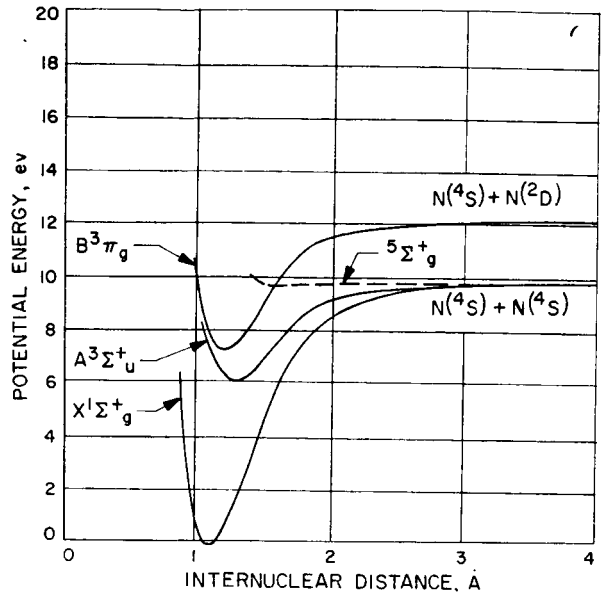

FIG. 5. — Energy level diagram of molecular nitrogen.

that this emission is pressure independent between 1 and 80 mm Hg. These observations require that if the reactions in equations 3-7 are a proper explanation of the nitrogen afterglow, the denominator in equation 8 has to fulfill the following condition :

$$(9)\quad \frac{k_{1d}}{A_1}\,[M] > 1.$$

Since the lowest pressure where the pressure independence was observed was 1 mm Hg, $[M] = 3 \times 10^{16}$ molecules cm^{-3}. The deactivation coefficient k_{1d} may not be larger than 10^{-10} $cm^3\,sec^{-1}$, hence this requires that the transition probability A_1 must be less than $3 \times 10^5\,sec^{-1}$. If further laboratory experiments show that the deactivation coefficient or the transition probability exceeds these limits, then KISTIAKOWSKY's idea of a collision-induced transition has to be given up.

The effective rate coefficient listed in Table III for the emission of the firstpositive bands, k_1, is equal to the following combination of the coefficients from equation 8 :

$$(10)\quad k_1 = \frac{k_{1a}\,k_{1b}\,A_1}{(k_{1b} + k_{1c})\,k_{1d}}.$$

Another three-body chemiluminescent reaction of long-standing interest is the recombination of atomic oxygen and atomic nitrogen to form nitric oxide, and the consequent emission of the beta, gamma, and delta bands. These bands have been observed in the nitrogen afterglow since the discovery of that phenomenon. Relatively recently

it has been realized that the three-body recombination of atomic oxygen and atomic nitrogen leads to the emission of the beta, gamma, and delta bands of nitric oxide in a manner that is analogous to the emission of the first positive bands in the nitrogen afterglow (BARTH et al., 1959). The recombining atoms form a nitric oxide molecule in a $^2\Sigma$ state. A subsequent collision induces a transition to the $B^2\ \Pi$ state from which the beta bands radiate. This mechanism may be represented by the following reactions :

$$(11)\quad N + O + M \rightarrow NO(^2\Sigma) + M \qquad k_{2a},$$

$$(12)\quad NO(^2\Sigma) + M \rightarrow NO(B^2\ \Pi) + M \qquad k_{2b},$$

$$(13)\quad NO(^2\Sigma) + M \rightarrow NO + M \qquad k_{2c},$$

$$(14)\quad NO(B^2\ \Pi) \rightarrow NO(X^2\ \Pi) + h\nu \qquad A_2.$$

where the $h\nu$ in this case stands for beta band photons and the other symbols have meanings analogous to the similar symbols in the previous set of equations. An energy-level diagram of nitric oxide is shown in figure 6. The intensity of the beta bands is given in the following expression :

$$(15)\qquad I = \frac{k_{2a}\ k_{2b}}{k_{2b} + k_{2c}}\ [N]\ [O]\ [M].$$

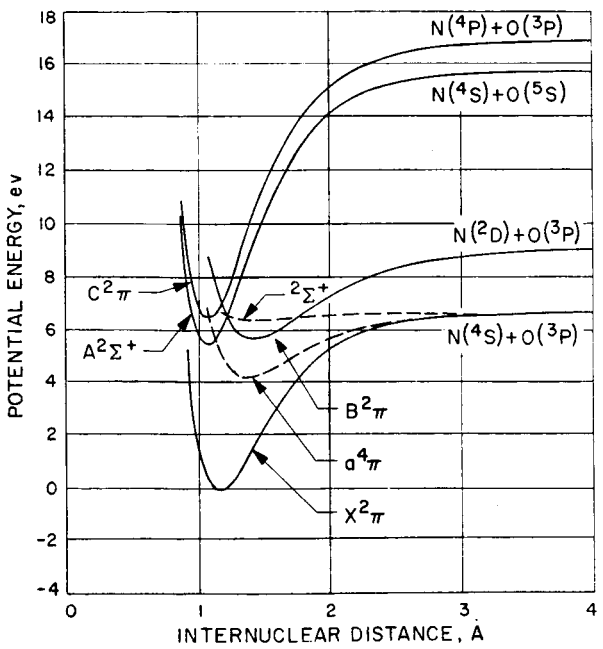

FIG. 6. — Energy level diagram of nitric oxide.

In some additional unpublished work, the author and PATAPOFF have shown that the intensity of the beta bands is directly proportional to pressure over the range 1 to 6 mm Hg and YOUNG and SHARPLESS (1963) report also that this emission is pressure dependent above 1 mm Hg. The laboratory report of pressure dependence of the intensity of the beta bands obviates the need for a deactivation term in equation 15. The rate coefficient of Table III is then equal to the following :

$$(16)\qquad k_2 = \frac{k_{2a}\ k_{2b}}{k_{2b} + k_{2c}}.$$

Still other experimental work by YOUNG and SHARPLESS (1962*a*) has shown that the delta bands of nitric oxide are independent of pressure between 0.2 and 10 mm Hg. As in the case of the nitrogen firstpositive bands, the pressure-independence challenges the concept of a collision-induced transition to bring the molecule into the upper state of the emission system. The emission of the delta bands from recombining nitrogen and oxygen atoms may be represented by the following equations

$$(17)\quad N + O + M \rightarrow NO(a^4\ \Pi) + M \qquad k_{2'a},$$

$$(18)\quad NO(a^4\ \Pi) + M \rightarrow NO(C^2\ \Pi) + M \qquad k_{2'b},$$

$$(19)\quad NO(a^4\ \Pi) + M \rightarrow NO + M \qquad k_{2'c},$$

$$(20)\quad NO(C^2\ \Pi) \rightarrow NO(X^2\ \Pi) + h\nu \qquad A_3,$$

$$(21)\quad NO(C^2\ \Pi) + M \rightarrow NO + M \qquad k_{2'd}.$$

with the intensity of the delta bands given by :

$$(22)\quad I = \frac{k_{2'a}\ k_{2'b}}{(k_{2'b} + k_{2'c})}\ [N]\ [O]\ [M]\ \frac{1}{\left(1 + \frac{k_{2'd}}{A_{2'}}\ [M[\right)}.$$

As in the case of the first positive bands, in order that the pressure independence be explained, the upper state of the emission bands must have a lifetime sufficiently long for significant deactivation to take place. If this requirement cannot be met, it is necessary to consider that the transition from the $a^4\ \Pi$ state to the $C^2\ \Pi$ state in equation 18 takes place without the necessity of a collision.

$$(23)\qquad NO(a^4\ \Pi) \rightarrow NO(C^2\ \Pi) \qquad k_{2'e}.$$

If equation (23) is substituted for equation (18) in the reaction mechanism, the intensity equation takes the following form :

$$(24)\qquad I = \frac{k_{2'a}\ k_{2'e}\ [N]\ [O]\ [M]}{k_{2'e} + k_{2'c}\ [M]}.$$

If the intermediate state $a^4\ \Pi$ is deactivated by collisions as in equation (19), equation (24) does become pressure independent. The effective rate

coefficient in Table III would then be equivalent to the following :

$$k_{2'} = \frac{k_{2'a}\, k_{2'e}}{k_{2'c}}. \tag{25}$$

YOUNG and SHARPLESS (1963) report the nitric oxide gamma bands to have a mixed pressure dependence. The reaction mechanism for this emission could be a combination of the mechanisms discussed here plus a contribution from still another reaction.

The three-body recombination of atomic oxygen to form excited molecular oxygen is a reaction of great importance in the upper atmosphere. The Herzberg bands and the atmospheric bands are prominent airglow features that arise from this recombination. The Herzberg bands were first produced in the laboratory in an oxygen afterglow by BROIDA and GAYDON (1954) and more recently in a laboratory source containing atomic oxygen as the only energetic species by BARTH and PATAPOFF (1962). The atmospheric bands were first produced in the laboratory by KAPLAN (1947) and later in an oxygen afterglow by BRANSCOMB (1952).

In contrast to the recombination mechanisms that have been discussed for molecular nitrogen and nitric oxide, the upper levels of molecular oxygen emissions may be reached directly by ground state oxygen atoms. The Herzberg bands arise from the transition $A^3\,\Sigma_u^+ - X^3\,\Sigma_g^-$ and the atmospheric bands from $b^1\,\Sigma_g^+$ to $X^3\,\Sigma_g^-$. See figure 7 for a potential energy diagram that shows these levels. The excitation and deactivation of the Herzberg band system may be represented by the following reactions :

$$O + O + M \rightarrow O_2\,(A^3\,\Sigma) + M \qquad k_{3a}, \tag{26}$$

$$O_2\,(A^3\,\Sigma) + M \rightarrow O_2 + M \qquad k_{3b}, \tag{27}$$

$$O_2\,(A^3\,\Sigma) + O \rightarrow O_2 + M \qquad k_{3c}, \tag{28}$$

$$O_2\,(A^3\,\Sigma) \rightarrow O_2 + h\nu \qquad A_3, \tag{29}$$

$$O_2\,(A^3\,\Sigma) + \text{wall} \rightarrow O_2 \qquad W_3. \tag{30}$$

In addition to molecular deactivation, the deactivation of the excited molecule by oxygen atoms, reaction 28, is important. Because of the long lifetime of the excited state, wall deactivation must be considered as well. The intensity of the Herzberg bands in terms of reactions 26 — 30 is given by the following expression :

$$I = \frac{k_{3a}\,[O]^2\,[M]}{1 + \frac{k_{3b}}{A_3}[M] + \frac{k_{3c}}{A_3}[O] + \frac{W_3}{A_3}}. \tag{31}$$

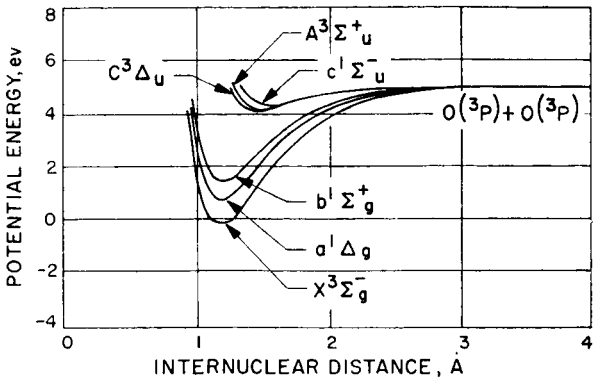

FIG. 7. — Energy level diagram of molecular oxygen.

The laboratory results by YOUNG and SHARPLESS (1963) show the Herzberg band emission to be independent of wavelength over the pressure range 0.8 to 65 mm Hg which indicates that molecular deactivation dominates. Their rate coefficient given in Table III should be equal to the following combination of coefficients :

$$k_3 = \frac{A_3\, k_{3a}}{k_{3b}}. \tag{32}$$

A set of reactions for the excitation of the atmospheric bands from oxygen atom recombination may be written in a form analogous to reactions 26 — 30. YOUNG and SHARPLESS (1963) also measured the emission rate of this band system and found that it did vary with pressure over the range 0.24 — 12 mm Hg. These results are best explained by equating their value as listed in Table III to the following coefficients derived from equation 31 and involving wall deactivation.

$$k_{3'} = \frac{A_{3'}\, k_{3'a}}{W_{3'}}. \tag{33}$$

In their paper on the oxygen afterglow, BROIDA and GAYDON (1954) suggested that a band system $A^3\,\Sigma - b^1\,\Sigma$ was present in the laboratory afterglow and the upper atmosphere airglow. In a spectroscopic study with higher resolution, BARTH and KAPLAN (1959) showed that this proposed BROIDA — GAYDON system could not be identified with either the laboratory or airglow spectra. CHAMBERLAIN (1958) has proposed a band system $B^3\Delta_u - a^1\Delta_g$ to explain some of the unknown spectral features in the night airglow. Some of these same features are found in the laboratory spectrum as well (BARTH and KAPLAN, 1959).

The three-body chemiluminescent reaction between nitric oxide and atomic oxygen has a history almost as long as that of the nitrogen afterglow.

The modern quantitative study of this reaction began with KAUFMAN (1958). More recently, BROIDA, SCHIFF and SUGDEN (1961) and CLYNE and THRUSH (1962) have been proponents of a reaction mechanism involving a collision-induced transition from a stabilized intermediate state, a mechanism analogous to that of the nitrogen afterglow. Using the notation and potential energy diagram figure 8, from BROIDA et al., (1961), the mechanism may be presented by the following equations :

(34) $NO + O + M \rightarrow NO_2\,(C) + M$ $\quad k_{4a}$,

(35) $NO_2\,(C) + M \rightarrow NO_2\,(B) + M$ $\quad k_{4b}$,

(36) $NO_2\,(C) + M \rightarrow NO_2 + M$ $\quad k_{4c}$,

(37) $NO_2\,(B) \rightarrow NO_2 + h\nu$ $\quad A_4$,

(38) $NO_2\,(B) + M \rightarrow NO_2 + M$ $\quad k_{4d}$.

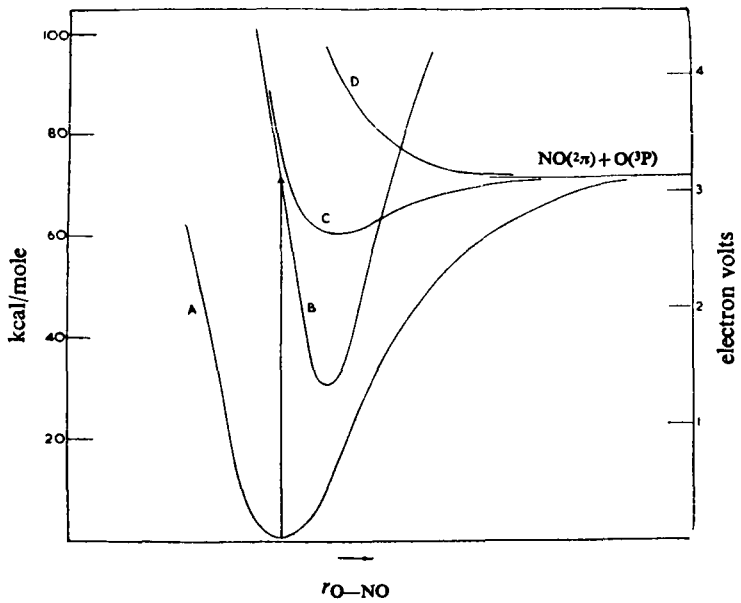

FIG. 8. — Energy level diagram of nitrogen dioxide. (Reproduced from BROIDA, SCHIFF and SUGDEN, 1961.)

The nitrogen dioxide states, B and C refer to levels in figure 8. The $h\nu$ refers to the emission bands of the greenish-yellow air afterglow. The intensity of this emission in terms of these reactions is given by :

$$(39)\quad I = \frac{k_{4a}\,k_{4b}}{(k_{4b} + k_{4c})}\,[NO]\,[O]\,[M]\,\frac{1}{\left(1 + \frac{k_{4d}}{A_4}\,[M]\right)}.$$

The rate coefficients reported in Table III by KAUFMAN (1958), FONTIJN and SCHIFF (1961), and CLYNE and THRUSH (1962) are independent of pressure over the pressure range available to the laboratory experimenters 0.2 — 4.3 mm Hg. Equation 39 may be made pressure-independent by having reaction 38 dominate reaction 37 ; then the rate coefficient of Table III is equivalent to the following :

$$(40)\qquad k_4 = \frac{k_{4a}\,k_{4b}\,A_4}{(k_{4b} + k_{4c})\,k_{4d}}.$$

CLYNE and THRUSH (1962) suggest that the ratio of k_{4d}/A_4 may be determined independently from data on the nitrogen dioxide fluorescence spectrum. These same experimenters report a negative temperature coefficient for the chemiluminescent reaction.

The chemiluminescence from the three-body recombination of carbon monoxide and atomic oxygen has been long observed in flames and, in fact, the emission has been called the CO flame bands. The production of these bands from a reaction between atomic oxygen and carbon monoxide was first shown by BROIDA and GAYDON (1953). This reaction is of current interest because of the possibility of its occurence in the night airglow of Mars and Venus. Two recent studies by CLYNE and THRUSH (1962) and by MAHAN and SOLO (1962) have shown the chemiluminescent reaction to be pressure independent. CLYNE and THRUSH (1962) have suggested a reaction mechanism that is analogous to the nitric oxide-atomic oxygen reaction. Ground state CO and O recombine into a state which undergoes a radiationless collision into the state that finally radiates. Figure 9, which is from their work, shows the energy

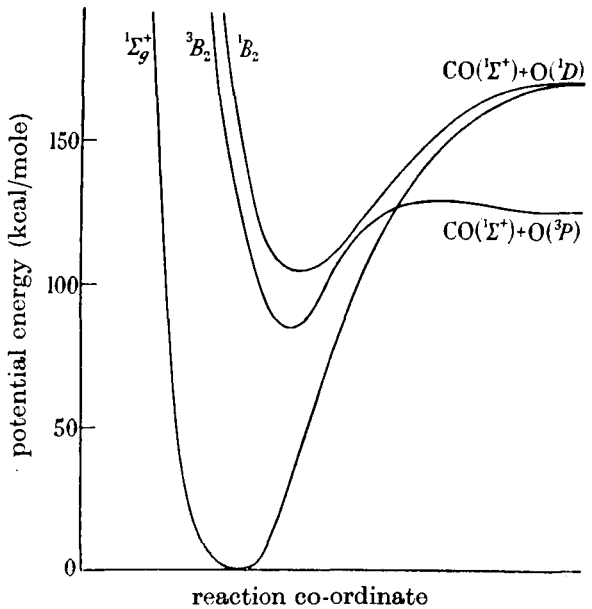

FIG. 9. — Energy level diagram of carbon dioxide. (Reproduced from CLYNE and THRUSH, 1962.)

levels appropriate to the following reaction mechanism :

(41) $CO + O + M \rightarrow CO_2\,(^3B_2) + M$ $\quad k_{5a}$,

(42) $CO_2\,(^3B_2) + M \rightarrow CO_2\,(^1B_2) + M$ $\quad k_{5b}$,

(43) $CO_2\,(^3B_2) + M \rightarrow CO_2 + M$ $\quad k_{5c}$,

(44) $CO_2\,(^1B_2) \rightarrow CO_2 + h\nu$ $\quad A_5$,

(45) $CO_2\,(^1B_2) + M \rightarrow CO_2 + M$ $\quad k_{5d}$.

The intensity of the carbon monoxide flame bands is then equal to :

$$(46)\quad I = \frac{k_{5a}\,k_{5b}}{(k_{5b} + k_{5c})}\,[CO]\,[O]\,[M]\,\frac{1}{\left(1 + \frac{k_{5d}}{A_5}\,[M]\right)}.$$

and the pressure-independent rate coefficient is equal to

$$(47)\qquad k_5 = \frac{k_{5a}\,k_{5b}\,A_5}{(k_{5b} + k_{5c})\,k_{5d}},$$

The rate coefficients reported by MAHAN and SOLO (1962) and CLYNE and THRUSH (1962) and listed in Table III have different temperature dependences. Even at room temperature the rates measured by the two experimental groups differ by a factor of 10 with the MAHAN-SOLO value being higher. In addition, MAHAN and SOLO (1962) reported that molecular oxygen was effective in deactivating the excited carbon dioxide and they took care to minimize the amount of oxygen present in their reactor. This means that the value of the deactivation coefficient in equation 45 is different depending on the nature of the deactivating molecule, and that the k_{5d} that one group measured may have been different from that which the other group measured. In attempting to evaluate the usefulness of chemiluminescent rate coefficients for application to the upper atmosphere, the higher reported value may be the most appropriate since it may indicate a lack of deactivating reactions. This criterion is opposite to that employed in evaluating the overall rate coefficients.

The following observation may be made after reviewing these five three-body recombination chemiluminescent mechanisms. Recombination into an intermediate state which then undergoes a radiationless transition appears to be the rule rather than the exception. The nature of this radiationless transition has not been clearly demonstrated by experiment. Whether or not a collision is always required to induce the transition is the key question.

UPPER ATMOSPHERE THREE-BODY REACTION

Three-body reactions play a role in determining the composition of the upper atmosphere and in contributing to the excitation of the night airglow. Calculations of the reaction rates of the three-body reactions in the upper atmosphere involving atomic nitrogen and atomic oxygen have been made by BARTH (1961*b*). Figure 1 of that paper, which is reproduced as figure 3 of the paper by BRANSCOMB in this volume, shows the particle densities in the upper atmosphere that are the results of the calculations. The only two three-body reactions which make an important contribution in determining the composition of the upper atmosphere are the recombination of atomic oxygen to form molecular oxygen and the reaction between atomic oxygen and molecular oxygen to form ozone. The first of these is important in the 90 — 110 km region and the second in the region between 30 and 90 km. Although the three-body reactions involving atomic nitrogen are rapid, a two-body reaction between atomic nitrogen and molecular oxygen determines the atomic nitrogen density.

The five three-body chemiluminescent reactions listed in Table III are potential contributors to the night airglow of planets. The rates of formation of excited molecules by three-body reactions were also calculated by BARTH (1961*b*). Figure 10 is a reprint of those results. The calculations were made using the overall rate coeffi-

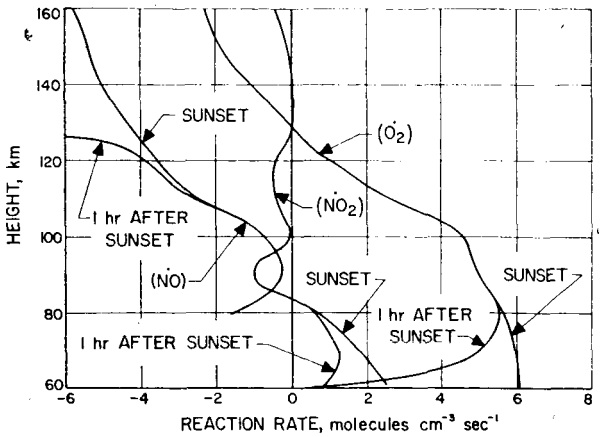

FIG. 10. — Calculation of reaction rates of three-body reactions in the upper atmosphere. (Reproduced from BARTH, 1961*b*.)

cients for the reactions corresponding to those in Table II of this paper. To determine the actual rate of emission from these reactions, it is necessary to multiply the results of figure 10 by the ratio of the appropriate chemiluminescent reaction rate to the overall reaction rate. For the five reactions listed in Table III, this requires a proper application of equations 10, 16, 25, 32, 33, 40 and 47. The atomic nitrogen density is far too low in the earth's atmosphere for reaction 1 of Table III to produce nitrogen first positive bands that are observable. The observation of nitric oxide bands actually offers a more sensitive technique of detecting atomic nitrogen in the upper atmosphere. However, the rate coefficient given in Table III and the calculation in figure 10 indicate that the intensity of the entire beta band system should be only of the order of 10^{-2} Rayleighs. However, in the airglow of a planet that has much less molecular oxygen than the earth, such as Mars, the intensity of this system may be greater (BARTH, 1961*c*). The intensity of the airglow contribution from nitricoxide gamma and delta bands and nitrogendioxide bands cannot be calculated because the laboratory experiments were not conducted at a pressure low enough to determine the pressure dependence of the emission. However, figure 10 shows that the variation with height of the nitrogen dioxide emission has a double maximum, one at 70 or 80 km and the other at 100 km. Measurements of the height distribution of the continuum of the night airglow by Naval Research Laboratory rocket experiments have shown a double maximum at these heights. (See fig. 8 of PACKER (1961).) The pressure dependence of the carbon-monoxide atomic-oxygen chemiluminescence has not been determined, and hence the calculation of its airglow intensity is not yet possible. It is not expected that this emission will contribute to the earth's airglow, but it may be important in the night airglows of Mars and Venus.

Disappointingly, the airglow intensity of the molecular oxygen Herzberg and atmospheric bands cannot be calculated from the results quoted in Table III. The pressure dependence of the Herzberg bands has not been measured, and the laboratory measurements of the atmospheric bands appear to be dominated by wall collisions. The workers who made the laboratory measurements recognized the difficulty in applying their results to the upper atmosphere, but it is not clear why this prompted them to state that the recombination of atomic oxygen is incapable of producing the observed airglow (YOUNG and SHARPLESS, 1962*b*). Their laboratory results do not prove this ; they are simply not applicable.

Information about the rate coefficients of the reactions leading to the emission of the Herzberg and atmospheric bands can be determined by examining the height profiles of the emissions obtained in rocket experiments (BARTH, 1962*a*). The altitude profile of the oxygen airglow that was presented by PACKER (1961) at the 1960 Symposium on Aeronomy is reproduced in figure 11. The maximum intensity of the Herzberg bands occurs at 95 km, while the calculated height profile in figure 10 shows a maximum at 80 km. These calculations were made for three-body excitation of molecular oxygen with no deactivation. The measurement of the maximum at 95 km shows that molecular deactivation must be occuring up to at least 95 km. The intensity of the Herzberg bands is described by equation 31 with the radiative term dominating above 100 km and the molecular deactivation term below 100 km.

$$\text{(41)} \qquad I = k_{3a}\,[O]^2\,[M] \quad > 100 \text{ km.}$$

$$\text{(42)} \qquad I = \frac{k_{3a}\,A_3}{k_{3b}}\,[O]^2 \quad < 100 \text{ km.}$$

Because the neutral particle density at 100 km, [M], is equal to 10^{13} particles cm^{-3}, k_{3b}/A_3 must be of the order of 10^{-13} cm^3 if molecular deactivation is to dominate. Since the observed Herzberg intensity is of the order of 1 kilorayleigh and the oxygen atom density at 100 km is 10^{12} cm^{-3}, k_3 from equation 32 is equal to 10^{-21} cm^3 sec^{-1}. The three-body rate coefficient, k_{3a}, then needs to have a value of the order of 10^{-31} cm^6 sec^{-1}.

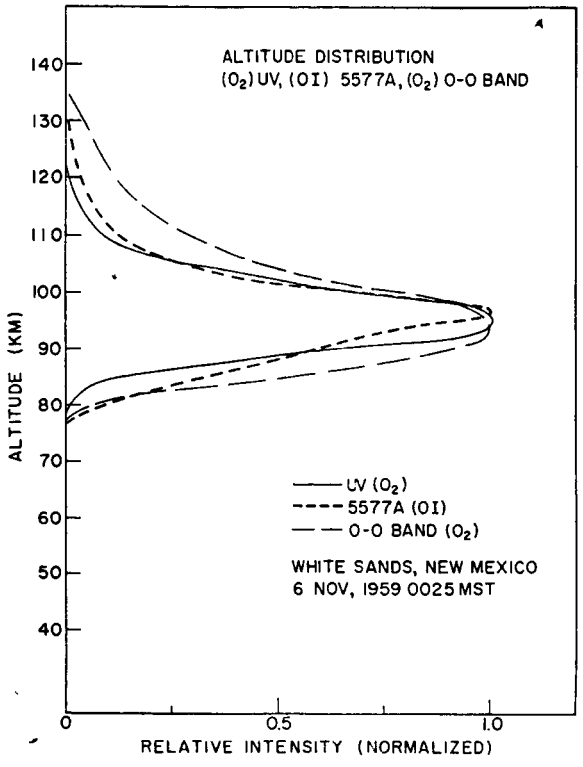

FIG. 11. — Measurements of the height profile of the oxygen night airglow by Naval Research Laboratory rocket experiments. (Reproduced from PACKER, 1961.)

The height profile of the atmospheric bands also shows a maximum near 95 km ; hence, the argument for molecular deactivation being prevalent up to this height applies here as well. Equations analogous to equation 41 and 42 will describe the intensity distribution. Since, however, the measured intensity of the atmospheric bands is 14.5 kilorayleighs (PACKER, 1961), the order of magnitude values for the rate coefficients become the following : $k_{3'} = 10^{-2)}$ cm^3 sec^{-1}, $k_{3'b}/A_{3'} = 10^{-13}$ cm^3, and $k_{3'a} = 10^{-33}$ cm^3 sec^{-1}. Because the intensity of the (0, 0) atmospheric band is determined by molecular deactivation below 100 km, the resonance reradiation of this band that has been calculated by CHAMBERLAIN (1954) does not have the opportunity to take place and produce the lowering of the intensity maximum that he predicted.

The most famous upper-atmosphere three-body reaction is what has been called the CHAPMAN mechanism of the 5577 A night airglow line of atomic oxygen. Thirty-three years ago CHAPMAN (1931) proposed with a great deal of insight that the energy source of the night airglow green line resided in the dissociated oxygen in the upper atmosphere. Since that time the theory has been amplified with a long-popular version having the oxygen atom becoming excited in a three-body reaction with two other oxygen atoms. A somewhat more complicated version of CHAPMAN's original idea is given here (BARTH, 1961*d*).

Two oxygen atoms recombine in a three-body collision to produce an oxygen molecule in an electronically excited state. This excited molecule will either radiate or undergo a deactivating collision with an oxygen atom. If the electronically excited molecule lies in certain vibrational levels, the electronic energy of the molecule may be transferred to the atom to produce an oxygen atom in a ^{1}S state from which the 5577 A line is subsequently radiated. The excited oxygen atom is also susceptible to deactivation. These reactions may be represented by the following set of equations :

$$(43) \quad O + O + M \rightarrow O_2^* + M \qquad k_{6a},$$

$$(44) \quad O_2^* + O \rightarrow O_2 + O^* \qquad k_{6b},$$

$$(45) \quad O_2^* + O \rightarrow O_2 + O \qquad k_{6c},$$

$$(46) \quad O_2^* + M \rightarrow O_2 + M \qquad k_{6d},$$

$$(47) \quad O^* \rightarrow O + h\nu \qquad A_6,$$

$$(48) \quad O^* + M \rightarrow O + M \qquad k_{6e}.$$

The excited oxygen molecule in equation 43 may be in either the $c^1\,\Sigma$ or $C^3\,\Delta$ state. (See fig. 7.) The excited atom in equations 44 and 47 is in the ^{1}S state. The $h\nu$ of equation 47 refers to the 5577 A line. The intensity of the 5577 A line from these reactions is given by the following expression :

$$(49)\ I = \frac{k_{6a}\, k_{6b}\, [O]^3\, [M]}{(k_{6b} + k_{6c})\, [O] + k_{6d}\, [M]} \cdot \frac{1}{\left(1 + \frac{k_{6e}}{A_6}\, [M]\right)}.$$

The deactivation rate coefficient of the excited atom, k_{6e}, has been measured by BARTH and HILDEBRANDT (1961) and found to be 4.5×10^{-15} cm^3 sec^{-1}. Using the value of 1.28 sec^{-1} for A_6, the radiative transition probability of the 5577 A line, leads to the result that the highest level in the atmosphere where atom deactivation can occur is 80 km, where the particle density is 3×10^{14} cm^{-3}. Observations of the green line in meteor wakes show little deactivation down to 80 km (HALLIDAY, 1960).

It has been argued that the intermediate metastable oxygen molecule is deactivated below 100 km by collisions with molecules, equation 46, and above 100 km by collisions with atoms, equation

45, (BARTH, 1962*b*). Using this assumption, the intensity of the 5577 A line, equation 49, will have the following dependences for the indicated altitude regions :

$$(50)\ I = \frac{k_{6a}\, k_{6b}}{(k_{6b} + k_{6c})}\, [O]^2\, [M] \qquad > 100 \text{ km.}$$

$$(51)\ I = \frac{k_{6a}\, k_{6b}}{k_{6d}}\, [O]^3 \qquad \begin{array}{l} < 100 \text{ km.} \\ > 80 \text{ km.} \end{array}$$

$$(52)\ I = \frac{k_{6a}\, k_{6b}\, A_6}{k_{6d}\, k_{6e}}\, \frac{[O]^3}{[M]} \qquad < 80 \text{ km.}$$

The argument for molecular deactivation being the dominant deactivation mechanism is based on an examination of the rocket results in figure 11. Above 100 km, both the Herzberg bands and the 5577 A line follow the same dependence with height. These height profiles are described by equation 41 for the Herzberg bands and equation 50 for the 5577 A line. Immediately below 100 km, the 5577 A intensity falls off more rapidly than the Herzberg bands which has been interpreted as indicating a dependence on a higher power of the atom density. Equation 51 gives the intensity dependence of the 5577 A line as the third power of the atomic oxygen density while equation 42 has the Herzberg bands dependent on the second power.

Some order of magnitude estimates may be made of the rate coefficients in the 5577 A mechanism. For the transition between molecular deactivation and atomic deactivation to occur at 100 km, where the neutral particle density [M] is ten times the oxygen atom density [O],

$$(53) \qquad (k_{6b} + k_{6c}) = 10\, k_{6d}.$$

Using the observed intensity of the 5577 A line of 250 Rayleighs, a layer thickness of 10^3 cm, and equations 50 and 51,

$$(54) \qquad \frac{k_{6a}\, k_{6b}}{k_{6d}} = 2.5 \times 10^{-34}\ \text{cm}^6\ \text{sec}^{-1}.$$

Since the overall rate coefficient for atomic oxygen three-body recombination is 2.8×10^{-33} cm^6 sec^{-1} (Table II), k_{6a} may be no greater than it and

$$(55) \qquad k_{6b} > 10^{-1}\, k_{6d} \approx 10^{-2}\, k_{6c}.$$

The mechanism requires that oxygen atoms be excited to the ^{1}S state in greater than 1 % of the reactions of atomic oxygen with the metastable oxygen molecules, equations 44 and 45. The molecular deactivation, equation 46, needs to be only one-tenth as effective as the atomic deactivation, equation 45.

CONCLUSION

Laboratory experiments have made a substantial contribution in determining the overall reaction rates of three-body reactions that are necessary for the calculation of atom densities in the upper atmosphere. The difficulties and limitations of laboratory apparatus in measuring the reactions of excited atoms and molecules and the rate coefficients of the chemiluminescence reactions have become apparent. There are some reactions that can best be measured in the upper atmosphere and, in the best tradition of geophysics, the study of these reactions in the geophysical environment may make a fundamental contribution to the science of reaction kinetics.

ACKNOWLEDGEMENT

Morris PATAPOFF conducted the literature search and evaluation that led to the rate coefficients tabulated in Tables II and III. This work was supported by the National Aeronautics and Space Administration under Contract NAS7-100.

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