STUDIES ON THE AFTERGLOW OF NITROGEN AND OXYGEN DISCHARGES

by

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B.Sc. (Hons), University of London, 1967

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF
THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF SCIENCE

in the Department
of
CHEMISTRY

We accept this thesis as conforming to the
required standard

THE UNIVERSITY OF BRITISH COLUMBIA

August, 1970
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The reactions:

\[ O_2(1\Delta_g) + O_2(1\Delta_g) \rightarrow O_2(1\Sigma^+) + O_2(3\Sigma^-) \]

and \[ O_2(1\Sigma^+) + \text{wall} \rightarrow O_2(1\Delta_g) + \text{wall} \]

have been studied here in a discharge flow system. Using two temperatures, the rate constant for wall deactivation was found to be \(3.8 \times 10^{-330} \exp\left(-\frac{330}{RT}\right) \text{sec}^{-1}\). It was concluded that the deactivation was not diffusion controlled as previously suggested but controlled by the surface deactivation process on the walls. The rate constant for production of \(O_2(1\Sigma^+)\) was found to be \(6.7 \times 10^4 \exp\left(-\frac{2000}{RT}\right) \text{litres mole}^{-1}\text{sec}^{-1}\), in reasonable agreement with the room temperature value determined by Arnold.

An upper limit of \(1.6 \times 10^6 \text{litres mole}^{-1}\text{sec}^{-1}\) was obtained for the rate constant of the reaction:

\[ N + O_2(1\Delta_g) \rightarrow \text{NO} + 0 \]

showing that the reaction is considerably slower than expected from comparison with the analogous reaction of ground state oxygen. This is rationalized by showing that the two reactions require different transition states.

Whilst studying the above reaction several surface catalysed glows from molecular nitrogen and nitric oxide were seen. These glows were found to require \(O_2(1\Delta_g)\) for their production and not atomic oxygen as previously thought. Several qualitative and spectroscopic experiments were performed and in the light of the information gained various possible mechanisms are discussed.
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ACKNOWLEDGEMENTS

The author wishes to express his gratitude to:

- Dr. E.A. Ogryzlo for his continued patience and guidance throughout this work.
- my colleagues in the laboratory for many helpful and instructive discussions.
- the University of British Columbia for a Teaching Assistantship.
- the many members of the technical staff in the Department.
- Mrs. V. Mottershead for typing the thesis.
PREFACE

Three major subjects, only slightly interrelated, are dealt with in this thesis. The first is concerned with the kinetics of various production and deactivation reactions taking place in a stream of 'singlet' oxygen; the second is a kinetic study of the reaction between atomic nitrogen and singlet oxygen and the third is a spectroscopic study of surface catalysed and homogeneous gas phase glows found in mixtures of atomic nitrogen and 'singlet' oxygen gas streams.

These three subjects have been divided and placed in two different sections in an effort to provide some organization to the diversity of material. Part I contains only the first subject, singlet oxygen kinetics, with very little reference to nitrogen chemistry. Part II contains both the second and third subjects, which have been placed together in a separate section in order to introduce the subjects of recombination and radiation in nitrogen and nitric oxide. In fact, very little singlet oxygen chemistry is required in Part II, thus making each part virtually autonomous. A division of the two major subjects of Part II has not been made since the subdivision of each main section in a parallel manner should enable the reader to pick out any particular topic. An examination of the 'contents' should make this clear.
PART I.

Production and Deactivation of $O_2(^1\Sigma^+)$ at Two Temperatures.
Spectroscopic Studies.

Singlet oxygen is a term which tends to be used rather loosely, but generally refers to a mixture of the first two electronically excited states of molecular oxygen. These are the \( a(^1\Delta_g) \) state and the \( b(^1\Sigma_g^+) \) state. The upper, \( b(^1\Sigma_g^+) \) state lies 0.65 eV above the \( a(^1\Delta_g) \) state which, in turn, lies 0.98 eV above the ground \( X(^3\Sigma_g^-) \) state as shown in Fig. 1 (1).

The existence of the \( O_2(^1\Delta_g) \) state was first predicted by Mulliken in 1928 (4) and later detected by Herzberg (5) in the infra-red solar spectrum where the atmospheric oxygen absorbs weakly in the 1.27\( \mu \)m region. Further confirmation of the presence of this band was provided by Ellis and Kneser (6) in absorption through liquid oxygen and by Van Vleck (7) in emission from a gaseous discharge. Later Harrison and Vallance-Jones (8) observed anomalous enhancement of the \( (2,3) \) Meinel \( N_2^+ \) band in the nitrogen nightglow that was probably due to the \( (0,1) \), \( (^1\Delta_g - ^3\Sigma_g^-) \) 'infra-red atmospheric' band at 1.58\( \mu \). The \( (0,0) \) transition at 1.27\( \mu \) was not observed at ground level due to reabsorption by the oxygen in the lower atmosphere. The transition was characterized by its nine branches - two R, two P, three Q, and one each of O and S branches which are characteristic of a \( (^1\Delta_g - ^3\Sigma_g^-) \) magnetic dipole transition. Vallance-Jones and Gattinger (9) have determined an Einstein A coefficient of \( 1.5 \times 10^{-4} \) sec\(^{-1} \) for the \( (0,0) \) transition.
Fig. I. Oxygen potential energy diagram as compiled by Gilmore (1).
The \( \text{O}_2 \) \( b(1\Sigma^+_g) \) state was first observed by the atmospheric oxygen absorption in the 'red' region of the solar spectrum. The \( \text{o} \) (0,1) transition at 8645 Å was observed by Meinel (10) in the airglow, the (0,0) band being reabsorbed as for the \( (1\Delta_g - 3\Sigma_g^-) \) transition. The spectrum has also been observed in emission from the aurora (11) and from discharged oxygen (12). The bands consist of two P and two R branches as expected for a magnetic dipole \( (1\Sigma^+_g - 3\Sigma_g^-) \) transition. Childs and Mecke (13) obtained a value for the Einstein A coefficient of the \( (3\Sigma_g^- - 1\Sigma_g^+) \) transition and subsequent determination (14) gave 

\[ A = 0.145 \text{ sec}^{-1} \]

in good agreement with the earlier work. Recently, however, Wallace and Hunten (15), on the basis of their own work together with the results of an unpublished report by Burch and Gryvnak, have suggested a value of 0.085 \( \text{sec}^{-1} \) for A.

**Singlet Oxygen from Discharge Systems.**

The discharge flow technique for studying the kinetics of fast reactions consists basically of a uniform flow tube with a controlled gas inlet at one end and a rapid pumping system at the other. The gases are regulated to flow at a uniform rate producing a linear time axis along the length of the tube. By observation at different points along the tube the variation of the reaction with time can be followed. Metastable species, for which the technique is usually used, can be produced by passing the particular gas through an electrodeless discharge. Other reactant gases can then be added to the stream prior to observation along the tube. By varying the flowrate the time dis-
placement can be varied over a considerable range, the only limitation being that the flowrate must be large compared with the diffusion rate through the gas (16).

A discharge through oxygen produces a relatively large quantity of atomic oxygen as well as excited molecular oxygen (17). Because of interference of this atomic oxygen in reactions of singlet oxygen, its selective removal by some means is necessary. It was found that by recombination of the atomic oxygen on a surface of mercuric oxide, a stream of ground state oxygen containing about 10% excited molecular oxygen could be produced (18)(19). This recombination process is achieved by placing a heated bead of mercury either before or after the microwave discharge causing mercuric oxide to form as a hot layer on the walls of the tube downstream of the discharge region. The precise function of the mercuric oxide is not well understood. A 20% increase in the \( \text{O}_2(\text{^1\Delta}_g) \) concentration on introduction of the mercuric oxide into the stream has been reported by Cairns and Samson (20) using photoionization techniques to measure the \( \text{O}_2(\text{^1\Delta}_g) \) concentration. This value has been confirmed by Whitlow and Findlay (21) by direct observation of the \((0,0), (\text{^1\Delta}_g - \text{^3\Sigma}_g^-) \) band at 1.27\( \mu \). The 14-fold enhancement of the 7619 \( \AA \) band on removal of the atoms reported by March et al (22) has not been confirmed by other workers.

In the present work a discharge flow system was used in which the singlet oxygen was produced by removal of the atomic oxygen with mercury. \( \text{O}_2(\text{^1\Delta}_g) \) concentrations of about 10% and \( \text{O}_2(\text{^1\Sigma}_g^+) \) concentrations of about
0.1% are formed in such systems (23). The concentration of other excited molecular states of oxygen is negligible.

It is possible to study a few quenching reactions of $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ without the presence of mercuric oxide to recombine the atomic oxygen provided the oxygen atoms do not react with the quencher. In order to minimize quenching by the atomic oxygen very small flowrates of discharged oxygen have been used, requiring special techniques for the detection of the low $O_2(^1\Delta_g)$ concentrations. Clark and Wayne (24) have used a photoionization technique employing the argon resonance lines at 11.70 eV and 11.61 eV to achieve a monochromatic light source. They compensated for absorption by $O_2(^1\Sigma_g^+)$ by comparison with the ion-current produced using the krypton line at 10.69 eV, since radiation of this energy cannot ionize the $O_2(^1\Delta_g)$ (see Fig. I). Since there is also some absorption by ground state oxygen a further correction, determined by measurement at various oxygen pressures, must be made.

Using this technique Clark and Wayne (24) have determined quenching constants for deactivation of $O_2(^1\Delta_g)$ by several gases. Their value for quenching by $O_2(X^3\Sigma_g^-)$ agrees well with that obtained by Findlay et al. (25) using irradiation of benzene-oxygen mixtures to obtain $O_2(^1\Delta_g)$. Values for the deactivation of both $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ by oxygen and nitrogen are shown in Table I. The values used are those suggested in the recent reviews by Wayne (26) and Zipf (27).
Table I.

Rate constant for quenching of $O_2(^1\Sigma_g^+)$ and $O_2(^1\Delta_g)$ by $N_2$ and $O_2$ in litres mole$^{-1}$sec$^{-1}$.

<table>
<thead>
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<th>Quenching Molecule</th>
<th>Rate constant in litres mole$^{-1}$sec$^{-1}$</th>
<th></th>
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<tbody>
<tr>
<td></td>
<td>$O_2(^1\Delta_g)$</td>
<td>$O_2(^1\Sigma_g^+)$</td>
</tr>
<tr>
<td>$O_2$</td>
<td>$1.4 \times 10^3$ (24)</td>
<td>$6 \times 10^4$ (27)</td>
</tr>
<tr>
<td>$N_2$</td>
<td>&lt; 40 (24)</td>
<td>$1.5 \times 10^6$ (35)</td>
</tr>
</tbody>
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Energy Pooling Processes.

Of particular interest in singlet oxygen chemistry are the double molecule 'energy pooling' processes which give rise to emission in the visible region of the spectrum. The collision of two $O_2(\Delta_g^1)$ molecules can produce, not only collision induced radiation at $1.27\mu$, but also emission at twice that energy (6340 Å). Bands involving both $O_2(\Sigma_g^+)$ and $O_2(\Delta_g^1)$ have been seen together with transitions from various vibrationally excited levels. These bands are listed in Table II together with their radiative lifetimes and wavelengths. The transitions were first seen by absorption in liquid oxygen (28) and later, by absorption in high pressure oxygen (29) and in emission from both chemical (30)(31) and discharge sources (32)(2). All bands are broad and lack rotational structure. A complete spectrum of discharged singlet oxygen is shown in Fig. II.

Two values have been quoted for the rate constant, $k_1$, of emission at 6340 Å:

$$I(6340) = k_1 [O_2(\Delta_g^1)]^2$$  \hspace{1cm} (1)

The first determination was by Browne (33)(34) who determined the $O_2(\Delta_g^1)$ concentration using an isothermal calorimeter and calibrated the absolute emission at 6340 Å by comparison with the known intensity of the emission from the NO$_2$ continuum produced by the recombination (3):

$$O + NO \rightarrow NO_2 + hv$$  \hspace{1cm} (2)
## Table II

Observed double molecule transitions in oxygen.

<table>
<thead>
<tr>
<th>Excited State</th>
<th>Transition to ground ( ^3\Sigma_g^- + ^3\Sigma_g^- ) state.</th>
<th>( v_{\text{excited}} - v_{\text{ground}} )</th>
<th>Wavelength (Å)</th>
<th>Lifetime* (secs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( ^1\Delta_g + ^3\Sigma_g^- )</td>
<td>0</td>
<td>12700</td>
<td>4 secs.</td>
<td></td>
</tr>
<tr>
<td>( ^1\Sigma_g^+ + ^3\Sigma_g^- )</td>
<td>-1</td>
<td>15800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^1\Delta_g + ^1\Delta_g )</td>
<td>0</td>
<td>7619</td>
<td>15 secs.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>8345</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>6340</td>
<td>1.5 secs.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>7030</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>5800</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^1\Delta_g + ^1\Sigma^+_g )</td>
<td>0</td>
<td>4800</td>
<td>1.7 secs.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1</td>
<td>5200</td>
<td></td>
<td></td>
</tr>
<tr>
<td>( ^1\Sigma_g^+ + ^1\Sigma^+_g )</td>
<td>0</td>
<td>4000</td>
<td>0.3 secs.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>+1</td>
<td>3800</td>
<td></td>
<td></td>
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</table>

* calculated from integrated absorption coefficients (2).
Fig. II. Spectrum of singlet oxygen between 8000 Å and 3500 Å as obtained by Gray and Ogryzlo (2). Taken using an RCA IP21 photomultiplier and uncorrected for spectral response. The dotted line shows the relative spectra at 300°K and the solid line at 150°K. Both spectra were taken at 10 torr.
He obtained a value of 0.09 litres mole\(^{-1}\)sec\(^{-1}\) for \(k_1\). Falick and Mahan (35) also made a determination in which they found a value for \(k_1\) of 0.03 litres mole\(^{-1}\)sec\(^{-1}\). They determined the \(O_2(^{1}\Delta_g)\) concentration by observation of the \(\Delta M_J = 1\) transition of the \(J = 2\) total angular momentum state, using a paramagnetic resonance spectrometer. The cavity was calibrated using a known pressure of ground-state oxygen.

Since, in the work to be described, the \(O_2(^{1}\Sigma_g^+)\) concentration was determined by monitoring its emission at 6340 A, the present work also includes an independent determination of \(k_1\).

Under normal conditions in a discharge flow system the \(O_2(^{1}\Sigma_g^+)\) concentration is in a steady state (32) between its production by the reaction:

\[
O_2(^{1}\Delta_g) + O_2(^{1}\Delta_g) \xrightarrow{k_3} O_2(^{1}\Sigma_g^+) + O_2(^{3}\Sigma_g^-)
\]

and its deactivation on the walls of the reaction tube:

\[
O_2(^{1}\Sigma_g^+) + \text{wall} \xrightarrow{k_4} O_2(^{3}\Sigma_g^-) + \text{wall}
\]

or \(O_2(^{1}\Delta_g)\)

Reaction (3) is an example of a non-radiative energy-pooling process, which has been called an energy dispropriation reaction (36). It was first proposed by Young and Black (37) to account for the steady state concentration of \(O_2(^{1}\Sigma_g^+)\). By determining the possible limits of \(k_4\) and from a knowledge of the \(O_2(^{1}\Sigma_g^+)\) and \(O_2(^{1}\Delta_g)\) concentrations they obtained an estimate for \(k_3\) of \(2 \times 10^{7}\pm0.5\) litres mole\(^{-1}\)sec\(^{-1}\). This value, however, was found to be high by several orders of magnitude (38). A determination
by Arnold and Ogryzlo (23) using non-stationary conditions gave a value for \( k_3 \) of \( 1.4 \times 10^3 \) litres mole\(^{-1}\)sec\(^{-1}\). Under these conditions the \( O_2(1\Sigma_g^+) \) concentration is governed by:

\[
\frac{d}{dt} [1\Sigma_g^+] = k_3 [O_2(1\Delta_g)]^2 - k_4 [O_2(1\Sigma_g^+)]
\]  

(5)

Since, under usual flow conditions, the \([O_2(1\Delta_g)]\) is approximately constant the first term on the right hand side of the above equation can also be taken as constant. \( k_4 \) can then be obtained from a knowledge of the rate of change of the \( O_2(1\Sigma_g^+) \) concentration. At steady state when \( \frac{d}{dt} [1\Sigma_g^+] = 0 \), equation (6) holds:

\[
k_3 [O_2(1\Delta_g)]^2 = k_4 [O_2(1\Sigma_g^+)]_{ss}
\]

(6)

and a knowledge of the \( O_2(1\Sigma_g^+) \) and \( O_2(1\Delta_g) \) concentrations gives \( k_3 \).

In the experiments to be described here a similar analysis is carried out. The temperature dependence of the change in the \( O_2(1\Sigma_g^+) \) concentration with time under non-stationary conditions, together with the variation of \([O_2(1\Sigma_g^+)/O_2(1\Delta_g)]^2\) with temperature allows the temperature variation of both \( k_3 \) and \( k_4 \). Determination of the \([O_2(1\Sigma_g^+)/O_2(1\Delta_g)]^2\) ratio was by comparison of the 7619 Å and 6340 Å bands, necessitating the determination of the absolute emission rate at 6340 Å mentioned earlier.
EXPERIMENTAL

The three experiments described here require, in each case, control and measurement of certain specific parameters, necessitating the use of three different flowtubes designed to meet the particular requirements of each experiment. The design of the gas inlets, controls, flow detectors, pressure gauges and pumping system, however, remained essentially the same since the flowtube design was altered only between conveniently placed ground glass joints. The general design of a flow system is shown in Fig. III. The particular variations on this design will be dealt with later.

The main oxygen flow through the system was controlled using an Edward's needle valve and the flowrate was determined from the pressure difference across a capillary measured using a differential manometer filled with dibutyl phthalate. This manometer was calibrated on known flowrates determined by collecting the quantity of gas passing through the system in a given time.

The added gas was contained in a 2 litre bulb and admitted to the flowtube by a similar system to that employed for the mainstream oxygen. It was found, however, that unless $P$, the pressure in the storage bulb, could be kept constant the flowrate could not be monitored using the familiar Poiseuille relationship:

$$F = \frac{r^4 \pi \Delta P(2P - \Delta P)}{16 \eta LRT}$$

where \( F \) = flowrate in mole sec\(^{-1}\).
Fig. III. Diagram of apparatus used for measuring the emission intensity along the tube using a photomultiplier and the absolute concentration of an excited species using an isothermal calorimeter.
DISCHARGE

LIGHT TRAPS,
* QUARTZ Hg (7mm. O.D.)

REFLECTOR

REACTANT • MULTIPLE JETS

CALORIMETRIC DETECTOR

Co FILTER WIRE SLITS

TO TRAPS AND PUMP

PHOTOMULTIPLIER
\[ \Delta P = \text{pressure difference across capillary in dynes/cm}^2 \]
\[ r,L = \text{radius, length of capillary in cms.} \]
\[ \eta = \text{viscosity of gas in poise.} \]
\[ T = \text{temperature (°K)} \]

This difficulty was overcome by determining \( \frac{dP}{dt} \) using a pressure gauge made by Texas Instrument Co. which could linearly measure pressure of up to one atmosphere to an accuracy of 0.02 torr. The decrease in pressure with time was then measured over a period of about 5 minutes and, using the volume of the storage bulb, the flowrate could be determined directly.

The oxygen was Matheson extra-dry grade which was used without further purification. The nitrogen dioxide was made from nitric oxide, obtained from Matheson Co. and purified as described in Part II. The bulb was filled to about 200 torr with nitric oxide and then to a pressure just below one atmosphere with pure oxygen. The gas was then solidified to 77°K, pumped on to remove excess oxygen and nitric oxide and eventually allowed to warm up to room temperature. This procedure was repeated several times until a pure white flaky solid was produced (36).

The three different flowtubes had similar singlet oxygen production systems. The discharge was maintained by power supplied through a 214L gas discharge cavity from an Electromedical Supplies 'Microtron' microwave generator with a continuous 2450 MHz output. The cavity could be tuned to resonance which, as well as producing a steadier discharge,
also minimized destructive interference with power reflected back along the leads. Although the unit had a maximum output of 200 watts, it was found that the singlet oxygen concentration increased only slightly with increasing power above 75 watts. In order to eliminate stray light produced by the discharge, the gas was passed through two conventional light traps before being admitted to the flowtube. The whole discharge area as well as the light traps were covered with flat, black paint.

The atomic oxygen was removed from the discharge products by distillation of a little mercury to form a surface of mercuric oxide on the walls of the tube. It was found that if the mercury was placed near the discharge, it could be maintained at a sufficient temperature to be effective by simply altering the position of the cavity along the tube.

The absolute $O_2(^1\Delta_g)$ concentration was determined by the isothermal calorimeter technique (19). This consists of deactivation of all the $O_2(^1\Delta_g)$ on an electrically heated wire known as a detector. The heat liberated by the $O_2(^1\Delta_g)$ is then matched by an appropriate decrease in the current through the wire, the difference providing an accurate measurement of the $O_2(^1\Delta_g)$ concentration. In practice the detector consists of a helically wound spiral of platinum wire, electroplated with cobalt. The circuit is shown in Fig. IV. In the absence of $O_2(^1\Delta_g)$, the bridge is balanced allowing the resistance, $R$, of the detector to be determined and the current, $i_o$, is measured using a potentiometer. The $O_2(^1\Delta_g)$ is then passed over the detector and the bridge rebalanced by decreasing the current. Thus by equalizing $R$ before and after the $O_2(^1\Delta_g)$ addition,
Fig. IV. Circuit for isothermal calorimeter.
-16-

P potentiometer terminal
C common "
G galvanometer "
T tapping key
the temperature of the detector is maintained at a constant value. The current \(i\) is again measured. The \(O_2(1\Delta_g)\) flowrate is given by:

\[
\frac{d [O_2(1\Delta_g)]}{dt} = \frac{\Delta(i)^2 R}{K E}
\]

where \(\Delta(i)^2 = i_o^2 - i^2\)

\(E = \) energy liberated per mole = 23 kcals. mole\(^{-1}\) for \(O_2(1\Delta_g)\)

\(K = 4.18 \text{ cal. secs. watts}^{-1}\)

The efficiency of the detector was checked by detection of the 6340 Å band downstream of the detector. In each case it was observed that >95% of the \(O_2(1\Delta_g)\) was removed from the stream.

The 7619 Å and 6340 Å bands were detected in all cases using an RCA 7265 photomultiplier (S20). The signal was chopped, amplified by a Tektronix 122 preamplifier and then fed into a PAR JB-5 lock-in amplifier where both phase and frequency were compared with a similarly chopped reference signal. Spectra were taken using a low resolution f/6.5 Bausch and Lomb grating monochromator with a slit width of about 1 mm. Very weak signals were isolated using interference filters to select the wavelength. For the 7619 Å band a Bausch and Lomb 337876 filter was used in conjunction with a Corning 2424 filter to eliminate the large first order 'window' at 3800 Å. For the 6340 Å band a Bausch and Lomb 337863 filter was used, the first order being in a region of low photomultiplier response as well as being well removed from any singlet oxygen bands or \(NO_2\) emission with which the apparatus was calibrated. The light cone collected was always about 30° which was easily sufficient for the purposes of this work.
Measurement of the absolute intensity of the 6340 Å emission as a function of the \( O_2^{1\Delta_g} \) concentration.

Apparatus similar to that shown in Fig. III was used in this experiment. The total \( O_2^{1\Delta_g} \) concentration was measured using an isothermal calorimeter which was placed at the end of a 25 cm. long, 3.5 cm. diameter flowtube. The 6340 Å emission was viewed across the tube with an RCA 7265 photomultiplier together with a suitable filter. The absolute intensity of the 6340 Å band was determined by comparison with the \( NO_2 \) continuum produced by the addition of \( NO_2 \) to atomic oxygen:

\[
0 + NO_2 \rightarrow NO + O_2 \quad (7)
\]

\[
0 + NO + NO_2 + h\nu \text{ (continuum)} \quad (2)
\]

The original atomic oxygen concentration was found using the end point of the \( O - NO_2 \) titration - when \([NO_2] > [O]\) no green continuum is seen. The actual atomic oxygen concentration for reaction (2) is given by:

\[
[O] = [O]_{\text{titration}} - [NO_2]_{\text{added}}
\]

and

\[
[NO] = [NO_2]_{\text{added}}
\]

Fontijn, Meyer and Schiff (3) have determined an absolute value for the total emission in the \( NO_2 \) continuum and have calculated a rate constant for reaction (2) of \( 3.8 \times 10^4 \) litres mole\(^{-1}\)sec\(^{-1}\). This value, however, represents the total \( NO_2 \) emission and since here only part of that emission is being observed, the rate constant must be reduced accordingly. This was done by taking the ratio of the shaded area to the total area under the continuum in Fig. V. The shaded area is the radiation of the continuum.
Fig. V. Relative intensity of the NO$_2$ continuum as a function of wavelength as given by Fontijn, Meyer and Schiff (3) compared with the relative intensity of the NO$_2$ continuum as seen by the photomultiplier through the filter.
modified by the filter transmission and adjusted to allow for the change in phototube response with wavelength. The curve is increased in height to match the continuum at its peak. Thus the change in filter transmission with wavelength is being used as a weighing factor with radiation at 6340 Å being a given weight of 1.

The second factor which had to be considered was whether all the light in the 6340 Å band would pass through the filter and how the 6340 Å band was modified by the filter transmission. This is illustrated in Fig. VI. The transmission curve of the filter was obtained using a parallel beam of light incident on the filter at 90°. The increased transmission to longer wavelengths due to the fact that a 30° cone of light was collected by the filter was found to be negligible. The total 6340 Å emission was thus given by:

\[ I(6340) = k_2 [0][NO] \frac{M_1}{M_2} \int_{-\infty}^{+\infty} F_S(\lambda)f(\lambda)d\lambda \int_{-\infty}^{+\infty} F_{6340}(\lambda)d\lambda \]

where \( k_2 \) = rate constant for reaction (2) = \( 3.8 \times 10^4 \) litres mole\(^{-1}\) sec\(^{-1}\).

\( F_S(\lambda), F_{6340}(\lambda) \) = function representing NO\(_2\) continuum and 6340 Å band respectively.

\( f(\lambda) \) = function representing filter transmission.

\( M_1, M_2 \) = recorded intensities of 6340 Å band and NO\(_2\) continuum respectively.
Fig. VI. Effect of filter on the 6340 Å band emission.
From Fig. V using the integrated areas under the curves:

\[
\int_{-\infty}^{+\infty} F_S(\lambda)f(\lambda)d\lambda / \int_{-\infty}^{+\infty} F_S(\lambda)d\lambda = 0.0145
\]

and from Fig. VI:

\[
\int_{-\infty}^{+\infty} F_{6340}(\lambda)f(\lambda)d\lambda / \int_{-\infty}^{+\infty} F_{6340}(\lambda)d\lambda = 0.458
\]

The atomic oxygen was produced by a microwave discharge of oxygen in the absence of mercuric oxide. A slight air afterglow was seen due to traces of nitrogen in the oxygen but this zero error was found to be negligible. To produce singlet oxygen the atomic oxygen was recombined by simply distilling mercury through the discharge until the characteristic red glow was seen.

**Measurement of the relaxation of \( O_2(1\Sigma_g^+) \) to steady state conditions as a function of temperature.**

A diagram of the flowtube used in this experiment is shown in Fig. VII. The uniform triple-walled tube was about 1 metre long and 1.9 cms. in diameter. The relative \( O_2(1\Sigma_g^+) \) concentration was measured by observation of the \((0,0)(1\Sigma_g^+ - 3\Sigma_g^-)\) transition at 7619 Å using an RCA 7265 photomultiplier together with a suitable filter. Opposite the photomultiplier was placed a polished aluminium reflector which not only increased the light input to the tube but also provided a constant back-
Fig. VII. Diagram of the apparatus used to measure the rate of change in the $O_2(\Sigma_g^+)$ emission at 7619 Å as a function of temperature.
ground for the emission. A rotating sectored disc was placed in front of the photomultiplier to chop the light input. The whole detection system was mounted on a platform which was moveable along the length of the tube. This arrangement allowed variation in the 7619 Å band intensity to be monitored as a function of distance along the tube.

The temperature in the flowtube was lowered by means of liquid nitrogen vapour, produced by placing a heating coil in a dewar of liquid nitrogen. The vapour was passed between the inner two walls of the triple-walled reaction vessel, the space between the outer two walls being evacuated. The temperature was measured with a copper-constantan thermocouple which was moveable along the inside of the tube in order to check for the uniformity of the gas temperature. This was found to vary by about 5% along the tube. The potential difference across the thermocouple was continuously monitored by means of a 10 mV strip chart recorder which was calibrated against a low temperature thermometer supplied by Fisher Scientific Co. by placing a thermometer and thermocouple in a series of stirred low temperature baths. The uniformity of the \( \text{O}_2 (^1\Delta_g) \) was checked using its emission at 6340 Å and found to be reasonably constant along the tube.

Measurement of the \( \frac{I(7619)}{I(6340)} \) ratio as a function of temperature.

For this experiment the flowtube consisted of a tube 1.9 cms. in diameter and 10 cms long surrounded by a jacket through which cold liquid nitrogen vapour could be passed, as in the previous experiment. A copper-
constantan thermocouple, placed in the gas stream was again used to measure
the temperature. Spectra were taken using a Bausch and Lomb f/6.5 mono-
chromator viewing the emission along the length of the tube. Scan times
were about 1 minute/200 Å. Some difficulty was encountered with frosting
of the observation window at low temperature, but its effect was reduced
by simply cleaning the window before each scan and then scanning the wave­
length range in both directions. The mean of the two scans was then taken.
The relative intensities of the 7619 Å band and the 6340 Å band were de­
termined by comparison of the region with the NO₂ continuum which was
produced in the cell by simply passing air through the discharge instead
of pure oxygen. The spectrum obtained was compared with the absolute
spectrum published by Fontijn, Meyer and Schiff (3). Thus any non-linearity,
such as phototube response, was eliminated.
RESULTS

The rate constant for 'dimol' emission at 6340 Å.

As mentioned earlier there have been two previous determinations of the rate constant for absolute emission at 6340 Å:

\[ I(6340) = k_1 [O_2(\Delta)^1_g)]^2 \]  \hspace{1cm} (1)

These determinations were made by Brown (33)(34) using an isothermal calorimeter and by Falick and Mahan (35) using paramagnetic resonance to measure the \(O_2(\Delta)^1_g\) concentration. Because the previous values differed by a factor of three, the present determination was performed to provide an independent test of \(k_1\) and to possibly allow a choice between the two values to be made.

\(O_2(\Delta)^1_g\) concentrations were measured using an isothermal calorimeter. The absolute emission at 6340 Å was obtained by comparison with the \(NO_2\) continuum produced by:

\[ O + NO \rightarrow NO_2 + hv \]  \hspace{1cm} (2)

The data is given in Table III. Absolute emission at 6340 Å was obtained by substitution in equation (8):

\[ I(6340) = \frac{k_2 [O][NO]}{M_1 A M_2} \]

where \(k_2 = \text{rate constant for reaction (2)} = 3.8 \times 10^4 \text{ mole}^{-1}\text{sec}^{-1}\). \(M_1, M_2 = \text{recorded intensities of 6340 Å band and } NO_2 \text{ continuum respectively.}\)
A = parameter adjusting transmission of 6340 Å band
and NO₂ continuum through filter = 0.032.

Substitution of I(6340), together with the O₂(¹Δg) concentrations into
equation (1) allowed an average value of 0.12 ± 0.04 litres mole⁻¹sec⁻¹
to be obtained for k₁. The principal error was due to the uncertainty in
the absolute intensity of the NO₂ continuum (3). This is in good agreement
with the value of 0.09 litres mole⁻¹sec⁻¹ reported by Brown (33)(34).

Mahan (35) has suggested that the discrepancy between the results of
the two determinations could be due to incomplete deactivation of all
vibrationally excited oxygen on the isothermal calorimeter. Assuming a
mean time for diffusion of the O₂(¹Δg) to the isothermal calorimeter of
10⁻³ secs and assuming deactivation at collision frequency, the O₂(¹Δg)
would be expected to be collected in about 1 cm. with a flowrate of
5 x 10² cms. sec⁻¹ used here. Further vibrational deactivation might
require anything up to 5 cms. In these laboratories it has been conventional
to use isothermal calorimeters forming coils about 2 cms. long. It is
thus conceivable that electronically deactivated O₂(¹Δg) might escape
the detector as vibrationally excited O₂(³Σg⁻). The O₂(¹Δg) conce-
tration would then appear falsely low even though all the 6340 Å emission
had been quenched, suggesting complete removal of the O₂(¹Δg) by the
detector.

The detailed experiments of Elias, Ogryzlo and Schiff (19) using
two isothermal calorimeters, however, show that this is certainly not
the case for recombination of atomic oxygen, which would presumably have
a similar O₂(³Σg⁻) vibrational deactivation process.
Table III

Intensity of emission at 6340 Å for different concentrations of $O_2(^1\Delta_g)$ and absolute emission calibration data.

<table>
<thead>
<tr>
<th>$O_2(^1\Delta_g)$ concentration expressed as a flowrate in moles. sec$^{-1}$</th>
<th>Recorded intensity of 6340 Å emission as seen by the photomultiplier (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5.97 \times 10^{-6}$</td>
<td>48/.02</td>
</tr>
<tr>
<td>$5.67 \times 10^{-6}$</td>
<td>39/.02</td>
</tr>
<tr>
<td>$7.03 \times 10^{-6}$</td>
<td>55/.02</td>
</tr>
</tbody>
</table>

Calibration conditions:

Flowrate of atomic oxygen = $2.45 \times 10^{-7}$ mole. sec$^{-1}$
Flowrate of nitric oxide = $4.96 \times 10^{-8}$ mole. sec$^{-1}$
Recorded intensity of NO$_2$ continuum as seen by the photomultiplier = 13/.002 (arbitrary units)
As far as Mahan's experiment is concerned, Westerberg (40) has criticized the use of the magnetic dipole transitions of oxygen for calibration of electric dipole transitions such as exhibited by \( \text{O}_2(\Delta_g) \). He states that the magnetic and electric field vectors of the microwave radiation are oriented at right angles to each other and even though they may be related in principle, in practice distortions of the field in the cavity for various reasons cause the theoretical calculations to be somewhat unreliable.

Thus the question of which of the two values for \( k_1 \) is correct, remains unanswered. The value of \( k_1 \) found in this work will be used here.

The temperature dependence of the rate of wall deactivation of \( \text{O}_2(\Sigma_g^+) \).

It has already been mentioned that the \( \text{O}_2(\Sigma_g^+) \) concentration is governed by the two reactions:

\[
\text{O}_2(\Delta_g) + \text{O}_2(\Delta_g) \rightarrow \text{O}_2(\Sigma_g^+) + \text{O}_2(\Sigma_g^-) \tag{3}
\]

\[
\text{O}_2(\Sigma_g^+) + \text{wall} \rightarrow \text{O}_2(\Sigma_g^-) + \text{wall} \tag{4}
\]

or \( \text{O}_2(\Delta_g) \)

This gives:

\[
\frac{d[1\Sigma_g^+]}{dt} = k_3[\Delta_g]^2 - k_4[\Sigma_g^+] \tag{5}
\]

At steady state:

\[
k_3[\Delta_g]^2_{ss} = k_4[\Sigma_g^+]_{ss} \tag{6}
\]
The first term on the right hand side of equation (5) is taken as constant since the $O_2(^1\Delta_g)$ concentration is approximately constant along the tube.

In order to independently vary the $O_2(^1\Sigma_g^+)$ concentration without changing the $O_2(^1\Delta_g)$ concentration it is necessary to disrupt the $O_2(^1\Sigma_g^+)$ production-deactivation balance. This was achieved by chance in the previous work of Arnold and Ogryzlo (23). Unfortunately, little is known of the reason why the necessary conditions were obtained in their apparatus. Great difficulty was encountered in trying to repeat their conditions in a normal glass apparatus which suggested that other factors might be involved apart from the initial formation of non-stationary concentrations in the discharge. (A decrease in the deactivation rate by a change in the slight mercuric oxide deposit on the walls, for instance). Other methods of producing non-stationary conditions were thus tried. These included a temperature drop ($500^\circ K \rightarrow 200^\circ K$) and introduction of glass wool into the flow system to increase the surface deactivation area, both of which were unsuccessful. It was eventually found that partial deactivation of the $O_2(^1\Sigma_g^+)$ on silver wire produced the required conditions which were optimum with about 50 cms. of silver wire (10 gauge) forming a grid across the tube.

The increase in the 7619 Å emission with distance along the tube after the silver wire is tabulated in Table IV for eight pressures and two temperatures. This data is plotted in Fig. VIII.

Combining equations (5) and (6) gives:

$$\frac{d[1\Sigma_g^+]}{dt} = k_4([1\Sigma_g^+]_{ss} - [1\Sigma_g^+])$$
Table IV

Intensity of 7619 Å emission as a function of distance along the tube at different pressures and temperatures.

1. Pressure = 2.90 torr  
   Temperature = 20°C

2. Pressure = 3.22 torr  
   Temperature = 20°C

<table>
<thead>
<tr>
<th>Distance along tube (cms.)</th>
<th>I(7619) arbitrary units</th>
<th>Distance along tube (cms.)</th>
<th>I(7619) arbitrary units</th>
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</thead>
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<td>15.0</td>
<td>30</td>
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</tbody>
</table>
Table IV (continued)

3. Pressure = 4.16 torr
   Temperature = 20°C

4. Pressure = 4.98 torr
   Temperature = 20°C

<table>
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<tr>
<th>Distance along tube (cms.)</th>
<th>I(7619) arbitrary units</th>
<th>Distance along tube (cms.)</th>
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Table IV (continued)

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### Table IV (continued)

7. Pressure = 4.20 torr  
Temperature = -69°C  

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<th>Distance along tube (cms.)</th>
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<th>I(7619) arbitrary units</th>
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<tr>
<td>30</td>
<td>22.2</td>
<td>30</td>
<td>23.0</td>
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8. Pressure = 5.00 torr  
Temperature = -69°C
which on integration gives:

\[ 2.3 \log_{10}(\left[ \frac{1}{\Delta} \right]_{ss} - \left[ \frac{1}{\Sigma} \right]_{ss}) = -k_4 t + \text{constant} \]  

(9)

Thus a plot of \(2.3 \log_{10}(I(7619)_{ss} - I(7619))\) against time will have a slope of \(-k_4\). The use of relative instead of absolute values of the \(O_2\left(\frac{1}{\Sigma} \right)\) concentration will only effect the constant of equation (9). This plot is shown in Fig. IX. The value of \(k_4\) is 215 ± 20 sec\(^{-1}\) at 20°C and 170 ± 20 sec\(^{-1}\) at -69°C, which combined in an Arrhenius equation gives \(3.8 \times 10^2 \exp \left(\frac{-330}{RT}\right)\) sec\(^{-1}\). These values represent a direct determination of \(k_4\) and are thus independent of any other constant.

\(k_4\) can be seen from Fig. IX to be independent of the total pressure of the system. The values given here actually represent all pressure independent loss mechanisms, including radiative deactivation. These latter processes, however, are negligible with lifetimes of 0.15 sec\(^{-1}\) for the \((\frac{1}{\Sigma} + \frac{3}{\Sigma})\) transition (13)(21) and 2.6 \times 10^{-3} sec\(^{-1}\) for the \((\frac{1}{\Sigma} + \frac{1}{\Delta})\) transition (18).

The temperature dependence of \(O_2\left(\frac{1}{\Sigma} \right)\) production from energy-pooling of \(O_2(\frac{1}{\Sigma})\).

From reaction (6) at steady state:

\[
\frac{1}{\Sigma} = \frac{k_3}{k_4}
\]

(10)

Using the rate constants that govern emission:

\[
I(7619) = k \left[ O_2(\frac{1}{\Sigma}) \right]
\]

(11)

\[
I(6340) = k_1 \left[ O_2(\frac{1}{\Delta}) \right]^2
\]

(1)
Fig. VIII(a). Relative intensity of 7619 Å emission of $^2 \Sigma_g^+$ as a function of distance along the tube at 20°C.

Fig. VIII(b). Relative intensity of 7619 Å emission of $^2 \Sigma_g^+$ as a function of distance along the tube at -69°C.
the ratio of $k_3/k_4$ can be determined:

$$\frac{k_3}{k_4} = \frac{k_1 I(7619)}{k_{11} I(6340)}$$

(12)

The experimentally determined $I(7619)/I(6340)$ ratio under differing conditions is shown in Table V. In order to measure the temperature variation of $k_3$ the temperature dependence of the other constants in equation (12) must be known. The only one that does not vary is $k_{11}$ since this represents the Einstein coefficient for spontaneous emission. Child and Mecke's value of 0.145 sec$^{-1}$ will be used here. The variation of $k_1$ with temperature has been previously determined by Arnold, Brown and Ogryzlo (34). By combining this temperature dependence with the room temperature value of 0.12 found here, $k_1$ was calculated to be $7.3 \times 10^{-2}$ litres. mole$^{-1}$sec$^{-1}$ at -79°C. This, together with the results of Table V gave a mean value of 10.8 litres. mole$^{-1}$sec$^{-1}$ for $k_3/k_4$ at 293°K and 2.34 litres. mole$^{-1}$sec$^{-1}$ for $k_3/k_4$ at 194°K. Thus, using the value for $k_4$ determined here of $3.2 \times 10^2 \exp\left(-\frac{330}{RT}\right)$sec$^{-1}$, $k_3$ was found to vary as $6.7 \times 10^4 \exp\left(-\frac{2000}{RT}\right)$litres. mole$^{-1}$sec$^{-1}$, giving a value of $2.3 \times 10^3$ litres mole$^{-1}$sec$^{-1}$ at room temperature. $k_4$ is known to vary with differences in wall surface. The justification for using the results of the determination of $k_4$ in this experiment is that little variation would be expected. This is because the same borosilicate glass of the same internal diameter, and cleaned in the same fashion, was used in each case.

Arnold and Ogryzlo obtained a value of 1320 litres. mole$^{-1}$sec$^{-1}$ for
Fig. IX(a). Plot of $\log_{10}(\Sigma_{ss} - \Sigma)$ against time at 20°C.

Fig. IX(b). Plot of $\log_{10}(\Sigma_{ss} - \Sigma)$ against time at -69°C.
\[ \text{LOG}_{10} (\Sigma_{SS} - \Sigma) \]

\[ \text{TIME (x } 10^{-3} \text{ SECS.)} \]

20°C
\[ \log_{10}(\Sigma_{SS} - \Sigma) \]

Time (\( \times 10^{-3} \) secs.)

2.48 torr
3.04 torr
4.20 torr
5.00 torr

-69 °C
Table V.

Ratio of $I(7619)/I(6340)$ at different pressures and temperatures.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Pressure (torr.)</th>
<th>$I(7619)/I(6340)$ observed</th>
<th>$I(7619)$ corrected for $I(6340)$ non-linearity.</th>
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</thead>
<tbody>
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$k_3$ at room temperature. Thus some agreement between these results is obtained which, with uncertainties of ±35% in their values, is not unreasonable.
**DISCUSSION**

The $O_2$($^1\Sigma_g^+$) surface deactivation coefficient $\gamma$ and the deactivation controlling process.

The rate constant for wall activation of $O_2$($^1\Sigma_g^+$) is dependent on the dimensions of the flowtube and is better expressed as a surface deactivation coefficient, $\gamma$, defined by:

$$\gamma = \frac{\text{rate of wall deactivation}}{\text{Total number of collisions with wall per sec.}}$$

$$= \frac{N_o V k_{\text{wall}}}{N_o c A} = \frac{2\pi}{c} k_{\text{wall}}$$

where

$N_o$ = number of molecules per unit volume

$V$ = volume of flowtube = $\pi r^2 L$

$k_{\text{wall}}$ = rate constant for wall deactivation ($k_4$)

$= 215 \text{ sec}^{-1}$ at $20°C$ and $170 \text{ sec}^{-1}$ at $-69°C$

$A$ = surface area of flowtube = $2\pi r L$

$c$ = mean molecular velocity = $\int_0^\infty c \frac{dN_o}{N_o}$

$$\sqrt{\frac{8RT}{\pi M}} = 1.46 \times 10^4 \sqrt{\frac{T}{M}} \text{ cms. sec}^{-1}$$

$M$ = molecular weight of oxygen.

Using the $k_{\text{wall}}$ values found here for borosilicate glass walls cleaned with 50% HNO$_3$, water and acetone, $\gamma = 9.3 \times 10^{-3}$ at $20°C$ and $8.9 \times 10^{-3}$ at $-69°C$ giving a value which is only slightly temperature dependent. The room temperature value can be compared with $3.7 \times 10^{-3}$ obtained by Arnold and Ogryzlo (23) and $1.0 \times 10^{-2}$ obtained by Izod and Wayne (41).
The value of $\gamma$ is large enough to require a check to see whether it is governed by the actual surface deactivation process at the wall or by the rate of diffusion of the gas to the wall. This is usually determined in a rather crude fashion by comparing the expected mean time of diffusion to the walls, $t$, with the observed lifetime for the deactivation, $t_{wall}$; if $t > t_{wall}$ the reaction can be regarded as diffusion controlled. Einstein's equation for the displacement $x$ executed by a particle during time $t$ in a medium of self diffusion coefficient, $D$, is given by:

$$x^2 = 2Dt_d$$

(13)

$D$ is given by: $D = \frac{1}{3\lambda\bar{c}}$ where $\lambda$ is the mean free path in cms. and $\bar{c}$ is the mean molecular velocity. Taking the mean distance traversed by any molecule before striking any wall to be $r$ (37), equation (13) gives, on substitution:

$$t_d = \frac{3r^2}{2\lambda\bar{c}}$$

(14)

$\lambda$ varies inversely with pressure and thus, using a standard value for $\lambda$ at room temperature and one atmosphere of $9.93 \times 10^{-6}$ cms. (42), equation (14) gives: $t_d = 4.1 \times 10^{-3}P$ for $P$ in torr. Typical pressures are about 2.5 torr. for which $t_d$ is about $1.3 \times 10^{-2}$ secs. This has to be compared with values of $t_{wall} (= 1/k_{wall})$ of $0.5 \times 10^{-2}$ secs at $20^\circ$C and $0.6 \times 10^{-2}$ secs at $-69^\circ$C, which gives $t_d > t_{wall}$ suggesting that the process is diffusion controlled.

There is, however, in this particular case an alternative mechanism
by which the $O_2(1\Sigma^+_g)$ energy can be transferred to the walls. This is by an energy exchange mechanism. Because of exact resonance with a neighbouring oxygen molecule, the $O_2(1\Sigma^+_g)$ exchange process should be fairly efficient. The low transition probability of the $(1\Sigma^+_g - 3\Sigma^-_g)$ transition, however, would be expected to restrict this exchange to a rate not much greater than collision frequency. Treating this exchange as a typical 'random-walk' problem, the rate of energy transfer to the walls at collision frequency can be expressed by a normal distribution curve. Thus if $r$ is the mean distance for a molecule to travel before reaching the walls (37):

$$r = \left( \frac{8n\lambda^2}{\pi} \right)^{\frac{1}{2}}$$

(15)

where $n =$ mean number of collisions for the energy to travel a distance $r$. Expressing the time required to reach the walls by:

$$t_{\text{ex}} = \frac{\text{number of collisions required to transfer energy to walls}}{\text{collision frequency}}$$

and substituting in with equation (15), gives:

$$t_{\text{ex}} = \frac{n}{(c/\lambda)} = \frac{\pi r^2}{8\lambda c}$$

(16)

Comparing equation (16) with equation (14) it can be seen that transfer of energy to the walls by this exchange mechanism is $4 \times$ faster than by a diffusion mechanism. This gives values of $t_{\text{ex}}$ of about $3.2 \times 10^{-3}$ secs and thus $t_d > t_{\text{wall}} > t_{\text{ex}}$ implying that $t_{\text{wall}}$ is not governed by the rate of transfer of $O_2(1\Sigma^+_g)$ to the wall but by the actual surface deactivation process at the wall.
Support for the fact that $k_{\text{wall}}$ is controlled by the surface deactivation process is given by the lack of its pressure and temperature dependence. Energy exchange and diffusion mechanisms would be expected to show a considerable variation with both temperature and pressure, whereas the lack of pressure dependence and small temperature dependence of a surface deactivation mechanism are in keeping with the results of both atomic oxygen (19) and nitrogen (44) wall recombination.

Further support is given by the original experiments of Young and Black (45) in which they compared directly the quenching rates of $N_2O$, $N_2$, and $CO_2$ against $k_{\text{wall}}$. A change in reaction tube diameter by a factor of 2.2 produced a similar change in the value of $k_{\text{wall}}$. This direct dependency on $r$ would be expected for a surface deactivation process but not for an energy exchange (equation (16)) or diffusion controlled (equation (14)) process. Young and Black also concluded that deactivation was controlled by a surface quenching mechanism.

The rate constant for deactivation of the $O_2(^1\Sigma_g^+)$ on the wall is about 215 sec$^{-1}$ at room temperature. This corresponds roughly to 1 collision in 100 which is comparable to methanol or ammonia in its quenching ability (38). The presence of water adsorbed to the surface of the glass might account for this.

The similarity of quenching rate on the wall with that involving normal quenching molecules suggests the possibility of a similar mechanism being used in each case. The relaxation of the $O_2(^1\Sigma_g^+)$ to $O_2(^1\Delta_g)$ or $O_2(^3\Sigma_g^-)$ can thus be represented by the general expressions:
where M represents the quenching molecule or wall. Information on which of the two processes is taking place could be gained by observing the effect of using a paramagnetic molecule as the quencher. The paramagnetism should effect the spin change in reaction (18), but have little effect on reaction (17). This is conveniently done by comparison of the quenching rates of oxygen and nitrogen shown in Table I. In the case of $O_2(1\Sigma_g^+)$ quenching, which must be by a spin change mechanism similar to reaction (18), oxygen is a better quencher than nitrogen. The reverse is true for $O_2(1\Sigma_g^-)$, implying no change in spin multiplicity and consequently quenching via reaction (17). The evidence is not foolproof but it seems likely that a spin allowed mechanism would be preferable to a spin forbidden mechanism requiring a greater conversion of electronic energy into vibrational energy. This also agrees with the theoretically predicted mixing of the $1\Sigma_g^+$ and $1\Delta_g$ states upon perturbation of the molecule with a component at right angles to the internuclear axis (46) facilitating this $1\Sigma_g^+ \rightarrow 1\Delta_g$ interconversion. Using this mechanism, however, it is very difficult to say what the slight activation energy of the wall deactivation process would represent.

It is possible that the observed temperature dependence is totally unconnected with the wall deactivation process but is simply due to a slowing up in the rate of transfer of the $O_2(1\Sigma_g^+)$ from the gas phase to the wall at lower temperature. Thus a slight contribution to the reaction
rate from the transfer process (using either the diffusion or energy exchange mechanism) at the lower temperature might result in a small temperature dependence without the corresponding pressure effect being noticed.

Energy pooling of two $O_2(\text{^1}\Delta^g)$ molecules to form $O_2(\text{^1}\Sigma^+)$. The energy pooling reaction:

$$O_2(\text{^1}\Delta^g) + O_2(\text{^1}\Delta^g) \rightarrow O_2(\text{^1}\Sigma^+) + O_2(\text{^3}\Sigma^-)$$

provides a conceptually rather simpler case than wall deactivation of $O_2(\text{^1}\Sigma^+)$. It can be regarded as an energy transfer in which one oxygen molecule loses energy in a $\text{^1}\Delta^g - \text{^3}\Sigma_g^-$ transition while the other gains energy by excitation from the $\text{^1}\Delta^g$ state to the $\text{^1}\Sigma^+$ state. This situation is illustrated in Fig. X. Energy transfer has been treated for large molecules as a resonance transfer process involving either long-range or coupled interactions (47)(48). In this case a collisional perturbation would be required to give the levels the exact resonance energy. Again little can be said about the magnitude of the observed temperature dependence of this reaction.
Fig. X. A diagramatic comparison (to scale) of possible transition energies of unperturbed molecules.
CONCLUSION

The rate constant for deactivation of the \( \text{O}_2(\Sigma_g^+) \) on the wall of the reaction vessel was found to be \( 3.8 \times 10^2 \exp(-\frac{330}{RT}) \) sec\(^{-1}\). It was concluded that this represented the actual process on the wall and not any diffusion controlled mechanism as previously suggested.

The rate constant for formation of \( \text{O}_2(\Sigma_g^+) \) from a bimolecular reaction involving \( \text{O}_2(\Delta_g) \) was found to be \( 6.7 \times 10^4 \exp(-\frac{2000}{RT}) \) litres. mole\(^{-1}\)sec\(^{-1}\).

The controversy over the value of the absolute emission rate at 6340 Å was not resolved. Both Browne's and Falick and Mahan's values still stand. An independent method of measuring the \( \text{O}_2(\Delta_g) \) concentration is really required. However, for all such methods known to date a calibration on an absolute standard is needed. This necessarily involves an isothermal calorimeter or a calibrated EPR cavity unless some other method can be devised.
PART II.

A Kinetic and Spectroscopic Investigation of the $N + O_2(^1\Delta_g)$ System.
INTRODUCTION

Of considerable interest to the study of chemical aeronomy is a knowledge of the rate constant for the homogeneous reaction between atomic nitrogen and $O_2(1\Delta_g)$ to form nitric oxide. Experiments performed to determine this rate constant will be described here, together with some work on the origin of various glows seen near the surface of certain metals exposed to these species. These glows involve the excited states of both molecular nitrogen and nitric oxide. Because of its direct bearing on the present work, a brief summary of the theories of radiative recombination of these molecules will be given. More extensive reviews can be found in the literature. (44)(49)

Gas-phase recombination of nitrogen atoms giving rise to the first positive emission of molecular nitrogen.

The well known Lewis-Rayleigh afterglow of nitrogen produced by the action of a high frequency electrodeless or condensed electrode discharge of the gas, has the characteristic yellow colour of the first positive emission of nitrogen $N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+)$ (see Fig. XI). The spectrum stretches from 5000 Å to 1.1μ in the infrared and consists of emission from all vibrational levels up to $v' = 12$ which is just below the dissociation energy of the nitrogen ground state at 9.76 eV. When two $N(^4S)$ atoms recombine to form molecular nitrogen, they can form any of the following states (50): $1\Sigma_g^+, 3\Sigma_u^+, 5\Sigma_g^+, 7\Sigma_u^+$. The last state is repulsive. The $B^3\Pi_g$ state cannot be populated directly necessitating involvement of the three lowest lying states. Mechanisms based on both
Fig. XI. $N_2$ potential energy diagram as compiled by Gilmore (1).
the $A^3\Sigma_u^+$ and $S\Sigma g^+$ states have been proposed.

One of the first attempts to provide a possible mechanism for the first positive emission was by Kistiakowsky and co-workers (51)(52) who, on the basis of a study of the variation in vibrational level population distribution of the $B^3\Pi_g$ state with temperature and with added foreign gases, suggested that the $B^3\Pi_g$ state was populated by a collision-induced transition from the $\Sigma g^+$ state, thus:

$$N_2(S\Sigma g^+) + M \rightarrow N_2(B^3\Pi_g) \nu' = 12,11,10 + M$$

(19)

The rate of population of the $B^3\Pi_g$ state required the $S\Sigma g^+$ state to be in equilibrium with atomic nitrogen:

$$N(4S) + N(4S) + M \rightarrow N_2(S\Sigma g^+) + M$$

(20)

In order to explain the smaller maximum in emission for the $B^3\Pi_g$, $\nu' = 6$ vibrational level and the increase in emission from the $\nu' = 4 \rightarrow 0$ vibrational levels in the first positive systems, Kistiakowsky et al proposed a series of cascade processes involving other intermediate species:

$$S\Sigma g^+ \overset{M}{\rightarrow} B^3\Sigma_u^- \nu' = 8,7,6 \rightarrow B^3\Pi_g \nu'' = 4,3,2$$

(21)

$$M \rightarrow 3\Delta_u \rightarrow B^3\Pi_g \nu' = 7,6,5$$

(22)

They also maintained that emission from the lower levels could be maintained by a direct collision-induced radiationless transition from the $N_2(A^3\Sigma_u^+)$ state around the $\nu'' = 8$ level.

Harteck, Reeves and Mannella (53) suggested that the $B^3\Pi_g$ state was populated in $\nu' = 6$ region from highly vibrationally excited $N_2(A^3\Sigma_u^+)$
molecules. They gave as evidence the fact that the first positive spectrum observed near the surface of certain metals involves only vibrational levels of this $\nu' = 6$ region which, because of the crossing of the potential curves, is the region of maximum overlap of the two wave functions.

Campbell and Thrush (54) endorsed this view by determining a rate constant of $6.2 \times 10^8$ litres$^2$ moles$^{-2}$ sec$^{-1}$: this, they maintain, is incompatible with population of the $B^3\Pi_g$ state from the $5\Sigma_g^+$ state, because the stabilization of this state is not high enough to provide a sufficient equilibrium population (reaction (20).) They therefore proposed that the $B^3\Pi_g$ state is populated by a collision-induced radiationless transition from the $A^3\Sigma_u^+$ and that the variation in population distribution with vibrational energy level reflects the ease with which crossing can take place at that particular level. Some evidence for this ($A^3\Sigma_u^+ - B^3\Pi_g$) crossing is provided by the breaking off of the forbidden Vegard-Kaplan emission from the $A^3\Sigma_u^+$ state above the $\nu'' = 6$ level (55).

Benson (56) has recently treated this system from a point of view of production via the $5\Sigma_g^+$ state. He shows that since the probability of the curve crossing ($5\Sigma_g^+ \rightarrow B^3\Pi_g$) is about $10^{-1} - 10^{-2}$ per collision there is an equilibrium set up between rotationally hot members of the 12th vibrational level of the $B^3\Pi_g$ state and free nitrogen atoms, without the intervention of a third body. Rotational quenching then populates the 12th vibrational level and this is followed by vibrational quenching populating the 11th, 10th and 9th levels in competition with emission.
Since neither Campbell and Thrush or Benson can satisfactorily exclude the possibility of each other's mechanism taking place the question of the recombination path to produce the first positive emission is still open. The principle emission spectra seen in molecular nitrogen are listed in Table VI.

Radiative recombination of nitric oxide.

Young and Sharpless (49) and Callear and Smith (57) have extensively studied the kinetics and mechanism of the recombination process:

$$\text{N}(^4S) + \text{O}(^3P) + \text{M} \rightarrow \text{NO}^* + \text{M}$$ (23)

They have concluded that the mechanism for recombination of N($^4S$) and O($^3P$) atoms involves formation initially into the NO($^4\Pi$) state (see Fig. XII) followed by a 'pre-association' crossing into the $C^2\Pi$ v = 0 state, giving rise to the $\delta$ bands ($C^2\Pi - X^2\Pi$). The $A^2\Sigma$, v = 0 state is then excited by both cascade radiation (the (0,0)($C^2\Pi - A^2\Sigma$) band being at 1.22 μ) and by collisional crossing from the $C^2\Pi$ and a $^4\Pi$ states. The $a^4\Pi$ state spontaneously populates the $b^4\Sigma$ state which, in turn, populates the $B^2\Pi$ state by means of a collision-induced transition. The various emission spectra seen from NO are listed in Table VII.

The homogeneous reaction between N($^4S$) and O$_2$(1$\Delta_g$).

The first estimate for the rate of the reaction:

$$\text{N} + \text{O}_2(1\Delta_g) \xrightarrow{k_{24}} \text{NO} + \text{O}$$ (24)

was made by Hunten and McElroy (58) who were interested in this reaction as a possible source of NO in the 90 km region of the upper atmosphere.
Table VI

Principle band spectra seen in molecular nitrogen.

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<thead>
<tr>
<th>Emission</th>
<th>Transition</th>
<th>Approximate spectral region</th>
<th>Type of transition</th>
</tr>
</thead>
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<tr>
<td>First positive system</td>
<td>$B'\Pi_g \rightarrow A'\Sigma_u$</td>
<td>5000 - 25000 Å</td>
<td>electric dipole</td>
</tr>
<tr>
<td>'Y' bands</td>
<td>$B'3\Sigma_u - B'\Pi_g$</td>
<td>6000 - 10800 Å</td>
<td>electric dipole</td>
</tr>
<tr>
<td>Vegard-Kaplan bands</td>
<td>$A'\Sigma_u - X'\Sigma_g$</td>
<td>2100 - 5000 Å</td>
<td>forbidden by $\Delta S = 0$ approximation</td>
</tr>
<tr>
<td>Lyman-Birge-Hopfield bands</td>
<td>$a'\Pi_g - X'\Sigma_g$</td>
<td>1200 - 2600 Å</td>
<td>magnetic dipole and electric quadropole</td>
</tr>
<tr>
<td>Second positive system</td>
<td>$C'\Pi_u - B'\Pi_g$</td>
<td>2800 - 5450 Å</td>
<td>electric dipole</td>
</tr>
<tr>
<td>Birge-Hopfield system</td>
<td>$b'1\Sigma_u - X'\Sigma_g$</td>
<td>930 - 1650 Å</td>
<td>electric dipole</td>
</tr>
<tr>
<td>$3\Delta_u - 3\Pi_g$ system</td>
<td>$3\Delta_u - 3\Pi_g$</td>
<td>22500 - 7700 Å</td>
<td>electric dipole</td>
</tr>
</tbody>
</table>
Fig. XII. NO potential energy diagram as compiled by Gilmore (1).
Table VII
Principle band spectra seen in nitric oxide

<table>
<thead>
<tr>
<th>Band</th>
<th>Transition</th>
<th>Wavelength</th>
</tr>
</thead>
<tbody>
<tr>
<td>β bands</td>
<td>$B^2Π - X^2Π$</td>
<td>5000 - 2000 Å</td>
</tr>
<tr>
<td>γ bands</td>
<td>$A^2Σ^+ - X^2Π$</td>
<td>2250 - 2800 Å</td>
</tr>
<tr>
<td>δ bands</td>
<td>$C^2Π - X^2Π$</td>
<td>1900 - 2400 Å</td>
</tr>
<tr>
<td>Ogawa bands</td>
<td>$b^4Σ - a^4Π$</td>
<td>7500 - 9000 Å</td>
</tr>
</tbody>
</table>
For the reaction:

\[ N + O_2 \xrightarrow{k_{25}} NO + O + 1.42 \text{ eV} \] (25)

the experimental data could be adequately reproduced using 
\[ k_{25} = 1.2 \times 10^{8.5 \frac{1}{2}} T \exp\left(\frac{3000}{T}\right) \text{ litres. mole}^{-1} \text{sec}^{-1}. \] Since reaction (24) has 0.98 eV more energy at the beginning and the activation energy of reaction (25) is only 0.28 eV, a first approximation to the rate constant was made by setting the exponential factor to unity giving 
\[ k_{24} = 1.8 \times 10^9 \text{ litres. mole}^{-1} \text{sec}^{-1} \] at 200°K.

From the concentrations of the constituents of the 90 Km region of the upper atmosphere and assuming steady state kinetics it was found that to successfully account for the NO concentration at that height a value for \( k_{24} \) of \( 1.8 \times 10^8 \text{ litres. mole}^{-1} \text{sec}^{-1} \) was required. Since no direct laboratory determination of this rate constant had been previously made, the present work was done in an attempt to verify these values.

**Surface catalysed emission of N\(_2\) and NO.**

About 1960, there appeared in the literature a series of three papers by Harteck, Reeves and Mannella (57)(58)(51) concerned with surface catalysed excitation of molecular nitrogen and nitric oxide produced with mixtures of the flowing afterglows of nitrogen and oxygen discharges. They observed three glows: (A) A red glow consisting of the nitrogen first positive emission bands, seen in the gas phase near surfaces of Co, Cu, Ni and Ag in the presence of the combined products of nitrogen and oxygen discharges. Emission is maximum from the \( \text{B}^3\text{II}_g \ v' = 6 \) level and no emission was seen for \( v' > 8 \). The glow extended 10-15 mm into the
gas phase. (B) A blue glow consisting of the NO $\beta$ bands, seen near the surface of nickel in the presence of the combined products of the nitrogen and oxygen discharges. (The red glow (A) was also present.) No NO $\gamma$ or $\delta$ bands were seen. The glow extended only a few millimetres into the gas phase. (C) A weak blue glow consisting of the $N_2$ second positive system ($C^{3}\Pi_u - B^{3}\Pi_g$) observed near copper maintained at 15-20°C in a nitrogen afterglow only. It extended about 2 mm. into the gas phase.

In their first paper (59), Harteck et al. proposed the following mechanism for the formation of the red (A) and blue (B) glows over nickel:

\[
N(4S) + O(3P) \xrightarrow{M} NO(B^2\Pi) \quad (26)
\]

formed on surface and goes into gas phase.

\[
NO(B^2\Pi) \rightarrow NO(X^2\Pi) + hv(\beta \text{ bands}) \quad (27)
\]

\[
N + NO(B^2\Pi) \rightarrow N_2(B^3\Pi_g) + O(3P) \quad (28)
\]

\[
N_2(B^3\Pi_g) \rightarrow N_2(A^3\Sigma_u^+) + hv \text{ (first positive bands)} \quad (29)
\]

This mechanism is successful in explaining the fact that the nitrogen first positive emission of the red glow was only from vibrational levels with $v' < 8$, since the maximum energy produced by reaction (28) is just sufficient to excite the $N_2(B^3\Pi_g)$ to the $v' = 8$ level.

Harteck et al. pointed to the slightly greater intensities of the transitions from the $NO(B^2\Pi)$ $v' = 0$ vibrational level for corroboration. The difficulty with this mechanism is that it is necessary to evoke some unique property of the metal in order to account for the absence of $\gamma$ and $\delta$ bands in the blue glow.
Harteck et al. later became doubtful of this theory when they found that the red glow produced over cobalt was rather more extensive than over nickel, giving a lifetime for the metastable species of $10^{-3}$ secs. This is incompatible with the upper limit for the $\text{NO}(B^2\Pi)$ lifetime of $10^{-6}$ secs. set by Keck et al. (61). Thus Harteck (53) proposed the idea of recombination of the nitrogen atoms into the $N_2(A^3\Sigma_u^+)$ state on the surface of the metal followed by diffusion into the gas phase where conversion to the $B^3\Pi_g$ state with $v' < 8$ takes place by a collision-induced radiationless transition. Harteck relegated the function of the atomic oxygen to some sort of 'conditioning' process on the metal surface. The blue glow from nickel was then produced by the reverse of reaction (28):

$$N_2(A^3\Sigma_u^+) + O(^3P) \rightarrow \text{NO}(B^2\Pi) + N(^4S) \quad (30)$$

The concentration of $N_2(A^3\Sigma_u^+)$ state would probably be controlled by the fast reaction:

$$N_2(A^3\Sigma_u^+) + N(^4S) \rightarrow N_2(X^1\Sigma_g^+) + N \quad (31)$$

Rate constants of $3 \times 10^9$ litres mole$^{-1}$sec$^{-1}$ (62) and $3 \times 10^{10}$ litres mole$^{-1}$sec$^{-1}$ (63)(64) have been determined for this deactivation process. From measurements on the intensity of the glow as a function of distance away from the cobalt surface, Weinreb and Mannella (65) have set an upper limit of $3 \times 10^8$ litres mole$^{-1}$sec$^{-1}$ for $k_{31}$, which, if Harteck is correct, involves high vibrational levels of the $A^3\Sigma_u^+$ state. The discrepancy between values quoted for high and low vibrational levels has then to be explained.
The weak blue glow (C) seen near the surface of copper in the nitrogen afterglow, Harteck (59) attributes to the nitrogen second positive system \((C^3Π_u - B^3Π_g)\). The extent of this glow into the gas phase, about 2 mm., eliminates the possibility of the metastable species being the \(C^3Π_u\) state since its radiative lifetime is too short (66). Some recent work by Stedman and Setzer (67) provides a possible excitation process:

\[
N_2(A^3Σ_u^+) + N_2(A^3Σ_u^+) \xrightarrow{k_{32}} N_2(C^3Π_u) + N_2(X^1Σ_g^+) \tag{32}
\]

They quote a value of \(1.25 \times 10^{10}\) litres mole\(^{-1}\) sec\(^{-1}\) for \(k_{32}\) which is based on a value for the \(N_2(A^3Σ_u^+)\) radiative lifetime of 2.0 secs given by Shemansky (68). If the metastable species is in fact the \(N_2(A^3Σ_u^+)\) state, then the production of the red glow on addition of discharged oxygen to this system is unexplainable using Harteck's theories.

The present work describes a re-examination of these glows in an attempt to clarify some of the confusion surrounding their production.
EXPERIMENTAL

The rate constant for the $N + O_2(1\Delta_g)$ reaction was determined in a conventional discharge-flow apparatus illustrated in Fig. XIII. The tube was about 1 metre long and 2.5 cms. in diameter with a quartz window attached to the downstream end of the tube through which spectra of the gaseous emission could be obtained. Two main inlets provided the discharged oxygen and nitrogen flows and four smaller inlets supplied nitric oxide for titration of the atomic nitrogen at different points along the tube. The flowrate control and measuring systems for both the main and added gases are identical to those described in Part I. Both discharges were optically isolated from the flowtube by means of blackened light traps.

The nitrogen used was ultra high purity grade obtained from Matheson Co. It still contained sufficient impurity to produce reasonable concentrations of nitrogen atoms (43) and was thus used without further purification. Nitric oxide was also obtained from the Matheson Co. and contained nitrogen dioxide, water and nitrogen as the main impurities. These were removed by passing the gas through soda lime followed by successive distillation at $-78^\circ$C with the initial and final fractions being discarded each time. The resultant was a pure white solid.

The singlet oxygen was produced by a mercury contaminated discharge as described earlier. Power to maintain the discharges was supplied through 214L gas discharge cavities from standard 2450 MHz microwave power supplies. Both cavities were cooled by blowing air through them. It was found that the atomic nitrogen concentration was roughly propor-
Fig. XIII. Flow apparatus used to measure decay of atomic nitrogen as a function of time.
Nitric oxide
Silica window
Monochromator

Nitrogen from discharge

Nitric oxide

Silica window

Monochromator

to McLeod gauge
to pump

Oxygen from discharge

Nitric oxide

Nitrogen from discharge
tional to the discharge power. To stop rapid recombination of the atomic nitrogen, the walls of the tube were 'poisoned' with orthophosphoric acid. This was then pumped on overnight, followed by several hours of exposure to atomic nitrogen before any attempt was made to measure experimental value. Between runs the apparatus was constantly under vacuum and the discharges were always run for about 1 hour before use. The method of switching on the apparatus always followed the same procedure: first the singlet oxygen discharge was switched on and the \( \text{O}_2(1\Delta_g) \) detected by its characteristic red glow. The molecular nitrogen was added through the other inlet and the apparatus left to check for the stability of the \( \text{O}_2(1\Delta_g) \) production system. Finally the nitrogen discharge was switched on. These precautions eliminated the possibility of incomplete recombination of the atomic oxygen by the mercury. The flowrate of \( \text{O}_2(1\Delta_g) \) was measured using an isothermal calorimeter and the total pressure was measured with a McLeod gauge which was usable between 0.1 torr and 5.0 torr.

The heterogeneous glows were first seen on the cobalt-plated platinum isothermal calorimeter situated at the downstream end of the above apparatus. The spectra of the cobalt and nickel glows in the visible and infrared were obtained by viewing the metal sideways across the tube. For the copper glows and the glows in the ultraviolet the metal was placed in a short cell, about 5 cms. long and 3 cms. in diameter, fitted with a silica window of about 1 mm. in thickness, through which the spectrum was obtained. Products of the nitrogen and oxygen discharges were mixed before entering the cell and were passed through several blackened light traps in order to eliminate stray light from the discharge. Entrance and exit ports in
this cell were made as wide as possible to stop streaming of the gases. This cell was fairly successful in minimizing the contribution to the spectrum of the Lewis-Rayleigh afterglow, except in the case of the blue copper glow which was particularly weak.

The spectra were taken in all cases using a Hilger-Watts f/4.5 monochromator. This instrument contains interchangeable quartz and glass prisms, the latter being used in the visible and infra-red because of the higher dispersion in those regions. Spectra were calibrated using an Ar/Ne lamp for the red end of the spectrum and a medium pressure mercury lamp for the blue end. Scan speeds were generally about 100 Å/minute. Detection devices varied according to the spectral region. Those used are listed in Table VIII. 'Photon-counting' techniques (69)(70) were found to give a definite improvement in signal-to-noise ratio using RCA IP28 and IP21 phototubes, but were about equal with phase sensitive detection techniques using an RCA 7265 phototube. For the liquid nitrogen cooled RCA 7102 phototube phase sensitive detection techniques were definitely superior. The RCA intrinsic germanium detector was a photoconductive device and thus could not be handled by the pulse discrimination techniques of 'photon-counting'. The electronics used for this 'photon-counting' apparatus were constructed of components supplied by Hamner Co. and consisted of a preamplifier, followed by a linear amplifier, an analyser and finally a linear ratemeter. The output of the ratemeter was recorded on a conventional strip chart recorder. Phase sensitive detection techniques have already been described.
Table VIII
Detection equipment

<table>
<thead>
<tr>
<th>Phototube (RCA)</th>
<th>Response</th>
<th>Approximate spectral range (Å)</th>
<th>Amplification system</th>
</tr>
</thead>
<tbody>
<tr>
<td>IP28</td>
<td>S5</td>
<td>2500 - 6000</td>
<td>photoncounting</td>
</tr>
<tr>
<td>IP21</td>
<td>S4</td>
<td>3200 - 6500</td>
<td>photoncounting</td>
</tr>
<tr>
<td>7265</td>
<td>S20</td>
<td>3200 - 8000</td>
<td>photoncounting, P.S. detection</td>
</tr>
<tr>
<td>7102 cooled to 77°K</td>
<td>S1</td>
<td>5000 - 11000</td>
<td>phase sensitive detection</td>
</tr>
<tr>
<td>intrinsic germanium photodiode cooled to 77°K</td>
<td>S25</td>
<td>8000 - 17000</td>
<td>phase sensitive detection</td>
</tr>
</tbody>
</table>
The surfaces of the cobalt and nickel were cleaned before use with 50% hydrochloric acid although cleaning was found to have little effect on the intensity of the glow. Both metals were of 'technical' grade and were in either wire or pellet form. More attention was paid to the surface of the copper since the glow was so weak. 'Analar' sheet copper was used and the surface cleaned with steel wool and an organic solvent. Of the methods tried, including cleaning with 50% nitric acid and depositing and removing layers by electrolysis, this was the only one that produced a reasonable glow. The copper sheet was aligned parallel to the entrance slit of the monochromator.
RESULTS

The homogeneous reaction between $N$ and $O_2(\Delta_g^1)$. Using the discharge-flow techniques, the predicted (58) rate constant for reaction (24) should produce an easily measurable change in the nitrogen atom concentration along the tube:

$$N + O_2(\Delta_g^1) \rightarrow NO + O \quad (24)$$

Atomic nitrogen concentrations were determined by titration with nitric oxide:

$$N + NO \rightarrow N_2 + O \quad (33)$$

which if $[N] > [NO]$, gives rise to blue emission from nitric oxide:

$$N + O + M \rightarrow NO^* + M \quad (23)$$

$$NO^* \rightarrow NO + \hbar\nu(\beta, \gamma \text{ and } \delta \text{ NO bands})$$

or, if $[N] < [NO]$ the green air afterglow is obtained:

$$NO + O \rightarrow NO_2 + \hbar\nu \text{ (continuum)} \quad (34)$$

At $[N] = [NO]$ no emission is seen. The end point is very sharp and it was found that detection by eye was as good as using photoelectric methods. The $O_2(\Delta_g^1)$ was determined by isothermal calorimeter. Preliminary experiments using EPR to detect the $O_2(\Delta_g^1)$ showed an insignificant change in the $O_2(\Delta_g^1)$ concentration on addition of atomic nitrogen to the system. It was therefore taken as constant along the tube. Typical data is shown
in Table IX and a plot of atomic nitrogen concentration against distance along the tube is shown in Fig. XIV.

It can be seen that very little change in the atomic nitrogen decay is apparent on addition of $O_2(^1\Delta_g)$. This indicates that the rate constant for reaction (24) is considerably slower than expected and allows only an upper limit, set by the sensitivity of the apparatus, to be placed on the rate constant. To determine this upper limit it is convenient to change the results of Fig. XIV into a straight-line plot, enabling comparison of slopes to be made. A kinetic analysis is thus required.

The main atomic nitrogen decay process in the presence of molecular oxygen is:

\[ N + O_2 \rightarrow NO + O \]  \hspace{1cm} (25)

followed by:

\[ N + NO \rightarrow N_2 + O \]  \hspace{1cm} (33)

Reactions (25) and (33) have rate constants of $10^5$ litres mole$^{-1}$ sec$^{-1}$ and $10^{10}$ litres mole$^{-1}$ sec$^{-1}$ respectively at room temperature (71). Removal of the atomic nitrogen by wall recombination and third order gas phase recombination is small compared with removal by reaction (25). Thus:

\[ \frac{d[N]}{dt}_1 = k_{25}[O_2]_1[N]_1 + k_{33}[N]_1[NO] \]

which for a steady state concentration of NO gives:

\[ \frac{d[N]}{dt}_1 = 2 k_{25}[N]_1[O_2]_1 \]  \hspace{1cm} (34)
Table IX.
Variation of atomic nitrogen concentration with distance along tube.

<table>
<thead>
<tr>
<th>Distance along tube (cms.)</th>
<th>$[N]$ with $O_2(^1A_g)$ moles. litre$^{-1}$(±0.1)</th>
<th>$[N]$ without $O_2(^1A_g)$ moles. litre$^{-1}$(±0.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>$1.45 \times 10^{-7}$</td>
<td>$1.71 \times 10^{-7}$</td>
</tr>
<tr>
<td>10</td>
<td>$0.94 \times 10^{-7}$</td>
<td>$1.03 \times 10^{-7}$</td>
</tr>
<tr>
<td>30</td>
<td>$0.52 \times 10^{-7}$</td>
<td>$0.55 \times 10^{-7}$</td>
</tr>
<tr>
<td>50</td>
<td>$0.20 \times 10^{-7}$</td>
<td>$0.00$</td>
</tr>
</tbody>
</table>

Conditions:

$[O_2] = 4.2 \times 10^{-5}$ moles. litre$^{-1}$

$[N_2] = 1.3 \times 10^{-5}$ moles. litre$^{-1}$

$[O_2(^1A_g)] = 1.6 \times 10^{-6}$ moles.litre$^{-1}$ (assumed constant along tube)

Total pressure = 2.00 torr.
### Table IX (cont.'d.)

<table>
<thead>
<tr>
<th>Distance along tube (cms.)</th>
<th>([N \text{ with } O_2(^1\Delta_g)]) moles. litre(^{-1}) (0.1)</th>
<th>([N \text{ without } O_2(^1\Delta_g)]) moles. litre(^{-1}) (0.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>(2.1 \times 10^{-7})</td>
<td>(2.1 \times 10^{-7})</td>
</tr>
<tr>
<td>10</td>
<td>(1.2 \times 10^{-7})</td>
<td>(1.3 \times 10^{-7})</td>
</tr>
<tr>
<td>30</td>
<td>(0.6 \times 10^{-7})</td>
<td>(0.7 \times 10^{-7})</td>
</tr>
<tr>
<td>50</td>
<td>(0.4 \times 10^{-7})</td>
<td>(0.6 \times 10^{-7})</td>
</tr>
</tbody>
</table>

**Conditions:**

\([O_2] = 3.5 \times 10^{-5}\) moles. litre\(^{-1}\).

\([N_2] = 2.3 \times 10^{-5}\) moles. litre\(^{-1}\).

\([O_2(^1\Delta_g)] = 1.2 \times 10^{-6}\) moles. litre\(^{-1}\) (assumed constant along the tube.)

Total pressure = 2.20 torr.
Fig. XIV. Plot showing decay of atomic nitrogen along tube.

The points represent the data in Table IX.
Pressure = 2.0 torr

Distance along tube (cms)

Atomic nitrogen concentration

$10^{-7}$ moles/litre -1
Distance along tube (cms)

Atomic nitrogen concentration $\times 10^{-7}$ moles litre$^{-1}$

Pressure = 2.2 torr
Similarly:

$$\frac{d[N]}{dt} = 2[N] \left( k_{25}[O_2]_2 + k_{24}[O_2(1\Delta_g)] \right)$$

(35)

The subscripts 1 and 2 refer to the absence and presence of $O_2(1\Delta_g)$ respectively. On integration equation (34) and (35) become:

$$\log_{10}[N]_1 = -2k_{25}[O_2]_1 t + \text{constant.}$$

$$\log_{10}[N]_2 = -2(k_{25}[O_2]_2 + k_{24}[O_2(1\Delta_g)]) t + \text{constant.}$$

A plot of $\log_{10}[N]$ against time thus gives straight lines of slope $-2k_{25}[O_2]_1$ and $-2(k_{25}[O_2]_2 + k_{24}[O_2(1\Delta_g)])$. This plot is shown in Fig. XV.

For a change in slope which is too small to be observed:

$$\frac{k_{25}[O_2]_2 + k_{24}[O_2(1\Delta_g)]}{k_{25}[O_2]_1} \leq \text{maximum possible slope.}$$

mean slope

where the maximum possible slope refers to the limit at which the difference in the two slopes would become noticeable. Taking this to be twice the possible error in the slope, the mean value of the two runs gives:

$$1.8 \geq \frac{k_{25}[O_2]_2 + k_{24}[O_2(1\Delta_g)]}{k_{25}[O_2]_1}$$

which using the approximation $[O_2]_1 = [O_2]_2$ becomes:

$$0.8 \geq \frac{k_{24}[O_2(1\Delta_g)]}{k_{25}[O_2]_1}$$

giving $k_{24} \leq 1.6 \times 10^6$ litres mole.$^{-1}$sec.$^{-1}$. 
Fig. XV. Plot of $\log_{10}[N]$ against time.
In a recent paper, Clark and Wayne (72) determined a value of $1.7 \times 10^6$ litres mole.$^{-1}$sec.$^{-1}$ for the deactivation of $O_2(^1\Delta_g)$ by atomic nitrogen, which they state represents an upper limit for this reaction. By comparison with deactivation rates of other species they state that the main deactivation process is probably reaction (24), which gives good agreement with the upper limit determined in this study.

**The red first positive glow from cobalt.**

The red glow seen near cobalt was first discovered by Reeves, Mannella and Harteck (59) in 1960. They found that the presence of discharged oxygen as well as discharged nitrogen was required for the formation of the glow and from this assumed that atomic oxygen played a necessary part in the formation mechanism.

A series of qualitative experiments were performed here to study this particular aspect of the glow in more detail. The following observations were noted:–

1. With molecular oxygen and discharged nitrogen, no glow was seen over the cobalt. Only on addition of discharged oxygen to the stream was the glow produced. Removal of the discharged oxygen by switching off the discharge or by closing a tap caused the immediate disappearance of the glow.

2. Distillation of mercury through the oxygen discharge causing complete removal of the atomic oxygen had very little effect on the intensity of the glow.

3. Addition of nitric oxide to a stream of discharged nitrogen, producing
atomic oxygen by the rapid reaction: \( \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \) \( (33) \)
resulted in only a very weak glow \((\sim10^{-4})\) of the intensity of the glow in
the presence of discharged oxygen.)

(4) A large flow of water vapour \((-10\% \text{ of the total flow})\) diminished the
glow only slightly \((<50\%)\).

Experiment (1) immediately suggests error in Harteck's assumption
of small quantities of atomic oxygen being necessary for the formation
of the glow. This is because of the absence of a glow with atomic oxygen
produced by the reaction:

\[ \text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O} \] \( (25) \)
The lack of atomic oxygen participation is further indicated by the results
of Experiment (3). Here atomic oxygen, produced by:

\[ \text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O} \] \( (33) \)
also results in an absence of strong emission.

Some constituent of discharged oxygen, however, is necessary for
production of the glow. Experiment (2) indicates that the active product
of the oxygen discharge is also present in singlet oxygen. This limits
the range of possible active species to \(\text{O}_2(\text{^1}\Delta_g), \text{O}_2(\text{^1}\Sigma_g^+)\) or vibrationally excited \(\text{O}_2(\text{^3}\Sigma_g^-)\). In Experiment (4), the water added was sufficient
to totally quench \(\text{O}_2(\text{^1}\Sigma_g^+)\) vibrationally excited \(\text{O}_2(\text{^3}\Sigma_g^-)\). The only
remaining possibility is \(\text{O}_2(\text{^1}\Delta_g)\).

The formation of the very weak glow in Experiment (3) can be attri­
buted to \(\text{O}_2(\text{^1}\Delta_g)\) production by energy transfer to ground state oxygen or,
more likely, to third order recombination from atomic oxygen:

$$O + O + M \rightarrow O_2(^1\Delta_g) + M$$  \hspace{1cm} (36)

A similarly weak glow which could be produced by an analogous mechanism was occasionally seen in the presence of molecular oxygen and discharged nitrogen.

Mercury vapour was shown to be unimportant since its concentration was varied in the stream without producing an effect on the glow. It can therefore be concluded that $O_2(^1\Delta_g)$, not atomic oxygen as originally assumed by Harteck, was necessary for the production of the red cobalt glow.

The spectrum of this glow in the region 5000 Å - 8000 Å was obtained and is shown in Fig. XVI. Harteck's characterization was checked by comparison with the normal Lewis-Rayleigh afterglow first positive emission shown in Fig. XVII. The peaks of the $B^3\Pi_g, v' = 12,11,10$ vibrational levels in Fig. XVI are probably due to some normal Lewis-Rayleigh emission which was always present. The spectrum of the red glow in the infrared was also recorded and shown in Fig. XVIII. Resolution is not good since wide slits had to be used. A comparison spectrum of the normal Lewis-Rayleigh afterglow is shown in Fig. XIX.

The homogeneous gas-phase effect of ground state and singlet oxygen on the normal Lewis-Rayleigh afterglow was checked. It was found that in a system 'poisoned' with orthophosphoric acid both $O_2(^3\Sigma_g^-)$ and $O_2(^1\Delta_g)$ had no effect on the glow. However, in an 'unpoisoned' system the spectrum in the presence of $O_2(^1\Delta_g)$ showed an increase in emission from the $B^3\Pi_g, v' = 6$ region. Later a red glow, similar to that observed over cobalt
Fig. XVIII. Spectra of cobalt catalysed first positive emission between 1.8 µ and 0.6 µ. Taken with a Hilger-Watts f/4.5 monochromator in conjunction with an intrinsic germanium detector. Slits 250 µ.

Fig. XIX. Spectra of Lewis-Rayleigh first positive emission between 1.8 µ and 0.6 µ. Taken with a Hilger-Watts f/4.5 monochromator in conjunction with an intrinsic germanium detector. Slits 250 µ.
The cobalt catalysed first positive glow.
The normal Lewis-Rayleigh first positive glow.

\[ \Delta V = 3 \]

\[ \Delta V = 2 \]

(0,0)

(2,3)

(0,1)

(1,2)

(2,4)(1,3)

(0,2)
Fig. XVI. Spectrum of cobalt catalysed first positive emission between 8000 Å and 5600 Å. Taken with a Hilger-Watts f/4.5 monochromator in conjunction with an RCA 7265 photomultiplier. Slits 100 μ.

Fig. XVII. Spectrum of usual Lewis-Rayleigh first positive emission between 8000 Å and 5600 Å. Taken with a Hilger-Watts f/4.5 monochromator in conjunction with an RCA 7265 photomultiplier. Slits 100 μ.
The cobalt catalysed first positive glow.
The normal Lewis-Rayleigh first positive glow.
was seen near the surface of the glass wall. The only effect on the gas-
phase infrared spectrum upon addition of $O_2(3\Sigma_g^-)$ or $O_2(1\Delta_g)$ to the Lewis-
Rayleigh afterglow was the appearance of the strong $NO(C^2\Pi - A^2\Sigma^+)(0,0)$
transition at 1.22 \mu.

The dependency of the red cobalt glow on the nitrogen atom concentration
was obtained by monitoring the intensity of the surface-catalysed (6,3)
band at 6600 A and comparing it with the intensity of normal Lewis-
Rayleigh first positive (11,7) band. Since the $O_2(1\Delta_g)$ was found to have
no effect on the population distribution of the first positive glow, the
intensity of this band can be taken as proportional to $[N]^2$. The results
of this are shown in Table X and a plot of the cobalt glow intensity
against the Lewis-Rayleigh afterglow intensity is shown in Fig. XX.

An attempt was made during these studies to determine whether the
$O_2(1\Delta_g)$ was involved in reaction at the surface of the metal or in the gas
phase. This was done by moving the cobalt upstream of the mixing region
of the nitrogen and oxygen afterglow. The result, however, was rather
inconclusive since the extent of $O_2(1\Delta_g)$ diffusion equalled that of the
glow and estimates of the direction of the intensity gradient were diffi-
cult.

As well as on cobalt and glass, the glow was also seen on copper,
silver and nickel. When a new piece of metal was placed in the gas stream,
the glow required about half an hour to reach maximum intensity, which
could then be maintained indefinately.
Table X

Variation of cobalt catalysed first positive emission with normal gas-phase Lewis-Rayleigh emission.

<table>
<thead>
<tr>
<th>Cobalt catalysed (6,3) first positive emission (arbitrary units)</th>
<th>Lewis-Rayleigh (12,7) first positive emission (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 ± 2</td>
<td>11 ± 2</td>
</tr>
<tr>
<td>20</td>
<td>22</td>
</tr>
<tr>
<td>28</td>
<td>38</td>
</tr>
<tr>
<td>48</td>
<td>49</td>
</tr>
<tr>
<td>36</td>
<td>45</td>
</tr>
<tr>
<td>30</td>
<td>39</td>
</tr>
<tr>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>42</td>
<td>46</td>
</tr>
</tbody>
</table>
Fig. XX. Graph of cobalt catalysed emission against Lewis-Rayleigh first positive emission showing direct dependence.
The blue NO $\beta$ band glow.

This glow was first seen by Harteck et al (60) over nickel. It has not been seen over any other metal. Similar tests (Experiments (1)-(4)) to those of the previous section were performed on this glow and similar results were obtained, showing that the reactive species from the oxygen discharge was not atomic oxygen as originally thought by Harteck et al, but $O_2(1\Delta_g)$.

The effect of NO addition on the intensity of the nickel catalysed glow is shown in Table XI and plotted in Fig. XXI. For comparison purposes the effect of NO addition on the NO $\beta$ bands produced by reaction (23) is also shown.

$$N + O + M \rightarrow NO^* + M \quad (23)$$

Since both glows were obtained under exactly the same conditions the gas-phase recombination glow can be regarded as the background radiation of the nickel-catalysed glow. In practice this was achieved by moving the nickel (magnetically) away from the entrance slit of the monochromator and repeating the NO addition. Little screening of the gas-phase glow from the monochromator slit by the nickel wire would be expected. It can be seen that, unlike the gas-phase glow, the nickel catalysed glow appears independent of the atomic oxygen concentration and directly dependent on the atomic nitrogen concentration.

Harteck (60) states that there is a complete absence of $\gamma$ and $\delta$ bands in the nickel-catalysed glow. This conclusion was not definitely verified in the present studies because of the difficulty in removing the gas-
Table XI

Variation of nickel NO $\beta$ band glow and its background glow on addition of nitric oxide.

<table>
<thead>
<tr>
<th>Nitric oxide concentration (Arbitrary units)</th>
<th>Intensity of (0,7)NO $\beta$ band in gas phase + nickel catalysed glow (Arbitrary units)</th>
<th>Intensity of (0,7)NO $\beta$ bands in gas phase (Arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.8</td>
<td>4.3</td>
</tr>
<tr>
<td>2</td>
<td>8.4</td>
<td>4.7</td>
</tr>
<tr>
<td>3</td>
<td>8.0</td>
<td>4.9</td>
</tr>
<tr>
<td>4</td>
<td>7.6</td>
<td>5.05</td>
</tr>
<tr>
<td>5</td>
<td>7.2</td>
<td>5.1</td>
</tr>
<tr>
<td>6</td>
<td>6.7</td>
<td>5.05</td>
</tr>
<tr>
<td>7</td>
<td>5.7</td>
<td>4.8</td>
</tr>
<tr>
<td>8</td>
<td>4.8</td>
<td>4.1</td>
</tr>
<tr>
<td>9</td>
<td>2.6</td>
<td>2.3</td>
</tr>
<tr>
<td>10*</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

* Nitrogen atom titration point.
Fig. XXI. Graph showing effect on nickel catalysed and normal gas-phase emission of NO β bands, of addition of nitric oxide to the 
N + O₂(¹Δ₉) stream. The titration point is arbitrarily put at 10 units of [NO].
Nitric oxide concentration (arbitrary units)

Relative intensity of (0,7)NOβ band

- Gas phase + nickel catalysed glow
- Gas phase glow
- Nickel catalysed glow
phase emission. However, a definite reduction in these bands compared with the intensities obtained in the normal recombination reaction (23) was apparent.

The spectra of the NO $\beta$ bands between 5000 Å and 4000 Å obtained over nickel and by gas-phase recombination are shown in Figs. XXII and XXIII. The effect of both $O_2(^3\Sigma_g^\text{-})$ and $O_2(^1\Delta_g)$ on individual NO $\beta$ bands produced by gas-phase recombination was checked. Intensities of the bands were seen to vary slightly between spectra. The band intensities are listed in Table XII.

Molecular oxygen was also found to cause overall quenching of the NO $\beta$ bands. This was observed by addition of oxygen to the NO $\beta$ bands produced by:

\[ N + NO \rightarrow N_2 + O \quad (33) \]
\[ N + O + M \rightarrow NO^* + M \quad (23) \]

A comparison of equal flowrates of argon and oxygen showed a considerable decrease in NO $\beta$ band emission with oxygen. This could possibly be due to competition with reaction (23) from the reaction sequence:

\[ N + O_2 \rightarrow NO + O \quad (25) \]
\[ N + NO \rightarrow N_2 + O \quad (33) \]

However, with an oxygen concentration of about $10^5$ litres mole.$^{-1}$ sec.$^{-1}$, the half-life for atomic nitrogen decay by reactions (25) and (33) ($k_{25} = 1 \times 10^5$ litres mole.$^{-1}$ sec.$^{-1}$ and $k_{33} = 1.5 \times 10^{10}$ litres mole.$^{-1}$ sec.$^{-1}$) would
Fig. XXII. Spectrum of nickel catalysed emission from NO $\beta$ bands. Taken with a Hilger-Watts $f/4.5$ monochromator in conjunction with an RCA IP21 photomultiplier. The fraction of the glow produced by background radiation (Fig. XXIII) is unknown. Slits 150 $\mu$.

Fig. XXIII. Spectrum of emission produced by conventional nitric oxide recombination. Taken with a Hilger-Watts $f/4.5$ monochromator in conjunction with an RCA IP21 photomultiplier. Slits 150 $\mu$. 
Nickel catalysed emission from the NO β bands
NO  β band emission from nitric oxide recombination
Table XII

Variation in the intensity of the NO β bands produced by different methods.

<table>
<thead>
<tr>
<th>Peak of NO β band</th>
<th>Intensity from $N + NO$ (arbitrary units)</th>
<th>Intensity from $N + O_2$ (arbitrary units)</th>
<th>Intensity from $N + O_2 + O_2(\Sigma^\Delta_g)$ (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(0,12)</td>
<td>2.3</td>
<td>2.3</td>
<td>3.3</td>
</tr>
<tr>
<td>(1,13)</td>
<td>0.8</td>
<td>1.3</td>
<td>2.4</td>
</tr>
<tr>
<td>(2,14)</td>
<td>0.6</td>
<td>0.5</td>
<td>0.95</td>
</tr>
<tr>
<td>(0,13)(3,15)</td>
<td>1.1</td>
<td>0.9</td>
<td>1.65</td>
</tr>
<tr>
<td>(1,14)</td>
<td>0.5</td>
<td>0.7</td>
<td>1.45</td>
</tr>
<tr>
<td>(2,15)</td>
<td>0.4</td>
<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>(0,14)(3,16)</td>
<td>0.6</td>
<td>0.8</td>
<td>1.45</td>
</tr>
<tr>
<td>(1,15)</td>
<td>0.2</td>
<td>0.3</td>
<td>0.6</td>
</tr>
<tr>
<td>(2,16)</td>
<td>0.4</td>
<td>0.5</td>
<td>0.9</td>
</tr>
<tr>
<td>(3,17)</td>
<td>0.6</td>
<td>0.8</td>
<td>1.3</td>
</tr>
<tr>
<td>(2,17)</td>
<td>0.4</td>
<td>0.4</td>
<td>0.7</td>
</tr>
</tbody>
</table>
be about 0.5 seconds. On this mechanism a trivial decrease in the NO β band intensity would be expected (flowrate = 5 x 10\(^2\) cms. sec\(^{-1}\). - observation within 20 cms.) - certainly not of the order of a factor of 10 observed here. It was also found that the β band intensity increased slightly on discharging the oxygen to form \(O_2(^1\Delta_g^\text{e})\), the complete recombination of atomic oxygen in the \(O_2(^1\Delta_g^\text{e})\) stream being checked by addition of excess nitric oxide.

The NO β band glow over nickel was always seen in the presence of the first positive red glow also seen near other surfaces. A variation in the relative intensities of the two glows could be made by varying the ratio of the atomic nitrogen concentration to the \(O_2(^1\Delta_g^\text{e})\) concentration. Predominance of the nickel catalysed NO β band glow required a smaller \([N]/[O_2(^1\Delta_g^\text{e})]\) ratio.

The blue copper glow.

This glow was very weak and was produced with discharged nitrogen alone. The copper was not maintained at room temperature as in the spectrum recorded by Harteck et al (53) but was allowed to be heated by the atom recombination. The effect of cooling the copper was tried but no obvious change in the colour or intensity of emission could be seen. The glow consisted of a blue emission extending about 2 mm. away from the copper surface under usual conditions. The spectrum was taken at lower pressure to eliminate as much of the gas phase Lewis-Rayleigh emission as possible. Under these conditions the glow was slightly more extensive. The spectrum
of this glow is seen in Fig. XXIV and the region between 5000 Å and 4000 Å is shown in more detail in Fig. XXV. Less resolution was possible in Fig. XXIV since a quartz prism was used instead of the glass prism employed for Fig. XXV. The strongest features of the spectrum were at 3247 Å and at 3274 Å, consisting of the CuI resonance lines. The CuI lines seen in the spectra are listed in Table XIII.

Summary of the experimental results on the surface-catalysed glows.

I. Surface catalysed red first positive emission.

1. Glow seen over a variety of metals and from 'unpoisoned' glass walls.

2. \( O_2(^1\Delta_g) \) required for production of glow.

3. Glow varies as \([N]^2\)

4. Increased population from the \( v' = 8, 6 \) levels relative to the \( v' = 12-9 \) levels compared with population distribution of Lewis-Rayleigh emission.*

5. Decreased population towards the \( v' = 0 \) level.

6. Lifetime of glow \( \sim 2 \times 10^{-3} \) secs (calculated for a diffusion distance of 1.5 cms. into gas phase)*

II(a). Nickel catalysed nitric oxide \( \beta \) band glow.

1. Glow seen only over nickel.*

2. \( O_2(^1\Delta_g) \) required to produce glow.

3. Glow varies as \([N]\). Independent of \([O]\).

4. Glow favoured by higher \([N]/[O_2(^1\Delta_g)]\) ratio than required for red first positive glow.
Fig. XXIV. Spectrum of the copper glow between 3200 Å and 5000 Å. Taken with a Hilger-Watts f/4.5 monochromator (quartz prism) in conjunction with an RCA IP28 photomultiplier. Slits 250 µ.

Fig. XXV. Spectrum of the copper glow between 4250 Å and 5600 Å. Taken with a Hilger-Watts f/4.5 monochromator (glass prism) in conjunction with an RCA IP21 photomultiplier. Slits 170 µ.
The graph shows a spectroscopic analysis with two distinct regions highlighting different wavelengths.

1. **Cu I** band is indicated at the top region of the spectrum, spanning wavelengths from 3200 Å to 3900 Å.
2. **NO β band** is marked at the bottom region, ranging from 4000 Å to 5000 Å.

The relative intensity of the emissions is indicated on the vertical axis, with values ranging from 0 to 6.
Table XIII

Copper I lines seen in blue glow.

<table>
<thead>
<tr>
<th>Wavelength of CuI lines (Å)</th>
<th>Approximate intensity corrected for detection response. (Arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2745</td>
<td>2</td>
</tr>
<tr>
<td>2766</td>
<td>5</td>
</tr>
<tr>
<td>2824</td>
<td>15</td>
</tr>
<tr>
<td>2961</td>
<td>10</td>
</tr>
<tr>
<td>3070</td>
<td>7</td>
</tr>
<tr>
<td>3094</td>
<td>4</td>
</tr>
<tr>
<td>3248</td>
<td>100</td>
</tr>
<tr>
<td>3274</td>
<td>58</td>
</tr>
<tr>
<td>5219</td>
<td>11</td>
</tr>
</tbody>
</table>
(5) Spectrum suggests a more even distribution through the vibrational energy levels than in the glow produced by radiative recombination of nitric oxide.

(6) Absence of γ and δ bands.*

(7) Lifetime of glow ~ 10^{-4} secs (calculated for a diffusion distance of 0.2 cms. into the gas phase).*

II(b) Nitric oxide β band glow produced in gas phase by normal nitric-oxide recombination.

(1) Glow quenched by ground state oxygen.

(2) Glow produced by O_2(^1Δ_g) addition.

III The blue copper glow.

(1) The spectrum shows a band emission and copper line emission.

(2) Lifetime of glow ~ 10^{-4} secs (calculated for a diffusion distance of 0.2 cms. into the gas phase).

* Results first obtained by Harteck et al. (53)(59)(60) and confirmed here.
DISCUSSION

The rate constant for the $N + O_2(\text{^1}g)$ reaction.

An upper limit of $1.6 \times 10^6$ litres mole.$^{-1}$sec.$^{-1}$ was obtained here for $k_{24}$, the rate constant for the reaction:

$$N + O_2(\text{^1}g) \rightarrow NO + O \quad (24)$$

This should be compared with $k_{25}$, the rate constant for the analogous reaction with ground state oxygen:

$$N + O_2 \rightarrow NO + O \quad (25)$$

which has a rate constant of $1.0 \times 10^5$ litres mole.$^{-1}$sec.$^{-1}$ at room temperature (71). Thus $k_{24}$ is less than $16 \times$ faster than $k_{25}$, not $10^3$ faster as required by Hunten and McElroy (58) to explain the concentration of NO in the 90 km region of the upper atmosphere. They calculated that a rate constant of $1.8 \times 10^8$ litres mole.$^{-1}$sec.$^{-1}$ would be required for $k_{24}$ in order to account for the NO concentration found by Barth (73) using rocket observation of the NO γ bands. These bands are emitted by a fluorescence mechanism of nitric oxide that is excited by absorption of sunlight around 2500 Å. He deduced a column density of $1.7 \times 10^{14}$ molecules cm$^{-2}$ above 85 km which is considerably greater than that originally predicted by Nicolet and Aiken (74) and Barth (75) using as the principle production and removal reactions:

$$N + O_2 \rightarrow NO + O \quad (25)$$

$$N + NO \rightarrow N_2 + O \quad (33)$$
Two reactions have so far been proposed to explain the increased steady state concentration of NO found experimentally. The first was the reaction:

\[ \text{O}_2^+ + \text{N}_2 \rightarrow \text{NO} + \text{NO}^+ \]  (37)

originally proposed by Nicolet (76). Upper limits for the rate of reaction (37) have been determined, however, showing that the reaction is too slow to explain the observed concentration (77)(78). The second reaction was reaction (24) proposed by Hunten and McElroy, which has already been discussed. The present work rules out reaction (24) as the major nitric oxide production process, again leaving the whole question of an explanation for the high oxide concentration unanswered.

The unexpected slowness of reaction (24) compared with the rate expected from comparison with reaction (25) (see earlier) can be rationalized by consideration of the transition states involved in the two processes. The reactions can be written:

\[
\begin{align*}
N(4S) + O_2(1\Delta_g) & \rightarrow NO(2\Pi) + O(3P) \\
S: & \begin{array}{c} 3/2 \\ 0 \\ 1/2 \\ 1 \end{array}
\end{align*}
\]  (24)

\[
\begin{align*}
N(4S) + O_2(3\Sigma^-) & \rightarrow NO(2\Pi) + O(3P) \\
S: & \begin{array}{c} 3/2 \\ 1 \text{g} \\ 1/2 \\ 1 \end{array}
\end{align*}
\]  (25)

The spin quantum numbers are written below each separate component in the reaction. If it is assumed that there is no change in the total spin state reaction (24) must proceed via a quartet (\(S = 3/2\)) and reaction (25) via a doublet or quartet (\(S = 1/2\) or \(3/2\)). Thus:
\[
\begin{align*}
N(^4S) + O_2(^1\Delta_g) &\rightarrow 4[N----0----=0] \rightarrow NO(^2\Pi) + O(^3P) \quad (38) \\
N(^4S) + O_2(^3\Sigma_g^-) &\rightarrow 2 \text{ or } 4[N----0----=0] \rightarrow NO(^2\Pi) + O(^3P) \quad (39)
\end{align*}
\]

where \([N----0----=0]\) represents the transition state. By comparison with the isoelectronic O-N-O molecule, the first doublet state would be expected to be below the first quartet state in \([N----0----=0]\) resulting in different reaction paths for the two processes. Hunten and McElroy's prediction of the reaction rate depended on the same transition state being used in both cases. The above argument shows that this is probably not true if the total spin is conserved throughout the reaction. For the opposite situation in which a spin change does take place (quartet \(\rightarrow\) doublet in reaction (38)), other considerations would be required and Hunten and McElroy's argument still would not stand.

The mechanism of the red first positive emission.

It was shown earlier that both atomic nitrogen and \(O_2(^1\Delta_g)\), as well as a surface, are necessary for the formation of the \(N_2(^3\Pi_g)\) state giving rise to the red nitrogen first-positive glow. Since no new or increased emission is seen near the surface in the absence of \(O_2(^1\Delta_g)\), the \(O_2(^1\Delta_g)\) must be involved in an actual formation process and not in selective removal of particular vibrational levels. Any mechanism proposed for the red glow must be able to explain not only this participation of the atomic nitrogen, \(O_2(^1\Delta_g)\) and the surface, but also the spectral distribution, the lifetime of the glow \((2 \times 10^{-3} \text{ secs using the data of Weinreb and} \quad \)
Mannella (65)) and the \([N]^2\) dependency shown in Fig. XX.

The populations of the vibrational energy levels of the \(B^3\Pi_g\) state are compared in Fig. XXVI. The relative population distribution of the different vibrational levels in the normal Lewis-Rayleigh glow is taken from Fig. VII of reference (52). This diagram should be treated with some caution since in several cases there is divergence between the theoretically predicted (79)(80) and the experimentally determined transition probabilities for different bands of one particular vibrational level. Bayes and Kistiakowsky (52) have suggested that this is due to an underlying band system \((B^1\Sigma_u^- \rightarrow B^3\Pi_g)\), and has calculated the \(B^3\Pi_g\) state population accordingly. It is this population distribution which is used in Fig. XXVI. The relative populations of the cobalt red glow vibrational levels are determined from the heights of the peaks in Figs. XVI and XVIII compared with Figs. XVII and XIX.

Harteck et al (53) suggested that surface catalysed recombination of atomic nitrogen to produce the red glow was via the \(N_2(A^3\Sigma_u^+)\) state, followed by collision-induced transfer to the \(B^3\Pi_g\) state, which then emitted. This is also the route suggested by Campbell and Thrush (54) for gas phase recombination of atomic nitrogen giving rise to Lewis-Rayleigh emission. If the mechanism of Campbell and Thrush is correct, the \(N_2(A^3\Sigma_u^+)\) state would be expected to have a fairly steady change in population through its vibrational levels, because of its formation by a termolecular collision process. In order to explain the \(B^3\Pi_g\) population of the red glow a large increase in population of the \(V' = 10-15\) levels
Fig. XXVI. The relative population of vibrational levels in the $B^3\Pi_g$ state of nitrogen. Shaded areas denote the cobalt-catalysed glow. Unshaded bars denote the normal Lewis-Rayleigh emission. Populations are arbitrarily equalized at $v' = 6$. 
of the $A^3\Sigma_u^+$ state would have to be proposed as well as rather erratic population distributions in the $v'' = 7$ and $v'' > 20$ regions (corresponding to $B^3\Pi_g^+ v' = 12-9$ respectively). A population distribution similar to that for gas phase recombination would seem more likely.

Harteck's mechanism would fare better if it were proposed that the $v' = 12-9$ levels of the $B^3\Pi_g$ state were populated via the $5\Sigma_g^+$ state as discussed by Benson (56), the $v' = 8-0$ levels by similar mechanisms to that of Harteck involving the $A^3\Sigma_u^+$ state with the lower $v' = 2-0$ levels enhanced by population from the $B^1\Sigma_u^-$ state as originally proposed by Bayes and Kistiakowsky (52). The particular vibrational distribution could then be produced by allowing formation of the $A^3\Sigma_u^+$ state but not the $5\Sigma_g^+$ state on the surface of the metal.

Both these mechanisms require the $O_2(^1\Delta_g)$ to be of little importance in the reaction and relegate its effect to a 'conditioning' process of the surface. The appearance of the glow over a wide variety of surfaces and the complete and immediate removal of the glow on switching off the $O_2(^1\Delta_g)$ stream imply the contrary. Because of its specific role in this reaction the most likely function of the $O_2(^1\Delta_g)$ is in the spin-change energy transfer process.

A possible mechanism using the $N_2(A^3\Sigma_u^+)$ state requires its production in high vibrational levels on a surface followed by diffusion into the gas phase where it forms the $^1\Pi_g$ and $^1\Delta_u$ states by an energy-pooling collision with $O_2(^1\Delta_g)$. Vibrational deactivation to the $v' = 0$ vibrational levels and then collisional transfer to the $B^3\Pi_g$ state might be expected.
to preferentially populate the \( v' = 6 \) and \( 8 \) levels without significant population of the \( v' = 12-9 \) levels. Thus:

\[
N + N + \text{cobalt surface} \rightarrow N_2(A^3\Sigma_u^+) + \text{cobalt surface}
\]

\[
N_2(A^3\Sigma_u^+) + O_2(1\Delta_g) \rightarrow N_2(a^1\Pi_g)^* + O_2(3\Sigma_g^-) \rightarrow N_2(w^1\Delta_u)^*
\]

\[
N_2(a^1\Pi_g)^* \rightarrow \text{vibrational} \quad N_2(a^1\Pi_g) \quad v = 0 \quad M \quad N_2(B^3\Pi_g) \quad v = 0 \rightarrow v' = 6, 8
\]

where the asterisk denotes vibrational excitation.

The strongest evidence so far against the \( A^3\Sigma_u^+ \) state as the metastable is the effect of atomic nitrogen on the glow. Weinreb and Mannella (65) have shown that the rate constant for the deactivation of the metastable species by atomic nitrogen is \(< 3 \times 10^8 \) litres mole.\(^{-1}\) sec.\(^{-1}\). The rate constant for deactivation of the \( N_2(A^3\Sigma_u^+) \) state, however, appears to be about \( 3 \times 10^{10} \) litres mole.\(^{-1}\) sec.\(^{-1}\) (63)(64).

Other metastable species apart from the \( N_2(A^3\Sigma_u^+) \) state can be proposed as intermediates of the states below 9.76 eV, the \( B^3\Pi_g \) with a first positive radiative lifetime of \( 6 \times 10^{-6} \) secs. (81) and the \( a^1\Pi_g \) state with a radiative lifetime to the ground state of \( 2.5 \times 10^{-5} \) (82) can both be eliminated as well as the \( B^1\Sigma_u^- \) state, the radiative lifetime of which would be expected to be comparable with first positive radiation. Of the remaining \( w^1\Delta_u, a^1\Sigma_u^- \) and \( 3\Delta_u \) states, the last has been extensively studied using nitrogen contaminated electrical discharges through argon. (83)(84).
The results obtained agree with those expected from a recent determination (85) of its position on the potential energy diagram by observation of the \((3\Delta_u - B^3\Pi_g)\) transition in the infrared. By comparison with the \((B^3\Pi_g - A^3\Sigma_u^+)\) transition and only compensating for the smaller \(v^3\) factor in the Einstein A coefficient, a lifetime of the order of seconds would be expected for the \(v' = 0\) \(3\Delta_u\) level, making it a suitable metastable species. Unfortunately mechanisms involving the \(3\Delta_u\) state have been found to produce a considerable increase in the first positive \(v' = 0\) emission (82). It can be seen from Fig. XVIII, that this is not so in the present case. The \(a'(1\Sigma_u^-)\) state has a lifetime of about 0.1 secs (86) and is thus a possible metastable species. The \(w(1\Delta_u)\) state would be expected to have a very fast radiative lifetime to the \(a(1\Pi_g)\) state.

One attempt was made to gain some insight into a possible intermediate by producing a stream of \(N_2(A^3\Sigma_u^+)\) using a low powered hollow cathode d.c. discharge to produce metastable Ar atoms in their \(3P^2, 3P^0\) states with about 11.6 eV of energy (67). This is enough to excite nitrogen to the \(C^3\Pi_u\) state, producing a small flame about 1 cm long consisting of the second positive \(C^3\Pi_u - B^5\Pi_g\) and first positive emission on addition of molecular nitrogen to the argon stream. The result of this radiative cascade process is the production of the \(N_2(A^3\Sigma_u^+)\) state in the absence of atomic nitrogen, which allows the \(A^3\Sigma_u^+\) state to last along the length of the tube. The \(N_2(A^3\Sigma_u^+)\) state was detected by the presence of the 2537 Å resonance line formed by energy transfer from the \(N_2(A^3\Sigma_u^+)\) state on addition of mercury vapour to the stream (87). No emission could be seen near the surface of
a cobalt plug placed in a stream of $N_2(A^3\Sigma_u^+)$ and $O_2(^1\Delta_g)$, although emission was easily detected when a small quantity of atomic nitrogen was added to the stream. Since $N_2(A^3\Sigma_u^+)$ appears to be rapidly quenched by ground state oxygen (88), the cobalt was moved to the mixing zone of the two streams. Again no emission was detected. The absence of a positive result does not necessarily disprove that the metastable species was the $N_2(A^3\Sigma_u^+)$ v = 0 vibrational level. This experiment illustrates the difficulty involved in testing possible mechanisms as well as the difficulty in interpreting the results of these tests.

The mechanism of the blue NO β band glow.

In connection with the reaction between atomic nitrogen and $O_2(^1\Delta_g)$ to form the NO β bands, two processes have to be considered - the surface catalysed emission and the gas phase effect of oxygen on the NO recombination process. The latter is the simpler system and will therefore be treated first.

It was found that emission from the NO($b^2\Pi$) state was quenched by ground state oxygen and produced by addition of $O_2(^1\Delta_g)$. This can be explained by an energy-pooling reaction between the $O_2(^1\Delta_g)$ and the NO($a^4\Pi$) state formed in the first step of the recombination process producing the $B^2\Pi$ state:

\[
\text{NO} (a^4\Pi) + \text{NO} (b^4\Sigma^-) \rightarrow \text{M} \rightarrow \text{NO} (b^2\Pi)
\]  
(40)

\[
\text{NO} (a^4\Pi) + O_2(^1\Delta_g) \rightarrow \text{NO} (b^2\Pi) + O_2(^3\Sigma_g^-)
\]  
(41)

The quenching effect of ground state oxygen on the NO($b^2\Pi$) state emission
is presumably due to the reverse of reaction (41). The absence of any marked selective quenching of the NO $\beta$ bands by oxygen (see Table XII) would be expected since the $B^2\Pi$ and $a^4\Pi$ potential curves appear to run almost parallel, suggesting that the $(0,0)$, $(1,1)$, $(2,2)$ etc. Franck-Condon factors and energy differences are all approximately the same. This, unfortunately, cannot be calculated exactly since there is some uncertainty in the position of the $a^4\Pi$ state. The possibility of energy-pooling by the reaction:

$$\text{NO}(a^4\Pi) + O_2(1\Delta_g) \rightarrow \text{NO}(b^4\Sigma^-) + O_2(3\Sigma^-)$$  \hspace{1cm} (42)$$
cannot be neglected. Similar arguments to those for the $B^2\Pi$ state would apply except that, from the positions of the potential curves, a greater population in the $B^2\Pi v' = 0$ state might be expected.

For the nickel catalysed glow, the diffusion distance of a few millimeters into the gas phase suggests a lifetime of $10^{-4}$ secs for the metastable species. Thus this metastable species can not be the NO$(B^2\Pi)$ state with a radiative lifetime of $10^{-6}$ secs (61). By analogy with the gas phase process, the metastable species would be expected to be the $a^4\Pi$ state which would require removal at a rate of 1 collision in $5 \times 10^3$ to explain the extent of the glow. This is about 1 collision in 20 with $O_2(1\Delta_g)$, which is not unreasonable. One major difference, however, exists between the surface catalysed and gas phase glows and this is the effect of addition of nitric oxide illustrated in Fig. XXI. It can be seen that the normal gas phase curve peaks at about halfway to the titration end point, i.e. when $[N] = [O]$ as expected from the kinetic analysis. The surface catalysed glow
does not follow this curve but appears directly dependent on the atomic nitrogen concentration and independent of the atomic oxygen concentration. A possible mechanism which would explain this would be a surface catalysed reaction between atomic nitrogen and ground state or singlet oxygen:

\[
\begin{array}{c}
\text{N} \\
\text{O} = 0
\end{array} + \left[ \begin{array}{c}
\text{N} \\
\text{O} = 0
\end{array} \right] \rightarrow \begin{array}{c}
\text{N} \\
\text{O} (^{2}\Pi)
\end{array}
\]

If either half of the reaction is rate controlling direct dependence on the atomic nitrogen concentration would result. Campbell and Thrush (54) suggested, from a consideration of the required surface coverage for the recombination of nitrogen atoms, that the process followed neither a Hinshelwood nor a Rideal type mechanism but that the atomic nitrogen must have considerable mobility on the surface of the walls. It is possible that such a mechanism is taking place here and facilitating the seemingly rather difficult reaction.

Mechanisms involving energy transfer from metastable molecular nitrogen can not be proposed, because the glow would then be seen over cobalt and copper as well as over nickel.

The copper blue glow.

The copper blue glow seen in these studies is certainly not the nitrogen second positive glow seen by Harteck et al (53). Its origin is unknown. No comparison with the glow obtained by Harteck et al over copper could be made since they did not publish a diagram of their spectrum. A systematic search to identify the present band system was made using the
data listed in references (89-92). The method of checking a particular band system was to find a transition which had its wavelength within ±20° Å of the wavelength of the two most intense peaks at 4957 Å and 4852 Å and then to search for other expected transitions from the same vibrational level.

The spectrum appears to consist of at least two groups of bands, which show a definite resemblance, suggesting a progression with $\omega_e = 2345 \pm 10 \text{ cm}^{-1}$. This $\omega_e$ value is unusually large, being comparable in spacing to the vibrational levels of ground state nitrogen. This suggests either $k$, the vibrational force constant is large or $\mu$, the reduced mass, is small, as in a hydride. The appearance of the spectrum suggests that the emission is either from a polyatomic molecule or from several closely spaced different electronic states in a diatomic molecule. There are several overlapping bands and this presents difficulty even in picking out a progression involving the two stronger bands. For the progression shown in Fig. XXV, $\omega_e = 410 \text{ cm}^{-1}$.

The existence of CuI lines is not surprising; they have been seen many times in active nitrogen (44).
CONCLUSION

The rate constant for the reaction:

\[ N + O_2(1_{\Delta g}) \rightarrow NO + O \]  

was found to have an upper limit of \(1.6 \times 10^6\) litres mole\(^{-1}\) sec\(^{-1}\) which is too slow to account for the concentration of nitric oxide in the 90Km region of the upper atmosphere.

The red glow seen over cobalt was found to require \(O_2(1_{\Delta g})\) for its production and vary as \([N]^2\). Its vibrational level population distribution differed from that obtained in the normal Lewis-Rayleigh after-glow.

The nickel-catalysed blue glow also required \(O_2(1_{\Delta g})\) for its production and varied as \([N]\). A more even distribution of population through the vibrational levels of the \(B^2\Pi\) state was obtained than in the normal radiative recombination of nitric oxide. Variations in the gas phase NO \(\beta\) band emission could be attributed to the reaction:

\[ NO(a^4\Pi) + O_2(1_{\Delta g}) \rightarrow NO(B^2\Pi) + O_2(3_{\Sigma g}^-) \]  

The copper blue glow was definitely not the second positive emission as originally stated by Harteck et al (53).

The testing of mechanisms suggested for individual glows is made extremely difficult by both the lack of method of obtaining isolated states as well as the lack of specific detection methods. One mechanism for the production of the red first positive glow, however, can be tested. This is the mechanism requiring production of the \(a^1\Pi_g\) state from the \(N_2(A^3\Sigma_u^+)\)
state by energy-pooling with \( O_2(1^1\Delta_g) \). The \( 1^1\Pi_g \) state can be produced by absorption of radiation in the 1300 Å region (Argon lamp). The production of the \( B^3\Pi_g \) state in the \( v'i = 6 \) level can then be checked. The success of the experiment depends on applying sufficient intensity at 1300 Å without masking the first positive emission with stray visible light. This might just be possible.
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POSTSCRIPT

A paper (93) by Weinreb and Mannella has been recently published dealing with the red first positive glow. They agree with the present work in that they also find the presence of $O_2(^1\Delta_g)$ necessary for the glow. They also show that the $O_2(^1\Delta_g)$ does not react at the surface of the metal but on a metastable species (which they assume is the $N_2(A^3\Sigma_u^+)$ state) diffusing into the gas phase. They then vary the quantity of discharged oxygen flowing into the system and obtain an estimate of the rate of reaction between the metastable nitrogen and the discharged oxygen, by measuring the variation of the glow with distance away from the surface. Assuming 20% $O_2(^1\Delta_g)$ in the discharged oxygen and a direct variation of the $O_2(^1\Delta_g)$ concentration with the total oxygen concentration they obtained $3 \times 10^9$ litres mole$^{-1}$sec$^{-1}$ for the reaction of the metastable nitrogen with $O_2(^1\Delta_g)$ giving rise to the glow. They assume that quenching by ground state oxygen is negligible, an assumption which is not necessarily valid. This might account for the good correlation between the half-life of the glow and the reciprocal of the total oxygen concentration.