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PLANETARY AERONOMY IX:
THE DARK SIDE AIRGLOW OF VENUS

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N. Jonathan and G. Doherty

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I. INTRODUCTION

Telescopic observations of Venus have shown a luminescence on the dark side which is similar to that which sometimes illuminates the whole moon during its first quarter.

Recent spectroscopic measurements have reported especially strong emission in the region 4410 - 4400 A.(1,2) The nature of the emissions is unestablished but the possibility has been suggested that this luminescence arises as a result of the reaction between atomic oxygen and carbon monoxide.(3)

The chemiluminescence arising from the reaction of carbon monoxide and atomic oxygen has been investigated by a number of workers.(4,5,6) A brief summary of their experimental methods and observations is perhaps in order.

(a) The first investigation was made by Broida and Gaydon(4) who studied the reaction, in a 1-liter Pyrex flask, of the atomic oxygen being produced in a discharge tube maintained by a 6000 V transformer. A weak blue glow was observed which was strongest at 3 mm Hg pressure and was not observable below 0.5 mm. The luminescence showed clean carbon monoxide flame bands with a complete absence of a continuum or O_2 bands. No attempt was made to measure concentrations of any of the species. It was postulated that the flow was caused by the luminescence from excited carbon dioxide molecules formed during the three-body reaction:

$$CO + O + M \rightarrow CO_2^* + M.$$

(b) During the course of our work, the results of a study of the reaction were published by Clyne and Thrush.(5) Oxygen atoms formed by dissociation of molecular oxygen or molecular oxygen and inert gas mixtures subjected to an electrodeless discharge were passed through a flow tube at about 1 mm of mercury pressure. Carbon monoxide was fed into this flow tube and the resulting light emission was observed by means of a photomultiplier. It was found that, over the pressure range 0.86 to 2.69 mm of mercury, the light emission was directly proportional to the atomic oxygen and carbon monoxide concentrations, and independent of the total pressure and amount of third body present. Hence, these workers found similar values for the light emission with oxygen and nitrogen as respective third bodies, but for neon and helium as third bodies the light emission was less. Therefore, they explained the reaction as being a three-body process involving atomic oxygen, carbon monoxide and the predominant species for stabilization of the excited state. The actual light emission is of the type

$$I_c = I_{oc} [O][CO] \quad .$$

The mechanism attributed to the reaction by these workers is given in detail in our discussion.

(c) Our attention has been drawn to a paper by Mahan and Solo,(6) which appeared after our own experimental work had been completed. The investigation of the light emission dependence was made by a somewhat different method from that of the other workers. They used a stirred reactor in the pressure range 0.56 to 1.6 mm Hg and studied the light emission as a function of the amount of carbon dioxide which was produced. Atomic oxygen was usually made by passing a mixture of 99% argon and 1% oxygen through a microwave discharge. By adding molecular oxygen directly to the reaction vessel, they were able to observe a quenching effect of the light emission which seemed to be in accordance with the Stern-Volmer quenching law. Significantly, they found that an increase in the total pressure caused the quantum yield to decrease, the quantum yield being defined as number of quanta emitted per unit amount of carbon dioxide produced. They observed that the amount of carbon dioxide produced approached a constant value as the amount of added molecular oxygen was increased, indicating to them that molecular oxygen could react with excited carbon dioxide molecules. They therefore propose a mechanism to explain their results, which involves two distinct two-body reactions resulting in the formation of both radiative and nonradiative carbon dioxide molecules. Full details of the mechanism are given in our discussion.

It can be seen that they suggest that the radiative CO_2 is formed by a bimolecular process and does not require a third body for stabilization. This explanation is, of course, directly opposed to that of Clyne and Thrush since it requires the light emission to be dependent upon the amount of third body present.

Since our experimental apparatus is similar to that of Mahan and Solo (but we make measurements in a different way), our result takes on an added interest as a comparison with those of the other workers in an attempt to bring some understanding into these apparently conflicting results.

II. EXPERIMENTAL

The design of a reaction cell for the study of a relatively slow reaction such as carbon monoxide and atomic oxygen is necessarily complicated since one requires a maximum light gathering power from an emission which does not approximate to a point source. We have used a reaction cell which is similar in many respects to the stirred reactor of Mahan and Solo and is based upon the design of multipath cells which are common in conventional absorption spectroscopy. The cell is shown in schematic form in Figure 1. It consists of a 50-liter, 3-necked Pyrex flask with a single path length of up to 18 inches. The gases are let into the cell through the two side arms of the flask. The center arm is connected to an oil booster pump backed by a Welsh mechanical pump which, working together, are capable of keeping the cell pressure at 10 microns of Hg when the flow rates are up to 70 standard cc's/minute. The bulb is coated on the outside with a layer of magnesium oxide between 1 and 2 mm thick. Magnesium oxide is an excellent diffuse reflector which gives a maximum of 97% reflectivity at this thickness. Magnesium oxide has an advantage over a conventional reflector in this type of system in that each reflection within the cell increases the light gathering power of the cell. The light emerges from a small aperture in the side of the cell which is sealed with a quartz window. Provided that this aperture is small, the light which is emitted can be made to approximate to a point source. It was therefore necessary to keep the aperture small in order to focus as much light as possible in the entrance slit of the

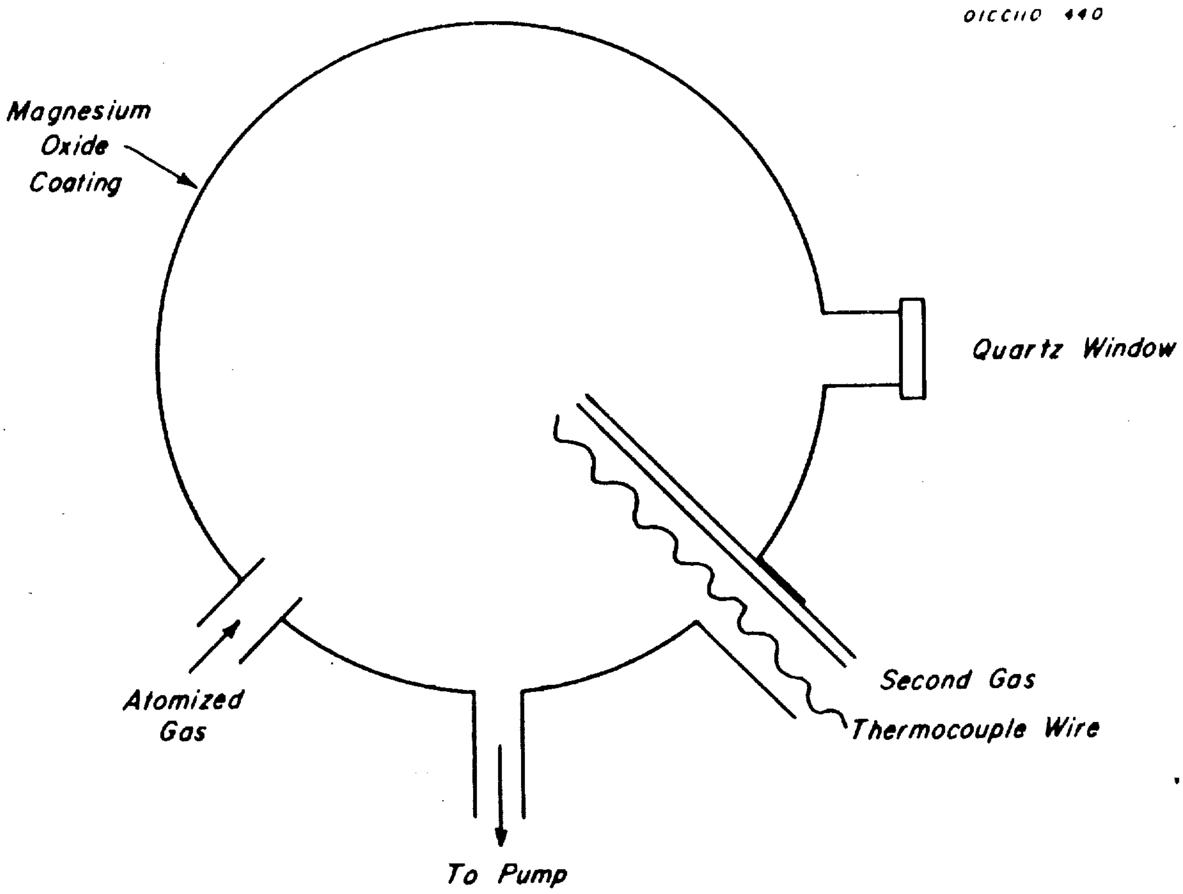

Figure 1. Reaction Cell for Observation of Chemiluminescence.

spectrometer. In order to investigate the temperature dependence of reactions, provision is made for heating the cell to a maximum of 700^{o}K by means of an external heating jacket which fits over the cell. This ensures uniform heating throughout the reaction volume. The temperature of the cell can be controlled by varying the voltage applied to the heating circuit. The temperature within the cell is measured by means of a calibrated thermocouple wire which enters the cell through one of the side arms. The pressure within the cell is measured on the two independently calibrated McLeod gauges which are also inserted through a side arm.

A block diagram of the apparatus used is shown in Figure 2. Molecular oxygen or a mixture of molecular oxygen and inert gas is passed, via a flowmeter and valve, through a microwave discharge unit. This partially dissociates the molecular oxygen which then enters the reaction vessel after first passing through the Wood's light trap. Carbon monoxide which has been purified by passing through a column of activated charcoal enters the reaction vessel through another side arm via a needle valve, a calibrated flowmeter and a liquid nitrogen trap (on the low pressure side of the needle valve) to remove any last traces of impurities. It is worth noting that most samples of tank carbon monoxide contain a certain quantity of iron carbonyl. Failure to remove this and other impurities gave an intense spectrum containing many of the bands of cuprous chloride. No spectroscopic evidence was found for the presence of these bands after purification.

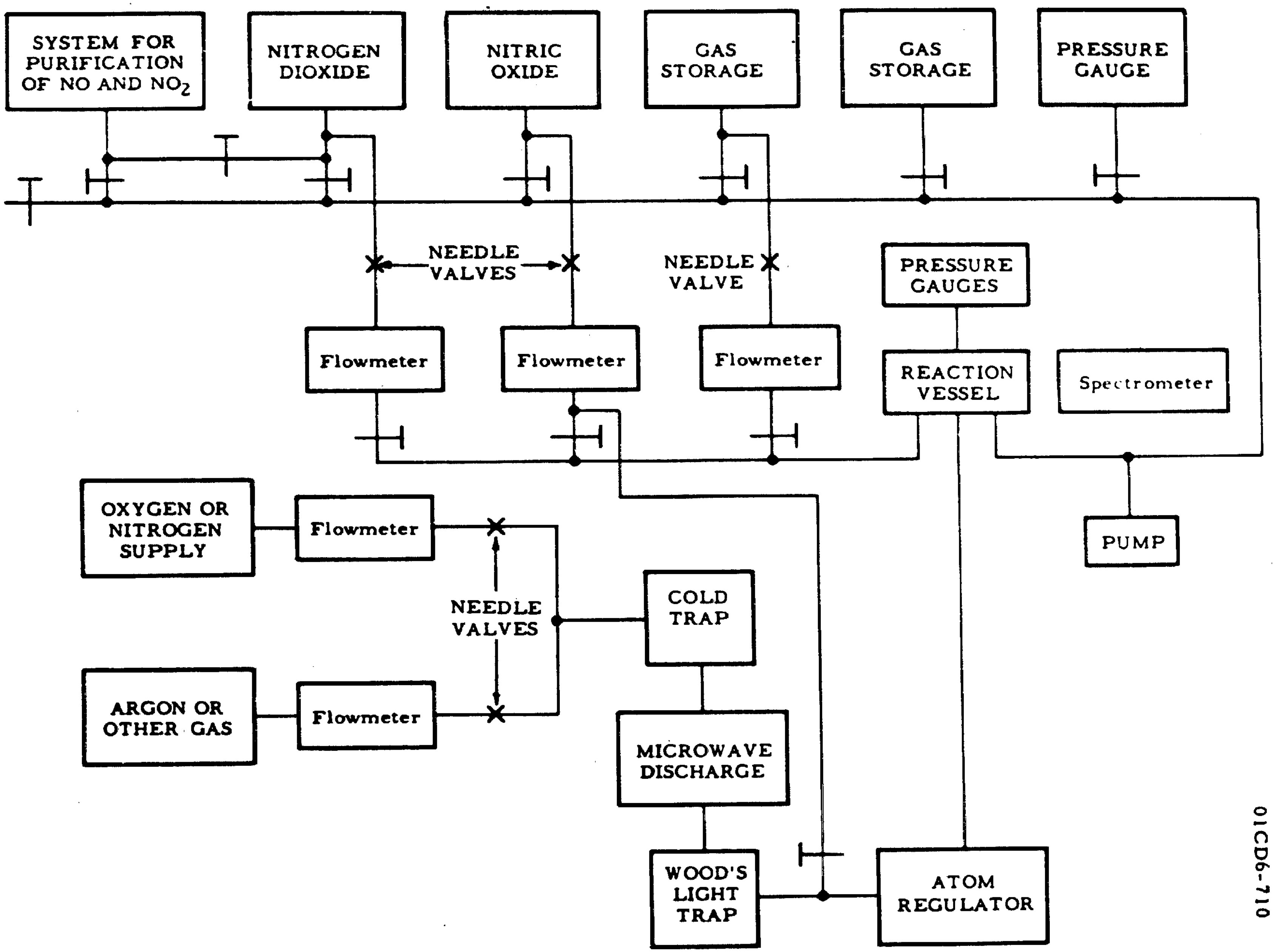

Figure 2. Block Diagram of Apparatus for Observation of Chemiluminescence.

All the flowmeters used during the experimental program were calibrated directly on the system for all gases which passed through them, using the apparatus which is shown diagramatically in Figure 3. The flow path of the gas is self-explanatory, the volume which passed through the flowmeter being measured at atmospheric pressure which avoided the necessity for correcting the results for the pressure at which the flowmeters were operating.

The steady state concentration of oxygen atoms in the reaction vessel was measured at the end of each set of readings by titration with nitrogen dioxide. The well-known reaction goes according to the equation

$$O + NO_2 \rightarrow NO + O_2 \quad ,$$

which is very much faster than the light emitting reaction

$$O + NO \rightarrow NO_2 + h\nu \quad .$$

Hence, when NO_2 is in excess, there is no light emission. It is easily seen that maximum light emission will occur when the nitrogen dioxide concentration is equal to one-half that of the oxygen atom concentration. In practice, there is a marked asymmetry to the curve at pressures above 100 microns. An example is shown in Figure 4. This can be explained as being due to the decay of the oxygen atom concentration owing to wall collisional recombination since the residence time within the vessel is

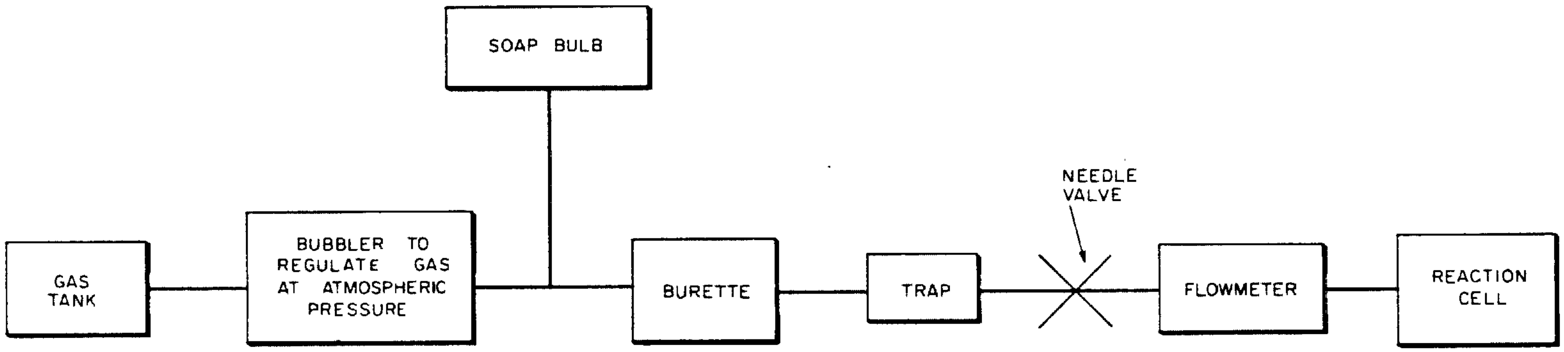

Figure 3. Block Diagram of Apparatus for Calibration of Capillary Flowmeters.

between 20 and 60 seconds. In Figure 4, the intercept A with the X axis is the point of no light emission and is, hence, the point at which the nitrogen dioxide concentration is equal to the oxygen atom concentration. Alternatively, one can say that the oxygen atom flow rate entering the bulb is equal to the nitrogen dioxide flow rate entering the bulb. This statement can be made since there is virtually no depletion of the oxygen atoms by wall collisions in the cell, owing to the rapidity of the reaction with nitrogen dioxide. At point B, the position of maximum light emission, the situation is somewhat different. Here, we have maximum light emission since the oxygen atom concentration is equal to the nitric oxide concentration. The number of oxygen atoms measured at this point, however, has been depleted by approximately the same number of wall collisions as the oxygen atoms in the carbon monoxide reaction, since the O + CO and O + NO reactions have approximately the same rate constant. Hence, the number of oxygen atoms present in the bulb is equal to double the number measured at the position of maximum light emission. The difference between this number and the number measured at the intercept A is a measure of the number lost by wall collisions at the particular operating pressure.

Two methods were used to observe the light emission from the carbon monoxide atomic oxygen reaction.

The spectral distribution of the light emission was observed using a Perkin-Elmer Model 112 G grating spectrometer, which had a single beam,

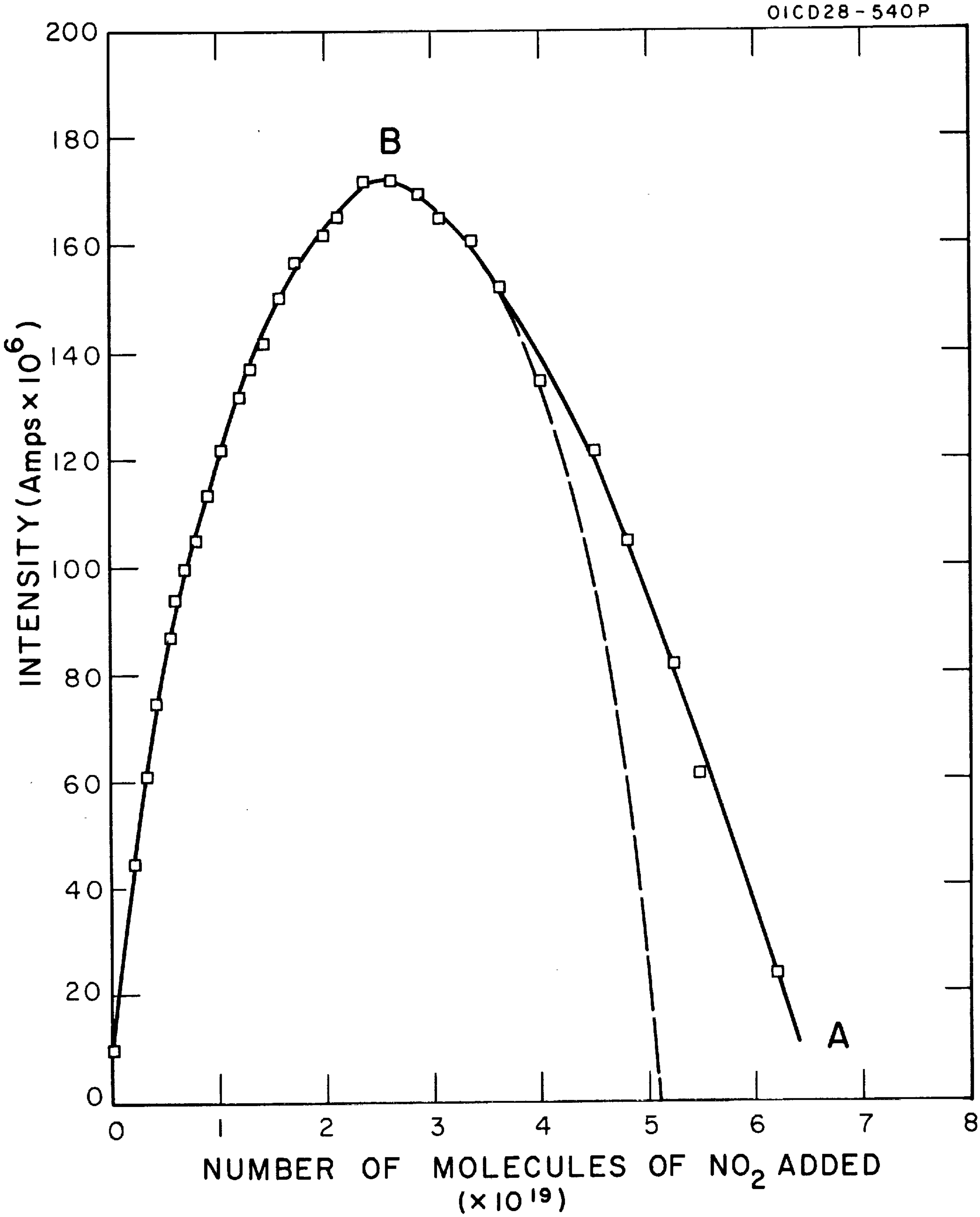

Figure 4. Plot of Intensity Against Amount of Nitrogen Dioxide Added at 350 microns of Mercury.

double pass monochromator. Attempts were made to record the spectrum in the region from 2000 A to 6000 A. Above 3500 A, a Pyrex filter was inserted in order to avoid the presence of higher orders from the grating. The radiation passing through the monochromator was chopped on its second pass using a chopping frequency of 13 cps. This avoided the detection of the unchopped first pass radiation since the resulting signal was fed into an amplifier tuned to the chopping frequency. The signal was detected at the exit slit of the monochromator by an E.M.I. number 9558B tri-alkali photomultiplier tube which was mounted in a specially designed light-tight housing. The spectral region between 2000 A and 6000 A were scanned automatically.

The over-all light emission was measured by mounting an RCA IP21 photomultiplier tube, in a light-tight housing, directly onto the aperture of the reaction cell. The resulting DC signal was fed into a Victoreen microammeter.

III. RESULTS

The spectrum of the luminescence was obtained between pressure limits of 0.5 mm and 1.5 mm of mercury and at varying flow rates of oxygen, atomic oxygen and carbon monoxide. Since the glow was very weak, 2 mm slits had to be employed on the monochromator; this consequently cut down on the degree of resolution available. Under these conditions the luminescence appeared as a continuum, varying only in intensity, extending between approximately 3300 A and 6200 A. In all probability this is the same continuum which has been reported as the carbon monoxide flame bands(4) and as the flame bands plus a larger number of unidentified bands,(6) by photographic techniques. Our results are not inconsistent with these since our degree of resolution with 2 mm slits would not be sufficient to resolve the bands suggested as being present. It is important to note, however, that very careful purification of the carbon monoxide is necessary. We found that if insufficiently pure carbon monoxide was used, then we obtained a much stronger light emission which consisted of a banded spectrum overlying an apparent continuum which appeared at somewhat longer wavelengths than the carbon monoxide-atomic oxygen continuum. The bands were readily identified as the emission from the CuCl system. It is to be noted that these bands are a frequent impurity in flames of burning carbon monoxide and also in the cool flame.

The experimental program was continued using the photomultiplier setup which was described earlier. In all experiments it was found that there was a certain amount of background emission which is always present in experiments with atomic oxygen in which a small amount of nitrogen impurity is present. The radiation is due to the well-known, light emitting, O + NO reaction. The emission from the oxygen atom-carbon monoxide reaction was obtained by subtraction of the microammeter readings obtained with and without carbon monoxide flowing.

The dependence of the glow on the concentration of carbon monoxide present was investigated in the following manner. Using a constant flow of molecular oxygen and maintaining a constant discharge, the flow rate of carbon monoxide added was varied from 0 to 8 standard cc's per minute. The light emission was then plotted as a function of the carbon monoxide concentration expressed in microns of mercury. The light emission was found to be linear with an increasing carbon monoxide concentration. A typical set of results are shown in Figure 5.

The light emission variation as a function of atomic oxygen concentration was determined in a similar way. The atomic oxygen concentration was varied while the carbon monoxide flow rate was kept constant. The results are given in Figure 6 which shows that the light emission increases linearly with increasing atomic oxygen concentration.

The effect of changing the amount of third body present was next established. The molecular oxygen flow rate was varied from 63×10^{19} to

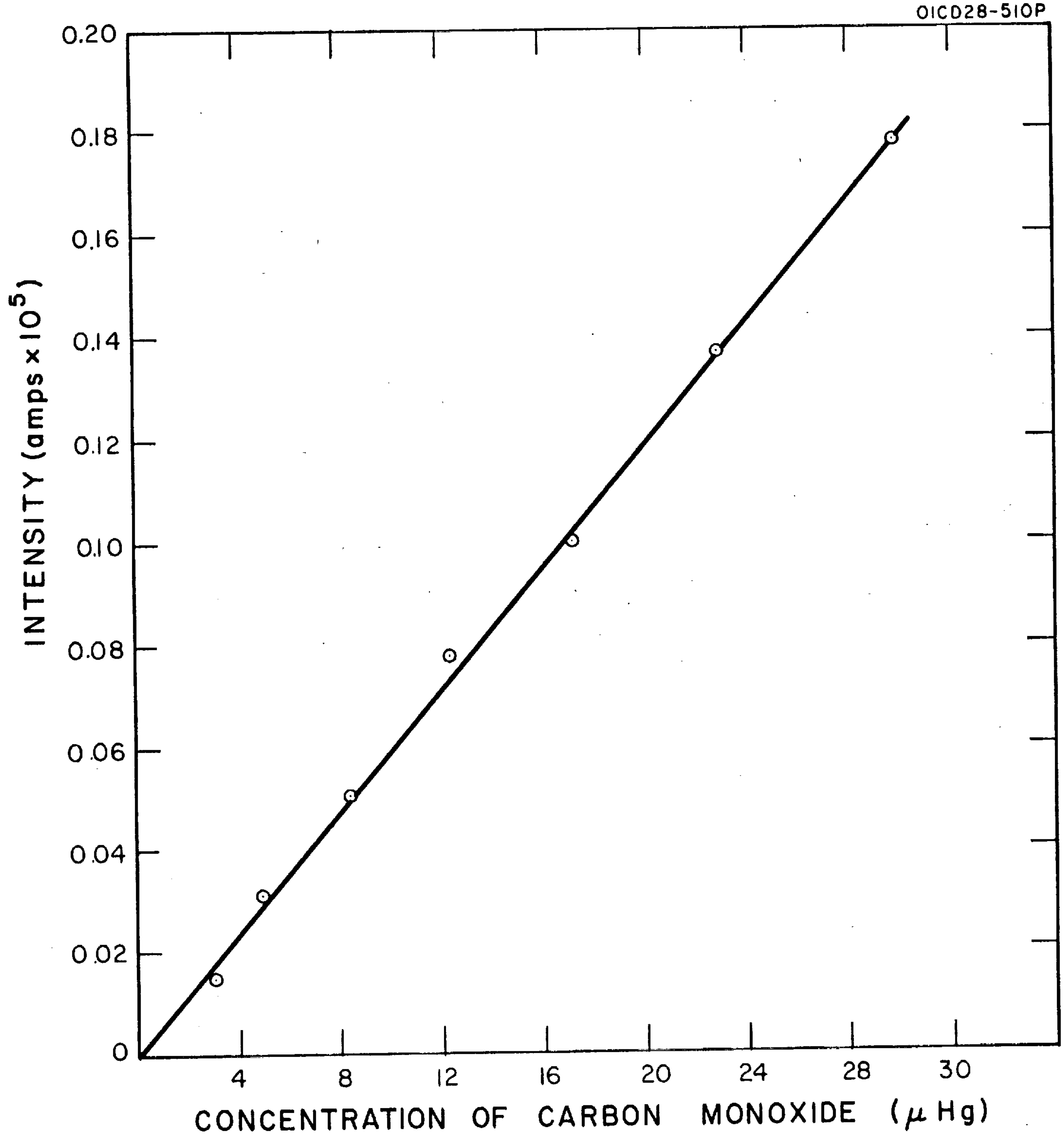

Figure 5. Graph of Light Emission Against Carbon Monoxide Concentration with Constant Oxygen Atom Concentration.

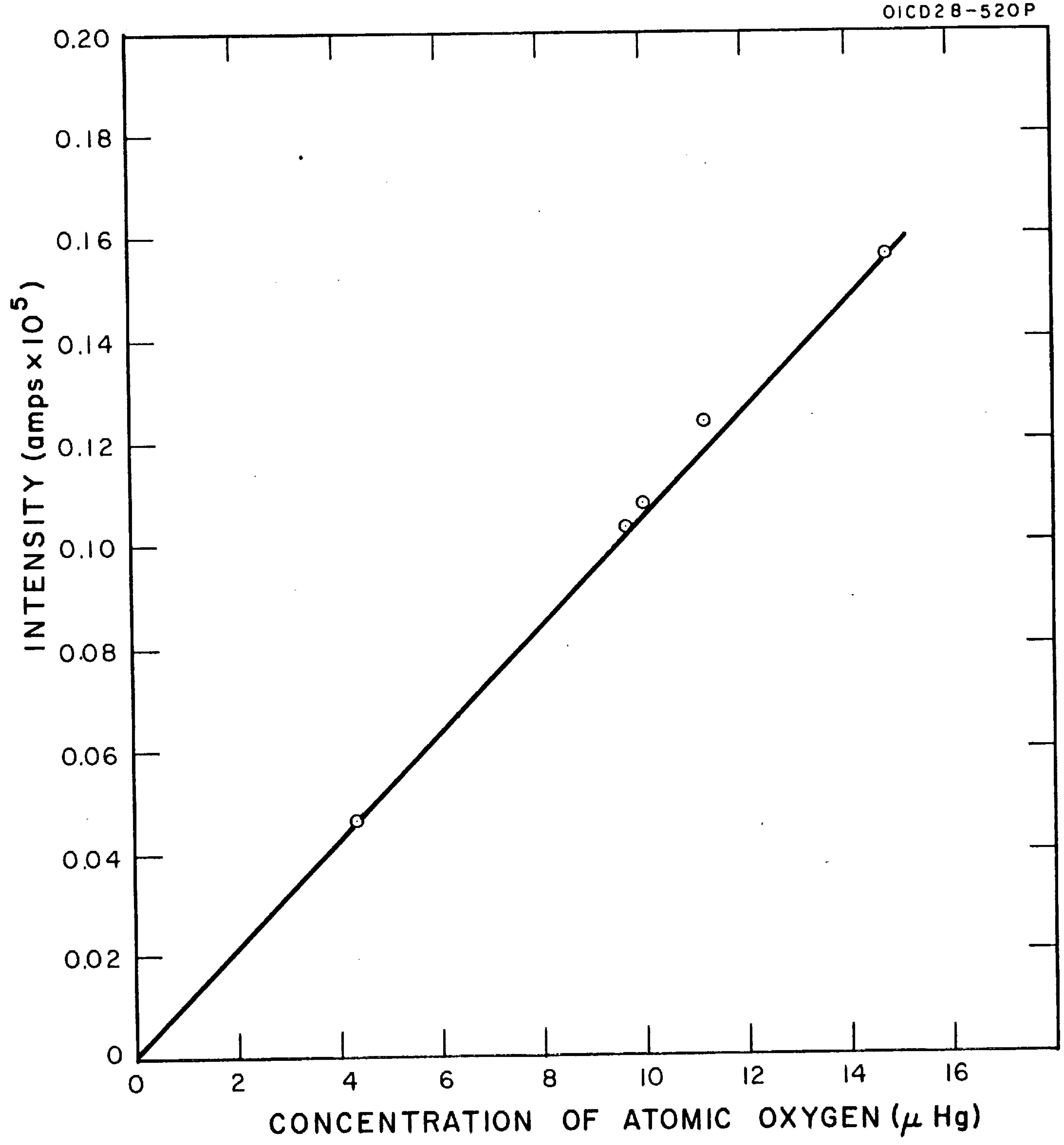

Figure 6. Graph of Light Emission Against Oxygen Atom Concentration with Constant Carbon Monoxide Concentration.

233×10^{19} molecules/min and varying amounts of carbon monoxide up to a maximum of 20×10^{19} molecules/min were added. In all cases, the predominant third body was molecular oxygen. The atomic oxygen concentration was measured in each case. Changes in the flow rate caused changes in the pressure of the reaction cell ranging from 230 microns to 430 microns. These pressure changes were always taken into account when concentration values for the species were established. The results are given in Table 1 and are summarized in Figure 7, along with some extra readings. Figure 7 gives a clear indication of the lack of effect of varying amounts of the third body.

The dependence of the light emission on the type of third body present was next investigated. The experiments were carried out by measuring the light emission using varying amounts of carbon monoxide with the molecular oxygen being diluted with either helium or argon so that the inert gas was the predominant third body. Subjection of these mixtures of gases to the microwave discharge gave atomic oxygen concentrations of the same order of magnitude as in the experiments described earlier. The results in Table 2 show that varying the type of third body present causes the light emission to change. More light is emitted with argon and helium than there is with oxygen as a third body. These results are shown graphically in Figure 8.

Since one fails to see any intensity change as a result of varying the amount of third body present, one would perhaps not expect to find a

TABLE 1

VARIATION OF INTENSITY OF LIGHT EMISSION WITH CHANGE IN THE AMOUNT OF THIRD BODY PRESENT

[CO] (microns Hg)	[O] (microns Hg)	[O][CO] (microns Hg)^2	[O$_2$] (microns Hg)	Pressure (microns Hg)	I (x10^5 amps)	I/[O][CO]
3.0	11.4	34	302.6	317	0.015	0.00044
4.9_5	11.4	56	301.65	318	0.031	0.00055
8.4	11.4	96	300.2	320	0.051	0.00053
12.3	11.3	139	299.4	323	0.078	0.00056
17.1	11.3	193	297.6	326	0.100	0.00052
22.8	11.2	255	296.0	330	0.137	0.00054
29.8	11.2	334	293.0	334	0.178	0.00053
2.5	13.7	34	390.8	407	0.022	0.00065
4.2	13.6	57	390.2	408	0.038	0.00067
7.2	13.5	97	389.3	410	0.050	0.00052
10.5	13.5	142	389.0	413	0.084	0.00059
14.7	13.4	197	387.9	416	0.118	0.00059
19.7	13.4	264	386.9	420	0.147	0.00056
25.8	13.3	343	384.9	424	0.188	0.00055
33.2	13.3	442	383.5	430	0.238	0.00054
3.6	4.6	17	223.8	232	0.008	0.00047
5.9	4.5	27	222.6	233	0.013	0.00048
10.0	4.5	45	220.5	235	0.023	0.00051
14.5	4.5	65	219.0	238	0.033	0.00051
20.3	4.4	89	216.3	241	0.047	0.00053
26.9_5	4.4	119	213.6	245	0.063	0.00053
34.6	4.3	149	210.1	249	0.088	0.00059
43.9	4.2	184	206.9	255	0.107	0.00058

TABLE 2

VARIATION OF INTENSITY OF LIGHT EMISSION WITH CHANGE IN NATURE OF THIRD BODY PRESENT

[CO] (μ Hg)	[O] (μ Hg)	[O][CO] (μ Hg)^2	[Ar] (μ Hg)	[O_2] (μ Hg)	[He] (μ Hg)	[P] (μ Hg)	I(x10^5amps)	I/[O][CO]
3.0	11.4	34		302.6		317	0.015	0.00044
4.9_5	11.4	56		301.6		318	0.031	0.00055
8.4	11.4	96		300.2		320	0.051	0.00053
12.3	11.3	139		299.4		323	0.078	0.00056
17.1	11.3	193		297.6		326	0.100	0.00052
22.8	11.2	255		296.0		330	0.137	0.00054
29.8	11.2	334		293.0		334	0.178	0.00053
4.6	6.7	31	915.5	34.8		962	0.040	0.0013
7.6	6.7	51	914.6	34.8		964	0.070	0.0013
12.9	6.7	86	911.4	34.6		966	0.115	0.0013
18.9	6.6	125	908.6	34.5		969	0.153	0.0012
26.3	6.6	174	905.3	34.4		973	0.195	0.0011
35.2	6.6	232	901.6	34.3		978	0.253	0.0011
2.4	5.8	14		24.8	537.0	570	0.014	0.0010
4.0	5.8	23		24.7	536.3	571	0.027	0.0012
6.7_5	5.7	38		24.6	535.4	572	0.038	0.0010
9.9	5.7	56		24.6	533.4	574	0.057	0.0010
13.9	5.7	79		24.5	532.9	577	0.075	0.0010
18.6	5.7	106		24.5	531.2	580	0.100	0.0009
24.4	5.7	139		24.4	529.5	584	0.125	0.0009
31.4	5.6_5	177		24.4	527.6	589	0.153	0.0009

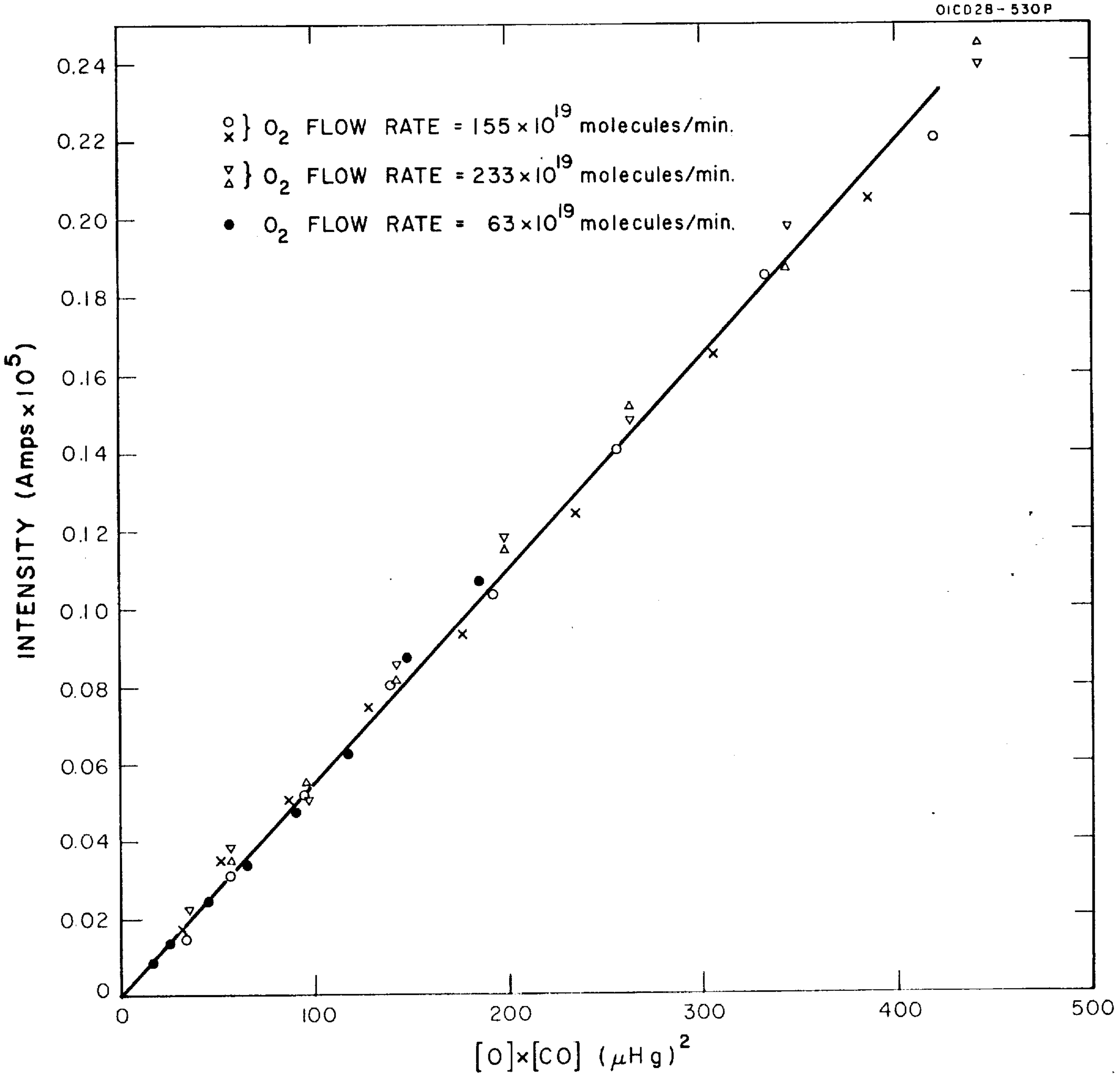

Figure 7. Plot of Intensity of Light Emission Against Concentration of Atomic Oxygen and Carbon Monoxide.

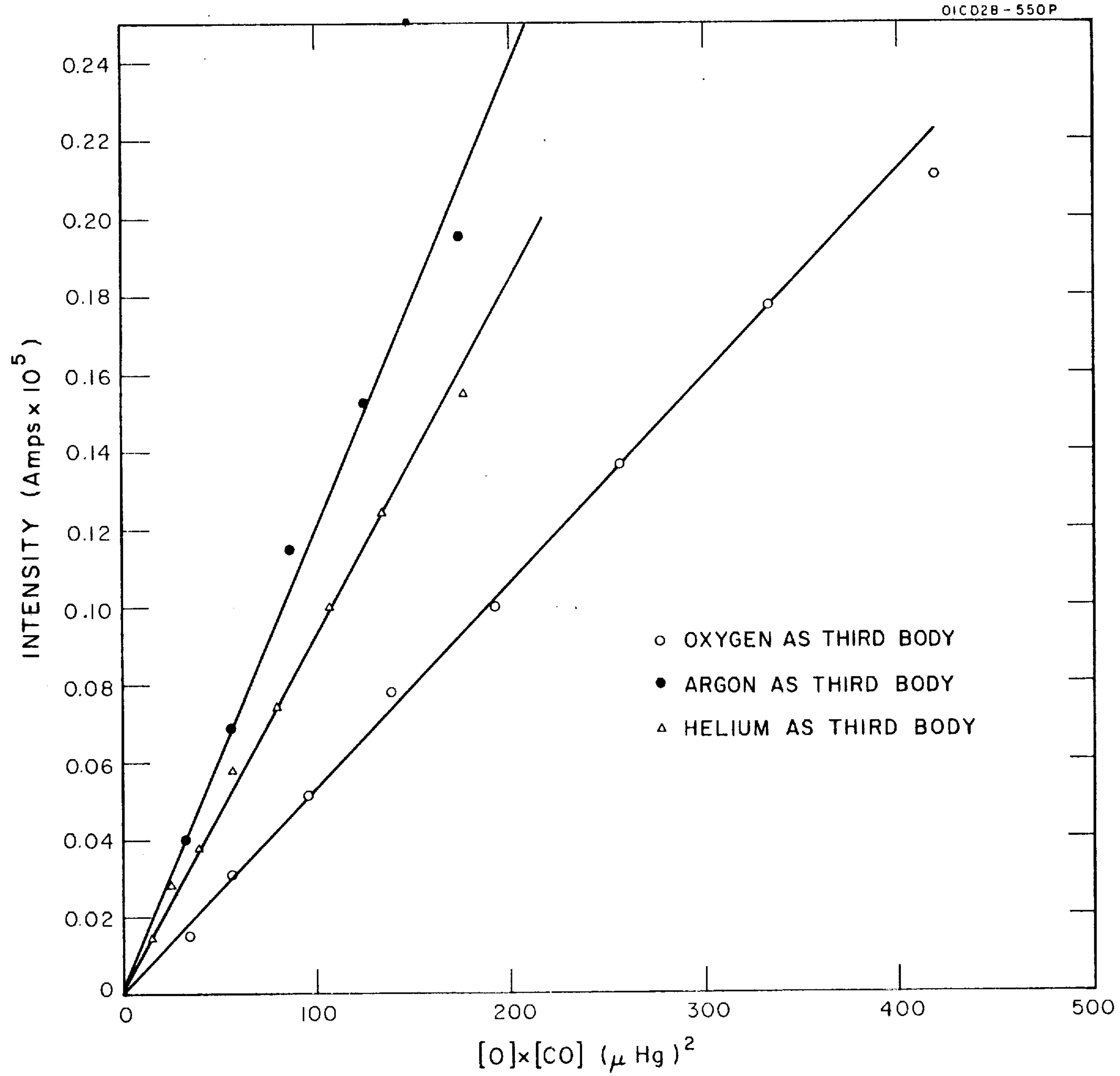

Figure 8. Effect of Variation of the Predominant Third Body on Intensity.

change with variation in pressure. This, however, was investigated over the pressure range 0.23 mm to 1.0 mm using oxygen as a third body and from 0.5 to 1.0 mm using argon as the predominant third body. The atomic oxygen concentration was measured at each pressure since it was quite sensitive to pressure effects. No significant change in the ratio of intensity to [O][CO] was observed over the pressure range studied. The ratio was, of course, different depending upon the predominant third body, as explained in the previous paragraph.

An attempt was made to observe the luminescence from the O + CO reaction at pressures below the 0.25 mm which have been described. By using the oil diffusion pump, the internal pressure of the cell was maintained at approximately 8 microns while the input flow rates were the same as those at higher pressures. This, of course, meant that the residence time of the gases in the reaction vessel was cut down drastically to under one second. Under these conditions, it was found that there was no resultant glow upon adding varying amounts of carbon monoxide. In fact, the normal oxygen "afterglow" was diminished. This "afterglow" which is due to the O + NO reaction was diminished according to the amount of carbon monoxide added in a fashion which suggested a Stern-Volmer quenching relationship. The results are shown in Figure 9. It was therefore concluded that under our conditions at 8 microns and $293^{\circ}K$, there was no significant light emission from the O + CO reaction and that carbon monoxide was a reasonably efficient quencher of the reaction. This presumably arose from deactivation of the excited NO_2 molecules during collision:

$$CO + NO_2^* \rightarrow CO + NO_2 \quad .$$

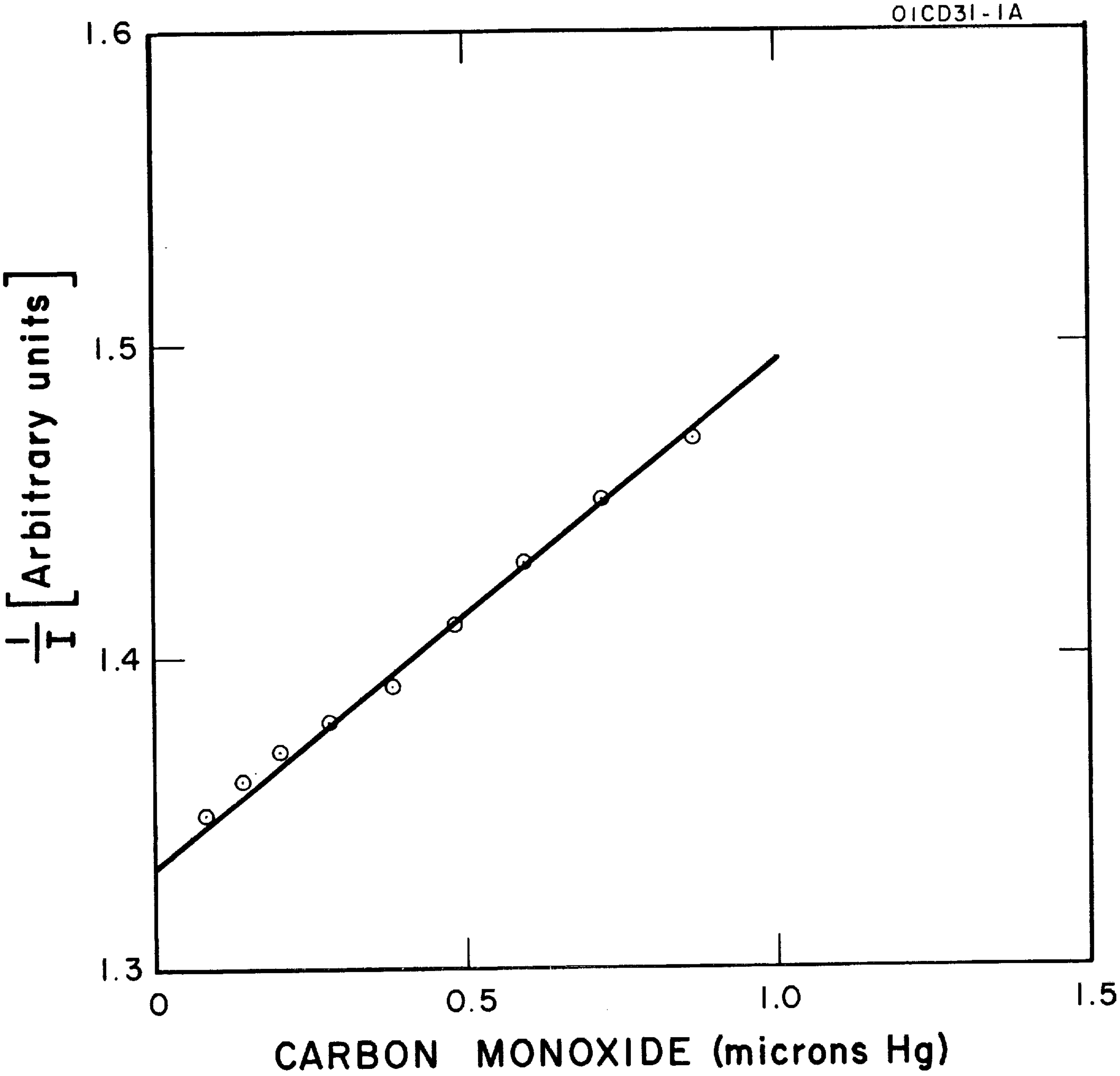

Figure 9. Effect of Adding Carbon Monoxide to the Oxygen "Afterglow" at Eight Microns Pressures.

IV. DISCUSSION OF RESULTS

In order to discuss and interpret the results which we have obtained, it is necessary, as a first step, to understand the results and interpretations of the other workers.(5,6) At this point, therefore, we will give a full account of their observations and what their interpretations entail.

A. RESULTS OF CLYNE AND THRUSH(5)

Their results are similar in all respects to ours except that they obtained less light emission from helium as the third body than from oxygen as the third body. The mechanism which they propose to account for their observations is given below.

Stabilization and Redissociation

$$O + CO + M \underset{k_{-1v}}{\overset{k_{1v}}{\rightleftharpoons}} CO^*_{2(v)} + M \quad .$$

Vibrational Energy Transfer

$$CO^*_{2(v)} + M \underset{k_{v',v}}{\overset{k_{v,v'}}{\rightleftharpoons}} CO^*_{2(v')} + M \quad .$$

Radiation

$$CO^*_2 \xrightarrow{k_{2v}} CO_2 + h\nu \quad .$$

Collisional Electronic Quenching

$$CO^*_{2(v)} + M \xrightarrow{k_{3v}} CO_2 + M \quad .$$

Applying a steady state treatment we get:

$$\left[CO_2^*\right]_v = \frac{[M]\left(k_{1v}[CO][O] + \sum_{v',v}\left[CO_2^*\right]_{v'}\right)}{k_{2v} + [M]\,k_{-1v} + k_{3v} + \sum_v k_{v,v'}} \quad . \qquad (A)$$

The total emission is given by

$$I = \sum_v k_{2v}\left[CO_2^*\right]_v \quad .$$

Rate of formation of CO_2 is given by

$$\frac{d\left[CO_2\right]}{dt} = \sum_v \left(k_{2v} + k_{3v}\,[M]\right)\left[CO_2^*\right]_v \quad .$$

Now if $k_{2v} \ll$ than all other terms in the denominator of Eq. (A), then the observed I depends on the nature of M but not on the pressure of the carrier gas.

However, if this is the case, then the rate of formation of carbon dioxide is dependent upon M; this is in disagreement with the results of Mahan and Solo.(6)

The over-all combination reaction is spin forbidden,

$$CO\left({}^1\Sigma^+\right) + O\left({}^3P\right) \rightarrow CO_2\left({}^1\Sigma_g^+\right) \quad .$$

Spin reversal occurs either:

(1) in the stabilization of a CO_2 molecule by a third body. This, it is claimed, would yield an increased intensity since oxygen

(which has a triplet ground state $^3\Sigma_g^-$) would facilitate spin reversal. On the other hand, it might be argued that the CO_2 would not be produced in an excited state and, if it were, then the molecular oxygen might be a more efficient quencher of the excited species to the ground state than, say, helium.

(2) in the radiationless transition between two states before or after radiation. This transition could occur before or after the emission process; however, if it occurs after emission, it implies the presence of a very low-lying triplet state for CO_2, since the emitting state cannot lie more than 130 kcal/mole above the ground state of CO_2 and emission is observed below 3000 A (95 kcal/mole). No low-lying singlet or triplet state of CO_2 has been detected spectroscopically and none is expected. Clyne and Thrush, therefore, concluded that the emission is a singlet-singlet transition to the ground state of CO_2 and that spin reversal occurs in the radiationless transition between two excited states before emission.

(3) in the radiative process. This, however, would be expected to decrease I by accelerating the rate of quenching of triplet CO_2 molecules relative to the rate of emission.

Hence, Clyne and Thrush favor the second explanation given above. However, if one is prepared to accept all the data in the Mahan and Solo paper, then this mechanism cannot be correct since the rate of production of CO_2 would be dependent on the concentration of M.

B. RESULTS OF MAHAN AND SOLO(6)

These workers claim that an increase in the total pressure (over the range 0.56 - 1.9 mm Hg) decreases the quantum yield — the quantum yield is defined as the light emitted per unit amount of carbon dioxide. The data from which they draw this conclusion are reproduced in Table 3. However, as can be seen from Figure 10, the data can equally well show that the light emission is directly proportional to the amount of carbon dioxide produced. This would indicate that the light emission was not pressure dependent over the pressure range 0.56 to 1.9 mm of Hg. It is believed that, within these workers' probable limits of experimental uncertainty, this is a legitimate straight line plot.

Further studies by these workers indicate that the light emission is quenched considerably by the addition of small quantities of molecular oxygen when the predominant third body was argon. This quenching was in apparent agreement with the Stern-Volmer quenching law. It was also found that small amounts of molecular oxygen increased the amount of carbon dioxide formed, indicating to them that there was a secondary reaction between the excited carbon dioxide and molecular oxygen, thus:

$$CO_2^+ + O_2 \rightarrow CO_2 + 2O$$

and

$$CO_2^* + O_2 \rightarrow CO_2 + 2O \quad .$$

TABLE 3

ABSOLUTE QUANTUM YIELDS* (MAHAN AND SOLO)

Run	CO	O_2 x 10	Ar	CO_2 x 10^3	Flow Rate	Pressure	$(\text{Quantum Yield})^{-1}$	Intensity
1A	0.27	0.39	0.25	0.82	20.9	0.56	500	164
1B	0.38	0.58	0.37	1.6	14.4	0.81	580	276
2A	0.75	0.34	0.20	0.65	34.4	0.98	480	135
2B	1.0	0.49	0.31	0.88	24.4	1.4	530	166
3A	1.34	1.6	0.41	0.37	17.9	1.9	780	47
3B	1.09	1.3	0.35	0.28	21.6	1.6	660	42

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* All quantities except Flow Rate, Quantum Yield and Intensity are in mm. Flowrate is in units of liters/min, Quantum Yield is the number of quanta emitted divided by the total number of carbon dioxide molecules produced, and the Intensity is in arbitrary units.

When the molecular oxygen reached a value of approximately 10% of the total amount of third body present, then the production of carbon dioxide became independent of the molecular oxygen.

It was found that over the pressure range 0.18 to 1.44 mm, the rate of production of carbon dioxide was independent of the third body M. They, therefore, concluded that the over-all rate of production of CO_2 went according to the equation $d(CO_2)/dt = k(CO)(O)$.

The following mechanism was used by them to explain their results:

$$O + CO \xrightarrow{k_1} CO_2^+ \quad \text{nonradiative}$$

$$O + CO \xrightarrow{k_2} CO_2^* \quad \text{radiative}$$

$$CO_2^+ + M \xrightarrow{k_3} CO_2 + M$$

$$CO_2^* + M \xrightarrow{k_4} CO_2 + M$$

$$CO_2^* \xrightarrow{k_5} CO_2 + h\nu$$

$$\left[CO_2^+\right] = \frac{k_1[O][CO]}{k_3[M]}$$

$$\left[CO_2^*\right] = \frac{k_2[O][CO]}{k_4[M]+k_5}$$

$$\begin{aligned} d\left[CO_2\right]/dt &= k_3[M]\left[CO_2^+\right] + k_4[M]\left[CO_2^*\right] + k_5\left[CO_2^*\right] \\ &= k_1[O][CO] + \frac{k_2k_4[M][O][CO]}{k_4[M] + k_5} + \frac{k_2k_5[O][CO]}{k_4[M] + k_5} \\ &= k_1[O][CO] + \frac{k_2[O][CO]k_4[M] + k_5}{k_4[M] + k_5} \\ &= \left(k_1 + k_2\right)[O][CO] \quad . \end{aligned}$$

Hence, the rate of production of carbon dioxide is independent of M.

$$I = k_5\left[CO_2^*\right] = \frac{k_2k_5[O][CO]}{k_4[M] + k_5} \ .$$

It can be seen that the light emission is dependent upon [M].

The above mechanism can explain all the results of Mahan and Solo; but as can be seen, it cannot be reconciled with the results of Clyne and Trush or with our own results, since the light emission is dependent upon pressure. However, as we have shown, these results could probably equally well show that the light emission is not pressure dependent. (See Figure 10.)

We think it is therefore necessary to give a mechanism which will explain both our observations and those of the other two sets of workers. We attempt to do this with the following mechanism.

The over-all combination reaction is spin forbidden:

$$CO\left({}^1\Sigma^+\right) + O\left({}^3P\right) \rightarrow CO_2\left({}^1\Sigma_g^+\right) \ .$$

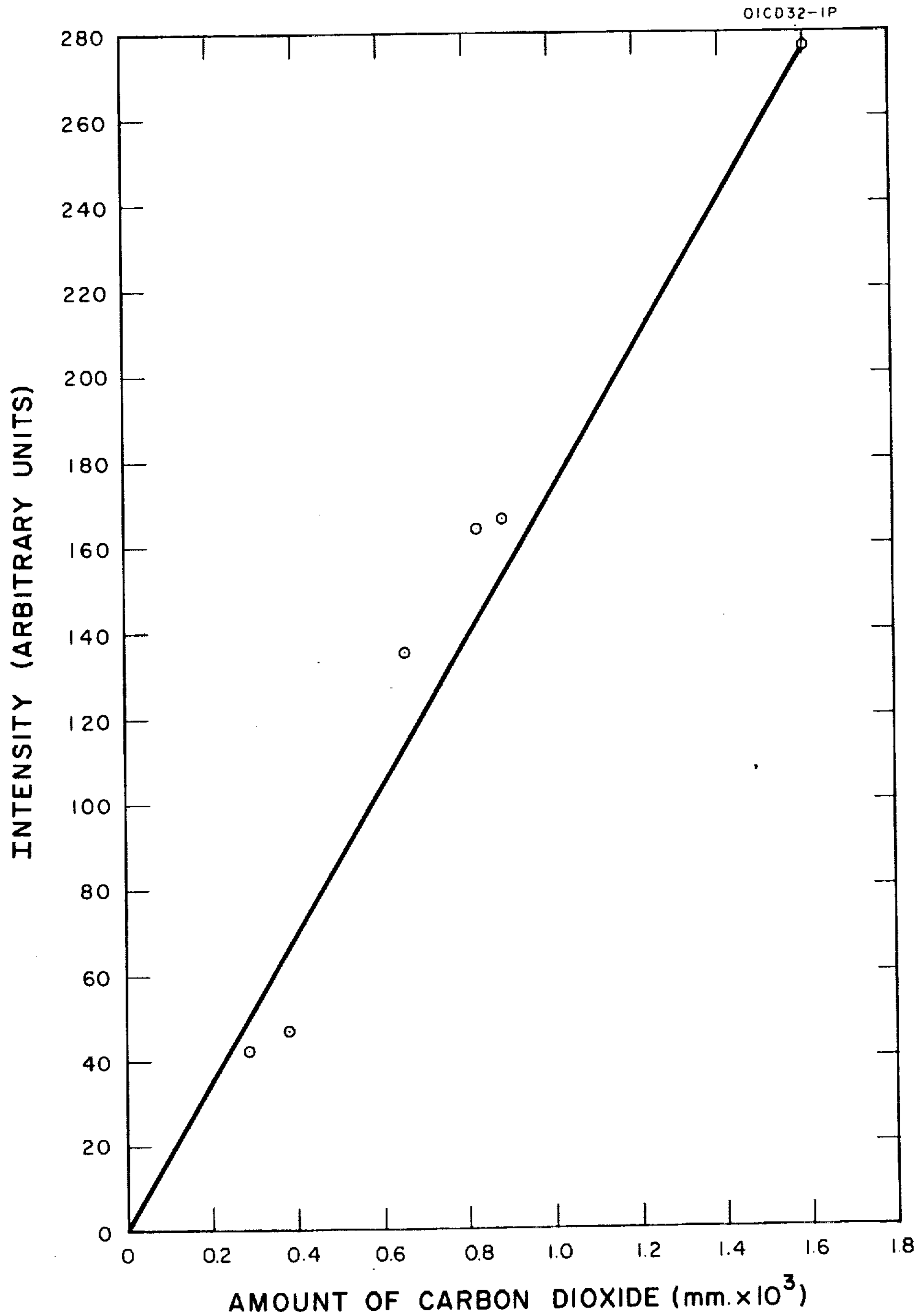

FIG. 10

INTENSITY OF LIGHT EMISSION AS FUNCTION OF CARBON DIOXIDE PRODUCED (DATA OF MAHAN & SOLO)

If, however, spin reversal occurs in the stabilization of the excited CO_2 molecules by a third body, then we might write the mechanism as

$$O + CO \xrightarrow{k_1} CO_2^+ \tag{1}$$

$$CO_2^+ + M \xrightarrow{k_2} CO_2^* + M \tag{2}$$

$$CO_2^+ + M \xrightarrow{k_3} CO_2 + M \tag{3}$$

$$CO_2^* + M \xrightarrow{k_4} CO_2 + M \tag{4}$$

$$CO_2^* \xrightarrow{k_5} CO_2 + h\nu \tag{5}$$

If molecular oxygen is present in any significant amount, then reactions (2) and (3) are facilitated since the ground $\left({}^3\Sigma_g^-\right)$ state of oxygen would be expected to facilitate spin reversal. Hence, while it is possible for the stabilization to give CO_2 in an excited singlet state, as in reaction (2), it is also probable that reaction (3) will occur, which gives CO_2 in its ground singlet state. It is therefore believed that the statement of Clyne and Thrush that the stabilization of the excited CO_2 molecule by molecular oxygen would lead to an increased I value is not necessarily true, since the "quenching" effect of reaction (3) would also become more evident. It might be argued also that it is difficult to avoid the molecular oxygen or the atomic oxygen playing a dominant part as the third body, since if it is only present in small quantities, then it would be expected to be several orders of magnitude more efficient than an inert gas. Our results (i.e., the light emission is increased with argon or helium as the apparent predominant third body) are, therefore, not in disagreement with this theory since reaction (3) would decrease at least in relation to reaction (2) even if atomic and molecular oxygen were not present in significant quantities.

It is necessary at this point to see if our mechanism will fit the observations of Mahan and Solo. These will be taken in turn.

(1) The absolute quantum yield decreases with pressure over the range 0.56 to 1.9 mm Hg. As we have shown in Figure 10, we believe that these results could equally well be interpreted as showing that the quantum yield is independent of pressure. However, one can take another approach. The relative amount of molecular oxygen present in these workers' experiment (Table 3) varies from 3.5 to 8.4 percent. This is probably sufficient to make the molecular oxygen play a major role as the third body. It can be argued that even if one agrees that the quantum yield decreases, then from the limited amount of data available, if I is assumed constant, the amount of CO_2 formed increases as O_2 increases. This also would not be contradictory to our observations.

If we accept our observations that the light emission is independent of pressure, then our mechanism is consistent with this:

$$\left[CO_2^+\right] = \frac{k_1[O][CO]}{k_2[M] + k_3[M]}$$

$$\left[CO_2^*\right] = \frac{k_2[M]\left[CO_2^+\right]}{k_4[M] + k_5} = \frac{k_1k_2[M][O][CO]}{k_2[M] + k_3[M]} \times \frac{1}{k_4[M] + k_5}$$

$$\frac{dI}{dt} = k_5\left[CO_2^*\right] = \frac{k_1k_2k_5[M][O][CO]}{k_2[M] + k_3[M]} \times \frac{1}{k_4[M] + k_5} .$$

Thus, provided that k_4, the quenching of the excited electronic state is very small, then the observed light emission will be independent of pressure but will depend upon the nature of the third body [M].

(2) The relative quantum yield decreases in apparent agreement with a Stern-Volmer quenching law as small amounts of molecular oxygen are added. Again, it is noted that the molecular oxygen is never present in quantities of less than 1.5 percent and is gradually increased to 20 percent. Hence, the reactions

$$CO_2^+ + O_2 \rightarrow CO_2^* + O_2 \tag{6}$$

$$CO_2^+ + O_2 \rightarrow CO_2 + O_2 \tag{7}$$

predominate and the CO_2^+ is preferentially placed in a nonexcited singlet state.

(3) Small amounts of molecular oxygen increase the amount of carbon dioxide formed. This is interpreted by Mahan and Solo as evidence for the chain-branching mechanism

$$O_2 + CO_2^+ \rightarrow CO_2 + 2O$$

$$O_2 + CO_2^* \rightarrow CO_2 + 2O \quad .$$

It may not be necessary to postulate this explanation, however. We can again argue that the addition of small amounts of molecular oxygen will increase the degree of importance of reactions (6) and (7). The belief that these are more efficient than reactions (2) and (3) where M is nitrogen or argon would cause the required increase in CO_2 produced.

(4) The reaction is first order with respect to both oxygen atoms and carbon monoxide, but zero order with respect to total pressure. Our mechanism yields the following expression for the production of carbon dioxide.

$$\begin{aligned}\frac{d\left[CO_2\right]}{dt} &= k_3[M]\left[CO_2^+\right] + k_4[M]\left[CO_2^+\right] + k_5\left[CO_2^*\right] \\ &= \frac{k_1k_3[M][O][CO]}{k_2[M] + k_3[M]} + \frac{k_1k_2k_4[M][O][CO]}{(k_2[M] + k_3[M]\; k_4[M] + k_5)} \\ &\quad + \frac{k_1k_2k_5[M][O][CO]}{(k_4[M] + k_5)(k_2[M] + k_3[M])}\end{aligned}$$

The rate of production of carbon dioxide is independent of M provided that k_4 is very small. Hence, our mechanism does not conflict with the data of Mahan and Solo.

V. CONCLUSIONS

It is interesting to note that ours is the third mechanism to be proposed for this reaction, and it is felt that it is the only one which is not in conflict with experimental observations.

Before we can draw any positive conclusions as to the importance of the reactions to the Venus airglow, a study should be made at higher temperatures. It might, however, be noted that at room temperature the luminescence is at least a factor of 2000 less than the O + NO reaction.

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