KINETICS OF THE CHEMILUMINESCENT REACTION

BETWEEN OZONE AND NITRIC OXIDE

by

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INTRODUCTION

(A) Spectra of the 03-NO Chemiluminescence and its Mechanism:

In early work this chemiluminescence was confused with that from the oxygen atom - nitric oxide reaction. Indeed it has turned out that their spectra and mechanisms are quite similar, so that an understanding of the 0-NO reaction (which was investigated first) will facilitate understanding of the 0_3 -NO reaction.

The O-NO chemiluminescence, when first observed, was called the "air afterglow" or "oxygen afterglow". Thomson (17) subjected oxygen to an electrodeless discharge at low pressures and observed a yellow-green glow, which persisted for some time after the discharge was turned off. Air under the same conditions also gave this glow.

Lord Rayleigh (13) postulated a reaction between ozone and nitric oxide to account for this chemiluminescence, although when he mixed these two gases, no afterglow appeared. He reported that the afterglow spectrum was continuous, extending from 4200 - 6700Å.

The conditions necessary for the afterglow were investigated later in more detail by Lewis (25) and Herzberg (26). Stoddart (15) reported 28 or 30 weak diffuse bands over the range 4200 - 6700Å for the afterglow spectrum. About the same time, Newman (16) reported at least 29 diffuse bands superimposed upon a continuous spectrum in the same range. The emitter was taken to be NO₂, and oxygen atoms,

rather than ozone were shown to be responsible for the afterglow (7, 14).

The mechanism for the 0-NO chemiluminescence was first investigated by Kaufman (21, 27). He concluded that the continuum in the afterglow spectrum might arise from

 $0 + N0 \longrightarrow N0_2 + h\nu$

but this would not yield the complex system of bands. By varying separately the quantities [0], [NO] and [M], where M is an inert molecule, he found that the emission intensity I varied jointly as the concentrations thus

$$I = k [0] [N0]$$

and was independent of [M] and the nature of M (in the torr pressure range).

The mechanism suggested by this author was

$$0 + NO + M \longrightarrow NO_2^* + M \quad (1,1')$$
$$NO_2^* \longrightarrow NO_2 + h\nu \quad (2)$$
$$NO_2^* + M \longrightarrow NO_2 + M \quad (3)$$

where NO_2^* represents a molecule in an excited state. Under steady-state conditions for NO_2^* ,

$$I = k_2 \left[NO_2^* \right]_{SS} = \frac{k_2 k_1 \left[NO \right] \left[O \right] \left[M \right]}{k_2 + (k_3 + k_1^2) \left[M \right]}$$

In the experimental pressure range, $(k_3 + k_1)$ [M] $\gg k_2$;

$$I = \frac{k_1 k_2}{(k_3 + k_1')} [N0][0]$$

As Kaufman pointed out, however, the ratio $k_1/(k_3 + k_1)$ would be expected to vary for different M, since there is no reason why all M should have similar relative efficiencies in reactions (1), (1') and (3).

The molecule NO_2^* has generally been taken to be in an excited electronic state. In consideration of available spectroscopic data of the molecule, Broida, Schiff and Sugden (24) presented an elaborated scheme which included two excited states of NO₂, (B) and (C):



where (C) is the higher energy state, and undergoes transition to (B) by a resonance transfer process.

The work of Clyne and Thrush (22) supported the now generally accepted scheme, which is as follows:

$$0 + NO + M \longrightarrow NO_{2}^{*} + M \qquad (1)$$

$$NO_{2}^{*} \longrightarrow NO_{2} + h\nu \qquad (2)$$

$$NO_{2}^{*} + M \longrightarrow NO_{2} + M \qquad (3)$$

The emission intensity will be expressed by

$$I = \frac{k_1 k_2 [0] [N0] [M]}{k_2 + k_3 [M]}$$
$$= \frac{k_1 k_2}{k_3} [0] [N0] \qquad (I)$$

where $k_3 [M] \gg k_2$.

The ratio k_1k_2/k_3 would not necessarily be constant for different gases, for reasons given by Kaufman above. Clyne and Thrush found that this ratio did indeed change somewhat from gas to gas. This fact had been envisaged in the expanded scheme of Broida, Schiff and Sugden (24).

The proportionality (I) was found to be valid in the pressure range 0.85 - 400 microns according to Doherty and Jonathan (99) and in the range 3 - 20 microns, according to Reeves, Harteck and Chace (20), although at these pressures the inequality $k_3 [M] \gg k_2$ may not hold.

The parallel spectroscopic and kinetic investigations of the 0_3 -NO reaction were begun only recently. As no discharge is necessary to produce this radiation, it is not called an "afterglow", although NO₂ undoubtedly is responsible for the emission in both cases. The upper state of the NO₂ may, however, differ in the two cases.

Tanaka and Shimazu (7) compared spectra of the 0-NO and 0_3 -NC reactions in the same apparatus. All their work was done at a total pressure of a few torr. The 0_3 -NO emission was produced by mixing directly pure ozone and pure nitric oxide in a flow system. At low flows it appeared very red, but at high flows more yellowish. In this case the heat of reaction probably decomposed some ozone, and the resulting oxygen atoms existed long enough to produce the 0-NO flame.

If, however, the ozone producing the red flame was discharged before mixing, the yellow-green flame appeared instead. Cessation of the discharge brought back the red glow.

The discharged ozone showed no ultraviolet absorption bands, and hence had been destroyed.

For the red flame, they reported 24 diffuse bands and a continuum in the range 4300 - 6300 Å. The resolution was limited and the results indicated that the 0-NO and 0_3 -NO spectra were rather similar.

Better spectra were made later by Greaves and Garvin (10) who reported some 65 unresolved bands overlying an apparent continuum in the range 5900 - 10,850 Å. The absolute emitted intensity increased continuously toward longer wavelengths and probably extended much further into The partial pressures of 0_3 , NO and 0_2 diluent the infrared. were 5 torr, 60 torr and 140 torr respectively. Under these conditions the concentration of oxygen atoms was very small, and the O-NO radiation did not interfere. The exothermicity of the 03-NO reaction, 47.5 kcal./mole (8), corresponds to an einstein of radiation at 6000 Å, which agrees with their short wavelength cut-off of 5900 Å. The exothermicity of the 0-NO reaction, 72.7 kcal./mole, corresponds similarly to an einstein of radiation at 3834 Å, which can account for the radiation below 6000 Å observed by Tanaka and Shimazu.

Clyne, Thrush and Wayne (12) obtained spectra of this radiation and listed 12 bands in the range 7140 - 8500 Å; they obtained the intensity distribution photoelectrically from 6000 - 8750 Å. Their results were similar to those of Greaves and Garvin. They also compared these data with those from the thermal emission of NO₂, as observed by themselves and by Kondratiev (28). They concur with the suggestion of Greaves and Garvin that electronically excited NO₂ is responsible for the chemiluminescence.

Furnival (19) has reported spectrophotometric measurements of the red emission. Under appropriate conditions, she also obtained the spurious O-NO afterglow as observed by Tanaka and Shimazu. The total pressure, for the red flame, was a few torr with nitrogen as diluent. In the range 5900 - 10,500 Å she reported 54 bands upon a continuum, and the results substantiate those of Greaves and Garvin (10) and Clyne, Thrush and Wayne (12).

At the time of initiation of the present work, no mechanism for this chemiluminescence had been established. That one for 0-NO, however, provides a good analogy, so that for the 0_3 -NO system we can write

03	+	NO>	NO2	+	°2	(4)
⁰ 3	+	NO>	NO ² 2	+	°2	(4*)
	NO	ž>	N02	+	h u	(2)
NO [*] 2	+	$M \longrightarrow$	NO2	+	М	(3)

(B) <u>Reactions of Ozone</u>:

The reactions reported below are those which either would occur in the 03-NO system used in this work, or are otherwise related to the problem under study.

----- Nitrogen Dioxide -----

The stoichiometry of this reaction was first established by Wulf, Daniels and Karrer (43) who showed that one

mole 0_3 reacted with one mole $N_2 0_4$ in the gas phase at room temperature. The overall reaction was

 $0_3 + 2NO_2 \longrightarrow N_2O_5 + O_2$

and one gas could be "titrated" against the other, using the disappearance or appearance of brown fumes as end-point.

The rate constant has been measured at constant volume in the temperature range $13 - 29^{\circ}$ C by Johnston and Yost (44). Its value at room temperature was 6.7 x 10^{-17} cc./ molecule/sec. and the activation energy was approximately 7 kcal./mole. The NO₂ concentration as a function of time was determined by chopped-beam absorption photometry (4400 -4800 Å). The total pressure was near one atmosphere with oxygen as diluent. Since ozone does not react directly with N₂O₁, the mechanism was

> $NO_2 + O_3 \longrightarrow NO_3 + O_2$ rate-determining $M + NO_2 + NO_3 \longrightarrow N_2O_5 + M$ fast

Ford, Doyle and Endow (45) also measured the rate constant at room temperature, using a stirred flow reactor with one atmosphere nitrogen. Its value was 3.3×10^{-17} cc./ molecule/sec. The effluent stream was analyzed continuously for NO₂ with a photocolorimeter using flowing m-phenylenediamine, and for ozone by absorption photometry (2537 Å).

----- Nitrogen Pentoxide -----

This was first studied in detail by Schumacher and Sprenger (46) who observed that the disappearance of ozone depended upon the two-thirds power of ozone concentration and of N_2O_5 concentration. By optical absorption, they were able to follow the concentration of the intermediate species NO_3 ; the mechanism, elaborated by Johnston (63), is

$$M + N_{2}O_{5} \implies NO_{2} + NO_{3} + M \quad (5, 6)$$

$$NO_{3} + NO_{3} \implies 2NO_{2} + O_{2} \quad (7)$$

$$NO_{2} + O_{3} \implies O_{2} + NO_{3} \quad (8)$$

It is thus not a true 03-N205 reaction.

Assuming steady-state concentrations for NO_2 , NO_3 and N_2O_5 ,

$$- d[0_3]/dt = (k_5 k_8/k_6)^{2/3} (2k_7)^{1/3} [N_2 0_5]^{2/3} [0_3]^{2/3}$$

The values of all rate constants in this expression have been tabulated by Schott and Davidson (64).

----- Photolysis of Dry Ozone -----

The early work was reviewed by Schumacher (48), and Kistiakowsky's (49) was the least ambiguous. For photolysis with both red and ultraviolet light, kinetic considerations ruled out the primary steps

$$\begin{array}{rcl} 0_{3} & + & h\nu \longrightarrow 0_{3}^{*} \\ 0_{3}^{*} & + & 0_{3} \longrightarrow 30_{2}^{*} \\ 0_{3}^{*} & + & M \longrightarrow 0_{3} + & M \end{array}$$

Rather he suggested

$${}^{0}_{3} + h\nu \longrightarrow {}^{0}_{2} + 0$$
 (9)

$$^{0} + ^{0}_{3} \longrightarrow 20^{2}_{2} \tag{10}$$

 $0 + 0_2 + M \longrightarrow 0_3 + M$ (11)

where the formation of 0^{3*}_{2} can lead to a chain reaction to explain high quantum yields ($\emptyset > 2$):

This could account qualitatively for the variation of \emptyset , 0.1 to 3.6, at 6200Å (50, 51)

At shorter wavelengths (3130 to 2080Å) \emptyset was as high as 6.7 (52, 53). Heidt and Forbes adopted Schumacher's scheme, adding

 $0_3 + h\nu \longrightarrow 0^*_2 + 0$

and obtained the asymptotic approximation

$$\frac{1}{\emptyset} = \frac{1}{2} + \frac{k_{11}[0_2][M]}{2k_{10}[0_3]}$$

where most of the gas was 0_2 . Up to this time, 0_2^* was assumed to be an electronically excited molecule.

The work of McGrath and Norrish (47, 54, 55) helped to identify the atomic and molecular states in reactions (9), (10) and (12). In flash photolysis they observed Schumann-Runge absorption bands for O_2 molecules in their ground electronic state. These molecules, formed in reaction (10), possessed up to 17 quanta of vibrational energy and were rotationally cold. Thus for ultraviolet light, and in consideration of spin and energetic principles, they wrote

$$\begin{array}{rcl} 0_{3} &+& h\nu &\longrightarrow & 0_{2}({}^{1}\Delta g) &+& 0({}^{1}D) \\ 0({}^{1}D) &+& 0_{3} &\longrightarrow & 0_{2}^{\dagger}({}^{3}\Sigma \widetilde{g}) &+& 0_{2}({}^{3}\Sigma \widetilde{g}) & (14) \\ 0_{2}^{\dagger}({}^{3}\Sigma \widetilde{g}) &+& 0_{3} &\longrightarrow & 20_{2}({}^{3}\Sigma \widetilde{g}) &+& 0({}^{1}D) \end{array}$$

where $O_2^{\dagger}({}^{3}\Sigma_{g}^{-})$ is the chain propagator. The termination steps are (11) and (13) and

$$0 + 0 + M \longrightarrow 0_2 + M$$
$$0 \xrightarrow{\text{wall}} \frac{1}{2}0_2$$

Benson, however, in contrast to this, has suggested that the chain is photon-propagated (35, 56, 57):

$$0_2(^3\Sigma_u) \longrightarrow 0_2(^3\Sigma_g) + h\nu (2000Å)$$
 (16)

$$0_3 + h\nu (2000\text{\AA}) \longrightarrow 0_2 + 0(1\text{D})$$

However, reaction (15) is 4 kcal./mole endothermic, while (14) is 138 kcal./mole exothermic, and will more likely be favoured. McGrath and Norrish also believe that the radiation from reaction (16) would be of longer wavelength than 3000Å, and could not produce a photon chain because ozone absorbs so weakly in this region. Schumacher (58) also agrees with these conclusions.

The existence of energy chains in the red light photolysis of ozone has been a matter of contention (47, 58). On energetic grounds, McGrath and Norrish believe that the 0-atom produced in reaction (9) in this case is ${}^{3}P$, which cannot lead to a chain as depicted in reaction (15). Data for the energetics of this reaction are given in Table 1 (from reference 65):

TABLE	1
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		°2	· · · · · · · · · · · · · · · · · · ·
	β	"∆	'Σ
		$\lambda,$ å	
0 (3p)	11,400	5,900	4,600
0 ('D)	4,100	3,100	2,600

Limiting Wavelengths for Production of $0_2 + 0$ from 0_3

Recently Castellano and Schumacher (59) reinvestigated the photolysis in the region 5800 - 6200Å with extreme care. The highest value of \emptyset observed was 2, indicating the absence of any excited 0_2 molecules.

Following the work of McGrath and Norrish, Fitzsimmons and Bair (60) have measured the distribution and relaxation of vibrationally excited 0_2 from ozone flash photolysis. They were able to measure the concentration of the species

$$0_2^{\ddagger} (^{3}\Sigma_{g}^{-}), \nu'' = 13 \text{ to } 19$$

as a function of time. The relaxation rate constants were large and this was interpreted as an efficient transfer of energy between 0_3 and 0_2^{\ddagger} , taking place in single quantum steps.

---- Thermal Decomposition of Ozone -----

The pyrolysis of ozone, at first sight, would seem to be a relatively simple process. Ostensibly there are only three chemical species concerned $(0, 0_2, 0_3)$ and all contain nothing but oxygen. After 25 years' research, however, Tolman and Wulf (66) in 1927 still had just cause to say that the kinetics of "...this bothersome chemical change [were] entirely in doubt..." Previous authors' results disclosed discrepancies of such order which belied the apparent simplicity of the system.

It has turned out that ozone decomposition is an excellent example of a chemical change which is extraordinarily sensitive to the presence of trace impurities acting as catalysts. Indeed, the clarification of this "bothersome chemical change" may be said to have advanced in step with the effective elimination of these impurities.

Results of earlier work (67 - 74) were summarized by Wulf and Tolman as follows (all work was done with a dilute 0_3 in 0_2 solution). The reaction was followed manometrically and generally at 100° C and above. At room temperature the rates of decomposition were very erratic and seemed first order. At higher temperatures the reaction was second or mixed first and second order (corresponding to "monomolecular" and "bimolecular" rate constants k_A and k_B respectively). The rate constant would increase during a run and might or might not change markedly with different wall materials, vessel shape and surface-to-volume ratio. Increasing the $0_2/0_3$ ratio usually (but not always) decreased the rate.

The most consistent second-order rate constant k_B at 100°C was circa 2.7 x 10⁻²² cc./molecule/sec. and the activation energy lay in the range 25.9 to 38.3 kcal./mole.

The mechanism thought to be operative was first given by Jahn (69):

$$^{\circ}_{3}$$
 $\stackrel{\circ}{\longrightarrow}$ $^{\circ}_{2}$ + 0 (fast equilibrium) K₁
0 + $^{\circ}_{3}$ $\stackrel{\sim}{\longrightarrow}$ 20₂ (rate determining) (17)

and the rate of ozone disappearance would be

$$-\frac{d[0_3]}{dt} = 2k_{17} [0]eq [0_3] = \frac{2k_{17} K_1 [0_3]^2}{[0_2]}$$
(II)

which shows the second-order behaviour and inverse effect of $\begin{bmatrix} 0_2 \end{bmatrix}$. Doubt was cast on its strict applicability by Tolman and Wulf (66), who showed that the number of 0_3 -0 collisions was too small for observed rates of reaction.

Further work (75 - 82) yielded more detailed but not conclusive information. Addition of inert gases was found to inhibit the monomolecular reaction and accelerate the bimolecular, in the order of decreasing efficiency $CO_2 > N_2 > Ar > He$. The value of k_A was about 2 x 10⁻⁴ sec.⁻¹ at 100^oC. Anomalously high rates and occasional explosions were presumed to arise from energy chains, as in the following:

"MONOMOLECULAR" <u>DECOMPOSITION</u> $0_3 \rightarrow 0 + 0_2$ $0 + 0_3 \rightarrow 20^*_2$ $0^*_2 + 0_3 \rightarrow 20^*_2$ $0^*_2 + 0_3 \rightarrow 0^*_3 + 0_2$ $0^*_2 + 0_3 \rightarrow 0^*_3 + 0_2$ $0^*_2 + 0_3 \rightarrow 0^*_3 + 0_2$ $0^*_2 + 0_3 \rightarrow 0^*_3 + M$ $0^*_2 + M \rightarrow 0_2 + M$ Garvin's work (42) at 157 - 287° C, however, showed no evidence of chains and could be described by the Jahn relation, equation (II).

Benson and Axworthy (35) re-interpreted the results of Glissman and Schumacher (80) and Garvin (42). From these and their own results they concluded that there was no need to postulate energy chains or surface effects, or to include the reaction

$$^{0}_{3}$$
 + $^{0}_{3}$ \longrightarrow $^{30}_{2}$

Abnormally high rates could be accounted for by the existence of temperature gradients in the reacting gases, as suggested by Harteck and Dondes (82). In accordance with Garvin's suggestion, they gave a modified Jahn mechanism:

where a steady-state [0], rather than an equilibrium concentration is assumed, and $k_{17} \gg k_{18}$.

$$- \frac{d \left[0_{3}\right]}{dt} = 2k_{17} \left[0\right]_{ss} \left[0_{3}\right] = \frac{2k_{17}k_{18} \left[0_{3}\right]^{2} \left[M\right]}{k_{11} \left[0_{2}\right] \left[M\right] + k_{11} \left[0_{3}\right]} (III)$$

In two limiting cases, we can write

(a) Pure ozone:
$$k_{17} \begin{bmatrix} 0 \\ 3 \end{bmatrix} \gg k_{11} \begin{bmatrix} 0 \\ 2 \end{bmatrix} \begin{bmatrix} M \end{bmatrix}, M = 0_3$$

$$- \frac{d \begin{bmatrix} 0 \\ 3 \end{bmatrix}^2 = 2k_{18} \begin{bmatrix} 0 \\ 3 \end{bmatrix}^2$$
(IV)

(b) Dilute ozone:
$$k_{17}[0_3] \ll k_{11}[0_2][M], M = 0_2$$

$$- \frac{d[0_3]}{dt} = \frac{2k_{17}k_{18}[0_3]^2}{k_{11}[0_2]}$$
(V)

Efficiencies of inert gases (relative to ozone) in reaction (18) were also found. Equations (III), (IV) and (V) could clarify previous order-of-reaction anomalies, and also the fact that O_2 accelerates the reaction in pure ozone and decelerates it in dilute ozone; addition of inert gas under any conditions accelerates it.

In the following paragraphs, the rate constants quoted are those at room temperature, and the experimental temperature range follows the value of the activation energy.

From their data and existing thermodynamic values, Benson and Axworthy (85) derived the following: k_{17} , 2.3 x 10^{-15} cc./molecule/sec., activation energy 6.0 kcal./mole (70 - 110 C); k_{18} , 3.3 x 10^{-26} cc./molecule/sec., 24.0 kcal./ mole (70 - 110^oC).

Zaslowsky et al. (34) decomposed 100% ozone at 115 - 130^OC; the data were completely compatible with equation (IV), without energy chains. The values were: k_{18} , 2.7 x 10⁻²⁶ cc./molecule/sec., 24.3 kcal./mole.

In shock-tube experiments, Jones and Davidson (84) obtained rate constants at 416 - 637°C consistent with previous values at lower temperatures: k_{17} , 3.4 x 10⁻¹⁵ cc./molecule/ sec., 5.6 kcal./mole. Through flash absorption, moreover, they recorded the presence of vibrationally excited 0₂ molecules, $\gamma'' = 10$ to 17, which they say result from

$$0(^{3}P) + 0_{3} \longrightarrow 0_{2}^{\ddagger} + 0_{2}$$

although McGrath and Norrish (47, 54) doubt the ability of

3P atoms to form chains by this method, as do also Schumacher and Castellano (59, 86).

The results of Pshezhetskii et al. (83) at 70 - 170°C could also be described without energy chains.

The value 2.5 x 10^{-14} cc./molecule/sec. for k_{17} was obtained by Phillips and Schiff (18) using mixed streams of discharged oxygen and an 0_3 -Ar mixture, and following reaction with a mass spectrometer.

----- The Rate of the 03-NO Reaction -----

Previous work on the measurement of this rate constant is described below, where all pressures are in torr. The results are summarized in Table 2 which follows the descriptive material.

Johnston and Crosby (1) followed the reaction at -43 and -75°C. The partial pressures were: ozone and nitric oxide, 0.1; nitrogen, 700. Ozone was determined in situ by optical absorption photometry (2537 Å). The 1:1 stoichiometry was established by reacting excess 03 or excess NO and determining 03 and NO₂ by optical absorption at 2537 and 4360 Å respectively.

Goyer (6) confirmed the 1:1 stoichiometry of the reaction, analyzing for ozone by the potassium iodide method and for NO₂ by optical absorption (3500 - 4800Å). The partial pressures were: ozone, 0-10; nitric oxide, 0.4 - 100. The total pressure was one atmosphere at room temperature, the diluents being O₂, N₂ and water vapour.

Ford, Doyle and Endow (2) used dry air at atmospheric pressure as diluent at room temperature and reactant partial pressures of 10^{-4} . Ozone was measured by optical absorption (2537Å) and NO₂ by a continuous colorimetric method. The reactants were made in situ by photolysis of NO₂ at 3660Å:

 $NO_{2} + h\nu \longrightarrow NO + 0$ $O + O_{2} + M \longrightarrow O_{3} + M$ $O_{3} + NO \longrightarrow NO_{2} + O_{2}$

Borok (3, 4) used reactants at pressures about 10^{-2} with nitrogen and oxygen as diluents at one atmosphere at 60°C. Product NO₂ was determined continuously by a photocolorimeter using flowing m-phenylenediamine, calibrated gravimetrically. Initial ozone was determined iodometrically. The rate constant was calculated from NO concentrations required for full oxidation, and from residence times of reactants in the reaction zone.

Marte, Tschuikow-Roux and Ford (11) measured the rate of reaction in a supersonic nozzle, from - 28 to + 72° C. The partial pressures were: ozone, 2 x 10^{-2} ; NO, 2; N₂, 200. Ozone was determined by optical absorption (2537Å).

Clyne, Thrush and Wayne (12) measured the rate between - 57 and + 49°C. The partial pressures were: 03, 5 x 10⁻³; NO, 2 x 10⁻²; Ar, 2. Ozone concentrations were determined by using the resulting emission as a monitor. In this case, [M] and [NO] are constant, and so the expression $I = I_0 \frac{[03][NO]}{[M]}$ reduces to

$$I = I_0^{\dagger} \begin{bmatrix} 0_3 \end{bmatrix}$$

This gives relative concentrations; presumably the initial flowrate was determined by the iodometric method.

Using a mass spectrometer to follow 0_3 and NO concentrations, Phillips and Schiff (18) measured the rate at room temperature. The partial pressures were: 0_3 , 7 x 10^{-2} ; NO, 16 x 10^{-2} ; N₂, 0.5.

The pre-exponential factor A for the 03-NO rate constant has been calculated by Herschbach and Johnston (9). It was derived in three ways, viz., (a) using a detailed form of the activated complex theory, (b) using a cruder method of hydrocarbon analogy and (c) using the simple collision theory. A more refined activated complex calculation was reported by Ford et al. (11); theoretical and experimental values are compared in Table 2.

(C) Purpose of the present work:

At the time of initiation of this work, there existed no data on the mechanism of the chemiluminescence of the 0_3 -NO reaction. It was therefore of interest to explore this problem, particularly since previous work on the 0-NO chemiluminescence suggested a similar mechanism by analogy. The relative quenching efficiency of various inert gases for this chemiluminescence could also be found without difficulty, and might provide information on the excited molecule NO_2^* which is responsible for the chemiluminescence. TABLE 2

EXPERIMENTAL AND THEORETICAL PARAMETERS FOR

THE OZONE-NITRIC OXIDE REACTION

Authors	Reference	Rate Con cc./mole X 10 ¹ 27°C	stant cule/sec. 4 60°C	Activation Energy kcal./mole	Temperature Range °C	Pre-exponential Factor cc/molecule/sec. X 10 ¹²
Johnston and Crosby	1	2.0*	2.8*	2.50	- 75 to -43	1.3 (experimental)
Ford, Doyle and Endow	2	5.0	-	-	-	-
Borok	3,4	-	6.5	-		-
Marte et al.	11	3.0	4.2	2.50	- 28 to+72	2.0 (experimental) 1.3 (theoretical)
Clyne et al.	12	1.5	2.3*	2.46	- 57 to +49	1.0 (experimental)
Phillips and Schiff	18	2.1	-	-	-	-
Herschbach and Johnston	. 9	-	-	-	-	0.73 (act.complex) 1.1 (hydrocarbon analogy) 78 (collision theory)

* extrapolated value † requires a "normal" steric factor, about 10-2

Unfortunately, the results of Clyne, Thrush and Wayne (12) on this problem were published during the course of the present work. The present work, however, was continued for the following reasons:

(i) the mechanism for the chemiluminescence proposed by Clyne, Thrush and Wayne needed substantiation, and their values for relative quenching efficiencies for inert gases needed confirmation.

(ii) the data for testing the mechanism were to be obtained by different and independent methods. In their work, Clyne, Thrush and Wayne first established that, under experimental conditions, the emission intensity could be used to monitor the ozone concentration. For testing the mechanism, simultaneous ozone concentration and emission intensity measurements were needed; in their system these quantities were not measured independently.

In the present work, ozone concentration was determined at all times by optical absorption at 2537 $\stackrel{o}{A}$ (believed to be the most reliable method), and emission intensity was detected independently by a separate phototube.

(iii) The present work extended the total pressure range to 20 torr; previous work had been done at 3 torr or below.

(iv) The temperature range for measurement of the O_3 -NO rate constant was extended to 300° C; the temperature used in all previous work did not exceed 72° C.

(v) The data of Clyne, Thrush and Wayne were derived

from experiments in which the maximum removal of NO and 0_3 was only 5% of the initial value. In the present work, the reaction was followed to 60% reaction or farther.

EXPERIMENTAL

(A) Cylinder Gases Used:

OXYGEN (Therapy USP, 99.5%, Liquid Carbonic Canadian) was used exclusively for making ozone. At first it was passed through a foretrap at -78°C to remove water before entering the ozonizer; however, the presence of the small amount of this impurity did not affect significantly the ozone production, and the trap was later removed

The following gases were treated as indicated before entering the main flow system.

HELIUM (99.99%, Matheson of Canada and Air Reduction Canada) was passed at atmospheric pressure through a trap at liquid air temperatures.

CARBON DIOXIDE (Canadian Liquid Air) was passed at atmospheric pressure through a trap at -78°C.

NITROUS OXIDE (>98%, Matheson of Canada) was passed through a trap at -78° C at atmospheric pressure.

SULPHUR HEXAFLUCRIDE (>98%, Matheson of Canada) was used without further purification.

ARGON (Canadian Liquid Air) was passed at atmospheric pressure through a trap at -78°C.

NITROGEN (Standard Grade, Canadian Liquid Air) was passed at atmospheric pressure through a trap at liquid air temperatures.

NITRIC OXIDE (>99%, Matheson of Canada) was passed through a column of Caroxite (acidic oxide absorber, Fisher) to remove NO₂ and condensed at liquid air temperatures. It was then evaporated into two 12-liter storage bulbs and the high boiling fraction, consisting mainly of N_2O_h , was discarded.

(B) Manufacture and Storage of Ozone:

For kinetic studies, the method of ozone production will depend upon several factors, some of which are: (i) quantity desired and the rate at which it is used, (ii) purity, (iii) efficiency and ease of preparation and (iv) mode of use (gas, liquid or solid phase).

The simplest and safest procedure for making gaseous ozone consists of passing oxygen through the discharge and using it immediately, with or without other inert gases. If oxygen-free ozone is wanted, the ozonizer mixture $(2 - 15\% 0_3)$ in 0_2 at room temperature and one atmosphere) may be condensed below -183° C in a vacuum system, and oxygen pumped off (ozone boiling point -112° C, melting point -193° C). It is then evaporated into a storage bulb and inert gas may be added. Convenient amounts of ozone may be accumulated in this way.

In this method, however, there is much danger of ozone detonation. Both gas- and liquid-phase decompositions of ozone are extremely sensitive to trace impurities, especially hydrocarbons. Thorp (32) has discussed this at length and urges the following precautions: (a) oxygen for ozonization must be as pure as possible; (b) organic stopcock lubricant must be absent; (c) metal surfaces and mercury vapour from manometers must be excluded; (d) all glassware must be scrupulously clean; (e) liquid or gaseous ozone must not be subjected to any sudden application of localized energy, e.g., stopcock friction, static electricity and abrupt rise in temperature.

Despite the hazard, this method has been used widely in the past. Representative procedures have been described by Benson and Axworthy (35) and Zaslowsky et al. (34).

This method, without evaporation of the ozone, has been used by a few authors (36, 37, 38) to prepare solid and liquid ozone for reaction with hydrogen atoms.

Certain materials (such as "activated" charcoal) possess an enormous effective surface area per gram and adsorb a variety of chemical species. Now, to bring ozone into contact with carbon black is dangerous (39), but alumina and silica gels have adsorptive properties of sufficient magnitude to overweigh any decomposing effects. Indeed, at low enough temperatures, ozone on silica gel decomposes to a negligible extent; the bonding power between ozone and silica gel is so great as to lower appreciably its chemical reactivity. It can be subjected to astonishing amounts of chemical, thermal and mechanical shock without developing spontaneous decomposition leading to detonation (30, 32).

This adsorbent power of silica gel was first exploited for determination of ozone in air, by concentrating enough ozone at liquid oxygen temperature for it to be measured by standard iodometric methods. Edgar and Paneth (4) separated 0_3 and NO_2 this way by fractional distillation at $-120^{\circ}C$.

The amount of ozone adsorbed per gram of gel is a definite function of temperature and partial pressure of ozone in the gas phase. Adsorption isotherms have been obtained (30, 31) and sample curves are shown in Fig. 1. This behaviour is

FIGURE 1

ADSORPTION	ISOTHERMS	FOR	OZONE	ON	SILICA	GEL
------------	-----------	-----	-------	----	--------	-----

T _l :	-140°C
Т2 :	- 130
^т з [:]	- 120
т ₄ :	-110
т ₅ :	-100
^т 6 [:]	-90
^T 7:	-78.5



well suited to supplying ozone (with or without carrier gas) at a particular rate for flow experiments. For large flows, the ozone may be desorbed at a higher temperature than that at which it was adsorbed. The amount of gel, its loading and the adsorption and desorption temperatures may be chosen to yield a practically constant flowrate of ozone for any desired length of time.

The overriding attraction of this method of using ozone is its great safety and insensitivity to shock of any kind, and is attested by the author and others (41).

In Fig. 2 is shown the Siemens-type ozonizer used. Cylinder oxygen passed first through the manostat M and then into the annular spaces of two condensers in series. The outside of each condenser was wrapped with several thicknesses of aluminum foil, taped in place, and mercury was placed in the inside tubes. 8000 v.a.c., obtained from a Variac and a 12,000-volt cold cathode fluorescent lighting transformer, was applied across the 2-3 mm. gap. The current in the ozonizer under normal operating conditions was approximately six milliamperes.

The $0_3/0_2$ mixture, approximately 3 mole % 0_3 , flowed at 200 cc.(S.T.P.)/min. into a double-U trap shown in Fig. 3, filled with 900[±] 1 grams of silica gel (14-20 mesh, Fisher). The gel had previously been heated in vacuo at 120° C for six hours to drive off water. The trap was then cooled to -78° C with a dry-ice/ethanol mixture. The level of cold liquid was always above that of the gel in the trap. The temperature of

FIGURE 2

OZONIZER

ST:	Splash trap
S:	Stopcock
M:	Manostat
Al:	Aluminum foil



FIGURE 3

DOUBLE-U TRAP OF SILICA GEL






the liquid on all sides of the trap was explored with a copperconstantan thermocouple probe, and was found to be uniform within [±]2°C. The greatest source of temperature imbalance arose from the heat of adsorption of ozone on the gel. This was approximately 12 kcal./mole (30), and at the gas flowrate used, the rate of energy dissipation was about 3 cal./min. All the ozone was adsorbed from the gas phase by the gel and the exhaust gas passed into the atmosphere. If ozone was generated continuously, the gel was saturated in about three days. At this point, the flow of gas was reduced to 60 cc. (S.T.P.)/min. to keep the gel saturated and at atmospheric pressure, until ozone was needed for an experiment. The ozonizer was equipped with a mercury blow-off and splashtrap to prevent a possibly dangerous pressure build-up.

The capacity of the gel column may be derived from Fig. 1. In the present apparatus, the partial pressure of ozone was about 23 torr and the temperature was -78.5° C; hence the loading was 5.5 g./100 g. and the total amount of ozone at saturation was about 50 grams.

The main impurities in the oxygen used for making ozone were water and nitrogen. After passage through the ozonizer, the gas stream contained these possible chemically active impurities: H_2O , H_2O_2 , $NO_2(N_2O_4)$ and N_2O_5 . As the gas stream entered the double-U trap, these were deposited as a fine white powder immediately above the gel column. The vapour pressures of these substances at $-78^{\circ}C$ were as follows (100, 101):

$$p_{N_2O_5} \ll p_{N_2O_4} = 3.5 \times 10^{-2} \text{ torr}$$

 $p_{\rm H_20_2} \ll p_{\rm H_20}$ (ice) = 5.6 x 10⁻⁴ torr

In an experiment, the partial pressure of ozone above the gel was of the order of 20 torr, so that the ratio $\begin{bmatrix} 0_3 \end{bmatrix}$ / [chemically active impurity] was about 600:1.

(C) Main Apparatus

The flow system, of Pyrex glass, is represented schematically in Fig. 4. The volume V_c was 2.22 liters.

The densities at 25° C of the manometric liquids in M_2 and M_3 were measured with a Christian Becker Chainomatic specific gravity balance. M_2 contained Octoil hydrocarbon fluid of density 0.980_9 g./cc., and M_3 contained silicone cil (Dow Corning # 200 fluid, 10 centistokes) of density 0.929_{0} g./cc. The difference in levels in M_2 was read from a steel rule graduated in 0.5 mm.; that in M_3 from graph paper in 0.05 inch. Both liquids were degassed in vacuo. It was found that the silicone fluid absorbed gases exposed to it, and so the evacuated arm of M_3 was continuously pumped when in use.

The tilting McLeod gauge TM was used only for measuring ultimate pump vacua, since its accuracy in the range 1 - 5 torr varied by 0 - 10%, when compared with H₂SO₄ and silicone oil manometers read with a cathetometer.

All mercury in manometers was covered with a layer of silicone oil or dibutylphthalate to exclude mercury vapour as much as possible from the system. The McLeod gauge, when not in use, was isolated by S₂₂.

GENERAL APPARATUS

s _i :	One-way stopcock
ss _i :	Two-way stopcock
^M 1, ^M 4:	Mercury manometers
^M 2:	Octoil manometer
^M 3:	Silicone oil manometer
C ₁ :	Capillaries with differential manometers
N _i :	Needle valves
v _c :	Known volume
B _l :	Mercury bubbler
^B 2, ^B 3:	Dibutylphthalate bubblers
T _i :	Traps
MC:	Mixing chamber
TM:	Tilting McLeod gauge
HW:	Hot wire
0Z:	Ozonizer
SG:	Silica gel trap
D:	10-liter Dewar flask



Stopcocks in the ozone flow line were lubricated with Kel-F # 90 halocarbon grease (Minnesota Mining and Manufacturing Co.) and all others with Dow Corning High Vacuum Silicone grease. The halocarbon substance was never visually attacked by ozone, but the silicone quickly became "grainy" and lost its lubricating properties.

The needle-values N_1 , N_2 and N_3 were stainless-steel (fine control, W. Edwards and Co.) and N_{\downarrow} was glass-teflon (Fischer-Porter).

Most of the ozone emerging from the reaction tube was destroyed by the hot wire HW. It was a length of B.& S. # 18 nichrome wire in a 25-cm. coil, heated electrically to orange-redness with a Variac. Trap T_{μ} contained silica gel (3-8 mesh) at -78°C to adsorb NO₂ and NO from the gas stream.

The reaction tube, shown in Fig. 5, was 22 mm. I.D. A movable jet for NO was at the gas entrance end. Six equally spaced holes (diameter 0.25 ± 0.03 mm.) were blown on the circumference of the bulb, which moved axially along the tube, aided by glass guides. A movable copper-constantan thermocouple probe, encased in a thin layer of glass, also with glass guides, was at the gas exit end. This probe could be moved along the entire length of the tube and beyond the furnace. Veeco Quick Vacuum Couplings (with rubber 0-rings) were sealed to the glass by Epoxy resin.

The apparatus shown in Fig. 5 was enclosed in a light-tight box of black plastic curtain.

REACTION TUBE AND ASSOCIATED APPARATUS

- PM: 1P21 photomultiplier
- Q: Quartz absorption cell



SCALE, 1:3

(D) Analytical Methods for Gaseous Ozone:

Thorp (32) has compiled a bibliography of more than 240 references on this subject, which may be summarized as follows.

(a) Reaction with Iodide in Neutral Solution:

The extensive literature on this method attests to its popularity and its unsettled nature. The reaction stoichiometry is usually taken to be

 $0_3 + 2I^- + H_2 0 \longrightarrow 0_2 + I_2 + 20H^-$

and the liberated iodine may be titrated with thiosulphate. When large amounts of ozone react, the solution becomes increasingly basic, causing spurious ozone decomposition and hence low ozone determinations. Acid solutions give erroneously high results, and so buffers are sometimes used to They must not, however, favour ozone demaintain pH 7. composition themselves or interfere in the iodometric chemical For greatest precision this method should be processes. checked against more reliable methods (e.g. the pressure change at constant volume for the conversion $0_3 \rightarrow \frac{3}{2} 0_2$) and solution volumes, titration times and temperature should all Also, iodide can be oxidized to iodine by other be uniform. substances, such as nitrogen- and chlorine-oxides.

(b) Catalytic Decomposition Calorimetry:

The heat liberated in the change

 $0_3 \rightarrow \frac{3}{2} 0_2; \Delta H = -34.5 \text{ kcal./mole}$

may be detected with thermocouples when the ozone is decomposed catalytically and adiabatically. The sensitivity of this method would of course depend upon the efficiency of the catalyst, sensitivity of the detecting device, flow of the gas and the extent of adiabatic conditions realized.

(c) Fluorescence and Photometry:

Ozone oxidizes dihydroacridine and the resulting compound fluoresces; the light intensity may be measured and calibrated. Ozone also decolorizes fluorescein in a predictable manner, but in both these cases the action is not specific and the solvent may interfere.

(d) Thermal Conductivity:

The use of a catharometer has been described by Zhitnev (87) for detecting ozone in air or oxygen. The device uses semi-conductor thermoresistors with a thin covering of glass; the peak height from a balancing circuit voltage was a linear function of percentage ozone in the range 0-10%. Its reproducibility depends upon the constancy of catharometer temperature, of bridge current and of the rate of gas flow through the instrument.

(e) Other Chemical Methods:

At various times the reaction of ozone with rubber, aldehydes, arsenite, arsenate, bromide, ferrous ammonium sulphate, nitrite, sulphite, manganite, etc. were tried, but all were less reliable than the iodometric method.

(f) Absorption Spectrophotometry:

The absorption coefficient of gaseous ozone has been determined in the range 1000\AA - 25 microns (32) with particular

attention to the ultraviolet and visible regions. The best work, using $\geqslant 95\%$ ozone, was done by Vigroux (88), Ny and Choong (89), Inn, Tanaka and Watanabe (90, 91), DeMore and Raper (92) and Hearn (93). In the latter two the concentration of ozone present was determined from the pressure change during decomposition; this avoids chemical determinations and gives independent and absolute coefficients. The other authors used the iodometric method.

Thus the use of the Beer-Lambert law allows the most precise and reliable ozone determinations, especially at the pronounced absorption peak near 2550\AA . The only serious drawback to this method would be the presence of other absorbing species in the light path. In the 0_3 -NO system used by the author, this is not important; hence this method was used in the present work.

The ultraviolet absorption cell Q is shown in Figures 5 and 6. It consisted of four flat quartz plates, 29 mm. x 26 mm. x 1.5 mm. with 45° edges so that they could be cemented together with Epoxy resin. The optically polished plates were made from fused, clear SiO₂ (Pursil 453, Quartz et Silice, Paris, France) and each transmitted 97% of radiation at 2537Å. The round ends of the reaction tube were flared to the same square shape of the cell and were connected to it with Epoxy resin. The final inside dimensions were: 23.0 \pm 0.2 mm. (horizontally) and 24.0 \pm 0.2 mm. (vertically).

The light source S shown in Fig. 6 was a small quartz Pen-Ray lamp (low pressure mercury discharge, Black Light

ULTRAVIOLET ABSORPTION CELL FOR OZONE ANALYSIS

- S: Mercury lamp
- C: Collimator
- L: Quartz lens
- Q: Quartz cell
- M: Aluminum front-surface mirrors
- F.S.: Filter solutions
- F: Corning glass filter
- P.M.: 1P28 photomultiplier



Eastern Corp., Model 11/SC-1). Its strongest line was at 2537Å; the next strongest at 4358Å, and the ratio between these two intensities was about 13:1. A pencil of rays about 2 mm. diameter was selected by the collimator C and quartz lens L. The beam passed eight times through the cell; all traversals were co-planar. The total light path was therefore 18.8 ± 0.2 cm. The mirrors M were front-surface evaporated aluminum (V. Avarlaid, McGill University, and Canadian Arsenals Ltd., Toronto). Their reflectivities at 2537Å were measured (as described on p.62) and lay in the range 95 \pm 5%.

The mirrors surrounding the cell were cemented to balsa wood spacers upon a plexiglas platform supported by a layer of polyurethane foam as cushion. The units were held in place on a frame of plexiglas by fine threaded rods and nuts, which afforded the delicate adjustment for reflection angles.

The beam, emerging from the cell, passed through the quartz-windowed cell F.S. filled with two filter solutions (94) to isolate 2537Å radiation. The first was a 2.5 cm. length of 4.2 mg. 1,4-diphenylbutadiene (Matheson, Coleman and Bell) in 250 ml. 2-propanol (boiling range 82.2 - 82.4°C). The second was a 5 cm. length of an aqueous solution of NiSO₄.6H₂O, 240 g./l. and $CoSO_4.7H_2O$, 45 g./l. (C.P. reagents). The beam then passed through the Corning glass filter F (C.S. # 7-54, 1 mm.) into the 1P28 photomultiplier P.M., operated at 900 v.d.c. for greatest signal-to-noise ratio.

The optical transmission of the filter solutions and

glass filter were measured with a Unicam spectrophotometer (Model SP 500), and the results for the important lines of the mercury lamp are given in Table 3.

TABLE 3

TRANSMISSION FRACTIONS OF VARIOUS MEDIA FOR LIGHT AT MERCURY WAVELENGTHS

Wave- length mµ	5 cm. NiSO _L -CoSO _L in water	2.5 cm. diphenyl- butadiene in 2-propanol	Corning filter 7-54	Quartz windows (total)	Total trans- mission
254 313 365 405 436 546 577	0.5 0.86 3.7 x 10-5 10-10 1.6 x 10-5 7.6 x 10-5 1.3 x 10-2	5.8 x 10 ⁻² 0.34 1.0 1.0 1.0 1.0	0.60 0.84 0.78 0.24 4 x 10-2 0 0	0.50 1.0 1.0 1.0 1.0 1.0 1.0	8.7×10^{-3} 9.8 × 10^{-6} 2.4 × 10^{-11} 6.4 × 10^{-7} 0 0

These total transmissions were also verified from time to time with a Beckmann DK spectrophotometer. The ratio of the intensities transmitted at 2537 Å and the next strongest was circa 10^3 . The 1P28 photomultiplier (S-5 response) had negligible sensitivities for wavelengths greater than 7000 Å.

The diphenylbutadiene solution was susceptible to deterioration upon long exposure to ultraviolet light; both solutions were replenished monthly and new stock solutions were made twice yearly.

The filter solutions were placed in the light beam <u>after</u> it had passed through the cell, and it passed through the organic phase first. This was necessary because (a) 2537 Å

radiation caused both quartz and organic solution to fluoresce, causing a spurious photomultiplier current, and (b) this fluorescence was of such a wavelength that the Corning filter transmitted it but the NiSO₄-CoSO₄ solution did not (i.e., it was in the neighbourhood of 4000 Å).

Spectra of the mercury lamp radiation, both with and without filters interposed in the light path were photographed, using a Hilger Quartz Spectrograph Model E518, quartz optics and Ilford N40 plates. The table which follows gives the exposure details for the spectra seen in Fig. 7. In all cases the setting of the diaphragm of the spectrograph was 5.

TABLE 4

Plate	Spect- rum	Physical arrangement	Slit width mm.	Collimator setting	Exposure time, minutes
I I	(a) (b)	lamp only lamp only	0.075	9.0 7.5	0.5
II II	(a) (b)	lamp only lamp plus inorganic selt solution	0.015 0.015	7.0 7.0	0.5 4
II	(c)	lamp plus inorganic salt solution plus diphenylbutadiene solution	0.015	7.0	20

EXPOSURE DETAILS FOR MERCURY LAMP SPECTRA

The spectra confirm in a qualitative manner the quantitative transmission measurements made with the Unicam spectrophotometer as given in Table 3.

The output current of the 1P28 (ca. 10^{-8} ampere) was

SPECTRA OF THE PEN-RAY MERCURY LAMP







led into a Model Al200R Ratio-Linear Photometer (Analytical Instruments, Inc.). It was used as a simple one-channel current amplifier, and the pertinent circuit is shown in Fig. 8. The output of this amplifier was 0 - 50 millivolts and was displayed on a Leeds and Northrup Speedomax Azar Recorder, Model H.

For greatest precision in determining ozone concentration, it was necessary to know how much extraneous noise this amplifier introduced. To determine this a test voltage of -50 millivolts ± 0.02% from a dry cell and dropping resistors was substituted for the photomultiplier current at the point indicated in Fig. 8. The output at the recorder terminals was measured with a manual potentiometer (Tinsley, Model 3184D). It had an average deviation of 0.13%, which was considered good for this type of amplifier.

(E) Measurement of Chemiluminescence Intensity:

This was accomplished with the 1P21 photomultiplier PM, Fig. 5, whose position was not changed during the course of all experiments. Its photocathode was 6 cm. from the reaction tube surface, and a 1.5 mm. collimating slit was made from the edges of two opaque microscope slides cemented to the housing.

This photomultiplier was operated near 1180 v.d.c. from a battery pack. The precise value of this voltage was unimportant, but it was necessary that the same value be used for every experiment. To this end, the circuit in Fig. 9 was used. In practice, R_2 and R_3 (fine and coarse controls

CURRENT-AMPLIFIER SECTION OF THE RATIO-LINEAR PHOTOMETER

Range resistor values:

R _l :	50K ± 1%
R2:	166K ± 3.6%
R ₃ :	500K ± 1%
R ₄ :	1.67M ± 1.8%
^R 5 [:]	5M ± 1%
R ₆ :	16.6 M± 5%
R ₇ :	50M ± 5%



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SUPPLY VOLTAGE CIRCUIT FOR PHOTOMULTIPLIERS

 R_1 :1.1K wire-would R_2 :0 - 500K continuous R_3 :0 - 10M continuous R_4 :1M \pm 5%, carbonA:Photomultiplier anodePC:Photomultiplier photocathode



respectively) were adjusted until the stable voltage across R_1 was 0.13000 volt, as measured with a manual potentiometer.

The battery voltage, upon the closing of the DPST switch, was allowed to stabilize for ten minutes, after which its variation was less than 1 part in 10^4 during the time of an experiment.

(F) Calibration of Inert Gas Flowmeter:

The quencher gas flowmeter is shown as N_3 and C_3 in Fig. 4. Before these and in series with them was placed the system shown in Fig. 10. It consisted of an inverted burette through which the gas flowed, and a trap after it. The blowoff assured that the gas was at the measured atmospheric pressure. As the gas moved up the burette, it carried a scap bubble film with it, and the rate at which it swept out the known volume was measured with a stopwatch. The trap, cooled with liquid air, dry-ice/acetone mixture or CCl₁ slush (-23°C) according to the gas passing through, removed water vapour before it entered capillary C3. The differential pressure drop Δh across the capillary was also noted. The flowrate was changed by adjustment of N₂.

Under steady flow conditions, the mole flow was the same at all points in the flow system. The time-differentiated form of the ideal gas law is

$$P \frac{dV}{dt} = \frac{dn}{dt} RT = fRT$$

where f is the mole flow. P is the partial pressure of inert

MEASUREMENT OF GAS FLOW FOR FLOWMETER CALIBRATION



gas in the burette, and if ΔV is the volume swept out in time Δt , the mole flow may be calculated from

$$f = \frac{P}{RT} \cdot \frac{\Delta V}{\Delta t}$$

A plot of f (micromoles/sec.) versus Δh (cm.Hg) could be made, which was almost always linear. In some cases this plot had a slight curvature. Instead, the data could be re-plotted as a log-log relation, which would then be more precisely linear, but less sensitive.

It is interesting to note that the Poiseuille law predicts that the relation is not linear, but that f is proportional to $(\Delta h)^m$, where m should be about 2, in the conditions realized in this work. The fact that m was more nearly unity indicated that Poiseuille's law could not be applied in the actual conditions used (e.g., the capillary was "drawn out", and hence the radius was not constant).

(G) Experimental Check of Ozone Extinction Coefficient:

(1) THE "GIVEN" VALUE:

The Beer-Lambert law, in the form used for gases,

is

$$\log_{10} (I_0/I_t) = A = \langle \langle \rangle x$$

where

- I_o is the transmitted light intensity with no (or non-absorbing) gases in the light path
- It is the transmitted light intensity with ozone in the light path
- α_{λ} is the extinction coefficient in cm.⁻¹ for ozone at wavelength λ .

x is the light path in cm. through the gas, reduced to S.T.P.

If the pressure of ozone is P atm., its temperature $T^{O}K$ and the actual light path 1 cm., then

$$A = \alpha_{\lambda} \left\{ \begin{array}{c} P & x & \frac{273}{T} \end{array} \right\}$$
$$= \alpha_{\lambda} \left\{ \begin{array}{c} RT \left[03 \right] \\ N_{0} \end{array} \right\} \times \begin{array}{c} \frac{273}{T} \end{array} \right\}$$

where

R is the gas constant

 N_0 is Avogadro's number $\begin{bmatrix} 0\\ 3 \end{bmatrix}$ is in molecular units

Rearranging, we have

$$A = \left\{ \frac{d_{aR} \times 273}{N_{o}} \right\} \begin{bmatrix} 0 \\ 3 \end{bmatrix} 1$$

where the term in brackets is the extinction coefficient in molecular units. Substituting in this equation the values

we obtain

 $A = 4.95 \times 10^{-18} [0_3] 1$

for $\begin{bmatrix} 0_3 \end{bmatrix}$ in molecules/cc.

(ii) THE "EXPERIMENTAL" VALUE:

First the ozone content of the mixture from the ozonizer was determined iodometrically from five consecutive samples, for constant conditions of voltage and flowrate in the ozonizer. Each sample, exactly 300 bubbles, was passed into a 5% KI solution, buffered according to Boelter, Putnam and Lash (96). Only one bubble tower was used, as preliminary experiments with two towers in series showed that more than 99.8% of the ozone was absorbed in the first. The liberated iodine was titrated immediately with $0.005M \operatorname{Na}_2 \operatorname{S}_2 \operatorname{O}_3$, with Thyodene as indicator. The thiosulphate solution had previously been standardized against KIO₃, according to Kolthoff and Sandell, p. 594 (95).

The pertinent chemical equations are

⁰ 3 one mole	+	2KI	+	H ₂ 0 →	2KOH +	°2	+ I ₂ cne mole
2Na2 two mole	52 ⁰ 2	3 +	I2 one mole	>	^{Na} 2 ^S 4 ⁰ 6	+	2NaI

The number of moles 0_2 represented by 300 bubbles was determined by displacement of water. The data are as follows: Number of bubbles for 100 cc.: 411 Atmospheric pressure: 753 torr Temperature of water: 23°C = 296°K Vapour pressure of water: 22 torr The required quantity, n_{0_2} , is obtained from

$$n_{0_{2}} = \frac{PV}{RT}$$

$$= \frac{(753 - 22)(100)}{(62,360)(296)} \cdot \frac{300}{411}$$

$$= 2.89 \times 10^{-3}$$

If the titration required v ml. thic sulphate, this corresponds to $n_{0,3}$ moles of ozone given by

$$n_{0_3} = 2.5v \times 10^{-6}$$

The mole percent. 0_3 was then given by $n_{0_3} \times 100/n_{0_2}$ and the data are given in Table 5. The average 0_3 content was found to be 2.91 mole %.

TABLE 5

ICDOMETRIC ANALYSES OF CZONIZER MIXTURES

FROM THE SAME STREAM UNDER CONSTANT CONDITIONS

Analysis number	Milliliters thiosulphate for titration	Moles 03 in sample	Mole % 03 in sample
1 2 3 4 5	34.5 31.8 35.4 30.6 35.9	$\begin{array}{r} 8.63 \times 10^{-5} \\ 7.95 \times 10^{-5} \\ 8.84 \times 10^{-5} \\ 7.65 \times 10^{-5} \\ 8.98 \times 10^{-5} \end{array}$	2.99 2.75 3.06 2.65 3.11
		Avera	age: 2.91

OF FLOWRATE AND VOLTAGE

Five consecutive ozonizer samples of the same output at different pressures were then analyzed optically by bleeding the gas into the absorption cell and noting I_0 , I_t and the total pressure. The partial pressure of ozone, P_{0_3} , was calculated from its mole fraction as found previously, and was converted to concentration units as in the previous section. The data are in Table 6.

TABLE 6

OPTICAL ANALYSES OF OZONIZER MIXTURES

FROM THE SAME STREAM UNDER CONDITIONS AS

PREVIOUSLY, OF DIFFERENT TOTAL PRESSURES

Room temperature: 23°C

Analysis number	3 I _O Arbi uni	It tary ts	$\left(\frac{I_{o}}{I_{t}}\right)$	log (I _o /I _t)	Total pressure P _{tot} , torr	Partial pressure of ozone, PO3, torr	[03] molecules/ x 10 ⁻¹⁵
12345	96.7	17.2	5.63	0.751	8.97	0.261	8.53
	95.0	58.9	1.61	0.207	2.44	0.0711	2.32
	94.3	75.5	1.25	0.0970	1.26	0.0366	1.20
	94.5	22.1	4.28	0.631	6.90	0.201	6.56
	95.1	45.7	2.08	0.318	3.79	0.110	3.59

In Fig. 11 is plotted A (obtained from I_0/I_t) versus $\begin{bmatrix} 0_3 \end{bmatrix}$ (obtained from iodometric calibration). The slope (by the method of least squares) is 9.22 x 10^{-17} cc./molecule, so that the extinction coefficient is 9.22 x $10^{-17}/18.8$ or 4.91 x 10^{-18} cc./molecule/cm. By the same method the intercept is -0.005. These values are to be compared with the literature values 4.95×10^{-18} cc./molecule/cm. and zero. Such close agreement is partly fortuitous, considering the uncertainties in iodometric analysis and ozonizer output stability.

(H) Measurement of Reflectivity of Aluminum Mirrors:

In Fig. 12 is seen a sketch of the apparatus used. The filter F, C.S. # 7-54, 5 mm., reduced the intensity of the 2537 Å radiation selected by the filter solutions SNS.

In (a), without the mirror, the phototube was placed

TEST FOR THE BEER-LAMBERT LAW FOR OZONE



MEASUREMENT OF MIRROR REFLECTIVITIES

L:	Mercury lamp
SNS:	Filter solutions
QL:	Quartz lens
F:	Glass filter
PC:	Photocathode
M:	Mirror



ł

so that the beam was focussed on its photocathode. The measured signal was I_a , representing the original unreflected lamp intensity.

In (b), the mirror was interposed in the light beam and the phototube was again placed at the correct focal distance. The signal was I_b , representing the reflected intensity.

For all six mirrors used, I_b/I_a was 0.95 ± 0.05. During the time of measurement, the observed variation in the mercury lamp intensity was ± 1%. The reflectivity of each mirror was essentially the same over its entire area.

(I) Furnace Design:

A furnace, of 1000 watts maximum power, was constructed for following the reaction up to 300°C. It is shown diagrammatically assembled in Fig. 13, dissembled in Figs. 14 and 15.

The entire furnace consisted of aluminum plates, through which the center hole (diameter 27 mm.) was drilled longitudinally. Layers 1, 3, 4, 5 and 7 and bases of layers 2 and 6 were $\frac{1}{2}$ " thick. The frames of layers 2 and 6 were made from $\frac{3}{8}$ " aluminum strip to form the heater troughs.

In order to heat the reacting gases evenly, the elements were made in three sections, Fig. 16. All consisted of B. & S. # 24 nichrome wire, 1.63n/ft. Sections A and C both contained 5 feet of wire, section B, 10 feet. The wire was insulated from the aluminum by and sandwiched between thin asbestos sheet wetted for snug fit. The leads were drawn through double-hole porcelain insulators placed in the frame. The units were dried overnight at $105^{\circ}C$.

THE FURNACE LAYERS ASSEMBLED


FURNACE LAYERS 1, 2, 6 and 7



FURNACE LAYERS 3, 4 and 5





HEATER ARRANGEMENT



The pairs of sections A, B and C of layers 2 and 6 were joined in series, and each pair was supplied from a separate Variac.

When the plates were bolted together with the reaction tube inside, they were completely surrounded by four layers of $\frac{1}{4}$ " asbestos board.

(J) Temperature Profiles

The temperature of the heated gases in the reaction tube could be measured directly with the movable thermocouple probe. A typical temperature profile, for an air flowrate of approximately 350 micromoles/sec. is seen in Fig. 17. The resistance of each heater was known, and the calculated wattages for this profile were:

> Section A: 158 Section B: 70 Section C: 197

The shape of the profile was independent of the helium carrier/ quencher pressure in the range 2 - 20 torr. For the distance 3 - 33 cm. in the furnace, the temperature was $T^{OK} \pm 2.5\%$ or better, for all temperatures used in the range T = 373 to 573.

(K) <u>Nitric Oxide Flow Measurement:</u>

The flowrate of NO was obtained for each experiment by the P-V-T method, using a "two-bulb" technique. The components concerned, in Fig. 4, were V_c , S_5 , S_6 , M_2 and the 24-liter storage volume. During reaction S_5 and S_6 were open, and both volumes were used as a supply reservoir (at pressures

A TYPICAL TEMPERATURE PROFILE



near one atmosphere).

For finding the flowrate, S_5 was closed and the pressure in the known volume V_c diminished with time, as shown by M_2 . When a measurable pressure difference was attained, S_6 was closed and S_5 opened to provide a continuous flow for reaction. If a pressure difference Δp appeared in time Δt , the flowrate was

$$f_{\rm NO} = \frac{dn}{dt} = \frac{\Delta p}{\Delta t} \cdot \frac{V_c}{RT}$$

where T is ambient temperature.

During the time Δt , the flowrate decreased somewhat because the supply pressure in V_c decreased. The value of Δp was about 5 torr, which, in a reservoir at 700 torr, constituted less than 1% error.

(L) <u>Procedure for a Typical Experiment:</u> (with reference to Fig. 4)

The mercury lamp (on a Sola Constant-Voltage transformer) and the photomultiplier battery voltage were turned on and allowed to stabilize.

(1) Preparation of the gel column for use:

The ozonizer and gas flow were turned off, and the gel trap SG was evacuated with the secondary pump through S_{18} . An auxiliary hot wire destroyed ozone before the pump. The gel was flushed four times with carrier gas through SS_4 and SS_5 , alternately being filled to 70 cm.Hg and evacuated to 7 cm.Hg as measured on M_h . (ii) The gases used:

The quencher gas and its flowrate (which constituted almost the entire flow) were chosen with the intention of finding its relative quenching efficiency for $NO_2^{\ddot{v}}$. Its flow was started through the system S_{10} to S_{16} , and was read off from its flowmeter calibration.

The carrier gas for the ozone would generally be identical to the quencher gas, except SF_6 , CO_2 and N_2O , which would be more or less completely adsorbed on the silica gel column. In these cases, helium was used as carrier gas, because it was adsorbed to a limited extent only, and its quenching efficiency was small, compared with SF_6 , CO_2 and N_2O .

The carrier gas flow was started through S_{13} to S_{17} . The main hot wire HW was turned on (to decompose ozone before the pump) and trap T_4 was brought to -78°C (to trap nitrogen oxides before the pump during reaction). The ozone/carrier flow was allowed to stabilize for at least 45 minutes. The flow of ozone was controlled by N_4 and C_4 , the carrier flow by C_2 and N_2 .

(iii) Measurement of initial ozone concentration:

In this optical measurement, the value of I_0 was obtained by by-passing the ozone/carrier flow through S_{20} , leaving only quencher gas (non-absorbing) in the light beam. Three or four consecutive measurements were taken. The total pressure was measured with M_3 , and the gas temperature at the absorption cell was measured with the thermocouple probe. (iv) Measurement of nitric oxide flow:

NO was then introduced through S_7 . After its flow had become stable, as indicated by the flowmeter C_1 , the flowrate was determined as described on p. 76.

(v) Measurement of ozone concentration as a function of time:

These data would yield a value for the rate constant of the 0_3 -NO reaction. I₀ and I_t values were found for different reaction distances (i.e., different NO inlet positions). Three or four determinations were taken with the inlet at each position.

(vi) Measurement of emission intensity as a function of time:

The emission intensity was next measured as a function of reaction distance in a similar manner. Two readings were taken at each position and they agreed within $\pm 5\%$.

(vii) Measurement of reaction temperature:

The temperature profile in the reaction tube was next determined. In room temperature experiments, the thermocouple was placed at the absorption cell, and the temperature was taken as a function of reaction distance. In experiments using the furnace, the NO inlet was placed at the beginning of the "plateau" temperature region, and readings were taken downstream therefrom.

(viii) "Check" measurements after cessation of reaction:

The NO flow was stopped and initial ozone concentration redetermined. It was always within $\pm 3\%$ of the starting value.

The 1P21 dark current (no reaction) was determined as a function of NO jet position. This was necessary because (i) part of the NO entry tubing was outside and light-tight enclosure and transmitted light longitudinally; (ii) since the emission lay beyond 6000 Å where 1P21 was rather insensitive, maximum applied voltage was used, making it very sensitive to stray light.

(ix) Preparation for next run:

The ozone supply was used for as many as four consecutive runs. During this time, the silica gel column at the carrier entrance end became bleached of its dark-blue colour, the remainder staying as it was. The NO_2/N_2O_3 mixture in T_4 was desorbed in vacuo at $100^{\circ}C$, the ozonizer started and the gel column was re-saturated overnight.

(A) The Experimental Data:

The description of the quantity is followed by its symbol.

- (i) Before Reaction:
 - (a) Initial ozone concentration, 0_3 oo
 - (b) Gas temperature of this measurement, T_{00}
 - (c) Flowrate of carrier gas by the soap film method, f_c
 - (d) Flowrate of quencher gas from calibrated flowmeter, f_a
 - (e) Room temperature, T_A
 - (f) Total pressure (03, carrier, quencher), $P_{\rm qr}$
- (ii) During Reaction:
 - (a) Ozone concentrations at various reaction distances, $\begin{bmatrix} 0 \\ 3 \end{bmatrix}$ t
 - (b) Emission intensities (with photometer range number) at various reaction distances, I_{Ma}
 - (c) For initial nitric oxide flowrate, f_{NO} : Δp and Δt
 - (d) Total pressure (03, NO, products, quencher, carrier), P¹_m
 - (e) Temperature of gas at ozone measurement, T
 - (f) Reaction temperature at various reaction distances
- NOTE: In room temperature experiments, items (e) and (f) were identical.
 - (iii) After Reaction:
 - (a) Dark current of 1P21 photomultiplier at the NO jet positions used, I_{dc}

03

(b) Check on initial ozone concentration,

(B) <u>Calculation of concentrations from flowrates</u>:

Example, Experiment 45: In this run, argon was both carrier and quencher. $T_A = 22^{\circ}C = 295^{\circ}K$ $f_C = 155 \text{ micromoles/sec.} (1 \text{ micromole} = 1 \times 10^{-6} \text{ mole})$ $f_q = 1390 \text{ micromoles/sec.}$ $T_{00} = 23^{\circ}C = 296^{\circ}K$ $P_T = 12.52-2.73 = 9.79 \text{ inches silicone oil}$ $P_T = 12.54-2.72 = 9.82 \text{ inches silicone oil}$ For f_{N0} : $\Delta p = 10.7_1-3.7_2 = 6.99 \text{ cm. Octoil}$ $\Delta t = 60 \text{ seconds}$ NO flowrate: $f_{NO} = \frac{V_C}{RT_A} \cdot \frac{\Delta p}{\Delta t}$ $= \frac{2.22}{(62.4)(295)} \times \frac{(6.99)(0.98)}{(60)(13.5)}$

= 10.2 micromoles/sec.

Initial ozone concentration:

$$\begin{bmatrix} 0_3 \end{bmatrix}_{00} = \log_{10}(I_0/I_t) \times 10.75 \times 10^{15}$$

= log (94.7/46.9) x 10.75 x 10¹⁵
= 0.3054 x 10.75 x 10¹⁵
= 3.29 x 10¹⁵ molecules/cc.

Confirmatory determinations of $\begin{bmatrix} 0 \\ 3 \end{bmatrix}_{oc}$ yielded, in molecules/cc. x 10^{-15} : 3.18, 3.26, 3.15, 3.17, 3.17; average, 3.20 x 10^{15} molecules/cc.

Total pressure expressed in molecular units:

$$\left\{ \begin{array}{l} \mathbf{P}_{\mathrm{T}} \right\} \begin{array}{l} \frac{N_{\mathrm{O}}}{\mathrm{RT}_{\mathrm{OO}}} &= \left\{ \frac{(9.79)(0.92)(25.4)}{13.5} \right\} \begin{array}{l} \frac{6.02 \times 10^{23}}{(62,400)(296)} \\ &= 559 \times 10^{15} \text{ molecules/cc.} \end{array}$$

Initial flowrate of ozone, f_0 , may be calculated from the time-differentiated form of Dalton's law, viz:-

$$\frac{\mathbf{f}_{03}}{\mathbf{f}_{03} + \mathbf{f}_{c} + \mathbf{f}_{q}} = \frac{\begin{bmatrix} 0_{3} \end{bmatrix}_{00}}{\begin{bmatrix} 0_{3} + \text{ carrier + quencher} \end{bmatrix}}$$

In this experiment, argon is both carrier and quencher, so that

$$f_{0_3} = \frac{[0_3]_{00} f_{argon}}{[0_3 + argon] - [0_3]_{00}}$$
$$= \frac{(3.20 \times 10^{15})(1390 + 155)}{(559 - 3) \times 10^{15}}$$
$$= 8.90 \text{ micromoles/sec.}$$

In all experiments, the heat of reaction was such as to raise the reaction temperature above ambient. This difference amounted to as much as 20° C. For experiment 45 the data were:

TABLE 7

Variation of Reacting Gas Temperature with Reaction Distance

Position	Reaction Distance cm.	Thermoc'ple E.M.F. mv.	Temperature T _o ,°C
x1	2	1.94	48
x5	13	1.88	47
x8	32	1.40	35

The reaction was 60-70% finished at 13 cm., and so the average temperature over this interval was taken as the "true" reaction temperature, T_R , which was $321^{\circ}K$ in this case. The ozone concentrations measured directly during reaction correspond of course to T_R . Initial ozone and nitric oxide, as well as inert gas concentrations were evaluated also according to T_R .

Now the mole flowrate is determined solely by flowmeters and is independent of reaction temperature. The total molecular concentration at T_R may be calculated from P_T^1 as before:

$$\begin{array}{rcl} \texttt{all species} &=& \underline{(9.82)(0.92)(25.4)(6.02 \times 10^{23})} \\ && (13.5)(62,400)(321) \end{array} \\ &=& 519 \times 10^{15} \text{ molecules/cc.} \end{array}$$

The total flowrate, $\mathbf{f}_{\boldsymbol{\tau}},$ in reaction is

	f ₀₃ +	f_{NO}	+	f _{argon}
=	8.90 +	10.2	+	15 45
=	15 64 mi	cromole	s/s	ec.

This relation holds exactly because in the reaction

 $0_3 + N0 \longrightarrow N0_2 + 0_2$

the number of moles in invariant. Side reactions, changing the total number of moles, are relatively insignificant in conditions realized in this work.

The concentrations at ${\tt T}_R$ follow as before:

$$\begin{bmatrix} 0_{3} \\ 0_{3} \end{bmatrix}_{0} = \frac{f_{0}_{3}}{f_{T}} \cdot \begin{bmatrix} \text{all species} \end{bmatrix}$$
$$= \frac{8.90}{1564} (519 \times 10^{15})$$
$$= 2.96 \times 10^{15} \text{ molecules/cc.}$$

Similarly

$$[NO]_{O} = 3.38 \times 10^{15} \text{ molecules/cc.}$$

$$[Ar] = 513 \times 10^{15} \text{ molecules/cc.}$$

(C) Calculation of Reaction Time:

The gas flow in reaction is assumed to be laminar, i.e., there is no longitudinal mixing. The ideal gas law for flowing gas in reaction is

$$\frac{dV}{dt} = \frac{f_{T}RT_{R}}{P_{T}} = A \frac{dx}{dt}$$

where A is the internal cross-sectional area of the reaction tube and dx/dt is the linear gas velocity. The internal diameter was 22 mm., so that the area was $(3.1416)(2.2)^2/4$ or 3.8 cm.²

Hence

$$\frac{dx}{dt} = \frac{(1564 \times 10^{-6})(62,400)(321)}{(3.8)(17.2)}$$

= 480 cm./sec.

where P_T^{i} is 17.2 torr. The reciprocal of this number is the time equivalent of distance, i.e., 2.08 milliseconds/cm.

- (D) Integrated Rate Expressions:
 - (i) Non-stoichiometric conditions:

The rate of ozone disappearance is given by

$$-\frac{d[0_3]}{dt} = k_{\mu}^{\text{tot}} [0_3] [N0]$$

where k_{4}^{tot} is the overall rate constant, referring to the production of both excited and unexcited NO₂. The rate of

disappearance of ozone by

 $0_3 + N0_2 \longrightarrow N0_3 + 0_2$

is negligible under experimental conditions.

Let

z = concentration of ozone which has reacted $A_0 = \begin{bmatrix} 0_3 \end{bmatrix}_0$ and $A = \begin{bmatrix} 0_3 \end{bmatrix}$ $B_0 = \begin{bmatrix} N0 \end{bmatrix}_0$ and $B = \begin{bmatrix} N0 \end{bmatrix}$

Then

$$-\frac{dA}{dt} = -\frac{d(A-z)}{dt} = \frac{dz}{dt} = k_{\downarrow}^{tot} (A_0-z) (B_0-z) (VI)$$

which when rearranged and integrated is

$$\ln (B/A) = (B_0 - A_0) k_{4}^{tot} t + \ln(B_0/A_0)$$

or $\log(B/A) = 0.434(B_0 - A_0) k_{4}^{tot} t + \log(B_0/A_0)$

The requisite data for Experiment 45 are given on page 189. Since the reaction stoichiometry is 1:1

 $B = B_0 - (A_0 - A)$

Fig. 18 shows a plot of log(B/A) vs. t, and the slope S is given by

$$S = 3.48 \text{ sec.}^{-1} = 0.434(B_0 - A_0)k_{4}^{\text{tot}}$$

$$\cdot \cdot k_{4}^{\text{tot}} = \frac{S}{0.434(B_0 - A_0)} = \frac{3.48}{(0.434)(0.42 \times 10^{15})}$$

$$= 1.9 \times 10^{14} \text{ cc./molecule/sec.}$$

A TYPICAL SECOND-ORDER RATE PLOT

(Non-stoichiometric conditions)



(ii) Near-Stoichiometric conditions:

When A_0 is very close to B_0 , the quantity B/Ahardly changes with time, and the % uncertainty in $(B_0 - A_0)$ becomes very large. Hence it is better to proceed as follows (from reference 29):

Put $\Delta = (B_0 - A_0)$ $\therefore B = B_0 - (A_0 - A) = A + (B_0 - A_0) = A + \Delta$

The rate expression (VI) then becomes, upon substitution

$$-\frac{dA}{dt} = k_{\downarrow}^{tot}A(A + \Delta) \qquad (VII)$$

If we substitute in (VII) the relation A' = A + $\Delta/2$, we obtain

$$-\frac{dA'}{dt} = k_{4}^{\text{tot}} \left\{ A' + \Delta/2 \right\} \left\{ A' - \Delta/2 \right\}$$
$$= k_{4}^{\text{tot}} \left\{ (A')^{2} - \Delta^{2}/4 \right\} = k^{\text{tot}} (A')^{2} \left\{ 1 - (\Delta/2A')^{2} \right\}$$
(VIII)

In Experiment 35, Δ was 0.60 x 10¹⁵ molecules/cc. The term in brackets in equation (VIII) was initially 0.99 and

0.95 at two-thirds reaction; it may be replaced by its "constant" average value

$$1 - \frac{\Delta^2}{4A_0^{\prime}A_f^{\prime}}$$

and the equation may be integrated to give

$$1/A' - 1/A'_{o} = k_{\mu}^{tot}t \left\{ 1 - \Delta^2/\mu A'_{o}A'_{f} \right\}$$

Fig. 19 shows a plot of 1/A' vs. t. The slope is

$$S = 1.06 \times 10^{-14} \text{ cc./molecule/sec.}$$

$$\therefore k_{l_{4}}^{\text{tot}} = \frac{S}{1 - \frac{\Delta^{2}}{l_{4}A_{o}^{\dagger}A_{f}^{\dagger}}} = \frac{1.06 \times 10^{-14}}{1 - \frac{(0.60)^{2}(10.l_{4})(2.81)10^{-2}}{l_{4}}}$$
$$= \frac{1.06 \times 10^{-14}}{0.07} = 1.1 \times 10^{-14} \text{ cc/molecule/sec.}$$

The expression $\left(1 - \Delta^2 / 4A_0^{\dagger}A_f^{\dagger}\right)^{-1}$ is here called " Δ -correction".

(E) Confirmation of Reaction Order:

0.97

The best methods of determining reaction order require that the initial reactant concentrations be varied In the present work the speed of self-heating of widely. the reaction, and measured concentration uncertainties made this impractical.

If, however, the reactants are present in stoichiometric concentrations, the over-all order may be found as follows (after Van't Hoff). The rate law

$$-\frac{dA}{dt} = k_{l_{\downarrow}}^{tot} A^{X}B^{y}$$

reduces to

$$-\frac{dA}{dt} = k_{\downarrow}^{tot} A^{x + y}$$

and so

$$\log(-dA/dt) = \log k_{4}^{tot} + (x + y)\log A$$

Fig. 20 shows the ozone concentration profile for Experiment 51 in which A_0/B_0 was 1.01; tangents to the curve were drawn and Table 8 shows the pertinent variables, which

A TYPICAL SECOND-ORDER RATE PLOT

(Near-stoichiometric conditions)



A TYPICAL OZONE-DISAPPEARANCE CURVE



TABLE 8

THE OVERALL REACTION ORDER BY THE METHOD OF VAN'T HOFF

Reaction time t, sec. $x \ 10^{+3}$	0	10	30	60
Uzone concentration A molecules/cc.x 10^{-15}	3.52	2.10	1.25	0.70
-dA/dt molecules/cc./sec. x 10 ¹⁰	19	6.6	3.1	1.0
$\log (-dA/dt)$	17.28	16.82	16.50	16.01

(F) Mechanism for chemiluminescence:

The proposed mechanism for the chemiluminescence is given on page 6 and is as follows:

$$NO_{2}^{*} \longrightarrow NO_{2} + h\nu \qquad (2)$$
$$NO_{2}^{*} + M \longrightarrow NO_{2} + M \qquad (3)$$

The resulting kinetic expression, following the example on page 3 is

$$I = \frac{k_2 k_{\perp}^{*} [0_3] [NO]}{k_3 [M]} = I_{sp} \frac{[0_3] [NO]}{[M]}$$

where I_{sp} is the "specific intensity".

THE OVERALL REACTION ORDER DETERMINED BY THE METHOD OF VAN'T HOFF

A: Ozone concentration, molecules/cc. slope = dA/dt: Rate of reaction, molecules/cc./sec.



Upon rearrangement, this is

$$\frac{[v_3][NO]}{I} = \frac{k_3[M]}{k_2 k_1^{T}}$$
(IX)

so that, <u>in a single experiment</u>, the quantity on the L.H.S. should be invariant with reaction time (the nature and concentration of M do not change).

In practice, the intensity as measured, $I_{\mu a}$, contained a dark current I_{dc} , so that the corrected intensity was

$$I_c = I_{\mu a} - I_{dc}$$

The I_c values were normalized to photometer range # 2 (Fig. 8) to give values of I_r. Table 9 shows the derivation of I_r for experiment 35.

TABLE 9

CALCULATION OF Ir VALUES FROM EXPERIMENTAL DATA

FOR EXPERIMENT 35					
Reaction time, t sec. x 10 ³	I _{µa} (range) Arb:	I _{dc} itrary	I _c units,	I.U.	
4.44 8.88 13.3 20.0 28.8 37.7 53.3 71.0	101 (2) 70 (2) 142 (3) 96 (3) 66 (3) 142 (4) 95 (4) 68 (4)	6 4 7 6 21 20 18	95 66 135 89 60 121 75 50	95 66 45 20 12 7.5 5.0	

For convenience, the quantity $\begin{bmatrix} 0_3 \end{bmatrix} \begin{bmatrix} NO \end{bmatrix} / I_r$ will be designated hereafter by Φ . In Fig. 22 the Φ -values for

VARIATION OF **\$** WITH REACTION TIME IN EXPERIMENT 35

 $\mathbf{\Phi}: \qquad (\text{molecules/cc.})^2/\text{I.U. x } 10^{-28}$



Experiment 35 are plotted versus reaction time. This increase of $\mathbf{\Phi}$ with reaction time is not totally accounted for by experimental uncertainty, and this behaviour appeared in almost all runs, irrespective of the nature and concentration of M.

This indicated that, in the R.H.S. of Equation (IX), any combination of the following changes may be taking place as reaction proceeds: k_3 increasing, [M] increasing, k_2 decreasing, $k_{\downarrow}^{\#}$ decreasing. In the present work, the pertinent changes were:

- (a) temperature of reaction decreased somewhat during reaction
- (b) $\rm O_3$ and NO disappeared with simultaneous appearance of $\rm NO_2$ and $\rm O_2$

Since reaction (2) is a radiative step, and reaction (3) an energy transfer, their activation energies would be small; that for (μ^*) , the formation of an energy-rich molecule, would be relatively large. The activation energy for the overall 03-NC reaction is circa 2.5 kcal./mole; since the activated complex may be the same in this process as in reaction (μ^*) , they may be expected to be of the same order of magnitude. The decrease of k_{μ}^* as reaction proceeds might account for some of the Φ -increase.

The R.H.S. of equation (IX) can be written, for Experiment 35, as

$$\frac{k_{3,(He)}}{k_{2}k_{4}^{2}} \left\{ He \right\} + \alpha \left[0_{2} \right] + \beta \left[NO_{2} \right] + \delta \left[NO_{3} \right] \right\} (X)$$
Now α , λ and δ would not be expected to be very different
among themselves, and since helium was in large excess, the $O_{2,2}$

 O_3 and NO terms would not substantially change the value of the expression. However, since NO_2^{\times} is being quenched, β might very well be relatively large, so that increase in $[NO_2]$ during reaction would significantly affect the expression.

Another way of checking this explanation would be to investigate the dependence of Φ upon concentration of inert gas M. If the last four terms in the expression for Φ in (X) were small relative to the first term in brackets, then one would expect a linear plot between Φ and M. However, linear plots were not obtained and in fact, depended upon the reaction time "t". This is to be expected if the β [NO₂] term made a significant contribution. It is possible, however, to compare experiments with different values of M at reaction times which correspond to the same amount of NO₂ in each experiment. This can be done as follows:

Since $[NO_2] = [O_3]_0 - [O_3]$, its value must be large enough so that the uncertainties in $[O_3]_0$ and $[O_3]$ do not introduce prohibitive error. For example, let us consider the runs with helium as quencher (Experiments 35 - 39). For Experiment 35, the value 1.50 x 10^{15} molecules/cc. for $[NO_2]$ would appear at 13.3 milliseconds, i.e., $[O_3]_0 - [O_3] =$ $(3.26 - 1.77) \times 10^{15} = 1.49 \times 10^{15}$ molecules/cc. The corresponding \oint -value at 13.3 milliseconds may be read off from a plot such as Fig. 22. Its value is 8.8 x 10^{28} (molecules/cc.)²/I.U. and is entered in Table 10.

In this way, the Φ -values for a series of runs with the same inert gas were all evaluated at the same $[NO_2]$. Table 10 shows the Φ -data and the relative quenching efficiencies for
TABLE 10

₫ DATA FOR VARIOUS GASES AT ROOM TEMPERATURE

 P_T :Total pressure, torrinert gas:molecules/cc. x 10⁻¹⁵ Φ :(molecules/cc.)²/I.U. x 10⁻²⁸"slope" from Figure 23, molecules/cc./I.U. x 10⁻¹¹Rel. eff:Relative quenching efficiency (N₂ = 1)

Expt. No.	Р¦	[N20]	₫
56 57 58 59	19.2 2.77 8.80 13.8	534 27.8 216 374	39.4 2.2 8.6 24.0
Slope:	7.45	Rel. eff	1.4
Reference	NO2 concentration:	1.70 x 1015 molec	ules/cc.

NITROUS OXIDE AS QUENCHER

SULPHUR HEXAFLUGRIDE AS QUENCHER

Expt. No.	P! T	SF6	₫
78 79 80 81	2.43 7.27 12.7 17.3	25.4 177 345 486	2.1 19.0 39.2 71.0
Slope:	14.7	Rel. eff.	2.7
Reference	NO2 concentration:	1.70 x 1015 molecu	les/cc.

HELIUM AS QUENCHER

Expt. No.	Pt T	He	Ð
35 36 37 38 39	11.4 18.8 14.7 5.36 8.88	350 583 453 160 271	8.8 11.8 10.6 3.6 7.8
Slope:	1.84	Rel. eff.	0.34
Reference	NO2 concentration:	1.50 x 10 ¹⁵ molecul	es/cc.

Expt. No.	۲' _T	[Ar]	₫
45 46 47 48	17.2 3.27 12.1 7.84	513 90.2 358 230	12.6 0.8 5.8 7.1
Slope:	2.51	Rel. eff.	0.46
Reference	NO2 concentration:	2.00 x 1015 molecul	es/cc.

ARGON AS QUENCHER

NITROGEN AS QUENCHER

Expt. No.	Ρţ	N ₂]	ē
40 41 43	16.6 8.28 4.13	507 250 122	20.6 8.2 2.4
Slope:	5.41	Rel. eff.	1.0
Reference	NO2 concentration:	1.50 x 10 ¹ 5 molecul	es/cc.

CARBON DICXIDE AS QUENCHER

Expt. No.	۳i	[co ²]	Ð
50 51 52 53	2.70 19.9 8.63 14.4	28.0 523 207 386	2.0 140.0 13.9 27.0
Slope:	7.53	Rel. eff.	1.4
Reference	NO2 concentration:	1.70 x 1015 molecul	es/cc.

different gases at room temperature. In Fig. 23 the data are plotted.

(G) Calculations for the Rate Constant for Overall Reaction at Elevated Temperatures

The site of ozone concentration measurement was beyond the furnace, and always near room temperature; hence observed ozone concentrations were referred to reaction temperature with the use of Charles' Law.

For calculating reaction times, the temperature profile in Fig. 24 was used, where T_{EXT} is the "external" temperature, which is here taken as the "average" temperature $(T_{o} + T_{R})/2$. The linear velocities in the T_{EXT} and T_{R} regions were found as before.

On pages 205-217 are given the data for elevated temperature runs. The reaction distances used in Experiment 64 were used for all subsequent experiments, except where indicated.

The rate constant was found from near-stoichiometric conditions only. This was done because, for lower ozone concentrations, the percent. error in measured $\begin{bmatrix} 0_3 \end{bmatrix}$ would have been prohibitive; for higher ozone concentration, the heat of reaction would have introduced too great a temperature drop during reaction. The Δ -correction was always between 1.0 and 1.1, indicating the validity of this method for all twelve experiments. Results for all temperatures are given in Tables 11 and 12, and these data are plotted in Fig. 25.

It has been shown (12) that the disappearance of ozone in this reaction takes place by two paths simultaneously,

PLCT OF DATA FROM TABLE 10

 $\Phi: \qquad (molecules/cc.)^2/I.U. \times 10^{-28}$













TEMPERATURE PROFILE USED FOR CALCULATING THE LINEAR VELOCITY FOR ELEVATED TEMPERATURE REACTIONS

T _{EXT} :	Temperature	beyond	furnace,	(T _o +	T _R)/2
--------------------	-------------	--------	----------	-------------------	--------------------

T _{oo} :	Temperature	of	ozone	measurement	without
00	reaction				

To: Temperature of ozone measurement during reaction



TABLE 11

RATE CONSTANTS FOR 03 + NO NEAR ROOM TEMPERATURE

- k: cc./molecule/sec. x 10¹⁴
- т: 317 ± 8°к
- 1/T: 3.15 ± 0.07 x 10⁻³ °K⁻¹

EXPT. NO.	k	LOG ^k + 14
34	2.6	0.42
35	1.1	0.04
36	1.4	0.15
37	1.4	0.15
38	1.3	0.11
39	1.0	0.00
40	1.6	0.20
41	1.5	0.18
43	1.8	0.26
45	1.7	0.23
46	2.4	0.38
47	1.9	0.28
48	2.0	0.30
50	1.9	0.28
51	1.7	0.23
52	1.7	0.23
53	1.9	0.28
56	1.9	0.28
57	2.2	0.34
58	3.0	0.48
59	1.9	0.28
78	2.8	0.45
79	1.9	0.28
80	1.6	0.20
81	1.5	0.18
Average	1.8 ± 0.5	0.25

TABLE 12

RATE CONSTANTS FOR 03 + NO AT ELEVATED TEMPERATURES

.

EXPT. NO.	т , °К	$\frac{1}{T}, \circ_{K} - 1 \times 10^{3}$	k x 10 ¹⁴ cc./molecule/ sec	LOG k + 14
64	380 ± 10	2.64 ± 0.06	3.2	0.51
65			4.3	0.63
66			3.4	0.53
67			2.8	0.45
e		Average	3.4 ± 0.5	0.53

68	495 ± 10	2.00 ± 0.04	2.8	0.45
69			4.0	0.60
72			7.4	0.87
73			5.9	0.77
		Average	5.0 ± 1.7	0.67

74	574 ± 10	1.74 ± 0.03	8.8	0.94
75			9.2	0.96
76			12	1.1
77			7.4	0.87
		Average	9.4 ± 1.7	0.97

ARRHENIUS PLOT FOR THE 03-NC RATE CONSTANT

, mean value of $\log_{10}k$ (with its standard deviation) at a single temperature



viz., (4) producing unexcited NO_2 and (4^{*}) producing excited NO_2 :

so that the rate equation is, more precisely,

 $-d \left[0_{3}\right]/dt = (k_{4} + k_{4}^{*}) \left[0_{3}\right] \left[NO\right] = k_{4}^{tot} \left[0_{3}\right] \left[NO\right]$ If k_{4}^{tot} be written as

$$k_{l_{4}}^{\text{tot}} = A_{l_{4}}^{\text{tot}} \exp(-E_{l_{4}}^{\text{tot}}/\text{RT})$$
 (X1)
 $\therefore \log_{10}k_{l_{4}}^{\text{tot}} = \log_{10}A_{l_{4}}^{\text{tot}} - \frac{E_{l_{4}}^{\text{tot}}}{2.3\text{RT}}$

From a least squares calculation, the slope of the line of the Arrhenius plot is

The uncertainty in $E_{l_4}^{tot}$ may be estimated from experimental data as follows (29). Let the rate constants at two temperatures T_1 and T_2 be $k_{l_4}(T_1)$ and $k_{l_4}(T_2)$ respectively. The Arrhenius equation (XI) can be written as

$$\mathbf{E}_{4}^{\text{tot}} = \frac{\mathbf{R}\mathbf{T}_{1}\mathbf{T}_{2}}{(\mathbf{T}_{2}-\mathbf{T}_{1})} \cdot \ln \frac{\mathbf{k}_{4}(\mathbf{T}_{2})}{\mathbf{k}_{4}(\mathbf{T}_{1})}$$

Assuming errors ΔT_1 , ΔT_2 , $\Delta k_{l_1}(T_1)$ and $\Delta k_{l_1}(T_2)$ are independent and random,

$$\begin{pmatrix} \Delta E_{l_{4}}^{\text{tot}} \\ E_{l_{4}}^{\text{tot}} \end{pmatrix}^{2} = \left(\frac{T_{2}}{T_{1} - T_{2}} \right)^{2} \left(\Delta T_{1} \\ T_{1} \\$$

If we substitute the values

$$T_{1} = 317 \pm 8^{\circ}K$$

$$T_{2} = 575 \pm 10^{\circ}K$$

$$k_{4}(T_{1}) = 1.8 \pm 0.5 \times 10^{-14} \text{cc./molecule/sec.}$$

$$k_{4}(T_{2}) = 9.4 \pm 1.7 \times 10^{-14} \text{cc./molecule/sec.}$$

we obtain

$$\left(\frac{\Delta \mathbb{E}_{4}^{\text{tot}}}{\mathbb{E}_{4}^{\text{tot}}} \right)^{2} = \left(\frac{575}{258} \right)^{2} \left(\frac{8}{317} \right)^{2} + \left(\frac{317}{258} \right)^{2} \left(\frac{10}{575} \right)^{2} + \left\{ \ln 5 \cdot 2 \right\}^{-2} \left\{ \left(\frac{0 \cdot 5}{1 \cdot 8} \right)^{2} + \left(\frac{1 \cdot 7}{9 \cdot 4} \right)^{2} \right\}$$

$$= 32 \times 10^{-4} + 4 \cdot 6 \times 10^{-4} + 4 \cdot 1 \times 10^{-2}$$

$$= 4 \cdot 4 \times 10^{-2}$$

$$\therefore \frac{\Delta \mathbb{E}_{4}^{\text{tot}}}{\mathbb{E}_{4}^{\text{tot}}} = 0.21$$

so that we may write

$$k_{4}^{\text{tot}} = 5.0 \times 10^{-13} \exp(-2100 \pm 440/\text{RT}) \text{cc/molecule/sec.}$$

(H) Determination of the Absolute Value of I_{sp}:

(i) USE OF A STANDARD CHEMILUMINESCENT REACTION:
 Relative values for the specific intensity I_{sp}

have already been obtained (pp.97-108). Absolute values may be found if the 1P21 photomultiplier is "calibrated" with a chemiluminescent reaction of known specific intensity.

Let the phototube current for the 0_3 -NO emission at wavelength λ in the apparatus be $i(\lambda)$; then

$$i(\lambda) = I_{sp} \frac{[0_3]NO}{[M]} G^{S_{\lambda}}$$

where

G is the geometrical factor (fraction) for this apparatus

 S_{λ} is the sensitivity of the 1P21 at wavelength λ

For a selected wavelength interval λ_{1} to λ_{2} ,

$$\mathbf{i} = \mathbf{I}_{sp} \frac{\left[\mathbf{0}_{3}\right]\left[\mathbf{N}\mathbf{0}\right]}{\left[\mathbf{M}\right]} \quad \mathbf{G} \quad \int_{\lambda_{i}}^{\lambda_{2}} \mathbf{s}_{\lambda} \, d\lambda \qquad (XII)$$

Similarly, if in the same apparatus the 1P21 views light from the standard reaction $0 + NO_2 \longrightarrow NO + h\nu$ through a filter of transmission f_{λ} , the phototube current will be, for wavelength interval λ_2 to λ_3 ,

$$i_{s} = I_{sps} [0] [N0] G \int_{\lambda_{2}}^{\lambda_{3}} f_{\lambda} d\lambda$$
 (XIII)

For simplification, we shall use the relations

$$i_{sp} = \frac{i \left[M\right]}{\left[03\right]\left[N0\right]}$$
(XIV)

$$\mathbf{i}_{sps} = \frac{\mathbf{i}_s}{\left[0\right]\left[N0\right]}$$
(XV)

where isp and isps are corresponding "specific" phototube currents. Hence from equations (XII) to (XV),

$$\frac{\mathbf{i}_{sp}}{\mathbf{i}_{sps}} = \frac{\mathbf{I}_{sp}}{\mathbf{I}_{sps}} \int_{\lambda_{l}}^{\lambda_{2}} d\lambda \qquad (XVI)$$

where the required quantity I_{sp} is the only unknown.

(ii) CALIBRATION EXPERIMENT:

(a) Specific Phototube Currents:

The experimental arrangement is shown in Fig. 5. The NO jet was placed 10.0 cm. upstream from the photomultiplier collimator.

Nitrogen atoms were produced by a microwave discharge through nitrogen (Raytheon Diathermy Unit, Model CMD-13, 2450 megacycles) just before the entrance to the furnace. The Natoms were titrated with NO so that an equivalent concentration of 0-atoms were produced by the fast reaction

 $N + NO \longrightarrow N_2 + O$

and intensity readings were taken for different NO flowrates beyond the endpoint. Welch pumps 1402 and 1397 were used in parallel to obtain a high linear velocity, for minimum 0-atom decay in the 10-cm. distance.

The data are (the symbols have their usual denotation):

 $T_{A} = 28^{\circ}C$ $f_{N_{2}} = 127 \text{ micromoles/sec.}$ $P_{T} = 0.68 \text{ torr}$ $I_{dc} = 4 (4)$

A Wratten filter # 70 (Eastman Kodak Company) was placed before the collimating slit to reduce the emission intensity to a At visual endpoint:

$$I_{\mu a} = 15$$
 (4); $I_c = 11$ (4); $I_r = 1.1$
 $f_{NO} = 2.42$ micromoles/sec

b First NO increase:

$$I_{\mu a} = 145$$
 (4); $I_c = 141$ (4); $I_r = 14.1$
 $f_{NO} = 2.58$ micromoles/sec.

c Second NO increase:

$$I_{\mu a} = 140$$
 (3); $I_c = 139$ (3); $I_r = 46.2$
 $f_{NO} = 2.75$ micromoles/sec.

d Third NO increase:

$$I_{\mu a} = 195$$
 (2); $I_c = 195$ (2); $I_r = 195$; $f_{NO} = 3.44$
micromoles/sec.

e Fourth NO increase:

$$I_{\mu a} = 155$$
 (1); $I_c = 155$ (1); $I_r = 515$
 $f_{NO} = 5.13$ micromoles/sec.

In Fig. 26 is plotted I_r vs. f_{NO} ; the x-axis intercept is 2.45 micromoles/sec. which was the initial 0-atom flowrate.

Allowance must be made for the fact that the 0-atoms decayed somewhat in the 10 cm. distance, by the reactions

- $C + NO + M \longrightarrow NO_2 + M$ (1)
 - $0 + NO_2 \longrightarrow NO + O_2$ (19)
- $0 + 0 + M \longrightarrow 0_2 + M$ (20)

Under experimental conditions, $k_{19} \gg k_1 [M]$ so that the rate of 0-atom removal by reactions (1) and (19) was

$$R_{NO} = 2k_1 [0] [NO] [M]$$

INTENSITY OF THE O-NO EMISSION AS A FUNCTION OF NITRIC OXIDE FLOWRATE



and [NO] is constant since NO is regenerated in reaction (19). The rate of removal of 0-atoms by reaction (20) is

$$R_{\text{REC.}} = k_{20} \left[0\right]^2 \left[M\right]$$

$$\frac{R_{REC.}}{R_{NO}} = \frac{k_{2O}[O]}{2k_{1}[NO]}$$

where, at room temperature, $k_1 = 3.9 \times 10^{-31} \text{ cc}^2/\text{molecule}^2/\text{sec.}$ $k_{20} = 2.8 \times 10^{-33} \text{ cc}^2/\text{molecule}^2/\text{sec.}$

and [0] / [NO] was at most 19. Hence

$$\frac{R_{REC}}{R_{NO}}$$
 \leq 0.07

and we can write, in an approximation,

$$- d[0]/dt \doteq 2k_1[0][N0][M] = K[0]$$

which upon integration is

$$\begin{bmatrix} 0 \end{bmatrix} = \begin{bmatrix} 0 \end{bmatrix}_{0} \exp(-Kt)$$
For example, in step e, $\begin{bmatrix} NO \end{bmatrix} = 4.61 \times 10^{14} \text{ molecules/cc.}$
 $t = 10.6 \text{ milleseconds}$

$$K = (2)(3.9 \times 10^{-31})(0.42 \times 10^{15})(0.46 \times 10^{15})(23 \times 10^{15})$$

$$= 8.1 \text{ sec.}^{-1}$$

$$\therefore \begin{bmatrix} 0 \end{bmatrix} = (0.42 \times 10^{15})\exp(-8.1 \times 10.6 \times 10^{-3})$$

$$= 0.39 \times 10^{15} \text{ molecules/cc.}$$

The data for steps <u>b</u> to <u>e</u> are summarized in Table 13, where I_r is equated with i_s . The value of i_{sps} for our purposes is 2.54 x 10^{-27} I.U.cc.²/molecule².

TA	BL	Ξ]	3
_	_	-		_

DETERMINATION OF THE SPECIFIC INTENSITY OF THE O-NO EMISSION IN THE APPARATUS					
Run	NO molecules/ cc.x 10-14	[] molecules/ ec.x 10-14	[0][N0] (molecules/ cc.) ² x 10-28	Ir Arbit'y units, I.U.	isps <u>I.U.cc.²</u> molecule ² x 10 ²⁷
(b) (c) (d) (e)	0.20 0.48 1.57 4.27	4.18 4.16 4.07 3.87	0.85 1.97 6.40 16.5	14.1 46.2 195 515	1.7 2.3 3.1 3.1

For the O_3 -NO reaction, from Table 10 for $M = N_2$,

i _{sp}	н	$\frac{I_r [N_2]}{[0_3][N0]} =$	$\frac{\left[\mathbb{N}_{2}\right]}{\Phi} =$	1 5.41 x 10 ¹¹
	=	1.85 x 10 ⁻¹	.2 _{I.U.cc./m}	olecule

(b) Sensitivity Integrals:

The relative sensitivity curve for the 1P21 is given in Fig.27; since the 0_3 -NO emission begins at 6000 Å, this radiation was detected in the range 6000 - 7000 Å.

In the O-NO experiment, the Wratten filter, whose transmission is given in Table 14, limited the range detected to 6500 - 7000 Å.

TA	BL	Ε	1	1
				_

	TRAN	ISMISSION	OF WRATT	EN FILTE	R 70	
A	6500	6600	6700	6800	6900	7000
f	0.006	0.105	0.35	0.55	0.70	0.79

The sensitivity of the detecting system was then $\mathrm{S}_{\pmb{\lambda}}\;\mathbf{f}_{\pmb{\lambda}}$, whose

RELATIVE SENSITIVITY OF 1P21 PHOTOMULTIPLIER, 6000-7000Å



S_A, RELATIVE SENSITIVITY OF IP2I

132B

curve is shown in Fig. 28. Hence

$$\frac{\int_{3\lambda}^{7000} s_{\lambda} d\lambda}{\int_{5\lambda}^{7000} s_{\lambda} f_{\lambda} d\lambda} = 3.8$$

(c) Values for I_{sps} and I_{sp} :

The spectral distribution of the 0-NO and O_3 -NO emissions are shown in Figs. 29 and 30 respectively (23, 12). The specific intensity for any wavelength interval is proportional to the area under the curve in that interval. Hence by direct measurement,

$$I_{sps} = 0.11 I_{sps}(total) = 0.11 \times 6.4 \times 10^{-17}$$

= 0.70 x 10⁻¹⁷ cc./molecule/sec.

If it is assumed that the intensity of the 0_3 -NO emission increases linearly from 7000 to 11,000 Å, and that one-half the total intensity resides at wavelengths less than 11,000 Å, then

$$I_{sp} = 0.03 I_{sp} \text{ (total)}$$

Substituting these values in (XVI), we have

$$\frac{1.85 \times 10^{-12}}{2.54 \times 10^{-27}} = \frac{0.03 I_{sp}(total)}{0.70 \times 10^{-17}} \times 3.8$$

$$\cdot I_{sp}(total) = 4.5 \times 10^{-2} \text{ sec.}^{-1}$$

RELATIVE SENSITIVITY OF THE SYSTEM (1P21 + Wratten filter 70)



SPECTRAL INTENSITY DISTRIBUTION OF THE O-NO EMISSION





SPECTRAL INTENSITY DISTRIBUTION OF 03-NO EMISSION


DISCUSSION

The rate constant for the 03-NO reaction was obtained in this work on the basis of ozone disappearance rates, in common with most previous measurements. Hence these values may be compared directly, and the corresponding composite Arrhenius plot is given in Fig. 31.

The results of the present work are compared with extrapolated values from the work of Clyne, Thrush and Wayne (12) in Fig. 32. These were taken from their data in the form

$$k_{\downarrow}^{\text{tot}} = k_{\downarrow} + k_{\downarrow}^{*} = A_{\downarrow} \exp(-E_{\downarrow}/\text{RT}) + A_{\downarrow}^{*} \exp(-E_{\downarrow}^{*}/\text{RT})$$

where k_{\downarrow} and k_{\downarrow}^{*} are the rate constants for the formation of ground-state and excited NO₂:

$$0_3 + NO \longrightarrow NO_2 + 0_2 \qquad (4)$$

$$0_3 + NO \longrightarrow NO_2^* + 0_2 \qquad (4*)$$

and $A_{4} = 8 \times 10^{-13}$ cc./molecule/sec. $E_{4} = 2.4$ kcal./mole $A_{4}^{*} = 4.5 \times 10^{-13}$ cc./molecule/sec. $E_{4}^{*} = 4.2 \pm 0.3$ kcal./mole

The dotted line shows a slight upward curvature, indicating that the disappearance of ozone through the path of higher activation energy, $(4^{\#})$, is becoming appreciable. The fraction, \measuredangle , of k_4^{tot} contributed by $k_4^{\#}$ may be calculated straightforwardly from their data:

FIGURE 31

SUMMARY OF 03 + NO RATE CONSTANTS

× this work
Clyne, Thrush and Wayne, ref. (12)
Borok, refs. (3) and (4)
Marte, Tschuikow-Roux and Ford, ref. (11)
Johnston and Crosby, ref. (1)
A Phillips and Schiff, ref. (18)
Ford, Doyle and Endow, ref. (2)



FIGURE 32

COMPARISON OF PRESENT WORK WITH RESULTS OF CLYNE, THRUSH AND WAYNE





$$\frac{1}{\alpha} = 1 + \frac{A_{\underline{l}}}{A_{\underline{l}}^{\underline{c}}} \cdot \frac{\exp(-E_{\underline{l}}/RT)}{\exp(-E_{\underline{l}}^{\underline{c}}/RT)}$$
$$= 1 + 1.8 \exp \left\{ (E_{\underline{l}}^{\underline{c}} - E_{\underline{l}})/RT \right\}$$
$$\alpha = \frac{1}{1 + 1.8 \exp (1800/RT)}$$

For the temperatures used in the present work, Table 15 shows values of \mathbf{A} expected herefrom:

•••

TABLE 15

FRACTION OF $k_{l_{1}}^{tot}$ CC	ONTRIBUTED	ΒY	к ^ж Ц
----------------------------------	------------	----	------------------

т, ⁰ к	d
318	0.03
380	0.05
495	0.08
575	0.1

These figures are approximate only, since $(E_{\downarrow}^{*} - E_{\downarrow})$ has an uncertainty of at least \pm 300 cal./mole and A_{\downarrow}^{*} is known to within a factor of \downarrow .

In the present work, the temperature dependence of k_{\downarrow}^{*} was not found, and the precision of measurement does not justify assignment of curvature to the Arrhenius plot. However, it may be shown that these results are compatible with the following most reliable conclusions of the work of Clyne, Thrush and Wayne (assuming that their value for E_{\downarrow} is not reliable).

(i)
$$E_{\mu}^{*} = 4.2 \text{ kcal./mole}$$

(ii) $A_{\mu}^{*} \stackrel{\bullet}{=} A_{\mu}$

If we assume $A_{4}^{*} = A_{4} = A$, then we may say, approximately

$$k_{\downarrow}^{\text{tot}} = A \left\{ \exp(-E_{\downarrow}/\text{RT}) + \exp(-4200/\text{RT}) \right\}$$

or
$$\log \left\{ k_{\downarrow}^{\text{tot}} - A \exp(-4200/\text{RT}) \right\} = \log A - E_{\downarrow}/2.3\text{RT}$$

The quantity on the L.H.S. may be plotted versus 1/T, using several likely values for A (in the L.H.S. expression). The desired value for A is that one to which the intercept of the curve corresponds. The slope of the curve yields the desired value of E_{j_1} .

The data for the four experimental temperatures are given in Table 17, where two trial values for A were used. The data are plotted in Fig. 33. The desired value for A is evidently between 1 x 10^{-13} and 9 x 10^{-13} cc./molecule/sec. The intercept is -12.3 and the slope is $-470^{\circ}K^{-1}$, so that

$$A = \text{antilog} (\overline{13.7})$$

= 5 x 10⁻¹³ cc./molecule/sec

and

 $E_{\mu} = (470)(2.3)(1.99) = 2.1 \text{ kcal./mole}$ which values agree, within experimental error, to those of Clyne, Thrush and Wayne.

The value of I_{sp} of this work, for N₂ at 318 ± 8°K was found to be 0.045 sec.⁻¹. This in in fair agreement with the value of Clyne, Thrush and Wayne

The relative quenching efficiencies of the inert gases in reaction (3), found in the present work, are compared with other authors' results below:

TABLE 16

SF6	02	^N 2	Ar	Не	^H 2	^N 2 ⁰	^{C0} 2	^{NO} 2	NO	сн ₄	CF4	^н 20	Reference
2.7 - 3.5	1.1 0.8 1.1	1.0 1.0 1.0 1.0 1.0	0.46 0.6 0.68	0.34 - 0.68	- 1.3 0.5 1.4 -	1.4 2.9 2.1	1.4 3.0 2.4	- 16 3.5 2.3 1.9	- - 1.9	- - 1.9	- - 3.6	- - 6.4	This work 12 102 105 106

RELATIVE QUENCHING EFFICIENCIES OF INERT GASES FOR NO5

The results illustrate the general rule that the probability of energy transfer by a molecule increases with the number of constituent atoms, i.e., with the number of degrees of freedom offered by the molecule. However, in the extreme case of SF_6 (or H_2O), this efficiency is only about an order of magnitude greater than that for the simplest monatomic gas, He.

The quenching efficiency of NO_2 might be expected to be considerably larger than those of other molecules, since in this case the frequencies of emission correspond to frequencies of absorption. The values of Baxter (102), Kaufman (105) and Neuberger and Duncan (106) are considerably different; these are for quenching NO_2 fluorescence excited by Hg 4358 and 4047 Å.

TABLE 17

DATA FOR DETERMINING APPROXIMATE VALUES OF "A" AND $\mathbf{E}_{j_{\perp}}$ FROM THE PRESENT WORK

 k_{\downarrow}^{tot} : 1/T: $A \exp(-\frac{1}{200/RT})$: $\left\{ k_{\downarrow}^{tot} - A \exp(-\frac{1}{200/RT}) \right\}$: A:

cc./molecule/sec. x 10¹⁴ o_K-1 x 10³ cc./molecule/sec. x 10¹⁴ cc./molecule/sec. x 10¹⁴ cc./molecule/sec.

k ^{tot}	1/T	-4200/RT	өхр (-4200/RT)	A exp (A=1 x 10 ⁻¹³ (a)	-4200/RT) A=9 x 10 ⁻¹³ (b)	k 4 -1 (-4200 (a)	ot A exp D/RT) (b)	$\log \left\{ k_{4}^{\text{tot}} - A \right\}$	4 + . exp(-4200/RT)} (b)
	2.25	((7	0.0010	0.010	0.11	1 70	1 (0	0.05	0.00
1.0	3.15	-0.07	0.0013	0.013	0.11	1.79	1.69	0.25	0.23
3.4	2.64	-5.55	0.0039	0.039	0.35	3.36	3.05	0.53	0.48
5.0	2.00	-4.26	0.0141	0.141	1.27	4.86	3.73	0.69	0.57
9.4	1.74	-3.68	0.0252	0.252	2.27	9.15	7.13	0.96	0.85

FIGURE 33

PLOT OF DATA FROM TABLE 17

• for A = 9×10^{-13} cc./molecule/sec. X for A = 1×10^{-13} cc./molecule/sec.



The short wavelength cut-off for the 0_3 -NC emission is 6000 Å; hence the values derived from studies on fluorescence represent efficiencies for NO₂ molecules in higher energy states.

In the derivation of these quenching efficiencies, it was assumed that the intensity distribution of the O_3 -NO chemiluminescence was independent of $[O_3]$, [NO] and [M], as found by Clyne, Thrush and Wayne (12). Only the shortest wavelengths (6000 - 7000 Å) were detected for intensity measurements.

The increase in the quantity \oint in a single run may be accounted for as mentioned before (pp. 103 ff.). For example, the data for Experiment 36 are as follows:

TABLE 18

Reaction time milli- seconds	Temp of C	erature gases ^o K	[N02] molecules/cc. x 10 ⁻¹⁵	$(molecules/cg)^2/I.U. x 10^{-28})^2/I.U.$
4.24	41	311;	1.00	1.16
67.8	31	304	2.76	1.85

DATA FOR EXPERIMENT 36

The expression for Φ in this case may be written as

$$\Phi = \frac{k_3, He}{k_1^2 k_2} \left\{ He + \sigma NO_2 \right\}$$
 (XVII)

where σ is the quenching efficiency of NC₂ relative to helium, which from Table 16 is 45. The predicted ratio of the Φ 's at the two temperatures is

$$\frac{\Phi}{2} \frac{314}{304} = \frac{(k_{l_{1}}^{*})_{304}}{(k_{l_{1}}^{*})_{314}} \cdot \frac{\{ \mathbb{H}e + 45 \mathbb{N}o_{2} \}}{\{ \mathbb{H}e + 45 \mathbb{N}o_{2} \}}$$
(XVIII)
$$= exp(-0.23) \{ 0.89 \} = 0.71$$

using the activation energy for k_{4}^{*} as given by Clyne, Thrush and Wayne. Experimentally, this ratic was 0.63, indicating that, within experimental uncertainty, the data are consistent with this interpretation.

In runs with a more efficient inert gas (CO_2, N_2O_1, SF_6) , Φ changes very little or, within experimental uncertainty, is constant. In such cases, σ in equation (XVII) is much smaller and the concentration ratio in equation (XVIII) is more nearly unity.

There remains the possibility that product NO_2 in reaction (4)

 $0_3 + NC \longrightarrow NO_2 + O_2$ (4) will compete with NC for 0_3 , through the reaction

 $0_3 + N0_2 \longrightarrow N0_3 + 0_2$ (8) so that the rate constant, based upon ozone disappearance would contain a contribution from reaction (8). The only measurement of the activation energy for this reaction was reported by Johnston and Yost (144) for the temperature range 286 to 302° K. In this temperature range, k_8 was

5.8 x 10^{-13} (T) $\frac{1}{2}$ exp(-7000 ± 600/RT) cc./molecule/sec.

and Table 19 contains data for comparison:

Extrapolated values for k_8 compared with k_4^{tot}								
in cc./molecule/sec.								
	318	380	495	575				
kg	1.6 x 10-16	1.1 x 10-15	1.1 x 10 ⁻¹⁴	3.1 x 10-14				
$\frac{k_8}{k_{l_{\downarrow}}tot}$	9 x 10 ⁻³	4 x 10 ⁻²	0.2	0.3				

TABLE 19

If the k_8 values are correct, k_4^{tot} at the higher temperatures are significantly in error.

It is imperative, therefore, to determine whether the actual ozone-disappearance rates indicate this competition. To this end the following curve-matching technique may be used (104). Using the symbols

$$a = [N0]$$

$$b = [0_3]$$

$$\theta = \int_0^t b dt$$

$$x = \theta k_{l_1}^{tot}$$

$$y = k_8 / k_{l_1}^{tot}$$

we may write

 $(b_0-b)/a_0 = (2 - e^{-x} + e^{-xy})/(y-1)$ (XIX)

if $c_0 = 0$, where a_0 , b_0 and c_0 are initial concentrations.

A curve relating $(b_0-b)/a_0$ to $\log_{10}\theta$ is first drawn

from experimental data. The ozone profile for Experiment 75 is given in Fig. 34, and the necessary data for this curve, given in Fig. 35, are below:

TABLE 20

Experimental data for curve-matching technique

 $a_0 = 1.90 \times 10^{15} \text{ molecules/cc.}$ $b_0 = 1.63 \times 10^{15} \text{ molecules/cc.}$

Time interval, milliseconds	θ molecule-sec./cc. x 10 ⁻¹¹	log 0	b _o -b a _c
0 - 2.5	36	12.56	0.17
0 - 5	66	12.82	0.28
0 - 7.5	92	12.96	0.37
0 - 15	146	13.164	0.56
0 - 22.5	182	13.260	0.66
0 - 30	205	13.312	0.71
0 - 37.5	221	13.344	0.76
0 - 45	235	13.372	0.80

Next, data for curves of $(b_0-b)/a_0$ vs. log x are calculated according to equation (XIX). Since θ lies between 30 x 10¹¹ and 240 x 10¹¹ molecule-sec./cc. and k_4^{tot} between 7 x 10⁻¹⁴ and 11 x 10⁻¹⁴ cc./molecule/sec., the range of x will be 0.2 to 2.5.

Curves for y = 0.1, 0.01 and 0.5 are found in Fig. 36. It will be noted that, as y decreases, the shape FIGURE 34

OZONE CONCENTRATION PROFILE FOR EXPERIMENT 75





CURVE-MATCHING TECHNIQUE TO DETERMINE k8/k4



--X - X - Calculated, y = 0





CURVE-MATCHING TECHNIQUE TO DETERMINE k_8/k_4^{tot}

$$\triangle$$
 y = 0.5
• y = 0.1
× y = 0.01



TABLE 21

				<u>a</u>					
	5//1				У	- = 0.1			
	x								
	0.2	0.5	1.0	1.5	2.0	2.5			
log x	-0.70	-0.30	0.00	0.18	0.30	0.40			
xy	0.02	0.05	0.10	0.15	0.20	0.25			
e-x	0.82	0.61	0.37	0.22	0.14	0.08			
0-xy	0.98	0.95	0.91	0.86	0.82	0.78			
(b ₀ -b)/a ₀	-2.39	-2.61	-2.88	-2.93	-2.98	-3.00			

Calculated data for curve-matching technique

of the curve more nearly resembles the experimental curve in Fig. 35. Hence $k_8 \ll k_4^{\text{tot}}$, contrary to the predicted result using the values for activation energy and pre-exponential factor of Johnston and Yost (44). Their values must therefore be held in doubt. In Fig. 35 the limiting case (y = 0) is represented as the dashed curve, displaced so that it coincides with the experimental curve. Furthermore, as a check,

:.
$$\log x = \log k_{4}^{tot} + \log \theta$$

:. $\log k_{4}^{tot} = -13.2 = \overline{14.8}$
:. $k_{4}^{tot} = 6 \times 10^{-14} \text{ cc./molecule/sec.}$

which is of the right order of magnitude and confirms the essential reliability of the method.

The results of this work are seen to be in general agreement with those of Clyne, Thrush and Wayne, although the methods used are somewhat different, and, it is believed, those used in the present work are superior in some respects.

These authors established the mechanism for the chemiluminescence in systems where the maximum removal of NO and O_3 was 5% of their initial values, e.g. where

$$p_{NO}^{o} < 5 \times 10^{-3} \text{ torr}$$

 $p_{O_{3}}^{o} < 5 \times 10^{-4} \text{ torr}$
 $p_{Ar}^{p} = 1.3 \text{ torr}$

Thus, for constant [NO], they found $I \leq [0_3]$ and for constant $[0_3], I \leq [NO]$. By varying [M], they also concluded

$$\frac{I}{[^{0}3][^{NO}]} = \frac{I_{sp}}{[^{M}]}$$

where I_{sp} is a constant. Now they do not state in their publication how $\begin{bmatrix} 0_3 \end{bmatrix}$ was derived, or even how ozone was made. If $\begin{bmatrix} 0_3 \end{bmatrix}$ was determined by the iodometric method, such concentrations are unreliable to the extent that this chemical determination is so. In contrast to this, the present work utilized the optical absorption method, believed to be the most dependable.

Having established the relation $\begin{bmatrix} 0 \\ 3 \end{bmatrix} \ll I/\begin{bmatrix} NO \end{bmatrix}$, these authors proceeded to find k_4^{tot} , under conditions approximately as above, through the following kinetic analysis:

$$d[0_{3}]/dt = -k_{4}^{tot} [0_{3}][N0]$$

$$d \ln [0_{3}]/dt = -k_{4}^{tot} [N0]$$

$$\ln [0_{3}] = \ln [0_{3}]_{0} - k_{4}^{tot} [N0] t$$

$$\ln (I/[N0]) = \ln (I_{1}/[N0]) - k_{4}^{tot} [N0] t (XX)$$

where I_i is the intensity at t = 0. Hence the intensity of emission is used here as ozone monitor.

In the present work, however, the quantities $\begin{bmatrix} 0_3 \end{bmatrix}$ and I were measured <u>independently of each other</u>, during a single run. Hence the data for the determination of k_4^{tot} are independent of whatever value "I" may have. Again, equation (XX) is true only if $\begin{bmatrix} M \end{bmatrix}/I_{\text{sp}}$ is constant in a single run, i.e., if $k_{3,M} \begin{bmatrix} M \end{bmatrix} \gg k_{3,NO_2} \begin{bmatrix} NO_2 \end{bmatrix}$ where M is an inert gas.

SUMMARY AND CONTRIBUTIONS TO KNOWLEDGE

(1) A flow system was used to determine the rate constant k_4^{tot} of the gas-phase 0_3 + NO reaction. This rate constant was based upon the rate of disappearance of ozone, and ozone concentration in reaction was determined by optical absorption at 2537Å.

(2) The data fitted second-order integrated rate expressions, and when the reactants were in stoichiometric concentrations, the total reaction order was found to be 1.8.

(3) Rate constants at room temperature (318 \pm ⁸⁰K) did not show significant dependence upon total pressure in the range 3 to 20 torr, for the inert gases N₂, Ar, He, CO₂, N₂O and SF₆.

(4) An Arrhenius activation energy was obtained for k_{4}^{tot} by carrying out the reaction in a tube within an aluminum furnace of large capacity. Side reactions were shown to be negligible with respect to the one under scrutiny; the expression for the rate constant may be written as

 $k_{ll}^{\text{tot}} = 5.0 \times 10^{-13} \exp(-2100 \pm 440/\text{RT}) \text{ cc./molecule/sec.}$

in the temperature range 318-575°K.

(5) The intensity of chemiluminescence from the reaction was measured independently of ozone concentration, and the data were shown to be consistent with the following mechanism:

$$^{0}_{3} + N^{0} \longrightarrow N^{0}_{2} + ^{0}_{2} \qquad (4^{*})$$

$$NO_2^* \longrightarrow NO_2 + h\nu$$
 (2)

 $NO_2^* + M \longrightarrow NO_2 + M$ (3)

where NO_2^* is an excited molecule and M an inert atom or molecule.

(6) The kinetic analysis yielded relative values of k_3 (or quenching efficiencies) for the inert gases mentioned above. For N_2 as unity, these were: He, 0.34; Ar, 0.46; CO_2 , 1.4; N_2O , 1.4 and SF₆, 2.7.

(7) Indirect evidence was obtained which suggested that NO₂ is a very efficient quencher for the chemiluminescence, in agreement with the relative quenching efficiency of Clyne, Thrush and Wayne.

(8) The emission detection system was "calibrated" with the standard 0 + NO chemiluminescent reaction, and the value for I_{sp} in the expression

$$I = \frac{I_{sp} \left[0_{3}\right] \left[N_{0}\right]}{\left[N_{2}\right]}$$

was found to be 0.045 sec.⁻¹ at 318° K. The value of k_{4}^{*} derived from this was 2 x 10^{-17} cc./molecule/sec., in fair agreement with Clyne, Thrush and Wayne.

(9) The values for k_{μ}^{tot} were shown to be consistent with the equation

$$k_{\downarrow}^{\text{tot}} = k_{\downarrow}^{*} + k_{\downarrow}$$
$$= A_{\downarrow} \exp(-E_{\downarrow}^{*}/\text{RT}) + A_{\downarrow} \exp(-E_{\downarrow}/\text{RT})$$

where $k_{j_{\downarrow}}$ refers to the reaction yielding ground-state NO₂

$$0_3 + N0 \longrightarrow N0_2 + 0_2 \tag{4}$$

as suggested by Clyne, Thrush and Wayne.

(A) Ultraviolet Absorption of Gases other then Ozone:

By direct observation, no absorption at 2537Å could be detected in the apparatus, at the pressures used, for 0_2 , N₂, Ar, CO₂, N₂O, He, NO and SF₆. Extinction coefficients for NO₂ and N₂O₄ were obtained elsewhere (97). They were, at 25°C; NO₂, 3.1 x 10⁻²⁰ cc./molecule/cm.; N₂O₄, 3.7 x 10⁻¹⁹ cc./molecule/cm. The ratio



was therefore 0.075.

The "absorbances", A, of each gas is given by the Beer-Lambert law

$$A_{0_3} = \ln(I_0/I_t)_{0_3} = \epsilon_{0_3}I_{0_3}$$
 (XXI)

$$A_{N_{2}O_{4}} = \ln(I_{0}/I_{t})_{N_{2}O_{4}} = \epsilon_{N_{2}O_{4}} \left[N_{2}O_{4}\right] \quad (XXII)$$

Dividing (XXII) by (XXI), we have

$$\frac{A_{N_{2}}\circ_{4}}{A_{0_{3}}} = \frac{\epsilon_{N_{2}}\circ_{4}}{\epsilon_{0_{3}}} = \frac{1}{0.075} \frac{[N_{2}\circ_{4}]}{[0_{3}]}$$
(XXIII)

For a 1% error in $\begin{bmatrix} 0_3 \end{bmatrix}$ due to absorbance by $N_2O_{l_1}$, we must have, from (XXIII)

$$0.01 = 0.075 \frac{[N_20]_1}{[0_3]}$$

$$\frac{N_20_{l_1}}{[0_3]} = 0.13$$

or

It will be shown that, at all times in this work, the ratio $\left[N_2O_4\right]/\left[O_3\right]$ was always much less than this value.

In the most unfavourable case (at the lowest temperature 35°C) the equilibrium constant K_p for

was 0.3183 atmosphere (98). From this value the degree of dissociation may be deduced as > 99.9%.

Thus, for a 1% error in $\begin{bmatrix} 0_3 \end{bmatrix}$, the fraction of ozone, x, which must have reacted, will be

$$\frac{\begin{bmatrix} N_2 O_{1_1} \end{bmatrix}}{\begin{bmatrix} O_3 \end{bmatrix}} = 0.13 < \frac{10^{-3} \begin{bmatrix} N_0 \\ 0 \end{bmatrix}}{\begin{bmatrix} O_3 \end{bmatrix}} = \frac{10^{-3_x}}{(1-x)}$$

$$\therefore x > 0.99.$$

i.e., at more than 99% reaction; in practice, x was never more than 0.90, and interference from N_2O_4 was negligible under all conditions. Similarly it may be seen that the same was true for NO_2 .

(B) Variation of 1P28 Photomultiplier Supply Voltage:

The effect of this variation upon the ozone concentration as measured may be analyzed into two parts, viz., (i) effect of phototube voltage on the output, and (ii) effect of output variation (uncertainty in I_0 and I_t) in the Beer-Lambert law.

(i) VOLTAGE-OUTPUT RELATION:

The gain of the 1P28 is an approximate logarithmic function of the applied voltage, i.e., $G = (kV)^n$

where

G is the gain k is a proportionality constant V is the applied voltage n is the number of multiplying stages

Taking differentials, we have

$$dG = nk^n V^{n-1} dV$$

and dividing by G,

$$\frac{dG}{G} = n \frac{dV}{V}$$

or for small changes,

$$\frac{\Delta G}{G} = n \frac{\Delta V}{V}$$

For a 1P28, n = 9 and we can write

(% uncertainty in gain or output) = 9(% uncertainty in voltage) and so the uncertainty in I_0 and I_t is almost an order of magnitude greater than that in applied voltage.

(ii) CONCENTRATION-INTENSITY RELATION:

From the above, the ratio I_0/I_t will have an uncertainty, for $\pm x\%$ uncertainty in both I_0 and I_t ,

$$\frac{I_{\circ} \stackrel{+}{=} x\%}{I_{t} \stackrel{+}{=} x\%} \stackrel{=}{=} \frac{I_{\circ}}{I_{t} \stackrel{+}{=} 2x\%}$$

where $I_t \doteq I_o$.

The Beer-Lambert law may be stated as

$$I_0/I_t = e^{kcl} = e^{\overline{E}}$$

 $\therefore \ln(I_0/I_t) = \ln I_0 - \ln I_t = kcl = E$ (XXIV)

Taking differentials, we have

$$dE = kldc = -d(lnI_t) = -dI_t \qquad (XXV)$$

for constant 1.

Dividing (XXV) by (XXIV), we have

$$\frac{dE}{E} = \frac{dc}{c} = \frac{-dI_t}{EI_t} = \frac{-dI_t}{EI_c e^{-E}}$$
(XXVI)

so that the relative uncertainty in concentration is a minimum when Ee^{-E} is a maximum, for a given value of dI_t/I_c .

Differentiating Ee^{-E} with respect to E and equating to zero, we obtain

$$e^{-E}(1-E) = 0$$

which is satisfied when E = 1, i.e., when

$$I_o/I_t = e$$

which corresponds to 36.8% transmission. At this transmission, we have from (XXVI),

(% uncertainty in concentration) = 2.7(% uncertainty in I_o/I_t) or in symbols

$$U_{c} = FU_{t}$$

Now for any transmission other than 36.8%, F will be larger than 2.7; however, within certain limits it does not vary greatly. The actual behaviour is shown in Fig. 37 (from reference 95).

In the present work, the transmission lay between 0.4 and 0.9. The value of U_{I_t} , arising chiefly from amplifier

FIGURE 37

THE UNCERTAINTY FACTOR "F" IN THE APPLICATION OF THE BEER-LAMBERT LAW



= _____

noise, was 0.01 or less.

(C) Decomposition of Ozone in the Ultraviolet Beam:

It might be supposed that the analytical beam of 2537Å radiation would decompose some ozone in its path. An einstein at this wavelength corresponds to about 112 kcal./ mole; the energy of activation for ozone decomposition is 24 kcal./mole.

By direct observation, however, there was no detectable decomposition. Static mixtures representative of actual conditions were introduced into the absorption cell, and the transmission showed no significant change over a one-minute period.

(D) Justification for Assumption of Laminar Flow:

This is necessary for calculating reaction times (p.87). For the flow of a fluid through a tube, the degree of turbulence may be estimated by calculation of the Reynolds number, Re, according to

$$Re = \frac{vd\rho}{\eta} \quad (unitless)$$

where

v is the linear velocity of the fluid d is the diameter of the tube ρ is the density of the fluid η is the viscosity of the fluid

For Experiment 45,

v =
$$480 \text{ cm./sec.}$$

d = 2.2 cm.
 $P = 3.5 \times 10^{-5} \text{ g./cc.}$ (17.2 torr at 320°K)
 $\eta = 2.21 \times 10^{-4} \text{ dyne-sec./cm.}^2$ (argon)

$$\therefore Re = \frac{(480)(2.2)(3.5 \times 10^{-5})}{2.21 \times 10^{-4}}$$

Turbulence is said to be "present" when Re reaches values in the range 500 - 3000 (103). The experimental Reynolds number is below the "threshold" value, indicating that turbulence will not seriously invalidate assumption of laminarity in this work.

- (E) Justification of the Assumption that Change in Reactant Concentration Down the Reaction Tube arises only from Reaction:
 - (1) NEGLIGIBLE VISCOUS PRESSURE DROP DOWN THE TUBE:

Since the flow is laminar, we may apply the

Poiseuille law

$$f = \frac{\pi r^4 (p_2 - p_1) (p_2 + p_1)}{161 \eta RT}$$
$$= \frac{\pi r^4 \Delta pP}{8 \eta RT}$$

where $\Delta p \ll p_2 \doteq p_1 = p$.

Hence the fractional viscous pressure drop is

$$\left(\frac{\Delta p}{P}\right) = \frac{8\eta \, \text{lRTf}}{\pi \, P^2 r^4}$$

where, as typical values (Experiment 45),

1 = 30 cm. η = 2.21 x 10^{-l_4} dyne-sec./cm.² R = 6.24 x 10^{l_4} cc.-torr/^oK-mole
$$T = 320^{\circ}K$$

$$r = 1.1 \text{ cm.}$$

$$f = 1.56 \text{ x } 10^{-3} \text{ mole/sec.}$$

$$P = 17.2 \text{ torr (1 torr = 1333 dynes/cm.^2)}$$

$$\cdot \cdot \left(\frac{\Delta p}{P}\right) = \frac{(8)(30)(2.21 \text{ x } 10^{-4})(6.24 \text{ x } 10^{4})(320)(1.56 \text{ x } 10^{-3})}{(17.2)^2(3.14)(1.1)^4(1333)}$$

$$\doteq 1 \text{ x } 10^{-3} \text{ or } 0.1\%$$

(ii) NEGLIGIBLE LONGITUDINAL MIXING:

In a steady laminar flow of reacting gases through a tube, there will be set up a concentration gradient along the length, which will not alter with (laboratory) time. There will be diffusion from regions of higher concentration to those of lower (back diffusion at the jet and forward diffusion down the tube).

We can write, for the mass balance of species at a given position along the tube,

$$D \frac{d^2 C}{dx^2} - v \frac{dC}{dx} - kC^n = C$$

where

D is the diffusion coefficient C is the concentration of the species x is the distance along the tube k is the rate constant for removal of this species by reaction n is the order of this reaction v is the linear velocity

Now for diffusion to be negligible in comparison with linear velocity, we must have

$$D \frac{d^2 C}{dx^2} \ll v \frac{dC}{dx}$$

Now

$$\frac{dC}{dx} = \frac{dC}{dt} \cdot \frac{dt}{dx} = \frac{kC^{n}}{v}$$
$$\therefore \quad \frac{d^{2}C}{dx^{2}} = \frac{d}{dx} \left(\frac{dC}{dx} \right) = \frac{knC^{n-1}}{v} \cdot \frac{dC}{dx} = \frac{k^{2}nC^{2n-1}}{v^{2}}$$

Our conditions must satisfy,

$$\frac{nDk^2C^{2n-1}}{v^2} \ll \frac{vkC^n}{v}$$
$$\frac{nDkC^{n-1}}{v^2} \ll 1$$

Now in Experiment 45 n = 2

••••

$$D \doteq 5 \text{ cm} \cdot \frac{2}{\text{sec.}}$$

$$k = 2 \times 10^{-14} \text{ cc./molecule/sec.}$$

$$C = 3 \times 10^{15} \text{ molecules/cc.}$$

$$v = 480 \text{ cm./sec.}$$

$$\frac{nDkg^{n-1}}{v^2} = \frac{(2)(5)(2 \times 10^{-14})(3 \times 10^{15})}{(480)^2}$$

$$= 3 \times 10^{-3}$$

(F) Decomposition of Ozone at High Temperatures:

Rates of pyrolysis of ozone, even at the highest temperature used in this work, were negligible compared with the 0_3 -NO rate being measured.

The pertinent czone reactions are

$$0_{3} + M \rightleftharpoons 0_{2} + 0 + M \qquad (18, 11)$$

$$0_{3} + N0 \longrightarrow N0_{2} + 0_{2} \qquad (4)$$

$$0_{3} + 0 \longrightarrow 20_{2}$$

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The maximum rate of decomposition will be

$$-d[0_3]/dt = R_M = 2k_{18}[0_3]M$$

The rate of reaction with NO is

$$-d \boxed{0_3}/at = R_{NO} = k_{l_1} \boxed{0_3} \boxed{NO}$$
$$\cdots \qquad \frac{R_M}{R_{NO}} = \frac{2k_{18}}{k_{l_1}} \boxed{NO}$$

The expression for k_{18} , for M = He, is 2.6 x 10^{-9} exp(24,000/RT) cc./molecule/sec. (35). At 575°K, the highest temperature used in the present work, this is 1.8 x 10^{-18} cc./molecule/sec.

In the most unfavourable case, Experiment 77, we have

$$\frac{R_{\rm M}}{R_{\rm NO}} = \frac{(2)(1.8 \times 10^{-18})(354 \times 10^{15})}{(9 \times 10^{-14})(1.95 \times 10^{15})}$$

$$= 7 \times 10^{-3}$$

(G) Justification of the Steady-State Treatment:

In part, this requires

For a first approximation, we can write (pp.2,97),

$$\begin{bmatrix} NO_2^* \end{bmatrix}_{ss} = \frac{k_{l_1}^* \begin{bmatrix} O_3 \end{bmatrix} \boxed{NO}}{k_3 \begin{bmatrix} M \end{bmatrix}}$$
(XXVII)

In a typical room temperature case,

$$[M] = 9 \times 10^{16} \text{ molecules/cc.}$$

$$\begin{bmatrix} 0_3 \end{bmatrix} = \begin{bmatrix} NO \end{bmatrix} = 1.5 \times 10^{15} \text{ molecules/cc.}$$

$$k_{l_1}^{\#} = 7.8 \times 10^{-16} \text{ cc./molecules/sec.}$$

To estimate k₃, Clyne, Thrush and Wayne (12) derive a value of 5 x 10⁻¹⁶ cc./molecule for the ratio k₃/k₂ (M = N₂ or 0₂) from Baxter (102). If the radiative half-life of NO₂, $\mathcal{T}_{\frac{1}{2}}$, is of the order of 10⁻⁷ second, then k₂ is $\ln 2/\mathcal{T}_{\frac{1}{2}}$ or about 7 x 10⁶ sec.⁻¹

Hence k_3 is $l_1 \times 10^{-9}$ cc./molecule/sec., and substituting in (XXVII), we have

$$\frac{\left[N0^{*}_{2} \right]_{ss}}{\left[0^{3} \right]} = \frac{(7.8 \times 10^{-16})(1.5 \times 10^{15})}{(4 \times 10^{-9})(9 \times 10^{16})}$$
$$= 3 \times 10^{-9}$$

The steady-state treatment also assumes that

From (XXVII) we have

$$d\left[\operatorname{NO}_{2}^{*}\right]_{ss}/dt = \frac{k_{l_{1}}^{*}}{k_{3}\left[\operatorname{M}\right]} \cdot d\left[\operatorname{O}_{3}\right]^{2}/dt$$
$$= \frac{2k_{l_{1}}^{*}\left[\operatorname{O}_{3}\right]}{k_{3}\left[\operatorname{M}\right]} \cdot d\left[\operatorname{O}_{3}\right]/dt$$
$$\cdot \frac{d\left[\operatorname{NO}_{2}^{*}\right]_{ss}/dt}{d\left[\operatorname{O}_{3}\right]/dt} = 2\frac{\left[\operatorname{NO}_{2}^{*}\right]_{ss}}{\left[\operatorname{O}_{3}\right]}$$
$$= 6 \times 10^{-9}$$

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DATA FOR RUNS AT ROOM TEMPERATURE

Reaction time, seconds x 10^3
Ozone concentration, molecules/cc. x 10^{-15}
Nitric oxide concentration, molecules/cc. x 10-15
cc./molecule x 10 ¹⁶
$(molecules/cc.)^2 \times 10^{-30}$
Intensity of chemiluminescence, arbitary units, I.U.
$(molecules/cc.)^2/I.U. \times 10^{-28}$
Initial flowrate of nitric oxide,
Flowrate of inert carrier and quencher gases
Total pressure during reaction

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f^o_{NO}: 10.3 micromoles/sec.
f_{He}: 206 micromoles/sec.
P'_T: 2.61 torr

[He]: 74.5 x 10^{15} molecules/cc. [NO]₀: 3.73 x 10^{15} molecules/cc.

Linear velocity: 440 cm./sec.

t	A	A,	<u>1</u> A'
0	3.42	3.58	2.80
4.54	1.75	1.91	5.24
9.10	1.41	1.57	6.37
13.7	1.21	1.37	7.30
20.5	0.91	1.07	9.40
29.6	0.70	0.86	12
38.7	0.57	0.73	14
54.6	0.40	0.56	18
72.7	0.27	0.43	23

 f_{NO}^{o} : 10.9 micromoles/sec. **f**_{He}: 989 micromoles/sec.

[He]: 350×10^{15} molecules/cc.

P_T¹: 11.4 torr

Linear velocity: 451 cm./sec.

t	A	В	AB	$\frac{B}{A}$	$Log\frac{B}{A}$	٩١	1 A'	I _r	₫
0	3.26	3.86		1.19	0.074	3.56	2.81		
4.44	2.38	2.98	7.09	1.25	0.097	2.68	3.73	95	7.5
8.88	1.98	2.58	5.11	1.30	0.115	2.28	4.39	66	7.7
13.3	1.77	2.37	4.20	1.34	0.127	2.07	4.83	45	9.3
20.0	1.51	2.11	3.18	1.40	0.146	1.81	5.53	30	10.6
28.8	1.23	1.83	2.25	1.49	0.173	1.53	6.54	20	11.3
37.7	1.06	1.66	1.76	1.57	0.195	1.36	7.35	12	14.7
53.3	0.85	1.45	1.2	1.71	0.232	1.15	8.68	7.5	16.4
71.0	0.66	1.26	0.83	1.91	0.281	0.96	10.4	5.0	16.6

f^o_{NO}: ll.7 micromoles/sec.
f_{He}: l719 micromoles/sec.

[He]: 583×10^{15} molecules/cc.

 P_T^{L} : 18.8 torr

Linear Velocity: 472 cm./sec.

t	A	В	AB	$\frac{B}{A}$	$\text{Log}_{\overline{A}}^{\underline{B}}$	A'	<u>1</u> אי	I _r	₫
0	3.26	3.96		1.22	0.085	3.61	2.77		
4.24	2.26	2.96	6.68	1.31	0.117	2.61	3.84	58	11.6
8.47	1.87	2.57	4.80	1.37	0.138	2.22	4.51	4 1	11. ₉
12.7	1.57	2.27	3.56	1.45	0.160	1.92	5.21	30	11.8
19.1	1.27	1.97	2.50	1.55	0.190	1.62	6.18	20	12.4
27.6	1.10	1.80	1.98	1.64	0.214	1.45	6.90	12	16. ₈
36.0	0.85	1.55	1.3	1.8	0.26	1.20	8.33	8.2	16. ₁
50.8	0.64	1.34	0.86	2.1	0.32	0.99	10	5.0	17.2
67.8	0.49	1.19	0.59	2.4	0.38	0.84	12	3.2	¹⁸ .5

 f_{NO}^{o} : 11.3 micromoles/sec.

f_{He} : 1300 micromoles/sec.

[He]: 453×10^{15} molecules/cc.

P^I_T : 14.7 torr

Linear velocity: 457 cm./sec.

t	A	В	AB	B A	$log\frac{B}{A}$	A'	<u>1</u> <u>A</u> '	Ir	₫
0	3.12	3.94		1.26	0.101	3.53	2.84		
4.38	2.25	3.07	6.90	1.37	0.135	2.66	3.76	70	9.9
8.76	1.85	2.67	4.94	1. 44	0.159	2.26	4.42	48	10. ₄
13.1	1.56	2.38	3.71	1.53	0.184	1.97	5.07	35	10.6
19.7	1.28	2.10	2.69	1.64	0.215	1.69	5.92	23	11.6
28.4	1.03	1.85	1.91	1.85	0.268	1.44	6.94	13	14.2
37.2	0.87	1.69	1.5	1.9	0.29	1.28	7.82	9.1	16.2
52.5	0.60	1.42	0.85	2.4	0.37	1.01	9.90	5.6	15.2
70.0	0.48	1.30	0.62	2.7	0.43	0.89	11	3.6	17. ₁

 f_{NO}^{o} : 9.29 micromoles/sec.

f_{He} : 426 micromoles/sec.

 P_T^1 : 5.36 torr

 $[H_{\Theta}]$: 160 x 10¹⁵ molecules/cc.

Linear velocity: 422 cm./sec.

t	A	В	AB	$\frac{\mathbf{B}}{\mathbf{A}}$	$Log\frac{B}{A}$	A۱	<u>1</u> A'	I _r	Þ
ο	3.04	3.49		1.15	0.060	3.27	3.06		
4.74	2.07	2.52	5.22	1.22	0.086	2.30	4.35	160	3.26
9.48	1.71	2.16	3.70	1.26	0.101	1.94	5.16	110	3.36
14.2	1.46	1.91	2.79	1.31	0.117	1.69	5.92	79	3.5 ₃
21.3	1.26	1.71	2.15	1.36	0.132	1.49	6.72	49	4.3 ₈
30.8	1.04	1.49	1.55	1.43	0.156	1.27	7.87	33	4.76
40.3	0.87	1.32	1.2	1.5	0.18	1.1	9.1	23	5.0 ₂
56.9	0.71	1.16	0.82	1.6	0.21	0.94	11	13	6.3 ₅
75.8	0.56	1.01	0.57	1.8	0.26	0.79	13	8.5	6.7 ₀

 f_{NO}^{o} : ll.l micromoles/sec.

f_{He} : 743 micromoles/sec.

[He]: 271×10^{15} molecules/cc.

 P_{T}^{l} : 8.88 torr

Linear velocity: 438 cm./sec.

t	A	В	AB	B A	$Log\frac{B}{A}$	A۱	1 <u>1</u> ,	I _r	₫
0	3.25	4.04		1.24	0.094	3.65	2.74		
4.57	2.28	3.07	7.01	1.35	0.130	2.68	3.73	107	6.5 ₅
9.14	1.93	2.72	5.25	1.41	0.149	2.33	4.30	75	7.0 ₀
13.7	1.68	2.47	4.15	1.47	0.167	2.08	4.81	51	8.10
20.6	1.45	2.24	3.25	1.55	0.189	1.85	5.41	35	9.4 ₀
29.7	1.19	1.98	2.36	1.66	0.221	1.59	6.30	22	10.6
38.8	1.03	1.82	1.87	1.77	0.247	1.43	7.00	14	13.1
54.8	0.84	1.63	1.4	1.9	0.29	1.2	8.1	8.8	15.6
73.1	0.71	1.50	1.1	2.1	0.33	1.1	9.1	5.6	18.8

f⁰_{NO} : 10.2 micromole/sec.

 f_{N_2} : 1507 micromole/sec.

 P_{T}^{1} : 16.6 torr

 $[N_2]$: 507 x 10¹⁵ molecules/cc. Linear velocity: 473 cm./sec.

t	A	В	AB	B A	$\mathbf{Log}_{\overline{\mathbf{A}}}^{\mathrm{B}}$	A'	<u>1</u> A'	1 _r	Ē
о	2.63	3.43		1.30	0.115	3.03	3.30		
4.24	2.14	2.94	6.30	1.37	0.138	2.54	3.94	31	20.4
8.47	1.85	2.65	4.90	1.43	0.156	2.25	4.45	23	21. ₄
12.7	1.55	2.35	3.64	1.52	0.181	1.95	5.13	18	20.2
19.0	1.24	2.04	2.53	1.65	0.216	1.64	6.10	13	20.1
27.5	0.94	1.74	1.63	1.85	0.267	1.34	7.47	8.1	20.1
36.0	0.79	1.59	1.24	2.02	0.305	1.19	8.44	5.6	²² ·1
50.8	0.58	1.38	0.81	2.4	0.38	0.98	10	3.2	25.2
67.7	0.µµ	1.24	0.54	2.8	0.45	0.84	12	1.9	28.3

8.13 micromoles/sec. f_{NO}^{o} :

f_{N2}: P₁: 713 micromoles/sec.

8.28 torr

 $[N_2]$: 250 x 10¹⁵ molecules/cc.

Linear velocity: 454 cm./sec.

t	A	В	AB	A۱	<u>1</u> A'	I _r	₫
0	2.94	2.85		2.89	3.46		
4.41	2.27	2.18	4.94	2.22	4.51	65	7.6 ₀
8.82	1.86	1.77	3.29	1.81	5.53	48	6.9 ₂
13.2	1.66	1.57	2.61	1.61	6.21	35	7.4 ₀
19.8	1.42	1.33	1.89	1.37	7.30	24	8.0 ₁
28.7	1.22	1.13	1.38	1.17	8,55	14	10.1
37.5	1.07	0.98	1.05	1.02	9.8	9.2	11. ₄
52.8	0.88	0.79	0.70	0.83	12	5.4	13.0
70.6	0.79	0.70	0.55	0.76	13	3.1	17.6

f^o_{NO}: 8.07 micromoles/sec.

f_{N2}: 338 micromoles/sec. P³/_T: 4.13 torr

 $[N_2]$: 122 x 10¹⁵ molecules/cc.

Linear velocity: 443 cm./sec.

t	A	В	AB	A B	$Log\frac{A}{B}$	A۱	<u>1</u> A'	1 _r	₫
0	3.19	2.91		1.10	0.039	3.05	3.29		
4.52	1.98	1.70	3.36	1.17	0.066	1.84	5.44	171	1.96
9.03	1.74	1.46	2.54	1.19	0.076	1.60	6.25	121	2.1 ₀
13.5	1.56	1.28	2.00	1.22	0.086	1.42	7.04	84	2.3 ₈
20.3	1.36	1.08	1.47	1.26	0.100	1.22	8.20	48	3.1 ₀
29.4	1.16	0.88	1.02	1.32	0.120	1.02	9.80	29	3.5 ₁
38.4	1.02	0.74	0.76	1.3 ₈	0.14	0.88	11.	18	4.17
54.2	0.92	0.64	0.59	1.4 ₄	0.16	0.78	13.	11	5.26
72.3	0.83	0.55	0.46	1.5 ₁	0.18	0.69	15.	8.0	5.7 ₃

f⁰_{NO}: 10.2 micromoles/sec.

f_{Ar}: 1545 micromoles/sec.

 P_T^1 : 17.2 torr

[Ar]: 513 x 10^{15} molecules/cc.

Linear velocity: 480 cm./sec.

t	A	В	AB	B A	$Log\frac{B}{A}$	A'	<u>1</u> A'	Ir	₫
0	2.96	3.39		1.15	0.059	3.18	3.15		
4.17	2.10	2.53	5.32	1.21	0.081	2.32	4.31	48	11.2
8.33	1.92	2.35	4.52	1.22	0.088	2.14	4.68	36	12.5
12.5	1.64	2.07	3.40	1.26	0.101	1.86	5.38	29	11.7
18.8	1.37	1.80	2.47	1.31	0.119	1.59	6.30	21	11.8
27.1	1.09	1.52	1.66	1.40	0.145	1.31	7.64	14	12.2
35.4	0.90	1.33	1.2	1.5	0.17	1.12	8.93	8.6	14.0
50.0	0.65	1.08	0.70	1.7	0.22	0.87	12	5.1	13.6
67.7	0.51	0.94	0.48	1.8	0.27	0.73	14	3.2	14.9

f^o_{NO}: 9.22 micromoles/sec.

f_{Ar}: 237 micromoles/sec.

 P_{T}^{l} : 3.27 torr

 $[Ar]: 90.2 \times 10^{15}$ molecules/cc.

Linear velocity: 418 cm./sec.

t	A	В	AB	A۱	1 A'	Ir	₫
0	3.36	3.51		3.44	2.91		
4.78	1.87	2.02	3.77	1.95	5.13	598	0.63
9.56	1.42	1.57	2.23	1.50	6.67	358	0.62
14.4	1.22	1.37	1.67	1.30	7.70	178	0.94
21.5	1.03	1.18	1.21	1.11	9.01	83	1.46
31.1	0.89	1.04	0.94	0.97	11	38	2.45
40.6	0.75	0.90	0.68	0.83	12	24	2.85
57.4	0.63	0.78	0.48	0.71	14	12	3.9 ₄
76.5	0.49	0.64	0.31	0.57	18	7.3	4.25

f^o_{NO}: 9.90 micromoles/sec.

f_{Ar}: 1059 micromoles/sec.

 P_{T}^{l} : 12.1 torr

[Ar]: 358 x 10¹⁵ molecules/cc. Linear velocity: 471 cm./sec.

t	A	В	AB	B A	$Log\frac{B}{A}$	A۱	<u>1</u> <u>A</u> '	Ir	₫
0	2.94	3.34		1.14	0.055	3.14	3.19		
4.25	1.86	2.26	4.20	1.22	0.086	2.06	4.86	77	5.46
8.50	1.55	1.95	3.02	1.26	0.100	1.75	5.72	57	5.3 ₁
12.8	1.33	1.73	2.30	1.30	0.114	1.53	6.54	կկ	5.3 ₀
19.1	1.05	1.45	1.52	1.38	0.140	1.25	8.00	29	5.26
27.6	0.86	1.26	1.2	1.46	0.17	1.06	9.44	16	7• ² 3
36.1	0.74	1.14	0.84	1.5 ₄	0.19	0.94	11	11	7•9 ₇
51.0	0.54	0.94	0.51	1.7	0.24	0.74	14	5.9	8.66
68.0	0.45	0.85	0.38	1.9	0.28	0.65	15	3.3	11.5

f^o_{NO}: 8.38 micromoles/sec.

f_{Ar}: 662 micromoles/sec.

[Ar]: 230 x 10^{15} molecules/cc.

 P_{T}^{1} : 7.84 torr

Linear velocity: 458 cm./sec.

t	A	В	AB	A'	1 A'	I _r	₫
0	2.78	2.91		2.85	3.51		
4.37	1.99	2.12	4.22	2.06	4.86	106	3.9 ₈
8.74	1.68	1.81	3.04	1.75	5.72	82	3.7 ₁
13.1	1.41	1.54	2.17	1.48	6.76	60	3.6 ₁
19.7	1.24	1.37	1.70	1.31	7.64	37	4.73
28.4	1.02	1.15	1.17	1.09	9.17	22	5.27
37.2	0.87	1.00	0.86	0.94	11	13	6.62
52.4	0.70	0.83	0.58	0.77	13	7.2	8.06
69.8	0.61	0.74	0.45	0.68	15	4.4	10.2

f^o_{NO}: 8.92 micromoles/sec. f_{He}: 126 micromoles/sec. f_{CO2}: 75.1 micromoles/sec. P¹_T: 2.70 torr

EXPERIMENT 50

 $\begin{bmatrix} CO_2 \end{bmatrix}$: 28.0 x 10¹⁵ molecules/cc. [He]: 47.1 x 10¹⁵ molecules/cc.

Linear velocity: 426 cm./sec.

t	A	В	AB	A'	$\frac{1}{A'}$	I _r	₫
0	3.23	3.33		3.28	3.05		
4.70	1.77	1.87	3.31	1.82	5.50	236	1.4 ₀
9.40	1.54	1.64	2.53	1.59	6.28	129	1.96
14.1	1.36	1.46	1.99	1.41	7.09	83	2.4 ₀
21.2	1.13	1.23	1.39	1.18	8.48	48	2.90
30.5	0.90	1.00	0.90	0.95	11.5	29	3.12
39.9	0.76	0.86	0.65	0.81	12	20	3.27
56.4	0.59	0.69	0.40	0.64	16	11	3.7 ₉
75.1	0.43	0.53	0.22	0.48	21	6.6	3.3 ₈

f⁰_{NO}: 10.4 micromoles/sec.
f_{He}: 229 micromoles/sec.
f_{CO2}: 1585 micromoles/sec.
P¹_T : 19.9 torr

 $\begin{bmatrix} C_0 \\ 2 \end{bmatrix}: 523 \times 10^{15} \text{ molecules/cc.}$ $\begin{bmatrix} H_0 \\ 2 \end{bmatrix}: 75.5 \times 10^{15} \text{ molecules/cc.}$

Linear velocity: 482 cm./sec.

t	A	В	AB	A۱	<u>1</u> אי	Ir	₫
0	3.52	3.49		3.50	2.86		
4.15	2.40	2.37	5.69	2.38	4.20	16	35.0
8.30	2.30	2.27	5.23	2.28	4.39	12	42.8
12.5	1.98	1.95	3.86	1.96	5.11	9.6	40.2
18.7	1.66	1.63	2.71	1.64	6.10	6.8	39 . 9
27.0	1.35	1.32	1.78	1.33	7.52	4.5	39.6
35.3	1.10	1.07	1.18	1.08	9.26	3.0	39.4
49.8	0.87	0.84	0.73	0.85	12	1.6	⁴⁴ •7
66.4	0.74	0.71	0.52	0.72	14	0.90	57.5

f^o_{NO}: 9.47 micromoles/sec.
f_{He} : 134 micromoles/sec.
f_{CO2}: 600 micromoles/sec.
P^I_T : 8.63 torr

 $\begin{bmatrix} CO_2 \end{bmatrix}$: 207 x 10¹⁵ molecules/cc. [He]: 46.1 x 10¹⁵ molecules/cc.

Linear velocity: 462 cm./sec.

t	A	В	AB	A۱		I _r	₫
0	3.11	3.26		3.19	3.14		
4.34	2.25	2.40	5.40	2.33	4.30	43	12.5
8.67	1.87	2.02	3.78	1.95	5.12	32	11.7
13.0	1.62	1.77	2.87	1.70	5.88	24	12.0
19.5	1.37	1.52	2.08	1.45	6.90	15	14·3
28.2	1.13	1.28	1.45	1.21	8.27	8.8	16.5
36.8	0.94	1.09	1.03	1.02	9.80	5.7	18.1
52.0	0.80	0.95	0.75	0.88	11	3.2	23.6
69.3	0.71	0.86	0.61	0.79	13	1.9	32.8

f^o_{NO}: 10.2 micromoles/sec.
f_{He}: 134 micromoles/sec.
f_{CO2}: 1160 micromoles/sec.
P¹_T: 14.4 torr

 $\begin{bmatrix} CO_2 \end{bmatrix}$: 386 x 10¹⁵ molecules/cc. [He]: 44.6 x 10¹⁵ molecules/cc.

Linear velocity: 478 cm./sec.

t	A	В	AB	B A	$Log\frac{B}{A}$	A'	<u>1</u> A'	I _r	₫
0	3.05	3.40		1.11	0.047	3.33	3.00		
4.19	2.19	2.54	5.56	1.16	0.065	2.37	4.22	20	27.4
8.38	1.90	2.25	4.28	1.18	0.073	2.08	4.81	15	28.0
12.6	1.62	1.97	3.20	1.21	0.085	1.80	5.55	12	26.4
18.8	1.33	1.68	2.24	1.26	0.101	1.51	6.63	8.3	27.0
27.2	1.04	1.39	1.45	1.34	0.127	1.22	8.20	5.5	26.4
35.6	0.86	1.21	1.05	1.41	0.148	1.04	9.60	3.7	28.2
50.3	0.70	1.05	0.74	1.5	0.18	0.88	11	2.1	34.7
67.0	0.54	0.89	0.49	1.6	0.22	0.72	14	1.1	42.9

 f_{NO}^{o} : 10.7 micromoles/sec. f_{He} : 145 micromoles/sec. f_{N2}0: 1625 micromoles/sec. P_T^1 : 19.2 torr

 $[N_20]$: 534 x 10¹⁵ molecules/cc. [He]: 47.6 x 10^{15} molecules/cc.

Linear velocity: 483 cm./sec.

t	A	В	AB	A۱	$\frac{1}{A}$	I _r	₫
0	3.25	3.50		3.38	2.96		
4.14	2.34	2.59	6.06	2.47	4.05	16	38.8
8.28	2.14	2.39	5.12	2.27	4.41	12	43.8
12.4	1.86	2.11	3.92	1.99	5.03	9.5	51.8
18.6	1.53	1.78	2.72	1.69	5.92	6.9	39.4
26.9	1.21	1.46	1.77	1.34	7.47	4.7	37. ₇
35.2	0.91	1.16	1.06	1.04	9.58	3.1	34.3
49.7	0.75	1.00	0.74	0.88	11	1.7	42.9
66.3	0.57	0.82	0.47	0.60	17	1.0	47.4

 f_{NO}^{o} : 9.12 micromoles/sec.

 f_{He} : 136 micromoles/sec.

f_{N2}0: 74.9 micromoles/sec.

 P_T^l : 2.77 torr

 N_2]: 27.8 x 10¹⁵ molecules/cc. He]: 50.5 x 10¹⁵ molecules/cc.

Linear velocity: 429 cm./sec.

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1.9 ₇
2.21
2.29
2.71
2.99
3.3 ₈
3.43
3.61

ron:	8.18 micromoles/sec.
f _{He} :	130 micromoles/sec.
r _{N2} 0:	645 micromoles/sec.
	8.80 torr

 \mathbb{N}_{2} : 216 x 10¹⁵ molecules/cc. He: 43.6 x 10¹⁵ molecules/cc.

Linear velocity: 474 cm./sec.

t	A	В	AB	A B	$Log\frac{A}{B}$	A'	<u>1</u> A'	I _r	₫
0	3.07	2.74		1,12	0.049	2.90	3.45		
4.22	2.16	1.83	3.95	1.18	0.072	1.99	5.03	35	11.2
8.44	1.86	1.53	2.84	1.22	0.085	1.69	5.92	27	10.2
12.6	1.49	1 .1 6	1.73	1.29	0.109	1.32	7.58	21	8.3
19.0	1.24	0.91	1.13	1.4	0.14	1.07	9.35	13	8.8
27.4	1.03	0.70	0.72	1.5	0.17	0.86	12	8.0	9.0
35.9	0.79	0.46	0.36	1.7	0.24	0.62	16	5.5	6.6
50.7	0.71	0.38	0.27	1.9	0.27	0.54	18	3.0	9.1
67.5	0.59	0.26	0.16	2.3	0.35	0.42	24	1.7	9.1

f^o_{NO}: 10.2 micromoles/sec.
f_{He}: 131 micromoles/sec.

f_{N20}: 1140 micromoles/sec.
P_T¹: 13.8 torr

 $[N_20]$: 374 x 10¹⁵ molecules/cc. [He]: 43.0 x 10¹⁵ molecules/cc.

Linear velocity: 486 cm./sec.

t	A	В	AB	B A	$\log \frac{B}{A}$	A۱	$\frac{1}{A}$	I _r	₫
0	2.99	3.34		1.12	0.048	3.17	3.16		
4.12	2.19	2.54	5.56	1.16	0.065	2.37	4.22	21	27.0
8.24	1.90	2.25	4.28	1.18	0.073	2.08	4.81	16	27.3
12.3	1.61	1.96	3.16	1.22	0.086	1.79	5.60	12	25.9
18.5	1.26	1.61	2.03	1.28	0.107	1.44	6.95	8.5	23.9
26.7	1.01	1.36	1.37	1.35	0.130	1.19	8.41	5.6	26.6
35.0	0.87	1.22	1.07	1.4	0.15	1.05	9.50	3.7	29 . 2
49.4	0.66	1.01	0.67	1.5	0.19	0.84	10	21	31.4
65.8	0,53	0.88	0.46	1.7	0.22	0.71	11	1.3	35.4

 f_{NO}^{o} : 9.73 micromoles/sec.

f_{He} : 108 micromoles/sec.
f_{SF6}: 66 micromoles/sec.

 P_{T}^{1} : 2.43 torr

SF₆: 25.4 x 10^{15} molecules/cc. [He]: 41.6 x 10^{15} molecules/cc.

Linear velocity: 418 cm./sec.

t	A	В	AB	B A	$Log\frac{B}{A}$	A۱	$\frac{1}{A}$,	Ir	₫
0	3.31	3.75		1.13	0.054	3.53	2.84		
4.77	1.84	2.28	4.19	1.24	0.093	2.06	4.86	206	2.03
9.54	1.40	1.84	2.58	1.31	0.119	1.62	6.17	125	2.07
14.3	1.13	1.57	1.77	1.39	0.143	1.35	7.41	85	2.08
21.5	0.91	1.35	1.22	1.5	0.17	1.13	8.88	48	2.5 ₅
31.0	0.76	1.20	0.91	1.6	0.20	0.98	10	26	3.47
40.6	0,56	1.00	0.56	1.8	0.25	0.78	13	18	3.1 ₆
57.3	0.37	0.81	0.29	2.2	0.34	0.59	17	10	2.9 ₄
76.4	0.23	0.67	0.15	2.9	0.46	0.45	22	6	2.5 ₅

f^o_{NO}: 10.3 micromole/sec.
f_{He}: 109 micromole/sec.
f_{SF6}: 482 micromole/sec.

 P_T^1 : 7.27 torr

 $[SF_6]: 177 \times 10^{15} \text{ molecules/cc.}$ [He]: 40.1 x 10¹⁵ molecules/cc. Linear velocity: 433 cm./sec.

t	A	В	AB	B A	$\operatorname{Log}_{\overline{\mathbf{A}}}^{\operatorname{B}}$	1 _r	₫
0	2.73	3.79		1.39	0.143		
4.62	1.87	2.93	5.48	1.57	0.195	27	20.2
13.9	1.21	2.27	2.75	1.88	0.273	13	20.7
30.0	0.97	2.03	1.0	2.1	0.32	5.3	18.8
55.4	0.32	1.38	0.44	4.3	0.64	1.0	44

- f_{NO}^{o} : 10.4 micromoles/sec.
- \mathbf{f}_{He} : 110 micromoles/sec.
- f_{SF6}: 940 micromoles/sec.
- P_T^1 : 12.7 torr

SF₆: 345 x 10¹⁵ molecules/cc. Hel: 40.4 x 10¹⁵ molecules/cc.

Linear velocity: 435 cm./sec.

t	A	В	AB	B A	$\log \frac{B}{A}$	I _r	Þ
0	2.99	3.80		1.27	0.105		
4.61	2.13	2.94	6.26	1.38	0.140	16	40.1
13.8	1.58	2.39	3.78	1.51	0.179	9.1	41.6
30.0	0.97	1.78	1.73	1.8	0.26	4.7	36. ₈
55.3	0.51	1.32	0.67	2.6	0.41	2.3	29. ₁

- f_{NO}^{o} : 11.1 micromoles/sec.
- f_{He} : 110 micromoles/sec.
- fsr: 1320 micromoles/sec.
- PT : 17.3 torr

 $[SF_6]$: 486 x 10¹⁵ molecules/cc. [He]: 40.4 x 10¹⁵ molecules/cc.

t	A	В	AB	B A	$\log \frac{B}{A}$	I _r	₫
0	3.06	4.08		1.33	0.125		
4. 64	2.24	3.26	7.30	1.45	0.163	11	65.7
13.9	1.44	2.46	3.55	1.71	0.232	5.2	68.3
30.2	0.89	1.91	1.69	2.2	0.33	1.9	89.0
55.7	0.48	1.50	0.72	3.1	0.50	0.54	132

Linear velocity: 431 cm./sec.

RATE CONSTANT DATA FOR RUNS AT ELEVATED TEMPERATURES

t:	Reaction time, seconds x 10^3
A, A':	Ozone concentrations, molecules/cc. x 10^{-15}
1/A':	Reciprocal concentrations, cc./molecule x 10^{16}
f ^o NO:	Initial flowrate of nitric oxide
f _{He} :	Flowrate of helium as carrier-quencher
P' : T	Total pressure during reaction
T _R :	Reaction temperature
T _{EXT} .:	Temperature beyond furnace
Т.:	Temperature of ozone measurement

 f_{NO}^{o} : 10.8 micromoles/sec. T_{R} : 377°K f_{He} : 1935 micromoles/sec. T_{o} : 302°K P_{T}^{i} : 21.1 torr T_{EXT} : 340°K

[He] at T_R : 530 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 575 cm./sec. at T_{EXT} : 519 cm./sec.

 $[NO]_{O}$ at T_R: 2.97 x 10¹⁵ molecules/cc.

Temperature		Тo		TR	
Distance cm.	t	A	A	A'	<u>1</u> אי
0	0	3.52	2.81	2.89	3.46
2	3.86	2.35	1.88	1.96	5.10
7	13.5	1.50	1.20	1.26	7.94
15	29.0	0.92	0.73	0.81	12.3
25	46.4	0.64	0.51	0.59	17.0
48	86.4	0.35	0.28	0.36	28.0

f _{NO} :	9.19 micromoles/sec.	T _R :	379°K
f _{He} :	429 micromoles/sec.	т _о :	298°K
P_T^1 :	5.16 torr	T _{EXT} :	339°K

He at T_R : 126 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 541 cm./sec. at T_{EXT} : 485 cm./sec.

 $[NO]_{o}$ at T_{R} : 2.72 x 10¹⁵ molecules/cc.

Temperature	т _о		T _R	
t	A	A	A1	<u>1</u> A'
0	3.36	2.65	2.69	3.72
4.18	2.08	1.64	1.68	5.96
14.6	1.45	1.14	1.18	8.48
31.3	0.92	0.73	0.77	13.1
49.8	0.57	0.45	0.49	20.5
92.4	0.30	0.23	0.27	36.8

 f_{NO}^{o} : 9.05 micromoles/sec. T_{R} : 382°K f_{He} : 906 micromoles/sec. T_{o} : 295°K P_{T}^{l} : 10.4 torr T_{EXT} : 339°K

[He] at T_R : 258 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 558 cm./sec. at T_{EXT} : 496 cm./sec.

 $[NO]_{o}$ at T_{R} : 2.58 x 10¹⁵ molecules/cc.

Temperature	Т _о		T_{R}	
t	A	A	A۱	<u>1</u> אי
0	3.69	2.84	2.71	3.69
4.02	2.44	1.87	1.74	5.75
14.1	1.73	1.33	1.20	8.33
30.2	1.19	0.92	0.79	12.7
48.1	0.82	0.63	0.50	19.8
89.2	0.64	0.49	0.36	27.6

 f_{NO}^{o} : 10.6 micromoles/sec. T_{R} : 382°K f_{He} : 1408 micromoles/sec. T_{o} : 296°K P_{T}^{i} : 15.8 torr T_{EXT} : 340°K

[He] at T_R : 394 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 568 cm./sec. at T_{EXT} : 506 cm./sec.

 $[NO]_{o}$ at T_{R} : 2.96 x 10¹⁵ molecules/cc.

Temperature	To		Τ _R	
t	A	A	A1	1 A'
0	3.45	2.67	2.82	3.55
3.96	2.21	1.71	1.86	5.38
13.9	1.53	1.18	1.33	7.52
29.7	0.92	0.71	0.86	11.6
47.3	0.61	0.48	0.63	16.0
87.7	0.27	0.21	0.36	27.9

> Linear velocities: at T_R : 658 cm./sec. at T_{EXT} : 527 cm./sec.

 $[NO]_{O}$ at T_{R} : 2.25 x 10¹⁵ molecules/cc.

Temperature	Т _о		TR	
t	A	A	A۱	<u>1</u> A'
0	3.36	2.06	2.16	4.63
3.88	2.41	1.48	1.58	6.33
13.6	1.68	1.03	1.13	8.85
29.1	1.12	0.69	0.79	12.7
44.3	0.68	0.42	0.52	19.3
79.3	0.50	0.30	0.40	24.8
f_{NO}^{o} : 8.98 micromoles/sec.
 T_{R} : 496°K

 f_{He} : 826 micromoles/sec.
 T_{o} : 298°K

 P_{T}^{l} : 10.3 torr
 T_{EXT} : 397°K

[He] at T_R : 197 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 663 cm./sec. at T_{EXT} : 530 cm./sec.

 $[NO]_o$ at T_R : 2.15 x 10¹⁵ molecules/cc.

Temperature	To		TR	
t	A	A	A۱	<u>1</u> A'
0	3.44	2.08	2.12	4.72
3.77	2.35	1.42	1.46	6.85
13.2	1.75	1.05	1.09	9.17
28.3	1.04	0.63	0.67	15.0
43.2	0.72	0.44	0.48	21.1
77.5	0.58	0.35	0.39	25.9

 f_{NO}^{o} : 10.0 micromoles/sec. T_{R} : 495°K f_{He} : 1337 micromoles/sec. T_{o} : 298°K P_{T}^{I} : 15.1 torr T_{EXT} : 397°K

[He] at T_R : 289 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 935 cm./sec. at T_{EXT} : 750 cm./sec.

 $[NO]_{o}$ at T_{R} : 2.17 x 10¹⁵ molecules/cc.

Temperature	Тo		${}^{T}R$	
t	A	A	A1	<u>1</u> A'
0	3.40	2.04	2.11	4.74
2.72	2.19	1.31	1.38	7.25
9.52	1.50	0.90	0.97	10.3
20.4	0.94	0.57	0.64	15.7
31.1	0.59	0.36	0.43	23.6
55.8	0.40	0.24	0.31	32.6

 f_{NO}^{o} : 11.5 micromoles/sec.
 T_{R} : 575°K

 f_{He} : 1904 micromoles/sec.
 T_{o} : 301°K

 P_{T}^{I} : 20.7 torr
 T_{EXT} : 438°K

[He] at T_R : 400 x 10¹⁵ molecules/cc.

Linear velocities: at ${\tt T}_{\rm R}$: 758 cm./sec. at ${\tt T}_{\rm EXT}$: 578 cm./sec.

 $[NO]_{o}$ at T_{R} : 2.41 x 10¹⁵ molecules/cc.

Temperature	To		Τ _R	
t	A	A	A۱	<u>1</u> A'
0	3.15	1.91	2.16	4.63
3.31	2.01	1.22	1.47	6.80
11.6	1.27	0.77	1.02	9.80
24.8	0.63	0.38	0.63	15.8
38.0	0.30	0.18	0.43	23.2
68.4	0.15	0.092	0.34	29.2

 f_{NO}^{o} : 8.89 micromoles/sec. T_{R} : 575°K f_{He} : 426 micromoles/sec. T_{o} : 298°K P_{T}^{I} : 5.20 torr T_{EXT} : 437°K

[He] at T_R : 83.7 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 806 cm./sec. at T_{EXT} : 613 cm./sec.

 $[NO]_{o}$ at T_{R} : 1.73 x 10¹⁵ molecules/cc.

ire	Т _о		$T_{\rm R}$	<u> </u>
t	A	A	A'	<u>]</u> A'
0	3.43	1.80	1.76	5.69
11.5	1.71	0.90	0.86	11.6
24.6	0.93	0.49	0.45	22.3
44.4	0.54	0.29	0.25	40.8
65.5	0.47	0.24	0.20	49.0
	t 0 11.5 24.6 44.4 65.5	To t A 0 3.43 11.5 1.71 24.6 0.93 44.4 0.54 65.5 0.47	T_0 T_0 tA03.4311.51.710.9024.60.930.4944.40.540.2965.50.470.24	Ire T_0 T_R tAA'03.431.801.7611.51.710.900.8624.60.930.490.45 44.4 0.540.290.2565.50.470.240.20

 f_{NO}^{o} : 9.52 micromoles/sec. T_{R} : 575°K f_{Ho} : 802 micromoles/sec. T_{o} : 298°K P_{T}^{i} : 9.79 torr T_{EXT} : 437°K

[He] at T_R : 161 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 792 cm./sec. T_{EXT} : 602 cm./sec.

 $[NO]_{o}$ at T_{R} : 1.91 x 10¹⁵ molecules/cc.

Temperat	ure	To		Τ _R	······································
Distance cm.	t	A	A	A۱	<u>1</u> אי
0	0	3.17	1.63	1.77	5.65
7	11.7	1.87	0.68	0.82	12.2
15	25.2	1.19	0.33	0.48	21.0
31	45.4	0.74	0.11	0.25	40.8

 f_{NO}^{o} : 6.77 micromoles/sec. T_{R} : 574°K f_{He} : 1299 micromoles/sec. T_{o} : 299°K P_{T}^{I} : 14.7 torr T_{EXT} : 437°K

[He] at T_R : 244 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 846 cm./sec. at T_{EXT} : 645 cm./sec. NO₀ at T_R : 1.27 x 10¹⁵ molecules/cc.

ıre	Т _о		TR	
t	A	A	A1	<u>ן</u> אי
0	2.68	1.40	1.33	7.52
11.0	1.77	0.93	0.86	11.7
23.6	1.09	0.57	0.50	20.0
42.5	0.43	0.22	0.15	65.8
	t 0 11.0 23.6 42.5	To t A 0 2.68 11.0 1.77 23.6 1.09 42.5 0.43	To To t A A 0 2.68 1.40 11.0 1.77 0.93 23.6 1.09 0.57 42.5 0.43 0.22	T_0 T_R tAA'02.681.401.3311.01.770.930.8623.61.090.570.5042.50.430.220.15

f ^o N0:	10.8	micromoles/sec.	T _R :	575 ⁰ к
f _{He} :	1918	micromoles/sec.	T _o :	299 ⁰ K
P_T^1 :	21.1	torr	T _{EXT} :	437 ⁰ к

[He] at T_R : 350 x 10¹⁵ molecules/cc.

Linear velocities: at T_R : 870 cm./sec. at T_{EXT} : 662 cm./sec.

 $[NO]_{o}$ at T_{R} : 1.95 x 10¹⁵ molecules/cc.

Temperature		Т _о		T _R	
Distance cm.	t	A	A	A'	<u>1</u> אי
0	0	3.50	1.83	1.89	5 .3 0
7	10.7	1.16	0.61	0.67	15.0
15	22.9	0.66	0.34	0.40	24.8
31	41.3	0.40	0.21	0.27	37.4

BIBLIOGRAPHY

1.	Johnston, H.S. and Crosby, H.J., J. Chem. Phys., 22, 689 (1954)
2.	Ford, H.W., Endow, N. and Doyle, G.J., J. Chem. Phys. <u>26</u> , 1337 (1957)
3.	Borok, M.T., Russian J. Phys. Chem. <u>34</u> , 129 (1960)
4.	Borok, M.T., Russian J. Phys. Chem. <u>35</u> , 1123 (1961)
5.	Johnston, H.S. and Crosby, H.J., J. Chem. Phys. <u>19</u> , 799 (1951)
6.	Goyer, G.G., Can. J. Chem. <u>34</u> , 1730 (1956)
7.	Tanaka, Y. and Shimayu, M., J. Sci. Res. Inst. (Tokyo) 43, 241 (1949)
8.	Altshuller, A.P., J. Phys. Chem. <u>61</u> , 251 (1957)
9.	Herschbach, D.R. and Johnston, H.S., J. Chem. Phys. 25, 736 (1956)
10.	Greaves, J.C. and Garvin, D., J. Chem. Phys. 30, 348 (1949)
11.	Marte, J.E., Tschuikow-Roux, E. and Ford, H.W., J. Chem. Phys. <u>39</u> , 3277 (1963)
12.	Clyne, M.A.A., Thrush, B.A. and Wayne, R.P., Trans. Far. Soc. <u>60</u> , 359 (1964)
13.	Strutt, R.J., Proc. Phys. Soc. <u>23</u> , 66 (1910)
14.	Spealman, M.L. and Rodebush, W.H., J. Amer. Chem. Soc. <u>57</u> , 1474 (1935)
15.	Stoddart, E.M., Proc. Roy. Soc. <u>147A</u> , 454 (1934)
16.	Newman, J.H., Phil. Mag. <u>20</u> , 777 (1935)
17.	Thompson, J.J., Phil. Mag. <u>32</u> , 321 (1891)
18.	Phillips, L.F. and Schiff, H.I., J. Chem. Phys. <u>36</u> , 1509 (1962)
19.	Furnival, S.G., M. Sc. thesis, McGill University, 1965.
20.	Reeves, R.R., Harteck, P. and Chace, W.H., J. Chem. Phys. <u>41</u> , 764 (1964)
21.	Kaufman, F., Proc. Roy. Soc. <u>247A</u> , 123 (1958)

- 22. Clyne, M.A.A. and Thrush, B.A., Proc. Roy. Soc. <u>269A</u>, 404 (1962)
- 23. Fontijn, A., Meyer C.B. and Schiff, H.I., J. Chem. Phys. <u>40</u>, 64 (1964)
- 24. Broida, H.P., Schiff, H.I. and Sugden, T.M., Trans. Far. Soc. <u>57</u>, 259 (1961)
- 25. Lewis, B., J. Amer. Chem. Soc. <u>51</u>, 665 (1929)
- 26. Herzberg, G., Zeit. für Phys. <u>46</u>, 878 (1928)
- 27. Kaufman, F., J. Chem. Phys. <u>28</u>, 352 (1958)
- 28. Kondratiev, V., Phys. Zeit. d. Sowjetunion <u>11</u>, 320 (1937)
- 29. Benson, S.W., The Foundations of Chemical Kinetics, McGraw-Hill, 1960.
- 30. Cook, G.A., Kiffer, A.D., Klumpp, C.V., Malik, A.H. and Spence, L.A., Advances in Chemistry Series <u>21</u>, 44 (1959)
- 31. Kobozev, N.I., Eremin, E.N., Terekhova, M.G. and Mal'tsev, A.N., Russian J. Phys. Chem. <u>34</u>, 899 (1960)
- 32. Thorp, C.E., <u>Bibliography of Ozone Technology</u>, two volumes, Armour Research Foundation, 1955
- 33. Noyes, W.A. and Leighton, P.A., <u>The Photochemistry of</u> <u>Gases</u>, American Chemical Society Monograph, 1941.
- 34. Zaslowsky, J.A., Urbach, H.B., Leighton, F., Wnuk, R.J. and Wojtowicz, J.A., J. Amer. Chem. Soc. <u>82</u>, 2682 (1960)
- 35. Benson, S.W. and Axworthy, A.E., J. Chem. Phys. <u>26</u>, 1718 (1957)
- 36. Kobozev, N.I., Eremin, E.N. and Nekrasov, L.I., Zhur. Fiz. Khim. <u>30</u>, 2580 (1956)
- 37. Martinez, F., Urbach, H.B. and Zaslowsky, J.A., J. Phys. Chem. <u>67</u>, 714 (1963)
- 38. Giguere, P.A. and Chin, D., J. Chem. Phys. <u>31</u>, 1685 (1959)
- 39. Lamneck, Jr., J.H., J. Chem. Eng. Data 5, 233 (1960)
- 40. Edgar, J.L. and Paneth, F.A., J. Chem. Soc. <u>1941</u>, 511
- 41. Kaufman, F., private communication
- 42. Garvin, D., J. Amer. Chem. Soc. 76, 1523 (1954)

- 43. Wulf, O.R., Daniels, F. and Karrer, S., J. Amer. Chem. Soc. <u>44</u>, 2398 (1922)
- Ц4. Johnston, H.S. and Yost, D.M., J. Chem. Phys. <u>17</u>, 386 (1949)
- 45. Ford, H.W., Doyle, G.J. and Endow, N., J. Chem. Phys. 26, 1336 (1957)
- 46. Schumacher, H.-J. and Sprenger, G., Zeit. Anorg. Chem. 182, 139 (1929)
- 47. McGrath, W.D. and Norrish, R.G.W., Proc. Roy. Soc. <u>254A</u>, 317 (1960)
- 48. Schumacher, H.-J., J. Amer. Chem. Soc. <u>52</u>, 2377 (1930)
- 49. Kistiakowsky, G.B., Z. Physik. Chem. <u>117</u>, 337 (1925)
- 50. Schumacher, H.-J., Z. Physik. Chem. <u>B17</u>, 405 (1932)
- 51. Schumacher, H.-J., and Beretta, U., Z. Physik. Chem. B17, 417 (1932)
- 52. Heidt, L.J. and Forbes, G.S., J. Amer. Chem. Soc. <u>56</u>, 2365 (1934)
- 53. Heidt, L.J., J. Amer. Chem. Soc. <u>57</u>, 1710 (1935)
- 54. McGrath, W.D. and Norrish, R.G.W., Proc. Roy. Soc. <u>242A</u>, 265 (1957)
- 55. Ibid., Nature <u>180</u>, 1272 (1957)
- 56. Benson, S.W., J. Chem. Phys., <u>26</u>, 1351 (1957)
- 57. Ibid., <u>33</u>, 939 (1960)
- 58. Schumacher, H.-J., J. Chem. Phys. <u>33</u>, 938 (1960)
- 59. Castellano, E. and Schumacher, H.-J., J. Chem. Phys. <u>36</u>, 2238 (1962)
- 60. Fitzsimmons, R.V. and Bair, E.J., J. Chem. Phys. <u>40</u>, 451 (1964)
- 61. Schumacher, H.-J. and Sprenger, G., Z. Physik. Chem. <u>2B</u>, 266 (1929)
- 62. Schumacher, H.-J., Z. Elektrochem. <u>37</u>, 674 (1931)
- 63. Johnston, H.S., J. Amer. Chem. Soc. <u>73</u>, 4542 (1951)
- 64. Schott, G. and Davidson, N., J. Amer. Chem. Soc. <u>80</u>, 1841 (1958)

- 65. Taube, H., Trans. Far. Soc. 53, 656 (1957)
- 66. Wulf, O.R. and Tolman, R.C., J. Amer. Chem. Soc. <u>49</u>, 1183ff (1927)
- 67. Warburg, E., Ann. Physik. 9, 1286 (1902)
- 68. Clement, K.J., Ann. Physik. 14, 341 (1904)
- 69. Jahn, S., Z. Anorg. Chem. 48, 260 (1906)
- 70. Perman, E.P. and Greaves, R.H., Proc. Roy. Soc. <u>80A</u>, 353 (1908)
- 71. Clarke, H.E. and Chapman, D.L., J. Chem. Soc. <u>93</u>, 1638 (1908)
- 72. Chapman, D.L. and Jones, H.E., J. Chem. Soc. <u>97</u>, 2463 (1910)
- 73. Griffith, R.O. and McKeown, A., J. Chem. Soc. <u>127</u>, 2086 (1925)
- 74. Belton, J.W., Griffith, R.O. and McKeown, A., J. Chem. Soc. <u>129</u>, 3153 (1926)
- 75. Riesenfeld, E.H. and Bohnholtzer, W., Z. Physik. Chem. 130, 241 (1927)
- 76. Riesenfeld, E.H. and Schumacher, H.-J., Z. Physik. Chem. <u>138A</u>, 268 (1928)
- 77. Riesenfeld, E.H. and Wassmuth, E., Z. Physik. Chem. <u>142A</u>, 397 (1929)
- 78. Ibid., <u>8B</u>, 315 (1930)
- 79. Schumacher, H.-J. and Sprenger, G., Z. Physik. Chem. <u>6В</u>, 446 (1930)
- 80. Glissman, A. and Schumacher, H.-J., Z. Physik. Chem. <u>21B</u>, 323 (1933)
- 81. Ritchie, M., Proc. Roy. Soc. <u>146A</u>, 848 (1934)
- 82. Harteck, P. and Dondes, S., J. Chem. Phys. <u>21</u>, 2240 (1953)
- 83. Pshezhetskii, S. Ya., Morozov, N.M., Kamenetskaya, S.A., Siryayskaya, V.N. and Gribova, E.I., Russian J. Phys. Chem. <u>33</u>, 402 (1959)
- 84. Jones, W.M. and Davidson, N., J. Amer. Chem. Soc. <u>84</u>, 2868 (1962)
- 85. Benson, S.W. and Axworthy, A.E., J. Chem. Phys. <u>42</u>, 2614 (1965)

- 86. Castellano, E. and Schumacher, H.-J., Z. Physik. Chem. <u>34</u>, 198 (1962)
- 87. Zhitnev, Yu. N., Russian J. Phys. Chem. <u>37</u>, 1158 (1963)
- 88. Vigroux, E., Ann. de Phys. <u>8</u>, 709 (1953)
- 89. Ny, T.-Z. and Choong, S.P., Chin. J. Phys. <u>1</u>, 38 (1933)
- 90. Inn, E.C.Y. and Tanaka, Y., J. Opt. Soc. Amer. <u>43</u>, 870 (1953)
- 91. Inn, E.C.Y., Tanaka, Y. and Watanabe, K., J. Chem. Phys. 21, 1651 (1953)
- 92. DeMore, W.B. and Raper, 0., J. Phys. Chem. <u>68</u>, 412 (1964)
- 93. Hearn, A.G., Proc. Roy. Soc. <u>78</u>, 932 (1961)
- 94. Kasha, M., J. Opt. Soc. Amer. <u>38</u>, 929 (1948)
- 95. Kolthoff, I.M. and Sandell, E.B., <u>Textbook of Quant-</u> itative Inorganic Analysis, Third Edition, New York, 1952
- 96. Boelter, E.D., Putnam, G.L. and Lash, E.I., Anal. Chem. 22, 1533 (1950)
- 97. Hall, T.C. and Blacet, F.E., J. Chem. Phys. 20, 1745 (1952)
- 98. Verhoek, F.H. and Daniels, F., J. Amer. Chem. Soc. <u>53</u>, 1250 (1931)
- 99. Doherty, G. and Jonathan, N., Dis. Far. Soc. <u>37</u>, 73 (1964)
- 100. International Critical Tables III, 207 (1928)
- 101. <u>Handbook of Chemistry and Physics</u>, Chemical Rubber Publishing Co., 1961
- 102. Baxter, W.P., J. Amer. Chem. Soc. <u>52</u>, 3920 (1930)
- 103. Melville, H. and Gowenlock, B.G., <u>Experimental Methods in</u> <u>Gas Reactions</u>, p. 23, Macmillan and Co., London, 1964.
- 104. French, D., J. Amer. Chem. Soc. 72, 4806 (1950)
- 105. Mayers, G.H., Silver, D.M. and Kaufman, F., J. Chem. Phys. <u>49</u>, 718 (1966)
- 106. Neuberger, D. and Duncan, A.B.F., J. Chem. Phys. <u>22</u>, 1693 (1954)

