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ELECTRON SPIN RESONANCE INVESTIGATION
INTO THE KINETICS OF SOME GAS-PHASE REACTIONS

by

Larry T. Cupitt

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

Thesis Director's Signature:

Graham P. Glass

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<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. H₂S reactions</td>
<td>55</td>
</tr>
<tr>
<td>1. O + H₂S results</td>
<td>55</td>
</tr>
<tr>
<td>2. H + H₂S results</td>
<td>63</td>
</tr>
<tr>
<td>3. Discussion</td>
<td>66</td>
</tr>
<tr>
<td>C. O₂ (¹Δg) + H reaction</td>
<td>86</td>
</tr>
<tr>
<td>1. Results</td>
<td>86</td>
</tr>
<tr>
<td>2. Discussion</td>
<td>88</td>
</tr>
<tr>
<td>D. O + C₂H₂ reaction</td>
<td>97</td>
</tr>
<tr>
<td>1. Results</td>
<td>97</td>
</tr>
<tr>
<td>2. Discussion</td>
<td>97</td>
</tr>
<tr>
<td>IV. CONCLUSION AND ACKNOWLEDGEMENTS</td>
<td>110</td>
</tr>
<tr>
<td>V. APPENDIX OF COMPUTER PROGRAMS</td>
<td>111</td>
</tr>
<tr>
<td>VI. FOOTNOTES</td>
<td>118</td>
</tr>
</tbody>
</table>
INTRODUCTION

The purpose of this paper is to detail the results of some investigations into the kinetics of several gas-phase reactions made using the combined techniques of electron spin resonance (ESR) spectroscopy and fast-flow vacuum systems. Such a combination permits convenient investigation of rapid gas-phase reactions involving free-radicals and atoms.

Throughout this study, reactive atomic species were generated by passing a reagent-diluent mixture through a microwave discharge. The atom-diluent mixture then passed into the reaction tube where a second reagent gas was added through a small movable probe. Typically, flow conditions in the reaction tube yielded linear flow velocities of 10 to 20 m/sec at pressures of around 130 Nm⁻². Atom and reagent concentrations seldom exceeded a few per cent of the total concentration. The quartz reaction tube was mounted so that it passed through the non-movable ESR detection cavity. By varying the inlet probe position, concentration vs. probe position profiles could be measured. Since the probe position can be related to the reaction time by the linear flow velocity, the experimentally measured profiles were easily converted into the concentration vs. reaction time plots needed for kinetic calculations.

In this paper several different reactive systems are discussed. One reaction of concern is

\[ \text{O} + \text{H}_2\text{S} = \text{OH} + \text{SH}, \]

which gives rise to a number of subsequent reactions in a complicated chain-reaction mechanism. One reaction in the mechanism is
H + H₂S = H₂ + SH,

and this reaction was examined in isolation both with and without molecular oxygen being present. Other reactions considered herein include

\[ \text{H} + \text{O}_2(^{1}\Delta_g) = \text{products, and} \]

\[ \text{O} + \text{C}_2\text{H}_2 = \text{products.} \]

This latter reaction is well-known and was used only as a standard reaction to evaluate the usefulness of a specially-designed heated flow tube.

The paper itself is divided into three major sections. The first section is an introduction, in which the theoretical background of the experimental techniques is discussed and the equations necessary for the quantitative use of ESR spectroscopy are derived. The second section describes the equipment and materials used for the experiments. The experimental results are listed and discussed in the final section.

General Background.

Practically all chemically reactive gas-phase systems involve atoms or molecular fragments known as free-radicals somewhere in the reaction scheme. Usually, the radical concentration is assumed to be so small that steady-state approximations apply.¹ Such an approach may or may not be valid. In addition, if a detailed knowledge of the mechanism is desired, radical concentrations must be known. Once the rates of the individual reactions are known, calculation of the over-all reaction rate is simple.

Because of the importance of measuring atom-radical concentrations, a number of quantitative techniques have been developed.
These techniques include\textsuperscript{2} Wrede-Harteck gauges,\textsuperscript{3} catalytic probes,\textsuperscript{4} gas titrations,\textsuperscript{5} chemiluminescence,\textsuperscript{6} mass spectral analysis,\textsuperscript{7} absorption and emission spectroscopy,\textsuperscript{8,9} and ESR spectrometry.\textsuperscript{10,11} Each of these methods has its own distinct advantages and disadvantages, but ESR is surely one of the most powerful methods of radical detection and measurement.

The basic principles of ESR spectroscopy have been widely and thoroughly discussed.\textsuperscript{12} Whenever a species possessing electronic spin is placed in a strong magnetic field, the energy levels are split in accordance with the allowed orientations of the spin magnetic moment. Transitions between the Zeeman levels can then be effected by the magnetic vector of radiation of the proper energy. If there is an imbalance between the populations of the various levels, energy absorption will occur. The classic ESR experiment requires an unpaired electron, but a spin magnetic moment is not necessary for transitions to be observed. For example, \( \text{O}_2 (^1\Delta_g) \), hereafter denoted by the symbol \( \Delta \), produces a spectrum which arises from transitions between the split levels of the orbital angular momentum. (While such a spectrum is technically not an ESR spectrum since there is no "spin," the term ESR will be used throughout this paper to refer to transitions arising from Zeeman effects involving electrons.) In more complicated species, the spin, orbital, and rotational angular momenta may all couple to give a number of Zeeman levels and transitions. In hetero-nuclear diatomic species, transitions may occur because of the interaction of a permanent electric-dipole moment with the electric component of the incident microwave radiation, giving rise to electric-dipole transitions.
The ESR spectrometer is the device used to observe and measure the energy absorptions. The instrument uses a high-Q resonating cavity operating at a fixed frequency in a d. c. magnetic field. Usually the magnetic field is varied and the absorption is measured as a function of the field strength. Also, a phase-sensitive, differential method of detection is employed, and the device therefore displays a first-derivative type of absorption curve.

Some of the advantages of using ESR spectroscopy for gas-phase work like that conducted during this study are: 1. The technique is versatile and unambiguous. A large number of atoms and radicals have been detected, and the spectra are so distinct that ambiguities in identification seldom occur. 2. Concentration measurements can be quite precise. Relative concentrations are accurate to within the limits imposed by signal-to-noise ratios, while absolute concentration measurements can be easily made to an accuracy of about 10%. 3. The method is fairly sensitive.

Disadvantages include: 1. The instrumentation is expensive and complex. Care must be taken to avoid effects like power saturation and over-modulation while attempting to make quantitative measurements. 2. Concentration measurements are averaged over a fairly large volume in the cavity. As long as the concentration variation across the detection point is consistent, the observed absorption should reasonably represent the radical concentration at the center of the detection area. This problem may also be lessened by using a fast-flow reaction system so that a large spatial distance represents only a small time interval.

Throughout this study, the kinetic measurements were made using ESR
in conjunction with a fast-flow vacuum system. Use of the flow system with its spatial-time correlation permitted reaction time determinations to be related to position of the probe introducing the second of the reactive species. The linear flow velocities of 10 to 20 m/sec made the measurement of rapid reaction rates possible. Fast-flow systems do, however, have some severe limitations which must be considered.

Flow Line.

In an ideal flow system, all the gaseous molecules would move down the flow tube at the same rate with no molecules traveling opposite to the bulk flow. The gas would be homogeneous across the tube and the pressure would remain constant along the flow line. Experimentally, diffusion, wall effects, and viscosity all combine to create a non-ideal situation. Axial and radial concentration gradients and viscous pressure drops are all factors which must be considered in the use of fast-flow systems.

The condition for negligible back diffusion can be shown to be: $\frac{Dk}{v^2} \ll 1$, where $D$ is the diffusion constant, $k$ is a first-order removal rate constant and $v$ is the bulk linear flow velocity. For O atoms diffusing into molecular oxygen at a pressure of $133 \text{ Nm}^{-2}$, $D = 270 \text{ cm}^2 \text{ sec}^{-1}$. With a reasonable estimate of $k = 5 \text{ sec}^{-1}$, it is obvious that, if back diffusion is to be ignored, $v$ must be greater than 30 cm/sec. Since the flow rates used in these investigations exceeded 1000 cm/sec, axial concentration gradients were neglected.

Radial concentration gradients can be investigated by examining solutions to the continuity equation. Since approximate values for the valous parameters indicate that radial concentration differ-
ences should be less than 1% under the conditions of the experiments described herein, the effects of radial concentration gradients were also neglected. Poirier and Carr recently published a paper on the use of tubular flow reactors for kinetic studies over extended pressure ranges in which they calculated and accounted for the radial concentration gradients. Since their experimental calculations substantiated the results of co-workers using similar experimental conditions and neglecting concentration gradients, it is felt that the effects of these gradients may safely be ignored in this thesis.

One final effect to be considered is that of viscous pressure drop down the flow tube. Poiseuille's law indicates that the pressure drop along the flow tube is given by

\[(p_2)^2 - (p_1)^2 = 16 \frac{f \pi \eta RT}{\pi r^4}, \quad [1]\]

where \(p_1\) is the pressure in dynes cm\(^{-2}\), \(\lambda\) is the length of the flow tube reaction section and \(r\) is the radius. \(f\) is the mass flow in moles/sec, \(\eta\) is the viscosity in g/cm-sec, and \(R\) and \(T\) are the gas constant and the absolute temperature. For the experimental conditions used in these studies, the pressure drop along the 20 cm reaction section may approach about 10% of the measured pressure. This is too large an effect to simply ignore, and corrections for the pressure drop were made in all appropriate calculations.

Having examined the experimental techniques employed for these investigations and having recognized some of the limitations and restrictions of these methods, the equations needed to use ESR spectroscopy quantitatively may now be developed.

ESR as a Quantitative Tool.

The validity of using ESR spectroscopy as a quantitative tool
has been well established. The necessary theory will be outlined again however, because of the importance of the subject to this thesis.

Van Vleck and Weisskopf have demonstrated that for a pressure-broadened non-saturated microwave transition, the imaginary part of the susceptibility, \( \chi'' \), is given by the expression

\[
\chi''_{ij} = (\omega/kT) f(\omega-\omega_0) \frac{N}{Z} \exp(-E_i/kT) |\mu_{ij}|^2,
\]

where \( \omega \) is the incident angular frequency, \( \omega_0 \) is the resonant angular frequency, \( f(\omega-\omega_0) \) is a normalized lineshape, \( N \) is the number of absorbing species in the sample, \( Z \) is the partition function, \( E_i \) is the energy of the absorbing state, \( i \), relative to the ground state, and \( |\mu_{ij}|^2 \) is the square of the absolute value of the transition matrix element in the direction of the microwave (electric or magnetic) field.

In conventional ESR experiments, the incident radiation is held constant while the magnetic field \( H \) is swept. To be applicable to the usual ESR experiment, equation [2] must be transformed into a function of the magnetic field. This can be accomplished by using the relationship

\[
f(\omega-\omega_0) = \left( \frac{h}{2\pi g_{\text{eff}}^2} \right) f(H-H_0),
\]

where \( g_{\text{eff}} = \left( \frac{h}{2\pi} \frac{d\omega_0}{dH_0} \right) \) and \( f(H-H_0) \) is another normalized lineshape.

Substituting and integrating over all \( H \), one finds

\[
\int \chi''_{ij} = (hv_0/kT) \frac{N}{g_{\text{eff}}^2Z} \exp(-E_i/kT) |\mu_{ij}|^2,
\]

where \( v_0 = \omega_0/2\pi \). The above equation is obviously valid for any single transition. If the observed line is the result of unresolved multiple transitions, the above equation must include a summation over contributing transitions. Including the summation term and rearranging the equation [4] into a form more suitable for quantitative calculations, one derives
\[ N = \frac{\varepsilon_{\text{eff}}}{h} \frac{\beta Z k T}{\nu_0} \int x'' \, dH \sum_i \exp(-E_i/kT) |\mu_{ij}|^2 \]  \[5\]

Quantitative calculations may now be made using the ESR determined value of \( f x'' \, dH \), once \( \varepsilon_{\text{eff}}, Z, E_i \), and \( |\mu_{ij}|^2 \) are evaluated.

Attention will now be directed toward calculating the necessary variables to determine the quantitative expressions for the atoms, radicals and molecules examined during this work. Of concern are the atoms O, S, H, and N; the diatomic radicals OH, SH, and SO; and the molecules NO and \( \text{O}_2 \) (\( ^3\Sigma \) and \( ^1\Delta_g \)).

Magnetic Dipole Transitions.

\( ^3\Sigma \) Oxygen Molecule.

The interaction of the ground state \( ^3\Sigma \) oxygen molecule\(^{20}\) with a magnetic field has been extensively studied by Tinkham and Strandberg.\(^{21}\) Their work includes both theoretical and experimental identification of many of the \( ^3\Sigma \text{O}_2 \) lines, along with an attempt to predict theoretically the intensities of various lines.

Since the term \( |\mu_{ij}|^2 \) represents the average squared matrix element of the interaction of the absorbing species with the microwave energy, for a \( ^3\Sigma \) molecule this term is given by

\[ |\mu_{ij}|^2 = \frac{\langle g \mathbf{S}_{\text{rf}} \cdot \mathbf{S}_{ij} \rangle}{\langle H_{\text{rf}}^2 \rangle} = \frac{g^2 \beta^2}{\langle S_{\text{rf}} \rangle^2} |(S_{ij})|^2 \]  \[6\]

where \( g \) is the Landé \( g \) factor and \( (S_{ij}) \) is the component of \( S \) along \( H_{\text{rf}} \).

The usual analysis of the matrix term\(^{17,19,21,22}\) is accomplished using ladder operators. \( H_{\text{rf}} \) is expanded as \( H = H^+ \mu_+ + H^- \mu_- + H^z \mu_z \),

where \( H^\pm = (\mu_x \mp i \mu_y)/\sqrt{2} \) and \( \mu_\pm = (\mu_x \pm i \mu_y)/\sqrt{2} \) and \( x, y, \) and \( z \) are Cartesian co-ordinate directions with the static magnetic field
being applied in the z direction. Letting \( S_\pm = (S_x \pm i S_y) \), one finds
\[
H_{\text{rf}} \cdot S_{ij} = H^+ (S_+ \rangle_{ij} / \sqrt{2} + H^- (S_- \rangle_{ij} / \sqrt{2} + H_z (S_z \rangle_{ij} .
\]
[7]

Expansion in terms of ladder operators offers the advantage that, since the selection rules for the operators are all different, for any given transition only one term on the right of equation [7] will contribute. For example, for a \( \Delta M = 1 \) transition
\[
|<S_x\rangle_{ij}|^2 = \frac{\int_{\text{sample}} |H^+|^2 d\tau}{\int_{\text{cavity}} H^2 d\tau} \frac{|(S_+ \rangle_{ij}|^2}{2} \equiv f_+ \frac{|(S_+ \rangle_{ij}|^2}{2} .
\]
[8]

All of the \( S \) matrix elements will have coefficients, \( f \), which are filling factors representing the fraction of the microwave energy available in the sample to effect the particular matrix element. These filling factors are defined as in equation [8]. Finally for a \( \Delta M = \pm 1 \) transition, one finds
\[
|<S_x\rangle_{ij}|^2 = (f_\pm (S_\pm \rangle_{ij} + (S_x \rangle_{ij})^2) = f_x |(S_x \rangle_{ij}|^2 + f_y |(S_y \rangle_{ij}|^2 .
\]
[9]

Assuming that all radiation perpendicular to the externally applied magnetic field is equally likely to induce a transition without further regard to the particular spatial orientation (i.e., \( |S_x|^2 = |S_y|^2 \)), one finds
\[
|<S_x\rangle_{ij}|^2 = (f_\pm/2) (4|(S_x \rangle_{ij}|^2).
\]
[10]

The desired matrix term is therefore given by
\[
|u_{ij}|^2 = (g B^2) (f_\pm/2) (4|(S_x \rangle_{ij}|^2) .
\]
[11]

Noting that the Boltzmann factor is approximated by \( \exp(-B(K+1)/kT) \), Tinkham and Strandberg tabulated the term \( T_{ij} = (4|(S_x \rangle_{ij}|^2) \times \exp(-B(K+1)/kT) \) for a number of identified lines at 300 K. (Cf. Table I of reference 21.) Pertinent data, including values of \( g_{\text{eff}} \), given by Tinkham and Strandberg is reassembled in Table I.1. for several \( ^3\Sigma \) \( \text{O}_2 \) lines.
The value of the rotational partition function is approximated at room temperature and above by \( Z_{O_2} = 3kT/2\hbar B \), where \( B \), the rotational constant, has a value of 43102 Hz. At 300 K the partition function has a value of 217.

The data above permits one to calculate for the \( ^3\Sigma \) \( O_2 \) line (e), (the line most commonly used during this research)

\[
N_{O_2} = 55.4 \left( \frac{2kT}{h\nu_0} \right) \chi''_{O_2} \left( \chi''_{O_2} \right) \text{dH} \tag{12}
\]

\( ^1\Delta_g \) Oxygen Molecule.

The ESR spectrum of \( ^1\Delta_g \) \( O_2 \) below 10 kG in the X-band frequency range consists of four lines which are transitions of the type \( \Delta M_J = 1 \) between the five possible \( M_J \) values of the \( J = 2 \) "ground state" of the \( ^1\Delta_g \) excited level of \( O_2 \). A thorough analysis of the spectrum of the molecule has recently been accomplished by T. A. Miller.

For a singlet state molecule, the matrix term needed is

\[
|\mu_{ij}|^2 = \frac{<g_L^2 \beta^2 (L^2 - 1/2) |E_{ij}|^2 >}{<H^2>} \tag{13}
\]

The analysis is analogous to that for the ground state molecule above and leads to the conclusion

\[
|\mu_{ij}|^2 = (g_L^2 \beta^2) \left( \frac{f_+}{2} \right) (4 |(L^2)_{ij}|^2) \tag{14}
\]

Using the direction cosines given in Table 4.4 by Townes and Schawlow, one may calculate for a \( \Delta M_J = +1 \) transition,

\[
|\langle L^2 \rangle_{ij}|^2 = \frac{1}{4} \left( \frac{\hbar^2}{J(J+1)} \right)^2 (J(J+1)-M(M+1)) \tag{15}
\]

For these transitions \( J = A = 2 \) and \( g_L \sim -1 \), and the calculated matrix term is found to be

\[
|\mu_{ij}|^2 = (4/9) \beta^2 f_+ , \text{ for } M_J = 0 \text{ or } -1, \text{ and} \tag{16}
\]

\[
|\mu_{ij}|^2 = (8/9) \beta^2 f_+ , \text{ for } M_J = -2 \text{ or } +1. \tag{17}
\]

From symmetry arguments it can be shown that the rotational
TABLE I.1. Data for O$_2$ (^3E)

<table>
<thead>
<tr>
<th>LINE</th>
<th>TRANSITION</th>
<th>$dv/dH$ MHz/G</th>
<th>$g_{eff}$</th>
<th>$I_c$</th>
<th>$H$ Gauss</th>
</tr>
</thead>
<tbody>
<tr>
<td>B</td>
<td>5 4 $\rightarrow$ 6 1 $\rightarrow$ 2</td>
<td>1.84</td>
<td>1.32</td>
<td>0.37</td>
<td>5353.2</td>
</tr>
<tr>
<td>C</td>
<td>1 1 $\rightarrow$ -1 $\rightarrow$ 0</td>
<td>1.96</td>
<td>1.40</td>
<td>0.78</td>
<td>5583.8</td>
</tr>
<tr>
<td>E</td>
<td>1 2 1 $\rightarrow$ 2</td>
<td>1.74</td>
<td>1.25</td>
<td>1.34</td>
<td>6087.5</td>
</tr>
<tr>
<td>G</td>
<td>5 6 $\rightarrow$ 4 -2 $\rightarrow$ -1</td>
<td>1.74</td>
<td>1.25</td>
<td>0.57</td>
<td>6509.3</td>
</tr>
<tr>
<td>F</td>
<td>1 2 0 $\rightarrow$ 1</td>
<td>1.42</td>
<td>1.01</td>
<td>1.45</td>
<td>6710.2</td>
</tr>
<tr>
<td>K</td>
<td>1 2 -1 $\rightarrow$ 0</td>
<td>1.33</td>
<td>0.95</td>
<td>1.15</td>
<td>7254.3</td>
</tr>
<tr>
<td>J</td>
<td>3 4 -1 $\rightarrow$ 0</td>
<td>1.68</td>
<td>1.20</td>
<td>1.36</td>
<td>8575.2</td>
</tr>
</tbody>
</table>

1. $g_{eff} = (\hbar/\beta) (dv/dH)$.
2. $I_c = (4|S_x|^2) \exp(-\frac{-E(K+1)}{kT})$ at $T = 300$ K.
3. Field strength reported by Tinkham and Strandberg at frequency of 9476.75 MHz.
partition function of the $^1\Delta_g$ $O_2$ molecule is approximately $kT/B$, which at 300 K has the value of 147. Since the transitions occur within the "ground state" of the excited molecule, the exponential term equals 1. Using the above values, and setting $g_{eff}$ equal to $2/3$, one can calculate for either of the two central lines

$$N_{O_2}(^1\Delta_g) = 36.7 \left(\frac{2kT}{h\nu_0\beta_f}\right) \int x_{ij}'' \, dh.$$  \[18\]

Simple Atomic Transitions.

For atomic transitions of the type $\Delta J = 0$, $\Delta M_J = \pm 1$, the matrix term $|\mu_{ij}|^2$ has been shown$^{17,19,26}$ to be

$$|\mu_{ij}|^2 = \left(\frac{e}{2}\right)^2 (g^2\beta^2)(J-M_J)(J+M_J+1),$$  \[19\]

where $g$ equals the atomic Landé g factor, $g_{at}$.

Substitution into equation [5] yields for atoms showing simple Zeeman effects,

$$N_{at} = \frac{2}{h\nu_0\beta_f g_{at}} \int \frac{x_{ij}'' \, dh}{J-M_J(M_J+1) \exp(-E_J/kT)}.$$  \[20\]

where $J$ and $M_J$ refer to the lower state involved in the transition. Oxygen Atom.

The generally unresolved six line spectrum of atomic oxygen$^{27}$ consists of four lines arising from $\Delta M_J = \pm 1$ transitions between the five $M_J$ levels of the $^3P_2$ ground atomic state, along with 2 lines resulting from similar transitions in the $^3P_1$ state which lies 156.5 cm$^{-1}$ above the ground state. (In addition, one other level, the $^3P_0$ state which lies 226.5 cm$^{-1}$ above the ground state, is significantly populated at room temperature, but since $J = 0$, it obviously can not contribute to the ESR spectrum.)

For purposes of calculating the partition function, the $M_J$ levels may be regarded as degenerate and the partition function at 300 K
is thus
\[ Z_0 = \sum (2J+1) \exp(-E_j/kT) = 5\exp(-0.0) + 3 \exp(-158.5/300k) + 1 \exp(-226.5) = 6.741 \]  \[ [21] \]

For the 6-line composite the summation term in equation [20] is found to equal 21.87. Finally, noting that \( g_j = 3/2 \), one calculates for the unresolved 6-line spectrum
\[ N_0 = 0.206 \frac{2kT}{h\nu_0 g_j} \int \chi''_{ij} dH \]  \[ [22] \]
or for the four major lines from the \( J = 2 \) state
\[ N_0 = 0.225 \frac{2kT}{h\nu_0 g_j} \int \chi''_{ij} dH \]  \[ [23] \]
Sulfur Atom.

Electronically the sulfur atom \(^{28}\) is analogous to the oxygen atom. The two low lying excited levels are at 396.8 and 573.6 cm\(^{-1}\) above the ground state. The resulting partition function at 300 K is therefore
\[ Z_S = 5 + 3 \exp(-396.8/300k) + \exp(-573.6/300k) = 5.507 \]  \[ [24] \]
The summation term for both the \( J = 1 \) and \( J = 2 \) transitions is 20.593. With \( g_S = 3/2 \), the resulting expression is
\[ N_S = 0.178 \frac{2kT}{h\nu_0 g_j} \int \chi''_{ij} dH \]  \[ [25] \]
Hydrogen Atom.

The H atom has a \(^2S_{1/2}\) ground state, and a single \( \Delta M_J = +1 \) transition would be expected. However, the nucleus has a spin of 1/2, and in the high field limit the hyperfine interaction splits the spectrum into a doublet with the lines separated by about 500 G. Since only the \((2M_J+1)(2M_1+1) = 4\) levels of the ground state are involved, the partition function simply has a value of 4. The summation term, for either one of the two lines, equals 1 and \( g_H = 2 \). The quantitative expression for one line is therefore
\[ N_H = 2 \frac{2kT}{h\nu_0 g_j} \int \chi''_{ij} dH \]  \[ [26] \]
Nitrogen Atom.

The ground state of the N atom is $^4S_{3/2}$. The transitions between the various $M_J$ levels are degenerate, but the spectrum is split into a triplet by the nuclear spin of 1.

Since the only significantly populated level is the ground state, the $(2M_J+1)(2M_I+1) = 12$ degeneracy means that $Z_N = 12$. $g_N = 2$, and the summation term for one of the triply degenerate lines is

$$\sum_{J, M_J} (J-M_J)(J+M_J+1) = 10,$$

so that for one line of the N triplet

$$N_N = 0.6 \frac{2kT}{h\nu_0} f_{M_2} \int \chi''_{ij} dH.$$  \[27\]

Electric-dipole Transitions.

As Beringer and Rawson \(^{29}\) point out in their investigation of the magnetic microwave spectrum of NO, certain molecules should be expected to exhibit intense electric-dipole ESR transitions. The ratio of intrinsic electric-dipole to magnetic-dipole transition intensities is $\mu_e^2/\beta^2$, where $\mu_e$ is the permanent electric-dipole of the absorbing species. For many molecules this ratio is so large that under easily obtainable experimental conditions (i.e., electric and magnetic microwave intensities throughout the sample are roughly equal) any contribution of magnetic-dipole transitions to the spectral intensities may be neglected.

Essentially the only difference in evaluating quantitative expressions like equation \([4]\) for electric-dipole, rather than magnetic-dipole, transitions is that evaluation of the matrix term $|\mu_{ij}|^2$ is slightly different. As with magnetic-dipole transitions, the matrix term is the product of two factors

$$|\mu_{ij}|^2 = f_E |\mu_x|^2,$$  \[27\]

where $f_E$ is a microwave electric field filling factor and $|\mu_x|^2$ is the
square of the absolute value of the transition element for the appropriate microwave electric field direction. (The cavity used almost exclusively throughout this study operated in the $\text{TE}_{01n}$ mode. In this mode, there are two filling factors: $f_{E,x}$ in which the microwave electric field is perpendicular to the applied external magnetic field, and $f_{E,z}$ in which the radiation and the field are parallel. Theoretical cylindrical symmetry of the $\text{TE}_{01n}$ mode implies that the two filling factors are equal; however, introduction of the flow system into the resonant cavity may cause an asymmetrical standing wave pattern, and the two filling factors should actually be considered unequal.)

Nitric Oxide.

The ESR spectrum of ground state $^2\Pi_{3/2}$ NO consists of $2J(2I+1) = 9$ lines of the type $\Delta M_J = 1$, $\Delta M_I = 0$. Each of the three $\Delta M_J = 1$ lines is split into a triplet by the nuclear spin of 1 on the nitrogen atom. Each of the nine lines is actually a doublet consisting of $+ \rightarrow -$ and $- \rightarrow +$ transitions between the members of the $\Lambda$ doublet. A summary of the transitions of NO is given in Table 1.2.

The matrix element for transitions between $\Lambda$-type doublets for Hund's case (a) molecules like NO is (Cf. page 190 of reference 25)

$$|\mu_{ij}|^2 = \mu^2 \Omega^2 / J(J+1).$$  \[29\]

The matrix element applies to the unperturbed intensity and therefore involves transitions between any particular $K_J$ states of the final level that are induced in three-dimensional isotropic radiation. Using the probability distribution among Zeeman levels given by Condon and Shortley, Westenberg derives the necessary matrix element $|\mu_x|^2$ in terms of $|\mu_{ij}|^2$ found in equation [29]. This derivation has been
TABLE I.2. Transitions of NO (J = 3/2, $^2\Pi_{3/2}$). Each line is actually a $\Lambda$ doublet.

<table>
<thead>
<tr>
<th>LINE</th>
<th>TRANSITION</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>$1/2, 1 \rightarrow 3/2, 1$</td>
</tr>
<tr>
<td>b</td>
<td>$1/2, 0 \rightarrow 3/2, 0$</td>
</tr>
<tr>
<td>c</td>
<td>$1/2, -1 \rightarrow 3/2, -1$</td>
</tr>
<tr>
<td>d</td>
<td>$-1/2, 1 \rightarrow 1/2, 1$</td>
</tr>
<tr>
<td>e</td>
<td>$-1/2, 0 \rightarrow 1/2, 0$</td>
</tr>
<tr>
<td>f</td>
<td>$-1/2, -1 \rightarrow 1/2, -1$</td>
</tr>
<tr>
<td>g</td>
<td>$-3/2, 1 \rightarrow -1/2, 1$</td>
</tr>
<tr>
<td>h</td>
<td>$-3/2, 0 \rightarrow -1/2, 0$</td>
</tr>
<tr>
<td>i</td>
<td>$-3/2, -1 \rightarrow -1/2, -1$</td>
</tr>
</tbody>
</table>
further discussed by T. A. Miller.\textsuperscript{31,32}

For one member of a $\Lambda$ doublet in an ESR transition from state
$$(J,M_J) \rightarrow (J,M_J+1),$$
the matrix term is given by

$$|\mu_r|^2 = \frac{|\mu_{ij}|^2}{6 \sum_{M_J=J}^{J-1} (J-M_J)(J+M_J+1)} (2J+1)(J-M_J)(J+M_J+1). \text{[30]}$$

Taking the electric-dipole moment of NO, $\mu_{\text{NO}}$, as 0.158 D,\textsuperscript{33}
and assuming that the lambda doublets are unresolved one calculates
the desired matrix term as $|\mu_{ij}|^2 = 0.0060 \ f_{E,x}$ for lines (a, b, c,
g, h, and i) and $|\mu_{ij}|^2 = 0.0080 \ f_{E,x}$ for lines (d, e, or f).

The rotational partition function of NO may be approximated by\textsuperscript{34}

$$Z_{\text{NO}} = 2(2I+1)(kT/\hbar B)(1+\exp(\Delta E/\hbar c)),$$ \text{[31]}

where $c$ is the velocity of light, $B$ is the rotational constant, and
$\Delta E$ is the energy difference between the lowest energy level $J = 1/2$,
$^2\Pi_{1/2}$ and the first excited (but non-existent) level $J = 1/2$, $^2\Pi_{3/2}$.
Taking $B = 1.696 \ \text{cm}^{-1}$, $\Delta E = 119.8 \ \text{cm}^{-1}$,\textsuperscript{35}
and $T = 300 \ \text{K}$, $Z$ has the
value 1150. The energy $E_i$ in the exponential term of equation [5] is
approximately equal to $\Delta E + 3B = 124.9 \ \text{cm}^{-1}$. The Boltzmann factor
thusly assumes a value of 0.549 at 300 K. From the data reproduced
in Table I.2. one finds $g_{\text{eff}} = 0.777$. Combining all the above values
and gives as a final result for one line of the large central triplet
(lines (d, e, f))

$$N_{\text{NO}} = 203200 \ (kT/\hbar \nu_0 f_{E,x}) \int \chi_{ij}'' \, dH. \text{[32]}$$

SH Radical.

The X-band ESR spectrum of SH consists of two groups of lines.
The high field group consists of $2J(2I+1) = 6$ lines of the type
$\Delta M = 1$, $\Delta M = 0$, $+ -$ with $I = 1/2$ for H. The second set of lines
occurs about 190 G below the first set and is composed of the
equivalent - + + transitions. Radford and McDonald have observed and partially analyzed the spectrum. The SH spectral lines are tabulated in Table I.3.

Electronically the SH radical has an inverted $^2\Pi$ ground state in which the lowest level $J = 3/2$ of $^2\Pi_{3/2}$ lies below the lowest level $J = 1/2$ of $^2\Pi_{1/2}$. The radical exhibits an intermediate Hund's case (a) and (b) angular momentum scheme. Since the transitions occur within the lowest lying energy level, $E_1 = 0$ and the Boltzmann term in equation [4] equals $1$.

The partition function $Z$ for $^2\Pi$ molecule which shows intermediate Hund's case (a)/(b) coupling is given by

$$Z_{SH} = 2(2I+1) \sum_{J = 1/2}^{\infty} (2J+1)\exp(-E_J/kT) + \sum_{J' = 3/2}^{\infty} (2J'+1)\exp(-E_{J'}/kT) ,$$  \[[33]\]

where $J$ refers to the $^2\Pi_{1/2}$ state and $J'$ refers to the $^2\Pi_{3/2}$ state. The energy levels are given by the term values

$$E_J = B((J+1/2))^2 - \Lambda^2 \pm (1/2)(4(J+(1/2))^2 + \lambda(\lambda - 4)\Lambda^2)^{1/2} ,$$  \[[34]\]

where the plus sign refers to the $^2\Pi_{1/2}$ and the minus sign to the $^2\Pi_{3/2}$ state. $B$ is the rotational constant, and $\lambda = A/B$.

Ramsey quotes values of $A$ and $B$ as $-376.9$ cm$^{-1}$ and $9.461$ cm$^{-1}$ respectively. Using these values and setting $A = 1$ for $\Pi$ molecules and $T = 300$ K, the partition function may be calculated by direct summation to be 113. The value of $g_{eff}$ has been measured as 0.838.

Dousmanis et al. have derived the matrix elements for the electric dipole moment transitions of the type $\Delta J = 0$ between the members of a $\Lambda$ doublet of a $^2\Pi_{3/2}$ state slightly perturbed by a $^2\Sigma$ state. This matrix term, like that found in equation [28] for NO above, refers to the unperturbed line intensity and is given by
TABLE I.3. Transitions of SH $^{2} \Pi_{3/2}$, $J = 3/2$ in order of decreasing magnetic field strength. Field measurements are at a frequency of 8850 MHz. Doublets (a), (b) and (c) are $+ \rightarrow -$ transitions. Doublets (d), (e) and (f) are $- \rightarrow +$ transitions.

<table>
<thead>
<tr>
<th>LINE</th>
<th>TRANSITION</th>
<th>FIELD</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_J, M_I \rightarrow M_J+1, M_I$</td>
<td>Gauss</td>
</tr>
<tr>
<td>(a)</td>
<td>$-3/2, 1/2 \rightarrow -1/2, 1/2$</td>
<td>7665</td>
</tr>
<tr>
<td></td>
<td>$-3/2, -1/2 \rightarrow -1/2, -1/2$</td>
<td>7659</td>
</tr>
<tr>
<td>(b)</td>
<td>$-1/2, -1/2 \rightarrow 1/2, -1/2$</td>
<td>7646</td>
</tr>
<tr>
<td></td>
<td>$-1/2, 1/2 \rightarrow 1/2, 1/2$</td>
<td>7640</td>
</tr>
<tr>
<td>(c)</td>
<td>$1/2, -1/2 \rightarrow 3/2, -1/2$</td>
<td>7625</td>
</tr>
<tr>
<td></td>
<td>$1/2, 1/2 \rightarrow 3/2, 1/2$</td>
<td>7620</td>
</tr>
<tr>
<td>(d)</td>
<td>$-3/2, 1/2 \rightarrow -1/2, 1/2$</td>
<td>7471</td>
</tr>
<tr>
<td></td>
<td>$-3/2, -1/2 \rightarrow -1/2, -1/2$</td>
<td>7465</td>
</tr>
<tr>
<td>(e)</td>
<td>$-1/2, 1/2 \rightarrow 1/2, 1/2$</td>
<td>7455</td>
</tr>
<tr>
<td></td>
<td>$-1/2, -1/2 \rightarrow 1/2, -1/2$</td>
<td>7450</td>
</tr>
<tr>
<td>(f)</td>
<td>$1/2, -1/2 \rightarrow 3/2, -1/2$</td>
<td>7441</td>
</tr>
<tr>
<td></td>
<td>$1/2, 1/2 \rightarrow 3/2, 1/2$</td>
<td>7436</td>
</tr>
</tbody>
</table>
\[ |\mu_r|^2 = \frac{\mu^2 (\Omega_1^2 (x-2\lambda)^2 + \Omega_2^2 (x+2-\lambda)^2 + 2\Omega_1\Omega_2 (x^2-(2-\lambda)^2))}{4X^2J(J+1)} \]  

where \( \Omega_1 = 1/2 \), \( \Omega_2 = 3/2 \), \( X^2 = 4(J+(1/2))^2 + \lambda(\lambda-4) \), and \( \mu \) is the electric dipole moment of SH, which has been measured\(^{41} \) as 0.62±0.06 D.

Substituting equations [35], [30], and [28] into [5] and evaluating, one finds

\[ N_{SH} = 2034 \left( \frac{kT\beta}{\hbar \omega E_x} \right) \int x''_{ij} \, dH \]  

for any single line of doublet (a), (c), (d), or (f), and

\[ N_{SH} = 1526 \left( \frac{kT\beta}{\hbar \omega E_x} \right) \int x''_{ij} \, dH \]  

for any single line of doublets (b) and (e). If the integrated intensity of any unresolved doublet is used, the numerical coefficient in the appropriate equation [36] or [37] should be halved.

OH Radical.

Electronically the OH radical is analogous to the SH radical discussed above: it is a \( \Pi \) molecule with an inverted ground state and shows intermediate Hund's case (a)/(b) coupling. As above, the spectrum of the \( \Pi_{3/2} \) state is two sextets, but the splittings are different and the spectrum differs slightly from that of SH. While each sextet of SH was essentially a triplet of doublets, in OH the sextet is a doublet of triplets. The triplets come from the \( 2J = 3 \) transitions of the form \( \Delta J = 0, \Delta M_J = 1 \), and are almost degenerate. The doublet effect is the result of the nuclear spin of 1/2 on the \( H \) atom. The low field sextet is again from the \( - \leftrightarrow + \) \( \Lambda \) component. The splitting between the \( \Lambda \) components in OH is large, being about 2550 G in the \( \Lambda \)-band range. In addition, there are a number of lines in the OH spectrum which arise from the higher rotational levels of the \( \Pi_{3/2} \) state.
In calculating the appropriate quantitative expressions for OH, only the lower sextet of the transitions of the \( J = 3/2, \Sigma_{3/2} \) state will be considered. The transitions involved in this sextet, occurring around 5800 G, are listed in Table I.4. A comparison of Tables I.4. and I.3. shows that lines A and B for OH are analogous to taking one line from each of the doublets (a), (b), and (c) for SH and combining them. In other words, the lines A and B of OH are composed of 2 lines of lesser intensity and 1 line of larger intensity. This fact must be considered when calculating the quantitative expression for either of the unresolved triplets A or B.

The equations quoted in the section on the SH radical for the partition function, energy levels, and matrix elements are equally applicable to OH. Of course, the parameters may have different values from those used for SH. For OH, \( B = 18.5 \text{ cm}^{-1}, \) \( I = 1/2, \) \( \Lambda = 1, \) \( g_{\text{eff}} = 0.935, \) \( \Omega_1 = 1/2, \) \( \Omega_2 = 3/2, \) \( \lambda = -7.504, \) and \( \mu = 1.660 \pm 0.010 \text{ D}. \)

Using the values above with an analysis identical to that used for SH, one may calculate for either of the unresolved triplets A or B

\[
N_{\text{OH}} = 36.6 \left( \frac{kT\beta}{h
\nu_0 f_{E,x}} \right) \int x_{ij}'' \, dH .
\]

SO Radical.

Below 10 kG the X-band ESR spectrum of \( \text{SO}^3 \Sigma \) consists of four strong lines due to transitions of the type \( JKM \rightarrow J'K+1M' \) where \( J = J' = 1. \) While the molecule exhibits intermediate Hund's case (a)/(b) coupling, it is usually described in terms of a Hund's case (b) basis. The spectrum has been completely analyzed by Daniels and Dorain, \(^{45}\) and by Carrington \textit{et al}. \(^{45}\) Table I.5. lists the transitions of interest, along with values of \( g_{\text{eff}} \) calculated from the measurements.
TABLE I.4. Transitions of OH ($J = 3/2, \, ^2\Pi_{3/2}$). All are $- \to +$ transitions.

<table>
<thead>
<tr>
<th>LINE</th>
<th>TRANSITIONS $M_J, M_I \leftrightarrow M_{J+1}, M_I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>$1/2, 1/2 \leftrightarrow 3/2, 1/2$</td>
</tr>
<tr>
<td></td>
<td>$-1/2, 1/2 \leftrightarrow 1/2, 1/2$</td>
</tr>
<tr>
<td></td>
<td>$-3/2, 1/2 \leftrightarrow -1/2, 1/2$</td>
</tr>
<tr>
<td>B</td>
<td>$1/2, -1/2 \leftrightarrow 3/2, -1/2$</td>
</tr>
<tr>
<td></td>
<td>$-1/2, -1/2 \leftrightarrow 1/2, -1/2$</td>
</tr>
<tr>
<td></td>
<td>$-3/2, -1/2 \leftrightarrow -1/2, -1/2$</td>
</tr>
</tbody>
</table>

TABLE I.5. X-band transitions of $^{32}$SO($^3\Sigma$) below 10 kG. Field measurements are for a frequency of 8762 MHz.

| LINE | FIELD Gauss | TRANSITION $J\kappa M \leftrightarrow J\kappa M + 1M$ | $-R_{\text{eff}}$ | $|\mu|^2$ (Debye)$^2$ |
|------|-------------|----------------------------------|------------------|----------------------|
| g    | 2845        | $111 \leftrightarrow 120$       | 1.14             | 0.116 $\mu^2 f_{E,x}$ |
| h    | 4642        | $111 \leftrightarrow 121$       | 0.69             | 0.200 $\mu^2 f_{E,z}$ |
| i    | 5944        | $110 \leftrightarrow 12-1$      | 0.64             | 0.102 $\mu^2 f_{E,x}$ |
| j    | 9110        | $110 \leftrightarrow 120$       | 0.61             | 0.0104$\mu^2 f_{E,z}$ |
of \( \frac{dv}{dh} \) tabulated by Daniels and Dorain and the dipole matrix elements calculated by Carrington et al.

As Carrington notes, the dipole matrix elements for the \( ^3\Sigma \) SO radical are dependent upon the magnetic field strength. (N.b., line (j) is strictly forbidden at zero magnetic field.) Over the X-band frequency range (8800 MHz - 9600 MHz), the dipole moment for line (j) varies by more than 7%.

However, the matrix dipole elements for the other three lines vary less than 1% over the X-band range, and the values given by Carrington for a frequency of 8762 MHz are adequate.

It should be noted that the matrix terms listed by Carrington need to be multiplied by the square of the permanent electric dipole of SO and the filling factor. These additional factors have been included in the matrix terms listed in Table I.5.

Another important feature of the SO spectra to be considered is the fact that lines (h) and (j) are \( \Delta M = 0 \) transitions. As such, lines (h) and (j) are excited by the component of the microwave electric field vector parallel to the magnetic field, while the \( \Delta M = 1 \) lines (g) and (i) are excited by the component perpendicular to the field. The filling factors for the two sets of lines are therefore different. This fact may be of experimental significance if \( f_{E,x} \neq f_{E,z} \).

Since the initial state of these transitions lies 10.7 cm\(^{-1}\) above the ground state, the Boltzmann factor in equation [5] may be calculated to be 0.95. At 300 K the partition function can be approximated by

\[
Z_{SO} = \frac{3kT}{h} = 871
\]

where \( B = 0.7179 \) cm\(^{-1}\).\(^{41}\) Using the reported value for the electric dipole moment of 1.55 \( \pm \) 0.02 D,\(^{41}\) one may use the data given above
to calculate

\[ N_{SO \text{ line(g)}} = 3944 \left( \frac{kT \beta / h \nu o f_{E, x}}{o f_{E, x}} \right) \int \chi''_{ij}(SO, \text{ line(g)}) \, dH \]  \[ N_{SO \text{ line(h)}} = 1384 \left( \frac{kT \beta / h \nu o f_{E, z}}{o f_{E, z}} \right) \int \chi''_{ij}(SO, \text{ line(h)}) \, dH \]

\[ N_{SO \text{ line(i)}} = 2515 \left( \frac{kT \beta / h \nu o f_{E, x}}{o f_{E, x}} \right) \int \chi''_{ij}(SO, \text{ line(i)}) \, dH \]

\[ N_{SO \text{ line(j)}} = 23600 \left( \frac{kT \beta / h \nu o f_{E, z}}{o f_{E, z}} \right) \int \chi''_{ij}(SO, \text{ line(j)}) \, dH \]  \[ N_{SO \text{ line(j)}} = 23600 \left( \frac{kT \beta / h \nu o f_{E, z}}{o f_{E, z}} \right) \int \chi''_{ij}(SO, \text{ line(j)}) \, dH \] .  \[ N_{SO \text{ line(j)}} = 23600 \left( \frac{kT \beta / h \nu o f_{E, z}}{o f_{E, z}} \right) \int \chi''_{ij}(SO, \text{ line(j)}) \, dH \]

Absolute Concentration Determinations.

In principle, evaluation of the variables in equation [5] above provides all the necessary information to allow the absolute determination of radical concentrations. In practice, however, determination of the magnitude of the integrated absorption is a formidable task since the experimentally measured absorption is dependent upon many instrumental factors, including operational settings, intrinsic sensitivity of the detection devices, and operational characteristics of the resonating cavity. The evaluation of all such instrumental parameters is sufficiently difficult to preclude the straight-forward application of equation [5] with any appreciable accuracy.

Krongelb and Strandberg have suggested an alternative method whereby the free-radical absorption is compared with absorption by a known concentration of a standard molecule. The problem therefore is merely that of a relative concentration measurement, and the instrumental parameters need not be numerically evaluated. It is possible therefore to derive expressions of the form

\[ N_R = Q_R \frac{\int \chi''_{ij}(R) \, dH}{\int \chi''_{ij}(\text{STD}) \, dH} \]  \[ N_{\text{STD}} \int \chi''_{ij}(\text{STD}) \, dH \]

where \( Q_R \) is a numerical factor which varies depending upon the particular absorption of the radical, \( R \), and the standard gas used. Obviously, for most practical application of equation [44] the radical \( R \) and the
standard gas must both have the same filling factor f. Table I.6. lists values of Q_R at 300 K for various absorption lines. The standard gas absorption used is^{19} O_2(^3Σ) line (e) for the magnetic-dipole transitions and any one of lines (d), (e), or (f) of NO for the electric-dipole transitions.

In practice, the ESR spectrometer displays a first-derivative curve of the absorption signal. In order to arrive at a numerical entity proportional to the integrated absorption, the ESR signals were integrated twice, as described in the experimental section, resulting in a value in terms of square inches. Sometimes however, the radical signal and the standard gas signal were measured with different instrumental settings. Whenever that occurred, the ratio of the integrated absorptions was converted to standard conditions using the following relationship

\[
\frac{\int_{x}^{y}(R) \, dh}{\int_{x}^{y}(STD) \, dh} = \frac{A_R}{A_{STD}} \frac{M_R}{M_{STD}} \frac{SL_R}{SL_{STD}} \frac{REC_R}{REC_{STD}} \frac{ST_R}{ST_{STD}} \frac{SF_R}{SF_{STD}} \frac{P_R}{P_{STD}}^{1/2},
\]

[45]

where A is the area measured, MA is the modulation amplitude, SL is the signal level, REC is the recorder sensitivity, ST is the time for a full sweep, SF is the size of the magnetic field swept, and P is the klystron power level used.

Sets of integrals necessary to determine absolute concentrations were measured only once or twice per experimental run. During the run, concentrations were determined from relative sizes of the first-derivative ESR absorption signal. The validity of the assumption that the radical concentration is proportional to the displayed first-derivative signal height has been shown both theoretically\textsuperscript{46} and experimentally. (Cf. references 17 and 19 for example)
### TABLE I.6. Values of $Q_R$ for several atoms/radicals. The standard gas for magnetic-dipole transitions is ground state molecular oxygen—line ($E$). The standard transition for electric-dipole transitions is any one of the three central lines in the NO spectrum.

<table>
<thead>
<tr>
<th>SPECIE</th>
<th>TRANSITION</th>
<th>$Q_R$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_2(^{1}\Delta_g)$</td>
<td>Either of the 2 central lines</td>
<td>0.664</td>
</tr>
<tr>
<td>O</td>
<td>6-line composite</td>
<td>0.00372</td>
</tr>
<tr>
<td></td>
<td>4 major lines</td>
<td>0.00407</td>
</tr>
<tr>
<td>S</td>
<td>6-line composite</td>
<td>0.00322</td>
</tr>
<tr>
<td>H</td>
<td>Either of the 2 lines</td>
<td>0.0361</td>
</tr>
<tr>
<td>N</td>
<td>Any one line of the triplet</td>
<td>0.00108</td>
</tr>
<tr>
<td>SH</td>
<td>Doublet (a), (c), (d), or (f)</td>
<td>0.000500</td>
</tr>
<tr>
<td></td>
<td>Doublet (b) or (e)</td>
<td>0.00376</td>
</tr>
<tr>
<td>OH</td>
<td>Line A or B</td>
<td>0.000180</td>
</tr>
<tr>
<td>SO</td>
<td>Line (g)</td>
<td>0.0194</td>
</tr>
<tr>
<td></td>
<td>Line (h)</td>
<td>0.00682$f_{E,E,z}$</td>
</tr>
<tr>
<td></td>
<td>Line (i)</td>
<td>0.0123</td>
</tr>
<tr>
<td></td>
<td>Line (j)</td>
<td>0.116$f_{E,E,z}$</td>
</tr>
</tbody>
</table>
EXPERIMENTAL

The flow line used in this study consisted of three major sections: (A), the discharge section in which the reactive atom/radical was generated; (B), the reaction section where the reagents were mixed and passed through the ESR detection cavity; and (C), the pumping region. Sections (A) and (B) are depicted in Figure II.1.

The discharge section is constructed from 12 mm o.d. pyrex and quartz tubing, and usually has three gas inlets. Diluent and other gases enter through inlet 1 and pass through a U-shaped section which may be immersed in liquid nitrogen and used as a trap. Two other inlets, one on each side of the microwave discharge cavity, permit the entrance of additional gases either upstream or downstream of the discharge. The diluent/discharge product mixture then passes through an extended ground glass 24/40 "through" joint into the quartz reaction section. The extension on the "through" joint is a length of 12 mm o.d. tubing which fits inside a 14 mm i.d. section attached to a normal 24/40 outer joint. This type of connection gives the flexibility needed for convenient assembly of the flow line without permitting large concentrations of the atoms/radicals to come into contact with stop-cock grease, a contaminant which can effect marked surface recombination.

Basically, the reaction section is merely a 20 mm i.d. quartz tube passing through the ESR cavity. An inlet, situated about 25 cm upstream from the detection cavity, leads to the pressure guage. Connected to the quartz tubing by a pyrex-vycor graded seal is a pyrex section with two more inlets: one inlet leads to the extended
Figure II.1. Schematic diagram of the normal configuration of the flow line.
"through" joint and the discharge section; the second inlet is a short (about 1 inch) piece of tubing, the cylindrical axis of which coincides with the cylindrical axis of the larger quartz tube. This last inlet permits the entrance of a moveable probe through which the second reagent is added. A vacuum-tight seal between the probe and the inlet is obtained by attaching to the inlet a short section of rubber tubing with an inside diameter approximately equal to the o.d. of the probe. The probe-rubber seal may be further improved by stretching a small Buna-N O-ring around the rubber tubing. The O-ring constricts slightly the rubber tubing to provide a firm, vacuum-tight seal while permitting the probe to be moved readily. The rubber-glass seal may be lubricated by a small amount of silicone grease. Depending upon the particular reaction tube used, either a 3 mm o.d. or a 6 mm o.d. inlet probe could be used. The probe could be varied over a range from 1 to approximately 20 cm upstream of the center of the ESR detection in order to provide the distance-dependent (time-dependent) reaction profiles needed for kinetic studies.

The reaction section is connected by large glass and aluminum piping to a 5 gallon dump tank and a Welch Duo-Seal model 1397 vacuum pump. The pump is rated at 400 l/min and is capable of providing linear flow velocities in the reaction section of from 15 to 20 m/sec at pressures of 25 to 300 Nm⁻². The dump tank serves two purposes: (1) it smooths the gas flow, making the linear flow velocity more steady, and (2) it is bolted firmly to the wall in order to prevent transfer of vibrations from the pump to the flow line.

The flow line was never used for kinetic studies without a thorough cleansing and preparation. It was washed with a detergent
solution, rinsed thoroughly with distilled water, cleaned with 10% hydrofluoric acid, rinsed again with distilled water, poisoned with an ortho-boric acid solution, dried under vacuum, and finally subjected to a period of atom/radical flow to finish preparation of the walls.

Two methods were used during this study to examine reaction rates at elevated temperatures. The first method utilizes an oven placed around the conventional flow tube, while the second involves the use of a specially-constructed heated flow tube.

Oven Heater.

The oven consisted of an 11.5 cm long stainless steel tube with an i.d. of 2.5 cm which fitted snugly inside a ceramic tube of equal length. Resistance heating wire and asbestos rope were wrapped evenly along the outside of the ceramic tube and fastened on the ends with copper wire ties. This section was centered inside a 10.9 cm i.d. aluminum tube 12.5 cm long. The space between the tubes was packed with rock-wool insulating material and the ends were sealed with temperature resistant cement. Temperature control in the oven was maintained by using a Variac voltage regulator. During experimental runs the temperature at the center of the oven was measured using an iron-constantan thermocouple placed between the flow tube and the oven center. The oven did not provide a step-function type temperature change, however, and it became necessary to obtain a temperature profile for the oven. Figure II.2. shows a composite profile, with temperatures at the center of the oven, $T_{MAX}$, ranging from about 360 K to 620 K. In the normalized graph, the ordinate is given by $y(x) = (T(x) - TRT)/(T_{MAX} - TRT)$, where $T(x)$ is the experimentally
Figure II.2. Plot of the normalized temperature profile along the flow tube produced by the oven described in the experimental section. The ordinate is given by \((T(x) - T_{RT})/(T_{MAX} - T_{RT})\), where \(T(x)\) is the measured temperature at any point, \(T_{RT}\) is the room temperature, and \(T_{MAX}\) is the highest temperature within the oven. The positive direction of the abscissa corresponds to the downstream direction along the flow tube. The zero point on the graph for the abscissa is the center of the highest temperatures of the oven and moves along the flow tube as a function of \((T_{MAX} - T_{RT})\). The unit of the x-direction is centimeters.
measured temperature at some point along the flow tube, TRT is the absolute room temperature, and TMAX is defined above. All temperatures are absolute. The experimentally determined values were measured using an iron-constantan thermocouple which could be inserted into the flow line. All the profiles were obtained at flow conditions similar to those used for the kinetic studies. As TMAX ranged from 360 K to 620 K, the temperature profile shape remained consistent, but its location with respect to the oven position changed. The distance from the upstream side of the inner stainless steel tube of the oven to the location of the zero point of the temperature profile, DZP, is given by

\[ DZP = 4.76 + 0.0031 \ (TMAX - TRT) \text{ cm.} \]  

[46]

The temperature profile shown in Figure II.2. was split into 5 regions and the curve in each section was fitted to the profile. The abscissa in the figure is distance measured in centimeters, with zero being the center of the maximum section of the curve. The ordinate is given by

\[ y(x) = 0.815 + (x + 4)/6 \]  \hspace{1cm} \text{(Region I)}

\[ y(x) = 0.99 - 0.02 \ (x + 1.5)(x + 0.5) \]  \hspace{1cm} \text{(Region II)}

\[ y(x) = 1.0 - (0.01/(1.5)^2)(x^2) \]  \hspace{1cm} \text{(Region III)}

\[ y(x) = 0.99 - 0.0223 \ (x - 1.5) - 0.0367 \ (x - 1.5)^2 \\
+ 0.003 \ (x - 1.5)^3 \]  \hspace{1cm} \text{(Region IV)}

\[ y(x) = 0.42 \ \exp(-0.4865 \ (x - 6)) \]  \hspace{1cm} \text{(Region V)}

To calculate the experimental temperature, \( y(x) \) must be multiplied by \( (TMAX - TRT) \) and added to TRT. Appendix I includes a computer program for calculating the \( E_a \) of the \( H \) atom-delta state molecular oxygen reaction in which a subprogram designed to calculate the
temperature as a function of distance down the flow tube is incorporated.

The shortness of the oven described above, along with its non-step-function temperature profile, combined to limit the oven's usefulness. Conventionally, reaction profiles are obtained by moving the inlet probe along the flow tube inside a long oven. With the oven above, this technique was impractical and the oven was useful only when an "on-off" method could be used. (See the results and discussion of the $H + \Delta g O_2$ system.)

Heated Flow Line.

A flow tube was constructed to permit the determination of reaction profiles at elevated temperatures and also allow radical detection at those temperatures. This flow line is illustrated in Figure II.3. and resembles an ordinary condenser. A 15 mm o.d. quartz flow line is surrounded by a quartz jacket through which heated air may be blown. The outside diameter varies along the flow tube. The section of 28 mm o.d. was chosen because it would permit a good flow of hot air and was a convenient size. The tube constricts to 22 mm o.d., where it passes through the end plates of the ESR cavity, and expands to 40 mm o.d. to fill the inner portion of the cavity. The quartz jacket was expanded to fit snugly inside the cavity so that insertion of the flow line into the cavity would cause a small a decrease in resonant cavity "Q" as was practicable. Hot air entered the jacket on the upstream side through a sidearm and exited through a hole downstream of the cavity. The inlet sidearm went through a 1/2-inch pyrex-copper seal, a 1/2-inch i.d. flexexpand and a copper reducing union to a hot-air gun. The nozzle of the hot-air
Figure II.3.
Specially-designed heated flow line
gun was held in place by asbestos tape and three screws set into the copper reducing union. Heating tapes, controlled by Variac "Power-stats," were used to maintain the temperature along the flow tube. Several temperature profiles for the system, plotting temperature against distance upstream from the ESR detection point, will be presented later.

Gas Flow Measurements.

The flow of reagent gases into the flow line was regulated and measured using either calibrated rotameters or manometer bulbs.

The rotameters were ordered from Matheson Gas Products Company and were convenient for gas flow rates of 50 to 1500 cc-cm of Hg/sec. Each rotameter was calibrated for the specific gas by collecting the gas over water and plotting the measured flow rate against the rotameter reading. Periodically the rotameters were cleaned and re-calibrated. During calibration and use, the delivery pressure of the gas was held at 5 psi above atmosphere on the upstream-side of the rotameter needle valve. During calibration, the pressure on the downstream-side of the rotameter was obviously 1 atmosphere since the gas was collected over water: the downstream-side pressure was duplicated during experiments by the insertion of a manometer and needle valve between the rotameter and the vacuum flow line.

Flow rates of reacting gases were usually determined using manometer bulbs. A manometer bulb is a container of known volume attached to a mercury manometer. Two types of manometer bulbs are depicted in Figure II.4. The manometer bulb is connected through a needle valve to the flow line and through a stop-cock to a large gas reservoir. The needle valve permits control of the gas influx rate
Figure II.4. (a)  
**Straight manometer bulb.**

Figure II.4. (b)  
**U-tube manometer bulb.**
while the reservoir provides the large gas reserve necessary to maintain constant flow rates throughout an experimental run. The reservoir was often connected directly, or through a low-pressure delivery gauge, to a tank of the appropriate gas.

The flow rate of gas out of the manometer bulb was determined by closing the bulb off from the reservoir and measuring the rate of pressure drop in the manometer bulb. Assuming ideal gas behavior, a manometer bulb like that depicted in Figure II.4. (a) has a flow rate given by the equation

$$\Phi = \Delta P \left( V_0 + (P_1 + P_2) \pi r^2 \right) / t$$  \hspace{1cm} [47]

where \( \Delta P \) is the change in pressure measured in cm of Hg and is positive, \( V_0 \) is the volume of the manometer bulb above the 0 cm level of the manometer, \( P_1 \) is the first pressure (measured in cm of Hg) and \( P_2 \) is the second, \( r \) is the radius of the tubing in the manometer, \( t \) is the time in seconds, and \( \Phi \) is the flow rate in cc-cm of Hg/sec. The flow rate from U-tube manometer bulbs like that in Figure II.4. (b) was calculated in a similar, but slightly different, manner. The range of flow rates which could be conveniently measured by any particular bulb is essentially determined by the magnitude of \( V_0 \). Most of the bulbs employed during this study had a standard volume, \( V_0 \), of about 80 cc and a conveniently measured flow rate range of about 2 to 15 cc-cm of Hg/sec.

Microwave Discharge.

The microwave discharge employed was a Raytheon Microtherm Unit supplying 120 watts of power at 2450 MHz. The output was measured by a Bendix Micro-Match Power/Standing Wave Ratio device, which was used to maximize the efficiency of the tunable discharge and to
maintain a constant power output during an experiment.

The tunable cavity on the discharge section of the flow line was essentially two axially mounted tubes connected on the ends. The outer tube was 48 mm in diameter and 130 mm long. The inner tube, with an i.d. of 15 mm, extended axially along the cylinder for 90 mm. From the other end of the cylinder a 55 mm screw-in section with a 15 mm i.d. completed the inner tube. A gap could be created in this tube by screwing the one section out, thereby tuning the cavity. Connected to the outer cylinder was a co-axial cable junction, an air inlet and an outlet.

For the work on the $\text{H}_2\text{O}_2(1\Delta_g)$ system, a second discharge was used attached to the 6 mm inlet probe. For this work a clip-on cavity from Optos Instrument Company was used with a second Microtherm unit.

ESR Spectrometer.

The ESR signals were recorded on a Varian V4502 spectrometer, usually operated in the low power mode. The magnet was a Varian nine-inch magnet with a 2 and 5/8 inch gap.

The ESR cavity employed in these experiments was a large-access cylindrical cavity which operated in the $\text{TE}_{01n}$ mode. Modeled after the Varian V4535 cavity, it differs from the commercial model in that the end plates are split, permitting them to be attached after the flow line is in place extending through the cavity. One other variation is that one solid end plate was designed which could be screwed into the cavity in order to alter the standing wave pattern inside and to increase the spectrometer sensitivity.

For quantitative measurements the first derivative signals were
integrated using a conventional integrating circuit employing a Union Carbide general purpose operational amplifier H 6010. The fifteen volt source required by the operational amplifier was supplied by a Philbrick Researches PR-30 regulated power supply.

The electronically-integrated signals were further integrated manually using a K & E planimeter model 62 0000.

McLeod Guage.

Early attempts to use a commercial rotating McLeod guage showed that the device was both insensitive and unreliable at pressures of about 130 Nm⁻². Since accurate pressure measurements are essential to fast-flow kinetic measurements, a McLeod guage was designed and constructed.

The internal diameter of a length of capillary tubing was calibrated by measuring the length of a known volume of mercury at various points along the tube. A linear portion of this calibrated tubing was then used as the closed, center tube of a McLeod guage. The total volume of gas trapped in the guage was determined by filling the closed tube with mercury and calculating the volume from the weight increase and reasonable estimates of meniscus effects. By compressing the trapped gas to a fixed volume in the center capillary tube, the sensitivity of the device is calculable, and the scale on the outside capillary is linear. Linearity of the pressure measuring scale permits more accurate reading of the pressure than is possible with the approximately quadratic scale of the conventional guage. By changing the fixed volume of gas trapped in the center capillary tube, the effective pressure-measuring range of the guage can be adjusted.

Experimental use of the device has demonstrated that it is very
reproducible, and reasonable estimates of errors in the calibrating measurements above indicate that the device is accurate to 1.3 Nm$^{-2}$ at a total pressure of 130 Nm$^{-2}$.

Gases.

Inert gases, N$_2$, O$_2$, and prepurified hydrogen were supplied by the Linde and the Big Three Industrial gas companies. The gases were used as delivered without purification.

Matheson Gas Products supplied two special gas mixtures used during this work. One was a mixture of N$_2$ with 500 ppm O$_2$, and the second was a mixture of He and 5.54% O$_2$. Most of the experiments in the O + H$_2$S study were carried out with the He/O$_2$ mixture.

Originally the H$_2$S used (Matheson 99.6%) was further purified by condensing the gas, pumping on the solid, evaporating the chemical and re-condensing the middle portion. The gas distillation cycle was repeated three times for each flask of gas prepared. However, experimental usage showed that such purification was unnecessary, and the process was discontinued.

Other gases used were NO (Matheson 98.5%), NO$_2$ (Matheson 99.5%), SO$_2$ (Matheson 99.9%), and C$_2$H$_2$ (Matheson 99.6%).

Miscellaneous.

All studies were conducted at 297 $\pm$ 3 K.

Computer analysis was carried out on both an IBM 1620 and an IBM 7094 computer.
RESULTS AND DISCUSSION

Two of the chemical systems known to produce large amounts of SO radical are: (1) the reaction of O and OCS,\(^4^8\) and (2) microwave discharge of SO\(_2\) in a diluent.\(^4^9\) These systems were investigated in an attempt to verify the validity of the quantitative expressions used for SO.

When subjected to a microwave discharge, a 1–3% mixture of SO\(_2\) in Ar produces significant quantities of both SO and O. Both of these radicals are relatively stable under the typical flow conditions used and can easily be pumped several meters along the flow tube. Introduction of nitrogen dioxide into the flow system removes both radicals via

\[
\text{NO}_2 + O \rightarrow \text{NO} + O_2 \quad \text{and} \quad \text{(a)} \\
\text{NO}_2 + \text{SO} \rightarrow \text{NO} + \text{SO}_2 \quad \text{.} \quad \text{(b)}
\]

If SO and O are the only species produced in the discharge which react with NO\(_2\), then gas titration techniques may be used to determine the total concentration of O and SO, and the gas titration result may be compared with the sum of the two radical concentrations as calculated by ESR.

Such an experiment was carried out in this study. A 3% mixture of SO\(_2\) in Ar was discharged in a microwave cavity 50 cm upstream from the ESR cavity. The spectra of both SO and O were observed and recorded as NO\(_2\) was added to the system. Titration curves similar to the one in Figure III.1. were obtained. From such curves the total concentration of reactive species could be measured. Similar titration curves were obtained whether the NO\(_2\) was introduced 7 cm or 20 cm
Figure III.1. Plot of concentration of O and SO against NO₂ flow rate. Concentration units are $10^{14}$ molecules cm⁻³, and the flow rate is in units of cm³-cm of Hg/sec.
upstream of the detection point, and the concentration measured by
the gas titration was therefore considered to be equal to the total
concentration at the cavity. This result also meant that the wall
recombination of the radicals could be assumed to be negligible.
From the titration curves like Figure III.1, comparison of the rates
of reactions (a) and (b) may be made.

Table III.1. lists the results of several titrations of the
SO$_2$/Ar discharge products with NO$_2$. The total reactive species con-
centration determined by gas titration is given in column one. Column
two gives the concentration of atomic oxygen determined by ESR spec-
troscopy. The next column lists the estimated SO concentration as
given by the difference of the first two columns. Column four gives
the concentration of SO calculated by ESR. All calculations for
the fourth column used the SO line (i) and one line of the central
triplet of NO.

Throughout this study the quantitative measurements of SO are
based on line (i) of the SO spectrum. Table III.2. compares the inte-
grated absorption of the four lines of the SO spectrum observed with
their theoretical values assuming cylindrical symmetry. The ratio of
the intensity of line (g) to (i) agrees with theory, but that for lines
(h) and (j) to (i) does not. This discrepancy may arise from the fact
that $f_{E,x} \neq f_{E,z}$. This explanation is supported by the observation that
line (h) tended to saturate at much lower power levels than did lines
(g) and (i). Since the filling factor for NO is the same as that for
lines (g) and (i), the larger line (line (i)) was used for all quanti-
tative work.

The NO$_2$ flow rates used above were calculated as described before
TABLE III.1. Table of SO + O concentrations from SO\textsubscript{2} discharge.

<table>
<thead>
<tr>
<th>[SO]+[O] from titration</th>
<th>[O] from ESR</th>
<th>[SO] difference from cols. (1) &amp; (2) ESR</th>
<th>[SO] from ESR</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.52</td>
<td>1.37</td>
<td>2.15</td>
<td>0.99</td>
</tr>
<tr>
<td>3.41</td>
<td>1.21</td>
<td>2.20</td>
<td>1.42</td>
</tr>
<tr>
<td>5.10</td>
<td>1.87</td>
<td>3.23</td>
<td>1.89</td>
</tr>
<tr>
<td>5.51</td>
<td>2.17</td>
<td>3.34</td>
<td>1.65</td>
</tr>
<tr>
<td>3.15</td>
<td>0.70</td>
<td>2.45</td>
<td>1.51</td>
</tr>
<tr>
<td>4.62</td>
<td>1.26</td>
<td>3.36</td>
<td>1.44</td>
</tr>
</tbody>
</table>

All concentrations are in units of $10^{14}$ molecules cm$^{-3}$.

TABLE III.2. Relative integrated intensities of lines of $^{32}$SO.

Lines were normalized with respect to line (i). Theoretical values are based upon the assumption that $f_{E,x} = f_{E,z}$.

<table>
<thead>
<tr>
<th>LINE (g)</th>
<th>LINE (h)</th>
<th>LINE (1)</th>
<th>LINE (1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>THEORY</td>
<td>0.63</td>
<td>1.82</td>
<td>1.00</td>
</tr>
<tr>
<td>MEASURED</td>
<td>0.70</td>
<td>1.43</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.66</td>
<td>1.43</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.70</td>
<td>1.53</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.59</td>
<td>1.29</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>1.45</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>----</td>
<td>1.45</td>
<td>1.00</td>
</tr>
</tbody>
</table>
using Δ(PV) measurements of gas flows out of a known volume. However, NO\textsubscript{2} is very corrosive and soon contaminates the walls of the Hg manometer used to measure the pressure. For this reason, a manometer bulb of the type shown in Figure II.4. (b) was often used, with the pressure measurements being made using the side of the manometer not in contact with the NO\textsubscript{2}. In addition, at reasonable pressures NO\textsubscript{2} exists to a certain extent in dimer form as N\textsubscript{2}O\textsubscript{4}, and the equilibrium must be accounted for in any gas flow measurements. The equilibrium constant was calculated as a function of pressure from the data tabulated by Verhoek and Daniels.\textsuperscript{50} This procedure gave the following room temperature equation:

\[ K_{eq} = 0.143641 - (0.0294908)(P), \]

where \( K_{eq} \) is the equilibrium constant and \( P \) is the pressure in atmospheres.

Because of the complexity of calculating NO\textsubscript{2} flow rates, the calculations were checked by trapping NO\textsubscript{2} at 77 K and comparing the calculated and the measured flow rates. The NO\textsubscript{2} flow rates were also checked several times using gas titration techniques. The atomic N from a nitrogen discharge was titrated with NO to produce atomic oxygen which was then titrated with NO\textsubscript{2}. Both of these methods demonstrated that NO\textsubscript{2} flow rates could be accurately determined.

The reaction system of

\[ \ce{0 + OCS = SO + CO} \] (c)

has recently been used by Miller\textsuperscript{31} to verify the accuracy of the SO quantitative expressions. Table III.3. gives the results of an experiment carried out to check Miller's results. The amount of atomic oxygen formed by discharging a mixture of 6\% O\textsubscript{2} in Ar was determined by ESR and NO\textsubscript{2} titration. A small flow of OCS was added a few centimeters downstream of the discharge in order to reduce the atomic oxygen to
TABLE III.3. Comparison of O and SO concentrations as given by ESR and titration of the O + OCS reaction system. Concentrations are in units of $10^{14}$ molecules cm$^{-3}$.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>4.18</td>
<td>2.42</td>
<td>0.60</td>
<td>3.02</td>
<td>2.98</td>
</tr>
</tbody>
</table>
about 50% of its initial concentration. The resulting concentration of SO was determined by ESR, and the sum of the O and SO concentrations was determined by NO₂ titration. The titrations are shown in Figure III.2, while the pertinent concentration values are listed in Table III.3.

SO Integrals—Discussion.

Because one of the major intermediate products in the oxidation reaction of H₂S is the radical SO, it is important to this study to be able to measure accurately the SO concentration. The quantitative expressions for SO as derived earlier have recently been verified by Breckenridge and Miller. 31 These experimenters apparently reacted atomic O completely with OCS via reaction (c) to form large amounts of SO which were then titrated with NO₂. In addition to verifying the reliability of ESR in determining the concentration of SO, Breckenridge and Miller demonstrate that reaction (a), first reported by Clyne et al., 49 proceeds stoichiometrically as written. A similar method was used in this laboratory to verify the above work, and the results were given above in Figure III.2 and Table III.3. It is obvious that this work substantiates the quantitative expressions for SO.

The reaction of O with OCS has been thoroughly studied and appears to be a straightforward reaction with well defined stoichiometry and few, if any, complicating steps. 6,7,48,51-54 It therefore seems unlikely that the reaction (c) would produce significant quantities of any species which may react with the NO₂ and destroy the reliability of the titration results.

The first quantitative expressions for SO were published by this researcher and G. P. Glass 55 and were in error by a factor of two. 31
Figure III.2. Plot of O removal vs. [NO₂] added. The O intensity is given in arbitrary units. ∅ is the titration of O when OCS flow = 0.0

# is the titration of O when OCS flow 4 cm³-cm of Hg/sec.
This error came about because equation [30] above, as given by Westenberg\textsuperscript{22} and used by Cupitt and Glass yields a matrix term twice the correct value.\textsuperscript{31,32} The matrix elements for SO were taken from Carrington\textsuperscript{45} and were calculated in a manner such that the correct matrix term was derived. The result then was that the originally published quantitative expressions gave SO concentrations which were a factor of two too large. (Actually the published ratios are not exactly a factor of 2 larger than those quoted herein since no correction was applied to the published ratios to account for the fact that $^{32}$S comprises only 95% of all sulfur, while the ratios given in this thesis do reflect this fact.) It should be noted that while the published ratios for OH\textsuperscript{22} and SH\textsuperscript{55} to NO were calculated using technically inaccurate equations, since the error appeared both in the numerator and denominator, the ratios should be reliable.

In reference 55 some experimental results from this lab were quoted which seemed to lend credence to the inaccurate transition calculations for SO. The data are reproduced in Table III.1. except this time the currently accepted quantitative expressions for SO determination have been used in column four. If the values in the fourth column are doubled, they agree to within ±15% with the value of SO given in column three. The concentrations in the third column have been determined by subtracting the ESR measured concentration of atomic oxygen (column two) from the total reactive species given in the first column as determined by gas titration. Using the inaccurate transition expressions originally published, the experimental and calculated values of SO roughly agreed, and this worker and Dr. G. P. Glass were led to conclude "this (agreement) gives some confidence that the transition probabilities for SO
are correct and useful. Unfortunately it does not constitute proof
since while it is certain that \( \text{NO}_2 \) does titrate \( \text{SO} \) and \( \text{O} \), it is not
certain that other species that react rapidly with \( \text{NO}_2 \) are totally
absent from the products of the \( \text{SO}_2 \) discharge."\(^5\)

The question then arises of why the experimental data with the
\( \text{SO}_2/\text{Ar} \) discharge gave apparent agreement with inaccurate theoretical
calculations. In seeking an answer, one needs to consider sources of
possible error in Table III.1. Column one could be incorrect if the \( \text{NO}_2 \)
flow rates were inaccurately measured. But the flow rates of \( \text{NO}_2 \) have
been thoroughly checked using a number of methods as described above in
the section outlining the results of the \( \text{SO} \) integral experiments. The
second column could be in error if either the theoretical or experi-
mental techniques used in calculating the \( \text{O} \) concentration by ESR are
incorrect. However, the theory has been shown to be valid by other
workers,\(^1\) and numerous checks of ESR-determined \( \text{O} \) concentrations com-
pared to gas titration determinations (using \( \text{N} + \text{NO} \) to form a known
amount of \( \text{O} \)) have demonstrated that the experimental technique used
throughout this study is valid. It seems unlikely, therefore, that
columns one and two should have any large error, and one is led to con-
clude that column three just must not represent the \( \text{SO} \) concentration
alone. This could occur either because the titration reactions form
some reactive species or because some reactive products are produced
in the discharge process in addition to the observed \( \text{O} \) and \( \text{SO} \). There
is an abundance of experimental data to indicate that the reaction of
\( \text{NO}_2 \) with both \( \text{SO} \) and \( \text{O} \) proceed simply and stoichiometrically without
the formation of complicating products.\(^3\),\(^4\),\(^5\) It is presently felt
that the apparent agreement of the experimental results with the theory
as published by Cupitt and Glass was merely fortuitous and was probably the result of the presence of some discharge product which would react rapidly with NO₂.

This conclusion conflicts, however, with the results presented by Clyne, et al.⁴⁹ These experimenters used a weak discharge through SO₂/Ar to examine the blue chemiluminescence characteristic of oxidation of sulfur containing compounds. They demonstrated that in their discharge system, the concentration of any species other than SO and O which could react rapidly with NO₂ was very small. By implication, the discharge system used in this lab should give O and SO as essentially the only products also. There are some differences between the two studies however. Clyne, et al. state, "the flow of nitrogen dioxide at the end-point was always greater, by a factor of about two, than the oxygen atom flow. .."⁴⁹ Examination of Table III.1. shows that under the experimental conditions of reference 55, the ratio of NO₂ flow to [O] (column one to column two) averages to 3, not 2. In addition, a slight deposition of a wall coating was observed just downstream from the discharge, while Clyne and co-workers report that they found no evidence of wall deposits. While reconsideration of the data may indicate that some species other than O and SO may have occurred in the experiments in this lab with a SO₂/Ar discharge, conclusive proof is not available and further investigation is warranted.

While some question still exists regarding the products of a SO₂/Ar discharge, the quantitative expressions derived earlier in this paper will be assumed to be correct and will be employed in subsequent investigations to be discussed. This seems to be a reasonable assumption since the quantitative expressions have been verified in two
different laboratories using a reaction system which has been shown, through extensive research, to be "clean," free of any complicating species.

As NO$_2$ is introduced into a mixture of O and SO, the radicals compete to react with the NO$_2$ available. Radical removal profiles like that shown in Figure III.1. provide enough information to permit determination of the ratio of reaction rate constants, $k_a/k_b$. In integrated form the relative reaction rate equals

$$\frac{k_a}{k_b} = \frac{\ln([O]/[O]_o)}{\ln([SO]/[SO]_o)} \quad [48]$$

where $[O]_o$ and $[SO]_o$ are the original O and SO concentrations. The relative reaction rate was calculated in this study as $0.63 \pm 0.06$. This value is very close to that quoted by Clyne, et al.$^{49}$ of $0.67 \pm 0.07$. Using Westenberg's$^{48}$ value of $k_a = 7.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, one calculates $k_b = 1.1 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. The agreement of the relative reaction rate between this study and that of Clyne and his co-workers does have some implications regarding the nature of any additional products formed in the SO$_2$/Ar discharge. If the postulated additional products reacted with NO$_2$ to produce either O or SO, the measured relative reaction rate would have differed from that of Clyne, et al. It can therefore be assumed that the reaction of NO$_2$ with any additional species present in the discharge mixture does not go to give either O or SO.

It was stated above that NO$_2$ titrations of O and SO at 7 cm and 20 cm from the center of ESR detection gave identical titration end points. This fact implies that since the additional 13 cm during which wall effects may occur had no effect on the experimentally determined
concentration, wall reactions involving O and SO may be safely ignored. This technique (titration at various points along the flow tube) has been used many times during this study and indicates that wall recombination of the species O, SO, H, and N is negligible under the experimental conditions employed.

Another method of estimating wall effects is to examine reaction profiles. Figure III.3. gives a reaction profile for the titration reaction $N + NO = O + N_2$. It demonstrates that the wall recombination rate constant of O is essentially zero. Figure III.8., which plots S concentration against distance, can be utilized to show that $k_{w,S} < 20 \text{ sec}^{-1}$. A co-worker J. E. Breen has measured the wall recombination rate constant$^{15}$ for OH in similarly prepared flow tubes as $k_{w,OH} = 125 \text{ sec}^{-1}$.

Since insertion of the moveable glass probe into the flow line provides more surface upon which wall reactions may occur, comparison of radical signals when the probe is withdrawn with the signals observed when the probe is fully inserted can give some idea of the surface reaction effects. Radicals which gave consistent signals under the experimental conditions used for these studies regardless of the probe location include O, H, N, and $^1\Delta_g$ O$_2$.

Because the above observations indicated that the wall removal rates of atoms/radicals were very small, these removal rates were usually neglected in the following kinetic studies. Of course, the standard gases employed, O$_2$ and NO, did not show any wall effects.

Before proceeding to a discussion of kinetics of several chemical systems, a few comments on the effects of the mixing zone may be appropriate. Under typical flow conditions, a mixing zone extends about 1.5-2.0 cm downstream from the moveable probe. In chemiluminescent
Figure III.3. Plot of $O$ intensity in arbitrary units vs. the distance between the ESR detection point and the inlet probe. $N$ was formed in the discharge, and $NO$ was added through the probe to form the observed $O$.

Flow velocity = 1890 cm sec$^{-1}$
reactions, the mixing zone appears as a conical glow extending from the inlet probe tip to the flow tube walls. Obviously, valid kinetic measurements cannot be obtained within this region because (1) localizations of concentration and heat may occur to increase the reaction rate within the mixing region and (2) the filling factor for ESR detection occupies more than just the mixing zone itself making measurements of concentrations in the inhomogeneous mixing zone difficult. One instrumental factor also hinders taking measurements within this region. Insertion of the moveable probe to about 2 cm of the ESR detection point begins to change the resonating characteristics of the ESR cavity, producing erroneous ESR signals. For these reasons, kinetic measurements were taken only outside the mixing region.

One final note should be made regarding SO concentration measurements by ESR. It was noted previously that the ratio of line (g) to (i) agrees with theory, but the ratio for lines (h) and (j) to (i) does not. The theoretical intensities assume cylindrical symmetry of the standing wave pattern in the cavity and therefore \( f_{E_x} = f_{E_z} \). The experimental evidence suggests that assumptions regarding the equality of filling factors need to be approached with caution. Indeed, it would be far better to avoid such assumptions and use only ESR signals which have identical filling factors as that of the standard gas used, in this case NO. Therefore, quantitative measurements of SO, when compared to NO, should involve only lines (g) and (i).

H\textsubscript{2}S Reaction Results—O + H\textsubscript{2}S.

Early experiments with the O + H\textsubscript{2}S system were designed to follow the supposedly pseudo-first order decay of atomic oxygen in a large excess of H\textsubscript{2}S. Figure III.4. shows some of these runs. It is obvious
Figure III.4. Decay of atomic oxygen in hydrogen sulfide rich mixtures. Total pressure for all runs was 80 Nm⁻². All experiments were conducted in the absence of molecular oxygen. Concentrations for the runs are (in units of 10¹⁴ molecules/cc): for #, [H₂S]₀ = 6.91, [O]₀ = 1.05; for X, [H₂S]₀ = 12.64, [O]₀ = 1.10; for O, [H₂S]₀ = 16.95, [O]₀ = 1.05.
from the curvature of the plots that the reaction in the presence of excess \( \text{H}_2\text{S} \) is not pseudo-first order. Further examination indicated that the reaction order was about 0.65, and it therefore became desirable to examine the reaction in near stoichiometric or atomic oxygen rich conditions.

The atomic oxygen in the excess \( \text{H}_2\text{S} \) studies was generated by discharging pure nitrogen gas and then titrating the N atoms with NO to form a known concentration of O via the reaction

\[ \text{N} + \text{NO} = \text{O} + \text{N}_2 \]  

(d)

and the reaction was investigated in the absence of molecular oxygen. However, the amount of atomic oxygen which may be produced in this manner is severely limited by the inefficiency of the nitrogen discharge process. Since it was desirable to increase the O/\( \text{H}_2\text{S} \) ratio and to keep the product formation high, a different, more efficient source of atomic oxygen was needed. A switch was therefore made to a 5.54% \( \text{O}_2 \) in He mixture. This permitted approximately a six-fold increase in initial atomic oxygen concentration without severely changing pressures or flow rates.

When \( \text{H}_2\text{S} \) was introduced into the discharged mixture of 5.54% \( \text{O}_2 \) in He, the spectra of O, H, and SO were easily observed. Complete reaction profiles are shown for various conditions in Figures III.5. and III.6. In these figures the transformation from distance along the flow tube to reaction time was made assuming the flow velocity to be constant. A small Poiseulle's law pressure drop makes the above assumption slightly inaccurate; however, the pressure drops effected by the experimental conditions of these experiments were not extreme and were taken into account in all calculations of rate constants.
Figure III.5. (a): Experimental reaction profiles depicting the observed radical concentrations as a function of time. The concentration units are $10^{14}$ molecules cm$^{-3}$, and [H] has been multiplied by 5.0 before being depicted. The abscissa is in units of msec. $[0]_0 = 6.00 \times 10^{14}$ atoms cm$^{-3}$. $[\text{H}_2\text{S}]_0 = 2.73 \times 10^{14}$ molecules cm$^{-3}$. Total pressure is 105 Nm$^{-2}$. 
Figure III.5. (b): Similar to figure III.5. (a), but with different initial conditions. 
$[O]_0 = 7.58 \times 10^{14}$ atoms cm$^{-3}$. 
$[O_2]_0 = 6.26 \times 10^{14}$ molecules cm$^{-3}$. Total pressure = 9.18 Nm$^{-2}$. 

CONCENTRATION, $10^{14}$ molecules cm$^{-3}$ 

TIME, usec 

0 2 4 6 8 10 12 

0 2 4 6 8 10 12
Figure III.6. Comparison of experimental and theoretically calculated concentrations of O, H, and SO in a very H₂S-rich mixture. \([O]_0 = 4.28 \times 10^{14}\) atoms cm\(^{-3}\). \([H₂S]_0 = 20.2 \times 10^{14}\) molecules cm\(^{-3}\). 0 on the graph represents the experimentally measured \([O]\); \(\ldots\) represents the theoretical O profile. The symbol \(\bar{H}\) on the graph represents \(5 \times [H]\) experimentally measured; \(\overline{\ldots\ldots}\) is the predicted profile of \(5 \times [H]_{\text{theoretical}}\). X is the experimental [SO] and the line \(\ldots\ldots\) indicates the predicted SO profile. The values of rate constants used to predict the concentration profiles are those calculated in this paper. A mixing zone region of 1 msec was assumed in the theoretical calculation.
The fact that the profiles do not always extrapolate smoothly through the origin indicates the presence of a definite mixing zone that extends approximately 2 cm downstream of the moveable inlet probe.

Figures III.5. and III.6. illustrate some important facts pertinent to the reaction scheme. For each O atom consumed, about 0.2 or less hydrogen atoms are formed. In addition, the amount of SO formed is less than the amount of O removed.

Since most kinetic runs were carried out with the 5.54% O₂ in He mixture in which approximately one-half of the molecular oxygen remained undissociated, an experiment was run to estimate the effect of the molecular oxygen on SO production. Atomic nitrogen was formed by discharging N₂ in the discharge cavity. A dual-inlet probe, in which a 3 mm o.d. inlet extends 2 cm beyond a second inlet with a 6 mm o.d., was used to titrate the atomic N with NO to form atomic O as described earlier. H₂S was then added through the inner inlet which was positioned 20 cm upstream of the ESR detection point, and O₂ was added through an upstream inlet. The concentration of SO was measured as a function of O₂ concentration. The results of these measurements are shown in Table III.4. Molecular oxygen was apparently of little effect, since the SO production was increased only by 5–10%.

Throughout this study numerous attempts were made to observe OH, SH, and S. OH was detected at short reaction times in a near stoichiometric mixture. For a reaction system of [H₂S]₀ = 1.16 x 10¹⁵ molecules cm⁻³, [O]₀ = 9.66 x 10¹⁴ atoms cm⁻³, and a time of 1.5 msec, [OH] ≈ 1.1 x 10¹³. The measurement is not very accurate, since the signal-to-noise ratio was approximately 2. Neither SH nor S radicals were ever detected during this study, and upper limits of 5 x 10¹¹ molecules cm⁻³ and 7 x 10¹¹
TABLE III.4. Effect of $O_2$ on SO formation. $[O]_o = 2.85 \times 10^{14}$ atoms cm$^{-3}$. Reaction time is 13 msec. $[SO]$ measurements are relative measurements. The SO concentrations in the $O_2$-rich mixture are averages of several runs. $O_2$ and $H_2S$ concentrations are in units of $10^{14}$ molecules cm$^{-3}$.

<table>
<thead>
<tr>
<th>$[H_2S]_o$ = 5.75</th>
<th>$[H_2S]_o$ = 1.66</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[O_2]_o$</td>
<td>$[O_2]_o$</td>
</tr>
<tr>
<td>[SO]</td>
<td>[SO]</td>
</tr>
<tr>
<td>0.00</td>
<td>5.15</td>
</tr>
<tr>
<td>2.25</td>
<td>5.25</td>
</tr>
<tr>
<td>6.00</td>
<td>5.72</td>
</tr>
<tr>
<td>10.3</td>
<td>5.62</td>
</tr>
</tbody>
</table>
atoms cm\(^{-3}\) could be placed on their concentrations.

During all kinetic runs, a blue chemiluminescence similar to that attributed\(^{49}\) to the third-body reaction of atomic oxygen and SO was observed.

Whenever \(\text{H}_2\text{S}\) was added in excess a pale yellow deposit, presumed to be sulfur, appeared on the flow tube walls. Both the rate of coating and the point of first appearance downstream from the inlet could be varied by changing the \(\text{H}_2\text{S}\) flow. Whenever the deposits were subjected to a flow of atomic oxygen, the deposits were removed from the wall and the characteristic blue glow mentioned above was seen. Whenever the atomic oxygen was in excess, no deposits were observed.

**H + H\(_2\)S Results.**

Introduction of \(\text{H}_2\text{S}\) into a dilute solution of atomic hydrogen in argon, resulted in the appearance of the ESR spectra of both SH and S. As the concentration of \(\text{H}_2\text{S}\) was increased, the concentrations of both radicals rose, reached a maximum and eventually fell. Figure III.7. depicts the radical concentrations as a function of initial \(\text{H}_2\text{S}\) concentration. The figure shows that the maximum [S] occurred at lower \(\text{H}_2\text{S}\) flow rates than the maximum SH concentration. It also shows that at low \(\text{H}_2\text{S}\) flow rates, the SH concentration, [SH], was proportional to the initial \(\text{H}_2\text{S}\) concentration, \([\text{H}_2\text{S}]_0\).

At low \(\text{H}_2\text{S}\) flow rates \((|\text{H}|_0/|\text{H}_2\text{S}]_0 > 10\), atomic sulfur was very stable and could be pumped 20 cm downstream with very little loss. This behavior is illustrated in Figure III.8. Under the conditions of this experiment [S] was measured as 95 \(\pm\) 10 \% \([\text{H}_2\text{S}]_0\), and no evidence was observed of solid polymer formation.

As the \(\text{H}_2\text{S}\) flow rate was increased so that the atomic hydrogen to
Figure III.7. Dependence of [S] and [SH] upon \([H_2S]_0\). Reaction time is 1.1 msec, flow velocity = 1820 cm sec\(^{-1}\), pressure = 79 atm\(^{-2}\), \([H]_0 = 3.44 \times 10^{14}\) atoms cm\(^{-3}\). [S] is in units of \(10^{13}\) atoms cm\(^{-3}\). [SH] is in units of \(10^{12}\) molecules cm\(^{-3}\).
Figure III.8. Plot of $[S]$ against distance along the flow tube. Pressure was 47 Nm$^{-2}$, with a flow velocity of 1380 cm sec$^{-1}$. $[H]_o = 4.71 \times 10^{14}$ atoms cm$^{-3}$. $[H_2S]_o = 2.00 \times 10^{13}$ molecules cm$^{-3}$.
hydrogen sulfide ratio approached unity, a yellow wall coating was formed several centimeters downstream of the H₂S inlet. Some attempt was made to measure the rate of hydrogen atom decay in such systems, but these attempts were abandoned when it became clear that the rate of H atom removal was dependent upon the extent of the wall coating. However, some measurements were taken before the wall coating became heavy, and the results of these measurements are displayed in Table III.5. The wall coating appeared and behaved identical to the yellow coating described above in the O + H₂S results. Introduction of O₂ into the discharge mixture removed the wall deposits and resulted in the appearance of the visible, blue chemiluminescence, characteristic of the presence of SO and O. Only a moderate amount of O₂ was needed to remove all trace of atomic sulfur, but the SH radical could be observed even at very high O₂ flow rates. Numerous kinetic runs showed that, when \([O_2]_o \gg [H]_o > [H_2S]_o\), SO production paralleled that in the O + H₂S system.

Figure III.9. depicts the dependence of H, O, and SH upon the initial H₂S concentration in the H/H₂S/large excess O₂ system. When the ratio \([H_2S]_o/[H]_o\) was greater than 0.3, the O atom concentration was proportional to the concentration of atomic hydrogen. The ratio \([H]/[O]\) was measured as \(6.50 \pm 0.70\) in a number of experiments; these results are recorded in Table III.6.

Table III.7. shows the results of many experiments in which the concentrations of all observable reaction species were measured. These experiments were performed over a wide range of pressures using a large excess of O₂.

H₂S Reactions—Discussion.

The oxidation of hydrogen sulfide has been extensively studied by
TABLE III.5. Concentration measurements in the absence of $O_2$. All concentrations are in units of $10^{14}$ molecules cm$^{-3}$. $t$ is the reaction time in msec.

<table>
<thead>
<tr>
<th>[H]$_o$</th>
<th>[H$_2$S]$_o$</th>
<th>t</th>
<th>[H]</th>
<th>[H$_2$S]$^a$</th>
<th>[SH]</th>
<th>$k_5/k_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.70</td>
<td>3.50</td>
<td>2.2</td>
<td>1.70</td>
<td>1.00</td>
<td>0.065</td>
<td>16</td>
</tr>
<tr>
<td>3.50</td>
<td>2.88</td>
<td>1.1</td>
<td>1.92</td>
<td>2.09</td>
<td>0.042</td>
<td>48</td>
</tr>
<tr>
<td>2.28</td>
<td>2.88</td>
<td>1.1</td>
<td>0.50</td>
<td>1.99</td>
<td>0.043</td>
<td>45</td>
</tr>
<tr>
<td>1.44</td>
<td>2.88</td>
<td>1.1</td>
<td>0.28</td>
<td>2.30</td>
<td>0.039</td>
<td>58</td>
</tr>
</tbody>
</table>

a. [H$_2$S] estimated as [H$_2$S]$_o$ - $1/2([H]_o - [H])$. 
Figure III.9. Dependence of H, SH, and O concentrations upon $[\text{H}_2\text{S}]_0$.

The reaction mixture contained a large excess of $O_2-[O_2] = 2.92 \times 10^{15}$ molecules cm$^{-3}$. Reaction time = 3.3 msec. Pressure = 89 Nm$^{-2}$. $[\text{H}]_0 = 4.90 \times 10^{14}$ atoms cm$^{-3}$. Approximate values of $[O]$ and $[\text{SH}]$ are given in units of $10^{13}$ and $10^{12}$ molecules cm$^{-3}$ respectively.
TABLE III.6. A comparison of the steady-state concentrations of O and H. All concentrations are in units of $10^{14}$ molecule cm$^{-3}$. Time is in msec.

<table>
<thead>
<tr>
<th>[H]$_0$</th>
<th>[H$_2$S]$_0$</th>
<th>TIME</th>
<th>[H]</th>
<th>[O]</th>
<th>[O$_2$]</th>
<th>[H]/[O]</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.70</td>
<td>3.37</td>
<td>3.73</td>
<td>1.40</td>
<td>0.23</td>
<td>26.4</td>
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<td>&quot;</td>
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</tr>
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<td>1.24</td>
<td>0.17</td>
<td>&quot;</td>
<td>6.96</td>
</tr>
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</table>

Average -- 6.50 ± 0.69
TABLE III.7. Concentrations of various species in the \( H + H_2S + O_2 \) reaction. Concentration units are molecules cm\(^{-3}\). \([H_2S]\) is taken as \(([H_2S]_o - [SO] - [SH])\).

<table>
<thead>
<tr>
<th>PRESSURE Nm(^{-2})</th>
<th>([H]_o \times 10^{-14})</th>
<th>([H_2S]_o \times 10^{-14})</th>
<th>([O_2] \times 10^{-14})</th>
<th>([H] \times 10^{-14})</th>
<th>([O] \times 10^{-13})</th>
<th>([SH] \times 10^{-12})</th>
<th>([SO] \times 10^{-14})</th>
<th>([H_2S] \times 10^{-14})</th>
<th>(k_5/k_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>65.3</td>
<td>10.0(^a)</td>
<td>3.32</td>
<td>0.0</td>
<td>3.9(^a)</td>
<td>0.00</td>
<td>2.9(^a)</td>
<td>----</td>
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<td>----</td>
</tr>
<tr>
<td>66.5</td>
<td>&quot;</td>
<td>3.22</td>
<td>7.9</td>
<td>4.6(^a)</td>
<td>1.5(^a)</td>
<td>1.6(^a)</td>
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</tr>
<tr>
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<td>75.0</td>
<td>3.0(^a)</td>
<td>1.0(^a)</td>
<td>1.1(^a)</td>
<td>----</td>
<td>----</td>
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</tr>
<tr>
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<td>1.19</td>
<td>2.26</td>
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</tr>
</tbody>
</table>

\(^a\) Concentration given in arbitrary units.

\(37.8 \pm 6.9\)
a number of investigators. Experimental techniques include flash photolysis,\textsuperscript{8.56} shock waves,\textsuperscript{57} flames,\textsuperscript{58,59} and conventional static systems.\textsuperscript{60} Despite the interest and wide range of experimental methods, the over-all mechanism is still not well understood. In particular, uncertainty still exists concerning some of the reactions of the SH radical, an intermediate produced in the oxidation process. Also, the reaction scheme by which \( \text{SO}_2 \) is formed is very unclear.

In an attempt to resolve some of these problems, several groups have attempted to isolate and examine particular segments of the oxidative process. Luitj, Dondes, and Harteck\textsuperscript{51,61} have examined the reaction of atomic oxygen with \( \text{H}_2\text{S} \) using mass spectral analysis. Unfortunately, this segment of the oxidation process proved too complex for straightforward analysis and an estimated "chain length" had to be used to approximate the rate constant. Timmons, \textit{et al}.\textsuperscript{62} have restudied this reaction using ESR. They measured the overall rate of removal of atomic oxygen over the temperature range 205-300 K and deduced an activation energy for the initial abstraction reaction of 0 and \( \text{H}_2\text{S} \) of 1.50 kcal mole\(^{-1}\). Unfortunately, they too had to resort to estimating a chain length in order to calculate the rate constant.

Analysis of the experimental evidence presented earlier in this paper indicates that the reaction of atomic oxygen with \( \text{H}_2\text{S} \) (when \( [0] \gg [\text{H}_2\text{S}] \)) can be explained using the following mechanism:

\[
\begin{align*}
\text{O} + \text{H}_2\text{S} & \rightarrow \text{OH} + \text{SH} \quad (1) \\
\text{O} + \text{OH} & \rightarrow \text{H} + \text{O}_2 \quad (2) \\
\text{H} + \text{H}_2\text{S} & \rightarrow \text{H}_2 + \text{SH} \quad (3) \\
\text{SH} + \text{O} & \rightarrow \text{H} + \text{SO} \quad (4) \\
\text{SH} + \text{H} & \rightarrow \text{H}_2 + \text{S} \quad (5)
\end{align*}
\]
SO + OH = SO₂ + H  \hspace{1cm} (6)
S + O₂ = SO + O  \hspace{1cm} (7)
O + SO + M = SO₂ + M  \hspace{1cm} (8)

The experimental data can be accounted for without reactions (6) and (8), but these are known reactions which have a minor effect and have therefore been included. Because of its importance to the overall reaction scheme, reaction (3) was also studied in isolation, and the results have been given above. The observed quantitative conversion (95 ± 10%) of H₂S to S in the H/H₂S system, along with the observation of the SH spectrum, confirms the earlier suggestion of Thrush\textsuperscript{63,64} that in the presence of excess atomic H, the intermediate SH formed from reaction (3) reacts to form sulfur via reaction (5) above or (9) below.

SH + SH = S + H₂S  \hspace{1cm} (9)

While the overall stoichiometry is the same, it is possible to differentiate between the two SH removal mechanisms by examining the dependence of [SH] upon [H₂S]₀. When atomic H is present in large excess, H₂S is consumed by an effectively first-order process and [H₂S]ₜ, the concentration at any arbitrary time, is proportional to [H₂S]₀. Using steady state theory to calculate [SH] one finds

[SH] = k₃/k₅ [H₂S] = k' [H₂S]₀ \hspace{1cm} \text{[49]}

if one assumes (5) to be the major removal mechanism, while use of reaction (9) leads to the expression

[SH] = (k₃/k₅) [H] [H₂S] \text{[H₂S]} \text{[H₂S]}₀^{1/2} = k'' \text{[H₂S]}₀^{1/2} \hspace{1cm} \text{[50]}

The linearity of [SH] vs. [H₂S]₀ shown in Figure III.7. strongly suggests that under the experimental conditions given, the dominant removal reaction is (5), and for this reason (5) was used in the reaction scheme, rather than (9). Further evidence of the insufficiency of reaction (9)
will be developed later.

Equation [49] permits one to calculate directly the ratio \( k_3/k_5 \) if the concentrations of \( H_2S \) and SH are known. Since ESR cannot detect \( H_2S \), it is impossible to measure the concentrations directly. It is possible to estimate the concentration from the stoichiometry, however. If \([H][H_2S]\), only reactions (3) and (5) occur, then \([H_2S]\) is given by

\[
[H_2S] = [H_2S] - (1/2) ([H]_0 - [H]) .
\]

Using this expression in equation [49] several estimates of \([H_2S]/[SH] = k_5/k_3\) were calculated. These estimates are given in Table III.5. Unfortunately, the ratio is not constant and no reliable estimate of \( k_5/k_3 \) can be made. Perhaps one reason for the inconstancy is that if \([H] \gg [H_2S]\) the resulting \([SH]\) is small and the absolute magnitude of \([SH]\) can be calculated only with considerable uncertainty because of the low signal-to-noise ratio. At higher \( H_2S \) flow rates, \([SH]\) is larger, but yellow wall deposits begin to form and the overall mechanism is less certain, and the expression for the \([H_2S]\) above has questionable validity.

The mechanism by which wall deposits are formed remains uncertain. The lack of decay by atomic S in Figure III.8. demonstrates that it does not appreciably react on the walls. Third body recombination of S is also too slow to be significant at the experimental pressures used. Perhaps in the presence of high \( H_2S \) concentrations, sulfur polymerization is initiated by the reaction

\[
S + SH = S_2 + H .
\]

An upper limit of about 2 \( k_5 \) can be placed on \( k_{10} \) since under the conditions given for Figure III.8., 95% of the initial \( H_2S \) reacted to form atomic sulfur via reaction (5). At higher \( H_2S \) flow rates [S] and [SH]
both increase and the reaction may assume some importance.

Addition of $O_2$ to the $H/\text{H}_2\text{S}$ reaction mixture resulted in the hindrance of wall deposit formation and the appearance of large quantities of $SO$. This can be explained by the known\textsuperscript{64} rapid reaction

\[ S + O_2 = SO + O \quad . \quad (11) \]

In addition, the $SH$ may then react with the resulting atomic oxygen via reaction (4) above or with $O_2$ to give $OH$ and $SO$ via

\[ SH + O_2 = SO + OH \quad . \quad (12) \]

The data displayed in the first three lines of Table III.5. indicates that the role of reaction (12) is minor. Addition of $7.9 \times 10^{14}$ molecules cm\textsuperscript{-3} of $O_2$ reduced the $[SH]$ to almost one-half of its original value. However, $[SH]$ decreased only about 30\% more when $[O_2]$ was increased nearly ten-fold. Reaction (12) requires the attainment of a low entropy "four-center" transition state, and it may be expected to be relatively slow. Reaction (4) however is analogous to the abstraction reaction (2) which is known to be very fast\textsuperscript{10}. In addition, it has been observed that in the $O/\text{H}_2\text{S}$ reaction system with no $O_2$ available, $SH$ is still rapidly removed and $SO$ produced. It therefore seems likely that in the $H/\text{H}_2\text{S}/O_2$ reaction system, (12) does not contribute significantly to $SO$ formation, while reactions (11) and (4) must be considered.

The reaction of atomic oxygen with $H_2S$ is too slow to be of importance under these experimental conditions\textsuperscript{61,62,65} and the overall reaction for the $H/\text{H}_2\text{S}/O_2$ system should be described by a mechanism consisting of reactions (3), (5), (4), and (11). Using the steady state concentrations for $O$ and $S$, one derives the expression

\[ k_4 [O] = k_5 [H] \quad . \quad [52] \]

The range of conditions over which expression [52] is valid was checked
by numerically integrating the rate equations pertaining to the above mechanism using values of $k_3$ and $k_{11}$ taken from the literature,$^9, ^{64}$ along with values for $k_4$ and $k_5$ derived during this study. The approximation $[52]$ is not valid when the reaction time is short (i.e., there has not been sufficient time to permit formation of the steady-state atomic oxygen concentration) and when the $H_2S$ flow rate is low. Since only one atom of oxygen is produced for every molecule of $H_2S$ consumed, the $[H_2S]_0$ must exceed the steady-state $O$ atom concentration in order for $[O]$ ever to attain the steady-state value.

The data displayed in Table III.5. were obtained under conditions such that the steady-state approximation should have been valid. The constancy of the ratio $[H]/[O]$ implies that the chosen mechanism is valid. Using expression $[52]$, $[H]/[O] = k_4/k_5 = 6.5 \pm 0.7$.

The results shown in Figure III.9. dramatically confirm the validity of neglecting reaction (9) in the mechanism above. If this reaction were a major source of $S$, then the steady-state $[O]$ would be proportional to $[SH]$. In the graph $[O]$ is clearly proportional to $[H]$, even when $[H]$ is at its smallest value and $[SH]$ is at its largest concentration. This implies that $k_5$ $[H]$ $[SH]$ must be greater than $k_9$ $[SH]^2$ for the experimental conditions used. From the data given, the upper limit for $k_9$ is $2 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. Strausz, et al.$^{66}$ have reported a value of $2.3 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$, but this value may be too high since the analysis did not take account of the third body reaction $SH + SH + M = H_2S_2 + M$ (12) which may be important at their experimental pressures of 50000 Nm$^{-2}$. Mihelcic and Schindler$^{67}$ have studied the $H/H_2S$ system with $H_2S$ in excess using extremely fast flow velocities. They report a value of
\( k_9 = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \). It therefore seems that the upper limit for \( k_9 \) calculated above is reasonable.

Applying the steady-state approximation to the [SH] predicted by the mechanism (3), (5), (10) and (4), one finds

\[
[53] \quad k_3 \ [H] \ [H_2S] = [SH] \ (k_5 \ [H] + k_4 [O])
\]

Setting \( k_4 = 6.5 \ k_5 \), this expression can be rearranged to give

\[
[54] \quad \frac{k_5}{k_3} = \frac{[H] \ [H_2S]}{[SH] \ ([H] + 6.5 \ [O])}
\]

Approximating \([H_2S]\) by \([H_2S]_0 - [SO] - [SH]\), one may calculate the ratio \( k_5/k_3 \) from the data in Table III.7. The ratio is listed in the table and has a value of 37.8 ± 6.9.

The relative rate constant ratios of \( k_4/k_5 = 6.5 \) and \( k_5/k_3 = 37.8 \) can now be used to assist in the determination of rate constants in the \( \text{O/H}_2\text{S} \) reaction system.

The mechanism seems reasonably well established. Reactions (2), (6), (7) and (8) are well known. Reactions (1), (3), (4) and (5) seem reasonable in view of the observed products and the observations made above. Certain other reactions should be considered however.

Based upon isotopic labeling experiments, Luiti, Dondes, and Harteck have demonstrated that the possible reaction

\[
[14] \quad \text{O} + \text{H}_2\text{S} = \text{H}_2 + \text{SO}
\]

cannot make a significant contribution to the reaction scheme. In addition, the reaction

\[
[15] \quad \text{OH} + \text{H}_2\text{S} = \text{H}_2\text{O} + \text{SH}
\]

may be neglected since Luiti, et al. reported that very little \( \text{H}_2\text{O} \) was produced. Indeed, to compete effectively with (2) under the experimental conditions employed herein, \( k_{15} \) must be of the order of \( 10^{-8} \) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \), a value well above the collisional rate constant.
In addition to the above reactions, several SO removal reactions could possibly be included in the mechanism. These reactions will be discussed more fully later, but, using the best literature values given for these reactions involving SO, the effect of these reactions on the concentration profiles are minimal.

Having proposed a reaction scheme which can account for the qualitative experimental results (i.e., it accounts for removal of O, growth and decay of atomic H, formation of SO, and rapid removal steps for the species OH and SH so that the steady-state concentrations of these radicals may well be below the observable limits of the instrument), it becomes useful to attempt to apply the mechanism to quantitative results.

The reaction rate constant $k_\text{l}$ could not be measured exactly using excess $\text{H}_2\text{S}$. The initial slopes for the curves in Figure III.4. indicate O removal rate constants on the order of $2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. This value is similar to the overall O removal rate measured by Luiti, et al., but must be divided by an approximate "chain length" to give a value of $k_\text{l}$. Due to the non-linearity of the curves in Figure III.4. and the difficulty of estimating an average chain length, along with the formation of wall deposits when $\text{H}_2\text{S}$ was in excess, a different method of analysis was used to determine rate constants in O-rich and near stoichiometric mixtures.

The coupled rate constants of the mechanism given above were integrated numerically in a method similar to that described by Bulhman, et al. A simple first order Newtonian integration was employed using a step size of $10^{-4}$ seconds. Tests on the program showed that the use of this step size introduced no significant error into the calculation. Integration was initiated at the first experimental point in order to
avoid the effects of the mixing zone. The values of [O], [H], and [SO] at this point were taken from experimental profiles, and the [H₂S] at this point was taken as [H₂S]₀ - [SO]. A steady-state treatment was applied to SH and OH, since calculations indicated that this approximation was valid at reaction times longer than 10⁻⁵ sec. At each step of the integration, a correction for viscous pressure drop was applied using the Poiseuille's law discussed above. Also, the instantaneous linear flow speed was calculated and was used to perform the transformation between reaction time and the distance along the flow tube.

Whenever the computed time (distance) exceeded that at which an experimental determination of the SO, H, or O concentration had been made, the integration procedure was halted, and the value of [O], [H], or [SO] was extracted and stored. The integration was resumed and continued to the next experimental point. This process was repeated until the last point was reached. Since the pressure changed constantly along the flow tube, the initial concentrations were different at each experimental point. Technically then, each experimental point requires a separate integration procedure. Since experimental runs often contained as many as 30 points, having to perform a separate integration for each point would consume a great deal of computer time. Calculations showed that, under typical reaction conditions with reasonable values for the rate constants, the multiple integration procedure could be approximated to about 2% throughout the time range of 0 to 15 msec by performing a single integration using the initial concentration values at the point midway between the closest and farthest experimental measurements. Such a procedure was used in order to save computer time.

For any assigned values of the rate constants, the degree of fit
between the calculation and experiment was taken to be

\[
\frac{\sum [(\Delta 0)]^2}{\Sigma [\Delta 0]_{\text{ex}}} + \frac{\sum [(\Delta S0)]^2}{\Sigma [S0]_{\text{ex}}} + \frac{\sum [(\Delta H)]^2}{\Sigma [H]_{\text{ex}}}
\]

[55]

where \([\Delta 0]_{\text{ex}}\) represents the experimentally measured 0 concentration at any given reaction time and \([\Delta 0]\) is the difference between the calculated and the experimental concentration at that point. The sum of the squares of the differences were divided by the experimental concentrations as a normalization procedure used to give equal weight to the fit of all three species.

For all calculations \(k_2\) was fixed at \(4.3 \times 10^{-11}\) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\), \(k_6\) at \(1.17 \times 10^{-10}\) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\), \(k_7\) at \(1.2 \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\), \(k_8\) at \(8.3 \times 10^{-31}\) cm\(^6\) molecule\(^{-2}\) sec\(^{-1}\), \(k_5\) was set to \(37.8\) \(k_3\), while \(k_4\) was taken as \(6.5\) \(k_5\). Calculations indicated that the values of \(k_4\) and \(k_5\) could be varied by a factor of two without significantly affecting the reaction profile. No attempt was made, therefore, to manipulate those two rate constants to improve the degree of fit. Initial values of \(k_1 = 1 \times 10^{-14}\) and \(k_3 = 1 \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\) were used and the fit was calculated using expression [55]. \(k_1\) was then varied in increments of \(5 \times 10^{-16}\) until expression [55] reached a minimum. \(k_3\) was then varied in increments of \(5 \times 10^{-14}\) until [55] again reached a minimum, and \(k_1\) was again varied to reduce the error calculated by [55]. The process was repeated until variation of \(k_1\) no longer improved the fit.

Table III.8. lists the values of \(k_1\) and \(k_3\) calculated of \(1.51 \times 10^{-14}\) and \(1.53 \times 10^{-12}\) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\). The average error for all points was less than 5% of the experimental value. At higher H\(_2\)S concentrations, the fit between the calculated and experimental results was only
TABLE III.8. Predicted rate constants for the best fit of experimental data. All concentrations are in units of $10^{14}$ molecules cm$^{-3}$, and all rate constants are in units of cm$^3$ molecule$^{-1}$ sec$^{-1}$.

<table>
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<th>$[O]_o$</th>
<th>$[H_2S]_o$</th>
<th>$10^{14} k_1$</th>
<th>$10^{12} k_3$</th>
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<td>0.70</td>
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</tr>
<tr>
<td>5.94</td>
<td>2.71</td>
<td>1.55</td>
<td>1.65</td>
</tr>
</tbody>
</table>

Average $1.51 \pm 0.35$ $1.53 \pm 0.54$
qualitative. Figure III.6. illustrates the fit obtained under excess [H$_2$S] conditions.

The correctness of the mechanism, at least for O-rich mixtures, is supported by the accuracy of the fit between the computed and experimental profiles, the constancy of the rate constants predicted in different experiments, and the reasonableness of these rate constants in the light of previously published data. Additional support for the mechanism comes from the comparison of the experimental [OH] and the [OH] calculated for the conditions described above for the one run in which OH was observed. The rate constants given in Table III.8. predict an [OH] of 4 x 10$^{11}$ molecules cm$^{-3}$ compared to the measured value of 1.1 ± 4 x 10$^{11}$ molecules cm$^{-3}$. Considering that the measurement is imprecise and occurred at the edge of the mixing zone where concentrations may be inordinately large, the agreement is reasonable.

The mechanism does break down when H$_2$S is in excess, but under those conditions yellow wall deposits form, on which oxygen and hydrogen atoms may react. Accounting for these heterogeneous reactions would be very difficult.

The earliest reported measurement of $k_1$ was made by Luiti, Donde, and Hartel. They used mass spectrometry to follow reagent decay. While the stoichiometry measured implied that the O + H$_2$S reaction was not second-order overall, they still used the standard integrated second-order equation to calculate an overall oxygen removal rate constant. This number was divided by the average chain length of 5 ± 1.5 which was estimated from product analysis to give a value of 4 ± 2 x 10$^{-14}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ for $k_1$. The mechanism suggested by Luiti, et al. consisted of reactions (1), (3), and (4). It is doubtful that the concept
of an unchanging average chain length is valid. The concept is inadequate because the proposed mechanism indicates that the chain length should vary as the ratio [H]/[O]. But this ratio obviously changes throughout the reaction and thus the "average chain length" varies continuously as a function of time. Similarly, the ratio will also be strongly influenced by the initial conditions, and the "average chain length" for one experiment may or may not be the same for another run.

Timmons, et al.\textsuperscript{62} have restudied the O + H\textsubscript{2}S reaction. At 300 K, they measured $k\textsubscript{1}$ as $2.82 \times 10^{-14}$ cm\textsuperscript{3} molecule\textsuperscript{-1} sec\textsuperscript{-1}. This value was estimated from data similar to that shown in Figure III.4. When H\textsubscript{2}S was in large excess, they obtained curved lines similar to those shown above. At lower H\textsubscript{2}S concentrations, however, straight line plots were obtained, and from these the rate constant $k\textsubscript{1}$ was measured. Timmons and co-workers assumed that the overall reaction was largely described by reactions (1), (2) and (4), and the effects of reaction (3) were neglected. Figure III.5. indicates that this assumption is inaccurate. In the roughly stoichiometric mixture shown in this figure, the ratio [O]/[H] has fallen to 13 after only 2 msec. In excess H\textsubscript{2}S, the ratio should be even less, as is indicated in Figure III.6. The ratio of $k\textsubscript{3}/k\textsubscript{1} = 101$ calculated above predicts that under the conditions shown in Figure III.5., reaction (3) is proceeding 7.5 times as fast as reaction (1). Even the most unfavorable values reported for $k\textsubscript{1}$ and $k\textsubscript{3}$\textsuperscript{9,61} indicate that reaction (3) would be proceeding at least 1.5 times as fast as (1). Obviously then, the data of Timmons et al.\textsuperscript{62} cannot be free of influence from reaction (3) as they assumed.

The lower value of $k\textsubscript{1}$ found in this study is supported by the experiments of Sharma, et al.\textsuperscript{52} They monitored the blue chemiluminescence
from the $O+SO$ reaction\textsuperscript{49} at very short reaction times using very low reactant concentrations. They measure a rate constant for production of $SO$, $k_{SO}$, in the $O/H_2S$ system of $1.7 \times 10^{-14}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. From the experimental data given in their paper it is possible to use the mechanism above to predict the reaction profiles for their experiment. These computations indicate that under the experimental conditions of Sharma, et al., the ratio $[O]/[H]$ is large. The effect of reaction (3) is therefore small, and $k_{SO} = 1-1.5 \ k_1$.

The value of $1.5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ calculated for $k_3$ from this study seems consistent with previously reported values of this rate constant. Mihelicic and Schindler\textsuperscript{67} report a value of $1.0 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ from an ESR study of the $H/H_2S$ system with very fast flow velocities. Similarly, Tae and Glass\textsuperscript{71} calculate a value of $1.5 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. Kurylo, Peterson, and Braun\textsuperscript{9} report a value of $0.70 \pm 0.05 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ in a flash photolysis study in which efforts to avoid interfering reactions were made. Perner and Franken\textsuperscript{72} have deduced a value of $1.28 \pm 0.28 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. Darwent, et al.\textsuperscript{73} studied the competitive photolysis of $H_2S$/halogen mixtures and measured the ratio of $k_3$ to the rate constants for the reactions,

\begin{align*}
H + I_2 &= HI + I \quad \text{(e)} \\
H + Br_2 &= HBr + Br \quad \text{(f)}
\end{align*}

Using their ratios in conjunction with the value of $k_5$ reported by Sullivan\textsuperscript{74} and $k_f$ given by Benson\textsuperscript{75}, $k_3$ can be calculated as $1.7 \times 10^{-12}$ and $3.6 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ respectively.

Taking the value of $k_3$ and the relative rate ratios derived above, one estimates $k_4$ as $3.7 \times 10^{-10}$ and $k_5$ as $5.6 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. \textsuperscript{76}
The estimate for $k_5$ is more than two orders of magnitude greater than that obtained by Mayer and Schieler$^{76}$ from their "bond-energy--bond-order" calculation. Since this calculation ignored the doubling in the repulsion brought about because of the two unpaired electrons on S ($^3P$), the real discrepancy is even larger. Mayer$^{77}$ has indicated that if this repulsion is taken into consideration, then the calculated activation energy should increase from 3.4 kcal mole$^{-1}$ to 6.2 kcal mole$^{-1}$. More recently, Langford and Oldershaw$^{78}$ have substantiated the higher value of $k_5$ by estimating the rate constant as about $2 \times 10^{-11}$ in a flash photolysis experiment. It therefore seems likely that the theoretical calculations of Mayer and Schieler are in error.$^{79}$

The value of $k_4$ derived above seems quite reasonable. The analogous reaction (2) is known to be very fast, and reaction (4) might be expected to be even faster than (2) since the bond strength of SH is less than that of OH, and the bond strength of the product SO is even stronger than that of O$_2$.

The calculation of the rate constants $k_1$ and $k_3$ can be influenced strongly by reactions removing SO. Two more such reactions which should be considered are

$$SO + SO = SO_2 + S \quad \text{and} \quad (16)$$

$$SO + O_2 = SO_2 + O \quad \text{.} \quad (17)$$

The rate constants for these reactions are listed in the literature and have the values $k_{16} = 10^{-14}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$ $^{53,80}$ and $k_{17} = 8.8 \times 10^{-19}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. These rate constants were used to calculate the amount of SO$_2$ to be formed via these reactions at various concentrations of [O]$_0$ and [H$_2$S]$_0$. The results are tabulated in Table III.9. and demonstrate the minor role of these reactions under the
TABLE III.9. Production of SO₂ predicted by various mechanisms in the O + H₂S reaction scheme. The time is 10 msec. Concentrations are in units of 10¹³ molecules cm⁻³. Predicted concentrations are calculated from a computer program using literature values for the rate constants of SO₂ producing reactions, along with rate constants predicted by this study.

<table>
<thead>
<tr>
<th></th>
<th></th>
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<th></th>
<th></th>
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<th></th>
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<tbody>
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<td>0.165</td>
<td>0.406</td>
<td>0.0004</td>
<td>0.014</td>
<td>0.585</td>
<td>6.76</td>
</tr>
<tr>
<td>100</td>
<td>40</td>
<td>0.645</td>
<td>0.993</td>
<td>0.001</td>
<td>0.106</td>
<td>1.75</td>
<td>18.3</td>
</tr>
<tr>
<td>100</td>
<td>60</td>
<td>1.23</td>
<td>1.51</td>
<td>0.002</td>
<td>0.341</td>
<td>3.09</td>
<td>31.6</td>
</tr>
<tr>
<td>100</td>
<td>80</td>
<td>1.76</td>
<td>1.85</td>
<td>0.003</td>
<td>0.748</td>
<td>4.36</td>
<td>45.3</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>2.17</td>
<td>1.96</td>
<td>0.004</td>
<td>1.33</td>
<td>5.46</td>
<td>58.6</td>
</tr>
<tr>
<td>100</td>
<td>150</td>
<td>2.59</td>
<td>1.53</td>
<td>0.006</td>
<td>3.28</td>
<td>7.41</td>
<td>83.6</td>
</tr>
<tr>
<td>100</td>
<td>200</td>
<td>2.63</td>
<td>1.05</td>
<td>0.008</td>
<td>4.87</td>
<td>8.57</td>
<td>89.4</td>
</tr>
<tr>
<td>100</td>
<td>400</td>
<td>2.73</td>
<td>0.473</td>
<td>0.010</td>
<td>6.94</td>
<td>10.2</td>
<td>91.1</td>
</tr>
</tbody>
</table>
experimental conditions used in this study. The exclusion of these reactions from the mechanism, therefore, should not cause any significant error.

\[ H + ^1\Delta_g O_2 \]

Results.

Introduction of a large excess of atomic hydrogen into a diluent/\n\[ ^1\Delta_g O_2 \] system resulted in the decrease of the singlet-delta-g oxygen signal. (Hereafter the symbol \( \Delta \) alone may be used to represent the \[ ^1\Delta_g O_2 \] molecule.)

Since both reactants, \( H \) and \( \Delta \), require energetic excitation to be formed in quantity at room temperature, a double discharge system had to be used. Figure III.10. illustrates the experimental set-up.

A 1-3\% mixture of \( H_2 \) in \( Ar \) was discharged in the usual manner. The \( \Delta \) was then admitted to the reaction section through a 6 mm o.d. inlet. The \( \Delta \) was formed within the probe by using a tunable, clip-on cavity connected to a second "Microtherm" unit. This second discharge also results in the formation of atomic oxygen, and this by-product may either be removed or merely ignored. Rate constant determinations were conducted under both conditions. The atomic oxygen can be easily removed from such a system by a wall coating of mercury downstream from the discharge.\(^{82,83}\) When a bead of mercury was heated to form the wall coating no atomic oxygen signal could be observed by ESR. This method of removing atomic O did present some difficulties however. The wall coating moved slowly downstream, finally entering the larger reaction tube, effecting rapid wall removal of atomic H. The flow line then had to be dismantled and cleaned. Also, the amount of \( \Delta \) generated fluctuated with the position of the inlet probe. Such behavior was not present when there was no mercury wall coating, and the fluctuation may be due
Figure III.10. Schematic diagram of double-discharge set-up used in $H + O_2 (^1D_g)$ investigation.
to changes in the discharge process resulting from small amounts of mercury vapor. As long as the probe remained fixed in position, the $\Delta$ signal remained constant. Therefore, inclusion of the mercury wall coating to remove any interference involving atomic oxygen did not permit measuring the decay of the $\Delta$ signal as a function of distance (time), and an "on-off" method had to be used. Using this technique, the signal is measured with the $H_2$ discharge on and off. Because gas dilution effects are negligible, the change in $\Delta$ signal may be attributed to interaction with the discharge products, namely $H$ atoms. The $H$ atom signal was also monitored for each point to insure that fluctuations in the $H_2$/Ar discharge efficiency could be taken into account. Table III.10 lists room temperature experimental conditions along with rate constants calculated by assuming an $H + \Delta$ reaction.

Table III.11 lists results of attempts to measure experimentally the numerical coefficient given in [18] above. This value was determined by assuming that the change in peak height of the ground state $O_2$ lines effected by turning on the oxygen discharge was equal to the sum of the concentration of $\Delta$ plus one-half the atomic oxygen concentration. The calculated values agreed whether the atomic $O$ was removed from the system or not. Some of the included points were obtained by co-workers.

Using the oven described in the experimental section above, an "on-off" technique was used to attempt to measure the activation energy of the reaction. Table III.12 lists $T_{MAX}$ of the oven along with the activation energy calculated.

The metastable $^1\Delta_g O_2$ molecule plays a major role in the chemistry of the upper atmosphere. The experimentally measured atmospheric concentration of $\Delta$ varies from $4 \times 10^{11}$ molecules cm$^{-3}$ at 50 km to
TABLE III.10. Experimental values of the room temperature rate constant for removal of $\Delta$ by H. Concentrations are in units of $10^{14}$ molecules cm$^{-3}$. The rate constants have units of cm$^3$ molecule$^{-1}$ sec$^{-1}$. The weighted average was calculated by multiplying each measured value by (M-1), where M is the number of points used to determine that specific value, and then finding the mean.

<table>
<thead>
<tr>
<th>$[\Delta]_0$</th>
<th>$[H]_0$</th>
<th>PRESSURE Nm$^{-2}$</th>
<th>$10^{14} k_{20}$</th>
</tr>
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<td>6.69</td>
<td>2.45</td>
<td>60.0</td>
<td>2.63</td>
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<td>5.73</td>
<td>2.96</td>
<td>58.5</td>
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<td>3.01</td>
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</tr>
<tr>
<td>5.47</td>
<td>3.03</td>
<td>58.5</td>
<td>1.11</td>
</tr>
<tr>
<td>5.62</td>
<td>3.03</td>
<td>58.5</td>
<td>2.00</td>
</tr>
<tr>
<td>9.50</td>
<td>2.60</td>
<td>60.0</td>
<td>1.00</td>
</tr>
<tr>
<td>1.20</td>
<td>6.60</td>
<td>77.2</td>
<td>1.12</td>
</tr>
</tbody>
</table>

Weighted Average $1.56 \pm 0.57$
TABLE III.11. Experimental determination of the numerical coefficient, C, in equation [18] for $\Delta$. All concentrations are in units of $10^{14}$ molecules cm$^{-3}$.

<table>
<thead>
<tr>
<th>$[\text{O}_2]_0$</th>
<th>$[\text{O}]_0$</th>
<th>$[\Delta]_0$</th>
<th>C</th>
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</thead>
<tbody>
<tr>
<td>100</td>
<td>----</td>
<td>13.0</td>
<td>40.3</td>
</tr>
<tr>
<td>115</td>
<td>----</td>
<td>7.88</td>
<td>35.1</td>
</tr>
<tr>
<td>114</td>
<td>----</td>
<td>7.16</td>
<td>36.5$^a$</td>
</tr>
<tr>
<td>105</td>
<td>----</td>
<td>6.52</td>
<td>32.0$^a$</td>
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<td>9.50</td>
<td>30.9</td>
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<tr>
<td>99</td>
<td>----</td>
<td>10.3</td>
<td>41.0</td>
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<tr>
<td>90</td>
<td>11.0</td>
<td>10.0</td>
<td>31.8</td>
</tr>
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</table>

Average $36.9 \pm 5.3$

$^a$ Argon and molecular hydrogen were present in the system also.
TABLE III.12. Activation energies giving the best fit in an Arrhenius expression for reaction (21) at various values of TMAX in the oven.

<table>
<thead>
<tr>
<th>TMAX K</th>
<th>$E_a$ kcal mole$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>332</td>
<td>6.25</td>
</tr>
<tr>
<td>344</td>
<td>5.85</td>
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<td>361</td>
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<tr>
<td>385</td>
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</tr>
<tr>
<td>412</td>
<td>4.65</td>
</tr>
<tr>
<td>431</td>
<td>4.55</td>
</tr>
</tbody>
</table>

Overall best value 4.70
> 1 \times 10^{10} \text{ molecules cm}^{-3} \text{ at 100 km. The } \Delta \text{ is produced by photolysis of ozone via}^{84-86}
\begin{equation}
0_3 + h\nu = (^1\Delta_g) \text{ O}_2 + 0 (^1D).
\end{equation}
Absorbing radiation between 1027 angstroms and 1118 angstroms, \Delta \text{ is a major source of positive ions in the D region of the ionosphere.}^{87}
The species also affects the negative ion equilibrium through reaction to remove \text{O}_2^- (^2\pi_g),^{88}
\begin{equation}
\text{O}_2^- (^2\pi_g) + \text{O}_2 (^1\Delta_g) = 2 \text{O}_2 (^3\Sigma_g) + e^-.
\end{equation}
The interaction of \text{H} and \Delta \text{ investigated in this study may be written}
\begin{equation}
\text{H} + \text{O}_2 (^1\Delta_g) = \text{Products}.
\end{equation}
If the interaction is chemical in nature, the reaction should proceed via
\begin{equation}
\text{H} + \text{O}_2 (^1\Delta_g) = \text{OH} + 0,
\end{equation}
which is 6 kcal mole\(^{-1}\) exothermic. This reaction would be followed by the known rapid reaction\(^{10}\)
\begin{equation}
0 + \text{OH} = \text{H} + \text{O}_2.
\end{equation}
\Delta \text{ may also be removed by a third-body reaction involving H,}
\begin{equation}
\text{H} + \text{O}_2 (^1\Delta_g) + M = \text{HO}_2 + M,
\end{equation}
where [M] is the concentration of all species present. The rate of removal of \Delta \text{ is therefore}
\begin{equation}
-d[\Delta]/dt = k'[\text{H}][\Delta] + k_{22}[\text{H}][M][\Delta],
\end{equation}
or in integrated form
\begin{equation}
\ln ([\Delta]_t/ [\Delta]_0) = (k'[\text{H}] + k_{22}[\text{H}][M])t,
\end{equation}
where \(t\) is the time and \(k'\) is the rate for reaction (20) without regard to the specific mechanism for the removal of \(\Delta\). The form of [57] permits use of the "on-off" technique: the \(t = 0\) value of \(\Delta\) is the signal observed when the discharge is off, while the signal of \(\Delta\) observed when the discharge is lit may be assumed to be the signal at time \(t\), determined
from flow parameters and the probe position.

Once [H], t and k_{22} have been determined, it is simple to calculate the bimolecular removal rate constant k'. Values of [H] and t are easily found from the experimental conditions. However, k_{22} has not been measured directly. It's value may be approximated by the rate constant for the analogous reaction involving the ground state molecule.

\[ H + O_2 (^3\Sigma) + M = HO_2 + M \] (23)

At the experimental pressures used of about 70 Nm⁻², the third-body effects are small. Setting k_{22} = k_{23} = 2.2 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1} (\text{Cf. reference 89}), one calculates a value of k' only 3% different from the value calculated if reaction (22) is neglected altogether. Table III.10. lists the corrected rate constants measured in a number of experimental runs at room temperature. When weighted according to the number of experimental points used to determine the rate constant, an average room temperature rate constant of \( 1.56 \pm 0.57 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \) is found.

Recently, Westenberg and DeHaas⁹⁰ have suggested that reaction (20) proceeds via physical deactivation rather than through the reactions (21) and (2). These authors admit that their conclusion is not definitive, but is drawn from analogy with the reaction

\[ N + O_2 (^1\Delta_g) = NO + O \] (24)

which they investigated. Using ESR, G. P. Glass⁹¹ was able to determine an upper limit for this reaction rate constant, k_{24}, of 7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}. Clark and Wayne⁹² used absorption spectroscopy to follow \Delta decay in the presence of excess N and measured a rate constant of k_{24} = 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} at 300 K. They also calculated a pre-exponential factor \( A \approx 2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1} \)
with an activation energy $E_a < 1.2$ kcal mole$^{-1}$. While Wayne and Clark argue that their measured rate constant can be attributed to reaction (24), Westenberg and DeHaas have shown conclusively that the removal of $\Delta$ must be physical in nature by examining product formation and atomic N removal in the presence of excess $\Delta$. Because of the stoichiometry involved in reactions (21) and (2), the analogy of physical deactivation for the $H/\Delta$ system reached by these authors is inconclusive. Indeed, several considerations argue against physical deactivation.

One may expect that (24) would proceed much faster than (21) since (24) is nine times as exothermic as (21). Obviously this result is not what is observed experimentally. The discrepancy may be understood in terms of the Wigner spin conservation rule, however. Reaction (24) must proceed through a quartet N-O-O intermediate. The isoelectronic molecule NO$_2$ is known to have several low-lying doublet states,$^{93}$ but no quartet states have yet been observed. This implies that reaction (24) should have a large activation energy (to attain a quartet state in the intermediate) and that the small activation energy measured by Wayne and Clark should not be attributed to the chemical reaction (24). However, the reaction for $H$ and $\Delta$, reaction (21), may proceed via a doublet intermediate.$^{94}$ The resulting larger pre-exponential factor for (21) implies that the transition state is much more accessible than the N-O-O intermediate. Indeed the higher activation energy of 4.7 kcal mole$^{-1}$ can easily be overcome by the 23 kcal mole$^{-1}$ excess energy of $\Delta$.

Additional evidence for the chemical nature of (20) is provided by examining the effect of adding $\Delta$ to a mixture of $H/O_2/Ar$. Atomic $H$ reacts with ground state oxygen via the following scheme
\[ H + O_2 + M = HO_2 + M \]  \hspace{1cm} (23)
\[ HO_2 + H = 2 OH \]  \hspace{1cm} (25)
\[ OH + OH = H_2O + O \]  \hspace{1cm} (26)
\[ O + OH = O_2 + H \]  \hspace{1cm} (2)

to provide minute traces of intermediate species. When \( \Delta \) is added to the scheme, reaction (21) should increase the atomic oxygen steady state concentration by about 50% under conditions typically used for these experiments. Two experimental determinations showed that the concentration increased by 43% and 76%.

One other point to consider is physical deactivation by some other species in the system. Deactivation rate constants have been measured for Ar, \( O_2 \), and \( H_2O \) and are much too small to account for the observed \( \Delta \) decay. Wall removal of \( \Delta \) has also been determined as \( 2 \times 10^{-5} \) sec\(^{-1} \) and should therefore be insignificant. Deactivation by atomic oxygen may also be neglected since the reaction rate constant was unaffected by the presence of large quantities of \( O \) from the \( O_2 \) discharge. The steady state concentration of the \( HO_2 \) species is about \( 10^{-3} \) that of \( H \).

In order to be competitive with the \( H \) reaction, the reaction rate for physical deactivation by \( HO_2 \) must be of the order of \( 10^{-11} \) cm\(^3\) molecule\(^{-1}\) sec\(^{-1}\). Such a large rate constant seems unlikely in view of the activation energy. Deactivation by \( OH \) also seems unlikely. The [OH]\(_{ss}\) is strongly affected by the concentration of atomic O. Since the value of \( k' \) was consistent whether or not \( O \) was present, one can conclude that \( OH \) has little effect on the rate of \( \Delta \) removal. The total reactive system is very complex however, and further experimentation into the roles of all the various species is justified.

In an attempt to measure the activation energy of the reaction (20),
"on-off" type measurements were made with the oven described above in the experimental section interposed around the flow tube between the inlet probe and the ESR cavity. Increasing the temperature had a marked effect upon the observed removal of $\Delta$. The temperature at the center of the oven was measured with an iron-constantan thermocouple and the temperature along the tube was determined using the calibrated temperature profile described earlier. A computer program was developed in which an activation energy was assumed and used with the temperature profile and oven temperature to calculate the resulting signal of at the cavity. The calculated and experimental results were compared and an error was calculated for each experimental temperature. The activation energy was then increased by an increment of 50 calories and the data was recalculated. Table III.12. gives the temperatures used along with the activation energy which gave the best comparison between the experimental and calculated values. A copy of the computer program is included in Appendix 1. The overall best fit for all experimental points was $E_a = 4.70$ kcal mole$^{-1}$. Using this value along with $k'$ above, the pre-exponential factor becomes $3.9 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$.

During these experiments it was possible to check the validity of the quantitative expression [18] for $\Delta$. The sum of $[\Delta]$ plus one-half of $[O]$ was assumed to be equal to the change in the ground state molecular oxygen effected by igniting the oxygen discharge. (Usually the atomic oxygen was removed by a HgO wall coating downstream of the discharge, and the total concentration change of the ground state oxygen could be taken as the $\Delta$ concentration.) Comparison of the integrated intensities then permits one to calculate the experimentally measured numerical coefficient of equation [18]. The theoretical coefficient in [18] for
one of the two central lines of the $\Delta$ signal is 36.7. Table III.11. lists the experimentally determined factors in the last column. The average of the eight values is $36.9 \pm 5.3$, which compares very favorably with the theoretical value above.

$O + C_2H_2$ Results.

Addition of acetylene to a dilute solution of atomic oxygen in argon resulted in the decrease of the atomic oxygen signal detectable and the emission of a pale blue glow from the reaction flow tube.

In excess acetylene, the removal of atomic oxygen should be pseudo-first order. Figures III.11. and III.12. show the decrease of atomic oxygen signal on a logarithmic scale versus distance at different temperatures. Table III.13. lists the rate constants calculated from the figures. Figure III.13. places these rate constants in an Arrhenius plot, along with other points taken from papers by Westenberg and DeHaas$^{96}$ and by Hoyermann, et al.$^{97}$

Figure III.14. shows temperature profiles for the specially designed high-temperature flow tube used for this study. The flow line has been fully described above in the experimental section. Table III.14. displays some information pertaining to pressure-drop calculations for this flow line.

$O + C_2H_2$ Discussion.

The reaction of atomic oxygen with acetylene has been examined by a number of experimenters.$^{96-113}$ It is not the purpose of this study to re-examine the reaction, but rather to use the reaction to investigate the characteristics of the flow tube described above which was designed to permit examination of reaction rates at elevated temperatures and to allow ESR detection of the species at the higher temperatures.
Figure III.11. Logarithmic plot of the decay of $O$ signal strength as a function of distance along the flow tube. Temperature = 295 K.

$O$—pressure = 73.4 Nm$^{-2}$; $k_{27} = 1.51 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$.

$X$—pressure = 136 Nm$^{-2}$; $k_{27} = 1.48 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$.

$#$—pressure = 250 Nm$^{-2}$; $k_{27} = 1.45 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$.

The experiments were conducted with a large excess of C$_2$H$_2$ to remove the atomic oxygen.
Figure III.12. Plot of O decay in the presence of excess C$_2$H$_2$. The atomic oxygen signal strength is plotted logarithmically against the distance between the ESR detection point and the probe inlet, measured in cm. The average temperature across the reaction zone was about 420 K.

X--pressure = 132 Nm$^{-2}$; $k_{27} = 10.5 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$.

O--pressure = 136 Nm$^{-2}$; $k_{27} = 8.8 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$.

#--pressure = 117 Nm$^{-2}$; $k_{27} = 7.6 \times 10^{-13}$ cm$^3$ molecule$^{-1}$ sec$^{-1}$. 
TABLE III.13. Rate constants and activation energy for the atomic oxygen--acetylene reaction. The rate constants have units of cm$^3$ molecule$^{-1}$ sec$^{-1}$.

<table>
<thead>
<tr>
<th>TEMPERATURE K</th>
<th>PRESSURE Nm$^{-2}$</th>
<th>$k_{27}$</th>
<th>$E_a$ (calories/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>295</td>
<td>71.8</td>
<td>1.51 x 10$^{-13}$</td>
<td></td>
</tr>
<tr>
<td>295</td>
<td>251.</td>
<td>1.45 x 10$^{-13}$</td>
<td></td>
</tr>
<tr>
<td>295</td>
<td>136.</td>
<td>1.48 x 10$^{-13}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.48 ± 0.02 x 10$^{-13}$</td>
<td>1.480</td>
</tr>
<tr>
<td>480</td>
<td>132.</td>
<td>10.5 x 10$^{-13}$</td>
<td></td>
</tr>
<tr>
<td>480</td>
<td>136.</td>
<td>8.8 x 10$^{-13}$</td>
<td></td>
</tr>
<tr>
<td>480</td>
<td>117.</td>
<td>7.6 x 10$^{-13}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>9.0 ± 1.2 x 10$^{-13}$</td>
<td>3100</td>
</tr>
</tbody>
</table>
Figure III.13. Arrhenius type plot of $\ln k$ vs $(1000/T)$, where $T$ is the temperature in degrees Kelvin. The points denoted by X were measured in this work. The points indicated by @ were taken from reference 96 by Westenberg and deñaaas. ¥ represents values of $k_{27}$ given by Hoyermann, et al., in reference 97.
Figure III.14. Plot of temperature profiles along the heated flow tube.

The graph plots the temperature in °C against the distance along the flow tube upstream from the ESR detection point. The distance is given in cm.
TABLE III.14. Calculated pressure drop along the heated flow tube for argon at 480 K.

<table>
<thead>
<tr>
<th>DISTANCE</th>
<th>PRESSURE</th>
<th>PRESSURE</th>
<th>PRESSURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>cm</td>
<td>Nm$^{-2}$</td>
<td>Nm$^{-2}$</td>
<td>Nm$^{-2}$</td>
</tr>
<tr>
<td>0</td>
<td>133</td>
<td>117</td>
<td>100</td>
</tr>
<tr>
<td>5</td>
<td>122</td>
<td>109</td>
<td>93.4</td>
</tr>
<tr>
<td>10</td>
<td>111</td>
<td>101</td>
<td>86.8</td>
</tr>
<tr>
<td>15</td>
<td>100</td>
<td>89.3</td>
<td>80.0</td>
</tr>
<tr>
<td>20</td>
<td>85.3</td>
<td>77.4</td>
<td>73.3</td>
</tr>
</tbody>
</table>
While the detailed reaction mechanism leading to chemi-ionization and chemiluminescence appears to be complex and in doubt, several workers have shown that in stoichiometric or acetylene-rich mixtures, approximately two O atoms are removed and two H atoms produced for each \( \text{C}_2\text{H}_2 \) molecule consumed. The proposed mechanism is therefore

\[
O + \text{C}_2\text{H}_2 = \text{CH}_2 + \text{CO} \quad (27)
\]

\[
O + \text{CH}_2 = \text{CO} + 2\text{H} \quad (28)
\]

Using this mechanism, the overall rate of removal of atomic O is

\[
-d[O]/dt = k_{27}[O][\text{C}_2\text{H}_2] + k_{28}[O][\text{CH}_2] \quad [58]
\]

Applying the steady-state approximation to \([\text{CH}_2]\), one derives

\[
-d[O]/dt = 2k_{27}[O][\text{C}_2\text{H}_2] \quad [59]
\]

which yields

\[
d(ln[O])/dt = -2k_{27}[\text{C}_2\text{H}_2] \quad [60]
\]

Figures III.11. and III.12. plot the logarithmic decay of \([O]\) against distance for several runs at 298 K and 480 K. The calculated rate constants are listed in Table III.13. The average rate constants yield an activation energy of 3100 cal mole\(^{-1}\).

The calculated room temperature rate constant of \(1.48 \times 10^{-13} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\) compares very favorably with the values reported in the literature. Using ESR and mass spectral analysis, Westenberg\(^{96}\) measured a value of \(1.47 \times 10^{-13} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\), while Brown and Thrush\(^{98}\) give a value of \(1.53 \times 10^{-13} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\). Arrington, et al.\(^{59}\) reported an overall rate constant of \(0.9 \times 10^{-13} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\), however their best data (Cf. footnote 14 of reference 96) yields a rate constant of \(1.4 \times 10^{-13} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\). Sullivan and Warneck\(^{100}\) report a value of \(k_{27}\) of \(1.50 \times 10^{-13} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\). Saunders and Heicklen\(^{101}\) deduce a value of \(2 \times 10^{-13} \text{ cm}^3\) molecule\(^{-1}\) sec\(^{-1}\)
Hoyermann, et al., report a rate constant of \(1.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\), but there is some doubt that this represents the \(k_{27}\) given above. In a subsequent paper they present a rate constant expression for \(k_{27}\) which yields a value of \(1.35 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\) at 300 K. Combourieu, et al., have found a value of \(1.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\) using mass spectral analysis.

Three experimentalists have examined the rate of reaction (27) at temperatures other than around 300 K. In a flame study, Fenimore and Jones inferred a value for \(k_{27}\) of about 1.5 to 3.0 \(\times \ 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\) across temperatures ranging from 1000 K to 1500 K. Westenberg and DeHaas and Hoyermann, et al., use ESR and mass spectral analysis to measure the temperature dependance of \(k_{27}\). Westenberg finds \(k_{27} = 3.3 \times 10^{-11} \exp(-3200/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\) for \(C_2H_2\) in excess over the temperature range 230-450 K. For the temperature range of 243-673 K, Hoyermann and co-workers derive \(k_{27} = 2.0 \times 10^{-11} \exp(-3000/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}\) for \(C_2H_2:O\) ratios of 1.0 to 5.5. The measured activation energy of 3100 calories mole\(^{-1}\) found in this study compares very favorably with the values of \(E_a\) in the Arrhenius expressions of references 96 and 97. The precision of the agreement is somewhat fortuitous though, since the rate constant at 480 K has such a large probable error.

The lack of precision of \(k_{27}\) and the drastic pressure drops shown in Table III.14. at 480 K demonstrate some of the problems involved in using this particular flow line to measure reaction rates at elevated temperatures. The usual procedure for measuring reaction rates above room temperature using fast flow systems is similar to that described above for the \(H + O_2 (^{1}A_g)\) system. A long oven is placed around the
flow tube to maintain a long heated portion, and the inlet probe is moved within the heated zone. Often a heat sink is placed between the oven and the ESR cavity to return the system to room temperature. (Cf. reference 98) ESR spectrometric measurements are carried out at room temperature and the rate constant at elevated temperatures is calculated by subtracting out the effect of the previously determined room temperature rate constant for the region between the oven and the ESR detection point. The advantage of the flow line used in this study is that it permits detection by ESR at the elevated temperature. This may be important if the mechanism changes with temperature or if one desires to observe high-temperature species, such as pyrolysis products. Indeed, there is some confusion regarding the mechanism of the \( \text{O} + \text{C}_2\text{H}_2 \) reaction. (See reference 114) It has been suggested that at high temperatures the endothermic abstraction reaction

\[
\text{O} + \text{C}_2\text{H}_2 = \text{OH} + \text{C}_2\text{H}
\]  

(29)

may proceed. It was hoped that the \( \text{O} + \text{C}_2\text{H}_2 \) reaction could be examined at about 300 °C in order to check for OH formation, but it was extremely difficult to heat the cavity to that temperature. Figure III.14. shows a temperature profile in which the flow tube was maintained at about 365 °C. For the temperature profiles depicted, the flow tube was wrapped with heating tape to roughly 3.5 cm from the coils. Obviously the heating tape maintained an even temperature along the flow tube, but there was a marked temperature drop-off inside the cavity (from 0 cm to 3.5 cm on the graph). This is one major problem in using the flow tube as presently designed.

Another shortcoming of the flow tube is that the inside diameter of the reaction tube is so small that large pressure drops are induced.
(Cf. Table III.14.) This limits practical use of the tube to only moderately fast reactions which will exhibit pseudo-first order behavior. It may have been flow aberration from pressure drops which caused the large uncertainty in the measurement of $k_{27}$ at 480 K.

Another factor which influences the use of a heated flow tube is that, due to the temperature dependence of many of the variables in equation [4], the integrated intensity, $\int \chi_{ij}^2 \, dH$, of the ESR signals varies with temperature. Table III.15. gives the intensity of several lines at 400 and 500 K compared to the intensity of the line at room temperature. It is obvious that sensitivity can be drastically reduced by using the ESR at high temperatures. In addition there is an instrumental effect. The sensitivity of the resonating cavity used during this work decreased by about a factor of 3 when the temperature inside the cavity was raised to around 200 °C.

In spite of the decrease in signal strength effected by elevating the temperatures, a cavity designed to detect species at high temperatures can be useful. Bruker\textsuperscript{115} has introduced an ESR cavity designed to permit observation of species at up to 1000 °C. The cavity is heated internally by a 0.0 to 5.0 amp direct current passing through a platinum film plated on the internal quartz tube. A similar heating element could be used with the present flow line to prevent the observed temperature drop-off inside the cavity. Indeed, with such a heating device, the need for the jacket on the flow tube does not exist. The reaction tube could then be enlarged to the full 1 inch o.d. permitted by the wide-access cavity employed, and the pressure drop effects would diminish. Heating tapes, or an oven fitted snugly against the resonance cavity end plate, could heat the external portion of the flow tube, with the
TABLE III.15. Relative intensities of several ESR lines at different temperatures. The intensity of each line at 300 K is taken as the normalized unity.

<table>
<thead>
<tr>
<th>SPECIE</th>
<th>LINE</th>
<th>300 K</th>
<th>400 K</th>
<th>500 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>line E</td>
<td>1.00</td>
<td>0.564</td>
<td>0.362</td>
</tr>
<tr>
<td>O</td>
<td>six line composite</td>
<td>1.00</td>
<td>0.721</td>
<td>0.562</td>
</tr>
<tr>
<td>H</td>
<td>either line</td>
<td>1.00</td>
<td>0.750</td>
<td>0.600</td>
</tr>
<tr>
<td>NO</td>
<td>any line</td>
<td>1.00</td>
<td>0.619</td>
<td>0.418</td>
</tr>
</tbody>
</table>
heating within the cavity being accomplished by the platinum film heating element. The cavity end plate could even be designed to serve as one end of the external oven. An adjustable end plate on the other end of the cavity would permit compensation for resonant frequency shifts found to accompany changes in the operating temperature of the cavity. It would also allow for tuning the cavity to the best sensitivity at any temperature and frequency.
CONCLUSION AND ACKNOWLEDGEMENTS

The purpose of this thesis has been to examine the reaction systems \( 0 + H_2S, H + H_2S, \) and \( H + O_2(1\Sigma_g^+) \). The results given herein demonstrate the utility of ESR spectroscopy, fast-flow techniques, and computer analysis in illucidating the kinetics of various rapid gas-phase reactions and suggest that these methods can be very powerful tools for examining complex radical reaction systems. The study of the particular reactions investigated may be very important in terms of pollution chemistry. The sulfur oxides formed in the \( H_2S \) reactions are known to be extremely detrimental pollutants in several of the larger cities of the nation. Better understanding of the formation mechanisms of these pollutants could be very useful in learning to limit their formation. In addition, there has been much recent speculation regarding the role of \( O_2(1\Delta_g) \) in the chemistry of the atmosphere. \( O_2(1\Delta_g) \) and other "singlet" molecules are considered to be important factors in atmospheric photo-chemical reactions. Finally, this paper provided a discussion of a specially-designed heated flow tube, along with an examination of some of the difficulties involved in using ESR spectroscopy at elevated temperatures.

In closing, this author wishes to acknowledge three people vital to the accomplishment of this study. I offer my thanks to Dr. C. P. Glass for his guidance, instruction and patience. To Dr. J. E. Breen I express my appreciation for the friendship, discussions, and assistance he offered. And finally, I would like to thank my wife for being just the way she is.
APPENDIX 1

Listing of the computer programs used in this study. The program used to calculate rate constants for the $O + H_2S$ system is shown on pages 112-115. The computer program for calculating the most appropriate activation energy in the $H + O_2 (^{1}A_g)$ system is given on pages 116, 117.
C THIS PROGRAM IS DESIGNED TO CALCULATE THE SET OF RATE CONSTANTS
C MOST CONSISTENT WITH EXPERIMENT FOR THE REACTION H2S + O
C DIMENSION DATE(2), TEXP(50), CEXP(50), CODE(50), D(50), CALC(50), CO(3)
C FACTR=16.0, CO(195E-4)*(7.5*1E-4)/31.4159
C CPCCM=(6.1*25E22)/(760, 0.02, 0.57*298.0)
C CSTD1=9.1, IF=13
C CSTD3=0, IF=11
C 200 READ (5, 201) DATE
C READ (5, 202) REF, PEXP, FLTOT, FLHHS, FLO
C
C C1=CSOD1
C C2=CSOD2
C C3=37.8*C3
C C4=6.5*C5
C C5=1.2F-16
C C6=8.3F-31
C 206 READ (5, 207) T, CO(T), DZEPD
C 207 FORMAT (15, 2E15.8)
C IF (I-3) 206, 208, 208
C 208 READ (5, 209) N
C 201 FORMAT (7A4)
C 202 FORMAT (F9.1, F5.2, F8.1, 2F6.2)
C 203 FORMAT (15)
C TEXP(I) IS THE TIME CALCULATED FOR THE GAS IN THE SYSTEM TO FLOW
C FROM ITS POSITION AT D(T) TO THE POINT DZERC
C DO 204 I=1, N

C 204 READ (5, 205) TEXP(I), CEXP(I), CODE(I), D(I)
C 205 FORMAT (2E15.8, I15)
C DPC=EXP(-10, 1-D(I))
C DAV=ZDERC*D(I)**2.0
C PINT=SQRT((PEXP**2)*(FLTOT**0.59)*FACTR)
C PAV=SQRT((PEXP**2.0)*FLTOT*(PEP*4.1-DAV)*FACTR)
C IC0=1
C 102 IC0+1
C EPHT=EXP(0.094)
C DIP1=1.0
C CTR=1.0
C CTR4=1.0
C DIP8=1.0
C K1=1
C K3=1
C 229 EPNO=C.
C EPB=EXP(C.
C EPSE=C.
C SUMJ=0.0
C SUMJ=0.0
C SUMSN=0.0
C
C T=C.
C 0=COD(1)
C *COD(2)
C COD(COD(3)**.5)*6
C HHS=(FLHHS/FLTOT)*PAV*CPCCM-S0
C SN=0.0
C DD=0.0

C
\text{OX} = C \cdot C
\text{DISI} = C \cdot C
I = 1
P = PIN
\text{0L} = 0
H = H
SO = SO
PCALC = SORT((PIN \cdot 2) - FLT0T \cdot DISt \cdot FACTR)
\text{AI} = C1 \cdot 0 \cdot HHS
A3 = C2 \cdot H \cdot HHS
OHSS = A1 / (C2 \cdot 0 + C6 \cdot SO)
SHSS = (A14 \cdot 0) / (C4 \cdot 0 + C5 \cdot H)
A2 = C2 \cdot 0 \cdot CHSS
A4 = C4 \cdot 0 \cdot SHSS
A5 = C5 \cdot H \cdot SHSS
A10 = C12 \cdot 0 \cdot 0 \cdot CPCCM \cdot P
CSO = C6 \cdot SO \cdot OHSS + A10
DEO = A1 - A2 - A4 + A5 - A10
CHSS = A3 - A3
CSO = A4 + A5 - DSO2
DH = OHSS - DEO + DSO2 - 2 \cdot C \cdot A10
\text{C} \text{ DOO IS AMOUNT OF O2 FROM AT 0. DOO IS AMOUNT OF O FROM O2}
DOO = A2
DOX = A5
\text{0} = (O + DBO \cdot DEO) \cdot PCALC / P
HHS = (HHS + PHSS \cdot DEO) \cdot PCALC / P
H = (H + OHSS \cdot DEO) \cdot PCALC / P
SO = (SC + SO + DEO) \cdot PCALC / P
O = (OP + YOP \cdot DEO) \cdot PCALC / P
P = PCALC
DIST = DIST + VEL \cdot DEO
T = T + DEO
\text{IF} (T \geq TEXP(1)) 1, 3, 5
P = SORT((P \cdot P \cdot 2 - 1) - FLT0T \cdot (REF + 4, 1 - 0 \cdot (1)) \cdot FACTR)
O2 = (H1 \cdot TEXP(1) - T + DEO) \cdot (O - 01) / DEO \cdot (P / PAV)
H2 = (H1 \cdot TEXP(1) - T + DEO) \cdot (H + H1) / DEO \cdot (P / PAV)
SOA = (SO + TEXP(1) - T + DEO) \cdot (SO - SO1) / DEO \cdot (P / PAV)
KODE = KODE(1)
GO TO (7, 8, 9, 1, KODE I)
7 CALCl(1) = 0
GO TO 11
8 CALCl(1) = H2
GO TO 11
9 CALCl(1) = SOA
11 P = PCALC
I = I + 1
12 \text{IF} (I \geq 1) 10, 10, 210
10 \text{IF} (T \geq TEXP(1)) 1, 3, 5
21 \text{J} = J + 1
22 \text{IF} (J \geq N) 214, 214, 215
214 KODE = KODE(J)
GO TO (211, 212, 213), KODE J
211 ERD = ERD + (CALC(J) - C EXP(J)) * (CALC(J) - C EXP(J))
SUM0 = SUM0 + C EXP(J)
GO TO 210

212 ERH = EH + (CALC(J) - C EXP(J)) * (CALC(J) - C EXP(J))
SUM1 = SUM1 + C EXP(J)
GO TO 210

213 ES0 = ES0 + (CALC(J) - (0.526 * C EXP(J))) * (CALC(J) - (0.526 * C EXP(J)))
SUMSO = SUMSO + C EXP(1) = 0.526
GO TO 210

215 TOTER = ERD / SUM0 + ERH / SUM1 + ER SO / SUM5
GO TO (310, 910, 330), ICON

310 GO TO (311, 312, 313), K1

311 FP INT = TOTER
K1 = 2
GO TO 318

312 IF (TOTER - ER INT) 315, 315, 314

313 IF (TOTER - ER TOT) 318, 316, 317

314 DIR1 = -1.0
K1 = 3
GO TO 318

316 C1 = C1 - 0.025 * DIR1 * COST1
GO TO 320

317 C1 = C1 - 0.05 * DIR1 * COST1
GO TO 320

318 ER TOT = TOTER

319 C1 = C1 + 0.05 * DIR1 * COST1
IF (C1) 320, 322, 209

320 ICON = ICON + 1.0
IF (ICON - ICON) 321, 325, 321

321 ICON = ICON + 1
ICON = 3
GO TO 328

330 GO TO (329, 331, 332), K3

332 K3 = 2
GO TO 328

331 IF (TOTER - ER TOT) 335, 335, 324

332 IF (TOTER - ER TOT) 333, 333, 324

333 C3 = C3 = 0.25 * DIR3 * COST1
GO TO 337

334 DIR3 = -1.0

335 K3 = 3
GO TO 328

336 C2 = C3 - 0.08 * DIR3 * COST1

337 ICON = 2
COST1 = 37.8 * C3
C3T4 = 0.8 * COST1
C4 = COST1
C5 = COST1
TOTER = TOTER
GO TO 209

338 ER TOT = TOTER
C3 = C2 + C4 + DIR3 * COST1
C5 = 37.8 * C3
C4 = 6.5 * C5
IF (C3) 337, 337, 209

339 ICON = 2

114
GO TO 209
910 WRITE (6, 901) DATE, C1, C3, C4, C6
 IF (C1) 912, 913, 914
 913 IF (C3) 912, 914, 915
 914 IF (C4) 912, 915, 916
 915 IF (C6) 912, 916, 917
908 WRITE (6, 904)
901 FORMAT (1X, 2A4/5H C1 = , IP1C.3/5H C2 = , 1E10.3/5H C3 = , E10.3/5H C4 = , 1E10.3/5H C6 = , E10.3)
904 FORMAT (7H J KODE CEXP CALC DISTANCE)
1 DO 902 IJ = 1, N
 902 WRITE (6, 923) IJ, KODE (IJ), CPRINT, CEXP, CALC (IJ), D (IJ), TEXP (IJ), PCTER
 IF (KODE (IJ) .LE. 3) CPRINT = CEXP (IJ) * C.526
 PCTER = (CALC (IJ) - CPRINT) / CPRINT
903 WRITE (6, 907) TOTER
907 FORMAT (15H ERROR = , E10.3)
1 WRITE (6, 205) NO, DX
905 READ (5, 990) ICODE
900 FORMAT (15)
906 WRITE (6, 906) DATE
906 FORMAT (1H END OF CALCULATION FOR , 2A4/)
909 STOP
END
DIMENSION PKHT(6), TEMPX(6), DLTV2ST(6), DC2CAL(6), DEV(6), PCNTER(6)

TPT=301.0

DLTV2ST = 1.0E-4

C1STD=1.12E-14

C3=3.0E-32

TP=1.0E16

R=1.6672

DLTV2ST = (22.1/16.4) * 1.15E15

VSTD=530.0

XMAX=30.0

TMAX=33.0/30.0

RT2=C3*TP

X=(ALOG(21.47/(16.4*C3*E3)))/(C1STD+RT3)*TMAX

CN 10,1=1,5

10 READ (5,1) PKHT(1), TEMPX(1)

WRITE (6,2) H

WRITE (6,3)

WRITE (6,4)

WRITE (6,5) (TEMPX(1), I=1,6)

CN 11,1=1,6

11 DLTV2ST(J)=PKHT(J)*C3*DLTV2ST/22.1

CN 85 C IF=400.0, 7000.50

EA=IFA

ER=0.0

CN 85 I INPLT=1,6

TLAST=33.1.0

TIME=0.0

IPNG=1

DIST=0.0

CP=100.0/10.0

GF=0.0

C = DISTANCE FROM TUBE PROBE TO UPSTREAM EDGE OF INNER METAL TUBE OF THE OVEN, HEREAFTER APPRECIATED IN-MET-TUBE

CP = DISTANCE FROM UPSTREAM EDGE OF IN-MET-TUBE TO THE ZERO POINT OF THE TEMPERATURE PROFILE (SEE PROFILE CURVES)

X = PARAMETER USED TO CALCULATE TEMPERATURE FROM DISTANCE ALONG FLOW TUBE

TEMP = TEMPERATURE, AT ANY POINT ALONG FLOW TUBE

DIST = DISTANCE DOWNSTREAM FROM PROBE

DP = DISTANCE FROM THE PROBE TO THE ZERO POINT OF TEMPERATURE

INPL = INTEGER VARIABLE USED TO DETERMINE WHICH EQUATION THE COMPUTER SHOULD USE TO EVALUATE TEMPERATURE

TEM = THE EXPERIMENTALLY MEASURED IN THE CENTER OF THE OVEN,

IT SHOULD BE THE HIGHEST TEMPERATURE INSIDE THE OVEN

TPT = THE ROOM TEMPERATURE

CP=2.3

DLTV2ST = DLTV2ST

TINORM=TEMPX(INPLT)-TP

C3=4.76+0.0021*TINORM

CP=DP+I/D

201 X=CP-CP=DIST-1.0

TEMP=TP+TINORM = 1.0E-15

T(E) 2011, 2011, 210

201 IPNG=2

202 X=CP-CP=DIST-1.0

TEMP=TP+TINORM = 1.0E-15

T(E) 2021, 2021, 210

202 INPL=3

116
08/27/71

202 X=DIST-DPZP
TEMP=TR1+TNOPM*(C.56-C.223*X-0.367*X**2+0.303*X**3)
IF (X.GE.1.5) IRNG=6
GO TO 210

204 X=DIST-DPZP-1.5
TEMP=TR1+TNOPM*(C.56-C.223*X-0.367*X**2+0.303*X**3)
IF (X.GE.4.5) IRNG=5
GO TO 210

205 X=DIST-DPZP-6.0
TEMP=TR1+TNOPM*(-C.42*EXP(-C.486*X))
IF (X.GE.10.0) IRNG=6
GO TO 210

206 TEMP=TR1
IRNG=7
C1=CISTD
RHRAT=1.0
VELOC=VSTD
GO TO 100

210 C1=CISTD*EXP((EA/(F*3C1.0))-(EA/(R*TEMP)))
RHRAT=TLAST/TEMP
TLAST=TEMP
HPROFL=1.0*301.0/TEMP
VELOC=VSTD*TEMP/301.0

100 CFD02=1.0+RHRAT*HPROFL*RT34+DLT02*HHRAT+HFR0FL*301.0/TEMP
DLT02=DLT02*RHRAT+DEN02*DELT
DIST=DIST+VELOC*DELT
TIME=TIME+DELT
IF (DIST.GE.4000) GO TO 999

800 DD=CALL(INPUT)=3L1M2
DEV(INPUT)=0.2*CALL(INPUT)-0.75*EXP(INPULT)
PCNTER(INP=DEV(INP,UT))=0.75*EXP(INPULT)

801 EKR=EKR+PCNTER(INP=UT)*PCNTER(INP=UT)
FAK=FA/ICO{C,0}

850 WRITE (6,6) FAK,(1002C:1(J),K=1,5),(DEV(K),K=1,5),FRCUT
1. FRAFORMAT(F=1.2,X=3.1)
2. FRAFORMAT (F=1.2,THOHAT CONCENTRATION IS,1PE14.2///
3. FRAFORMAT (F=1.2,THOHAT CONCENTRATION IS,1PE14.2///
4. FRAFORMAT (F=1.2,THOHAT CONCENTRATION IS,1PE14.2///
5. FRAFORMAT (F=1.2,THOHAT CONCENTRATION IS,1PE14.2///
6. FRAFORMAT (F=1.2,THOHAT CONCENTRATION IS,1PE14.2///
999 STOP
END
FOOTNOTES


2. Neither the list of techniques nor the footnotes given for each method is intended to be exhaustive.


31. T. A. Miller, W. H. Breckenridge, to be published.
32. In reference to equation [4] of reference 22, Miller states "we believe (the equation) is in error. Consider two cases (i) magnetic field energy\(\Delta\) doubling, (ii) magnetic field energy \(\Delta\) doubling. In case (i) the total intensity along the z axis is actually a sum of two sums, one for the \(\Delta M = +1\) sum given in (the equation) and an identical sum for \(\Delta M = -1\). The latter implies that (the normalization factor is 1/2 that given by Westenberg). Alternatively we can work out C in case (ii). Here it is appropriate to consider only \(M \rightarrow M+1\), but the total intensity is now given by the sum of the \(+ \leftrightarrow -\) and \(- \leftrightarrow +\) transitions, implying that a factor of 2 should be included inside the summation over \(M\) in (equation [4] of reference 22)." This factor of two would have the same effect as dividing the normalization constant by 2 above. In either case, the equation given by Westenberg is wrong by a factor of 2.


77. S. W. Mayer, private communication to G. P. Glass.
78. J. Oldershaw, communication cited in reference 79.
79. K. Schofield, pre-publication communication to G. P. Glass.
81. based on $k = 2.2 \times 10^{-12} \, \text{exp} (-7920/RT) \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{sec}^{-1}$ obtained by combining previous work (references 6, 54, 58).
88. F. C. Fehsenfeld, D. L. Albritton, J. A. Burt, H. I. Schiff, Canad. J.
94. E. F. Hayes, unpublished results.
97. K. Hoyermann, H. Wagner, J. Wolfrum, Z. Phys. Chem. (Frankfurt), 63,
102. K. Hoyermann, H. Wagner, J. Wolfrum, Z. Phys. Chem. (Frankfurt), 55,
    72 (1967).
    42, 608 (1965).


114. Mass spectral analysis data indicates that the reaction is not quite so clean as it could be. Specifically, the formation of CO is not correctly accounted for. In addition references 109–113 imply that at high temperatures the endothermic reaction \( \text{O} + \text{C}_2\text{H}_2 = \text{OH} + \text{C}_2\text{H} \) may proceed.

115. Bruker High-temperature resonator system B-ER 400 TE_{011} h T.