THE KINETICS OF RADIOLYTIC GAS PHASE REACTIONS BY
MODULATED MOLECULAR BEAM MASS SPECTROMETRY

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ABSTRACT

An experimental system was developed to enable on-line mass spectrometric analysis of gas phase radiolysis flow systems, and was applied to observation of the oxygen radiolysis system in particular. In this experimental system, energy from a beam of 1-MeV protons is deposited in the oxygen as it flows through a fast-flow reaction tube. A molecular beam source samples the flow gas, and the resulting molecular beam is then modulated and analyzed with a quadrupole mass spectrometer.

Experimentally determined quantities are the concentrations of atomic oxygen, molecular oxygen, and ozone as functions of reaction time, system pressure, and total absorbed dose. Operating parameters were in the following ranges:

System pressure:	[1.5 - 4.0] Torr
Irradiation time:	[0.2 - 0.3] sec
Total energy deposited:	[0.5 - 15] 10^{12} heV/cm ³
Dose Rate:	[0.2 - 20] 10^{20} heV/gm·sec

Observed concentrations of the radiolysis products atomic oxygen and ozone were of the order:

Atomic oxygen:	[5 - 40] 10^{12} atoms/cm ³
Ozone:	[3 - 20] 10^{13} molecules/cm ³

The ozone levels observed are substantially higher than those predicted by pre-existing chemical models, and the discrepancies cannot be explained in terms of increased g-values or of systematic errors in the measurement.

A modification to the chemical model is proposed, in which an excited vibrational state O_2^* is postulated as a precursor to ozone via the reaction:

Calculations including this modification indicate that agreement with the data is improved, although neither the agreement nor the explanation can be considered complete. It is concluded that further investigation of the low-pressure behavior in the oxygen radiolysis system is indicated, particularly with regard to the role of excited species in the chemical mechanism.

I. INTRODUCTION

A. Statement of Problem

The experiment described in this report has been developed to provide a new method for studying gas phase radiolysis systems. The technique involves a fast flow reaction tube which supplies reaction products to a modulated molecular beam. These products are then analysed by means of a quadrupole mass spectrometer. Reactions are initiated by radiolytic energy deposition in the gas as it flows through the reaction tube. The energy source used is a mono-energetic proton beam, generated by a 1 MeV Van de Graaff accelerator.

The oxygen radiolysis system was chosen for study because of its importance and apparent simplicity. The stable radiolysis product in this system is ozone, and the other mass spectrometrically observable product is the free radical atomic oxygen. The experimental system allows on-line measurement of the concentrations of O, O₂ and O₃ as functions of system pressure, total absorbed dose, and flow conditions.

There are two objectives to be gained in this project. The first and more general goal is the development of the experimental system. The second is to establish a specific chemical model for the oxygen radiolysis system, and to provide estimates of the radiolytic yields of the important species in this system.

B. Motivation

Fission fragment energy in a nuclear reactor can be used as an energy source for large scale chemical production. The direct use of fission energy in this way is an inviting prospect, since it is potentially efficient (i.e., not limited by the efficiency of thermal cycles) and

economic. Economic studies of large scale chemo-nuclear reactors have been made^{1,6,36} and one of the most important parameters determining the feasibility of such a plant is the specific radiolytic yield; i.e., the number of product molecules per unit energy deposited. If the end product is not a direct result of the energy deposition (e.g., ozone in the oxygen system), the yield depends on the pressure, temperature, etc., of the system, as well as on the energy deposition. For these products, plant design would require knowledge of the specific yield over a range of operating parameters, and preferably an understanding of the chemical mechanism. It is advantageous to measure such yields under controlled experimental conditions, in a smaller, more adaptable system than an actual pilot plant.

Although the oxygen system (radiolytic ozone production) has been the subject of numerous experimental studies^{3,10,16,17,33,34,40} it was felt that the experiment under consideration could add materially to the existing body of knowledge. One of the most important reasons for this conclusion is that the present system allows quantitative measurement of both atomic oxygen and ozone. All previous studies have measured only the product ozone, and while this procedure does determine the ozone yield over the range of temperatures and pressures studied, the chemical mechanism can be established more firmly if more than one component of the system are observed.

The particular system studied in the present experiment is also of general and ecological interest, since the bombardment of low pressure oxygen by high energy protons simulates the effect of solar flare protons in the upper atmosphere.

C. Design Philosophy

The present system was designed around an existing quadrupole mass spectrometer gas analysis system.³⁰ The bases for the selection of the remaining components are discussed briefly in the following.

The fast flow system is advantageous in that the kinetic analysis is very direct. In such systems the reaction time becomes simultaneous with elapsed flow time (see Section II-A). This simple characterization is possible only if the flow velocity is large enough to preclude back diffusion. The dimensions of the flow tube and the pumping speed of the main mechanical pump were chosen on this basis. A discussion of the fast flow requirements in the oxygen system can be found elsewhere.²²

The other experimental systems used to investigate oxygen radiolysis have employed closed cells, in which (with one exception¹⁰) irradiation was completed prior to analysis. Several of these used pulse techniques, so that the bulk of the chemical reactions occurred after irradiation. Two methods were used for the ozone detection, one a titration technique^{3,16,17,40} and the other employing spectrophotometry.^{3,10,33,34,40} The titration technique is relatively slow, the time to completion of the analysis being on the order of several minutes. The spectrophotometric technique is not limited in this way, although in only one case (the above mentioned exception¹⁰) was such analysis carried out simultaneously with the irradiation. It was felt that the present flow system, coupled with direct molecular beam sampling, would have two advantages over the previous systems. In the flow system, irradiation and chemical reaction occur simultaneously. Second, sampling times are comparable to the

characteristic reaction times of the important neutral reactions.

The primary reason for the choice of the Van deGraaff accelerator as the radiation source was its availability. There are, however, some advantages in the selection. The magnet-deflected proton beam is clean and monoenergetic, so that energy deposition analysis is straight-forward. Also, high energy protons present an intermediate case between very heavy fission fragments, with extremely dense ionization tracks and varying charge, and the electrons and gammas used in most of the previous radiolysis experiments.

Other subsystems of the apparatus, such as the proton current detection and differential pumping systems, evolved as the development progressed and are discussed in detail in Chapter III.

II. THEORETICAL MODEL

A. General

The fast-flow radiolysis system with on-line mass spectrometric analysis provides direct measurement of the concentrations of ozone and atomic oxygen as functions of oxygen pressure, reaction time, and energy deposition. Such data is meaningful only in the context of some particular theoretical model for which the system response can be predicted as a function of elementary physical parameters and compared to the measured results. For a homogeneous radiolysis system, the model should include source terms for all species produced directly by the radiolytic energy deposition, and all chemical reactions known (or suspected) to be important in the system. To establish the predicted system response, these features must then be brought together with the known energy deposition and flow system behavior (pressure, velocity, etc). To minimize ambiguity of interpretation, a sufficient number of parameters and rate constants should be known from independent sources so that the number of physical constants to be determined is compatible with the number and type of measurements made.

The chemical source term in radiolysis systems is related to the energy deposition rate $\dot{E}_d$ by the g-value, defined for each species as the number of atoms (or molecules or ions) of that species produced by 100 eV of deposited energy (see Section II-B-1). Therefore, given the g-value for any species i , the source term follows directly:

$$S_i \equiv \left\{ \begin{array}{l} \text{Production Rate} \\ \text{of Species } i \\ \text{particles/cm}^3 \cdot \text{sec} \end{array} \right\} \sim g_i \left\{ \frac{\text{Particles } i}{100 \text{ eV}} \right\} \dot{E}_d \left\{ \frac{\text{eV}}{\text{cm}^3 \cdot \text{sec}} \right\}$$

The chemical mechanism is introduced into the model via the chemical rate equations, which include a term for each reaction in which the species under consideration participates. For example, the reaction

contributes a term $T_{N1} = k_{N1}[O][O_2]^2$ to the rate equation for ozone, and a term $(-T_{N1})$ to that for atomic oxygen. The chemical reaction term R_i is then given by:

$$R_i \equiv \left\{ \begin{array}{l} \text{Rate of change of} \\ \text{species } i \text{ from} \\ \text{chemical reaction,} \\ \text{particles } i/\text{cm}^3 \cdot \text{sec} \end{array} \right\} = \sum_j T_j$$

where the sum is taken over all reactions involving species i , either as a product or a reactant.

The one-dimensional continuity equation (neglecting diffusion, see Section I-C) for the species i in a compressible flow radiolysis system is:²

$$\frac{\partial C_i}{\partial t'} = - \frac{\partial}{\partial z} (C_i v) + S_i + R_i$$

where C_i = concentration of species i , particles/cm³;

v = flow velocity, cm/sec;

z = distance travelled along flow tube, cm;

t' = total elapsed time.

Since the pressure drop in this system is quite small (<5%) the flow is to good approximation incompressible, so that the velocity is constant.

The system is assumed to be at steady state, which requires:

- (1) steady energy deposition along the length of the flow tube; and
- (2) that initial flow transients have died out. At steady state, the continuity equation reduces to:

$$v \frac{dC_i}{dz} = S_i + R_i$$

However, the reaction time (i.e., the residence time in the flow tube) is given by $t = z/v$, so that the above formula becomes:

$$\frac{dC_i}{dt} = S_i + R_i$$

This relationship applies to all chemical species in the system. All such equations taken together form a set of first order differential equations, usually coupled and non-linear, which must then be solved to predict the system response to the given model. If a sufficient number of rate constants and g-values are available, the solution can be compared with the measured concentrations to determine (1) the applicability of the model; and (2) the value, or at least order of magnitude, of any unknown parameters.

B. Source Terms

1. Primary g-Values

Primary products in a radiolysis system are those formed directly by the action of ionizing radiation. The primary products in the oxygen system are O , O^+ , O_2^+ and e^- , formed in the processes:

Here the symbol ($\rightsquigarrow$) denotes radiolytic energy deposition.

Excited states of molecular oxygen may also be formed:

where the excitation energy can in general be vibrational, rotational, or electronic. The only allowed electronic dipole transition for ground state $O_2(^3\Sigma_g^-)$ is:¹²

and a vertical transition (Frank-Condon Principle) will frequently transfer the molecule to an unbound state on the $(^3\Sigma_u^+)$ potential energy curve (Schumann-Runge Dissociation³¹). Other transitions (electric quadrupole, magnetic dipole or quadrupole) may occur, or transitions ordinarily forbidden may take place during collisions due to distortion of the wavefunctions. The two stable, low-lying singlet states of oxygen ($^1\Delta_g$ and $^1\Sigma_g^+$) are accessible through magnetic dipole transitions, and may be produced in significant quantities through secondary electron interactions.²⁴ However, such secondary processes have not been discussed in earlier analyses of the oxygen radiolysis system;^{10,16,39} and since $O_2(^1\Delta_g)$ and $O_2(^1\Sigma_g^+)$ are not observable with the present detection system, their production and subsequent reactions are not considered at length here.

For collisions with high energy protons the ionization and dissociation processes predominate, and the following model is limited to the four primary products O , O^+ , O_2^+ and e^- .

The g-values for primary products depend to some extent on the character of the ionizing radiation, but not on the particular chemical model or experimental system being used. They are, therefore, elementary parameters of the model, and are unambiguously defined for each primary species as the number of atoms (or ions, etc) of that species produced per heV deposited energy (1 heV = 100 eV).

The average energy required to form an ion pair in a gas depends on the identity of the gas, but is virtually independent of the character (charge, mass, velocity) of the ionizing radiation.³⁵ The value for oxygen is 30.9 eV/ion pair (measured with tritium β^{35}), so that the ion g-value is:

$$g_{ion} = (100/30.9) = 3.2 \text{ ion pairs/heV} .$$

This g-value applies directly to e^- , but must be modified to account for the production of both O^+ and O_2^+ . The latter are assumed to appear with the relative abundance observed in mass spectrometric fractionation, (0.83:0.17).¹⁷ The ion g-values are therefore:

$$g_{O^+} = 0.5$$

$$g_{O_2^+} = 2.7$$

$$g_{e^-} = 3.2$$

Atomic oxygen is produced in both the first (direct dissociation) and third (dissociative ionization) primary reactions, and the contribution to the g-value for atomic oxygen from the latter process is equal to g_{O^+} . Other contributions are less well defined, and g_O is considered to be an unknown (e.g., variable) parameter within the model.

2. Ozone G-Value*

Since ozone is a secondary product of the irradiation process, the G value here is defined as the differential product yield (again: the number of O_3 molecules produced per heV deposited energy). $G(O_3)$ depends on the detailed processes occurring in the system; e.g., on the number and kind of primary radiolysis products, on the kinetics of the reactions among all the species involved, and consequently on the physical parameters of the system (pressure, temperature, etc). It may also depend on the energy, charge, and mass of the particle depositing the energy, since the g-values of the primary products may be functions of the character of the ionizing radiation.

$G(O_3)$ is a somewhat ambiguous term, since there are several possible definitions, all of which are sometimes used. Among these are:

- (1) Initial G-value (lim $t \rightarrow 0$ of slope, $[O_3]$ vs E_d);
- (2) Forward G-value, including production but not consumption processes;
- (3) Average G-value, $[(1/t) \int G(t) dt]$.

Other definitions may occur depending on the system observed and the

* Capital G denotes a reaction product yield, while lower case g is used for direct yields.

measurements and means available for obtaining G. Measurements of $G(O_3)$ have been carried out under widely varying conditions. Several of the measured values are listed in Table 1.

3. Source Term

The source term S_i (particles produced/cm³·sec) is given by:

$$S_i = g_i \dot{E}_d$$

where g_i is the (primary) g-value for species i, and $\dot{E}_d$ is the energy deposition rate. $\dot{E}_d$ [heV/cm³·sec] is given by:

$$\dot{E}_d = \frac{\epsilon I_p [O_2]}{\pi a^2} \frac{10^{-2} \text{ heV}}{\text{eV}} \frac{6.242 \times 10^{12} \text{ protons}}{\mu\text{A} \cdot \text{sec}}$$

where ϵ = oxygen stopping power, 10^{-15} eV·cm²/proton·O₂ molecule.

ϵ is a well established quantity and is available in the literature.³⁹

I_p = proton current, μA

$[O_2]$ = oxygen concentration, molecules/cm³

a = reaction tube radius, cm.

This expression is derived assuming that all energy is deposited in the molecular oxygen; or, in effect, that the concentration of O₂ is much larger than the sum of the concentrations of all other species present. This assumption is made throughout the following analysis.

Table 1. Measured $G(O_3)$ values.

$G(O_3)$ Molecules /ev	Incident Radiation		System	System	Dose	Means of	Reference	
	Type	Energy (MeV)	Source	Pressure (torr)	Temperature (°K)	Rate eV/gm sec	Determination	
12.8 ± 0.6	e^-	n.a.	Fabatron Pulsed Electron Source	30- 800	(298) ?	10^{26} - 10^{27}	Slope of O_3 molecules pro- duced vs. energy absorbed (in single pulse).	Willis, et al. ^{3,40}
6.2 ± 0.6	γ	1-173 1-332	Co^{60} Gamma Cell 220	n.a.	77	10^{16}	"	"
10.2*	γ	"	Co^{60}	760	200 90	2×10^{14} eV-mm ⁻¹)	"	Johnson & Herman ^{16,17}
13.8	e^-	1.7 (Max)	Fabatron	750	295	6.2×10^{25}	Ratio of meas- ured av. $[O_3]$ to calculated absorbed dose.	Chormley, et al. ¹⁰
10.5	γ	1-173 1-332	Co^{60}	665	77 195	1.2×10^{15} 1.4×10^{16}	Slope of curve $d[O_3]/dE_d$	Sears & Sutherland ³⁴
(a) 6.2	F.F. Spectrum	F.F.	n-Irrad.	950	298	8.6×10^{18}	Unclear	Sears & Sutherland ³³
(b) 5.7			U-Pd foils.			8.6×10^{18}		
(c) 6.9						1.9×10^{19}		

*Initial value of slope with corrected $G(N_2)$ value of 10.0 in N_2O dosimetry.**Conversion factor: 1 r/hr = 1.73×10^{10} eV/gm-sec; 1 r/sec = 0.62×10^{14} eV/gm-sec.

n.a., not available

C. Detailed Chemical Mechanism

The full, detailed chemical mechanism (i.e., the set of all reactions that can occur within the system) is extremely complex, even without the complications that would be introduced if electronically excited states of the ions and molecules were considered. The primary species undergo charge transfer, clustering, recombination, etc., and the number of distinct species involved is quite large. Ten species were included in the calculations: the three neutral species O , O_2 , and O_3 ; and the ionic species O^+ , O_2^+ , O_4^+ , e^- , O_2^- , O_3^- and O_4^- . The chemical mechanism used for the detailed model calculations, including the primary processes and reactions among the above species, is given in Table 2.

The rate equations are derived as indicated in Section II-A. For example, O_3^- is produced in reaction (I-21) and reacts with O_2^+ , O_4^+ and O_3 in reactions (I-8), (I-12) and (I-22), respectively. The chemical reaction term $R_{O_3^-}$ is, therefore, given by:

$$R_{O_3^-} = k_{121}[O_3][O_2^-] - k_{18}[O_3^-][O_2^+] - k_{112}[O_3^-][O_4^+] - k_{122}[O_3^-][O_3]$$

Since O_3^- is not a primary product of the radiolysis, $S_{O_3^-} = 0$ and

$$\frac{d[O_3^-]}{dt} = R_{O_3^-} = k_{121}[O_3][O_2^-] - [O_3^-]\{k_{18}[O_2^+] + k_{112}[O_4^+] + k_{122}[O_3]\}$$

The other species are dealt with in the same way, and the resulting rate equations are listed in Table 3. The relative importance of the various terms in these rate equations and the assumptions made in their solution are discussed in Section II-D.

Table 2. Gas phase radiolysis of oxygen chemical mechanism.

A. <u>Primary Reactions</u>			
(P-1)	$O_2 \rightsquigarrow O + O$		
(P-2)	$O_2 \rightsquigarrow O_2^+ + e$		
(P-3)	$O_2 \rightsquigarrow O^+ + O + e$		
B. <u>Reactions of Neutral Species</u>			
<u>No.</u>	<u>Reaction</u>	<u>k, cm³/particle·sec</u>	<u>References</u>
(M-1)	$O + O_2 + O_2 \rightarrow O_3 + O_2$	$*6.5 \times 10^{-34}$	23
(M-2)	$O + O + O_2 \rightarrow O_2 + O_2$	$*2.7 \times 10^{-33}$	18
(M-3)	$O \rightarrow O_{ads}$	$**0.5$	23
(M-4)	$O_3 + O \rightarrow 2O_2$	9.3×10^{-15}	18
(M-5)	$O_3 + O_2 \rightarrow 2O_2 + O$	2.0×10^{-26}	18
C. <u>Ion Reactions</u>			
(I-1)	$O^+ + O_2 \rightarrow O + O_2^+$	2×10^{-11}	7,40
(I-2)	$O_2^+ + O_2 \rightarrow O_4^+$	2×10^{-11}	40
(I-3)	$O^+ + e \rightarrow O$	3.3×10^{-8}	40
(I-4)	$O^+ + O_2^- \rightarrow O + O_2$	2×10^{-6}	40
(I-5)	$O^+ + O_4^- \rightarrow O + 2O_2$	2×10^{-6}	40
(I-6)	$O_2^+ + e \rightarrow 2O$	1.7×10^{-7}	7,40
(I-7)	$O_2^+ + O_2^- \rightarrow 2O + O_2$	2×10^{-6}	40
(I-8)	$O_2^+ + O_3^- \rightarrow O + 2O_2$	NA	
	$[O_2^+ + O_3^- \rightarrow 3O + O_2]$		
(I-9)	$O_2^+ + O_4^- \rightarrow 2O + 2O_2$	2×10^{-6}	40

Table 2. Continued.

No.	Reaction	$k, \text{cm}^3/\text{particle} \cdot \text{sec}$	References
(I-10)	$\text{O}_4^+ + \text{e} \rightarrow 2\text{O} + \text{O}_2$	1.7×10^{-7}	40
(I-11)	$\text{O}_4^+ + \text{O}_2^- \rightarrow 2\text{O}_2 + 2\text{O}$	2×10^{-6}	40
(I-12)	$\text{O}_4^+ + \text{O}_3^- \rightarrow \text{O}_3 + 2\text{O}_2$	2×10^{-6}	40
(I-13)	$\text{O}_4^+ + \text{O}_4^- \rightarrow 2\text{O} + 3\text{O}_2$	2×10^{-6}	40
(I-14)	$\text{O}_2 + \text{O} + \text{e} \rightarrow \text{O}^- + \text{O}_2$	NA	
(I-15)	$\text{O}_2 + \text{O}_2 + \text{e} \rightarrow \text{O}_2^- + \text{O}_2$	$*1.4 \times 10^{-30}$	7,40
	$[\text{O}_2 + \text{e} \rightarrow \text{O}_2^-]$	NA	
(I-16)	$\text{O}^- + \text{O} + \text{O}_2 \rightarrow \text{e}$	2×10^{-10}	7
(I-17)	$\text{O}^- + 2\text{O}_2 \rightarrow \text{O}_3^- + \text{O}_2$	$*4 \times 10^{-31}$	7
(I-18)	$\text{O}^- + \text{O}_3 \rightarrow \text{O}_3^- + \text{O}$	5×10^{-10}	7
(I-19)	$\text{O}_2^- + \text{O} \rightarrow \text{O}_3 + \text{e}$	3×10^{-10}	7
(I-20)	$\text{O}_2^- + \text{O}_2 \rightarrow \text{O}_4^-$	7×10^{-11}	40
(I-21)	$\text{O}_2^- + \text{O}_3 \rightarrow \text{O}_3^- + \text{O}_2$	3×10^{-10}	7,40
(I-22)	$\text{O}_3^- + \text{O}_3 \rightarrow \text{O}_2^- + 2\text{O}_2$	3×10^{-10}	9

* $\text{cm}^6/\text{particle}^2 \cdot \text{sec}$.

** sec^{-1} .

NA: not available.

Table 3. Rate equations.*

$$\begin{aligned} \frac{d[O]}{dt} = & S_0 + [O^+]\{k_{11}[O_2] + k_{13}[e^-] + k_{14}[O_2^-] + k_{15}[O_4^-]\} \\ & + k_{18}[O_2^+][O_3^-] + 2[O_2^+]\{k_{16}[e^-] + k_{17}[O_2^-] + k_{19}[O_4^-]\} \\ & + 2[O_4^+]\{k_{110}[e^-] + k_{111}[O_2^-] + k_{113}[O_4^-]\} - [O]\{k_{N1}[O_2]^2 \\ & + k_{N3} + k_{N4}[O_3] + 2k_{N2}[O][O_2] + k_{119}[O_2^-]\} \end{aligned}$$

$[O_2]$ is given by the pressure profile; it is assumed that the sum of the concentrations of all other species is $\ll [O_2]$

$$\begin{aligned} \frac{d[O_3]}{dt} = & k_{N1}[O][O_2]^2 + k_{112}[O_4^+][O_3^-] + k_{119}[O_2^-][O] - [O_3] \\ & \{k_{121}[O_2^-] + k_{122}[O_3^-] + k_{N4}[O]\} \end{aligned}$$

$$\frac{d[O^+]}{dt} = S_0^+ - [O^+]\{k_{11}[O_2] + k_{13}[e^-] + k_{14}[O_2^-] + k_{15}[O_4^-]\}$$

$$\begin{aligned} \frac{d[O_2^+]}{dt} = & S_{O_2}^+ + k_{11}[O^+][O_2] - [O_2^+]\{k_{12}[O_2] + k_{16}[e^-] \\ & + k_{17}[O_2^-] + k_{18}[O_3^-] + k_{19}[O_4^-]\} \end{aligned}$$

* Although several reactions involving the negative ion O^- are shown in Table 2, these were not included in the final model because no rate constant could be located for the production reaction (I-14), and also because electron attachment to O_2 is likely to dominate ($[O_2] \ll [O]$).

Table 3. Continued

$$\frac{d[O_4^+]}{dt} = k_{12}[O_2^+][O_2] - [O_4^+]\{k_{110}[e^-] + k_{111}[O_2^-] + k_{112}[O_3^-] + k_{113}[O_4^-]\}$$

$$\frac{d[e^-]}{dt} = s_e - k_{119}[O][O_2^-] - [e^-]\{k_{113}[O^+] + k_{116}[O_2^+] + k_{110}[O_4^+] + k_{115}[O_2^-]^2\}$$

$$\frac{d[O_2^-]}{dt} = k_{115}[O_2^-]^2[e^-] + k_{122}[O_3][O_3^-] - [O_2^-]\{k_{114}[O^+] + k_{117}[O_2^+] + k_{111}[O_4^+] + k_{119}[O] + k_{120}[O_2] + k_{121}[O_3]\}$$

$$\frac{d[O_3^-]}{dt} = k_{121}[O_2^-][O_3] - [O_3^-]\{k_{118}[O_2^+] + k_{112}[O_4^+] + k_{122}[O_3]\}$$

$$\frac{d[O_4^-]}{dt} = k_{120}[O_2^-][O_2] - [O_4^-]\{k_{115}[O^+] + k_{119}[O_2^+] + k_{113}[O_4^+]\}$$

D. Solution Method for Complete Model

Since the coupled, non-linear rate equations arising from Table 3 cannot be solved in closed form, digital or analog* methods must be applied. The numerical technique selected is the Gill modification of the Runge-Kutta method.^{4,13} This is a fourth order method (i.e., the first truncated term in the corresponding Taylor series expansion is $O(h^5)$) which is modified (Gill) in an attempt at control of round-off errors. Variable step-size is allowed, and reasonable convergence was obtained setting the interval dt (limited to the range $10^{-9} < dt < 10^{-5}$ sec) proportional to $[O_4^-]$. However, even with careful selection of the method and step-size, the solution is time consuming and expensive. Because of the limits on the step-size required for convergence, each solution requires $\sim 10^6$ mesh points, and the gradient (e.g., all derivatives listed in Table 3) must be evaluated four times at each mesh point. Furthermore, the computation should be repeated a sufficient number of times to map the solution over the appropriate range of experimental parameters and theoretical variables. It is, therefore, essential to streamline the program as much as possible, and to this end several approximations were made.

The model itself was simplified by deleting those terms (i.e., reactions) considered to have an insignificant effect on the result. The terms deleted are: $T_{N5} = k_{N5}[O][O_2^-]$, $T_{I4} = k_{I4}[O^+][O_2^-]$.

* First order coupled differential equations of this type are ideally suited to analog solution. However, the present problem requires a system with greater capacity (e.g., ~ 25 multipliers) than was available, and this technique was not pursued.

$T_{111} = k_{111}[O_4^+][O_2^-]$ and $T_{119}[O][O_2^-]$. The magnitude of each of these terms is at most <0.1% of the largest term in the respective rate equation in which it appears.

The solution method is streamlined by applying the stationary intermediate approximation to some of the rate equations. The advantage of this procedure can be seen if one considers the physical situation described by the stationary intermediate assumption. Mathematically, the time derivative of the species in question is set equal to zero, but in fact the concentration of that species is not constant. For example, the stationary intermediate value for $[O^+]$ is obtained by setting:

$$d[O^+]/dt = S_{O^+} - [O^+]\{k_{11}[O_2] + k_{13}[e^-] + k_{15}[O_4^-]\} = 0$$

$$[O^+]_{SI} = \frac{S_{O^+}}{\{k_{11}[O_2] + k_{13}[e^-] + k_{15}[O_4^-]\}}$$

As the concentrations of the other species (O_2 , e^- , O_4^-) change, $[O^+]$ will rapidly adjust to bring $(d[O^+]/dt)$ back to zero. For a true stationary intermediate this adjustment is virtually instantaneous, and the derivative always remains near zero. However, because the derivative is essentially held constant over the finite steps in a numerical integration, any attempt to increase the step-size as the initial transients die out can cause the rapid adjustment to become a divergent oscillation. In other words, even though the actual value of the concentration is changing rather slowly, the maximum allowable step-size is still determined by the largest rate constant. Therefore, if a given species has reached a stationary intermediate state, it is

more economical to calculate the concentration directly from the analytical stationary intermediate expression, since the step-size can then be increased to a time interval commensurate with the remaining (slower) reactions. It should be noted that applying the stationary intermediate assumption to one or more rate equations reduces the number of mathematical constraints by one, and the proper solution is obtainable only if charge conservation is included explicitly.

The concentrations of O^+ and O_2^+ were found to reach their stationary intermediate values within 1 μsec (i.e., $<0.0005\%$ of the distance down the reaction tube), and the analytical expressions for the concentrations of these two species were used throughout. Stationary intermediate expressions were used for other ions only if the solution began to diverge.

The results of the theoretical calculations are discussed in Chapter IV.

E. Simple Model

Since the model is to be developed to predict the behavior of a specific experimental system in which the reactions occur simultaneously with the irradiation (c.f. Section I-C), it is conceptually most appropriate to use the detailed model described in Section II-D. However, the detailed model does not lend itself readily to qualitative interpretation (e.g., Does the ratio of $[O_3]:[O]$ increase or decrease with the system pressure?) without lengthy and expensive digital computation. For this reason it is desirable to construct a simplified model, by means of which the general trends to be expected in the system response can be understood in a clear, direct way.

The construction of such a model requires drastic simplification of the complete mechanism. The assumptions used and the resulting simplified model follow:

- (1) All ion reactions are complete instantaneously; i.e., the stationary intermediate approximation applies to all ion rate equations.
- (2) All reactions involving O_3^- are neglected.
- (3) The neutralization of O_2^+ results in the production of two neutral atoms of oxygen (either via reactions (I-6), (I-7) and (I-9), or (I-2) followed by (I-10), (I-11) or (I-13)).
- (4) The direct neutralization of O^+ is much less efficient than the charge transfer reaction (I-1), so that three neutral oxygen atoms are produced for every O^+ ion (one from reaction (I-1) and two from the subsequent neutralization of O_2^+).
- (5) Excited species are neglected.
- (6) The sum of the concentrations of all product species is $\ll [O_2]$.
- (7) $[O_2]$ is constant over the length of the flow tube.
- (8) All neutral reactions that are second order in the reactive species (e.g., O , O_3) can be neglected relative to reactions (N-1) and (N-3).
- (9) Reaction (N-5) is neglected because of its very small rate constant.
- (10) The energy deposition rate $\dot{E}_d$ is constant over the length of the flow tube.

These assumptions lead to the following two rate equations for $[O]$ and $[O_3]$:

$$d[O]/dt = S_0 - k_{N1}[O][O_2]^2 - k_{N3}[O] \quad (1)$$

$$d[O_3]/dt = k_{N1}[O][O_2]^2 \quad (2)$$

The source term S_0 is now given by:

$$S_0 = g(0)_{\text{eff}} \dot{E}_d \quad (3)$$

where

$$g(0)_{\text{eff}} = g_0 + 2g_{0_2^+} + 3g_{0^+} = g_0 + g_{0^+} + 2g_{e^-}$$

and $\dot{E}_d$ is the average value over the flow tube.

Since the differential equation for $[O]$ is decoupled from that for $[O_3]$, these equations can be solved in closed form using the boundary conditions:

$$[O]|_{t=0} = [O_3]|_{t=0} = 0$$

($t = 0$ at the oxygen inlet to the reaction tube).

The solutions for the irradiated section* of the reaction tube are:

$$[O] = (S_0/k_{\text{eff}})[1 - \exp(-k_{\text{eff}}t)] \quad (4)$$

$$[O_3] = (k_{N1}[O_2]^2/k_{\text{eff}})(S_0t - [O]) \quad (5)$$

*For the complete prediction of the system response these solutions must be extended to include the non-irradiated section of the flow system leading to the molecular beam source (see Sections III-B-2 and 3). The same differential equations apply, except that the source term is zero. This procedure is also required in the solution of the complete model.

where

$$k_{\text{eff}} \equiv k_{N1}[O_2]^2 + k_{N3}$$

In the context of this simple model the ratio $[O_3]:[O]$ increases with system pressure ($k_{\text{eff}} \sim p^2$) and is independent of the proton current and energy (both $[O]$ and $[O_3]$ are directly proportional to S_0). This predicted behavior can be compared with the data to determine the validity of the simplified model, although it might be anticipated that $[O_3]$ will be over-estimated (particularly through assumptions 2, 5 and 8). The complex model can be considered as a refinement and evaluated in terms of its ability to compensate for deficiencies in the predictions of the simple model.

III. EXPERIMENTAL DESCRIPTION

A. General Features

The quantities to be measured are the concentrations of atomic oxygen and ozone, as functions of pressure, flowrate, and proton beam intensity. The equipment to accomplish these functions can be divided broadly into three systems: (1) equipment for production and measurement of the proton beam; (2) the oxygen flow system; and (3) apparatus for identification and quantitative measurement of the radiolysis products. A schematic of the complete experiment is shown in Fig. 1, and the physical layout can be seen in the equipment photographs, Figs. 2, 3 and 4. Detailed schematics of the individual systems follow in later sections.

B. Apparatus

1. Production and Measurement of Proton Beam

a. Van de Graaff Accelerator. The proton beam is produced by a 1 MeV Van de Graaff accelerator (High Voltage Engineering Corporation, Model JN-1). This accelerator is provided with three exit ports, and the beam tube leading to the present experiment is positioned 15° off the axis of the accelerator. The beam is deflected into this tube by a 2900 gauss (maximum) bending magnet (H. V. Eng. Corp., Part No. 998-2) with a variable regulated power supply. The resulting beam consists only of mono-energetic protons. A set of jaws located approximately three quarters of the length down the tube is used with a feedback circuit to the corona control of the accelerator to stabilize the energy (hence position) of the beam.

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Fig. 2. Overall physical layout of experiment, wide angle view. The accelerator (control panels on right) is located behind the concrete shielding wall. Other equipment is clustered about the reaction and the beam port, which penetrates the wall at the upper center of the photograph.

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Fig. 3. Near view of (left to right) reaction tube, spectrometer head and vacuum cart, differential pumping system, and beam port. The flow system mechanical pump is located directly behind the wall, to the left of the beam port.

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Fig. 4. Alternate near view of (left to right) oxygen inlet system, proton current detection system, reaction tube, spectrometer electronics, and spectrometer vacuum system.

The area in which the remaining apparatus is located (the cave) is shielded from accelerator radiation by a wall of high density concrete 2 m high and 30 cm thick. Crevices and openings in this wall are packed with lead. The radiation level directly in front of the accelerator (i.e., ~1 m from the ground terminal) is monitored with a Remote Area Monitor (RAM) (Victoreen "VAMP", Model 8088) and the level inside the cave with an ion-chamber type survey meter (Victoreen, Model 440). A set of film-type dosimeters are located at selected positions within the cave to provide a permanent integrated-dose record, and the individual operating the experiment wears both a film badge and self-reading dosimeter. Under normal operating conditions the level observed with the RAM is 1-10 mR/hr. The access door to the accelerator area is interlocked to shut down the accelerator should any one attempt to enter during operation. No significant radiation levels were observed in any accessible areas of the cave.*

b. Proton Current Measurement. The measurement of the proton current must be done quite carefully, since this factor directly determines the energy deposition in the flowing reactant gas. A Faraday cup (the standard means of measuring such currents) cannot be used under the present circumstances, however, because the ions produced in the gas are also collected and result in large, spurious

* At one cm from the Ta foil (a location normally occupied by the detector head, see Section III-1-b) a level of 53 mR/hr was measured with the survey meter (metal shield removed). This radiation field is assumed to consist of ~60 kV X-rays and some secondary electrons.

currents. To surmount this problem a modified Faraday cup was constructed, in which the beam is stopped in a relatively thick tantalum foil (45 mg/cm^2). The proton beam intensity is then related to the production rate of tantalum K X-rays, the latter being monitored with a lead-shielded Ge(Li) detector (Canberra Industries, Model No. 7219/7600, 35 cm^3 , true co-axial). The output of this detector is amplified (Canberra Industries Spectroscopy Amplifier, Model 1417B), fed into a ratemeter (Canberra Industries Linear Ratemeter, Model 1480) and recorded simultaneously with either the measured current (for calibration, vacuum condition) or the output of the mass spectrometer. The background count-rate is established by manually interrupting the beam with a rotatable, cylindrical beam flag located between the two collimators (see Fig. 1). The calibration procedure is discussed in Section III-C-2. A schematic of the system is shown in Fig. 5, and pertinent data on tantalum are given in the following table.²⁵

Table 4. Tantalum

$Z = 73$

Fluorescent Yield $\omega_k = 0.94$

Characteristic X-Ray	Energy keV	Relative Intensity
$K_{\alpha 2}$	56.28	54
$K_{\alpha 1}$	57.54	(100)
$K'_{\beta 1}$	65.2	33
$K'_{\beta 2}$	67.0	8

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Fig. 5. Proton current detection system.

The one essential criterion for this detection system is that the measured response have a reproducible, one-to-one relationship to the proton current. Even though the ratemeter responds non-discriminately to all the various radiations entering the detector (i.e., does not select a single X-ray peak) the detector-ratemeter system met this criterion adequately (see Section III-C-2). Consequently it was not necessary to make use of the available resolution of the Ge(Li) detector.

2. Oxygen Flow System

Figure 6 shows the reaction tube in detail. Research grade oxygen gas (Matheson, Stated Purity 99.95%) is supplied at a controlled rate via a Granville-Phillips Calibrated Leak. The flowrate is measured with a Matheson dual-float flowmeter (Series R-2-15-D, Model 602) located between the gas bottle and the calibrated leak. (The calibration curve, ($\text{cm}^3 \text{O}_2/\text{min}$ at 1 atm, 70°F vs flowmeter reading) was factory supplied with the flowmeter.) All intermediate lines and fittings in the oxygen supply system are stainless steel.

The flow system itself is primarily a long pyrex tube, the inside surfaces of which have been treated with phosphoric acid to reduce wall recombination of atomic oxygen.²² The irradiated section is 1.56 cm I.D. and 57 cm long, measured from the oxygen inlet to the outlet. The second section (1.2 cm I.D., 7.7 cm L) provides the vertical offset between the proton beam and the spectrometer ionizer. (The vertical positions of these two features of the experiment are determined by the heights of the accelerator beam port and the spectrometer pump cart, which are offset by ~8 cm, and inflexible except within narrow

Fig. 6. Detailed schematic of reaction tube.

limits.) The molecular beam source (see Section III-B-3-a) is located at the end of another connecting horizontal section, whose dimensions are $L = 9.5$ cm, I.D. = 1.0 cm. The pressure tap (measurement of p_g) is located at the downstream end of the irradiated section, and leads to a Wallace-Tiernan absolute pressure gauge. The system is pumped by a liquid nitrogen trapped 70 cfm mechanical pump (Welch Duoseal, Model 1398H). Vacuum integrity is assured by helium leak testing.

Pressure and velocity profiles in this system are discussed in Appendix A. Under normal experimental conditions the pressure in the reaction tube is a few Torr, the flow rate 1-10 std cm³/sec, and the velocity 200-500 cm/sec.

Since the accelerator tube and beam port must be maintained at a relatively low pressure ($\sim 10^{-6}$ Torr), some means must be provided to maintain the pressure difference between the reaction chamber and beam port without appreciably disturbing the proton beam. Thin windows of various materials were tried for this purpose, but the attempts were not successful (see Appendix B). In the present system, the pressure difference is achieved by two-stage differential pumping, using two long channels (2.5 mm in diameter and 10 cm in length) which allow passage of the proton beam but provide adequate resistance to gas flow from the reaction chamber to the accelerator. A schematic and pressure-flow analysis of this system is given in Appendix C. The fraction of the total gas flow lost through the channels is $\sim 25\%$, which produces negligible pressure rise in the accelerator tube. However, the attainable beam current was reduced by roughly an order of magnitude (to a maximum of 1-3 μ a at

the Faraday cup) because of the extensive collimation by the two channels, and the alignment problems encountered were substantial.

3. Analysis of Radiolysis Products

a. Molecular Beam. The portion of the reacted gas analyzed by the mass spectrometer is sampled from the main flow stream by a molecular beam source. This source connects the reaction tube and the roughing chamber (see Fig. 1) and is comprised of approximately 5000 pores, each 11 μm in diameter, packed in a 1 mm^2 area. The characteristics of this source and the resulting molecular beam have been described previously.²⁰

The signal to the spectrometer is modulated by chopping the molecular beam with a rotating slotted cylinder. The chopper motor, located in the roughing chamber (Fig. 1), is a synchronous motor designed for operation at 400 Hz, 26 VAC (rms). Operation at other frequencies is achieved by powering the motor with a system of variable resistors and capacitors which provide the correct phase shift (90°) between the windings at each frequency. The coolest possible operation is obtained by applying the proper phase shift and using the lowest voltage at which the motor will still operate synchronously. This is important since the motor is not cooled except for conduction through the mounting bracket.

The motor runs at 1/2 the driving frequency, so that use of a two bladed chopper produces beam modulation at exactly the driving frequency, and the signal from the oscillator can be used directly as the reference for the lock-in amplifier.

b. Spectrometer System. The quadrupole head of the mass spectrometer is located in the spectrometer chamber (Fig. 1). The molecular beam enters this chamber through a 1 mm^2 collimating aperture, which connects the roughing and spectrometer chambers while allowing them to be differentially pumped. The roughing chamber is pumped by a liquid nitrogen trapped, 500 lit/sec oil diffusion pump and the spectrometer chamber by an ion pump. With ~ 2.5 Torr in the reaction tube, typical pressures in the roughing and spectrometer chambers are 3×10^{-6} and 2×10^{-8} Torr, respectively.

The spectrometer used is an Electronics Associates Inc. Model 250 Quadrupole Mass Spectrometer. The output from the spectrometer is fed directly into a pre-amp and then to a narrow-band, lock-in amplifier (Princeton Applied Research, Model HR-8). The output of the PAR is used to drive one channel of a two-pen chart recorder.

This gas analysis system (PAR-spectrometer-vacuum system) was developed prior to construction of the present experiment, and detailed discussion of its characteristics and principles of operation can be found elsewhere.³⁰ Calibration of the spectrometer system for the measurements particular to this experiment is discussed in Section III-C-1, and typical operating parameters can be found in Section III-D-2.

C. Equipment Calibration

1. Spectrometer

Consider a modulated molecular beam of the oxygen species O, O₂ and O₃ entering the ionizer of the mass spectrometer. In general, some fraction of each species will be ionized, and will result eventually in a signal voltage measured at the output of the lock-in amplifier. If, for example, S₁₆ is the resulting signal (less background) from the ionization of atomic oxygen (i.e., directly from the mass 16 parent neutral), the density of O-atoms in the ionizer is proportional to S₁₆ with the proportionality constant determined by the ionization cross section, the geometry of the ionizer, the electron energy, the electron multiplier characteristics, etc. The object of the spectrometer calibration is to determine the relationship of the measured signals S₁₆, S₃₂ and S₄₈ (from O, O₂ and O₃, respectively) to the relative abundances of the parent neutrals in the ionizer, and eventually their concentrations in the reaction tube.

a. Calibration for Atomic Oxygen. The concentration of atomic oxygen is determined by first obtaining the mass- (or mole-) fraction of atomic oxygen in the spectrometer ionizer, and then relating this fraction to the known gas pressure at the molecular beam source. For example, if the mole fraction of atomic oxygen at the molecular beam source is x_O)_{MBS}, then the concentration of atomic oxygen at this point is given by

$$[O]_{MBS} = x_O)_{MBS} [O_2]_{MBS}$$

where $[O_2]_{MBS}$ is the molecular oxygen concentration, and it is assumed that $[O_2] \gg [O]$ or $[O_3]$. $x_o)_{MBS}$ is related to the mole fraction in the spectrometer ionizer, $x_o)_{sp}$ (see discussion at end of this section), which in turn is related to the signal S_{16} by

$$x_o)_{sp} = \frac{\alpha_{16} S_{16}}{\sum_A \alpha_A S_A}$$

Here S_A is the signal at mass A from the parent neutral of mass A (only) with the summation taken over all species present, and α_A is a previously mentioned proportionality constant. Since in this case only O, O_2 and O_3 are present, and $[O_2] \gg [O]$ or $[O_3]$, $x_o)_{sp}$ is well approximated by:

$$x_o)_{sp} = \frac{\alpha_{16} S_{16}}{\alpha_{32} S_{32}}$$

The proportionality constant α_{32} contains a known factor $(1 + \gamma_{16}^{32})$, which reflects the fractionation of the parent molecule O_2 . γ_{16}^{32} is the cracking fraction, defined as:

$$\gamma_{16}^{32} \equiv \left\{ \frac{\text{number of ions of mass 16}}{\text{number of ions of mass 32}} \right\}$$

resulting from the ionization of parent neutral O_2 . The factor $(1 + \gamma_{16}^{32})$ can be included explicitly and the remaining constants lumped together in a single relative proportionality constant α_{16}^{32} ,

$$\alpha_{16}^{32} \equiv \frac{\alpha_{16} (1 + \gamma_{16}^{32})}{\alpha_{32}} .$$

The expression for the mole fraction of atomic oxygen then becomes:

$$x_o)_{sp} = \alpha_{16}^{32} \frac{S_{16}}{S_{32}(1 + \gamma_{16}^{32})}$$

and the calibration for atomic oxygen is equivalent to the determination of α_{16}^{32} .

The calibration measurement is accomplished by using a microwave discharge to generate relatively large amounts of atomic oxygen in a flow tube similar to the reaction tube in the present experiment. The concentration of atomic oxygen at various points downstream from the discharge is determined by NO_2 light titration, and the extrapolated value at the molecular beam source is compared with the mass spectrometer measurement to determine α_{16}^{32} . Detailed discussion of the procedures and equipment used is given in Appendix D, and the results are shown in Fig. 7. In this figure, the abscissa x_o is the extrapolated mole fraction of atomic oxygen at the molecular beam source, and the ordinate α_{16}^{32} is the ratio of x_o to the quantity $\{S_{16}/S_{32}(1 + \gamma_{16}^{32})\}$ (the latter having been corrected for O-atom wall recombination in the molecular beam source, see below). The "error bars" on the data points represent the range of values measured during the course of one run.

When a mixed gas is sampled by this measurement system, the ratio of any two species detected by the spectrometer will be the same as that delivered to the molecular beam source only if neither is selectively created or destroyed in the sampling process. If one species is particularly reactive (e.g., the free radical atomic oxygen) wall- or intermolecular collisions within the molecular beam source can result in losses that must be accounted for in the overall analysis. Although

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Fig. 7. Results of mass spectrometer calibration for atomic oxygen. Proportionality constant $\alpha_{16}^{32} = 1.0 \pm 0.05$.

the ratio of intermolecular-to-wall collisions in this particular source ($(2a/L) = 4.4 \cdot 10^{-2}$, $p_{O_2}^* = 3.81$ Torr) is quite high relative to other typical molecular beam sources,^{20,29} the primary homogeneous O-atom reaction requires a three-body collision ($O + 2O_2 \rightarrow O_3 + O_2$) so that the dominant loss mechanism is wall recombination. The latter results in a decrease of ~7% in the relative concentration of atomic oxygen transmitted by the molecular beam source (see Appendix E for detailed analysis).

b. Calibration for Small O-Atom Concentrations. The amount of atomic oxygen produced by proton irradiation is so small that under normal operating conditions it cannot be detected against the mass 16 signal from the cracking of molecular oxygen.[†] However, since the processes in the mass spectrometer ionizer have different threshold energies:

$O_2 \rightarrow O_2^+ + e^-$	12.21 eV
$O_2 \rightarrow O^+ + O + e^-$	18.73 eV
$O \rightarrow O^+ + e^-$	13.55 eV

it is possible to suppress the O_2 cracking by lowering the electron energy in the ionizer; i.e., there is a window in the electron energy range [13.55-18.73 eV] in which O^+ can be formed from O but not from O_2 .

To establish the response of the system to variable electron energy, the O_2 signal and cracking fraction profiles were observed. The results, normalized to unity at normal operating conditions ($E_{max} \sim 65$ eV, not critical since the O_2 signal exhibits a broad maximum in this range), are

[†]For the atomic oxygen concentrations produced in this system, the signal at mass-to-charge ratio 8 (O^{++}) is also too small to be detected against background.

shown in Fig. 8. E_0 in this figure is the threshold energy for O_2 ionization (12.21 eV), and the various symbols represent separate runs at different source pressures.

For the atomic oxygen measurements it is assumed that the behavior of $(S_{16}/S_{16,max})$ with the reduced energy coordinate $\{(E - E_0)/(E_{max} - E_0)\}$ is the same as that of $(S_{32}/S_{32,max})$, provided that the proper threshold energy is used; equivalently, $(S_{16}/S_{16,max})|_E = (S_{32}/S_{32,max})|_{E-\Delta}$, where $\Delta = E_{0,16} - E_{0,32} = 13.55 - 12.21$ eV. If S_{16} and S_{32} are measured at some value of electron energy (e.g., $E \sim 17$ eV), the fraction x_0 (in the ionizer) is then given by:

$$x_0 = \frac{S_{16}(E_{max})}{S_{32}(E_{max})^{32}(1 + \gamma_{16,max}^{32})} = \left(\frac{S_{16}}{S_{32}}\right)_E \left(\frac{S_{16,max}}{S_{16}}\right) \left(\frac{S_{32}}{S_{32,max}}\right) \left(\frac{1}{1 + \gamma_{16,max}^{32}}\right)$$

$$= \left(\frac{S_{16}}{S_{32}}\right)_E \left(\frac{S_{32}(E)}{S_{32}(E - \Delta)}\right) \left(\frac{1}{1 + \gamma_{16,max}^{32}}\right)$$

The ratio $\{S_{32}(E)/S_{32}(E - \Delta)\}$ can be obtained from Fig. 8, and is a slowly varying function of E (≈ 1.85 at $E = 16$ eV, and approaching 1.0 as $E \rightarrow E_{max}$).

c. Ozone Measurement. The ozone peak (mass 48) occurs in a low-background region of the mass spectrum, and the signal was observable without alteration of the spectrometer settings (i.e., at E_{max}). The expression for the mole fraction of ozone is similar to that for atomic oxygen, except that the fractionation of O_3 (resulting in both O_2^+ and O^+) must be included. The pertinent cracking fractions (measured at 60 eV), are:¹¹

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Fig. 8. Normalized mass 32 signal and oxygen cracking fraction as a function of ionizer electron energy. $E_0 = 12.21$ eV; $E_{max} \sim 65$ eV.

$$\gamma_{32}^{48} = 5.0$$

$$\gamma_{16}^{48} = 0.5$$

The mole fraction of ozone (again assuming $[O_2] \gg [O_3], [O]$) is, therefore, given by:

$$x_{O_3} = \frac{S_{49}(1 + \gamma_{32}^{48} + \gamma_{16}^{48})}{S_{32}(1 + \gamma_{16}^{32})}$$

(Note that $\gamma_{16}^{32} = 0.17$, see Fig. 8.)

The above expression contains the implicit assumption that α_{32}^{48} is unity if the proper cracking fractions are used. The measured value $\alpha_{16}^{32} = 1$ supports this assumption, since it implies that any ion extracted from the ionizer produces the same result at the output of the spectrometer system.

2. Proton Beam Detector

a. System under Vacuum. When the reaction tube is evacuated, the proton beam current can be measured directly (Keithley 410 micro-microammeter, Faraday cup biased to prevent escape of secondary electrons) and compared to the X-ray production rate (see Section III-B-1b) to establish the detector calibration. This procedure is repeated before each experiment run.

The resulting calibration (for 0.9 MeV protons) is shown in Fig. 9. In this figure the abscissa is the ratemeter output, and the ordinate the measured beam current. Various symbols differentiate sets of data taken on different days.

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Fig. 9. Proton current detector calibration. Best fit slope = $(1.495 \pm 0.125) [\mu\text{A}/(10^3 \text{ counts/sec})]$.

The scatter in the data is for the most part a result of two difficulties: (1) the very unstable behavior of the accelerator (and consequently the proton beam) combined with imperfectly matched time constants in the filtering circuits of the picoammeter and ratemeter; and (2) residual gas in the reaction tube. The first effect can scatter the data in either direction, while the second always lowers the measured current at constant countrate because the positive bias on the Faraday cup pulls electrons out of the ionized gas. (This effect is quite dramatic, and gives an early indication of incipient loss of vacuum integrity.) The line shown

$$\{I_p(\mu a) = (1.495 \pm 0.125) \times (\text{countrate} \times 10^{-3})\}$$

represents the best fit to the slope of a straight line through the origin (number of data points = 121).

b. System in Operation- O_2 Flowing. When gas is admitted to the reaction tube there is a noticeable decrease in the X-ray production rate. There are two possible explanations for this phenomenon: (1) decrease in X-ray yield/proton from proton energy loss in the gas; and/or (2) physical loss of protons on the walls of the reaction tube as a consequence of angular deflections in the collision processes occurring in the g. s.

The variation of the tantalum K X-ray yield with proton energy is shown in Fig. 10. The solid part of the curve is taken from the literature,²⁷ and the data points from vacuum calibration measurements at different accelerator voltages, with appropriate normalization. The proton energy loss as a function of pressure can be combined with this

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Fig. 10. Tantalum K X-ray thick target yield as a function of proton energy.

curve to predict the decrease in X-ray yield, Fig. 11 . (For details of this calibration see Appendix F).

The data points in Fig. 11 represent direct measurements of the relative countrate decrease. Because of the instability of the proton beam and the time required to stabilize the pressure in the reaction tube, this particular measurement is difficult and unreliable, although it does at least indicate the order of magnitude of the correction. The curve exists independently (it can be interpreted as a minimum correction), and appears reasonably adequate over the pressure range used.

A similar analysis for losses on the tube walls proved intractable, since it requires the full three-dimensional solution for the proton angular distribution (preferably energy dependent), with finite boundary conditions. It is possible, however, to derive some of the moments of the radial distribution for the idealized case of a semi-infinite, pure scattering medium. The second moment (see Appendix G) indicates that the RMS radial displacement is independent of the gas pressure, so that, within the accuracy of the approximations used, there should be no losses from deflection of protons into the tube walls. Consequently, no correction is used, although this approximation could be expected to become worse at higher gas pressures, and places an additional limit on the useable pressure range.

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Fig. 11. Relative count rate decrease as a function of oxygen pressure. The curve is the predicted decrease from proton energy in the gas.

D. Experimental Procedure

1. Start-Up

In the down-state (e.g., over night) all electronics and pumps are either off or on stand-by, with the exceptions of the ion pump, roughing chamber fore pump, differential system mechanical pump, and the Ge(Li) detector electronics. The accelerator tube, beam port, and all diffusion pumps are blanked off, and an auxiliary pumping line between the roughing chamber and the reaction tube is opened so that any accidental loss of vacuum (e.g., back through a mechanical pump during a power-out, or through a fracture in some part of the glass system) will not cause a full atmosphere differential on the molecular beam source.

Preliminary preparations for an experiment run therefore include:

(1) filling all cold traps with liquid nitrogen; (liquid nitrogen in the Ge(Li) detector cryostat is of course maintained continuously); (2) switching on all pumps and electronics (except the accelerator controls); and (3) setting all valves except the O_2 inlet for flow operation. After these initial operations the equipment is allowed to warm up and/or pump down for 1 to 2 hr until the accelerator tube has been evacuated to $\leq 10^{-6}$ Torr.

The accelerator is then started and tuned for maximum beam strength and stability; (the beam current must be $\geq 0.15 \mu a$ before the product signals (S_{16} , S_{48}) are observable above background). Because the Van de Graaff is quite old and uncooperative, this process can be time consuming (1 to 4 hr of continuous retuning); but since the reaction tube is still evacuated, the time is used for the dual purposes of

tuning and calibration of the proton detection system.

When an adequate beam current has been obtained, oxygen is admitted to the reaction tube, the flow allowed to stabilize and the full experiment begun.

2. Operation

Typical instrument settings and operating parameters are as follows:

a. Spectrometer.

Ionizer Emission Current = 0.5 ma

Filament Current = 1.9 a

Ion Energy = 45 eV

Focus Voltage = 90 V

Extractor Voltage = 40 V

Extractor Current = 0.01 ma

Electron Energy (max) = 65 eV

(0-Atom Measurement) = 17 eV

Electron Multiplier Voltage = 2.5 kV

b. Lock-In Amplifier.

Frequency (Chopper Modulation) = 200 hz

Time Constant = 0.3-10 sec

(6 db/octave filter)

Signal Q = 10

c. Ge(Li) Detector System.

Head Voltage = -3 kV

Amplifier Gain = 8.394

Input Impedance = 1 K Ω

Shaping = 2 μ sec

Ratemeter Time Constant = 10 sec

Range = 50-5000 cts/sec

d. Accelerator.

Proton Energy = 0.9 MeV

Jaw Feedback-Controller Sensitivity = 4.5

Magnet Current = 1.49 ma

Corona Current = 75 μ a

Proton Current (at detector) = 0.1-3.0 μ a

H₂ pressure, focus voltage and extractor position
adjusted for maximum beam current.

e. Oxygen Flowmeter.

Reading (Glass Float) = 5-12 cm

Pressure = 1 atm

The phase setting on the lock-in amplifier is determined for each measurement by nulling the signal (90° from maximum).^{*} The mass spectrometer is adjusted for unit resolution at each mass peak, and the center of mass control setting is optimized by tuning for the maximum signal output from the lock-in amplifier (monitored for this purpose with a digital D.C. voltmeter (Digitec Model z-200-B)).

^{*}The slight phase shift with mass number resulted from time-of-flight differences over the length of the quadrupole rods. These phase shifts were very small.

Data accumulation proceeds as follows. The O_2 signal and cracking fraction are established, adjusting the electron energy for the maximum mass 32 signal. The approximate background and beam-on count-rates are established with the Ge(Li) detector selecting the appropriate ratemeter scale (usually different with oxygen present than under vacuum). The atomic oxygen or ozone signal is then recorded simultaneously with the ratemeter output, rotating the beam flag at appropriate intervals to establish the background levels for both the count-rate and mass signal.

The electron energy in the mass spectrometer ionizer is reduced to ~17 eV (actual value measured with another digital D.C. voltmeter) for the atomic oxygen measurement, as discussed in Section III-C-1b. Center of mass and phase adjustments for this measurement are made with the larger, more stable mass 16 signal from O_2 cracking, before the electron energy is lowered.

The ozone measurement is made with the ionizer settings used for O_2 ; however, this signal is quite small and also reflects the instabilities in the proton beam, so that the phase and center mass adjustments are substantially more difficult, and must be checked repeatedly.*

Both the 0 and O_3 signals are of the order of tens of microvolts or less, and both are subject to the fluctuations in the proton beam, so that a relatively long time constant ($\tau = 10$ sec, lock-in amplifier) is used in their measurement. Although a 10 sec time constant is also used with the ratemeter, the two are not precisely matched and can result in random errors in the measurements (similar

*No ozone signal could be detected in the absence of the proton beam.

to those observed in the proton current detector calibration, see section III-C-2a).

A sample of the raw data (chart recorder output) is shown in Fig. 12, and a summary of all measured quantities and associated calibrations or corrections is given in the following table.

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Fig. 12. Sample of raw data. The upper trace is the ratemeter output, and the lower trace the output of the lock-in amplifier-mass spectrometer. Signals in the lower trace are labelled according to 1) mass:charge ratio; 2) full-scale setting of lock-in amplifier; (3) ionizer electron energy; and 4) time constant. ($\tau = 0.3$ s if not specifically indicated.) Spike labelled (?) in ratemeter trace is background the surge from temporary malfunction in accelerator. Chart speed = 10 in./hr.

Table 5.

Summary: Experimental measurements and calibrations.

Quantity Measured	Analysis Procedure/Calibration	Section
S_{16}	Subtract Background	
	Determine x_0 at maximum electron energy	III-C-1b
	Correct for losses in molecular beam source	III-C-1a, (Appendix E)
	Find $[O]$ from x_0 , $[O_2]$	IV-A
S_{32}	Subtract Background	
	Correct for fractionation	III-C-1a
S_{48}	Subtract Background	
	Determine x_{O_3} using γ_{32}^{48} , γ_{16}^{48} , S_{32}	III-C-1c
	Find $[O_3]$ from x_{O_3} , $[O_2]$	IV-A
Proton Energy, E (none)		
Count-rate	Subtract Background	
	Correct to vacuum condition	III-C-2b
	Determine proton current from vacuum calibration	III-C-2a
	Find energy deposition rate	II-B-3

Table 5. Continued.

Quantity Measured	Analysis Procedure/Calibration	Section
Pressure, p_s	Determine pressure profile Convert to $[O_2]$	(Appendix A)
Flowmeter Reading	Find flowrate (cm^3/min at 1 atm, 70°F) from calibration curve Correct to (std cm^3/sec)	III-B-2 (Appendix A)

IV. RESULTS

A. General

The measured concentrations of atomic oxygen and ozone are shown in Figs. 13 and 14, plotted vs energy deposition for the various flow conditions used. The concentrations are obtained by combining the measured mole fractions of O and O₃ (see Section III-C) and calculated O₂ concentration at the molecular beam source using the relationships:

$$[O] = x_0[O_2]$$

$$[O_3] = x_{O_3}[O_2]$$

Here again it is assumed that $[O_2] \gg [O]$ or $[O_3]$ (valid since all measured mole fractions were $\leq 2 \times 10^{-3}$). The total energy deposition (eV/cm³) is obtained by integrating the energy deposition rate (see Section II-B-3) over the irradiation time:

$$E_d = \int_0^{L_1} \dot{E}_d(dx/v)$$

where v is the flow velocity and L_1 the length of the irradiated section of the flow tube. The experimental parameters corresponding to each set of data are given in Table 6.

B. Comparison with Theoretical Models

1. Preliminary q_0 Values

The measured concentrations are interpreted by comparison with the theoretically predicted system response (c.f. Chapter II). Since both the full model* (Section II-C, Table 3) and the simplified model

*The full model referred to in this chapter is that used for the computer calculations, including all simplifications required for convergence (see Section II-D).

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Fig. 13. Measured atomic oxygen concentration (atoms/cm³ at molecular beam source) as a function of total energy deposited (heV/cm³) for various flow conditions.

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Fig. 14. Measured ozone concentration (molecules/cm³ at molecular beam source) as a function of total energy deposited (heV/cm³) for various flow conditions.

Table 6. Experiment parameters.

System Pressure p_s (Torr)	O ₂ Flowrate (std cm ³ /sec)	O ₂ at m.b.s.* (10 ¹⁶ molecules per cm ³)	Irradiation Time, t_1 (sec)**	Elapsed Time to m.b.s. (sec)	Proton Energy (MeV)	Proton Current Range† (ua)
1.72	5.46	0.849	0.293	0.347	0.90	1.0-2.1
2.12	6.74	1.18	0.260	0.310	0.90	0.2-0.4
2.50	7.95	1.50	0.240	0.287	0.90	0.1-0.3
2.92	9.30	1.84	0.229	0.275	0.90	0.1-0.5
3.45	11.0	2.35	0.211	0.255	0.94	0.1-0.7
3.92	12.5	2.82	0.200	0.243	0.91	0.1-0.8

*At molecular beam source, calculated from pressure and flowrate.

** $t_1 = \int dx/v$, integrated over the irradiated section of the flow tube.

†Represents range covered by data at each pressure, not specific data points.

(Section II-E) are parametric in the g-value for atomic oxygen, a value of g_0 must be selected before the theoretical response can be calculated. Two values were chosen for initial comparison.

a) $g_0 = 24$. This value represents an approximate upper limit for g_0 . I.e., it was assumed (Section II-B-1) that 3.2 ion pairs are produced per heV, with O_2^+ and O^+ in the ratio 0.83:0.17. If all ions are produced in their ground states, the minimum energy required for ionization (per heV) is:

$$(3.2) \times \{0.83(12.21) + 0.17(18.73)\} = 42.6 \text{ eV}$$

Therefore, a maximum of 57.4 eV/heV is available for dissociation, and using 5.12 eV for the O_2 dissociation energy,¹⁸ the maximum direct O-atom production/heV is:

$$2 \times (57.4/5.12) = 22.4 \text{ atoms/heV}$$

Adding the contribution from dissociative ionization ($g_{0+} = 0.5$) brings g_0 to 22.9. $g_0 = 24$ is used as a conservative value, allowing for some uncertainty in the cracking fraction.*

b) $g_0 = 7.5$. This value is the estimate for g_0 obtained by Willis et al.⁴⁰ following much the same line of reasoning used in the above calculation. Their result is lower because various excitation processes are included, and dissociation is assumed to occur via dissociative transitions to the $^3\Sigma_g^+$ and $^3\Sigma_g^-$ states, requiring an average energy of 9.0 eV. The $g(0)_{\text{eff}}$ for the simplified model:

* Reported values vary from 0.07 to 0.17.^{17,40}

$$g(0)_{\text{eff}} = g_0 + g_{0+} + 2g_{e-} = g_0 + 6.9$$

(Section II-E) that results with $g_0 = 7.5$ is 14.4, in reasonable agreement with the reported values for $G(O_3)$ (see Table 1) if it is assumed that each O-atom produces one molecule of ozone.

2. Theoretical System Response

Figure 15 shows the variation of $[O]$ and $[O_3]$ with system pressure (see Table 6 for corresponding flowrates and irradiation times) predicted with these g_0 values at $E_d = 2.5 \times 10^{12}$ heV/cm^3 . Also shown are the corresponding experimental results, taken from Figs. 13 and 14. (The data were extrapolated to the selected E_d value where necessary.) The measured O-atom concentration passes through a sharp maximum at $p_s = 2.5$ Torr. Values for the simple model with $g_0 = 24$ (not shown) can be obtained by multiplying the values for $g_0 = 7.5$ (curves labelled A) by the ratio of the resulting $g(0)_{\text{eff}}$, $(24 + 6.9)/(7.5 + 6.9) = 2.14$, since in the simple model both $[O]$ and $[O_3]$ are directly proportional to $g(0)_{\text{eff}}$.

The predicted variation of $[O]$ and $[O_3]$ with E_d under constant flow conditions ($p_s = 3.45$ Torr, $Q_1 = 2.35$ $\text{std cm}^3/\text{sec}$) is shown in Figs. 16 and 17 using $g_0 = 5$ (best fit to $[O]$ data, simple model).

3. Evaluation

As discussed in Chapter II, the first criterion for an acceptable theoretical model is that it adequately reflect all known physical processes. The model should also be capable of predicting within the range of experimental error* the magnitudes of $[O]$ and $[O_3]$ simultaneously

*Validity of the data is discussed in Section IV-C.

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Fig. 15. Measured atomic oxygen concentrations (top) and ozone concentrations (bottom) vs system pressure for $E_d = 2.5 \times 10^{12}$ eV/cm³. The curves are the calculated theoretical system response. Curves A: Simple model, $g_0 = 7.5$ ($g(O)_{eff} = 14.4$); Curves B: Full model, $g_0 = 24$; Curves C: Full model, $g_0 = 7.5$.

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Fig. 16. Comparison of the measured E_d - dependence of the atomic oxygen concentration with theoretical predictions for $p_c = 3.45$ Torr, $g_0 = 5$ [$g(O)_{eff} = 11.9$, best Simple-Model-fit to $[O]$ at this pressure].

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Fig. 17. Comparison of the measured E_d - dependence of the ozone concentration with theoretical predictions for $p_s = 3.45 \text{ Torr}$, $g_0 = 5$.

for any combination of system parameters (flowrate, pressure, energy deposited, etc.), since both these concentrations are measured and available for comparison. The calculation of the theoretical concentrations is dependent on the g -value for atomic oxygen, and g_0 can be varied to produce a reasonable fit to the data. However, since g_0 is an elementary physical quantity, the model is subjected to the additional constraints that g_0 be a constant in the range [0.5,24] atoms/heV (c.f. Section IV-B-1).

The simple model appears to give a better prediction than the complete model of some aspects of the measured system behavior (as for example in Fig. 16). However, in constructing the simple model, all loss processes except atomic oxygen wall recombination and the primary ozone formation reaction (reaction N-1, Table 2) were neglected, and it was assumed that two oxygen atoms were formed from the (instantaneous) neutralization of every ion pair. These approximations will tend to overestimate both $[O]$ and $[O_3]$, and the results of this model represent an upper limit for the theoretical concentrations of both species. (That is: an upper limit for any model which considers only reactions among the ten species listed in Section II-C.) In going to the full model, the calculated concentrations are reduced by up to 75% within the range of system parameters considered. This discrepancy between the result of the two models indicates that one or more of the assumptions made in the simple model is invalid; that, in fact, one cannot simply neglect all of the loss processes.

The simple model, therefore, fails to meet the first criterion (does not adequately reflect all known physical processes), and in fact cannot satisfy any of the cited requirements. Although a single g_0 -value ($g_0 = 5$) predicts the variation of $[O]$ with E_d (Fig. 16), no single g_0 value predicts the observed behavior of $[O]$ with system pressure (Fig. 15, curve A, top). Similarly, while $[O]$ vs E_d data can be matched fairly well at a given pressure with a single g_0 -value, the corresponding theoretical ozone concentrations are much too low (see Fig. 17). Even with $g_0 = 24$ [$g(0)_{\text{eff}} = 30.9$] the theoretical values of $[O_3]$ remain 30-50% too low, while for this g_0 value the calculated $[O]$ values are too high by factors of 2-5 over the pressure range considered.

The full model is as comprehensive as possible, but gives even less satisfactory agreement with the experimental results. With the maximum g_0 value ($g_0 = 24$) the calculated magnitudes of both $[O]$ and $[O_3]$ are still too low by as much as a factor of 2, and the ozone concentration by an approximately constant factor of 3 (Fig. 15, curve B). Furthermore, although the functional dependence of the $[O_3]$ vs E_d and $[O_3]$ vs p_s curves given by this model are in reasonable agreement with the measured results, neither the observed linear dependence of $[O]$ on E_d nor the apparent maximum at 2.5 Torr in the $[O]$ vs p_s curve is predicted.

The performance of both models is summarized in Table 7, and more briefly in the observation that neither meets the cited requirements. Clearly some explanation of the data is required beyond that obtainable from previously proposed chemical mechanisms.

Table 7. Evaluation of theoretical models.

	Simple Model		Full Model	
	Yes*	No	Yes*	No
Reflects known physical processes		X	X	
Predicts measured magnitudes of:				
atomic oxygen concentration	X**			X
ozone concentration		X		X
Predicts functional dependence of:				
[O] vs E_d , constant p_s	X			X
[O ₃] vs E_d , constant p_s		X	X	
[O] vs p_s , constant E_d		X		X
[O ₃] vs p_s , constant E_d		X	X	

* All judgements are subject to the conditions that g_0 be ≤ 24 . A "yes" indicates that performance is considered to be adequate, not necessarily irreproachable.

** Only with variable g_0 .

C. Validity of Data

Before any further conclusions regarding the theory can be drawn, one must explore the possibility that the substantial discrepancies between the measured concentrations (particularly the high ozone concentrations) and those predicted by the models may be the result of systematic errors in data acquisition. Errors originating in each of the three main subsystems of the experimental apparatus (c.f. Chapter III) will be examined with regard to: (a) sources of error and quantities affected; (b) probable direction (e.g., effect on end results); and (c) probable magnitude.

1. Production and Measurement of Proton Beam

a. Accelerator. Although the instability of the proton beam is potentially responsible for errors in several other systems, the only measurement directly involved with the accelerator is that of the proton energy. No calibration of proton energy was made during this experiment, but previous calibrations indicate that the meter reading can be expected to be within 10%, reading low if anything. The proton energy determines the energy deposition in the oxygen through the energy dependence of the stopping power. If the meter reading were 5-10% low, the calculated E_d values would be too high by 3-6%, tending to increase the apparent g_0 and $G(O_3)$.

b. Proton Current Measurement. The calculated energy deposition E_d is directly proportional to the proton current, so that any errors in the proton current measurement are propagated directly. There are three distinct sources of possible error in this system: (i) statistical uncertainty in the countrate; (ii) uncertainty in the calibration and

(iii) correction for the countrate decrease with increasing oxygen pressure.

The statistical uncertainty of course depends on the countrate, and is not constant over any set of data. Because the countrate decreases with increasing pressure (for constant current) statistical errors will be largest for high pressure, low E_d data, and conversely. Assuming that the uncertainty is proportional to the square root of the countrate and using $\tau = 10$ secs (ratemeter time constant) the range of error is from $\sim 1\%$ ($p_s = 1.72$ Torr, $E_d = 1.42 \times 10^{13}$ heV/cm³) to $\sim 18\%$ ($p_s = 3.92$ Torr, $E_d = 1.37 \times 10^{12}$ heV/cm³).

An estimate of the uncertainty in the ratemeter calibration can be obtained from Fig. 9 (Section III-C-2a), and errors from this source are of the order $\pm 8\%$.

The countrate correction (Section III-C-2b) presents somewhat greater difficulties. Although the measured X-ray yield decrease as a function of proton energy (Fig. 10) is quite reproducible and appears reliable, the calculated proton energy loss (Appendix F) used to correlate the measured yield decrease with oxygen pressure depends on the proton energy measurement. Errors related to the proton energy in this calculation are of opposite sign and of approximately the same magnitude as those discussed in Section IV-C-1a, so that the effects tend to cancel. The calculated curve in Fig. 11 should, therefore, predict the minimum countrate decrease within a few per cent. (I.e., both the energy loss and the yield decrease are physically unavoidable processes, and the calculations are based on experimentally well established quantities.) The fact remains, however, that the direct measurements

of this correction (such as they are) do not agree particularly well with the calculated curve. It is assumed that some of the discrepancy can be attributed to the difficulty involved in this particular measurement, and that the total uncertainty in this correction (presumably resulting from accumulated errors in the calculation and processes otherwise unaccounted for) is of the order of 10%.

2. Oxygen Flow System

The pertinent quantities measured in this system are the pressure, flowrate and physical dimensions of the flow system. The pressure ($[O_2]$) directly determines $[O]$ and $[O_3]$ (see Section IV-A), and all of the above quantities are involved in the determination of E_d .

The Wallace-Tiernan gauge used in the measurement of p_s had been calibrated previously against a precision mercury manometer, and was found to be accurate (above ~1 Torr) to within the precision with which it could be read (approximately $\pm 1\%$). Similarly, the flowmeter reading and the physical dimensions are accurate to the limitations of the respective scales, and although no estimate of the accuracy of the flowmeter calibration was available, the probable uncertainty in these measurements is of the order of a few per cent or less.

3. Analysis of Radiolysis Products

Errors arising in this system can be divided into three categories: those affecting both $[O]$ and $[O_3]$ equally, and those affecting either $[O]$ or $[O_3]$ selectively.

a. Errors Affecting both $[O]$ and $[O_3]$. The first category would include, for example, (linear) calibration errors in the instruments (chart recorder, lock-in amplifier, oscillator, etc). Such instrument

errors were avoided as much as possible by the appropriate calibration procedures, and their importance minimized by the use of signal ratios rather than absolute signal levels.

Another effect which applies equally to $[O]$ and $[O_3]$ is that of mismatched time constants (c.f. Section III-C-2a). The primary measurement in the determination of the concentration vs E_d data is the simultaneous measurement of the mass spectrometer signal, via the lock-in amplifier, and the countrate. Both these signals are filtered before being recorded, and "mismatched time constants" refers to the fact that the time constants of the filtering circuits, although nominally equal, are not in fact identical. The mismatching would have no effect if the signals were stable; however, since both are directly related to the magnitude of the proton beam (very unstable), a significant scattering of the data results. The errors so introduced can be in either direction, depending on whether the signal levels of a given reading were approached from above or below. The magnitude of such errors is assumed to be approximately equal to that encountered in the ratemeter calibration, $\pm 8\%$.

b. Atomic Oxygen Measurement. Errors specific to the atomic oxygen measurement can originate in the initial calibration, in the procedures for measuring small concentrations (by operating the ionizer at reduced electron energy, see Section III-C-2b), in uncertainties in the mass spectrometer and lock-in amplifier settings, and to a lesser extent in the small correction for wall recombination in the molecular beam source. The uncertainty in the initial calibration (large O-atom concentrations) is assumed to be $\pm 5\%$ (Fig. 7).

The small O-atom concentration procedure requires measurement of the electron energy in the mass spectrometer ionizer, which introduces an additional possible source of error. However, the importance of this measurement is minimized by observing both S_{16} and S_{32} during every O-atom measurement (before increasing the electron energy again), and putting the absolute energy dependence in the slowly varying function $\{S_{32}(E)/S_{32}(E - \Delta)\}$. A change in electron energy of 0.1 eV (at 17 eV) results in a change in this function of less than 1%, as opposed to ~10-15% in the $(S_{32}/S_{32,max})$ curve (Fig. 8) for example. No estimate is available for the errors introduced by the assumption that the normalized S_{16} and S_{32} vs electron energy curves are identical, although one would expect that any such errors would tend to cause over-measurement (observed value higher than actual value) as a result of the slightly lower binding energy of the outermost electron in the O_2 molecule.

It is assumed that uncertainties in the various control settings (phase, center-mass, resolution) are reflected in the reproducibility of signals under constant source conditions, approximately $\pm 5\%$. The overall uncertainty in the atomic oxygen measurement is considered to be of the order $\pm(10-15)\%$, with some possible bias toward over-measurement (reported values too high) as observed above.

c. Ozone Measurement. There are three primary sources of possible error in the ozone measurement: (i) the mass spectrometer control settings; (ii) the (assumed) calibration, and (iii) the cracking fraction.

The spectrometer and lock-in amplifier settings present greater difficulties in the ozone measurement than in that of atomic oxygen. For the O-atom measurement, the phase and center-mass settings can be

adjusted to maximize the large stable mass 16 signal from O_2 cracking. However, for the ozone measurement, such adjustments must be made directly on the product signal during irradiation. The instability of this signal (directly related to the instability of the proton beam, see Fig. 12) presents substantial problems when attempting to locate a relative maximum (adjustment of center-mass control). The instability combined with the relatively small magnitude (5-20 μV) of the signal results in some difficulty in locating the proper phase setting (null), particularly since arcing in the accelerator often produced spurious signal transients observable in the μV range of the lock-in amplifier. The phase setting is not as critical as the center-mass, since the only phase difference between O_2 and O_3 is that resulting from time-of-flight differences over the relatively short quadrupole section of the spectrometer itself. Errors in either of these settings (phase or center-mass) will cause the signal to be under-measured; i.e., the observed signal would be lower than it should be, possibly by as much as 15-20%, although a great deal of effort was spent in tuning and re-tuning during the course of the ozone measurements.

The mass spectrometer was not calibrated specifically for ozone, and it was assumed that the calibration was similar to that for atomic oxygen. The measured result for atomic oxygen, $\alpha_{16}^{32} = 1$ (Fig. 7), implies that the observed signal ratio $\{S_{16}/S_{32}(1 + \gamma_{16}^{32})\}$ is equal to the neutral atom density ratio in the ionizer: $x_0\}_{sp} \equiv (n_0/n_{O_2})$; or in other words that the two neutrals O and O_2 were ionized in the same ion-to-neutral proportion (O_2 ions including fractionated O^+) and that the resulting ions produced the same signal output per ion, regardless of the identity

of the ion. Since ozone is also one of the oxygen species, it was assumed that the above implications could be extended to include O_3 , and that $\alpha_{32}^{48} = 1$. This assumption would be invalid if ozone were preferentially ionized, for example, or if the O_3^+ ions produced unusually large numbers of electrons in the first stage of the electron multiplier.

The cracking fractions used in the ozone calculations (Section III-C-1c) were taken from the literature rather than being measured with the present equipment, and a certain amount of error could be expected as a consequence. However, the measurements cited were made at an electron energy of 60 eV, which is comparable to the values used in this experiment, and it may be noted that the observed cracking fraction for O_2 (Fig. 8) agrees fairly well with the values cited in the literature (e.g., Section III-B-1).

Recalling that the reported ozone concentrations appear to be anomalously high, one is particularly interested in the possibility of systematic errors tending to over-measure the ozone signals. As indicated, errors arising from uncertainties in the control settings are in the opposite direction. The same is probably true for errors in the assumed cracking fraction, since the electron energy, while of the order of 60 eV, was in general slightly higher (65-75 eV). Also, the measured O_2 cracking fraction, while again comparable to those from the literature, tended to be slightly higher, so that use of the cited cracking fractions for ozone would probably result in an under-estimate, if anything. The direction of any errors from the assumed calibration ($\alpha_{32}^{48} = 1$) is not clear, but there is no reason at present to believe that the possibilities mentioned are in fact true. On the contrary, the quantities of ozone

observed during the discharge experiments (calibration for atomic oxygen) were substantially lower than could be explained by the simple model, as was to be expected. (The simple model is that of Section II-E, with different source and boundary conditions. The low ozone level in discharge systems is assumed to result from the generation of large quantities of electronically excited O_2 molecules, see for example Kaufman and Kelso.²³)

The reported ozone concentrations, then, are subject to potentially large errors, but in general it appears that the bulk of such errors are in the direction of under-measurement. The overall error limits (maximum) on this measurement are considered to be of the order +25%, -10%.

Another effect, while not precisely a measurement error, could lead to misinterpretation of the data if sufficiently large. The relatively large volume of stagnant gas in the proton collector is under constant irradiation while the beam flag is open. Under these conditions the concentrations of O and O_3 within the collector build up to their steady state values and diffuse out into the main reaction stream, potentially resulting in a true increase in the concentrations (primarily $[O_3]$) at the molecular beam source. However, conservative calculations indicate an $[O_3]$ increase from this effect of $<0.1\%$.^{2,41}

D. A Modified Chemical Model

The high ozone concentrations observed cannot be explained by pre-existing chemical models, nor by systematic errors in the measurement. These facts suggest the existence of an additional step (or steps) in the mechanism. Some of the desired characteristics of such a step can be inferred from the observed discrepancies between

the data and the model calculations.

The primary consideration is that ozone should be produced very efficiently. It can be seen in Fig. 14 that the ratio of $[O_3]:E_d$ (related to $G(O_3)$) is in the range 20-40 molecules/heV, or in other words that the energy required to produce one ozone molecule is in the range 2.5-5.0 eV. Going back to the discussion of the maximum g_0 value (Section IV-B-1) it is clear that mechanisms requiring exclusively atomic oxygen as a precursor to ozone will require a minimum of 4 eV/molecule (maximum $g_0 \sim 24$), and such mechanisms are, therefore, energetically incapable of predicting the bulk of the ozone data. Also, the ratio $[O_3]:[O]$ in such systems is determined primarily by the rate constant k_{N1} ,

and the elapsed reaction time. These two quantities are quite reliable, and the fact that this ratio (apart from the absolute magnitudes of the concentrations) is substantially higher than that predicted by the models is another indication that ozone is apparently being produced in some more efficient way than via reaction N1.

One simple possibility is to postulate an (unspecified) excited state O_2^* , produced directly by the irradiation, which undergoes the subsequent reaction:

This reaction has been postulated by others^{9,17} but has not been discussed in detail. If the contribution to $[O_3]$ from such a reaction

were comparable to or greater than that from reaction (N-1), the resulting $[O_3]:[O]$ ratio would clearly increase. Also, the energetics involved are somewhat more favorable, since reaction (N-*) requires an excitation energy of $\sim 4 \text{ eV}^{18}$ (for a potential maximum of two ozone molecules per O_2^*) as opposed to 5.12 eV for direct O_2 dissociation,¹⁸ or $\sim 9 \text{ eV}$ for dissociative transitions to an unbound $O_2(^2\Sigma_u^+)$ state.⁴⁰

Sample calculations utilizing the simple model with this modification were carried out at $E_d = 2.5 \times 10^{12} \text{ eV/cm}^3$. Three unknown parameters are required for such calculations: g_0 , $g_{O_2^*}$ and k^* , and the rate equations are:

$$\frac{d[O]}{dt} = (g_0 + 6.9) \dot{E}_d - k_{N1}[O][O_2]^2 - k_{N3}[O] + k^*[O_2^*][O_2]$$

$$\frac{d[O_2^*]}{dt} = g_{O_2^*} \dot{E}_d - k^*[O_2^*][O_2]$$

$$\frac{d[O_3]}{dt} = k_{N1}[O][O_2]^2 + k^*[O_2^*][O_2]$$

The $[O_3]:[O]$ ratio increases as the term involving $g_{O_2^*}$ increases relative to g_0 . However, $g_{O_2^*}$ cannot increase indefinitely, since the energetics require an upper limit similar to that calculated previously for g_0 . The maximum $[O_3]:[O]$ ratio occurs with the minimum g_0 value. For this it is assumed that all direct production occurs via dissociative Schumann-Runge transitions, and that the ratio of dissociation to ionization is approximately the same as the ratio of the cross sections for these two processes. Using cross sections available in the literature^{5,31} this ratio is approximately 0.1. The minimum g_0 value

is, therefore, taken as $0.1 \times 2 \times 3.2 = 0.6$ requiring $(0.6)(9 \text{ eV}) = 5.4 \text{ eV/heV}$ and the energy remaining/heV is slightly over 50 eV (i.e., $100 - 5.4 - 42.6$). Each O_2^* must have on the order of 4 eV, so that the maximum $g_{O_2^*}$ is roughly 12.5.

The $[O_3]:[O]$ ratio also depends on the rate constant k^* . An estimate of the corresponding ground state rate constant (i.e., for $O_2 + O_2 \rightarrow O_3 + O$) is available in the literature.¹⁸ If it is assumed that the energy carried by the O_2^* molecule affects the rate constant only by reducing the activation energy, the resulting rate constant is of the order $1-10 \text{ (Torr-sec)}^{-1}$.

The results of the modified simple model using $k^* = 10 \text{ (Torr-sec)}^{-1}$ ($\sim 3 \times 10^{-16} \text{ cm}^3/\text{molecule-sec}$), $g_0 = 1.1$ (contribution from direct dissociation plus that from dissociative ionization $0.6 + 0.5$); $g(O)_{\text{eff}} = 8.0$, and $g_{O_2^*} = 12.5$ are shown in Fig. 18. While some improvement in the $[O_3]:[O]$ ratio has been obtained, the agreement is not particularly good. The ratio may be improved if the full model is used, since the dominant loss mechanism is atomic recombination (reaction N-2) as opposed to ozone decomposition (reaction N-4). However, it is to be expected that the result of full model calculations would be to lower both concentrations, as before, so that while the agreement with the $[O]$ data may be improved, the opposite is true of the $[O_3]$ data. It was felt that no particular advantages would be gained by extensive computer runs of the full model with this modification.

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Fig. 18. Comparison of modified simple model calculations with experimental results. Upper curve and data, ozone concentration; lower curve and data, atomic oxygen concentration. $E_d = 2.5 \times 10^{12}$ eV/cm³; $g_0 = 1.1$, $g(0)_{\text{eff}} = 8.0$; $g_* = 12.5$; $k^* = 10$ (Torr-sec)⁻¹.

The identity of the hypothetical state O_2^* cannot be determined, although it could be postulated that most of the energy is in vibrational excitation. A high vibrational state could carry the requisite amount of energy ($v \sim 21$), and an $O_2 - O_2^*$ complex would be expected to form at least one atom of atomic oxygen (dissociating along the vibrationally excited bond) even though the bond does not have enough energy for complete dissociation to two atoms and one O_2 molecule.

The postulated vibrationally excited state O_2^* could be formed in several possible ways. Interactions between protons and binding electrons with less energy transfer than that required for ionization or allowed electronic transitions are one possibility. Also, some of the molecules resulting from ion recombination may be in vibrationally excited states, and vibrational excitation of the O_2^- ion, for example, can occur at any energy above zero.³⁷ The first possibility carries the objection that energy transferred to a binding electron is not readily transformed into nuclear motion within the molecule (vibrational excitation). The last two possibilities mentioned limit the production of vibrationally excited species to quantities comparable to the ionization, which alone could not account for the ozone data.

It is concluded that the proposed mechanism modification is probably partially responsible for the very high ozone levels observed. The calculated $[O]$ and $[O_3]$ are both increased by inclusion of this modification, and the calculated ratio $[O_3]:[O]$ increased as well. All these changes are in the correct direction, as indicated by comparison of the data with the full model calculation. Furthermore, the term

in the rate equation resulting from the proposed modification is proportional to the system pressure (i.e., to $[O_2]$). Since this term and that from reaction (N-1) are postulated to be of comparable magnitudes at the pressures used in this experiment (1-5 Torr), one could expect the latter term ($T_{N-1}, \alpha p_5^2$) to dominate at the higher pressures used by other investigators.

However, this modification does not provide a full explanation. Assuming that such a reaction does occur, it seems unlikely that sufficient quantities of O_2^* can be produced to account for the observed ozone yields, even allowing for the large uncertainties in the data. Also, excited O_2 molecules generally decompose ozone rapidly. This effect has been observed for the two stable electronically excited states ($^1\Delta_g$ and $^1\Sigma_g^+$ 14,26,38) and is expected for molecules in high vibrational states.¹⁸

In looking for other explanations for the data, it was found that anomalously high ozone levels at low pressures were anticipated by Willis et al.⁴⁰ as a result of the high yields observed by these investigators in other radiolysis systems. Although such behavior was not found in their investigation of the oxygen system, the lowest pressure they used was 30 Torr, substantially above the pressure range in the present work. The high yields they did observe were attributed to acceleration of secondary electrons in transient electric fields, assumed to result from the very high dose rates and consequently high charge density in their apparatus. High dose rates are apparently considered to be of the order 10^{26} - 10^{27} eV/gm sec.^{3,40} as opposed to "low" dose rates used by other workers³⁴ of $\sim 10^{16}$ eV/gm-sec. On this basis, the

dose rates in the present experiment (in the range $[0.2-20] \times 10^{20}$ eV/gm-sec) are low-to-intermediate. The present results are, therefore, in support of the observations of Willis et al., but not of their interpretation. It may be noted that their explanation is apparently ad hoc, without supporting experiments to indicate the absence of this low pressure effect at low dose rates.

No further specific modifications of the model are proposed at this time, since greater complexity, either in the number of constants to be determined or in the number of species postulated, is not warranted by the present data. The very efficient ozone production reported here remains an anomaly, awaiting further investigation and clarification.

V. EXPERIMENTAL LIMITATIONS AND SUGGESTED IMPROVEMENTS

Since one of the objectives in this project was the development of the apparatus, several suggestions for the improvement of the system and procedures are discussed in the following.

Assuming that most of the major equipment remains unchanged (i.e., that any other radiolysis experiments are carried out with the same energy source) one of the most important measures to be taken is to improve the proton beam stabilization. Good beam stability would not only increase the reliability of the measurements (see Sections IV-C-3 and III-C-2a, and Fig. 12), but also substantially reduce the time required for each measurement. Beam stability improvement would require that the accelerator be extensively up-graded, and once this has been completed the proton energy calibration should be checked.

The system chosen for study is important. Calibration for each species to be observed is desirable, and if possible should be devised so that it can be repeated periodically. Any active species (e.g., a free radical such as atomic oxygen in the present system) will generally occur in very low concentrations, and will be very difficult to observe if its mass-to-charge ratio is the same as that of any large background signal. If this cannot be avoided, and if unusual measures must be taken to observe the active species (such as lowering the electron energy for O-atom measurements), calibration measurements should, if possible, be made under the same conditions as the actual measurements.

Returning the center-mass control at each mass peak during each run can be avoided by pre-setting the required voltages, accessible through individual switches. This has been done in other systems, and should be done here.¹⁹

The flow system operation should be modified so that the parameters (e.g., pressure, reaction time) are varied individually. Interpretation of such data would be much more straight-forward than that of the data shown in Fig. 15, for example, in which the reaction time increases simultaneously with decreasing pressure. Measurements varying the pressure at constant flowrate can be made by throttling the main pumping line.

The differential pumping system separating the main reaction chamber from the accelerator beam port seems to be the most workable system for maintaining the necessary pressure difference, although it is possible that some design could be devised to ease the alignment problems.

The proton current detection system should be modified to allow more efficient detection at higher system pressures, if possible. Careful selection of the target material and detector should be made to minimize signal variation with proton energy.

VI. CONCLUSION

The apparatus developed was found to provide a workable method for on-line radiolysis measurements, although severe limitations on the range of useable parameters (system pressure, total energy deposition) remain.

The measured concentrations of the two radiolysis products ozone and atomic oxygen cannot be predicted by pre-existing chemical models. The major discrepancy is between the high measured ozone concentrations and the substantially lower calculated values. This discrepancy cannot be completely explained by systematic errors in the measurements, although the experimental uncertainties are large.

Anomalously high ozone concentrations at low pressures were anticipated by Willis et al.⁴⁰ Although these investigators did not observe the effect, the lowest pressure they considered was a factor of 6 above the highest pressure used in the present work. The high radiolysis yields they observed in other systems at low pressures were explained as a high dose rate effect. This explanation does not appear applicable to the present experiment.

A proposed modification to the chemical model involving ozone production directly from the reaction of an excited state O_2^* is considered. This modification has several appropriate characteristics (increases the calculated $[O_3]$, $[O]$, and the ratio $[O_3]:[O]$; decreases in importance with increasing system pressure), but does not provide a completely explanation of the data.

The high ozone yields measured in the present study have not been observed by earlier workers, but since the experimental conditions

(low pressure, on-line measurement of both $[O]$ and $[O_3]$) cover a range not previously investigated, the results are not in direct contradiction to other measurements. Although the oxygen system has been investigated more exhaustively than any other radiolysis system, it is still not fully understood.

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APPENDIX A. PRESSURE-VELOCITY CALCULATION

The pressure drop in the reaction chamber (see Section III-B-2) is computed from the formula

$$p^2(x) - p_s^2 = G^2 \frac{RT}{M} f \frac{(L - x)}{R_H}$$

in which the logarithmic correction term for adiabatic compressible flow $[+2G^2(RT/M) \ln(p(x)/p_s)]$ has been neglected. In this expression:

$p(x)$ = pressure at x (measured from the O_2 inlet), [Torr].

p_s = pressure at the end of the irradiated section, [Torr].

G = mass flux = $\rho \bar{v}$, $[gm/cm^2 \cdot sec]$,

$$= Q_1 \left\{ \frac{std \text{ cm}^3}{sec} \right\} \left\{ \frac{10^{-3} \text{ lit}}{cm^3} \right\} \left\{ \frac{1 \text{ mole}}{22.415 \text{ std lit}} \right\} \left\{ \frac{M \text{ gm}}{\text{mole}} \right\} \left\{ \frac{4}{\pi D^2 \text{ cm}^2} \right\}$$

$$= 1.1817 (Q_1/D^2) [gmO_2/cm^2 \cdot sec]$$

R = gas constant = $8.314_3 \cdot 10^7$ erg/mole °K

T = temperature, [°K]

M = molecular weight of gas, [gm/mole]

f = Fanning friction factor, = $16/Re$ for $Re \equiv (DG/\mu) < 2100$ (easily satisfied by conditions in present system). [Dimensionless].

R_H = Hydraulic radius = $(D/4)$ for circular tubes, [cm].

L = length of irradiated tube, [cm].

D = diameter of flow tube, [cm].

μ = viscosity of flowing gas, [poise = gm/cm·sec]

*1 atm, 0°C.

ρ = gas density, $[\text{gm}/\text{cm}^3]$.

Data used for O_2 in the calculation are:

$M = 32.0 \text{ gm/mole}$

$\mu = 2.02 \times 10^{-2} \text{ cp (at } 300^\circ\text{K), calculated from}^{32}$

$$\frac{\mu}{\mu_0} = \frac{273.15 + C}{T + C} \left(\frac{T}{273.15} \right)^{3/2}$$

$\mu_0 = 0.0187 \text{ cp}$

$C = 138$ for T in the range $[290, 460]^\circ\text{K}$

$Q_1 = \text{flowrate} = Q_0 \left(\frac{\text{cm}^3}{\text{min}} \right) \left(\frac{273.15}{294.3} \right) \left(\frac{1 \text{ min}}{60 \text{ sec}} \right), [\text{std cm}^3/\text{sec}]$

$Q_0 = \text{measured flowrate, obtained from flow meter reading and calibration curve, } [\text{cm}^3/\text{min at } 70^\circ\text{F, 1 atm}].$

The velocity is determined from the pressure and flowrate using

$$\bar{v} = \frac{G}{\rho} = \frac{G(p)}{p(\rho)} = \frac{G}{p} \left\{ \frac{1 \text{ cm}^3 \cdot \text{torr} \times 6.025 \times 10^{23} \text{ molecules} \times 1 \text{ mole}}{3.54 \times 10^{16} \text{ molecules} \times 1 \text{ mole} \times 32 \text{ gmO}_2} \right\}$$

The pressure and velocity in the second and third sections of the flow system are determined in the same manner, using the appropriate dimensions and flowrate. The latter is given by $Q_2 = Q_1 - Q_c$, where Q_c is the flow loss to the set of pressure-reducing collimators (see Section III-B-2 and Appendix C).

APPENDIX B. PROTON BEAM WINDOWS

At first glance a thin window would seem to be the obvious means of maintaining a pressure differential while allowing high energy protons to pass relatively unperturbed. However, upon closer examination this is found to be true only for an ideal thin window, and unfortunately none of the windows tested was found to meet adequately all of the requirements. The criteria defining acceptable performance are:

- 1) That the energy loss of the protons be small; and
- 2) that the window remain intact under experimental conditions.

The first of these is critical primarily because of the proton current detection system used. As discussed in Section III-C-2, the X-ray yield of the tantalum foil decreases rapidly with proton energy, an effect so pronounced as to limit the useable range of oxygen pressure. Any further reduction in the proton energy (by the window) will decrease the range of operation even further.

Large energy losses in the window also correspond to large angular deflections of the protons, which in turn result in a substantial reduction in beam current through losses to the walls of the reaction tube. These losses also result in non-uniformity of energy deposition over the length of the tube.

Minimum energy degradation in the window implies: (a) that the window material have low Z , since the linear energy deposition is proportional to Z^2 ; and (b) that the window be extremely thin.

The second criterion (window integrity) imposes the further restrictions: (c) that the window have reasonably high thermal conductivity and/or melting point (i.e., so that it will not melt), since

aside from radiation the only mechanism available for heat removal is conduction to the mounting bracket; (d) that the material be inert to attack by the active chemical species generated in the reaction tube (ozone and atomic oxygen); and (e) that the window be sufficiently strong to withstand pressure differences of the order of 10 Torr.

Among the most promising windows tested were:

aluminum ($Z = 13$, $\rho = 2.7 \text{ gm/cm}^3$, $m.p. = 660^\circ\text{C}$), thickness $\sim 1 \text{ mg/cm}^2$.

beryllium ($Z = 4$, $\rho = 1.85 \text{ gm/cm}^3$, $m.p. = 1280^\circ\text{C}$), thickness
 $0.8 - 2 \text{ mg/cm}^2$.

carbon* ($Z = 6$, $\rho = 1.6 \text{ gm/cm}^3$, $m.p. = 3550^\circ\text{C}$), 1.2 mg/cm^2 .

"Formvar" (assumed to be primarily hydrogen, $Z = 1$) $30 \text{ } \mu\text{g/cm}^2$.

All of the windows except the Formvar were too thick, i.e., resulted in unacceptable energy degradation of the protons. The Formvar windows seemed to work quite well as long as they lasted, but did not survive over 1-2 hr of irradiation. It might be expected that the energy deposition in such a window (very thin, low Z) would be very small, so that the lack of cooling would not be particularly critical. However, whether by melting, chemical attack, or physical radiation damage, they did in fact fail, and did so catastrophically.

All of the windows tested failed eventually. The metal foils failed gradually (developed pin holes), presumably as a result of localized radiation damage and melting. The carbon windows survived the longest, but were clearly being chemically attacked, and visible amounts of

*The courtesy of Pfizer, Inc. in supplying samples of their experimental pyrolytic graphite film is appreciated.

carbon were deposited on the walls of the reaction tube for some distance downstream of the window.

Even if these problems could be overcome with a more suitable combination of window material and thickness, one is still faced with the problems of first obtaining such a thin foil of the selected material, and then mounting the window and pumping the system down without rupturing it.

As a consequence of these observations, the search for a suitable proton window was abandoned in favor of the differential pumping system described in Appendix C.

APPENDIX C. REACTION CHAMBER-BEAM PORT DIFFERENTIAL PUMPING SYSTEM

A schematic of the system devised to maintain the pressure difference between the reaction tube and the Van de Graaff accelerator tube is shown in Fig. C-1. The two collimators are identical cylindrical channels of radius $a_c = 1.25$ mm, length $L_c = 10$ cm. The pump between the two stages is a mechanical pump (Welch, 1397), pumping speed $S_1 \sim 6$ liters/sec. The second chamber (following the second collimator channel) is pumped by a 4 in. oil diffusion pump, pumping speed $S_2 \sim 50$ lit/sec. The second chamber is separated from the beam tube proper (beam tube radius $a_T = 2.5$ cm, length $L_T = 5$ m) by an annular disk, aperture radius = 0.5 cm. The 6 in. oil diffusion pump on the accelerator tube has a pumping speed $S_3 \sim 250$ lit/sec.

Adequate operation of this system is defined by two criteria:

- (1) that the pressure rise in the accelerator tube be $\leq 10^{-6}$ Torr;
- and (2) that the flow through the first collimator be an acceptably small fraction of the total flow in the reaction chamber, $(Q_c/Q_1) \ll 1$.

It is assumed that Q_c is sufficiently small that the pressure drop between the pressure tap (measurement of p_s , see Section III-B-2) and the first collimator is negligible. (These two points are separated by a length of pyrex tube 1.2 cm I.D., 10 cm long.) The flowrate Q_c is then determined by the pressure p_s and the conductance of the first collimator:²⁰

$$Q_c = KQ^*F(p_s/p^*)$$

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Fig. C-1. Reaction tube-beam port differential pumping system.

where

$K = \text{Clausing Factor} = [1 + (3L_c/8a_c)]^{-1}$ (for either collimator).

$Q^* = \text{flowrate through an ideal orifice of radius } a_c = \frac{p_s a_c^2}{2} \sqrt{\frac{2\pi RT}{M}}$

$R = \text{Gas constant}$

$T = \text{temperature, } ^\circ K$

$M = \text{molecular weight of effusing gas, [gm/mole]}$ (Note that the expression for Q^* assumes $p_1 \ll p_s$).

$F(p_s/p^*)$ is given by the Fryer formula:^{8,20}

$$F(\theta) = \frac{1}{\theta} \left\{ \frac{\pi\theta}{4} + \left(1 - \frac{\pi}{4}\right) \ln(\theta + 1) + \frac{\pi}{128} \left[\frac{3}{2} \theta^2 + \theta^3 + 1 - (\theta^2 + 1)^{3/2} \right] \right\}$$

$$\theta = p_s/p^*$$

$p^* = \text{source pressure at which the mean free path is equal to the channel diameter,}$

$$= \frac{kT}{4\pi a_c \sigma^2} = \frac{4.19 \times 10^{-3}}{2a_c} \text{ (Torr}\cdot\text{cm)} \text{ for } O_2 \text{ at } 300^\circ K.$$

The pressure p_1 can be obtained by equating Q_c to the flowrate sustained by the pump S_1 :

$$Q_c = p_1 S_1 = K Q^* F(p_s/p^*)$$

The same method can be applied to the second collimator to give p_2 .

p_4 can also be obtained in a similar manner, except that one must use the Clausing factor for the combined conductance of the aperture at the end of the second chamber and the beam tube. This is given by:

$$K \approx \left\{ 1 + \frac{3}{8} \frac{L_T a_p^2}{a_T^3} \right\}^{-1}$$

if Q^* is defined by

$$Q^* = \frac{a_p^2}{2} (p_2 - p_4) \sqrt{\frac{2\pi RT}{M}}$$

a_p = radius of aperture.

For $p_s = 3.87$ Torr, $Q_1 = 2.806$ std cm^3/sec (this corresponds to a flowmeter setting of 10, which is near the top of the range of operating conditions), application of the foregoing formulas results in:

$$Q_c = 0.824 \text{ std cm}^3/\text{sec} \approx 30\% \text{ of } Q_1$$

$$p_1 = 0.115 \text{ Torr}; p_2 = 4.4_3 \times 10^{-5} \text{ Torr}$$

$$p_4 = 1.3_4 \times 10^{-6} \text{ Torr.}$$

APPENDIX D. CALIBRATION OF SPECTROMETER FOR ATOMIC OXYGEN

To calibrate the spectrometer system for any chosen chemical species, one must find some absolute measurement of the quantity of this gas being used to drive the system. For atomic oxygen, a convenient and accurate method of determining the concentration is a pseudotitration with NO_2 .^{21,22} The reaction

produces a glow via the subsequent reaction:

This glow is most intense when the flow of added NO_2 is one-half that of the atomic oxygen. For larger flows of NO_2 the light intensity decreases, and at the end point is sharply extinguished. Either point in the titration is definitive, and in this calibration the point of maximum intensity was chosen.

The NO_2 used is drawn from a cylinder of liquid NO_2 (N_2O_4) (Matheson, stated purity 99.5% min). The pressure in the NO_2 system is measured with a mercury manometer (with a layer of oil to protect the mercury from attack by the NO_2), and the flowrate with a calibrated ball float flowmeter (Matheson Dual Float R-2-15-AAA, Model 600). The flowmeter calibration and safety procedures followed in handling the NO_2 are discussed at the end of this appendix.

A schematic of the calibration system is shown in Fig. D-1. It is similar to the main experiment except for the NO_2 system and inlet ports, and the use of the microwave discharge unit (Raytheon

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Fig. D-1. Equipment schematic, calibration of mass spectrometer for atomic oxygen.

Model PGM-10X2, 85 watt output at 2450 ± 25 Hz) to supply energy for the generation of active species. The section of the flowtube at the position of the microwave discharge is quartz. (Pyrex tubes in the discharge can melt, thereby blowing a hole in the flow tube, losing the vacuum, and causing temporary cardiac arrest in the operator.)

The calibration proceeds as follows. The oxygen flow is initiated and allowed to stabilize, and the mass 32 and mass 16 (cracked O_2) signals are measured. The discharge is then started and the spectrometer measurements repeated. (The concentrations of atomic oxygen produced by the discharge are large enough that the resulting signal can be readily distinguished from that produced by cracking of O_2). The NO_2 titration is then carried out at each of the three ports, starting with the farthest downstream. A photodiode provides a convenient direct measure of the light intensity, and the point of maximum intensity (flow of $NO_2 = 1/2$ flow of atomic oxygen) is found from a plot of photodiode voltage vs flowmeter setting. The ratio of atomic oxygen to O_2 at each port then gives a profile of x_0 vs distance which can be extrapolated to the position of the molecular beam source.

An example of the light intensity vs NO_2 flow profiles and the resulting x_0 vs distance profile are shown in Fig. D-2. The solid point is the mass spectrometer measurement, corrected for wall recombination in the molecular beam source.

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Fig. D-2. (a) Top, photo-diode voltage (light intensity) vs NO₂ flowmeter reading. NO₂ system pressure = 57.2 Torr. (b) Bottom, mole fraction atomic oxygen vs position in flow tube. O₂ flowrate = 1.9 std cm³/sec. Inlet pressure = 3.06 Torr; tube I.D. = 1.1 cm.

Calibration of NO₂ Flowmeter

The NO₂ flowmeter is calibrated by weighing the total throughput in a measured time interval at constant flowrate. Since liquid NO₂ (N₂O₄) boils at 70°F and the vapor phase is a dissociating gas (2NO₂ ⇌ N₂O₄) of variable composition depending on p and T, the calibration is done in situ, under the experimental conditions in which the flowmeter is to be used.

A schematic of the flowmeter calibration system is shown in Fig. D-3. A typical calibration measurement proceeds as follows. The needle valve on the NO₂ (N₂O₄) cylinder and the flow control valve (Nupro Very Fine Metering Valve, Catalog #2S, Viton A Body Seal) at the outlet of the flowmeter are adjusted concurrently until the desired pressure and flow have been established in the main pumping line. The flow is then diverted for a measured length of time to a sealable pyrex tube (evacuated mass 62.125 gm). This tube is immersed in a dewar of liquid nitrogen so that the flow is maintained by the cryopumping action of the tube itself. The tube and accumulated NO₂ (N₂O₄) are then removed and weighed on a precision balance. For this step the tube must be allowed to warm up enough so that moisture no longer condenses on the outside, but since the boiling point is 70°F (p_{vap} = 1 atm and rising) excessive warming will cause the tube to explode (a particularly untidy situation since liquid NO₂ (N₂O₄) is highly corrosive and the vapor poisonous).

After weighing, the pyrex tube is reconnected to the vacuum apparatus and the NO₂ pumped out the main line. The LN trap in this

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Fig. D-3. NO_2 flowmeter calibration system.

line retains (and cryopumps) the NO_2 , and any non-condensing gases are removed by the mechanical pump.

At the end of each day's run the trap is heated and flushed with dry nitrogen. The effluent is bubbled through a solution of NaOH, dried, and then put through a column of acid absorbant ("Indicarb", Fisher Scientific Co.) before being vented to the atmosphere. The working area is routinely monitored for excessive levels of NO_2 (Unico 400 Precision Gas Detector).

Results of the calibration are shown in Fig. D-4.

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Fig. D-4. NO₂ flowmeter calibration curves. (Matheson dual float R-2-15-AAA, Model 600 flowmeter)

APPENDIX E. ATOMIC OXYGEN WALL RECOMBINATION IN THE MOLECULAR BEAM SOURCE

Consider a single channel of the molecular beam source of length L and radius a , through which pass ℓ particles/sec. If $n(x)$ is the number density at some point x along the channel, then the total number of particles within an incremental volume ($\pi a^2 dx$) is $(n(x) \pi a^2 dx)$. The number of wall collisions per second in dx (assuming an isotropic angular distribution) is: $(2\pi a dx)(n(x) \bar{v}/4)$, where $\bar{v}$ is the thermal velocity of the particle in question:

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}.$$

The wall collision frequency is therefore

$$\nu = \frac{(2\pi a dx)(n(x) \bar{v}/4)}{(\pi a^2 dx) n(x)} = \frac{\bar{v}}{2a}$$

independent of x , $n(x)$ and dx , so that the total number of wall collisions per particle in traversing the length L is $N_W = \nu t_L = (t_L \bar{v}/2a)$, where t_L is the transit time in seconds:

$$t_L = \int_0^L \frac{dx}{v(x)} = \frac{\pi a^2}{\ell} \int_0^L n(x) dx.$$

Here $v(x)$ is the average velocity in the x -direction ($\neq \bar{v}$). Assuming a linear number density profile

$$n(x) = \left(\frac{p_s}{kT}\right) \left(\frac{L-x}{L}\right)$$

where p_s is the driving pressure behind the molecular beam source; and setting

$$\lambda = \frac{4a^3 p_s}{3L} \sqrt{\frac{2\pi}{mkT}} \quad (\text{Knudsen flow})$$

one obtains:

$$N_w = \frac{3}{8} \left(\frac{L}{a}\right)^2 \quad \text{wall collisions/particle}$$

The wall recombination coefficient γ can be interpreted as the probability that an atom colliding with the wall will recombine. If n atoms enter the channel, the number that survive the first collision is $n(1 - \gamma)$; and after the second collision, the number surviving is $n(1 - \gamma)^2$. Therefore, after N_w collisions/particle, the number that remain is $n(1 - \gamma)^{N_w}$, the number lost $n - n(1 - \gamma)^{N_w}$, and the fraction that recombine is $\{1 - (1 - \gamma)^{N_w}\}$.

For the molecular beam source in the present system, $a = 0.00055$ cm, $L = 0.025$ cm, $N_w = 775$ collisions per particle, $\gamma \sim 10^{-4}$ (conservative), and $\{1 - (1 - \gamma)^{N_w}\} \sim 0.07$.

APPENDIX F. PRESSURE DEPENDENCE OF TANTALUM K X-RAY YIELD

The average energy loss of a charged particle traversing a stopping medium such as the gas in the reaction tube is determined by the stopping power of the target material; i.e., a mono-energetic beam of protons (energy E_i) will undergo average energy loss $\overline{\Delta E} = E_i - E_f$, with E_f determined from (ref. Section II-B-3):

$$\int_0^L N dx = - \int_{E_i}^{E_f} \frac{dE}{\epsilon(E)}$$

Here $\epsilon(E)$ = stopping power $\equiv -(1/N)(dE/dx)$, eV - cm².

N = number density of stopping material, atoms/cm³.

L = linear distance travelled through stopping medium, cm.

If the protons reaching the tantalum target were mono-energetic (energy E_f), or if the X-ray yield/proton (Y) of the tantalum were independent of proton energy, the observed count rate would be:

$$(CR) = Y|_{E_f}$$

In the general case, however, Y is a function of E (see Fig. 10).

and should be integrated over the proton energy distribution. Such an integration was done numerically, using a slightly modified form of Landau's "universal" energy loss distribution:²⁸

$$X(\omega) d\omega = \frac{1}{\sqrt{2\pi}} \exp\{-1/2[\omega + \exp(-\omega)]\} d\omega$$

(see Fig. F-1). In this expression ω is the reduced energy variable

$$\omega = \frac{\Delta E - \Delta E_D}{E_0 Q}$$

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Fig. F-1. Landau's "universal" energy loss distribution.

ΔE_p is the most probable energy loss, Q the number of collisions, and E_0 the minimum energy loss per collision. The most probable energy loss is given by:

$$\Delta E_p = E_0 Q \left\{ \log \left(2Q - 2 - \frac{1}{2Q - 1} \right) - C + \frac{2Q - 1}{(2Q - 2)(2Q - 1) - 1} \right\}$$

where $C = 0.577$ is Euler's constant.

Although the above expressions are derived using the classical Thomson cross section, the present calculation was carried out using the experimental total ionization cross section⁵ to determine Q ($Q = N\sigma_{tot}L$); and setting

$$\bar{\omega} \equiv \int_{-\infty}^{\infty} \omega X(\omega) d\omega = 1.27 \approx \frac{\overline{\Delta E} - \Delta E_p}{E_0 Q} ,$$

where $\overline{\Delta E}$ is obtained from the stopping power. (Note that $X(\omega)$ is a normalized distribution, $\int X(\omega) d\omega = 1$.)

These relationships are sufficient to determine $\omega(\Delta E)$. The count rate (CR) is then proportional to:

$$(CR) \propto \int_{-\infty}^{\infty} Y(\omega) X(\omega) d\omega .$$

Figure F-2 shows the energy distribution $X(E)$ and the yield distribution $X(E) Y(E)$, $E = E_i - \Delta E$ for a typical set of operating conditions $\{p_s = 3.45 \text{ Torr}, Q_i = 2.32 \text{ std cm}^3/\text{sec}, \text{ proton source} = \delta(0.9 \text{ MeV})\}$. $Y(E)$ for this curve is normalized to unity at $E = E_i = 0.9 \text{ MeV}$.

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Fig. F-2. Energy distribution and corresponding Ta K X-ray yield distribution for 0.9 MeV protons incident on oxygen in the reaction tube.

APPENDIX G. AVERAGE DISPERSION OF PROTON BEAM IN A PURE SCATTERING MEDIUM

Consider a semi-infinite medium made up of a scattering layer of thickness L followed by a pure absorber. A well collimated, mono-energetic beam of protons is incident on the scattering medium at the origin of a coordinate system (x_0, y_0, z_0) , travelling in the z_0 direction. For relatively small values of L , the angular distribution of the protons in the scattering medium will be strongly peaked about the incident direction, and there will be some radial displacement from the z_0 axis. The average value $\langle r^2 \rangle^{1/2}$ of this displacement is to be found as a function of L and the properties of the scattering medium.

The differential scattering (Rutherford) cross section is:¹⁵

$$\frac{d\sigma}{d\Omega} = \left(\frac{2ze^2}{pv} \right)^2 \frac{1}{\theta^4}, \quad \theta_{\min} < \theta < \theta_{\max}$$

$$\frac{d\sigma}{d\Omega} = 0 \quad \text{otherwise.}$$

Here θ = scattering angle, measured from the incident direction;

p = momentum of proton;

v = velocity of proton;

z = proton charge (≈ 1);

Z = atomic number of scattering material;

e = electronic charge;

$$\theta_{\min} \approx \left\{ \frac{ze^2}{pva} \right\} \quad (\text{classical});$$

$$\theta_{\max} = \frac{2.74}{A^{1/3}} \left(\frac{mc}{p} \right);$$

a = radius of scattering particles, $= 1.4 a_0 z^{-1/3}$;

a_0 = Bohr radius;

A = mass number of scattering particles;

m = electron mass

It is assumed that the proton energy remains constant over the range to be considered (pure scattering), so that the mean free path λ is constant and is given by:

$$\lambda = \frac{1}{N\sigma}$$

where N is the number density of scattering atoms and $\sigma = \int (d\sigma/d\Omega) d\Omega$.

It is also assumed that the scattering angles are small, $\sin\theta \sim \tan\theta \sim \theta$.

The scattering process is perhaps most easily visualized if one considers three separate coordinate systems, (see Fig. G-1). One of these is the fixed (x_0, y_0, z_0) system, with the origin at the point where the proton beam enters the scattering medium. The other two coordinate systems are not stationary, but have their origins at the location of the particular collision being considered. One of the two systems (x', y', z') is parallel to the (x_0, y_0, z_0) system, while the other (x^*, y^*, z^*) is rotated such that the z^* -axis is colinear with the velocity vector of the proton approaching the collision. E.g., consider a proton about to undergo its n^{th} collision. This collision will occur at some point P_n with coordinates $(x_0, y_0, z_0)_n$, and the origins of both the $(*)$ and $(')$ systems will be at P_n . The velocity vector of this proton $\vec{v}_n$ has some orientation (θ'_n, ϕ'_n) with respect to the (x', y', z') axes, so that the (x^*, y^*, z^*) axes are generated by a double rotation through (θ'_n, ϕ'_n) . The proton then scatters in some direction (γ^*, ϕ^*) and is assumed to travel a distance λ before its next collision at P_{n+1} .

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Fig. G-1. Coordinate systems for proton scattering analysis.

The spherical coordinates of P_{n+1} in the $(*)$ -system are $(\lambda, \theta^*, \phi^*)$. Its coordinates in the $(')$ -system are then $(\lambda, \theta'_{n+1}, \phi'_{n+1})$ such that

$$\theta'_{n+1} \cos \phi'_{n+1} = \theta^* \cos(\phi'_n + \phi^*) + \theta'_n \cos \phi'_n$$

$$\theta'_{n+1} \sin \phi'_{n+1} = \theta^* \sin(\phi'_n + \phi^*) + \theta'_n \sin \phi'_n$$

or

$$(\theta'_{n+1})^2 = \theta^{*2} + \theta_n'^2 + 2\theta^* \theta'_n \cos \phi^*$$

(These are derived using the approximation $\sin \theta \sim \theta$, $\cos \theta \sim 1$.) Since θ^* is measured from the incident direction of the proton, the average value of any pertinent quantity (e.g., θ^{*2}) is given by

$$\langle \theta^{*2} \rangle = \frac{\int_{\Omega} \theta^{*2} \left(\frac{d\sigma}{d\Omega^*} \right) d\Omega^*}{\int_{\Omega} \left(\frac{d\sigma}{d\Omega^*} \right) d\Omega^*} =$$

$$\frac{\theta_{\min}^2}{\pi} \int_0^{2\pi} \int_{\theta_{\min}}^{\theta_{\max}} \left(\frac{\theta^{*2} \theta^* d\theta^*}{\theta^{*4}} \right) d\phi^*$$

$$\langle \theta^{*2} \rangle = 2\theta_{\min}^2 \ln \left(\frac{\theta_{\max}}{\theta_{\min}} \right)$$

Averaging the expression for $(\theta'_{n+1})^2$ over the cross section then gives a recursion formula for $\langle \theta_n'^2 \rangle$:

$$\langle \theta'_{n+1}{}^2 \rangle = \langle \theta^{*2} \rangle + \langle \theta_n'^2 \rangle .$$

The first collision is assumed to take place on the z_0 axis, $(x_0, y_0, z_0)_1 = (0, 0, \lambda)$, so that $\langle \theta_1'^2 \rangle = 0$ and in general

$$\langle \theta_n'^2 \rangle = (n-1) \lambda \theta^*{}^2 .$$

Returning to the fixed coordinate system (x_0, y_0, z_0) , the coordinates of the point P_{n+1} in this system are (double translation from the (')-system):

$$(x_0)_{n+1} = (x_0)_n + \lambda \theta_{n+1}' \cos \phi_{n+1}'$$

$$(y_0)_{n+1} = (y_0)_n + \lambda \theta_n' \sin \phi_{n+1}'$$

$$(z_0)_{n+1} = (z_0)_n + \lambda$$

The displacement from the z_0 axis of a proton undergoing its n^{th} collision is

$$r_n = \sqrt{(x_0)_n^2 + (y_0)_n^2} .$$

From the above expressions for $(x_0, y_0, z_0)_{n+1}$:

$$r_{n+1}^2 = r_n^2 + \lambda^2 \theta_{n+1}'^2 + 2\lambda \theta_{n+1}' \{ (y_0)_n \sin \phi_{n+1}' + (x_0)_n \cos \phi_{n+1}' \} ;$$

and averaging this expression over the cross section:

$$\langle r_{n+1}^2 \rangle = \langle r_n^2 \rangle + \lambda^2 \langle \theta_{n+1}'^2 \rangle = \langle r_n^2 \rangle + (n-1) \lambda^2 \langle \theta^*{}^2 \rangle$$

Setting $\langle r_1^2 \rangle = 0$ one finds:

$$\langle r_n^2 \rangle = \lambda^2 \langle \theta^*{}^2 \rangle \sum_{m=1}^{n-1} \langle m \rangle = \lambda^2 \langle \theta^*{}^2 \rangle \frac{n(n-1)}{2}$$

For large n ,

$$\langle r_n^2 \rangle \sim \frac{(n\lambda)^2 \langle \theta^2 \rangle}{2}$$

However, $(n\lambda)$ is the distance travelled through the scattering medium, $(n\lambda) \sim (z_0)_n$ (to the approximation $\sin\theta \sim \theta$), so that for a scattering layer of thickness L :

$$\langle r^2 \rangle^{1/2} \sim \frac{L \langle \theta^2 \rangle^{1/2}}{\sqrt{2}}$$

independent of the number density of the scattering medium.

For a scattering layer of O_2 80 cm thick and 0.9 MeV neutrons:

$$\sigma = \int_{\Omega} \left(\frac{d\sigma}{d\Omega} \right) d\Omega = \left(\frac{2Ze^2}{pv} \right)^2 \frac{\pi}{\theta_{\min}^2} = 1.72 \times 10^{-16} \text{ cm}^2$$

(c.f. experimental total ionization cross section at 0.9 MeV,⁵

$$\sigma_{O_2} = 1.65 \times 10^{-16} \text{ cm}^2)$$

$$\langle \theta^2 \rangle = 2\theta_{\min}^2 \ln \left(\frac{\theta_{\max}}{\theta_{\min}} \right) = 2.6 \times 10^{-7} \text{ radian}^2$$

$$\langle r^2 \rangle^{1/2} = 2.88 \times 10^{-2} \text{ cm}$$

As a check on the approximations: Assuming a (maximum) pressure of ~ 4 Torr

$$n \sim 3.6 \times 10^3, \quad n(n-1) \sim n^2$$

The maximum rms cumulative angle is then

$$(\theta^2)_{\max}^{1/2} \sim 0.1 \text{ radian}$$

$$\sin(\theta^2)_{\max}^{1/2} = 0.0998 \sim (\theta^2)_{\max}^{1/2}$$

The change in the cross section as a result of energy losses in the gas is $\leq 10\text{-}15\%$.

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