

CONF-740614-2

Mechanisms of Aerosol Formation from  $\text{SO}_2$ \*†

William P. Wood, A. W. Castleman, Jr., and I. N. Tang  
Brookhaven National Laboratory  
Upton, New York 11973

March 1974

The paper will be delivered by:  
Dr. A. W. Castleman, Jr.  
Leader, Atmospheric Chemistry Research Group  
Department of Applied Science - Bldg. 815  
Brookhaven National Laboratory  
Upton, New York 11973

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\* This research was performed under the auspices of the U. S. Atomic Energy Commission and was partially financed by the Department of Transportation under an interagency agreement.

† For presentation at the National Air Pollution Control Association meeting, Denver, Colorado, 10-13 June, 1974.

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### Abstract

Experiments were performed to elucidate some of the mechanisms of important reactions leading to aerosol formation involving  $\text{SO}_2$  and mixtures with  $\text{NO}_2$ . In one series, the rapid generation of a high number density aerosol was effected upon exposing 1 ppm of  $\text{SO}_2$  to ionizing radiation in the presence of moisture. Subsequent addition of  $\text{NH}_3$  led to further chemical conversion, the product being identified as  $(\text{NH}_4)_2\text{SO}_4$  by x-ray diffraction. Mass spectrometric studies of the gas phase showed the expected reaction sequence leading to the formation of  $\text{H}_3\text{O}^+$  hydrates and the hydroxyl radical. Additional experiments with an ion trap and appropriate free radical scavengers proved that aerosol formation did not involve an ion-molecule switching reaction; but, rather, the reaction of OH with  $\text{SO}_2$  was found to be an important initiating step. The kinetics of the oxidation and subsequent hydration reactions leading to aerosol formation are discussed.

In other experiments, a systematic investigation of aerosol formation involving  $\text{NO}_2$ ,  $\text{SO}_2$ , and water vapor was undertaken. In the absence of organic impurities, no dark reaction leading to aerosol formation was observed for concentrations up to 1000 ppm of the reacting gases. However, upon exposure to light,  $3000 \leq \lambda \leq 4900\text{\AA}$ , aerosol production occurred. At low reactant concentrations, the kinetics of particle formation are shown to depend directly on  $\text{SO}_2$  concentration. Above a certain minimum level, particle formation is independent of  $\text{NO}_2$ .

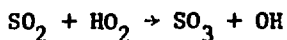
## Introduction

Although sulfur compounds are known to play a role in the formation of atmospheric aerosols under some conditions, the basic mechanisms leading to the production of sulfuric acid and other sulfate aerosols have not been well established. Clearly, a knowledge of the mechanisms is essential in order to understand the origin of the stratospheric sulfate layer and to establish the overall tropospheric sulfur cycle. Furthermore, data on the rates of the individual steps in the conversion are urgently needed as input to regional models used in forecasting, establishing emission standards, and assessing biological hazards, as well as for interpreting the results of field studies.

The homogeneous photooxidation of  $\text{SO}_2$  has been suggested<sup>(1)</sup> as one mechanism by which  $\text{SO}_2$  is converted to sulfuric acid in the atmosphere. Several evaluations<sup>(2-4)</sup> of the quantum yield of  $\text{SO}_2$  conversion have been made and the values vary over several orders of magnitude. The most recently reported value<sup>(4)</sup> of less than  $1 \times 10^{-9}$  seems to eliminate the homogeneous photooxidation as an important mechanism either in the troposphere or in the stratosphere.

The three-body oxidation of  $\text{SO}_2$  by O atoms has also been postulated<sup>(5)</sup> to explain the conversion of  $\text{SO}_2$ . However, the recent reevaluation of the rate constant by Davis<sup>(6)</sup> with  $\text{N}_2$  as the third body has shown the reaction to be almost four times slower than previously thought, and this mechanism is of only minor importance under most conditions.

Several authors<sup>(4,7-11)</sup> have raised the possibility that  $\text{SO}_2$  reaction with either OH or  $\text{HO}_2$  represents a prime conversion mechanism and, in the absence of high organic radical concentrations and catalytic surface sites, these do appear to be contenders as the most important reactant species. Payne et al<sup>(9)</sup> studied the reaction



and obtained an approximate rate coefficient of  $9 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . Preliminary measurements in this Laboratory<sup>(8,10)</sup> and elsewhere<sup>(7,9,11)</sup> have shown the reaction with OH to be third body, with the saturated two-body rate several orders of magnitude higher.

The objective of the present paper is to summarize our findings regarding the oxidation of  $\text{SO}_2$  to sulfuric acid droplets and sulfate particles in the presence of ionizing radiation, and to present evidence for the importance of the OH reaction mechanism. The results of some preliminary work on the reaction of  $\text{SO}_2$  with  $\text{NO}_2$  at low concentrations are also discussed.

#### Experimental Methods

The experiments with ionizing radiation are carried out in the flow system shown in Figure 1. Briefly, the apparatus consists of a 6-liter cylindrical reaction vessel which is completely shielded from room light to prevent the possibility of uncontrolled photo-induced reactions. Several inlet ports are located upstream from the reaction chamber where trace amounts (ppm range) of gaseous reactants are introduced into the carrier gas. The flow rate of each gas stream is controlled by a calibrated rotameter. Ultrahigh purity Argon was used as the carrier gas in the majority of the experiments and the flow rate was adjusted to 3000 cc/min in order to balance the gas flow-rate required to operate a condensation nuclei counter. This counter was used to continuously monitor the generation of aerosols in the reaction vessel and is capable of detecting condensation nuclei of the size range  $>.002\mu\text{m}$  in diameter; the minimum detection is taken to be one condensation nuclei/cm<sup>3</sup> (cn/cm<sup>3</sup>). Nitrogen was substituted as the carrier gas in some of the experiments. The valving (not shown) is arranged so that the carrier gas can be flowed over a water reservoir for humidification, or around it for making experiments under dry conditions.

After passing through the water reservoir (or after bypassing it),

the carrier gas is flowed over a tritium foil beta source. Tritium is a pure beta ( $\beta$ ) emitter, with a half-life of 12.4 years, and an energy of 18.6 kev. The activity of the source employed in these experiments was 250 millicuries and it was positioned within the flow stream so that the foil lined the inner wall of the pyrex tubing. Calibrated permeation tubes containing  $\text{SO}_2$  were obtained from A.I.D., Inc. and were utilized to produce concentrations of  $\text{SO}_2$  in the ppm range. Concentrations of  $\text{CO}$ ,  $\text{NO}$ , and  $\text{N}_2\text{O}$  in the ppm range were obtained by crimping  $1/8$ " stainless steel tubing and calibrating the flow of the particular gas through the tube.

Direct studies of the reaction between  $\text{SO}_2$  and hydroxyl radicals are carried out in a cylindrical quartz cell 1.4 cm in diameter and 44.0 cm long. This cell was equipped with suprasil quartz windows which permit the entrance of radiation down to  $1650 \text{ \AA}$ . A microwave discharge lamp containing 10%  $\text{N}_2$  in He at a total pressure of 1 mm is used as the source of vacuum ultraviolet radiation. This lamp emits a broad band of radiation from  $1650 \text{ \AA}$  to  $1950 \text{ \AA}$ . Mixtures of the gaseous reactants are added to the reaction cell and photolyzed for a given period of time. The mixture is then collected and analyzed by gas chromatography or mass spectrometry, as required.

Investigations of the photochemically induced aerosol formation in the ( $\text{SO}_2 + \text{NO}_2 + \text{H}_2\text{O}$ ) system are carried out in a 14-liter reaction vessel. This apparatus is equipped with heat transfer coils which enable the reactant gases to be precooled before entering the inlet mixing region. The entire apparatus is submerged in a vacuum Dewar which can be cooled to  $-50^\circ\text{C}$ , thereby permitting experiments to be performed at stratospheric temperatures. Monitoring of reactant concentrations is achieved with the use of several instruments including a  $\text{NO}_x$  analyzer, a gas chromatograph equipped with a flame photometric detector for  $\text{SO}_2$  analysis, and a hygrometer for monitoring water vapor concentrations. The vessel is equipped with an optically flat pyrex window which transmits light

of wavelengths  $>3000 \text{ \AA}$ . For these experiments, a medium pressure Hg lamp was used as the source of ultraviolet radiation.

A typical experiment designed to study the effect of ionizing radiation upon  $\text{SO}_2$  oxidation is made in the following manner. Initially, the reaction vessel is purged with carrier gas for thirty minutes before each run. The vessel's residence time was approximately two minutes at the flow rates employed. Clearly, the purging time was more than sufficient to clear the vessel of any residual aerosol. After purging, no background aerosol is detectable.

#### Summary of Results and Discussion

##### Aerosol Formation in the Presence of an Ionizing Source

A typical experimental series is described below and illustrated in Figure 2. Referring to the regions designated in the figure:

A. Dry argon containing 1 ppm of  $\text{SO}_2$  was flowed over the  $\beta$  source. No aerosol was produced.

B. Moist argon containing 1 ppm of  $\text{SO}_2$  was bypassed around the  $\beta$  source. This also produced no aerosol.

C.  $\text{SO}_2$  at 1 ppm was then flowed over the  $\beta$  source and moist argon was added downstream. No detectable aerosol was generated by this procedure as well.

D. Step C was reversed with moist argon passed over the  $\beta$  source and 1 ppm of  $\text{SO}_2$  was added downstream. As seen from the figure, this resulted in an aerosol concentration of  $2 \times 10^5$  particles/cm<sup>3</sup>.

E. Finally, the source of  $\text{SO}_2$  was isolated from the flow stream; with continued purging, this resulted in the decrease of the aerosol concentration to zero.

Additionally, trace quantities of  $\text{NH}_3$  were added to the reaction vessel which already contained aerosols. This resulted in the production of a white crystalline solid which coated the walls of the vessel. This solid was collected, subjected to x-ray diffraction analysis, and identified as ammonium sulfate. Sul-

furic acid was almost certainly the species with which the ammonia had reacted to form the sulfate.

An assessment of these and related experiments showed that the aerosol production in this system resulted either from (1) an ion-molecule switching reaction<sup>(12)</sup> or, (2) a free-radical conversion initiated by the water flowing over the  $\beta$  source.

A series of experiments were performed in order to assess the importance of (1). In these, a pair of charge plates were installed in the flow stream and positioned in such a manner that the carrier gas, after being exposed to the  $\beta$  source, passed through the potential field of the charge plates. The injection point for  $\text{SO}_2$  was located further downstream. The charged plates were spaced approximately 1 cm apart and a potential of up to 1000 V was applied between them. No noticeable decrease in particle production was observed, and this eliminated (1) as a significant mechanism in the conversion step.

The remaining possibility is that a free radical is responsible for the conversion of  $\text{SO}_2$  to sulfuric acid. Clearly the free radical must be one generated by the interaction of a high energy electron with the water vapor and carrier gas as they pass over the ionizing source. Related experiments<sup>(13)</sup> made in one of the ion-molecule clustering apparatuses in our Laboratory showed that a series of ion-molecule reactions between  $\text{H}_2\text{O}$  and  $\text{Ar}^+$  and  $\text{H}_2\text{O}^+$  lead eventually to the production of hydrated oxonium ions,  $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$  (where  $n$  is an integer); the free radical OH is produced as a by-product. OH readily recombines via a third body reaction, leading to the formation of  $\text{H}_2\text{O}_2$ . The rate coefficient for this termolecular reaction is  $1.6 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ . Subsequent reactions of the hydrogen peroxide with OH leads to the formation of  $\text{HO}_2$ ; the appropriate rate coefficient is  $1.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$ . There are additional reactions which are possible, and O and H atoms are also conceivable

constituents present in the system along with the OH, H<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub>.

In order to provide evidence as to which of the potential reactants is responsible for sulfurous acid formation, other experiments were made to study the effect of adding known concentrations of various free radical scavengers on the extent of aerosol production. A typical series of experiments, and the results, are shown in Figure 3. These were carried out by initiating aerosol formation in the usual manner and then adding the appropriate free radical scavenger along with the SO<sub>2</sub> and carrier gas at a point downstream from the radiation source, but prior to the reaction vessel.

The effects of adding the gases CO, N<sub>2</sub>O, and NO are seen from the results plotted in Figure 3. Changes in the reaction conditions were made at successively later times represented by the letters A - G designated on the figure:

A) Initially, moist argon containing 1 ppm of SO<sub>2</sub> was passed over the β source and the resultant aerosols were monitored until the concentration built up to a steady value and remained constant for at least 5 minutes.

B) Upon addition of 60 ppm of CO, the aerosol concentration decreased from an original value of  $2 \times 10^5/\text{cm}^3$  to  $7 \times 10^4/\text{cm}^3$ .

C) The source of CO was isolated from the system and the aerosol concentration returned to its original value.

D) Upon addition of 60 ppm of N<sub>2</sub>O, the aerosol concentration decreased from  $2 \times 10^5/\text{cm}^3$  to  $1.4 \times 10^5/\text{cm}^3$ .

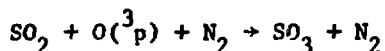
E) Isolating the source of N<sub>2</sub>O from the system, resulted in the aerosol concentration returning to its original value.

F) The addition of 60 ppm of NO reduced the aerosol concentration from  $2 \times 10^5/\text{cm}^3$  to an undetectable level.

G) Terminating NO addition to the system resulted in the aerosol concentration returning to its original value.

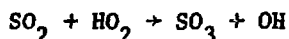


All experiments were made at ambient temperature and one atmosphere pressure. Rate coefficients for some of the possible reactions taking place in the system are given in Table I. The effect of the scavenger gas addition must be assessed in comparison to the ratio of SO<sub>2</sub> to scavenger concentration, with due consideration also being given to the rate of SO<sub>2</sub> oxidation by the appropriate species. Davis<sup>(6)</sup> has reported the rate constant for the following two reactions:



$$k = 7.7 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$$

and



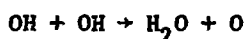
$$k = 0.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Considering the tabulated rate constants, and those given directly above, it was established that SO<sub>2</sub> was reacting with both OH and HO<sub>2</sub>, and that the conversion due to reaction with OH was quite significant. The conclusions, which are to be detailed elsewhere<sup>(14)</sup>, are summarized in what follows. The reaction of SO<sub>2</sub> with H<sub>2</sub>O<sub>2</sub> is relatively slow and may be neglected with respect to the other two species. Nevertheless, at the point of SO<sub>2</sub> (and scavenger gas) introduction, sufficient time has elapsed from the OH formation region for H<sub>2</sub>O<sub>2</sub>, and ultimately HO<sub>2</sub>, to have reached appreciable concentrations with respect to the OH.

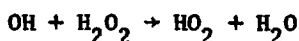
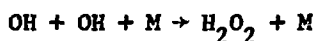
CO was the first gas chosen for addition. It readily reacts with OH, but would be expected to reduce the HO<sub>2</sub> concentration by only a negligible amount. If we assume only HO<sub>2</sub> was responsible for the aerosol formation, the addition of CO would not have been expected to produce such an appreciable effect. However, since CO is a poor scavenger for HO<sub>2</sub>, the effect observed from the addition of CO

as a scavenger gas did not rule out the existence of HO<sub>2</sub>. Nor was it a proof that HO<sub>2</sub> did not contribute to aerosol formation in this system. In fact, the observation that the aerosol production merely decreased to a new appreciable level upon the addition of CO suggests that reaction with some species other than OH also occurs to some extent. Species such as HO<sub>2</sub>, O, or H are the other possible contenders.

The likelihood of O(<sup>3</sup>P) being an important reactant is eliminated by relative concentration considerations. The O atoms are most plausibly produced in our system by the recombination of OH radicals via the following reaction:



Concurrently, the recombination of OH leads eventually to the formation of HO<sub>2</sub> radicals:



Using the appropriate rate constants given in Table I, it was calculated that the rate of O production is at least 25 times slower than HO<sub>2</sub> production. Furthermore, if the aerosol production were dominated by reaction with O(<sup>3</sup>P), the N<sub>2</sub>O would not have displayed the observed effect. Referring to Table I, it can be seen that its reaction with O(<sup>3</sup>P) would be negligible.

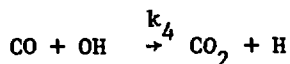
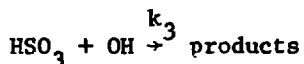
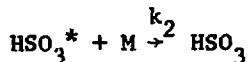
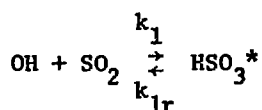
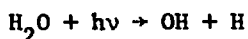
The possibility that H atoms initiated particle formation also seems very unlikely. Fair and Thrush<sup>(15)</sup> have shown the three-body addition rate to be less than  $1.4 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$ . Other experiments, not shown in Figure 3, were made to investigate the influence of O<sub>2</sub> addition on aerosol production. As shown in Table I, the three-body reaction of H with O<sub>2</sub> is fast at atmospheric pressure and, consequently, experiments made at 1 atmosphere O<sub>2</sub> pressure should have shown a substantial reduction of aerosol concentration due to H being scavenged. Instead, the production of aerosols actually increased, indicating that HO<sub>2</sub> radicals, rather than H atoms, were partially responsible for the production of sulfuric acid aerosol.

The role of HO<sub>2</sub> radicals in our system was further elucidated from NO

scavenger experiments. Referring to Figure 3, the large reduction due to the addition of 60 ppm of NO cannot be explained solely on the basis of OH scavenging. However, since NO is an effective scavenger for both HO<sub>2</sub> and OH, its addition is expected to result in a cumulative reduction in the aerosol concentration as observed.

Using the apparatus discussed in the Experimental Methods section, a series of photochemical experiments were initiated to directly measure the kinetics of the SO<sub>2</sub> reaction with OH. Briefly, these experiments were made by performing a steady-state photolysis of known mixtures of SO<sub>2</sub>, CO, H<sub>2</sub>O, and nitrogen carrier gas over a wide range of concentrations and pressures. In these experiments CO competes with SO<sub>2</sub> for OH, and the effect of varying concentration ratios on CO<sub>2</sub> production is measured. The source of hydroxyl radicals is the photochemical dissociation of water molecules by the vacuum UV radiation. Experiments made in the absence of water vapor indicated that the direct photo-induced reaction between CO and SO<sub>2</sub> provides a negligible source of CO<sub>2</sub> at the wavelengths employed in this study.

The data obtained from these experiments was interpreted according to the following mechanism:



The experimental results showed the reaction to be pressure dependent below 500 torr and pseudo bimolecular at higher values. This leads to a high pressure

limit for the ratio,  $r$ , of  $\text{CO}_2$  produced in the presence of  $\text{SO}_2$  to that without  $\text{SO}_2$ :

$$r = \frac{1}{1 + \frac{2k_1 [\text{SO}_2]}{k_4 [\text{CO}]}}$$

At the high pressure limit, a preliminary value of  $k_1 = 3.8 \times 10^{-13} \text{ cm}^3$  molecule<sup>-1</sup> sec<sup>-1</sup> is obtained. Depending on the altitude and presence of sources of pollution, OH concentrations between  $10^6$  and  $10^8$  molecules/cm<sup>3</sup> have been predicted. Therefore, particle formation from  $\text{SO}_2$  reactions with hydroxyl radicals is expected to be quite significant under some atmospheric conditions.

Additionally, experiments have been carried out to identify other reactions of atmospheric significance which can result in gas-to-particle conversion. Scoping experiments are presently being conducted on the ( $\text{NO}_2 + \text{SO}_2 + \text{H}_2\text{O}$ ) system. Preliminary results indicate that no dark reaction takes place between  $\text{NO}_2$  and  $\text{SO}_2$  for concentrations in the ppm range. Exposing the reaction mixture at  $-50^\circ\text{C}$  to ultraviolet radiation ( $3000 \text{ \AA} < \lambda < 5000 \text{ \AA}$ ), resulted in the rapid production of condensation nuclei when trace concentrations of  $\text{H}_2\text{O}$  vapor were present. Extinguishing the lamp resulted in the aerosol concentration returning to the detection limit. Initial experiments have shown the amount of aerosol produced to be directly proportional to the  $\text{SO}_2$  concentration and independent of  $\text{NO}_2$ , once a small critical concentration of  $\text{NO}_2$  is present. A wavelength study has shown that light in the region  $3000 \text{ \AA}$  to  $3660 \text{ \AA}$  to be responsible for aerosol production in this system. Additional studies are presently being conducted to further elucidate the mechanism and to identify the aerosol; these findings will be reported.

Table I. Rate Constants<sup>a</sup> for Reactions of H, O, OH, and HO<sub>2</sub>.

Reaction	$k/\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$	Reference
$\text{NO} + \text{O} + \text{M} \rightarrow \text{NO}_2 + \text{M}$	$7.0 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$	16
$\text{NO} + \text{HO}_2 + \text{M} \rightarrow \text{HNO}_3 + \text{M}$	$5 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$	7
$\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$	$2 \times 10^{-13}$	16
$\text{NO} + \text{H}_2\text{O}_2 \rightarrow \text{HNO}_2 + \text{OH}$	$< 5 \times 10^{-20}$	16
$\text{NO} + \text{OH} \xrightarrow{\text{M}} \text{HNO}_2$	$2 \times 10^{-12}$	17
$\text{N}_2\text{O} + \text{O}(^3\text{P}) \rightarrow \text{NO} + \text{NO}$	$4.4 \times 10^{-31}$	16 <sup>b</sup>
$\quad \quad \quad \rightarrow \text{N}_2 + \text{O}_2$	$4.4 \times 10^{-31}$	16 <sup>b</sup>
$\text{N}_2\text{O} + \text{H} \rightarrow \text{N}_2 + \text{OH}$	$1.1 \times 10^{-21}$	16 <sup>b</sup>
$\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$	$1.33 \times 10^{-13}$	16
$\text{CO} + \text{HO}_2 \rightarrow \text{CO}_2 + \text{OH}$	$< 10^{-19}$	16
$\text{CO} + \text{O}(^3\text{P}) + \text{M} \rightarrow \text{CO}_2 + \text{M}$	$4.29 \times 10^{-36} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$	18
$\text{SO}_2 + \text{H} + \text{M} \rightarrow \text{HSO}_2 + \text{M}$	$< 1.4 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$	15
$\text{OH} + \text{OH} + \text{M} \rightarrow \text{H}_2\text{O}_2 + \text{M}$	$1.6 \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$	19
$\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2 + \text{H}_2\text{O}$	$8 \times 10^{-13}$	16
$\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$	$1.8 \times 10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ sec}^{-1}$	16
$\text{OH} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}$	$1.6 \times 10^{-12}$	16

a. All values are for 298°K.

b. Extrapolation from high temperature data.

### Acknowledgement

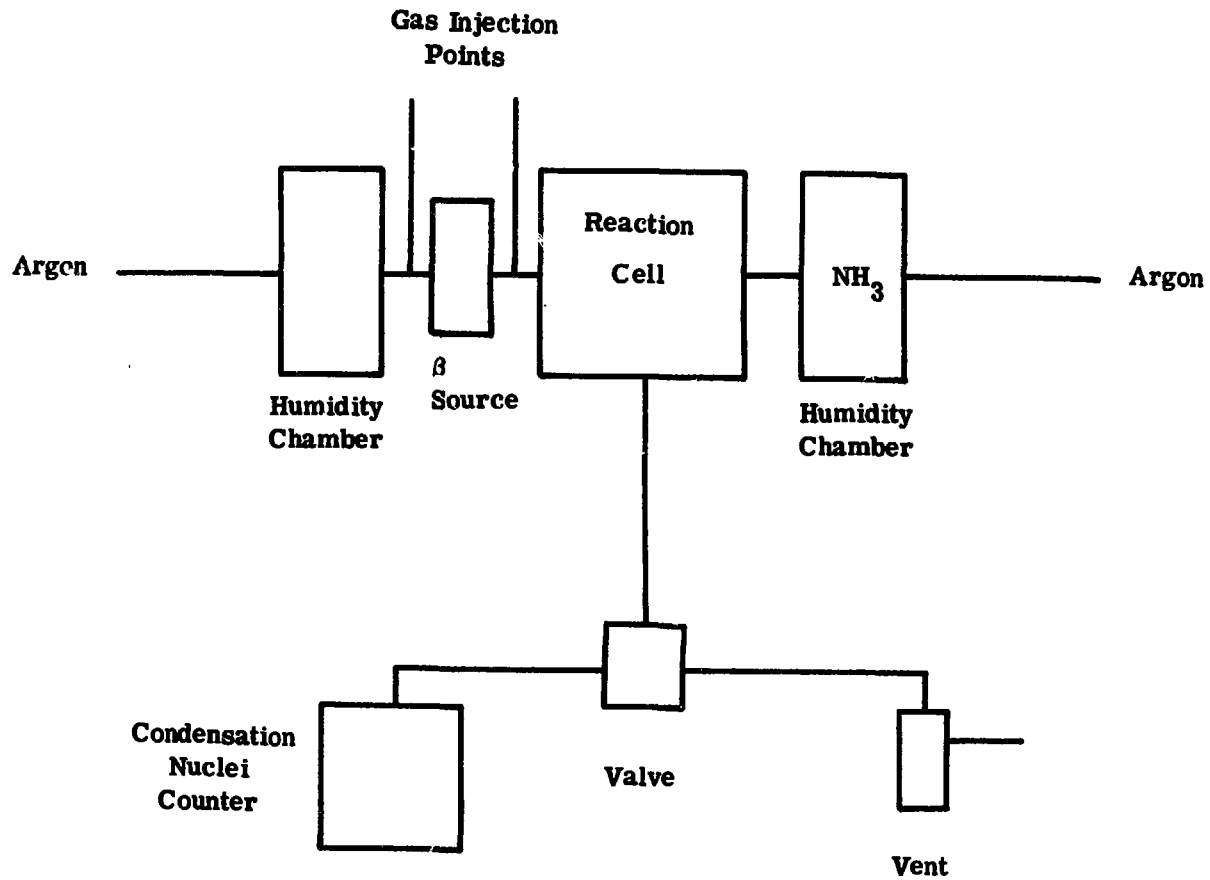
The authors wish to express their appreciation to Mr. H. R. Munkelwitz and Mr. Walter Kalinowski for their assistance in constructing the apparatus and in performing the experiments.

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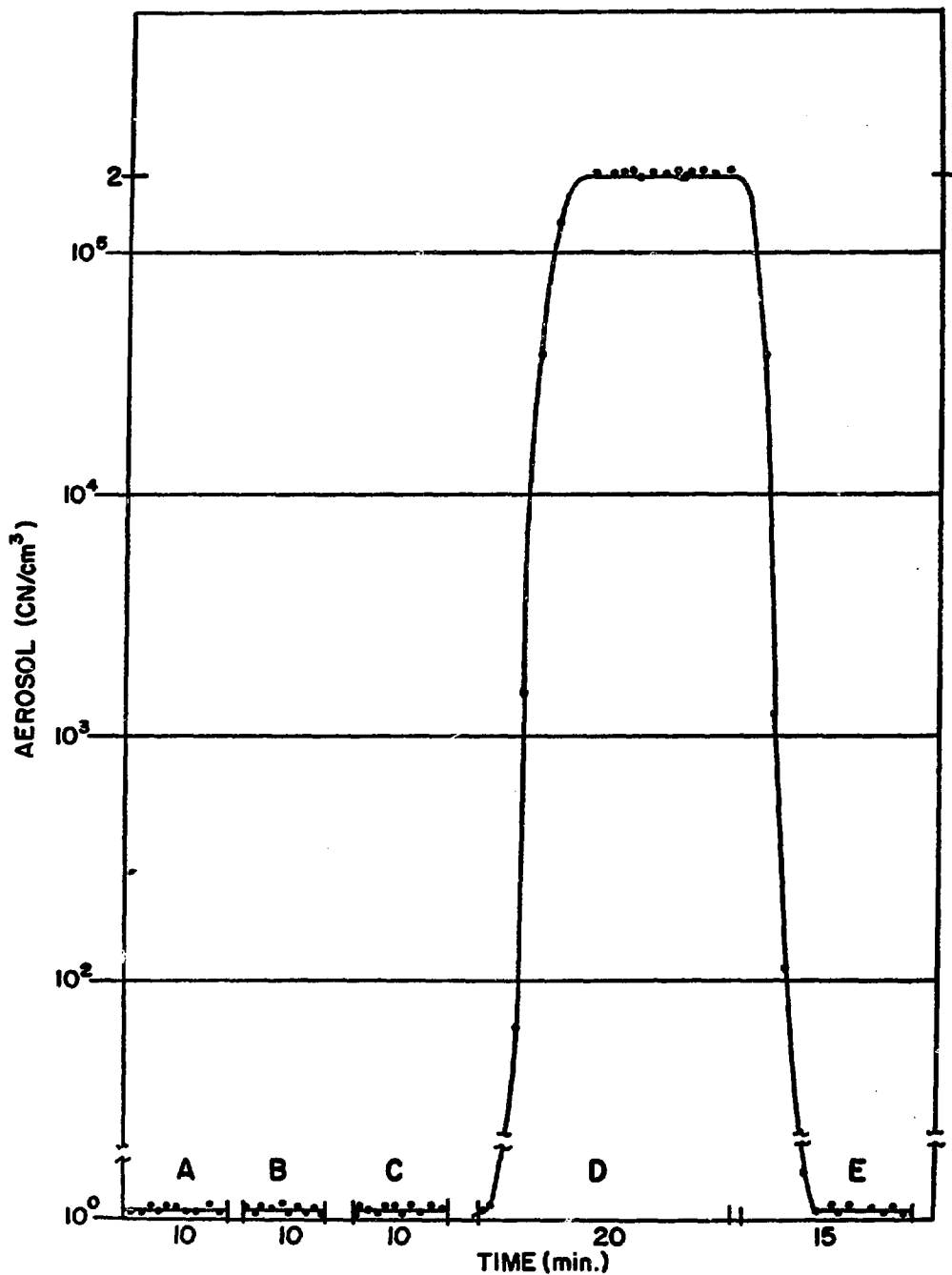
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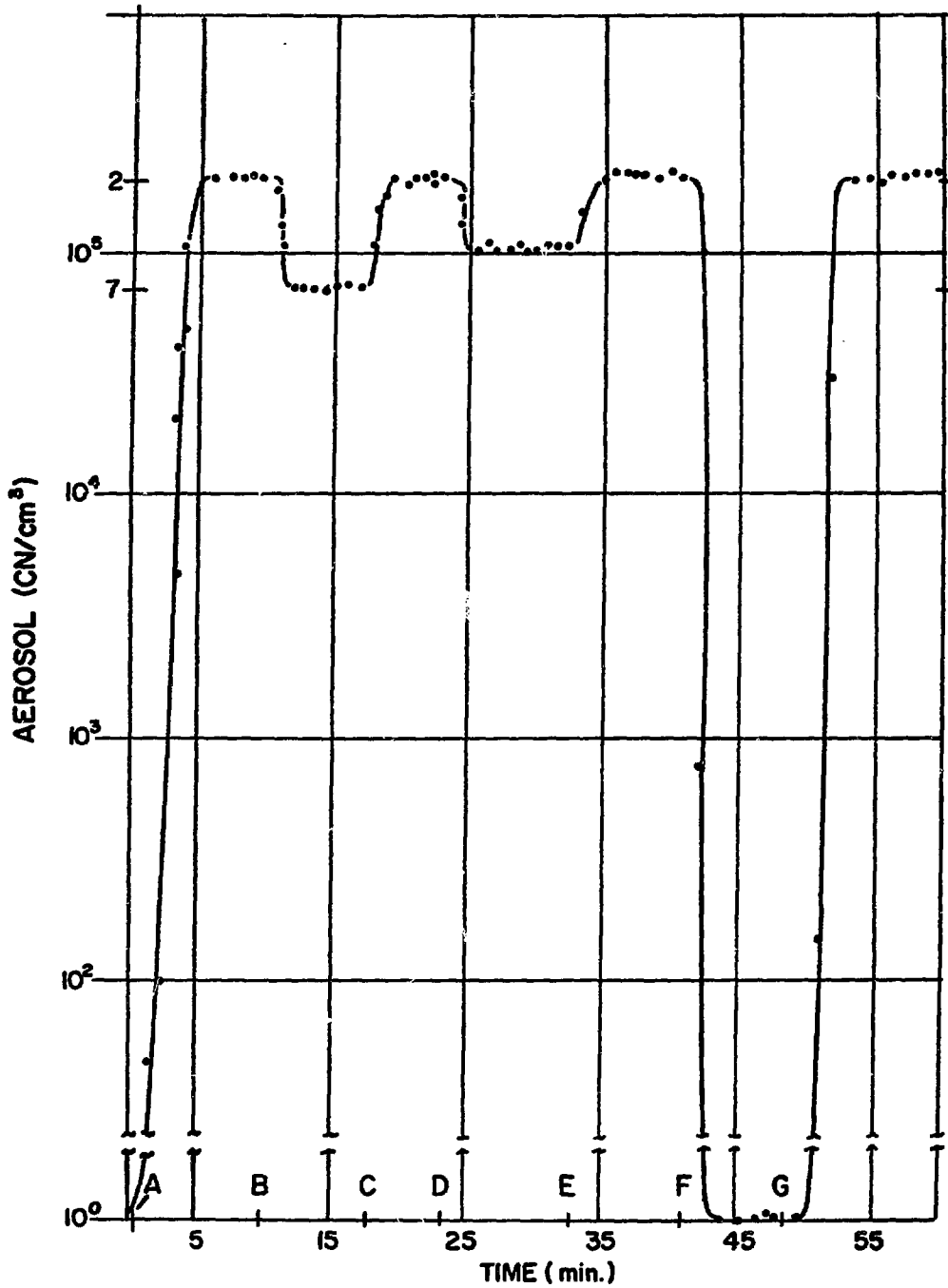
**Apparatus for Condensation Nuclei  
Formation by  $\beta$  Irradiation**

**FIGURE 1**



PLOT OF AEROSOL CONCENTRATION VS. EXPERIMENTAL CONDITIONS.

FIGURE 2



PLOT OF AEROSOL CONCENTRATION VS. ADDITION  
OF SCAVENGER GASES

FIGURE 3