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GAS-TO-PARTICLE CONVERSIONS OF SO_2-NO_2-H_2O-AIR GAS MIXTURES UNDER SPECIFIC UV IRRADIATION

BY

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ABSTRACT

In these series of experiments, mixtures of sulfur dioxide and nitrogen dioxide were irradiated in an absorption cell with monochromatic radiation found in the tropospheric region of the atmosphere. The irradiated mixtures were then introduced into a Wilson type cloud chamber to investigate the effects of these specific wavelength induced gas to particle conversions on nucleation. Results showed that sulfur dioxide could not be the sole agent for the formation of condensation nuclei. A mixture of sulfur dioxide and nitrogen dioxide irradiated at 3660 angstroms produced copious droplet formation identifying nitrogen dioxide as an integral reactant in nuclei production.

ACKNOWLEDGEMENTS

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I. INTRODUCTION

In these series of experiments, it is expected that a further knowledge of the nature of condensation nuclei formed by tropospheric radiation in the ultraviolet range will be enhanced. By using pure wavelengths of radiation found in the troposphere and stratosphere a knowledge of the gaseous compounds participating in nuclei production will be found. These nuclei can play an important role in both the local and general planetary environment.

The observation and study of atmospheric nuclei and aerosol is not a new field of atmospheric science, but the increasing concern over the quality of the urban environment has caused a renewal of interest in this subject. Any complete study of atmospheric aerosol should include the various factors that affect the role of conversion of gas phase pollutants into particulate matter. One of these factors may be the increasing volume of combustion products released into the atmosphere as a result of our technological society. Some believe, such as Schaefer[1], that technology is now a primary contributing factor to a slight and practically unrecognizable modification of our climate due to its addition of large amounts of exhaust gases and particulates into the atmosphere. It is hoped that a better understanding into the physics of the photochemical aspects of gas-to-particle conversions will lead to conclusions which may be used to help alleviate some aspects of these environmental problems.

Many and varying experiments have been done since the initial work of Tyndall and Aitken who first recognized the effect of sunlight in producing aerosol or haze. John Aitken(1839-1919) was the first investigator to identify the gas to particle conversion due to the action of sunlight. The initial particulate matter formed by these reactions were first identified and measured by him, and these particles are now called Aitken nuclei or condensation nuclei. Vohra and Nair[2] conclude that in these gas-to-particle reactions, there is an initial formation of small clusters or embryos of hygroscopic molecules with a radius of eight angstroms or less. Particle growth is further enhanced by the coagulation of these embryos, absorption of water vapor or both working simultaneously.

Aitken further postulated that sulfur dioxide, carbon monoxide, and hydrogen peroxide were the gases responsible for nuclei formation. Crane and Halpern, and also Farley[3] favored atomic oxygen as the primary agent in the production of these nuclei. In 1949, Vassail[4] suggested that simple hygroscopic molecules such as sulphuric and nitric acid would be suitable nuclei. Went[5] proposed that organic vapors such as olefins and terpenes produced by natural vegetation and some plankton were suitable reactants with the addition of sulfur dioxide and the oxides of nitrogen. Vohra, Vasudevan and Nair[2] found that the addition of ozone enhanced the production of nuclei. Haagen-Smit[6] measured ozone concentrations around 50 pphm in heavy smog in Los

Angles. However, Dunham[7] contends that ozone plays a very minor role in nuclei production.

Sulfur dioxide and the oxides of nitrogen however are relatively common in sizeable concentrations in most urban centers. There has been considerable evidence that sulfur dioxide plays a major role in the formation of photochemical aerosol. Megaw and Wiffen[8] showed that sulfur dioxide cannot be exclusively responsible for the production of aerosol in filtered air; Roddy[9] came to the same conclusion in his dissertation studies. Verzar and Evans[10] studying the influence of solar radiation on air contained in a polyethylene bag found that sulfur dioxide produced nuclei in the absence of sunlight, while hydrogen sulfide,and ammonia accelerated nuclei production only in the presence of sunlight. However, some doubts were later raised by McGreevy and T.C. O'Connor[11] concerning the possible effects of contamination upon this study.

Recently Jean Bricard and his coworkers have performed a series of experiments on irradiated mixtures of sulfur dioxide, nitrogen dioxide and water vapor resulting in some interesting conclusions.[12] As already noted, some researchers such as Megaw and Wiffen and Roddy felt that sulfur dioxide did not act as the sole agent for nuclei production, but that it needed a partner to enhance nuclei production. Bricard's experiments were designed to identify this unknown reaction partner of sulfur dioxide. In these series of experiments he was able to prove that sulfur dioxide added to a mixture of nitrogen(99%) and oxygen(1%) produced no nucleation under ultraviolet irradiation from a mercury arc. The addition of water vapor to the mixture did not alter the results. Nitric oxide was added to a nitrogen, sulfur dioxide and water vapor mixture which was then irradiated. No aerosol was produced. When, 2ppm of nitrogen dioxide was added to the same mixture and irradiated aerosol was formed.

In the second stage of his experiment, Bricard and his coworkers set up two containers, one whose contents would be irradiated with ultraviolet radiation, and the other darkened. In addition, the contents of one flask could be introduced into the other flask. Bricard irradiated 0.5ppm nitrogen dioxide in air with ultraviolet radiation, and then filtered and vented a sample into the darkened flask containing air. As a result, a weak production of aerosol, approximately 1000 particles per cubic centimeter, was formed. If this was repeated with the addition of sulfur dioxide in the darkened flask, a heavy aerosol consisting of approximately 20,000 particles per cubic centimeter was found.

When this procedure is reversed; that is, if sulfur dioxide was initially irradiated in the first flask and then introduced into the second flask containing air at one time and then air with the addition of nitrogen dioxide, no aerosol production was noted.

These experiments have seemed to prove that the direct irradiation of atmospheric concentrations of sulfur dioxide does not lead to significant production of aerosol. One could further conclude that some oxidation product of the nitrogen dioxide mixture is contributing along with the sulfur dioxide to produce enhanced nucleation.

To further substantiate this conclusion, it would be interesting to observe the effect of wavelength upon the nucleation. There has been some question over the wavelength interval which provides the primary energy for the photochemical reactions in the atmosphere. McHenry and Twomey[13] found the effective wavelength for nuclei formation to lie between 2345-2399 angstroms, whereas Vassail[4] found that the range between 1800-1850 angstroms was most effective. It is interesting to note that Roddy[14] observed that about 76% of the specific absorption rate of his radiation was due to the wavelengths of 3130 and 3025 angstroms. This is most valuable in that these wavelengths are above the atmospheric cut-off. So there seems to be some disagreement. On the whole, except for broad measurements of wavelength cut-offs for researchers' lamps, little or no concern seems to have been given to specific wavelengths used in the experiments that have been mentioned above.

It should, perhaps, be mentioned at this point that there has been general agreement that these nuclei are mostly electrically neutral. Also, heat or the temperature of the reaction vessels has no influence on the production of aerosol. Bricard states that there is no change in the nuclei count after raising the temperature of his reaction vessel by twenty degrees Centigrade[15]. Verzar and Evans[16] also state that the intensity of the light source affects the speed of the chemical reactions, but that it has no effect upon the end products.

II. PHOTOCHEMICAL REACTIONS

A. GENERAL INFORMATION AND NOTATION

The photochemical reaction begins with the absorption of solar radiation, which by the Stark-Einstein Law is the absorption of one photon by one molecule.

The immediate effect of photon absorption is the production of an excited state in the molecule with the extra energy above the ground state equal to the energy of the absorbed photon. It is now known that rotational or vibrational states do not lead to photochemical transitions. Only electronically excited molecules produce any photochemical reactions. Since most electronic spectra lie in the visible and ultraviolet, it is this part of the spectrum which is of importance in photochemistry.

The electronically excited molecule may undergo two transitions of importance in photochemical reactions. These are dissociation and direct reaction. In dissociation molecular bonds are broken leading to different species which may react with other molecules or other dissociation products to form new and different compounds. In a direct reaction, the excited molecule reacts with another molecule giving up its excitation energy to form a new product.

A term that is often used is the quantum yield, ϕ, of a reaction. This is defined as the ratio of the excited molecules reacting by that process to the number of photons absorbed or to the total number of excited molecules. Thus the maximum value that the quantum yield may take is one. If the molecules are reacting in several processes, the sum of the quantum yields of each process will be one, even though individual quantum yields might be quite small.

If (A) represents the concentration of our absorbing species, the rate of formation of the excited species, A^*, is given by,

$$d(A^*)/dt = (A)j(h\nu)\sigma_{eff} - (A^*)/\tau_{eff}$$

where $j(h\nu)$ is the photon flux in $cm^{-2}s^{-1}$, σ_{eff} is the effective cross-section for absorption, and τ_{eff} is the effective life-time of the excited state. The quantity $j(h\nu)\sigma_{eff}$ is often called the specific absorption rate, k_a, and has units of seconds^{-1} or hours^{-1}.

For a primary photochemical reaction yielding a product P, with primary quantum yield ϕ, the rate of formation of P will be,

$$d(P)/dt = k_a\phi(A) - L \text{ (a general loss term)}$$

where (A) is often given in molecules per cubic centimeter or liter for laboratory data or in parts per million (ppm) for pollution studies. The quantum yield is dimensionless.

B. SO_2 and NO_2 PHOTOCHEMICAL REACTIONS

In this study, the roles of sulfur dioxide and nitrogen dioxide under specific irradiation is investigated. Therefore, it is important to look at laboratory work in air pollution and aeronomy involving reactions of sulfur dioxide and nitrogen dioxide which may be of significance in the atmosphere.

Cadle and Allen[17] give typical concentrations for the oxides of nitrogen and also sulfur dioxide at 20 ppm or about $4.9\mathrm{X}\ 10^{11}$ molecules per cubic centimeter. While it should be noted that other compounds such as water, carbon monoxide and dioxide, and ammonia and methane may have concentrations of one to five orders of magnitude greater, these compounds are photochemically inert; with excitation and dissociation energies corresponding to photon wavelengths far less than the tropospheric cut-off.

Photochemical reactions involving sulfur dioxide and the various components of the atmosphere have been extensively studied. In the following reactions, reaction rate constants will be given when rate constant data has been published. One possible reaction is a three body reaction involving atomic oxygen:

$$SO_2+O+M \rightarrow SO_3+M \qquad k=2.7\mathrm{X}10^{-32}\mathrm{cm}^6\mathrm{mole}^{-2}\mathrm{s}^{-1} \quad M=O_2$$

Sulfur dioxide can not react with molecular oxygen or ozone in its ground state, so a photoexcitation is necessary for such reactions:

$$SO_2+ h\nu(3400\text{-}2900\mathrm{A}) \rightarrow SO_2^*(^3B_1)$$

$$SO_2^*+O_2 \rightarrow SO_3+O \rightarrow SO_4$$

$$SO_4+SO_2 \rightarrow 2SO_3$$

$$SO_4+O_2 \rightarrow SO_3+O_3$$

$$2SO_2^*+O_2 \rightarrow 2SO_3$$

$$3SO_2^*+O_3 \rightarrow 3SO_3$$

Finally SO_3 reacts strongly with water,

$$SO_3+H_2O \rightarrow H_2SO_4$$

Sulfuric acid molecules are hygroscopic. Hygroscopic molecules act as excellent condensation centers by effectively lowering the water vapor pressure over an aqueous solution compared to its vapor pressure over pure water. Water therefore tends to condense towards the sulfuric acid solution[18]. Sulfuric acid is widely believed to be the prime component of Aitken nuclei. Leighton[19] states that particulates from the above reactions consisted of droplets of moderately dilute sulfuric acid(about 43% at 50% relative humidity).

Research on reactions of the oxides of nitrogen has also been extensive; however, we will restrict ourselves to those reactions involving nitrogen dioxide as the primary reactant.

The most common reactions are:

$$NO_2+h\nu(\lambda<3660) \rightarrow NO+O(^3P)$$

$$NO_2+O+M \rightarrow NO_3+M \quad k=5.8X10^{-32}cm^6mole^{-2}s^{-1};\ M=N_2$$

$$NO_2+O_3 \rightarrow NO_3+O_2 \quad k=6.1X10^{-17}cm^3mole^{-1}s^{-1}$$

$$NO_3+NO_2+M \rightarrow N_2O_5+M \quad k=3.3X10^{-17}cm^6mole^{-2}s^{-1};\ M=N_2$$

$$N_2O_5+H_2O \rightarrow 2HNO_3$$

Nitric acid molecules are also hygroscopic and will enhance nucleation.

According to Leighton[20], some reactions may be eliminated as of any practical importance in the atmosphere. These reactions are:

$NO_2+O+M \rightarrow NO+O_2+M$

$NO_2+O+M \rightarrow NO_3+M$

$3NO_2+H_2O \rightleftarrows 2HNO_3+NO$

Furthermore, Leighton[21] states that oxygen(^3P) atoms contribute little in atmospheric photochemical reactions so that the reactions:

$SO_2+O \rightarrow SO_3$

$SO_2+O+M \rightarrow SO_3+M$

may also be neglected. However, little data has been collected on O(^3P) reactions and this should remain an open question. The prevalent opinion is that the oxygen atoms will quickly react with molecular oxygen to form ozone.

In an irradiated mixture of SO_2, NO_2, H_2O, and filtered air the following reactions may occur:

$NO_2+h\nu \rightarrow NO+O(^3P)$

$O_2+O+M \rightarrow O_3+M$

$SO_2^*+O_2 \rightarrow SO_4$

$SO_4+SO_2 \rightarrow 2SO_3$

$SO_4+O_2 \rightarrow SO_3+O_3$

$3SO_2+O_3 \rightarrow 3SO_3$

$SO_3+H_2O \rightarrow H_2SO_4$

$NO_2+O_3 \rightarrow NO_3+O_2$

$NO_2+NO_3+M \rightarrow N_2O_5+M$

$H_2O+N_2O_5 \rightarrow 2HNO_3$

It can be seen that for such a sequence to occur, atomic oxygen may be very important. While sulfur dioxide and water dissociation can occur only in the stratosphere with wavelengths less than 2400 angstroms, nitrogen dioxide dissociation is almost 100% complete below 3660 angstroms which is clearly in the region of tropospheric radiation. Nitrogen dioxide also has a strong absorption peak at 3130 angstroms, and sulfur dioxide has a peak at 3025 angstroms. These were important wavelengths in Roddy's observations as previously mentioned on page 5.

Special attention will be devoted to nucleation results around the strong absorption peaks of sulfur dioxide and nitrogen dioxide. These peaks in the tropospheric region are:

NO_2	3660A 3130A
SO_2	3400A 3025A 2940A

Results at the sulfur dioxide peaks will help to categorize the importance of reactions of the excited triplet state of sulfur dioxide. By controlling the oxygen component of the experimental environment, the importance of atomic oxygen and ozone in the previous chain of chemical reactions may be determined.

C. GAS TO PARTICLE CONVERSIONS

The end result of photochemical reactions is the formation of substances which finally result in atmospheric particulates. Gas to particle conversion which creates Aitken nuclei must initially involve homogeneous nucleation. In gas to particle conversion processes, higher vapor pressure organic substances may be converted into corresponding nitrites and nitrates, which are referred to generically as PANN. These possess a much lower vapor pressure so that concentrations of the material quickly become supersaturated. A clustering process, especially dealing with heterogeneous substances is a very difficult and little understood phenomenon. At the microscopic level, quantities such as surface free energy and vapor pressure have little significance, so that a classical formulation involving nucleation terms such as change in Gibbs free energy and chemical potential based on surface tension and vapor pressure, will not yield meaningful results for clustering of molecules having less than one hundred molecules. When dealing with aggregates of less than one hundred molecules, a statistical model must be developed. While many models have been proposed; there are still many shortcomings to be resolved. However; on the macroscopic scale, nucleation on liquid nuclei having a dissolved solute has been extensively developed, and since the macroscopic process leads to photographically detectable nuclei, a brief outline as given by Fletcher[22] will be presented.

Raoult's law describes the behavior of the vapor pressure of solutions through the equation:

$$p'/p = m$$

where p' is the vapor pressure over a plane surface of the solution containing a mole fraction m of water and p is the vapor pressure over pure water. It is sometimes necessary for solutions containing dissolved inorganic salts such as sodium chloride to include the van't Hoff factor i. When a mass m of a substance of gram molecular weight M is dissolved in water of gram molecular weight M_o to form a droplet of radius r and density ρ', the droplet contains effectively im/M moles of solute and $(\frac{4}{3}\pi\rho' r^3 - m)/M_o$ moles of water. Thus the mole fraction of water is given by:

$$m = \{1 + imM_o/M(\tfrac{4}{3}\pi\rho' r^3 - m)\}^{-1}$$

Since this will always be less than unity, it will have the effect of always decreasing the vapor pressure of the solution as compared to pure water.

From the Kelvin equation, the vapor pressure over a droplet of radius r at temperature T is:

$$p_r = p_\infty \exp(2\sigma/n_L kTr)$$

where p_∞ is the vapor pressure over a plane surface and σ is the surface free energy or surface tension, about 75.6 ergs/cm^2, and n_L is the number of molecules per cubic centimeter in the liquid phase, about 3.3×10^{22} cm^{-3}.

Combining the above equations, we get:

$$p_r' = p_\infty\{1+imM_0/M(\tfrac{4}{3}\pi\rho' r^3-m)\}^{-1}\exp(2\sigma'/n_L kTr)$$

When the mass of the solute is much smaller than the mass of the water or $m<<M_o$,

$$p_r' \simeq p_\infty\{1+(2\sigma'/n_L kT)/r - (imM_o/\tfrac{4}{3}\pi\rho' m)/r^3\}$$

or,

$$p_r' \simeq p_\infty\{1+a/r - b/r^3\}$$

where now $a \simeq 3.3X10^{-5}/T$ and $b \simeq 4.3im/M$

The critical radius and supersaturation for the droplet will be:

$$r^* = (3b/a)^{\frac{1}{2}}$$
$$S^* = 1+(4a^3/27b)^{\frac{1}{2}}$$

Vohra and Nair[23] have taken these equations and calculated the stable size in angstroms for these liquid nuclei of aqueous sulfuric acid for various relative humidities starting with sizes in the range of six angstroms for clusters of ten acid molecules. These droplets grow rapidly by coagulation and hydration to an easily detectable size. Their results are reproduced in Table I.

Reiss[24] has done a statistical formulation following the pattern of Frenkel and Zeldovich on the self-nucleation of dilute sulfuric acid-water vapor systems. He obtained a nucleation rate equation of the form:

$$I = \frac{\alpha_c p_a (4\pi R^*_{ab} n_G \Omega_{ab})}{(2\pi M_G kT)^{\frac{1}{2}}} \frac{4\pi R^{*2} n_G \exp(-\Delta G^*/kT)}{2\pi M_a kT}$$

where α_c is the accomodation coefficient, Ω_{ab} is a

TABLE I

STABLE PARTICLE SIZE

NUMBER OF ACID MOLECULES	STABLE PARTICLE SIZE 100% R.H.	60% R.H.
10	6.6	5.5
100	14.5	13.1
200	19.6	16.8
300	23.0	19.3
400	26.1	21.3
500	28.7	23.1
600	31.3	24.5
800	35.7	27.0
1000	40.2	29.2

complicated function of the surface energy of a binary liquid embryo, and n_G refers to the number of moles of the acid(A) and water(B) in the embryo. Doyle's[25] investigation into this rate equation for a binary system indicate rapid nucleation for small partial pressures of sulfuric acid, but this is difficult to verify due to the lack of confidence in vapor pressure data for sulfuric acid in such dilute quanities. Such rapid nucleation can be easily detected in the cloud chamber.

As a final comment on the effects that droplets of sulfuric acid might have in the atmosphere, the sulfuric acid may combine with ammonia by the reaction,

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4$$

to form ammonium sulfate which has been found by Junge[26] to be a major component of the continental aerosol in the large($.1\mu < r < 1\mu$) size range. The sulfuric acid droplets may further react with airborne dust particles to form calcium or magnesium sulfates and with sea-salt particles to form sodium sulfate. The importance of sulfate formation as quoted by Mason[27] is demonstrated by finding that ice and snow in central Greenland has a SO_4^- content about ten times higher than any other soluble component including Na^+ or Cl^- from sea water.

III. EXPERIMENTAL PROGRAM

The equipment and procedure that has been used in this experiment were done in such a way as to maximize the recording and identification of the end products of gas to particle conversions. To this end, the experiment has been kept as clean as possible, and losses of end products in the flow system has been reduced by requiring a compact configuration. The procedure is done in such a way as to maintain efficient operation in coincidence with the irradiation program and cloud chamber cycle.

A. DESCRIPTION OF EQUIPMENT

The equipment used in these experiments may be classified into three categories. These are the optical-irradiation system, gas flow system, and the nuclei counting system. A block diagram of the equipment set-up is shown in Figure 1.

The optical irradiation system is composed of the mercury light source, monochromator, irradiation cell, photomultiplier tube and recorder. The light source is a Hanovia 5000 watt mercury-xenon compact arc lamp with a spectral range of 2000-14,000 angstroms, and it is run at 4000 watts by a power supply capable of delivering a maximum of 60 volts at 90 amperes which is necessary for stable lamp operation. The McPherson 0.3 meter scanning monochromator operates between 1050-10,000 angstroms. It has a resolving power of 95% of the theoretical, and can

FIGURE CAPTION

Figure 1. Block Diagram of Experimental System. Items are as listed:

A. Mercury-Xenon Compact Arc Lamp

B. Monochromator

C. Irradiation Cell

D. Photomultiplier Tube

E. Chart Recorder

F. Gas Bottles consisting of Nitrogen, Oxygen, Sulfur dioxide, and Nitrogen dioxide.

G. Mixing Chamber

H. Filter

I. Flowmeter

J. Cloud Chamber

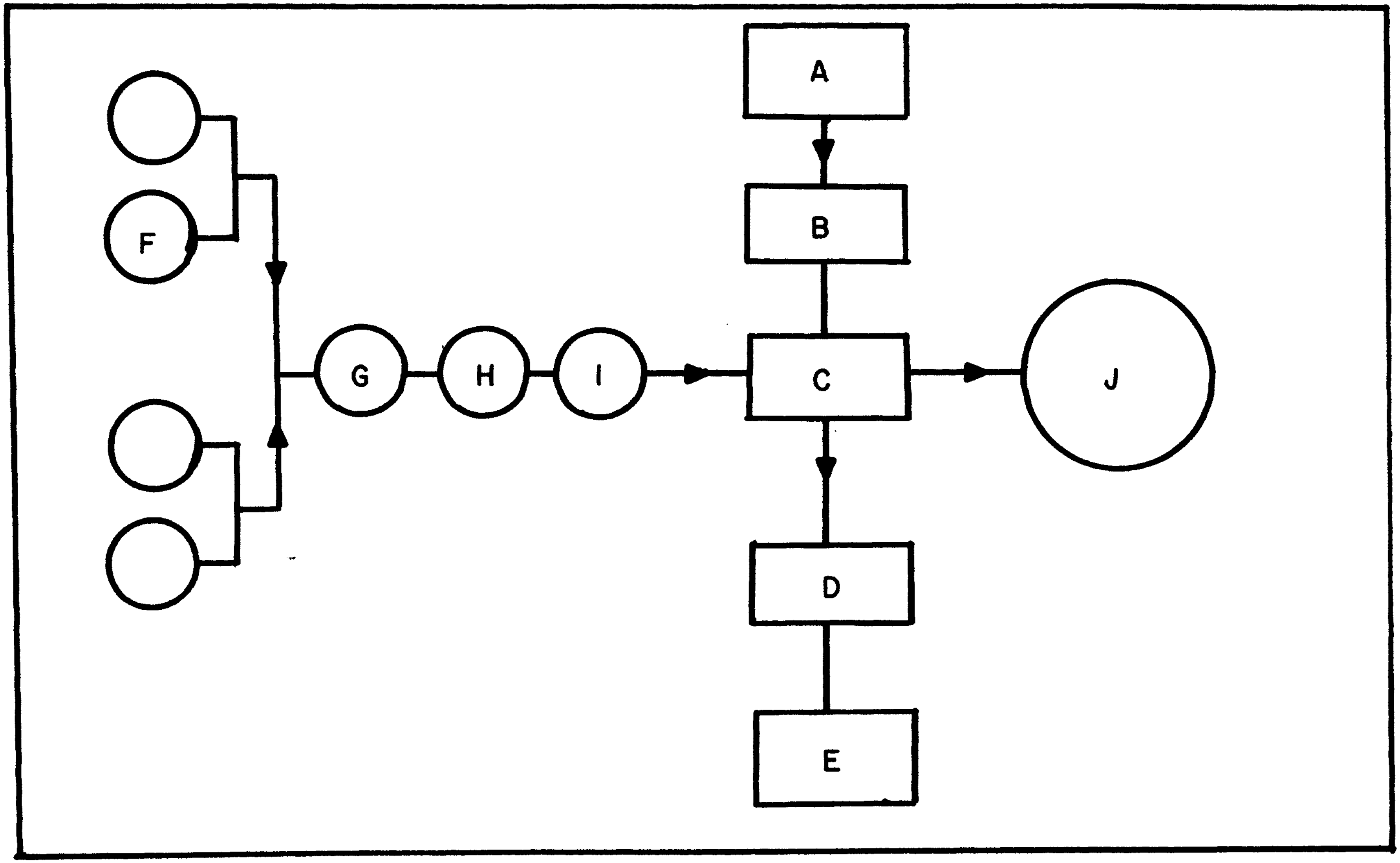

Figure 1. Block Diagram of the Experiment

give a resolution of 0.6 angstroms. Calibration using a known spectral source indicates it is accurate within one angstrom. The irradiation cell is a pyrex tube 61 cm. long and 3 cm. in diameter. Both ends of the tube are made from suprasil quartz windows made by Amersil Quartz. The inner diameter of the outlet of the tube which is so arranged that a nearly straight path is provided for the gas to enter the cloud chamber, minimizing diffusion losses which depend upon the tube inner diameter, length, and gas flow rate. The photomultiplier tube is a RCA IP28 nine stage tube which has a wavelength of maximum response at 3400±500 angstroms. This tube being connected to the chart recorder can give an indication of the light absorption inside the cell by measuring the drop in tube current as a function of wavelength. This is a means of checking for the possible production of certain molecular species that absorb radiation in the wavelength interval of interest.

The gas flow system is composed of the gas bottles, vernier needle control valves, mixing chamber, flowmeter, and absolute nuclei filter. The gases are all Matheson Research Grade or better(greater than 99.5% purity). In order to accurately control the flow of the gases, Nupro stainless steel micrometer needle control valves were used. These have the advantage of being able to preselect a precise flow rate that may be desired. The mixing chamber is a 2.1 liter steel cylinder used to thoroughly mix all gas components before entry into the adjacent tubes leading to the irradiation cell. The absolute nuclei filter is a Mine Safety Appliance Co. "ultra-filter" with a collection efficency of 99.9% on 0.3μ diameter particles. The flowmeter is a Matheson low range flowmeter capable of accurately measuring gas flow rates between 1 to 50 cubic centimeters per minute.

The absolute Aitken nuclei counter is a Wilson type expansion cloud chamber capable of producing supersaturation ratios from 1.30 to 4.00. A complete description of the cloud chamber system is given by J.L. Kassner Jr. *et al*[28]. A cut-away drawing of the cloud chamber itself is shown in Figure 2.

B. EXPERIMENTAL PROCEDURE

As a first step to ascertain the effect of monochromatic irradiation upon the gas sample contained in the irradiation cell, a static irradiation test was performed. The following procedure was used. The system was briefly connected to the vacuum and the instruments were turned on for a warm up period. A fresh gas mixture was then allowed to fill the irradiation cell. The scanning speed was set at 100 angstroms per minute and the initial wavelength was set on the monochromator. The recorder and scanning are commenced with careful marking of the initial wavelength on the recording paper. When the end of the wavelength interval is reached, the electrometer which serves as a

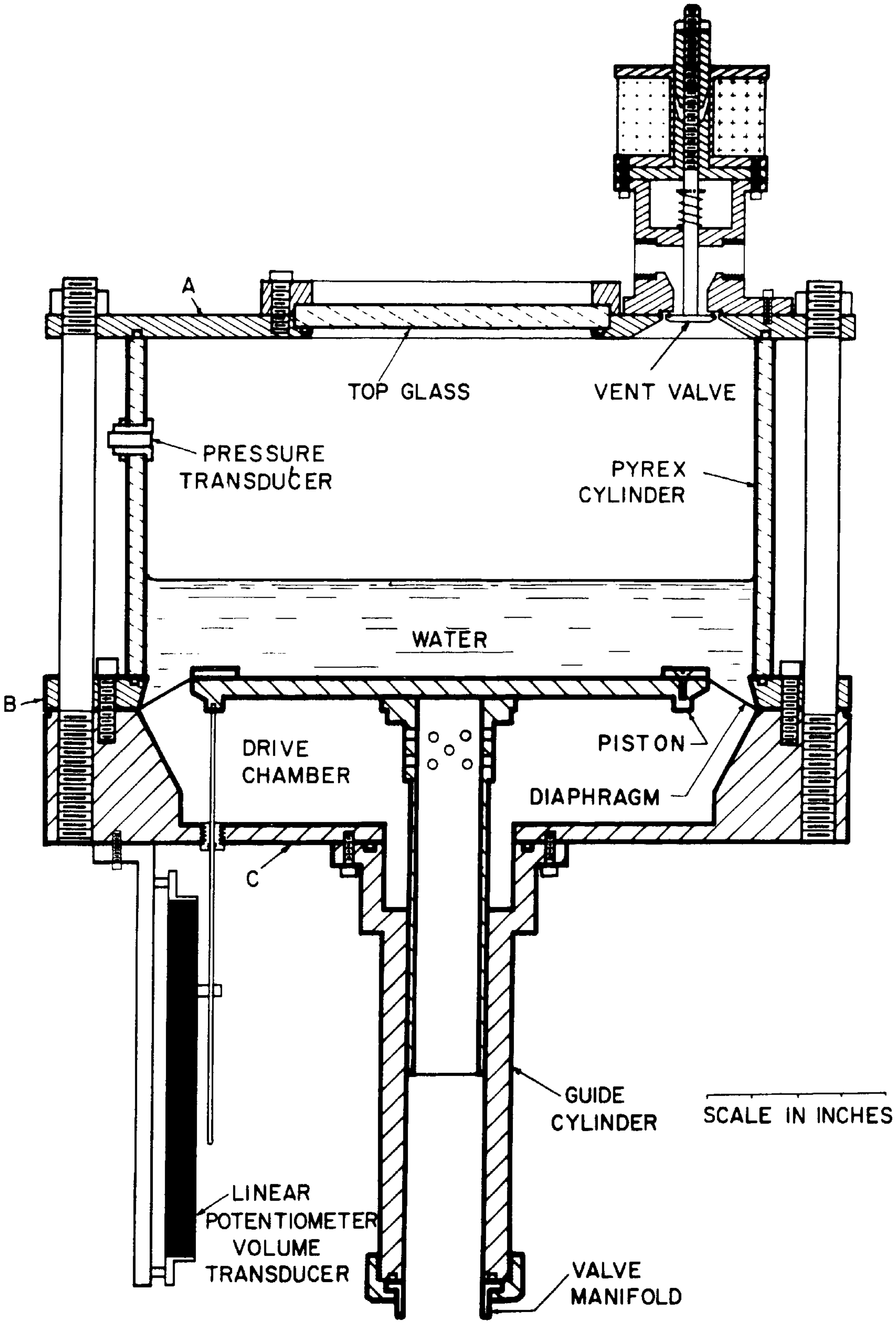

Fig. 2. Drawing of Cloud Chamber.

unity gain preamplifier for relaying the photomultiplier tube current output losses to the chart recorder, is turned off immediately, and then the recorder and the monochromator. Finally, the system is again evacuated. A calibration of the chart speed and scanning speed gives a very accurate determination of wavelength for the peaks which are recorded by measuring the distances in centimeters from the initial scanning point on the chart recorder paper.

In this manner with several gas mixtures, a visual determination of the photochemical reactions taking place can be observed. Also, by noting the characteristic absorption peaks, the identification of the molecular species undergoing the reaction is possible. The identification of the components may be used to eliminate specific chemical reactions or to judge their role in leading to particulate formation.

In the second stage of the experimental program, nuclei resulting from irradiation of the incoming gas sample with specific wavelengths will be initiated. However, first some preliminary considerations of the cloud chamber's preparation will be described. The cloud chamber is filled with fresh doubly distilled water and sealed. The chamber is then flushed with the gas which will serve as the condensing phase for the particular experimental run that is scheduled. Except for the initial run with sulfur dioxide which used nitrogen, the gas is "artificial air" composed of

80% nitrogen and 20% oxygen. The optical system is turned on with the monochromator already set at the initial wavelength to be used. The appropriate gas or gas mixture is selected and allowed to fill the irradiation cell. During this time the high pressure compact arc lamp had been turned on, and its power is being raised to its operating value of 4000 watts. The monochromator is set at a wavelength outside the absorption system of the gas under consideration. These wavelengths are 3500 angstroms for SO_2 and 4100 angstroms for NO_2. The gas sample is irradiated for fifteen minutes. The cloud chamber cycle is begun with the subsequent introduction of a sample of the irradiated gas into the chamber. A supersaturation spectrum at this wavelength is taken by counting the number of droplets formed at each different expansion ratio determined by the chamber sequence programmer. When this is finished, the cell is evacuated and a fresh gas is introduced. The monochromator is now set sequentially at a wavelength in the strong absorption system of NO_2 and SO_2. These wavelengths are 3660 and 3025 angstroms respectfully. After the experiments the camera which has been recording the droplet formation is removed and the film developed. The droplets are then counted from the negatives by projecting the images upon a screen containing a grid which determines the droplet count per cubic centimeter. The experimental program is summarized in Table II including the wavelengths and purpose of the run.

TABLE II.

EXPERIMENTAL SUMMARY

GAS MIXTURE	WAVELENGTHS	PURPOSE
SO_2	3500A	Nucleation due to SO_2+H_2O ?
	3025A	Nucleation due to $SO_2^*+H_2O$?
$SO_2+O_2+N_2$	3500A	Possible O_3 reactions?
	3025A	Same
NO_2	4100A	Nucleation due to NO_2+H_2O ?
	3660A	Nucleation due to $NO+O+H_2O$?
NO_2+SO_2	4100A	Nucleation due to $NO_2+SO_2+H_2O$?
	3660A	Formation of sulfuric acid ?

IV. DISCUSSION AND PRESENTATION OF RESULTS

A. REACTANT IDENTIFICATION

In the first part of this experiment, the goal was the identification of the reactants which form due to photochemical reactions. This identification of the reactants from various gas mixtures was accomplished through the examination of the absorption of specific wavelengths which can be displayed through a current drop in the transmitted beam traced on the chart recorder.

Fig. 3 displays the absorption as a function of wavelength for an interval between 4000 and 2900 angstroms for the irradiation of SO_2. The first peak occuring at 3965 angstroms is attributed to the calcium oxide present in the quartz windows of the irradiation cell. The next seven peaks represent strong absorption lines of SO_2 with the 3025 peak being the most important. It is evident then that the SO_2 in the irradiation cell is being excited by the reaction:

$$SO_2 + h\nu(3400\text{-}2900A) \rightarrow SO_2^*(^3B_1)$$

Fig. 4 is a graph of the absorption spectrum of a mixture of SO_2,N_2, and O_2 in equal proportions. Again the calcium oxide line is present. Also, two lines representing absorption by molecular nitrogen are present; these are the 3596 and 3371 angstrom lines. This spectrum has a major line at 3530 angstroms. The wavelength tables indicate that this is due to the presence of ozone. This would tend to

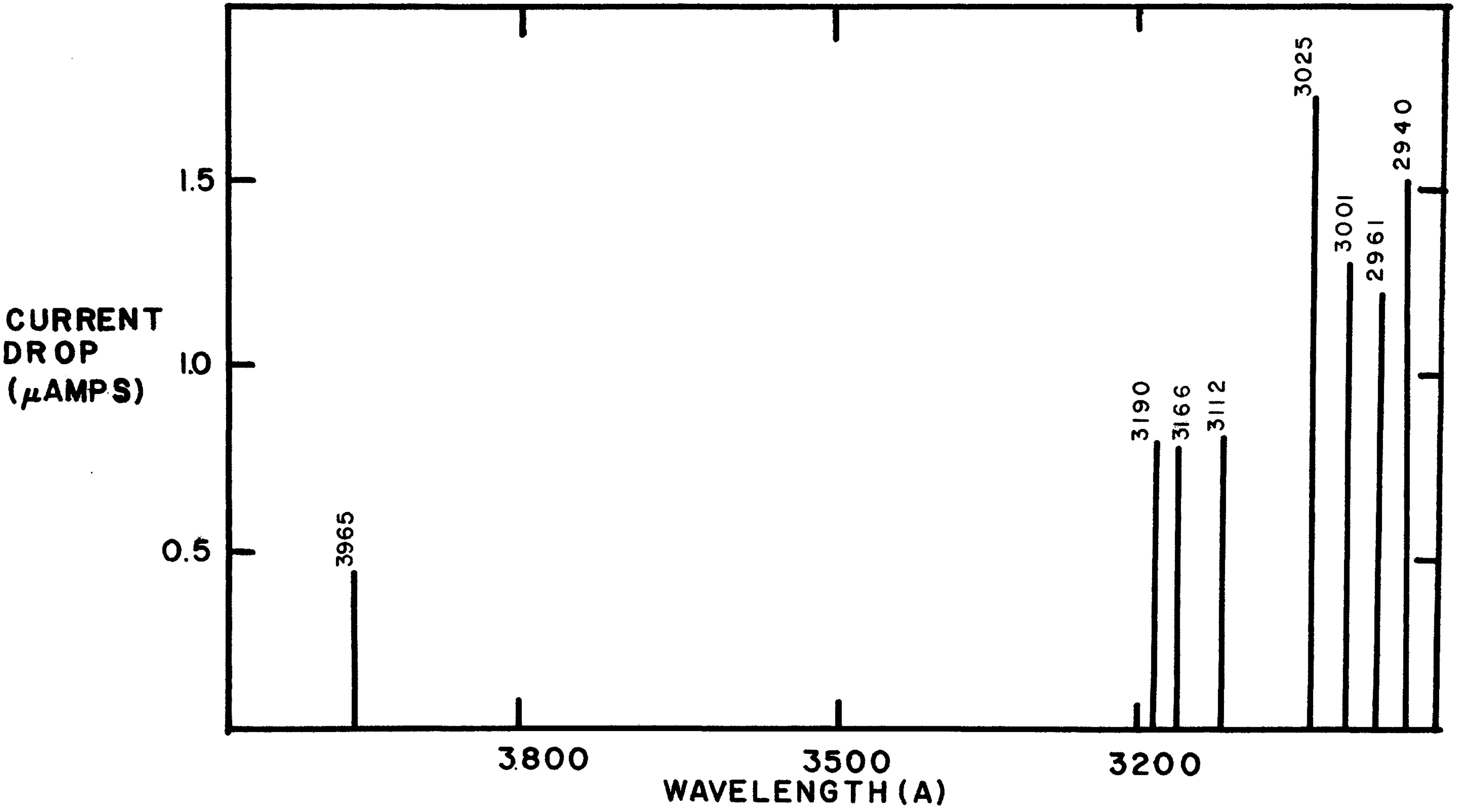

Figure 3. Absorption Curve of SO_2

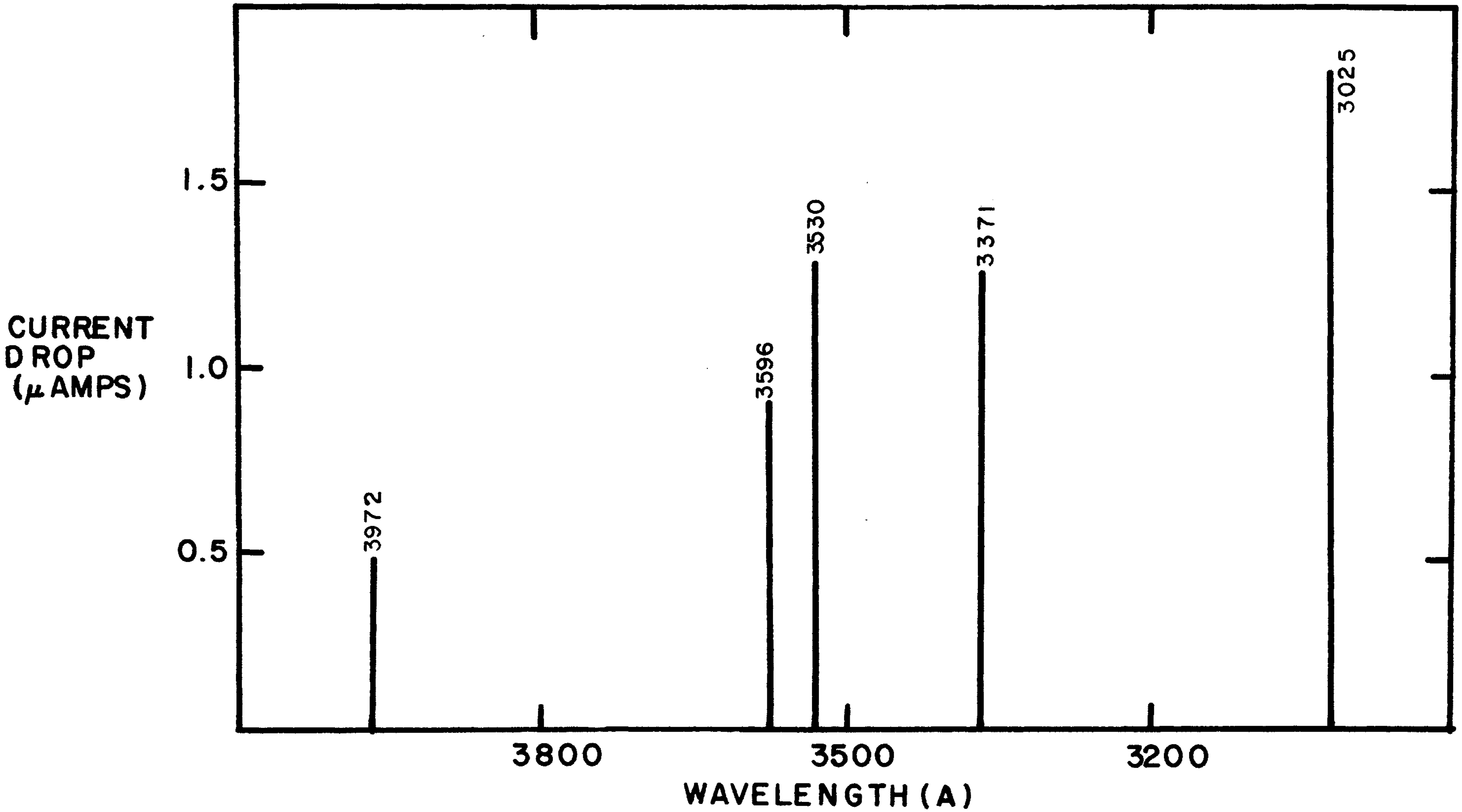

Figure 4. Absorption Curve of SO_2-O_2-N_2

support a proposal by Blacet[29]:

$$SO_2^*+O_2 \rightarrow SO_3+O \rightarrow SO_4$$

$$SO_4+O_2 \rightarrow SO_3+O_3$$

Also, the 3025 angstrom line appears indicating excited SO_2. Molecular oxygen shows no absorption spectra above 2595 angstroms.

Fig. 5 shows the absorption spectrum of pure NO_2. The wavelength interval for this gas or a mixture of it is between 4100 and 2900 angstroms. In this spectrum four major peaks are observed. The 4047 and 3130 angstrom peaks identifying the presence of NO_2 as expected are seen; in addition to these, there are the lines at 3648 and 3331 angstroms. These peaks indicate absorption by nitric oxide. The reaction that is taking place in the irradiation cell is:

$$NO_2+h\nu(\lambda<3660A) \rightarrow NO+O(^3P)$$

The atomic oxygen may now react with SO_2 to form SO_3. The SO_3 may then react with water to form sulfuric acid vapor.

Fig. 6 shows the absorption spectrum for a mixture of equal parts of sulfur dioxide and nitrogen dioxide between 4100 and 2900 angstroms. There are three peaks; the first is the 4047 angstrom peak again indicating strong absorption of NO_2. The 3585 angstrom peak identifies NO absorption. The last peak is at 3460 angstroms which is a strong absorption peak for SO_3. This spectrum is also interesting in what it does not show. The 3130 and the 3025 angstrom

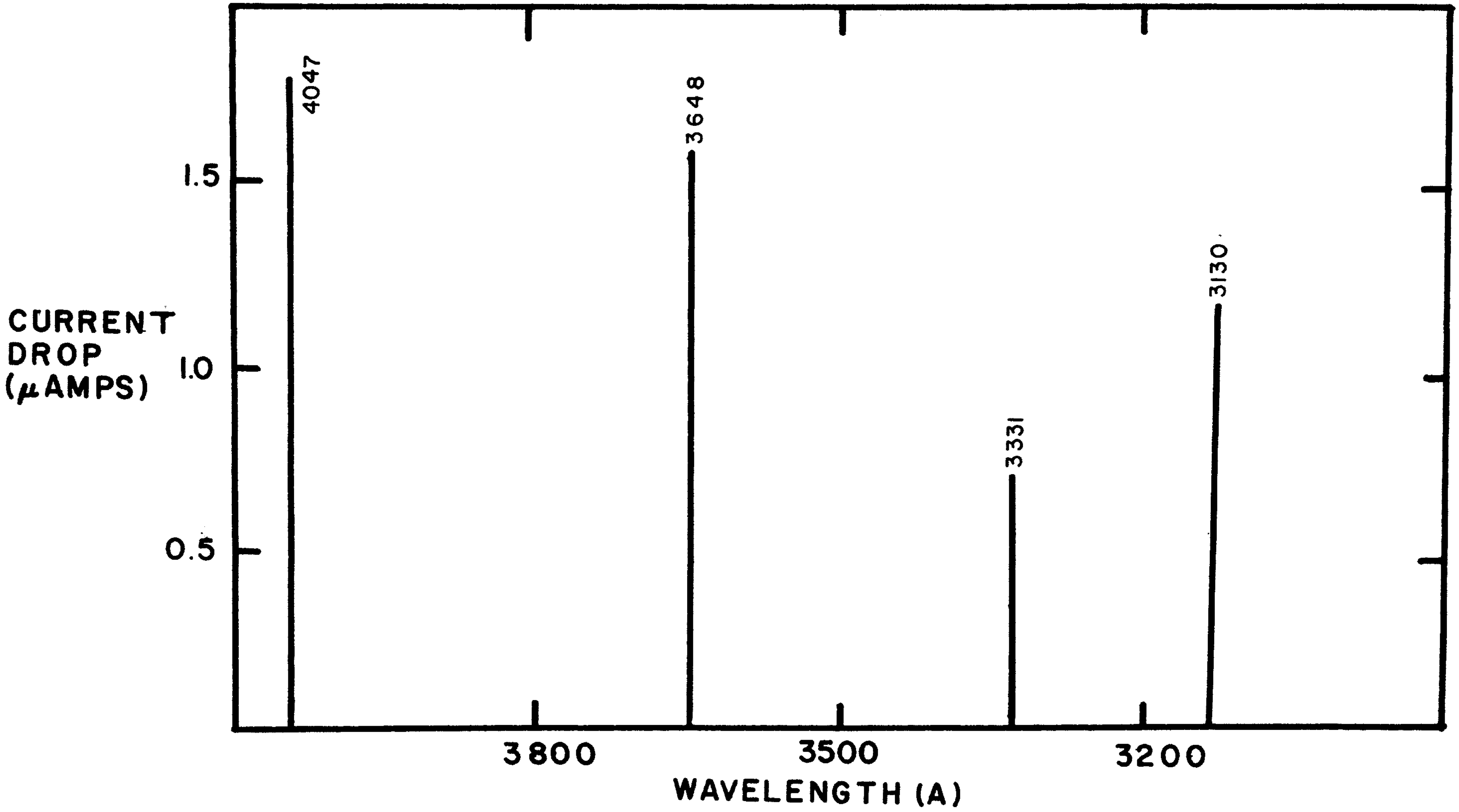

Figure 5. Absorption Curve of NO_2

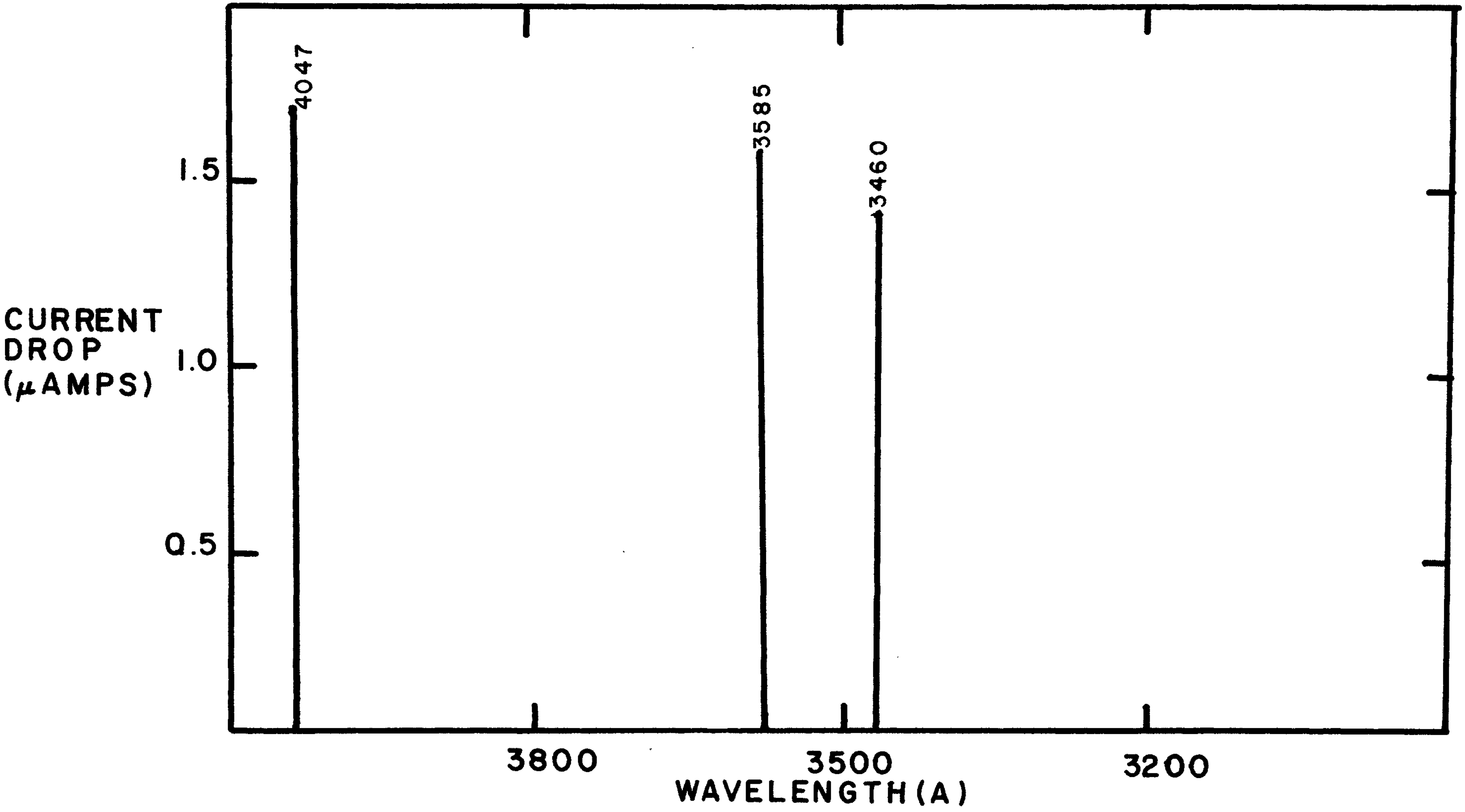

Figure 6. Absorption Curve of NO_2-SO_2

lines are missing. This would seem to indicate that when SO_2 and NO_2 are in equal proportions and exposed to radiation between 4100 and 2900 angstroms, the end result will be NO and SO_3. Sulfur trioxide may then react directly with water vapor to form sulfuric acid. The nitric oxide may be removed by the following reactions:

$$NO+O_2 \rightarrow NO_3$$

$$NO_3+NO_2+M \rightarrow N_2O_5+M$$

$$N_2O_5+H_2O \rightarrow 2HNO_3$$

However, the exact removal mechanism for NO is in doubt; and such a suggestion may be viewed as speculative.

B. PHOTONUCLEATION RESULTS

The purpose of the second stage of the experiment was to identify with the aid of the results of part one the probable end products of the gas to particle conversions produced by monochromatic radiation.

The first experimental run used sulfur dioxide as the impurity gas, and nitrogen was used as the condensing gas inside the cloud chamber. Fig. 7 shows the results of the irradiation of sulfur dioxide at 3025 angstroms. The results show clearly that there is little nucleation taking place. Results at 3500 angstroms ran between ten and twenty five droplets per cubic centimeter. It could be possible that the sulfur dioxide reacts with trace amounts of oxygen in its excited state to form sulfate radicals which eventually lead to sulfur trioxide formation causing

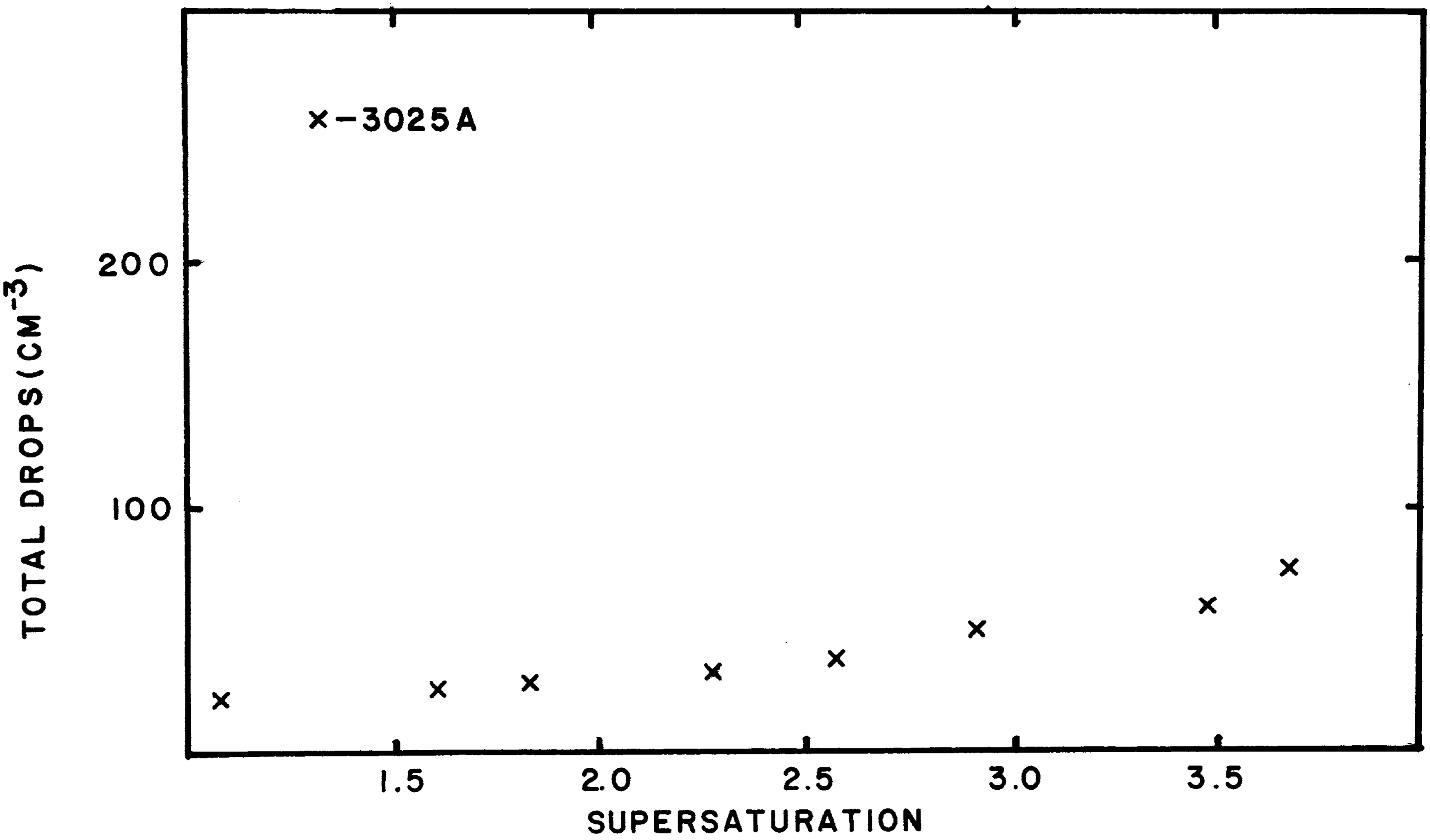

Figure 7. Supersaturation Spectrum of SO_2

sulfuric acid droplet formation. It also appears that neither excited nor ordinary sulfur dioxide and water vapor alone contribute significantly to nuclei production.

The next experimental run had sulfur dioxide, oxygen, and nitrogen in equal proportions for the impurity gas mixture with the "artificial air" as the gas inside the cloud chamber. In this case, as shown in Fig. 8, a more numerous droplet count was found which might indicate a greater efficency in photochemical particulate production. However, since the probable error in droplet counting is equal to the square root of the number of droplets counted, a large number of droplets must be counted to reduce the possible error in determining whether photochemical reactions are responsible for the higher droplet count at 3025 angstroms. Spectrographic evidence indicates the possibility of ozone participating in the production of nuclei. However, the results would tend to confirm that any ozone reactions would be slow and contribute little to the overall nucleation rate.

The third experimental run used nitrogen dioxide as the impurity gas with the "artificial air" as the condensing gas inside the cloud chamber. A higher droplet count than previously found probably indicates that nitrogen dioxide is more reactive with water vapor and molecular oxygen than sulfur dioxide. Fig. 9 shows that there is a difference larger than experimental error between the two sets of data.

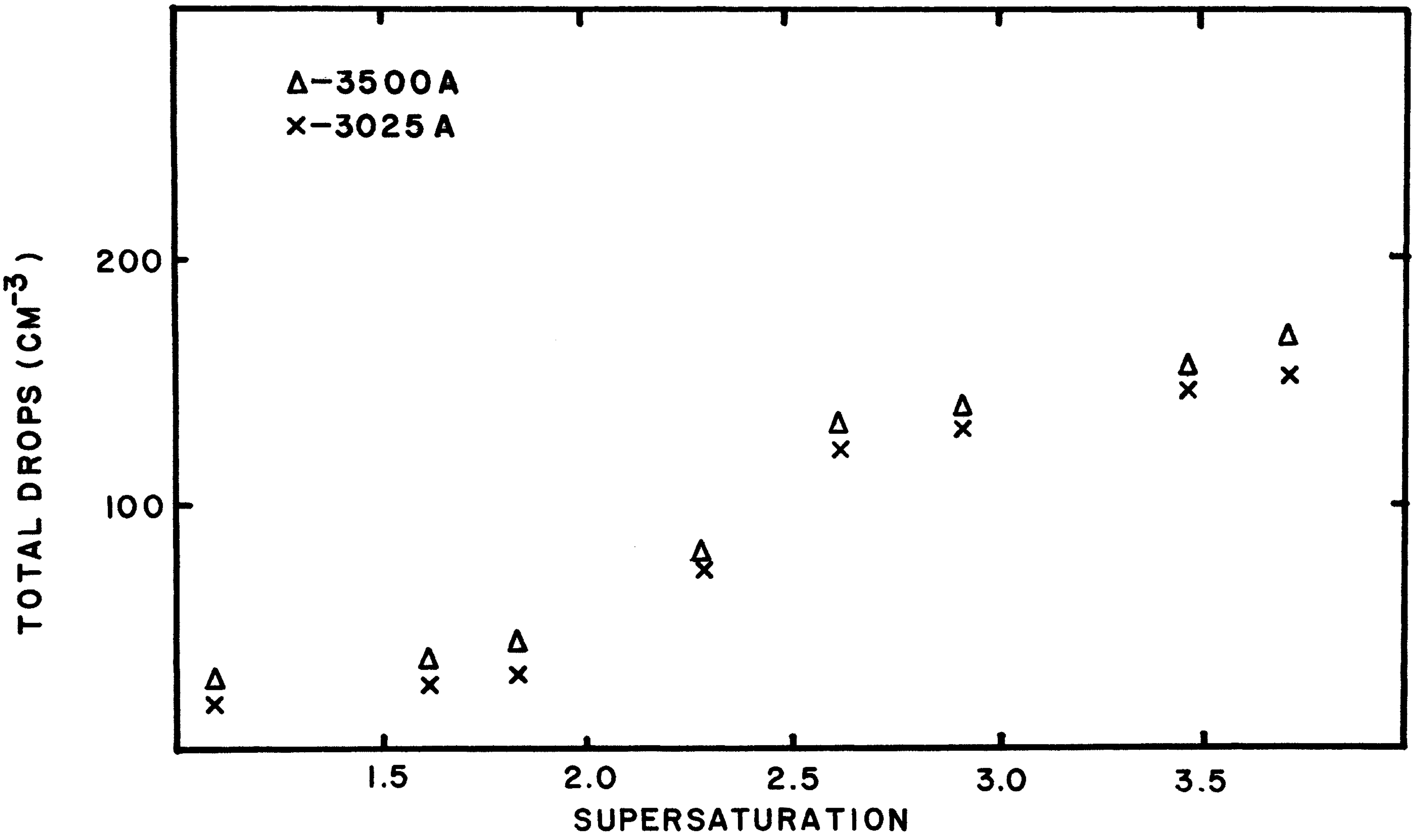

Figure 8. Supersaturation Spectrum of SO_2-O_2-N_2

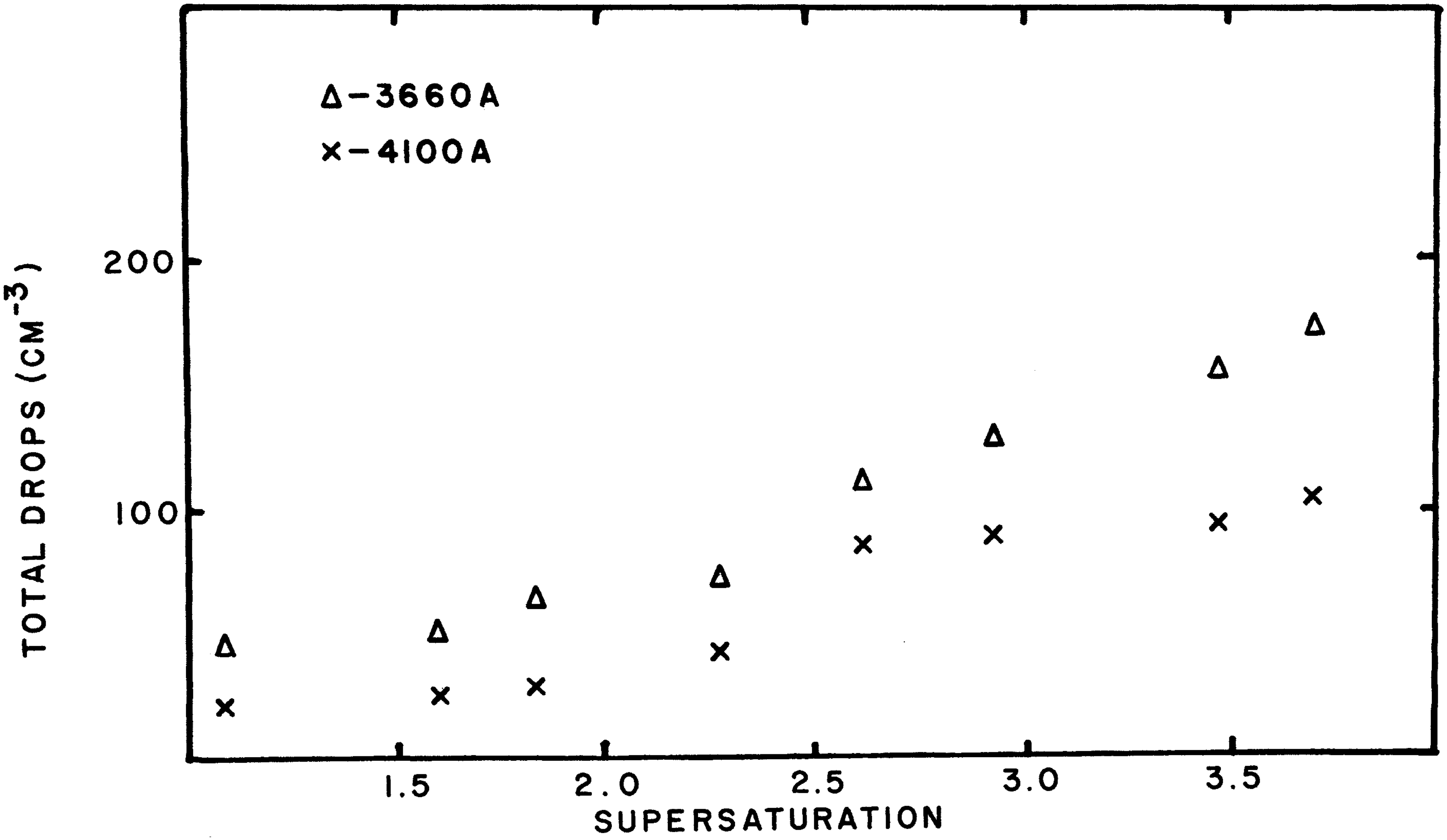

Figure 9. Supersaturation Spectrum of NO_2

The higher droplet count at 3660 angstroms is most likely due to the atomic oxygen which has been dissociated from the nitrogen dioxide molecule starting the following reactions:

$$NO_2+O \rightarrow NO_3$$

$$NO_3+NO_2 \rightarrow N_2O_5$$

$$N_2O_5+H_2O \rightarrow 2HNO_3$$

However, the intermediate reactions leading to the formation of nitrogen pentoxide are relatively slow thereby restricting rapid nucleation.

Fig. 10 shows the results of the last experimental run in which equal proportions of sulfur dioxide and nitrogen dioxide were used as the impurity gas with the "artificial air" again being used as the gas inside the cloud chamber. The droplet count due to irradiation at 4100 angstroms is relatively high compared to previous results. This higher count may be due to two effects. One, the end result of a reaction between the two gases could be hygroscopic or second; an additive effect of the reactions of the two gases with the water vapor and molecular oxygen found inside the cloud chamber. The latter scheme is the more probable of the two.

The droplet count due to the 3660 angstrom radiation is about four times greater than that due to the 4100 angstrom radiation. In this case, the reaction scheme appears to be clear. The atomic oxygen after being dissociated from the nitrogen dioxide molecule reacts with

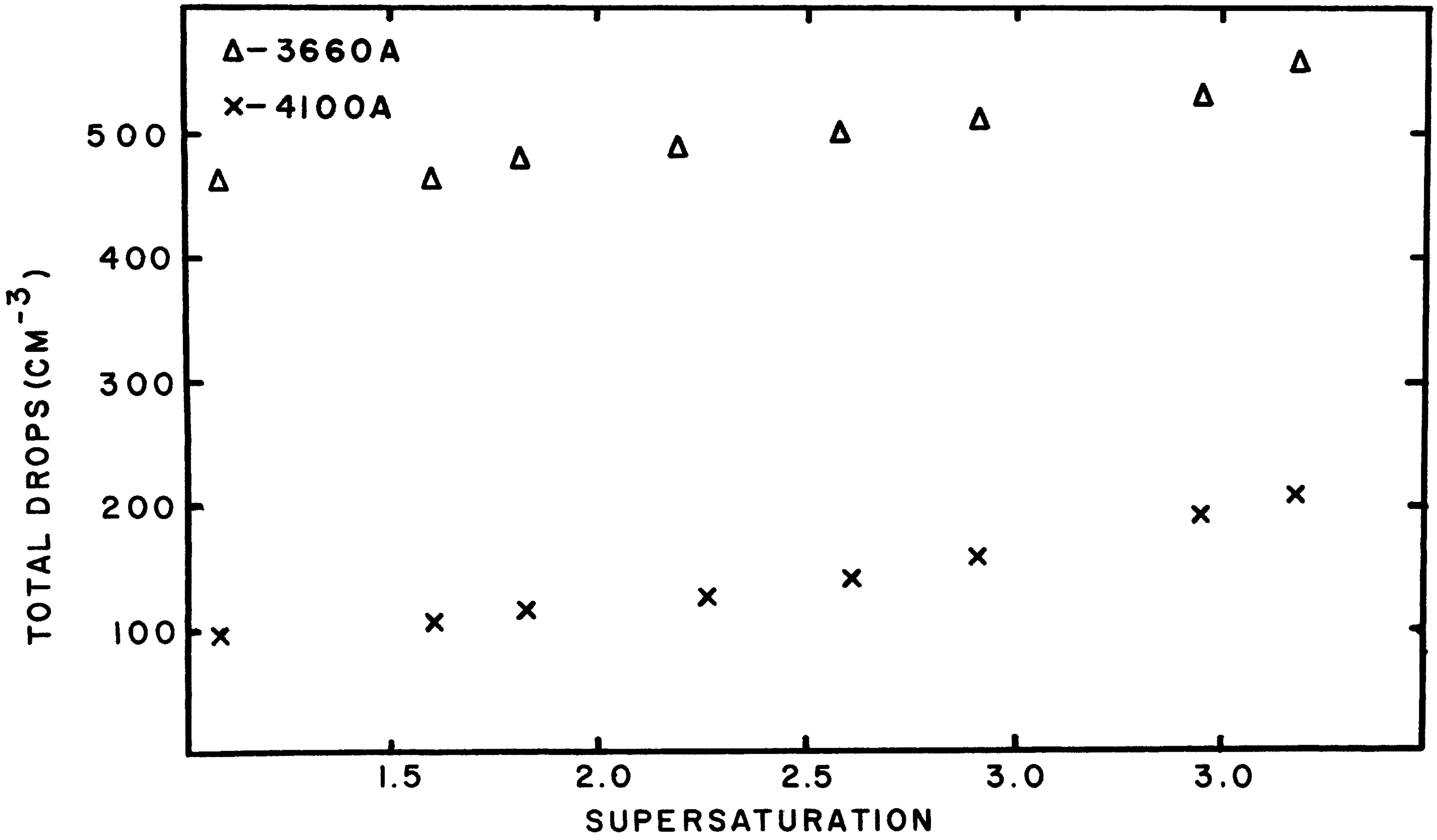

Figure 10. Supersaturation Spectrum of NO_2-SO_2

available sulfur dioxide molecules to form sulfur trioxide which then reacts with water vapor to form sulfuric acid droplets. The great number of droplets formed is an indication that this reaction chain is both fast and efficient. There is probably an additional number of droplets formed as a result of the reactions involving nitric oxide leading to formation of nitric acid droplets.

V. CONCLUSIONS

These experiments tend to confirm that sulfur dioxide by itself is not responsible for the production of large numbers of nuclei. This confirms the opinions of workers such as Roddy and Leighton. Many felt that sulfur dioxide had to have a reaction partner in order to enhance nuclei production. These experiments confirm this since neither sulfur dioxide nor nitrogen dioxide alone produced copious nuclei. Nitrogen dioxide was found to be the primary reaction partner of sulfur dioxide at wavelengths less than 3660 angstroms due to the creation of atomic oxygen by dissociation.

These experiments seem to suggest that for a short-term solution to air pollution that a decrease in nitrogen dioxide emissions would be in order. However, elimination of nitrogen dioxide might adversely affect the removal mechanism of sulfur dioxide and other components found in the atmosphere. Many pollutants are removed by the scavenging effect of rainfall, and the effect of sulfur dioxide and nitrogen dioxide on producing rain by providing additional nuclei or lowering of the critical activation supersaturation of existing nuclei for droplet growth might be substantial in the urban atmosphere.

The study is incomplete since hydrocarbons of the terpene and olefin family were not included, and studies of American smog especially in the Los Angles area show that hydrocarbons play an important role in smog creation. Without an overall reduction in the three major pollutants of sulfur dioxide, nitrogen dioxide, and hydrocarbons as opposed to reduction in just one; the choice would be between an "acidic" or dirty environment rather than a clean one.

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