GCA-TR-71-4-N

AE MASS SPECTROMETER ANTECHAMBER STUDY

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FINAL REPORT
Tasks 1 and 2
Contract No. NAS5-11368

Prepared for
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GODDARD SPACE FLIGHT CENTER
Greenbelt, Maryland

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ABSTRACT

The formation of CO_2 and H_2O in a gold plated antechamber has been investigated if a beam of oxygen is introduced. It has been found that at room temperature the formation of CO_2 and H_2O is negligibly small. However, at the top temperature (197°C), which could be achieved with the existing system, both products have been formed in significant quantities. Desorption of CO_2 and H_2O at this temperature is still slow and incomplete which accounts for the delayed response to the beam conditions. Although the catalytic reactions take place already with molecular oxygen, the reactions are significantly enhanced if the oxygen beam is partially dissociated.

SECTION 1

INTRODUCTION

The objective of the work under this contract was to investigate the effects of increased antechamber temperature on the absorption and desorption of CO_2, H_2O and O. This investigation had to be performed with the Atomic Beam System which was developed under contract NAS5-9188. For this investigation it was necessary to build a small oven around the antechamber and to attach a thermocouple to measure the temperature. The Atomic Beam System has been described in detail in the final report of the above mentioned contract or in the GCA Technical Report 70-4-N. Therefore only the modifications made under the new contract NAS5-11368 will be described here. The appendix contains a brief excerpt from the part of the above mentioned report which relates to the description of the instrument.

SECTION 2

MODIFICATIONS OF THE ATOMIC BEAM SYSTEM

It was found previously, that the degree of dissociation of oxygen depends very strongly on trace impurities in the gas stream. For instance, water vapor, nitrogen and sulfur hexafluoride increase the dissociation and hydrocarbons reduce the concentration of atomic oxygen. In the previously used atomic beam system, the concentrations of these trace impurities were not sufficiently under control. The discharge tube and reaction chamber were assembled from several pieces of pyrex pipes connected together with viton-A "O" ring seals. It is expected that some atomic oxygen was absorbed by the viton or reacted with hydrocarbons released from it. Therefore, a new inlet system was built from one single piece of pyrex pipe, thus eliminating all viton gaskets. Only one teflon gasket has been used to connect the discharge tube to the capillary array and the stainless steel vacuum chamber. Two inlets have been provided to the discharge tube: one for pure molecular oxygen, the second one for a controlled amount of a trace impurity which is added to enhance the dissociation. Both inlet lines are equipped with cold traps in order to remove water vapor and hydrocarbons. The ball type flow meter, which was previously used to measure the flow rate of the trace impurities, did not have sufficient sensitivity and accuracy. It has been replaced by the Pace flow meter, which was previously used to measure the NO_2 flow. The chemical titration technique has been abandoned since the degree of dissociation is well reproducible and can be measured adequately with the mass spectrometer if an open ion source is used. Elimination of the reaction chamber permits bringing the microwave discharge closer to the effusion nozzle, thus reducing losses of atomic oxygen due to recombination and absorption. The thermocouple manometer, which as been used previously to measure the pressure before the effusion nozzle, has been also eliminated, since it is not really necessary and might have contributed to some losses of atomic oxygen.

The sublimation pumps and the orb ion pump had to be disassembled to replace the filaments. Since the titanium deposits on the walls started to peel off, a general cleaning was required. The ultra-high vacuum flanges have lost the perfect finish essential for any ultra-high vacuum work because of the large number of bakeouts during the past five years. It was now much more difficult to get the old system vacuum tight. Nevertheless, it was finally possible to achieve in the main chamber, where the mass spectrometer ion source is located, a background pressure of 8×10^{-10} torr. Extreme care has been used to eliminate minute air leaks in the inlet system and to prevent any trace amount of nitrogen to be present in the oxygen stream. The release of methane from the titanium sublimation pumps was reduced to a tolerable amount by keeping the filaments slightly below sublimation temperature whenever the instrument was idling. Nevertheless, the background gas consisted predominantly of methane. A very small amount of fluorine was released from the gold electrodes of the ion source where it had been absorbed previously during work with sulfur hexafluoride.

SECTION 3

PERFORMANCE OF THE MODIFIED ATOMIC BEAM SYSTEM

The dissociation of molecular oxygen was investigated with a 90-degree magnetic mass spectrometer equipped with an open ion source which has been described in the second interim Final Report, GCA-TR-69-14-N. If ultra-pure oxygen from the Baker Corporation is introduced directly and the discharge tube is cooled with a fan, then 6.4 percent of molecular oxygen are dissociated. If the trap in the inlet gas line is cooled with liquid nitrogen, the dissociation drops down to 1.8 percent. This is an indication that trace amounts of impurities (probably water vapor) had enhanced the dissociation. The cleanest way to enhance the dissociation is to switch the fan off and wait about a minute until the new equilibrium temperature of the discharge tube is reached. The increased plasma temperature produces a dissociation of 3.1 percent.

Dissociation enhancement by water vapor is difficult to control. Instead, enhancement by hydrogen has been investigated. The advantage is that hydrogen can be introduced through a trap cooled with liquid nitrogen and the amount of hydrogen can be accurately measured with the flow meter. When the discharge is switched on, this hydrogen reacts in the discharge and water vapor is formed. A maximum dissociation of 7.7 percent is achieved if the 18 peak is 2 percent of the 32 peak. Dissociation of water vapor in the ion source produces a small fragment peak at mass 16 which contributes to the observed 16 peak. However, experiments with pure water vapor have indicated that the resulting 16 peak is less than 1 percent of the 18 peak. Since the 18 peak is only 2 percent of the 32 peak, the contribution to the 16 peak from dissociation of water vapor in the ion source is negligibly small. For most applications, enhancement of the dissociation of oxygen by hydrogen is a simple, reliable, and well-reproducible method which causes only a very slight increase of the background partial pressure of water vapor which can be easily removed by bake-out. However, for the investigation of the formation of H_2O by catalytic reaction of H_2 and atomic oxygen, the increased partial pressure of H_2O would represent an undesirable complication. In this case, enhancement of the dissociation by sulfur hexafluoride has been utilized. Here, the traps in the inlet lines are cooled with dry ice to eliminate water vapor without removing sulfur hexafluoride. Under these conditions, a maximum dissociation of 10.3 percent of the O_2 beam has been achieved (see Figure 1). Normally, the shutter in front of the antechamber has been kept closed during the pre-conditioning of the discharge tube with sulfur hexafluoride, in order to keep the contamination of the antechamber to a minimum. After this conditioning process, a degree of dissociation of 7 percent can still be achieved even after the sulfur hexafluoride gas flow has been stopped. It should be emphasized that, with the open ion source, the response to the shutter movement is instantaneous (see Figure 1) and

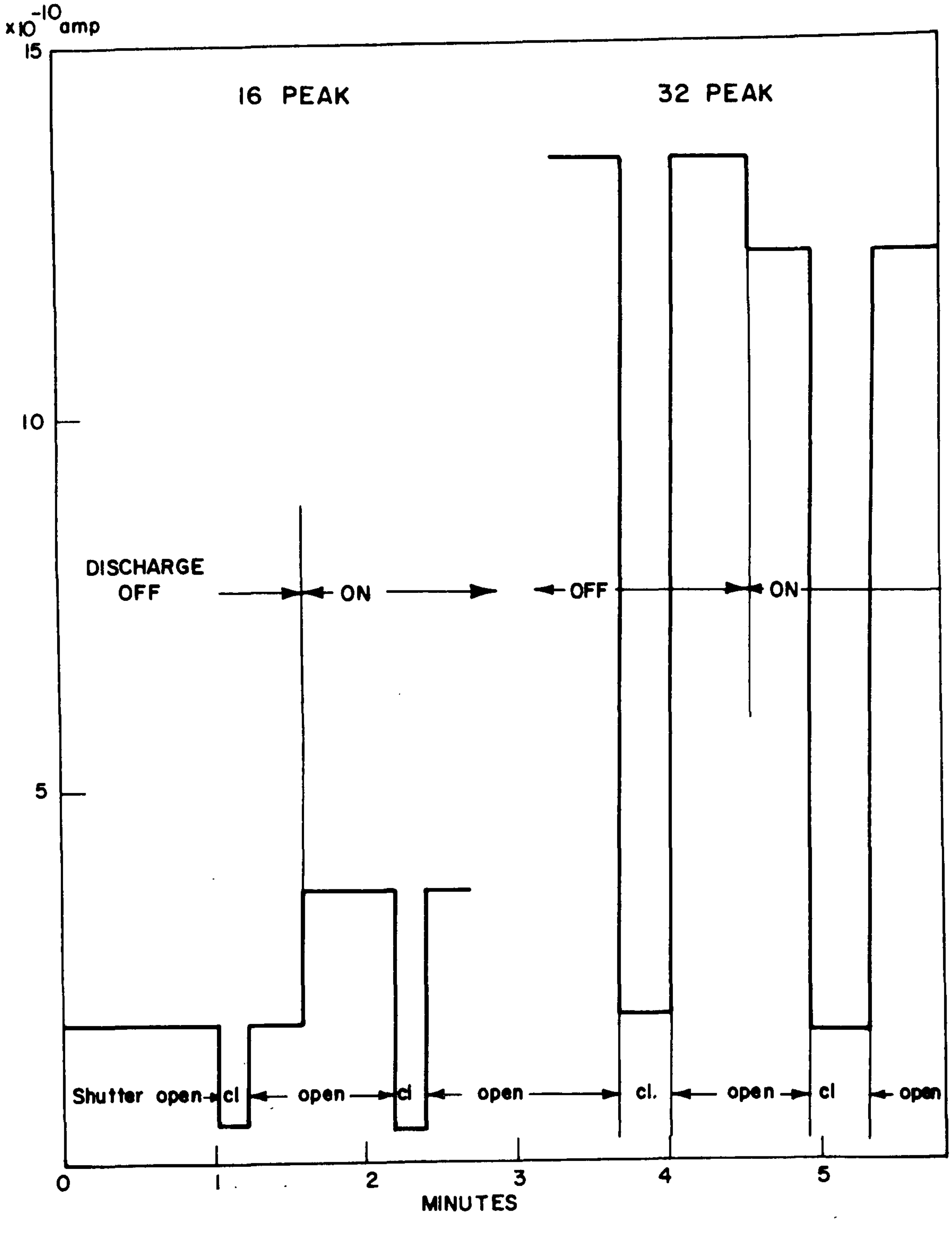

Figure 1. $O_2 + SF_6$ Beam, open ion source.

the reduction of the 32 peak when the discharge is turned on corresponds to the increase of the 16 peak if the different ionization cross sections and mass spectrometer transmissions are taken into account.

The elimination of the Viton O-rings resulted in a much cleaner beam which was demonstrated by investigation of the 44 peak. Previously, (see Figure 14 of GCA-TR-70-4-N, Section III) the CO_2 background increased from 0.5×10^{-3} of the 32-peak to 6×10^{-3} if the discharge was switched on. At present, the CO_2 background stays at 0.5×10^{-3} of the 32 peak and does not increase after the discharge is switched on. There is no detectable amount of CO_2 in the beam.

The H_2O background is also significantly reduced. A very small dependence on the discharge and on the shutter position is still visible. It is possible that a trace amount of water vapor is released from the walls of the pyrex glass discharge tube, especially if it is heated by the discharge. However, the variations of the 18 peak are negligibly small compared with the expected effect of the catalytic reaction to be investigated later.

SECTION 4

PROVISIONS FOR HEATING THE ANTECHAMBER

A small oven has been built and installed around the gold antechamber. The heating element was originally an iridium wire of 5 mil diameter and approximately 20 inches long. Iridium has been chosen because it resists oxidation. It is insulated from the antechamber by ceramic tubings mounted in a block of aluminum. This insulation is adequate for the small voltage drop along the wire but insufficient for the full ion accelerating voltage, usually 480 volts. Therefore an external insulation transformer had to be used.

A thermocouple wire has been attached to the entrance flange of the antechamber. The output voltage of the thermocouple has been calibrated against the temperature inside the antechamber, measured by a mercury thermometer. After this calibration, the thermometer has been removed and the antechamber with the San Marco ion source installed in the atomic beam system. After a few initial mass spectra have been taken, the instrument has been baked and the small oven was kept switched on overnight. Unfortunately in the morning the filament was burned out and all electrodes of the ion source had very low resistance to ground. Disassembly of the instrument and visual inspection revealed that the iridium deposits on the vacuum feedthrough connectors have spoiled the insulation. Complete disassembly was necessary and the insulators were cleaned by a careful sandblasting.

Now a molydenum wire has been installed in the oven, since molydenum has a somewhat higher melting point than iridium. Since the wire is insulated from the antechamber by ceramic tubes, it must be assumed that the temperature of the wire is much higher than the temperature of the antechamber. In order to avoid a repetition of the electrical breakdown, it was decided to increase the temperature of the antechamber very slowly and only enough to demonstrate a pronounced effect. Approximately 300 mass spectra were taken. First with the antechamber at room temperature 24°C; then with elevated temperatures of 98°C, 174°C, and 197C°. Finally, again at room temperature. The evaluation and comparison of data required normalization for multiplier voltage and electrometer sensitivity.

SECTION 5

RECOMBINATION OF ATOMIC OXYGEN IN THE ANTECHAMBER

In order to obtain the highest dissociation, a very small amount of SF_6 has been added to the O_2 beam. The results are shown in Figures 2 through 4. It can be seen that in contract to Figure 1, which was obtained with an open ion source, the discharge now reduces the 16 peak. The reduction of the 32 peak is less than previously because of the recombination of atomic oxygen in the antechamber. If this recombination were complete, then the 16 peak should be caused entirely by dissociation of molecular oxygen in the ion source and the relative decrease of the 16 peak should be equal to the relative decrease of the 32 peak (5 percent). Actually the decrease of the 16 peak is slightly less, thus indicating that a very small mount of atomic oxygen could pass the antechamber and enter the ion source. This effect is more pronounced in Figure 2 with the antechamber at 174°C than in Figures 3 and 4 with the antechamber at 24°C. Since many experiments have been performed between, it is possible that a change in the surface conditions instead of the temperature has caused the different behavior. The fact remains that about 5 percent of the total oxygen is lost if the beam has been partially dissociated.

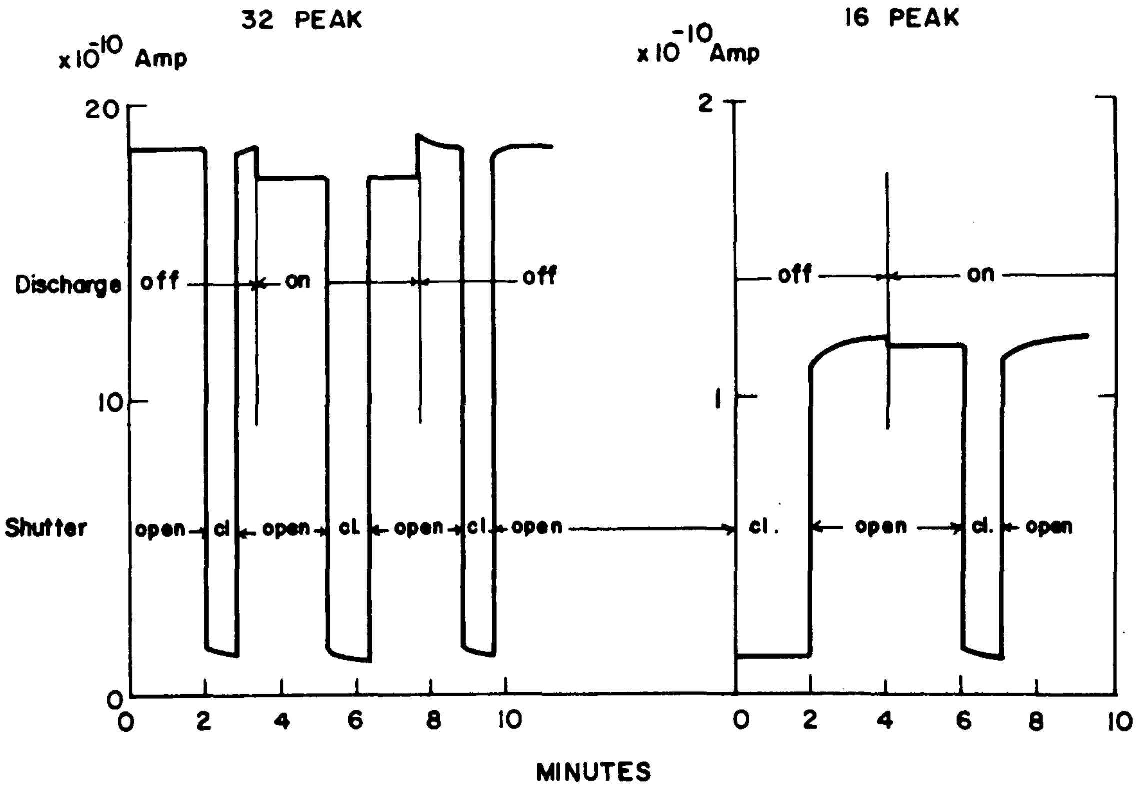

Figure 2. Beam: O_2 + 1% SF_6. Antechamber temperature 174°C. Recordings No. 120 and 121.

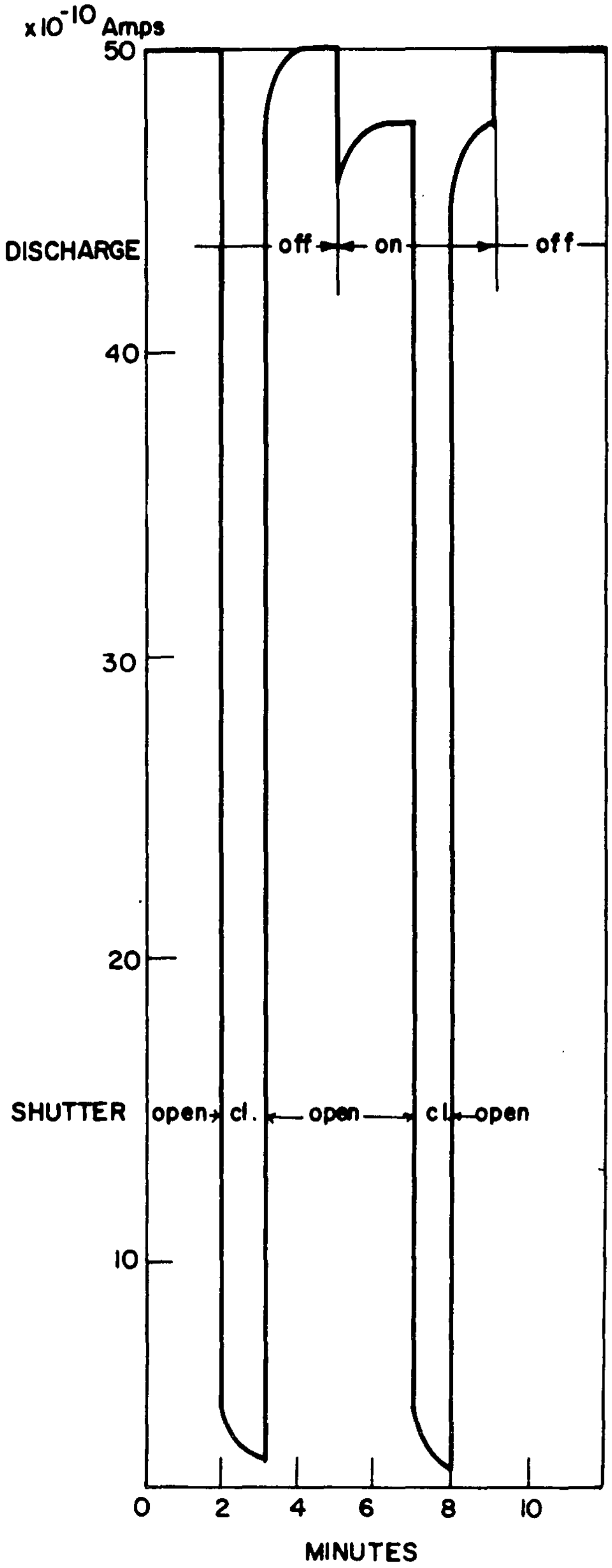

Figure 3. Beam: O_2 + 1% SF_6. 32-peak. Antechamber temperature 24°C. Recording No. 183.

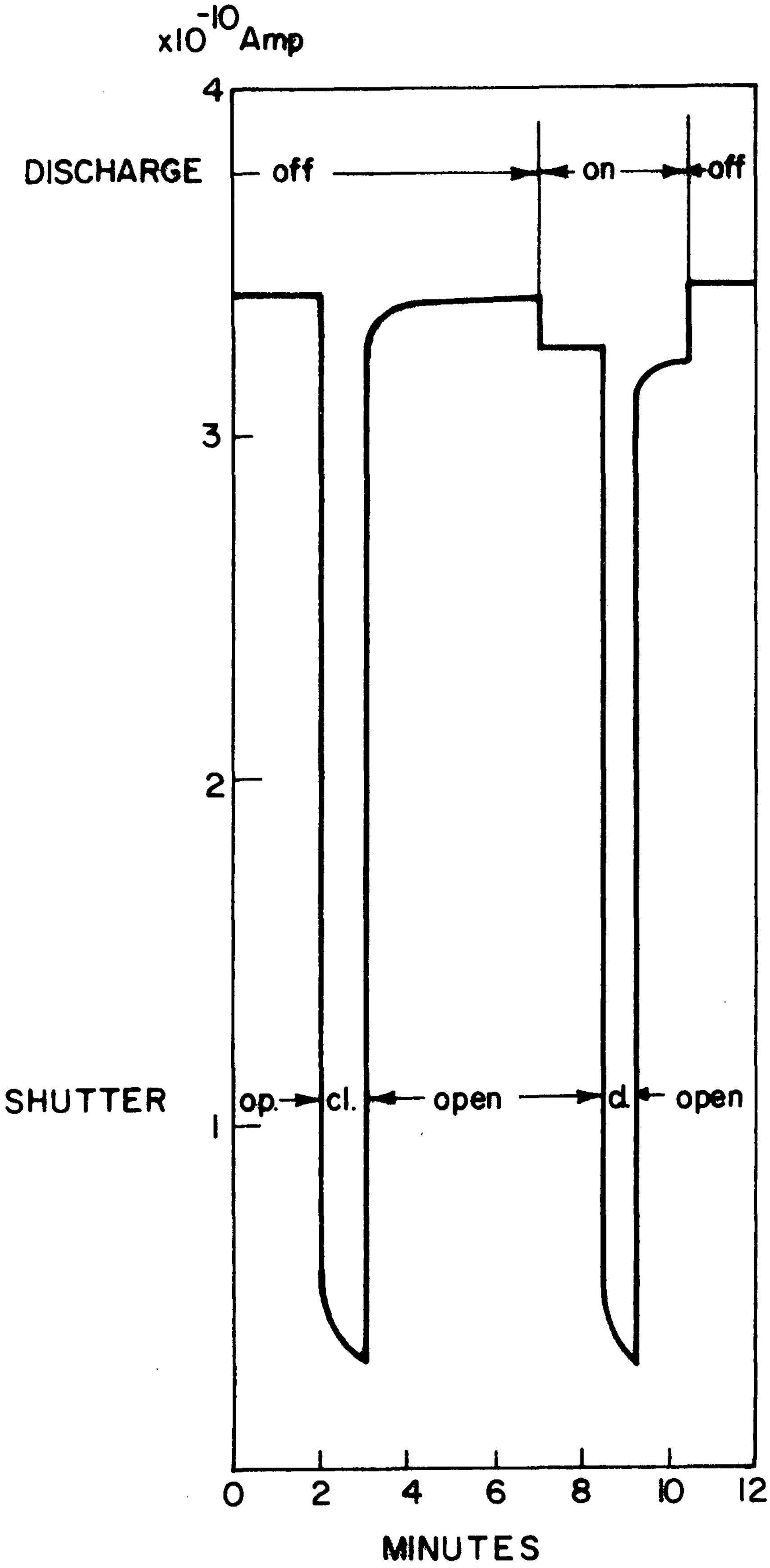

Figure 4. Beam: O_2 + 1% SF_6. 16-peak. Antechamber temperature 24°C. Recording No. 182.

SECTION 6

ABSORPTION AND DESORPTION PHENOMENA IN THE ANTECHAMBER

6.1 Absorption and Desorption of CO_2

A pure CO_2 beam has been introduced into the antechamber. The discharge was not in use and only the effect of the shutter has been studied. Figures 5 to 9 illustrate the results. Before Figures 5 to 8 had been started, the CO_2 flow rate had to be adjusted and the beam entered the antechamber for several hours. Therefore, the walls of the antechamber were well saturated. Only in Figure 9 the already well-known flow rate was adjusted first with the shutter in the closed position and with the antechamber well outgassed. One can see the very slow and gradual rise of the CO_2 partial pressure after the shutter is opened. This is an indication that a large amount of CO_2 is absorbed on the walls of the antechamber. Saturation has not been obtained completely and therefore the response to the shutter movement is not quite instantaneous. In both cases, Figures 5 and 9, the antechamber was at room temperature (24°C). The measurements at higher temperatures (Figures 6 to 8) are quite similar to Figure 5 which indicates that the temperature has little effect on the absorption and desorption of CO_2 within the temperature range investigated.

6.2 Absorption and Desorption of Water Vapor

In this case the beam consisted practically only of water vapor and the effect of the shutter position has been investigated. The discharge was not used during these measurements. Figures 10 through 13 show the results for increasing antechamber temperatures. The flow rate of the water vapor was adjusted before the recording shown in Figure 10 was started. Therefore, the beam entered the antechamber for about an hour and the walls were well saturated with water molecules. In the later recordings (Figures 11, 12 and 13) the already known flow rate was adjusted before the shutter was opened. In these cases one observes a more gradual increase of the 18 peak. On Figures 11 and 12 the response to the shutter movement is partially instantaneous and partially gradual. The instantaneous response disappeared at the highest temperature as shown in Figure 13. The slow rise on Figure 11 indicates that a large amount of water is absorbed if the wall is well outgassed. After saturation has been reached, very little water vapor is released from the wall when the shutter is closed and new saturation occurs quite rapidly after the shutter is opened. It was expected that at higher temperatures there will be less absorption and more and faster desorption. Comparison between Figures 10 and 13 shows that at the low temperature of 24°C the decrease of the 18 peak is more rapid when the shutter is closed. Apparently, the water molecules are strongly bound to the surface and most of them are not released at this low temperature. Since they still cover most

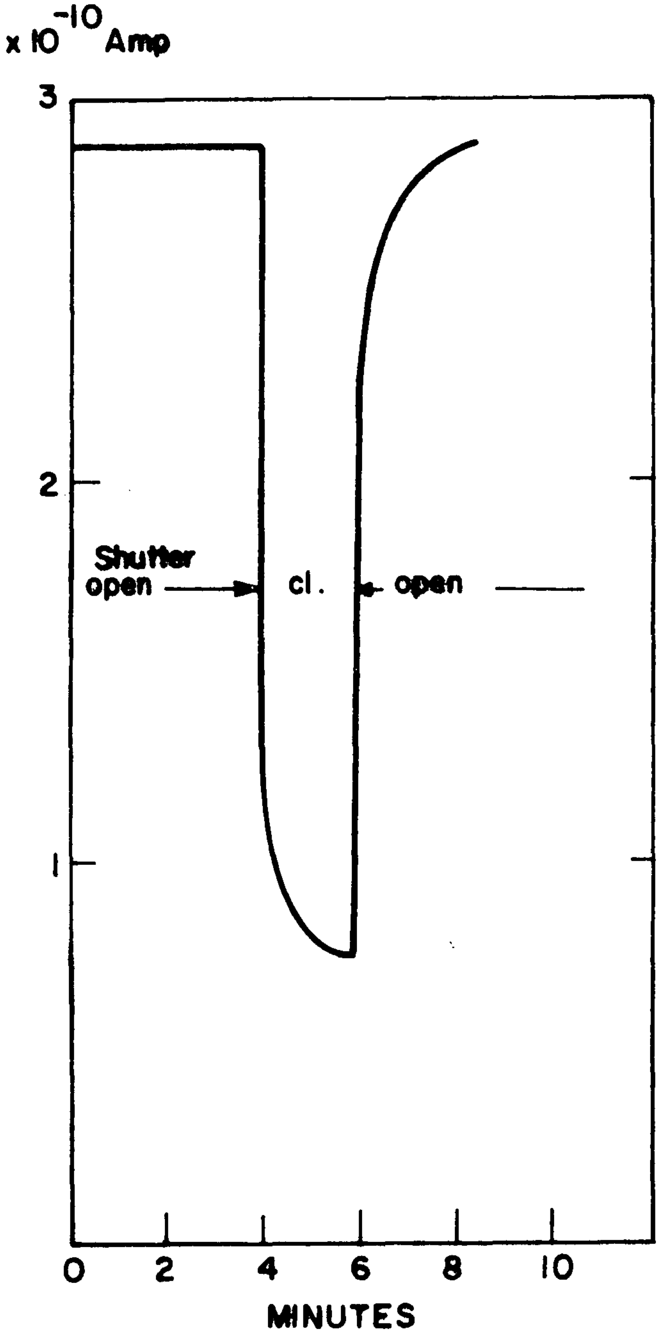

Figure 5. 44 peak, CO_2 beam. Antechamber temperature 24°C. Recording No. 90.

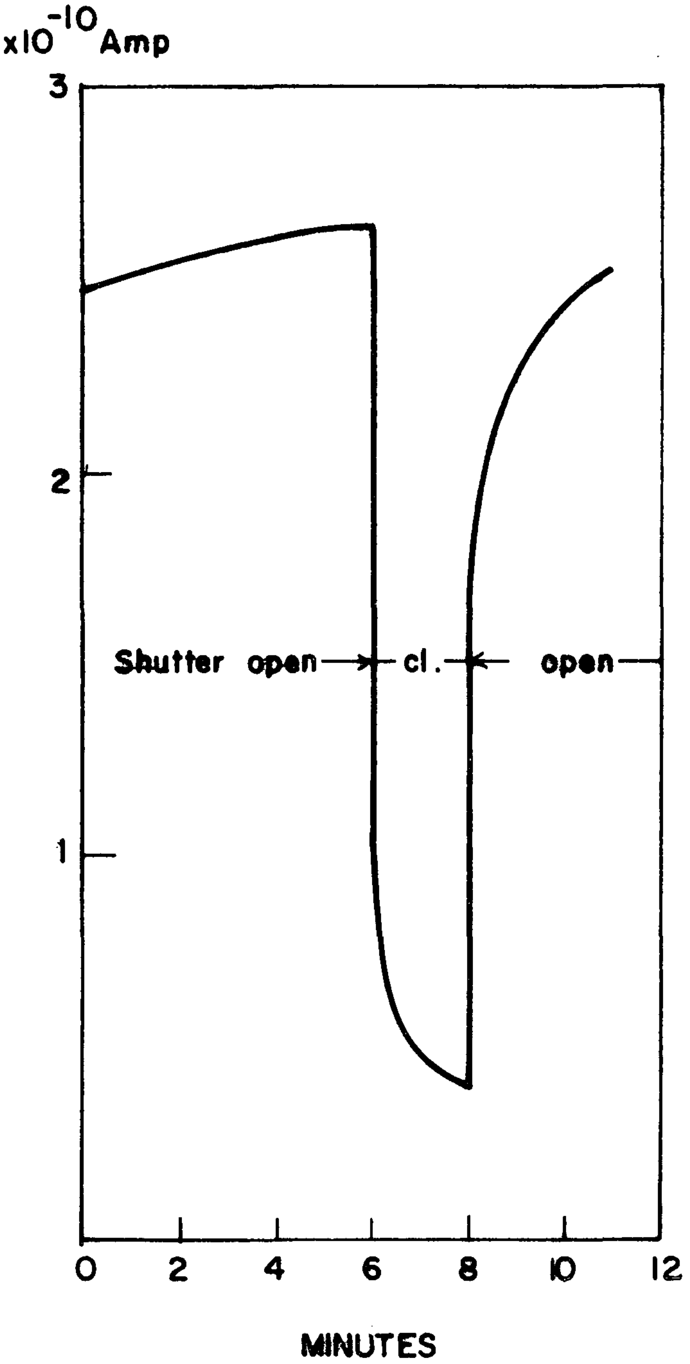

Figure 6. 44 peak, CO_2 beam. Antechamber temperature 98°C. Recording No. 104.

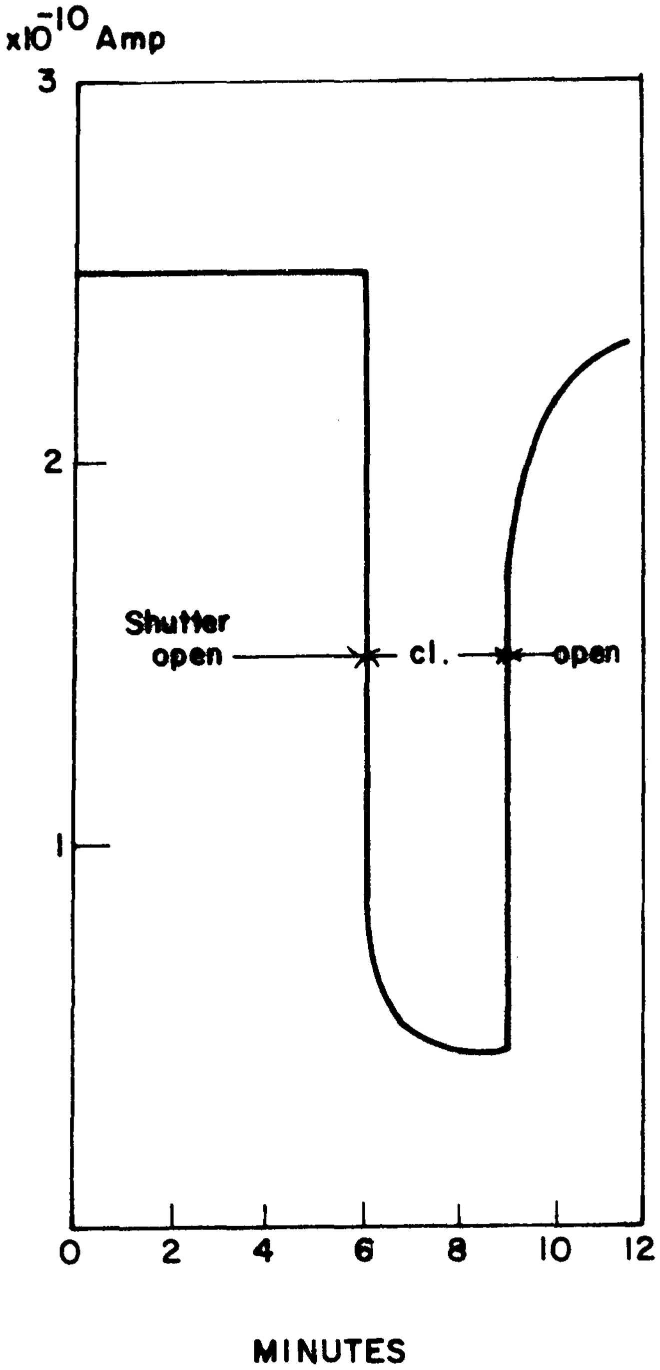

Figure 7. 44 peak, CO_2 beam. Antechamber temperature 174°C. Recording No. 135.

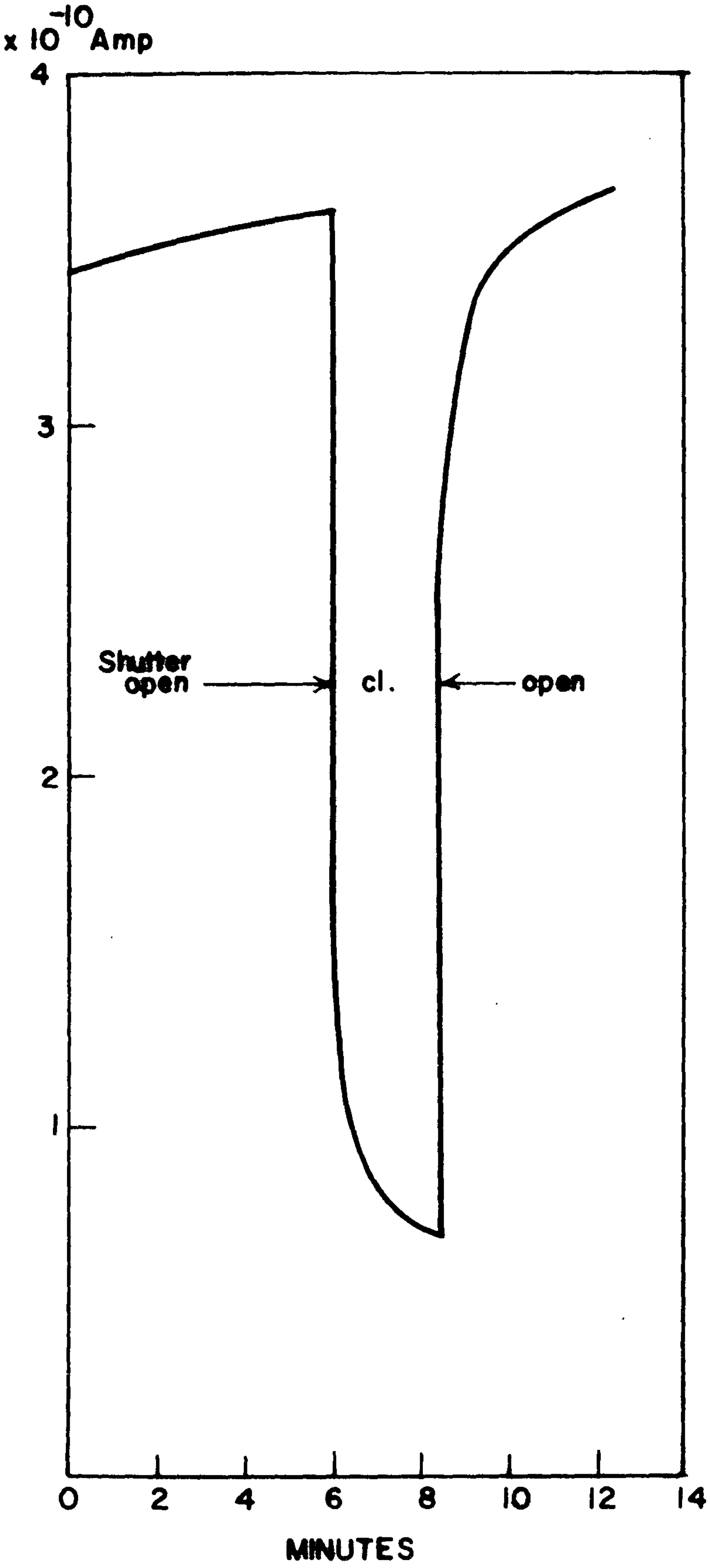

Figure 8. 44 peak, CO_2 beam. Antechamber temperature 197°C. Recording No. 157.

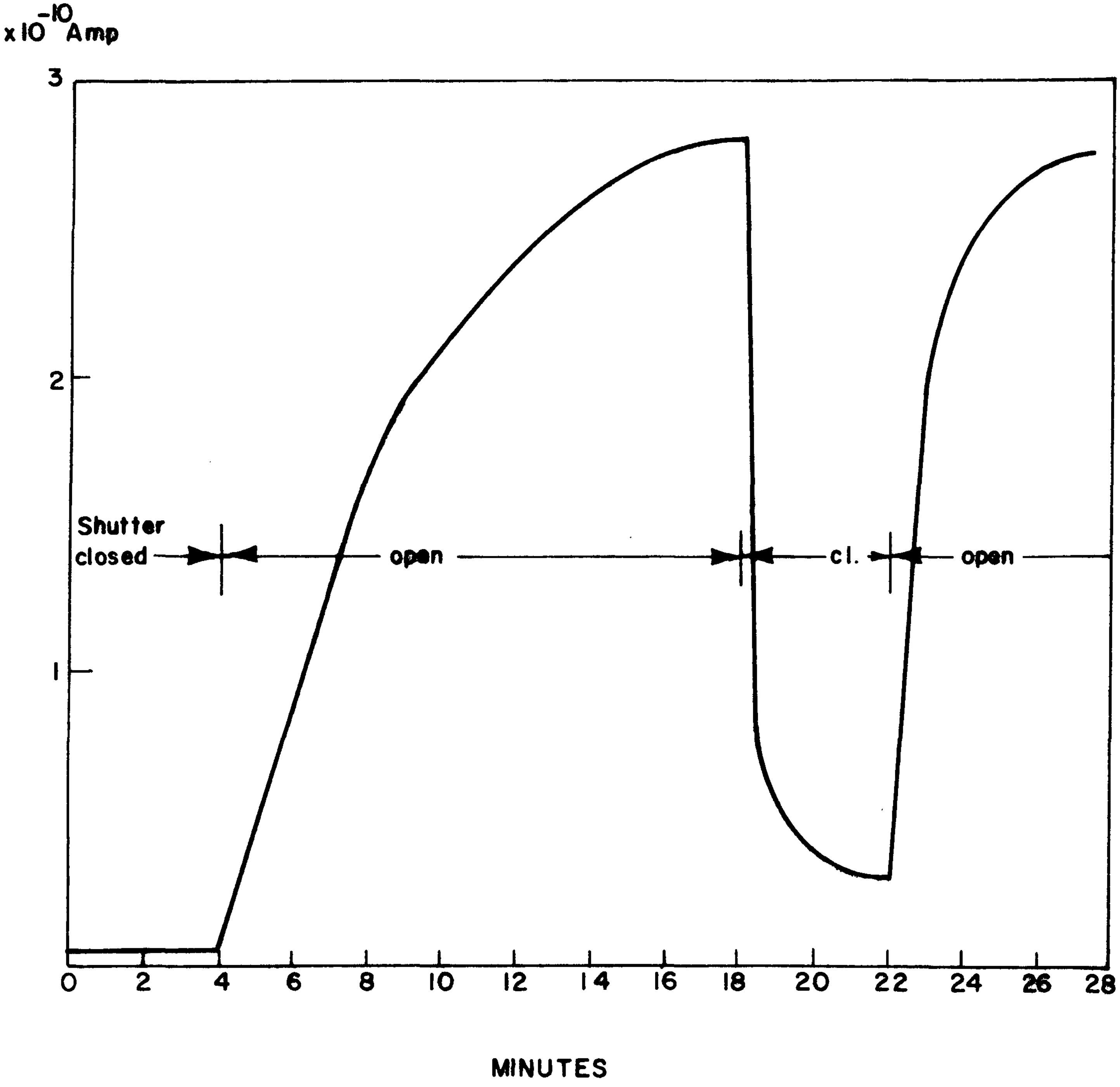

Figure 9. 44 peak, CO_2 beam, Antechamber temperature 24°C. Recording Nos. 165 and 166.

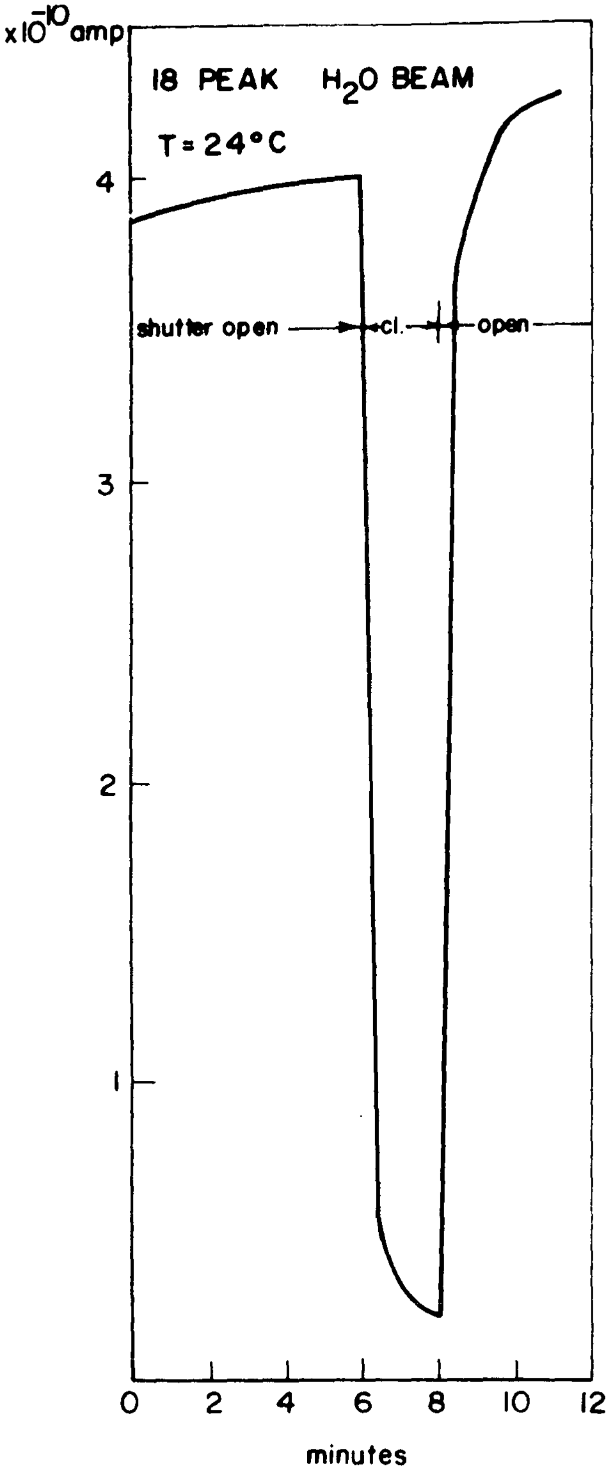

Figure 10. 18 peak, H_2O beam, T = 24°C. Recording No. 92.

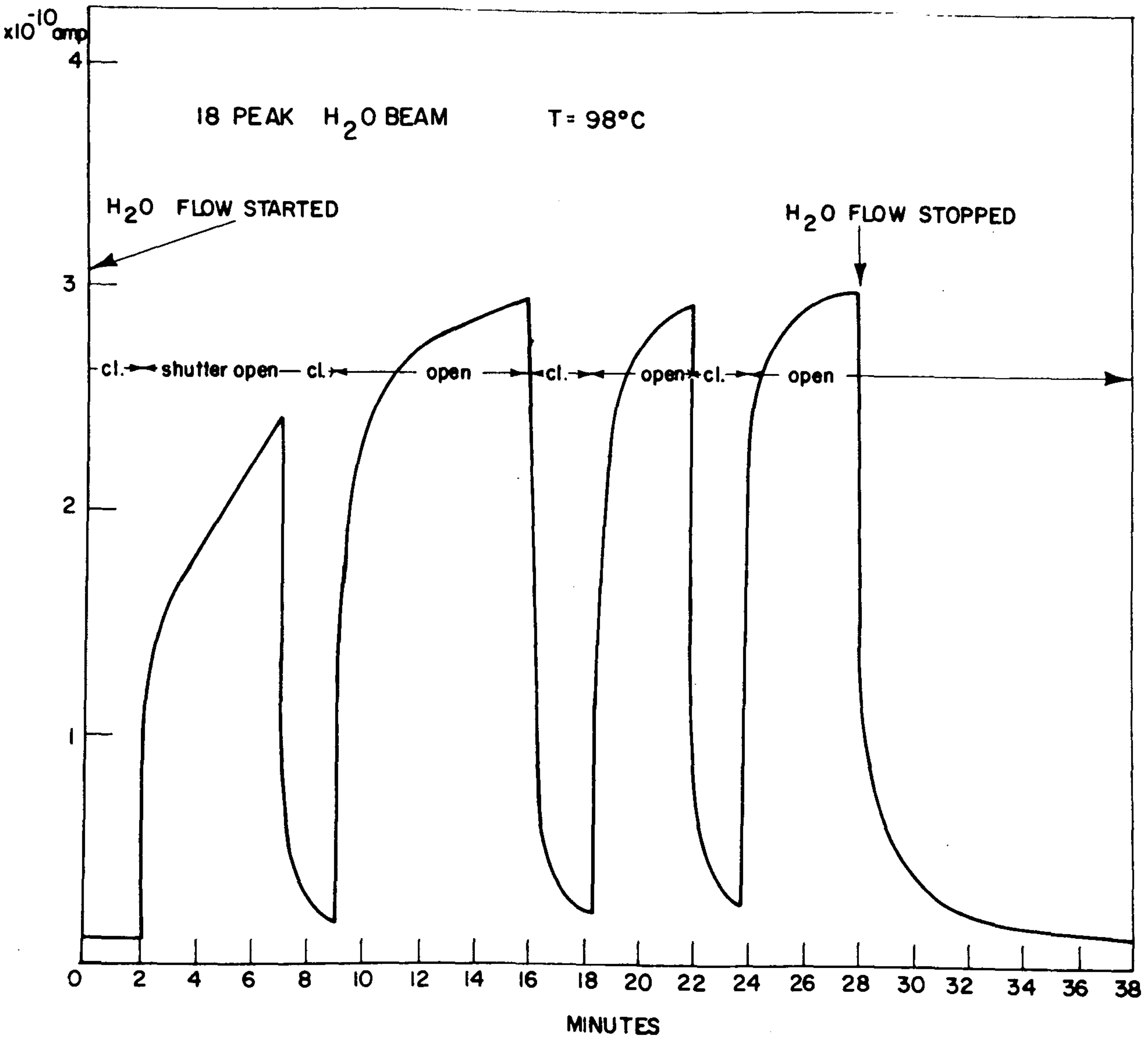

Figure 11. 18 peak, H_2O beam, T = 98°C. Recording Nos. 99-101.

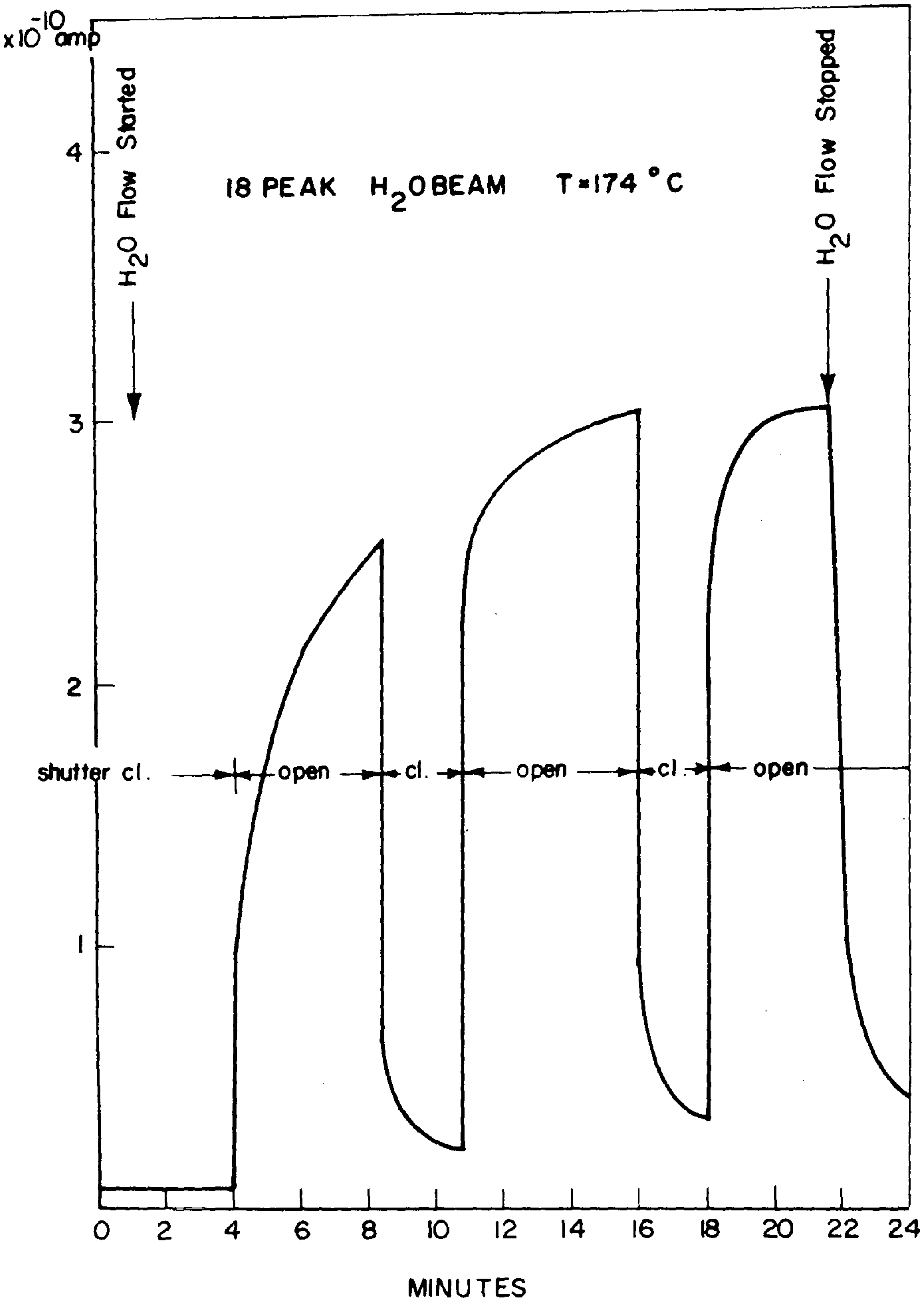

Figure 12. 18 peak, H_2O beam, T = 174°C. Recording Nos. 131-132.

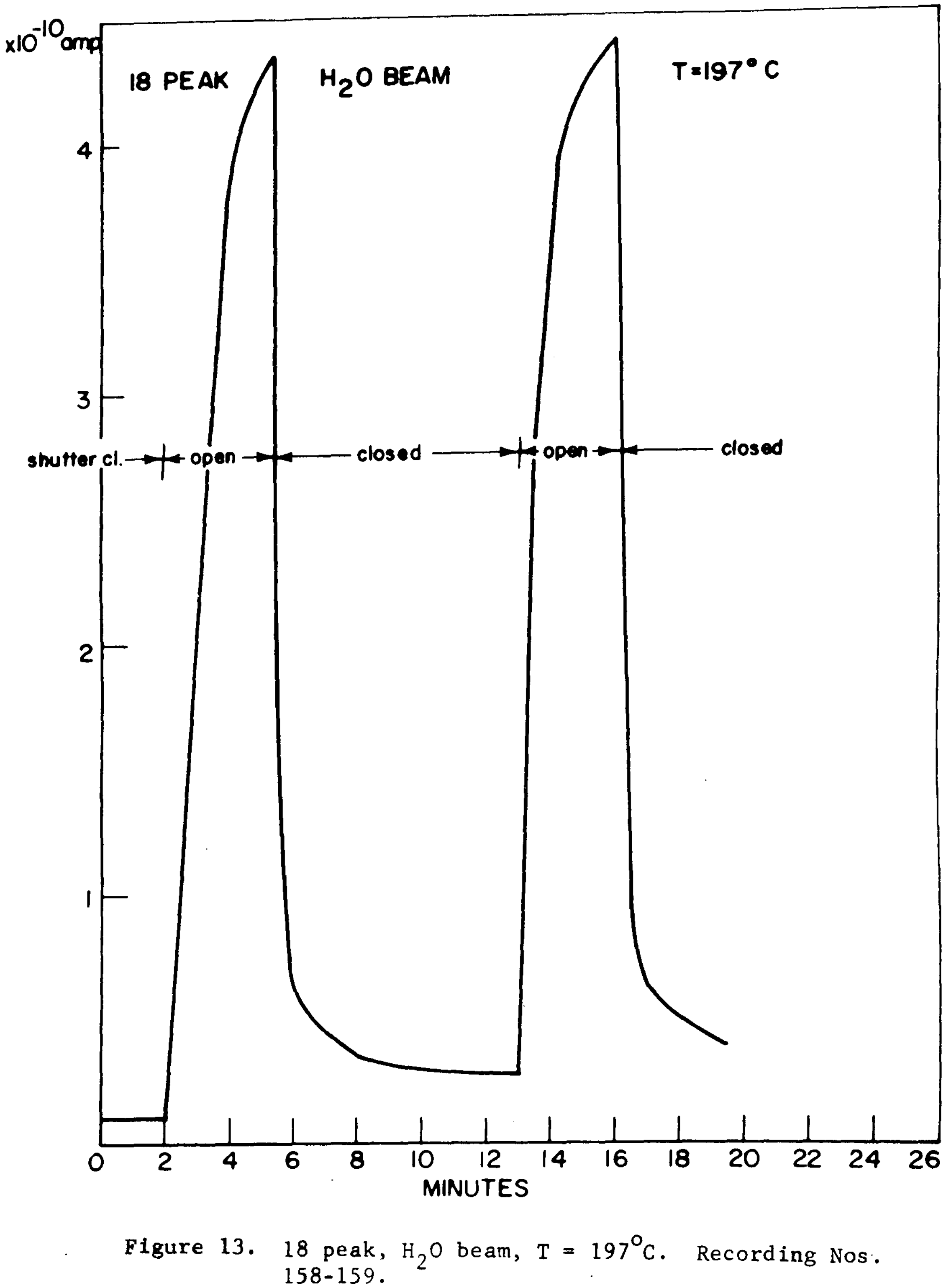

Figure 13. 18 peak, H_2O beam, T = 197°C. Recording Nos. 158-159.

of the surface when the shutter is re-opened very few places for absorption are available and the saturation pressure is obtained rapidly. The very slow increase of the peak height in Figures 11 and 12 before saturation is reached could be due either to absorption of water on the clean surface of the antechamber or in the gas inlet line. The latter assumption could be excluded since the total pressure in the mass spectrometer chamber stayed practically constant during the time when the increase of the 18 peak was observed.

Instantaneous response to the shutter movement would indicate that no absorption or desorption phenomena occur. This condition does not exist accurately. Even if the antechamber could be cooled sufficiently to form a solid layer of ice on the inside wall, water vapor molecules would still be absorbed and desorbed. On the other hand, if the antechamber is heated sufficiently to prevent absorption of water vapor, then absorption would occur in the ion source unless the whole system is kept at a high temperature. The temperature gradient over different parts of the antechamber ion source combination as well as the multiple wall collisions of the water molecules produce an average result which is not well suited for quantitative evaluation. In summation it can be said that water vapor is strongly absorbed on a clean gold surface and released only slowly and partially even at a temperature of about 200°C. The temperature effect is relatively small and an extension of the measurements towards higher temperatures would be desirable.

6.3 Absorption and Desorption of Oxygen

Investigations of the 32 peak with the open ion source have shown an instantaneous response to the shutter movement (see Figure 1). The response is still almost instantaneous with the closed ion source antechamber combination (see Figures 2 to 4). Steady state conditions are reached much more rapidly as with H_2O or CO_2. It was suspected that this is primarily the result of the much larger beam intensity. In order to check this hypothesis the oxygen flow was very much reduced and Figure 14 has been obtained. From the more gradual change of the 32 peak one can conclude that also for oxygen some absorption and desorption effects occur. However, they seem to be less pronounced as for CO_2 or H_2O.

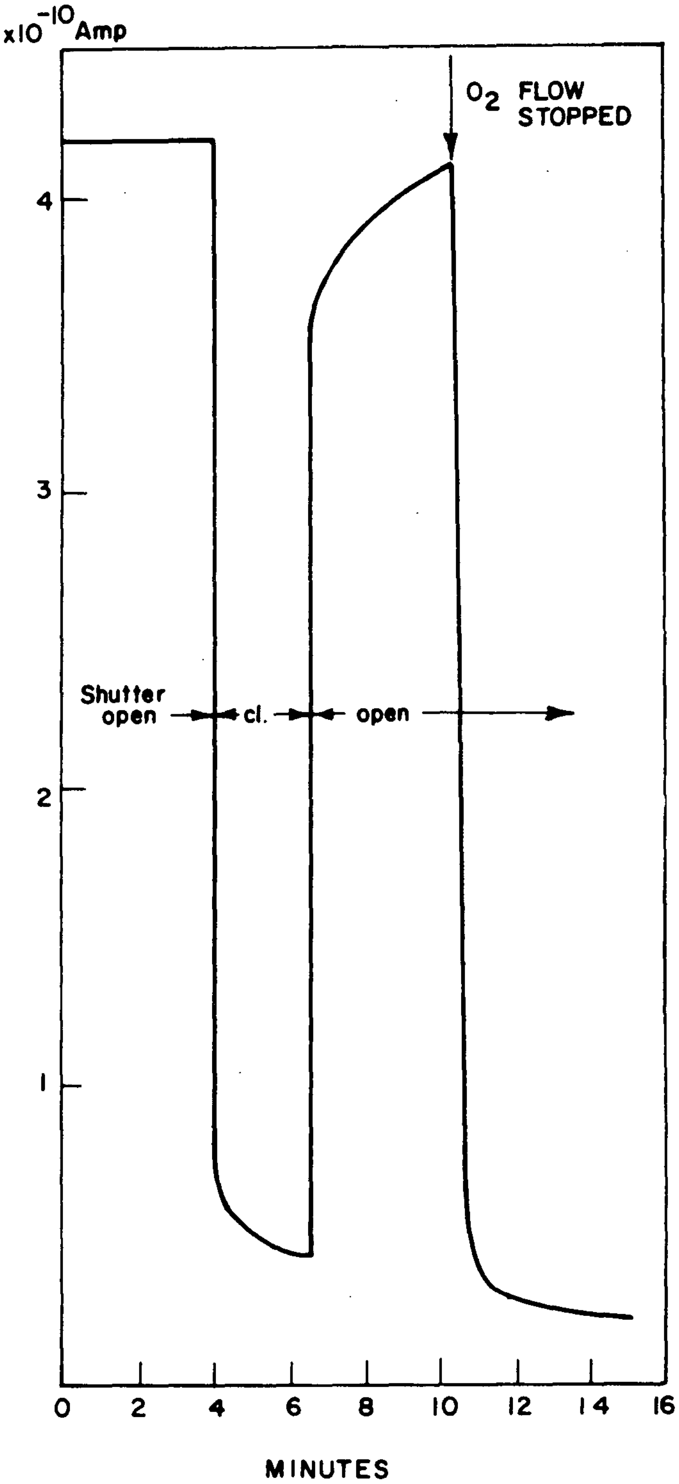

Figure 14. 32 peak. Beam O_2 with small flow rate. Antechamber temperature 98°C. Recording No. 108.

SECTION 7

INCREASE OF THE PARTIAL PRESSURE OF THE BACKGROUND GASES BY THE INTRODUCTION OF OXYGEN

7.1 Formation of CO_2 in the Antechamber by the Introduction of an Oxygen Beam

Figure 15 shows the behavior at room temperature at the end of all measurements, which was practically identical with the behavior at the beginning. The CO_2 background is first very small and increases very slowly and steadily when the oxygen beam is started. Movement of the shutter changes the pressure in the antechamber by more than one order of magnitude. Since this had no effect on the speed of rise of the CO_2 partial pressure, it must be concluded that CO_2 is not formed in the ion source or in the antechamber but rather in the Orb Ion Pump. Dissociation of the molecular oxygen in the microwave discharge had no effect whatsoever. The conclusion of these measurements is that the effect which was previously observed and described in GCA-TR-70-4-N was due to minute contamination in the beam inlet system probably from the viton gaskets. The elimination of the viton gaskets has eliminated this effect. This is in agreement with the results obtained with the open ion source which have been mentioned earlier. Based on this conclusion, it was assumed that increasing the temperature of the antechamber would have no effect on the 44 peak; but surprisingly the contrary was true.

The behavior of the 44 peak with moderately elevated temperature of the antechamber (98°C) is shown in Figure 16. A constant stream of O_2 plus approximately 2 percent SF_6 has been introduced. The 44 peak increases slowly but steadily if the shutter is opened and decreases if the shutter is closed. If the discharge is on and therefore approximately 10 percent oxygen is dissociated into atomic oxygen the increase of the 44 peak is faster and the effect of the shutter is partly instantaneous.

If the temperature of the antechamber is raised to 174°C, the behavior of the 44 peak (Figure 17) is essentially the same. In this case pure O_2 was first introduced into the system. At the marked moment SF_6 was added. One can see that the increased dissociation resulted in a more rapid increase of the 44 peak.

The most pronounced effect (see Figure 18) was achieved with the highest temperature (197°C) which could be obtained with the present apparatus. First pure O_2 has been introduced. The 44 peak did not increase as long as the shutter was closed or, at least, such an increase was negligibly small. If the shuter is opened, a sudden increase occurs, followed by a slower further increase. The reverse is true if the shutter is closed. The increase of the 44 peak due to molecular oxygen is now much larger, especially if part of the molecular oxygen is dis-

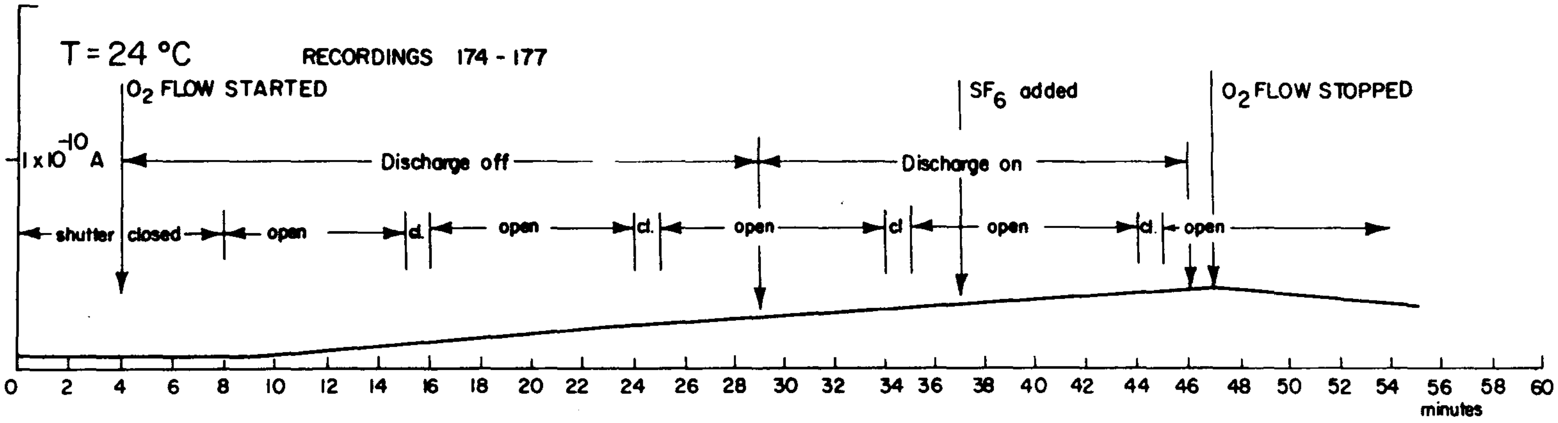

Figure 15. Height of 44 peak. Beam: O_2 + 2% SF_6; antechamber temperature 24°C.

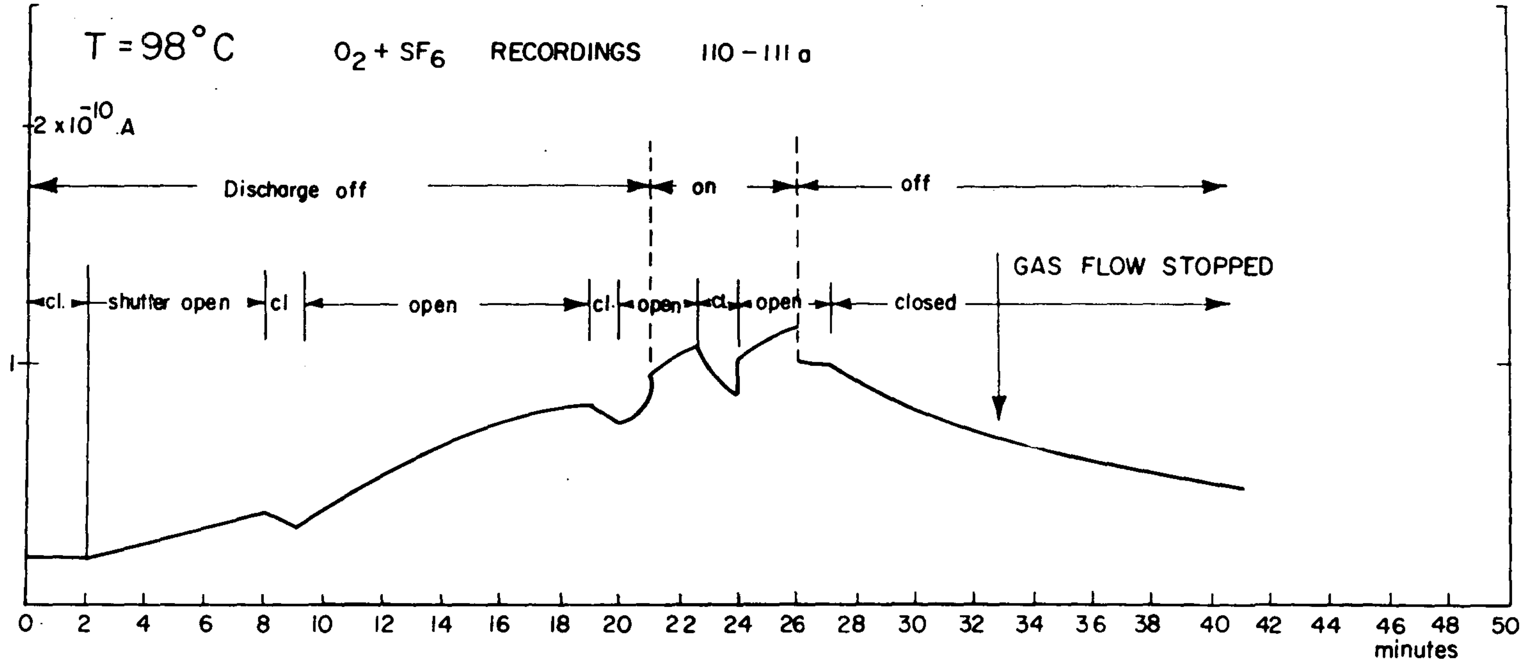

Figure 16. Height of 44 peak. Beam: O_2 + 2% SF_6; antechamber temperature 98°C.

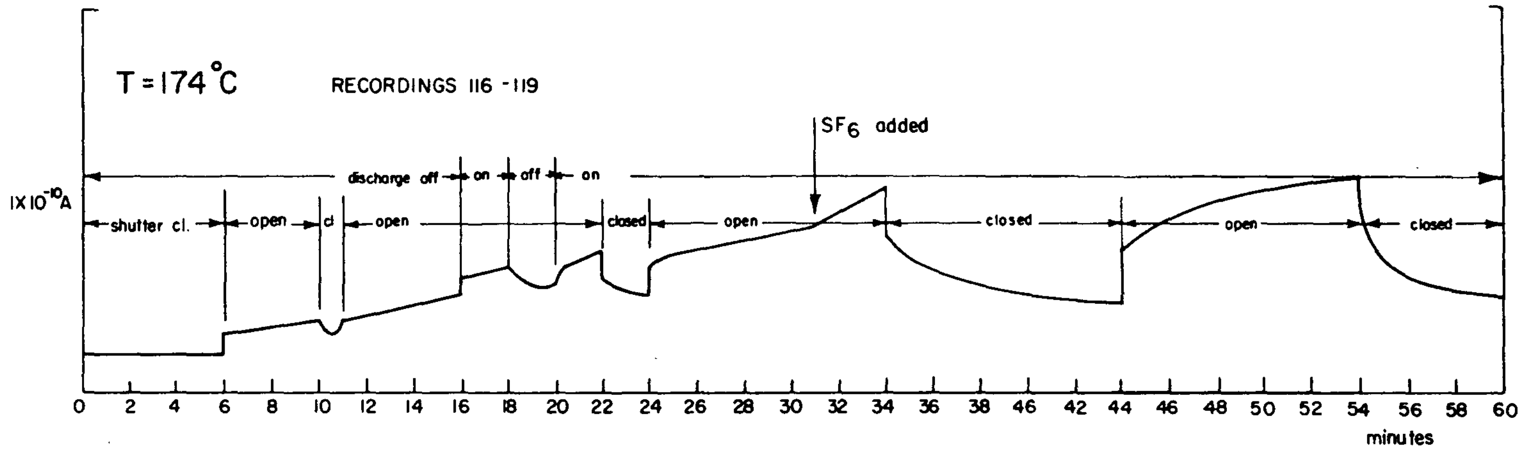

Figure 17. Height of 44 peak. Beam: First pure O_2, later 2% SF_6 added. Antechamber temperature 174°C.

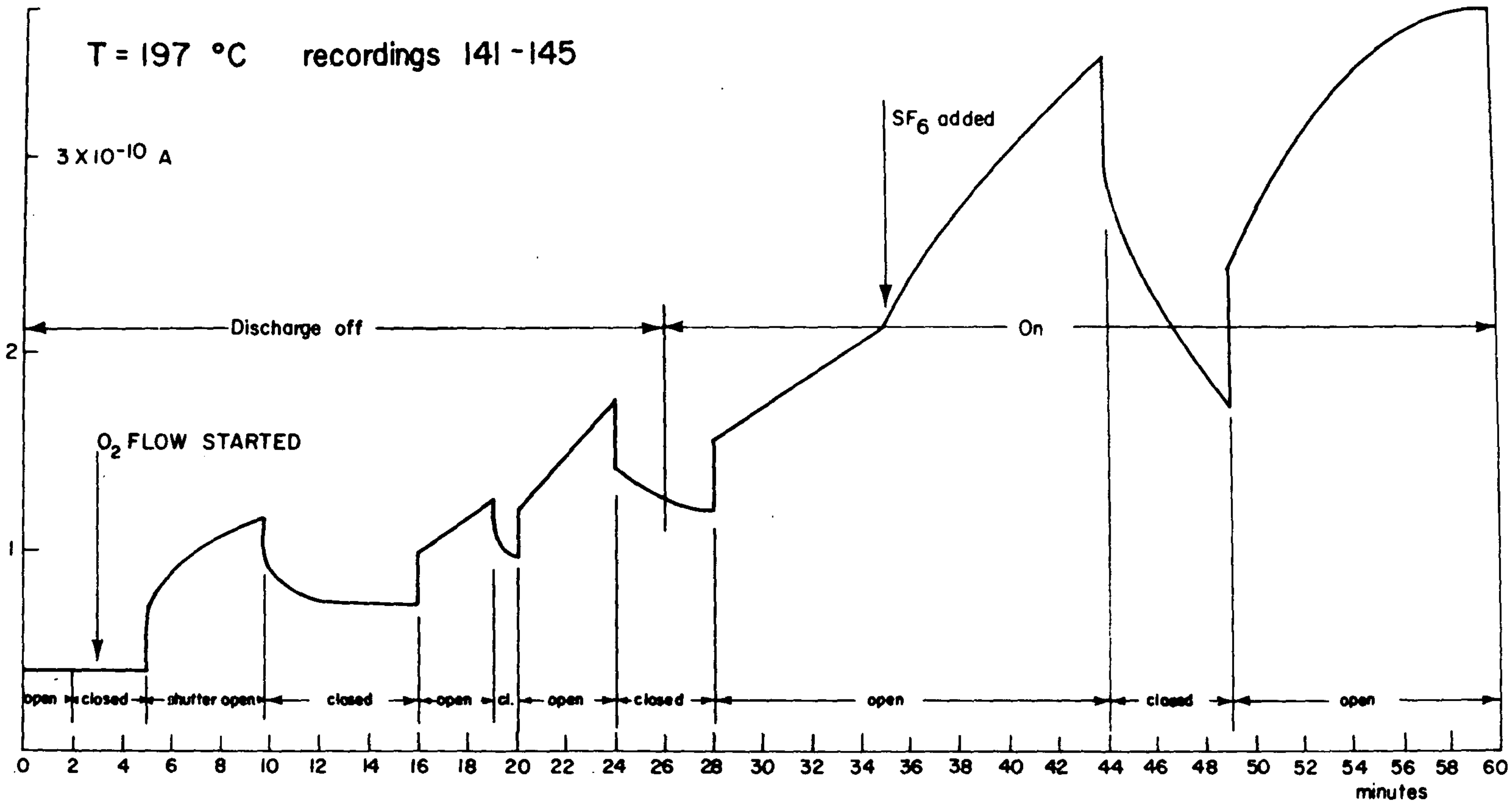

Figure 18. Height of 44 peak. Beam: First pure O_2, later 2% SF_6 added. Antechamber temperature 197°C.

sociated. If SF_6 is added to enhance the dissociation, the increase is even more rapid. In this case too, the movement of the shutter results first in a sudden change followed by a more gradual change of the 44 peak height. It should be mentioned that the increase of the 44 peak at this high temperature is 20 percent of the 32 peak (17×10^{-10}A) and therefore by far larger than the largest increase (3.5 percent) previously observed at room temperature (see Figure 18 of GCA-TR-70-4-N).

7.2 Increase of the 28 peak if Oxygen is Introduced

If the system is at a pressure below 1×10^{-9} torr, then the largest peak in the background spectrum is either hydrogen-1 or the peak at mass 28. An air leak would produce a peak at mass 28, however, the fragmentation peak at mass 14 and the oxygen peak 32 should also be visible. Since those peaks are negligible small, it must be concluded that the 28 peak is produced primarily by carbon monoxide. Carbon monoxide is a well-known trace impurity in most metals and is released under ultra-high vacuum conditions.

If a pure oxygen beam is introduced into the system, the 28 peak rises slowly and steadily (see Figure 19). Shutter position and the discharge have little effect on the 28 peak. This is an indication that carbon monoxide is produced on the filament of the Orb Ion Pump. A 28 peak is also produced by fragmentation of CO_2 in the ion source which accounts for the remaining superimposed small effect of the shutter and discharge on the 28 peak height. Therefore, the shutter effect is caused only indirectly, whereas the partial pressure of CO in the whole mass spectrometer chamber rises steadily to more than twice the background value. It must be concluded that there is always plenty of carbon monoxide around to produce a monolayer on the inner walls of the antechamber.

7.3 Production of Water Vapor by the Oxygen Beam

After pumping overnight the 18 peak is extremely small. If the antechamber is at room temperature and an oxygen beam is introduced, a very slight and slow increase of the 18 peak is observed. The shutter position and the discharge have practically no effect. It appears that the water vapor is produced either on the filament of the Orb Ion Pump, which is used to evacuate the main chamber, or released from the walls of this pump by replacement of physically absorbed water by chemically absorbed oxygen. This increase is barely noticeable and of no practical consequence.

If the temperature of the antechamber is increased to 174°C, the increase of the 18 peak becomes more noticeable (see Figure 20). Now the shutter position has a slight effect and also the discharge produces a slight increase in the rate of change of the 18 peak. A remarkable difference occurs if the temperature of the antechamber is increased to 197°C (See Figure 21). The 18 peak became much larger and the

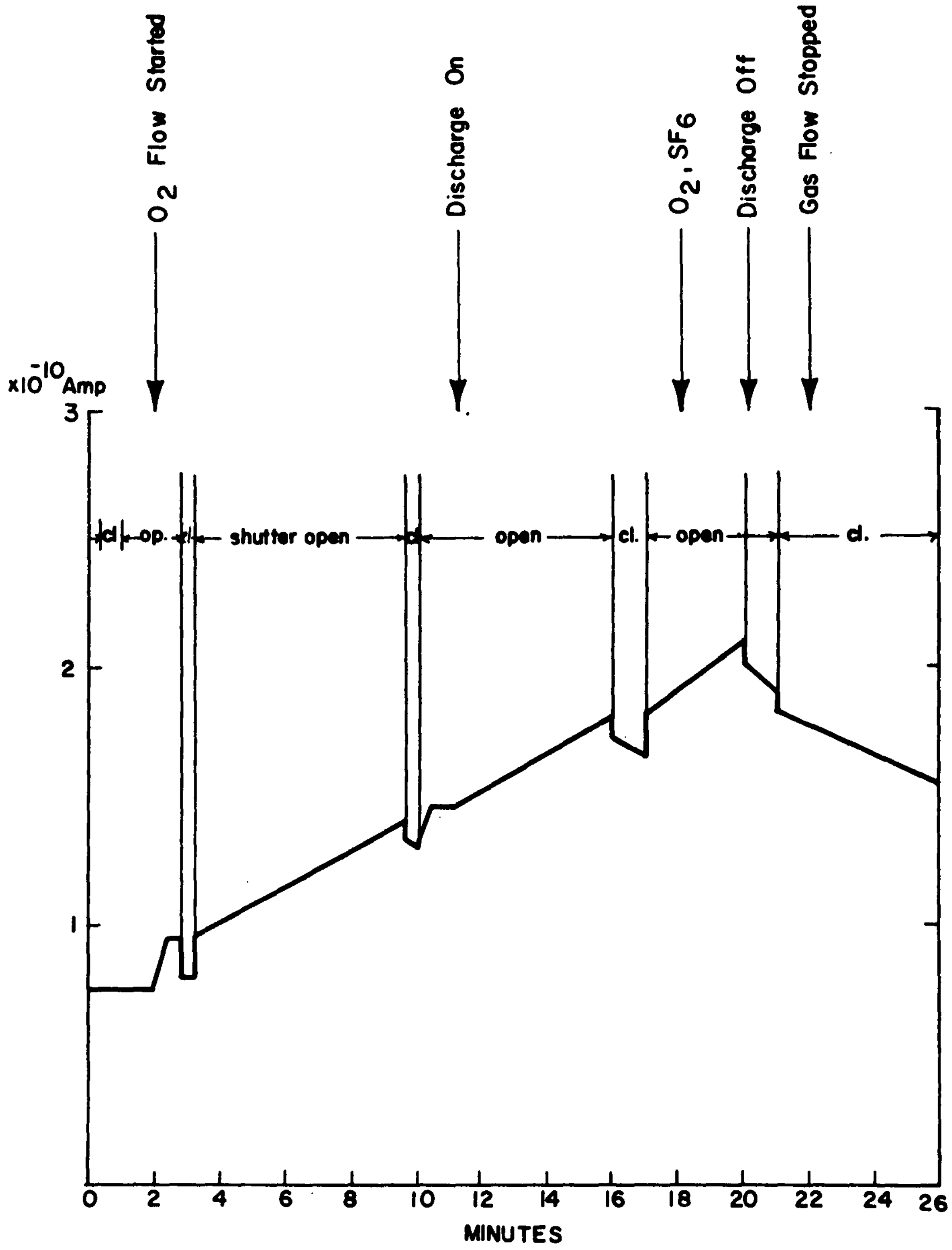

Figure 19. Height of 28 peak. Beam: First pure O$_2$, later 2% SF$_6$ added. Antechamber temperature 197°C. Recordings No. 161 and 162.

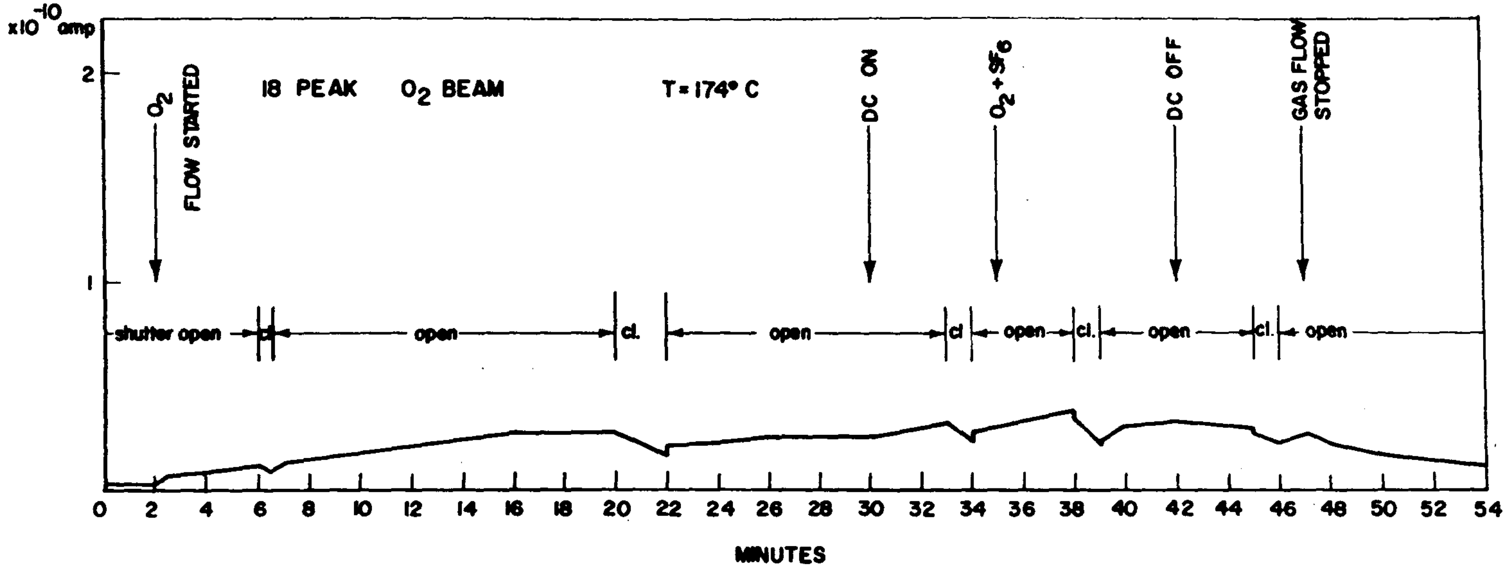

Figure 20. Height of 18 peak. Beam: First pure O_2, later 2% SF_6 added. Antechamber temperature 174°C. Recordings No. 127-130.

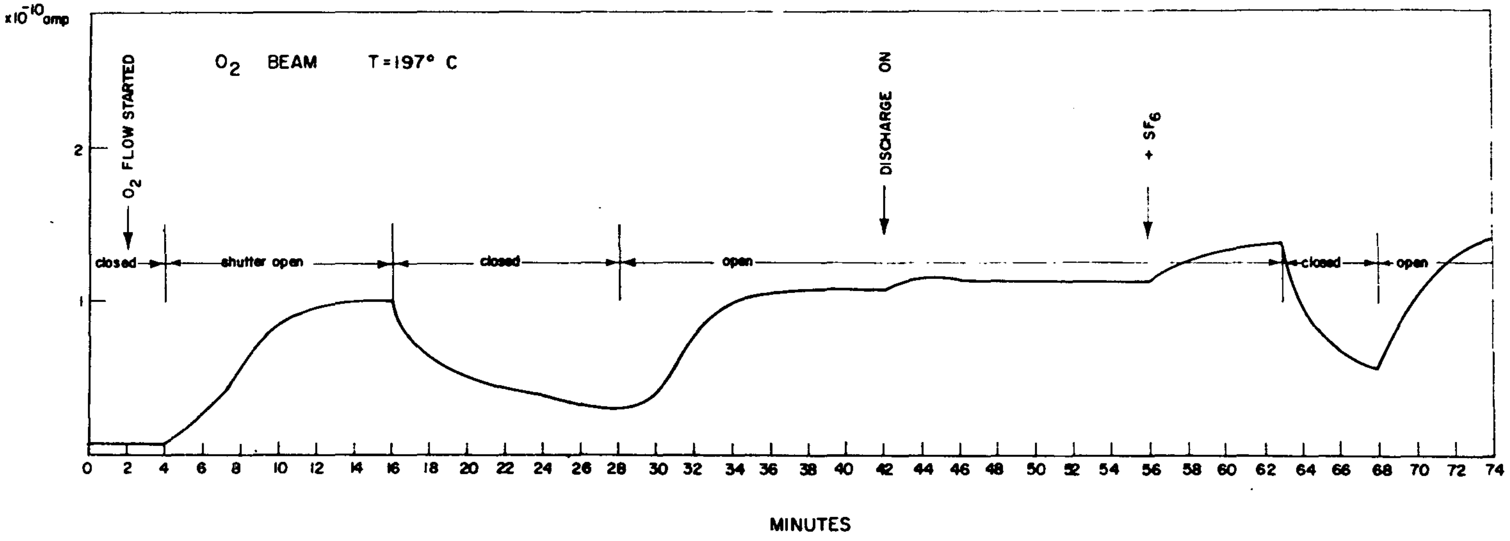

Figure 21. Height of 18 peak. Beam: First pure O_2, later 2% SF_6 added. Antechamber temperature 197°C. Recordings No. 147-152.

shutter position has a very pronounced effect. Atomic oxygen increases the 18 peak slightly which can be observed at the points where the discharge is switched on and also at the point where sulfur hexafluoride has been added. Since the only difference between Figure 20 and Figure 21 is the temperature of the antechamber, it must be assumed that the formation of the water molecules occurs on the wall of the antechamber. The most likely explanation is that the increased temperature improves the diffusion of hydrogen from the interior of the metal antechamber towards the surface and that this hydrogen is oxidized by a catalytic reaction on the wall.

SECTION 8

CONCLUSIONS

8.1 Production of CO_2 in the Antechamber

The elimination of the viton gaskets in the inlet system has practically eliminated the partial pressure rise of CO_2 and H_2O due to atomic oxygen which has been observed previously with the old atomic beam system when the antechamber was at room temperature. The remaining very small increase of the partial pressure of CO_2 and H_2O is quite insignificant and is not effected by the movement of the shutter or by partial dissociation of the oxygen beam. It must be produced in the Orb Ion Pump by interaction of O_2 with the hot filament and the titanium deposits. Since the filament temperature of the ion source is always the same and independent of the temperature of the antechamber and since no shutter effect was observed at room temperature, it must be concluded that the filament of the ion source does not contribute to the production of CO_2. The surprising observation of these measurements was the fact that the increase of the partial pressure of CO_2 and H_2O becomes much more pronounced if the antechamber is heated and becomes most significant at the highest temperature which could be reached with the present setup. The large increase of the 44 peak at the highest temperature of the antechamber must be caused by a reaction occurring on the walls, since all other parameters were kept constant. A reaction occurs already with molecular oxygen, but is increased significantly if part of the molecular oxygen is dissociated. It seems that the elevated temperature increases the mobility of absorbed CO and O_2 molecules; this contributes to the higher reaction rate.

Catalytic reactions can only occur if the catalyst, in this case, gold, is only partially covered by one of the two reactants, thus leaving absorption places open for the second reactant. The speed of formation of the reaction product depends on many parameters. Absorption and desorption measurements have shown only a minor effect caused by the temperature within the limited range from 24°C to 194°C. The large increase of the partial pressure of the reaction products at the highest available temperature indicates that diffusion processes play a major role. The kinetic energy of the reactant molecules will also contribute to the higher reaction rate at the higher temperature.

Unfortunately, experiments with enriched isotopes could not be performed under this contract due to the limited funds. Therefore only speculations are possible about the origin of the partner of the catalytic reaction with oxygen. In the case of CO_2 formation, the other reactant is probably CO from the background gas, which is always present in rather large amounts, especially if oxygen is introduced in the Orb Ion Pump.

8.2 Production of H_2O in the antechamber

The formation of water vapor is more difficult to explain, since the molecular hydrogen partial pressure in the system is negligibly small during the actual beam experiments. Only during pumpdown procedures a high partial pressure of molecular hydrogen has been observed, especially if new filaments in the titanium sublimation pumps, or a new titanium anode in the Orb Ion Pump has been used the first time. Later on, especially after bakeout of the whole system, the molecular hydrogen partial pressure became insignificantly low. On the other hand, especially under ultra-high vacuum conditions, the atomic hydrogen peak became by far the largest peak in the background spectrum. This peak is produced by surface ionization in the San Marco ion source if the electron beam strikes the inner walls of the ionization chamber. The atomic hydrogen peak is usually split into two peaks and the separation between the two peaks depends on the repeller voltage. The two peaks coincide if the repeller voltage is sufficiently small. Unfortunately, under this condition, the total intensity of all peaks is also relatively small. The relative intensity of the split hydrogen-1 peaks depend on the focusing and deflection adjustment of the electron beam. No correlation between the hydrogen-1 peak and the temperature of the antechamber has been found. Nevertheless these experiments have indicated that a large supply of atomic hydrogen is available on the surface of the gold plated ionization chamber, and therefore, most likely, also on the gold plated surface of the antechamber. This is the key for the interpretation of the observed water peaks.

It must be concluded that the hydrogen diffuses from the interior of the metal towards the inner surface of the antechamber where it recombines with oxygen. This diffusion process is also enhanced by the increased temperature of the antechamber.

APPENDIX*

THE NEW ATOMIC BEAM SYSTEM

The new atomic beam system is shown schematically in Figure 22. The system consists essentially of three chambers, CH-1, CH-2, and CH-3 which are differentially pumped. The atomic beam is formed at the effusion nozzle A_o and collimated by the apertures A_1 and A_2. Two opposing requirements have to be fulfilled. The distance between the effusion nozzle A_o and the mass spectrometer ion source IS must be as short as possible in order to obtain high beam intensity. Conversely, in order to obtain a high beam-to-background ratio, the pumping speed and with it the cross section of the three chambers must be large. Therefore, the cross sections of the chambers have been made rectangular: 12 inches wide and only 4 inches high. The chambers are made of welded stainless steel plates and are interconnected with ultra-high vacuum flanges and copper gaskets. The pressure in the chambers is measured by Bayard-Alpert gauges G-1, G-2, and G-3 which contain thoriated iridium filaments to resist oxidation. The atomic beam can be interrupted by a shutter located in front of the mass spectrometer ion source. This shutter is shown in the open position S_1 and in the closed position S_2. Chamber 1 carries the heavy gas load and is pumped by a 6-inch oil diffusion pump DP, isolated by a chevron baffle B-3 and a zeolite baffle B-4. The chamber can be separated from the pump with a 6-inch gate valve G.V. The chambers 2 and 3 are connected with chamber 1 over the ultra-high vacuum valve UHV-1 and UHV-2. These valves are kept open during the bakeout and outgassing period. They are closed during normal operation of the instrument. Chamber 2 is pumped by two titanium sublimation pumps. The titanium filaments Ti are surrounded by a cooling coil, CC. The short distance between the beam and the titanium layer on the cooling coil assures a very high pumping speed. The top chamber No. 3 is the main chamber which contains the mass spectrometer and must be pumped down to the lowest possible pressure. It is evacuated by a 6-inch Orb Ion Pump, OIP. A heavy wall pyrex glass pipe, GP, has been used for the discharge tube DCH and the reaction chamber, R, in order to insure against breakage. The gas inlet system has been transferred unchanged from the old atomic beam system. Also, the diffusion pump, the chevron baffle, the fore pump, many valves, and the microwave power supply as well as the photomultiplier have been transferred from the old system. A large oven can be rolled over the three chambers and permit bakeout up to about 350°C. The bottom plate of chamber 1 is outside the oven which permits use of a teflon nozzle at A_o and Vitron A gaskets in the gate valve, G.V. The automatic relay valve, ARV, closes in case of an electric power failure, and simultaneously switches off the diffusion pump. The diffusion pump will also be switched off by a thermostat control of the cooling water. Based on previous experience Convalex 10 has been used as diffusion pump fluid. Excessive pressure in chamber 1, as measured by gauge G_1 will also switch off the diffusion pump.

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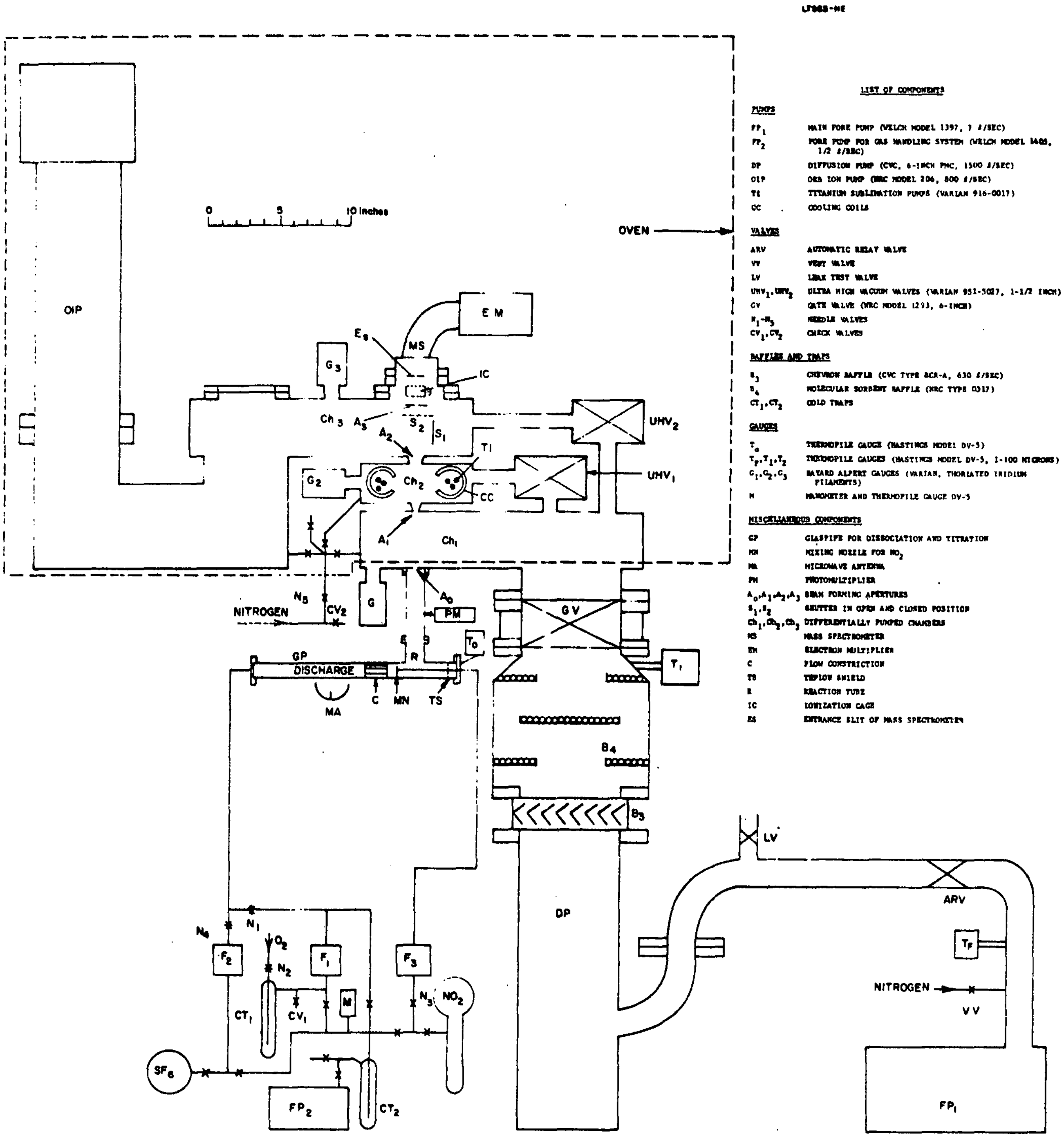
*Excerpt from GCA-TR-70-4-N.



LIST OF COMPONENTS

PUMPS

FP_1	MAIN FORE PUMP (WELCH MODEL 1397, 7 ℓ/SEC)
FP_2	FORE PUMP FOR GAS HANDLING SYSTEM (WELCH MODEL 1405, 1/2 ℓ/SEC)
DP	DIFFUSION PUMP (CVC, 6-INCH PMC, 1500 ℓ/SEC)
OIP	ORB ION PUMP (NRC MODEL 206, 800 ℓ/SEC)
TI	TITANIUM SUBLIMATION PUMPS (VARIAN 916-0017)
CC	COOLING COILS

VALVES

ARV	AUTOMATIC RELAY VALVE
VV	VENT VALVE
LV	LEAK TEST VALVE
UHV_1,UHV_2	ULTRA HIGH VACUUM VALVES (VARIAN 951-5027, 1-1/2 INCH)
GV	GATE VALVE (NRC MODEL 1293, 6-INCH)
N_1-N_5	NEEDLE VALVES
CV_1,CV_2	CHECK VALVES

BAFFLES AND TRAPS

B_3	CHEVRON BAFFLE (CVC TYPE BCR-A, 630 ℓ/SEC)
B_4	MOLECULAR SORBENT BAFFLE (NRC TYPE 0317)
CT_1,CT_2	COLD TRAPS

GAUGES

T_o	THERMOPILE GAUGE (HASTINGS MODEL DV-5)
T_F,T_1,T_2	THERMOPILE GAUGES (HASTINGS MODEL DV-5, 1-100 MICRONS)
G_1,G_2,G_3	BAYARD ALPERT GAUGES (VARIAN, THORIATED IRIDIUM FILAMENTS)
M	MANOMETER AND THERMOPILE GAUGE DV-5

MISCELLANEOUS COMPONENTS

GP	GLASPIPE FOR DISSOCIATION AND TITRATION
MN	MIXING NOZZLE FOR NO_2
MA	MICROWAVE ANTENNA
PM	PHOTOMULTIPLIER
A_0,A_1,A_2,A_3	BEAM FORMING APERTURES
S_1,S_2	SHUTTER IN OPEN AND CLOSED POSITION
Ch_1,Ch_2,Ch_3	DIFFERENTIALLY PUMPED CHAMBERS
MS	MASS SPECTROMETER
EM	ELECTRON MULTIPLIER
C	FLOW CONSTRICTION
TS	TEFLON SHIELD
R	REACTION TUBE
IC	IONIZATION CAGE
ES	ENTRANCE SLIT OF MASS SPECTROMETER

Figure 22. New atomic beam system.

MASS ANALYZER

In the San Marco experiments, the ion acceleration voltage is kept constant and different masses are measured at different collectors corresponding to different radii in the magnetic field. Such a mass analyzer was not available for the present investigations. A magnetic analyzer equipped with an electromagnet was used instead, which also allowed the ion energy to be kept constant. This analyzer is shown schematically in Figure 23. The scanning of the mass spectrum has been performed by changing the current through the magnet coil. The magnet has a pole gap of 3/8 in. and produces a field strength of 7,020 gauss for 7 amp magnet current. This corresponds to mass 615 if the ion energy is 480V which was kept constant during all experiments. Up to a magnet current of 4 amperes the field strength is proportional to the current and the mass is proportional to the square of the current up to mass 250. The position of the magnet is rather critical to obtain maximum resolution and sensitivity. The best position is shown in Figure 2. In this case, a resolution of 68 at half peak height has been obtained which is more than adequate for the present investigations. The valley between the 28 and 29 peaks was less than 0.3 percent.

The ion current has been measured with a multiplier model MM-1 of the focused mesh type manufactured by the Johnson Laboratories Inc. During the first days after installation this multiplier was rather noisy, but later the noise disappeared and the multiplier performed very well. The gain was more than an order of magnitude larger than the guaranteed value and did not deteriorate during half a year of extensive use despite the fact the system had to be exposed to atmospheric pressure many times.

The ion acceleration voltage was delivered by a Fluke power supply model 412B and the multiplier voltage by a Fluke power supply model 408A. The multiplier current has been measured and recorded with a Hewlett Packard XY recorder. The magnet current was delivered by Kepco Power Supply model KS 60-20M. The voltage drop on a 0.2 ohm resistor was used to drive the X-axis of the recorder. The Kepco Power Supply was used in the voltage regulation mode since the current regulation mode was too sluggish. The mass scan was performed by turning the built-in potentiometer with an external low speed motor. The desired mass range has been adjusted with a series resistor in the magnet circuit in such a way that the full output voltage of the power supply could be utilized. This was necessary to achieve adequate resolution of the potentiometer.

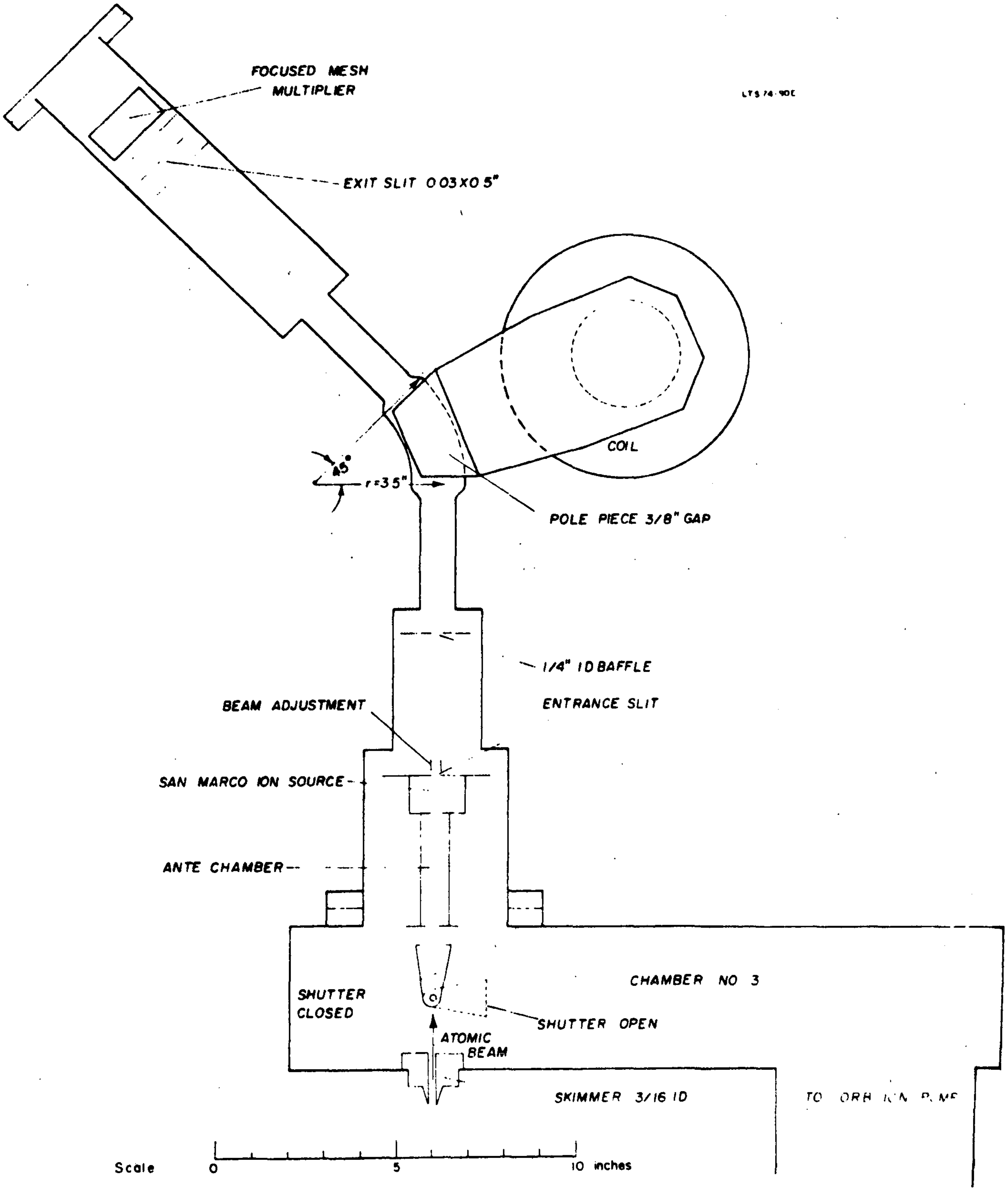


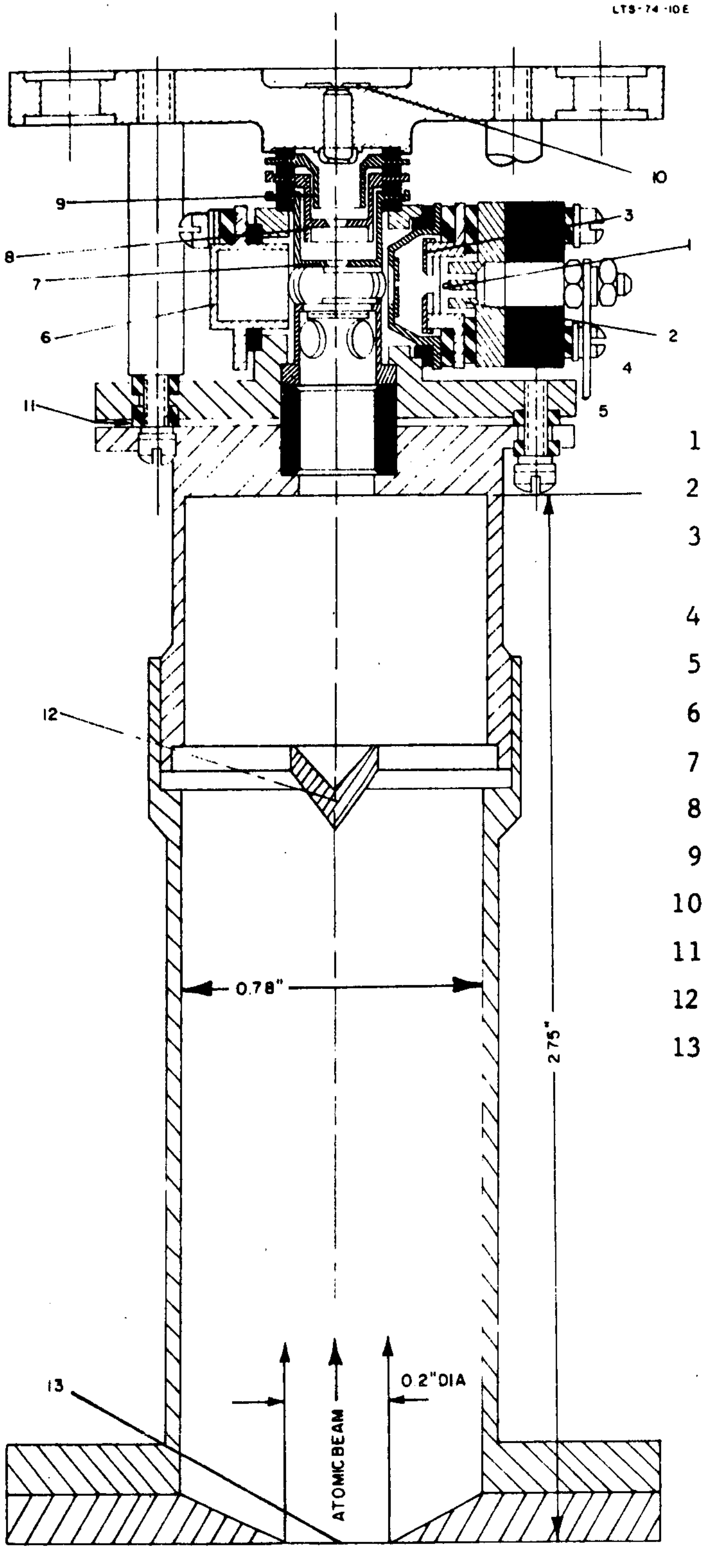
Figure 23. Magnetic mass analyzer.

ANTECHAMBERS

NASA has supplied three different antechambers; one made out of stainless steel with a pyrex glass liner, a second one also made of stainless steel but gold plated and the third one fabricated out of solid titanium. Each antechamber contains an insert (see #12 on Figure 24) which prevents the direct beam from entering the ionization region. Beam particles suffer a very large number of wall collisions before they can either reach the ionization region or escape through the entrance aperture. Because of this large number of wall collisions, all molecules leave the antechamber with the thermal velocity corresponding to the wall temperature, regardless of the actual value of the accommodation coefficient. This is the purpose of using the antechambers since they eliminate the uncertainty in the data evaluation which was disturbing with "half open" ion sources.

The antechambers are screwed on to the ion source at the interface #11 on Figure 1. Exchange of an antechamber requires venting the whole system with dry nitrogen and removing the mass spectrometer from the atomic beam system. Each antechamber was carefully cleaned with acetone before installation. Nevertheless, the first spectra always showed a very rich hydrocarbon background sometimes extending above mass 500. This hydrocarbon background disappeared completely after the first high temperature bake-out. The remaining background spectrum was quite similar to the one obtained with the plain San Marco source without an antechamber attached.

All present measurements have been performed with the gold plated antechamber.



1-filament
2-shield
3-electron focus electrodes
A and B
4-electron accelerator
5-ion repeller
6-anode
7-ion accelerator
8-ion focus A
9-ion focus B
10-exit slit 0.012 x 0.05 inches
11-interface
12-insert
13-atomic beam entrance
aperture

Figure 24. San Marco-C ion source with ante-chamber.