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FINAL REPORT

An Analytical and Experimental Investigation of Limited Operational Life of CO_2 Lasers to achieve a Non Flowing Sealed CO_2 Gas Laser

Prepared by

J. F. [illegible]

October 1967

Prepared under Contract No. NAS12-[illegible] by

HONEYWELL INC.
Radiation Center
Boston, Massachusetts

[illegible], Technical Monitor
Electronics Research Center
National Aeronautics and Space Administration
575 Technology Square
Cambridge, Massachusetts 02139

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An Analytical and Experimental Investigation of Limited Operational Life of CO_2 Lasers to Achieve a Non Flowing Sealed CO_2 Gas Laser

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SECTION 1
INTRODUCTION AND SUMMARY

This report relates the results obtained during the two-month contract NAS12-590, "An Analytical and Experimental Investigation of Limited Operational Life of CO_2 Lasers to Achieve a Non Flowing Sealed CO_2 Gas Laser."

The objective of this contract was to investigate the gaseous mechanisms which limit the operating life of a sealed CO_2 gas laser.

The particular areas investigated were:

1. The dissociation of pure CO_2 in a gas discharge.
2. The effects of water vapor and xenon upon dissociation.
3. Electrode material in regard to its influence upon clean-up rate.

Results to date indicate that the dominant CO_2 depletion mechanisms are due initially to dissociation followed by a steady clean-up of the dissociation products and the CO_2 by the electrodes.

The dissociation rate of CO_2 is strongly dependent upon additive gases and indirectly by a clean-up rate of a given electrode material. A combination of nickel electrodes and carbon dioxide with water vapor added has produced a very stable CO_2:CO:O_2 concentration. A system employing this combination could be expected to run for several hundreds of hours before total depletion of the CO_2 component occurs.

SECTION 2
PLAN OF INVESTIGATION

In order to determine the causes of limited operational life of a sealed CO_2 laser the following plan of investigation was undertaken.

The pyrex discharge tube (un-cooled) shown in Figure 1 was constructed and two electrodes were sealed in. The tube was filled with a known quantity of gas, and excited with a d-c power supply.

Mass scan recordings were made of the tube before filling, to obtain data on the background; of the tube when it was filled and before excitation; and then every half hour (during normal working day) after the discharge has begun.

The mass scan recordings are then measured, and the mass peaks are recorded for each mass number and put into tabular form. The data at this point is raw experimental data and must be modified. The raw data is presented as peak heights versus elapsed time (running time). The peak heights are converted to partial pressure by the partial pressure calibration curves.

At this point, the data represents a time history of a given quantity of fill gas and how it is affected by an electrical discharge.

The following questions may now be investigated:

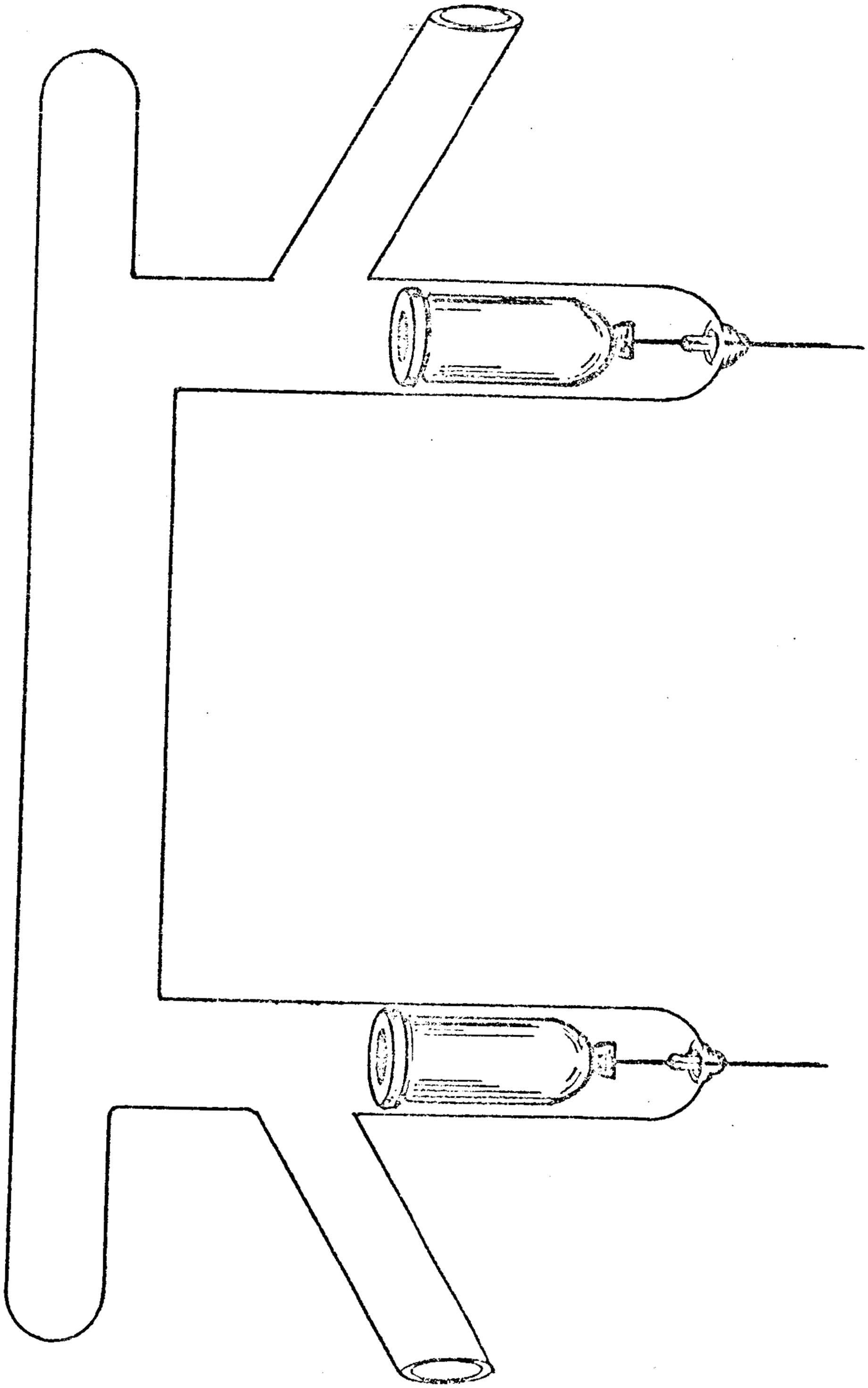

Figure 1 DISCHARGE TUBE

1. Does the gas composition remain unchanged?

2. If new compounds are formed:

   a. What are they?

   b. In what quantity?

3. Have contaminants evolved from the discharge tube and electrodes?

4. Is there a depletion of the fill gas?

To investigate these questions, consider the following sample data. Figure 2 represents a mass scan recording of the discharge tube at a pressure of 5×10^{-7} Torr. The mass peaks are identified according to their specific mass species. Next, the discharge tube is filled with 3 Torr of CO_2 (see Figure 3). At masses 44, 28, 22, 16, and 12 there is a significant increase in peak height. This set of peaks represents a partial cracking pattern for CO_2. Figure 4 is a mass scan recording showing what has happened to the gas composition after one-half hour of excitation. Figure 5 shows a plot of pressure vs elapsed time for mass peaks 28, 32, and 44 (CO_1, O_2, and CO_2).

Figures 2, 3, and 4 show that no new mass species are formed greater than 0.003 Torr of CO_2 pressure, and no contaminants (i.e., different from the existing species) have changed, and from Figure 5 there is at first a rapid depletion of mass 44 and then a slower, steady depletion of mass 44. At mass 28 and 32 the behavior is different, in that initially there is a rapid increase in partial pressure up to a peak value, and then a steady decrease in both 28 and 32. However, the decrease in 32 is greater than 28.

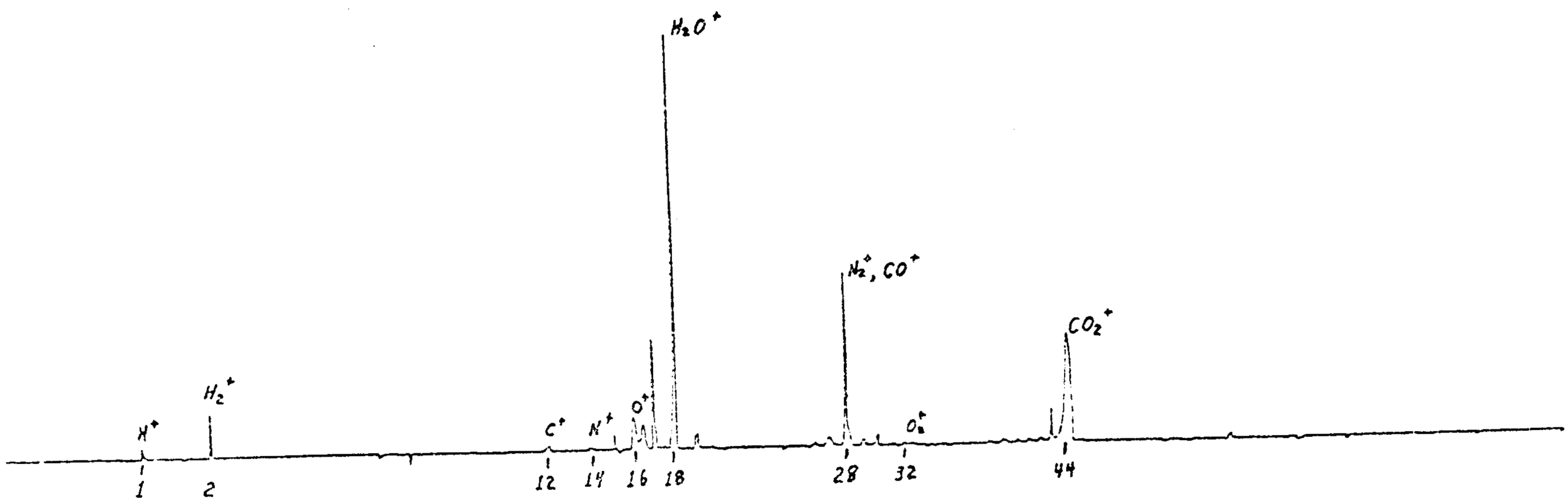

Figure 2 MASS SCAN BACKGROUND

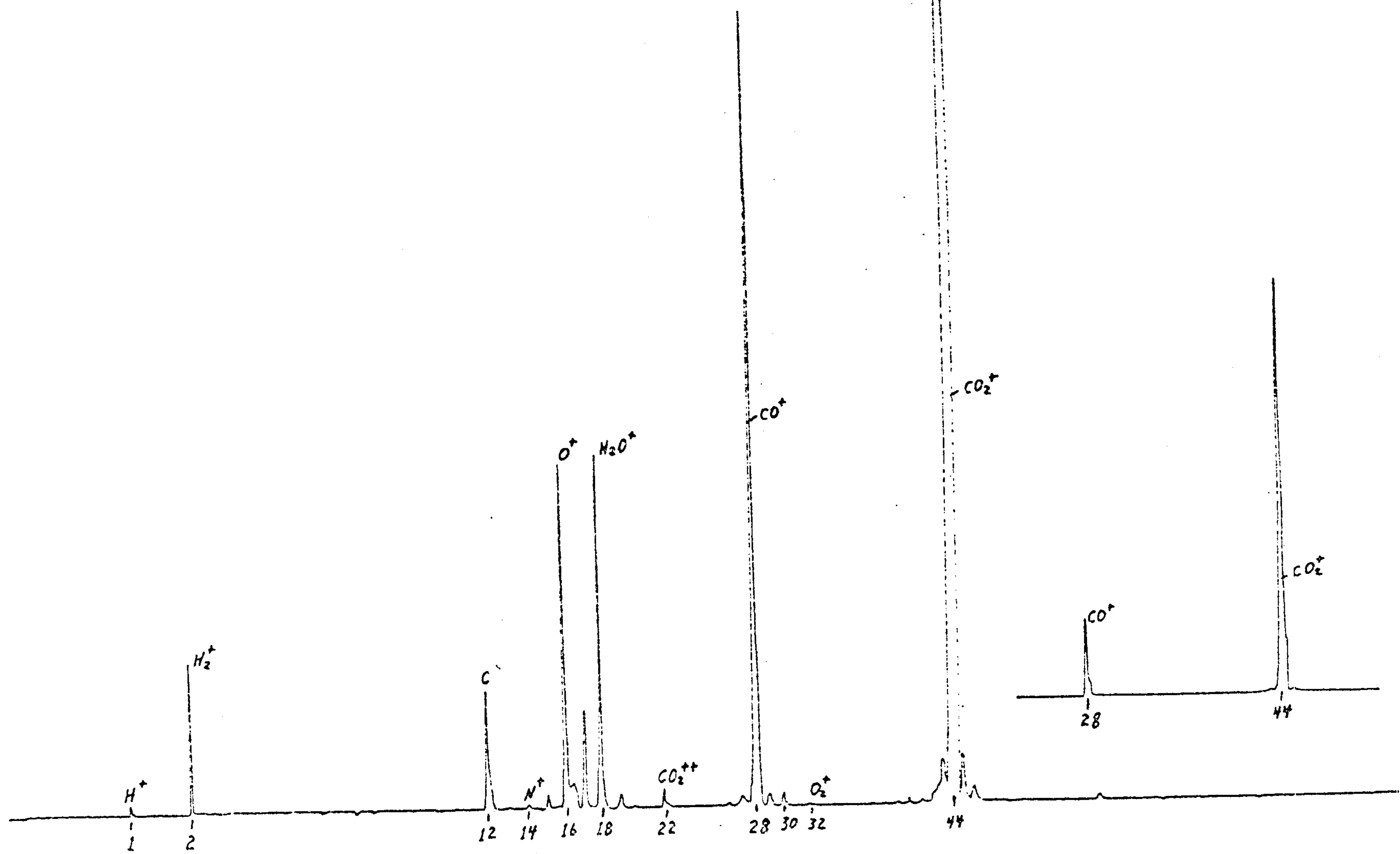

Figure 3 MASS SCAN 3 TORR CO_2

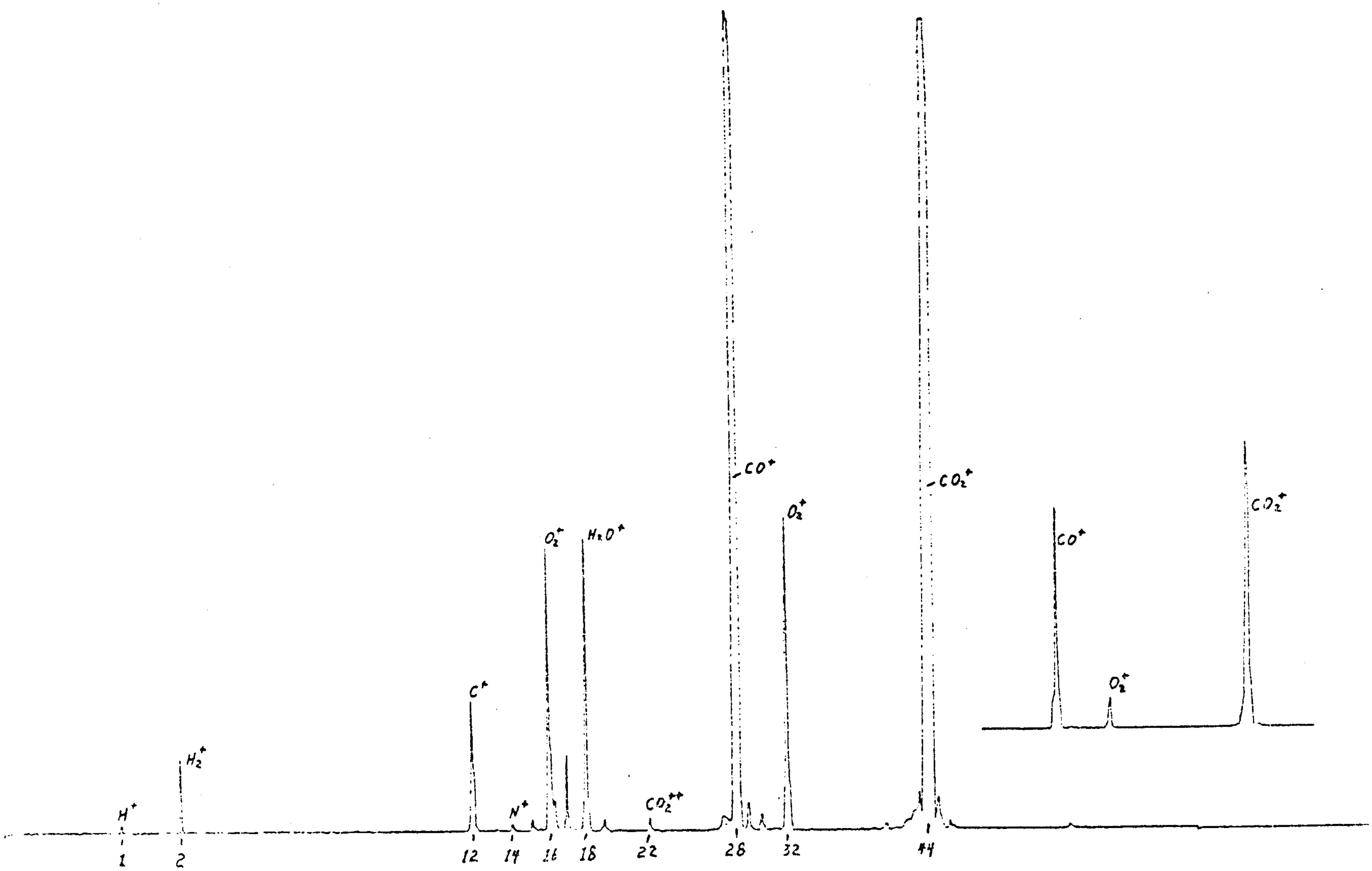

Figure 4 MASS SCAN AFTER 5 HR OF DISCHARGE

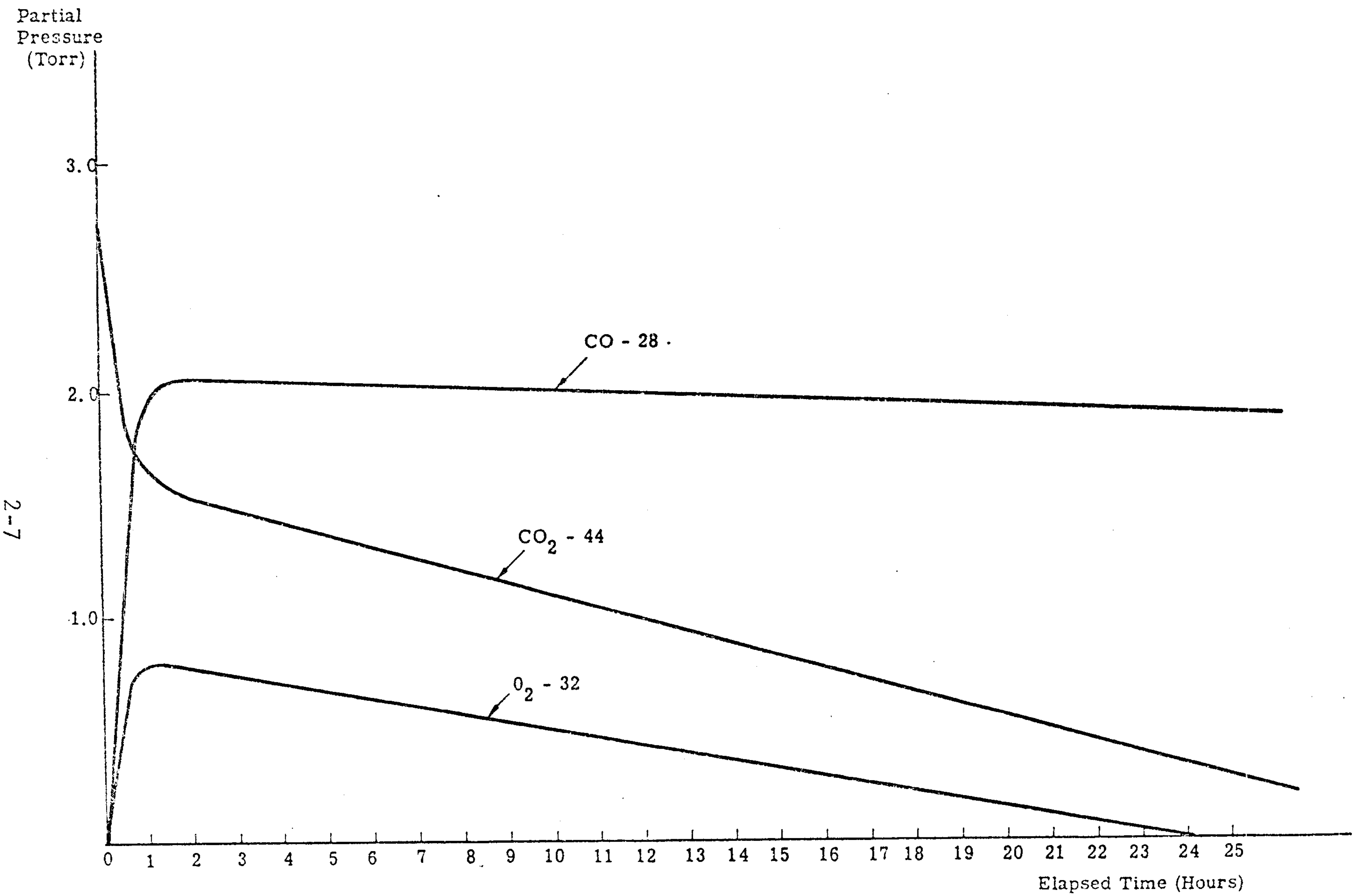

Figure 5 TIME HISTORY OF SEALED CO_2 GAS

From Figure 5, it appears that two distinct processes are occurring. The first one is very rapid and is completed in the first half hour. The second process is much slower and continues for a much longer time (24 hours).

Process one appears to be dissociation of the CO_2 molecule governed by the following chemical reaction

$$2CO_2 + \Delta E \rightleftarrows 2CO + O_2$$

Process two is a combination of dissociation and clean-up effects. Clean-up is a term used to describe any process which tends to reduce the gas species, e.g., absorption, adsorption, chemisorption, ion burial, etc.

The shapes of these curves are influenced by the non-instantaneous response of the mass analyzer due to diffusion time from the sample to the mass analyzer tube.

However, it was determined that a time significantly less than five minutes was required for dissociated species to appear at the analyzer tube.

SECTION 3
EXPERIMENTAL SETUP

The main vacuum system shown in Figure 6 consists of a high-speed mechanical vacuum pump, a 140 liter per second Vac Ion pump, and a Vac Sorb pump. All pumps are used to obtain a system pressure of from 5 x 10^{-8} Torr to 5 x 10^{-7} Torr. A manifold, which allows up to six gases to be mixed together, is used for gas handling. All gases used are J. T. Baker Research Grade gases with the exception of H_2O vapor which is provided from a vessel containing liquid H_2O at low pressure. Total pressure is measured with a Wallace-Tiernan 0-20 Torr absolute pressure gauge. To monitor relative pressure, several thermocouple gauges are used. To monitor the ultimate vacuum pressure, two Vac Ion gauges are used.

Discharge tubes (A and B) are made of pyrex glass and electrodes of various materials are sealed into the glass tubes. A Granville Phillips variable leak valve measures the gas flow into the mass analyzer tube (GE Partial Pressure Analyzer). The mass analyzer tube consists of a Nier-type electron-bombardment ion source, a 90-degree sector magnetic analyzer with a 5-cm radius of curvature, and a 10-stage electron multiplier ion detector entirely enclosed in a glass-metal envelope. A 6.5 kilogauss electromagnet provides a uniform magnetic field across the mass analyzer tube. A Bell (Model 110-A) Gaussmeter monitors the magnetic field strength. A voltage is generated in the gaussmeter proportional to the magnetic field strength of the electromagnet. This voltage is applied to the X drive of Electro Instruments

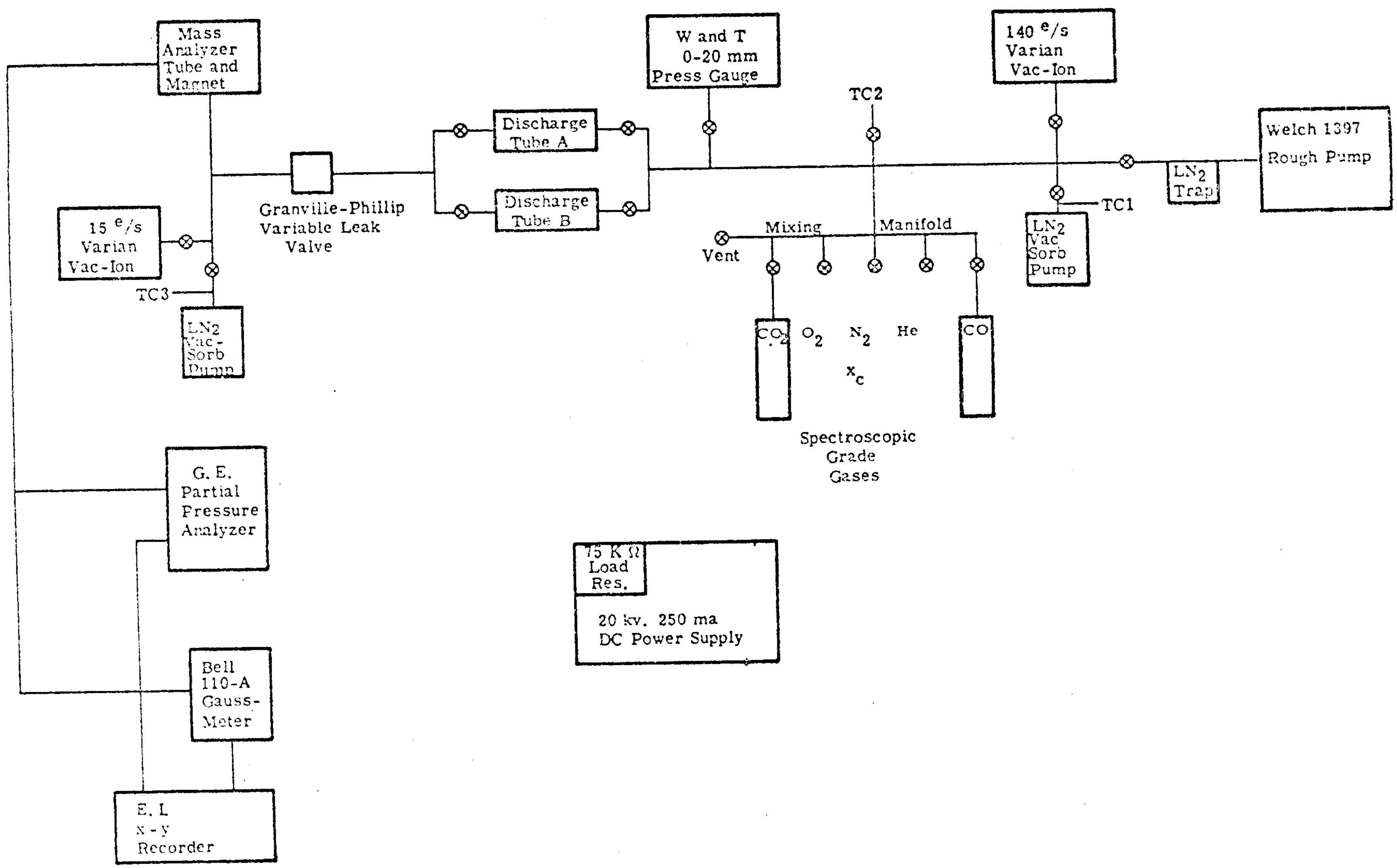

Figure 6 EXPERIMENTAL SET UP BLOCK DIAGRAM

X-Y recorder. The Y drive obtains its signal voltage from the electron multiplier output. Excitation of the discharge tubes is obtained from a NJE, 0-25 kv, 0-250 ma d-c power supply.

SECTION 4
SYSTEM CALIBRATION

Mass Peak Calibration

The magnetic field strength is monitored with a gaussmeter, and the output of this meter is a voltage proportional to the magnetic field strength. This voltage is applied to the X drive of the X-Y recorder. This results in motion along the chart paper which is dependent on the magnetic field strength. A calibration curve of mass number versus distance along the X axis can be plotted as shown in Figure 7.

Partial Pressure Calibration

Partial pressure is calibrated by the following procedure. Spectroscopically pure gases (CO_2, N_2, O_2, H_e, CO) are emitted into the discharge tubes at a measured absolute pressure (Wallace and Tiernan Gauge). The scan is made with the mass spectrometer. The heights of each peak are measured and the data is plotted (Figure 8) as a series of curves of partial pressure versus peak height for each mass peak.

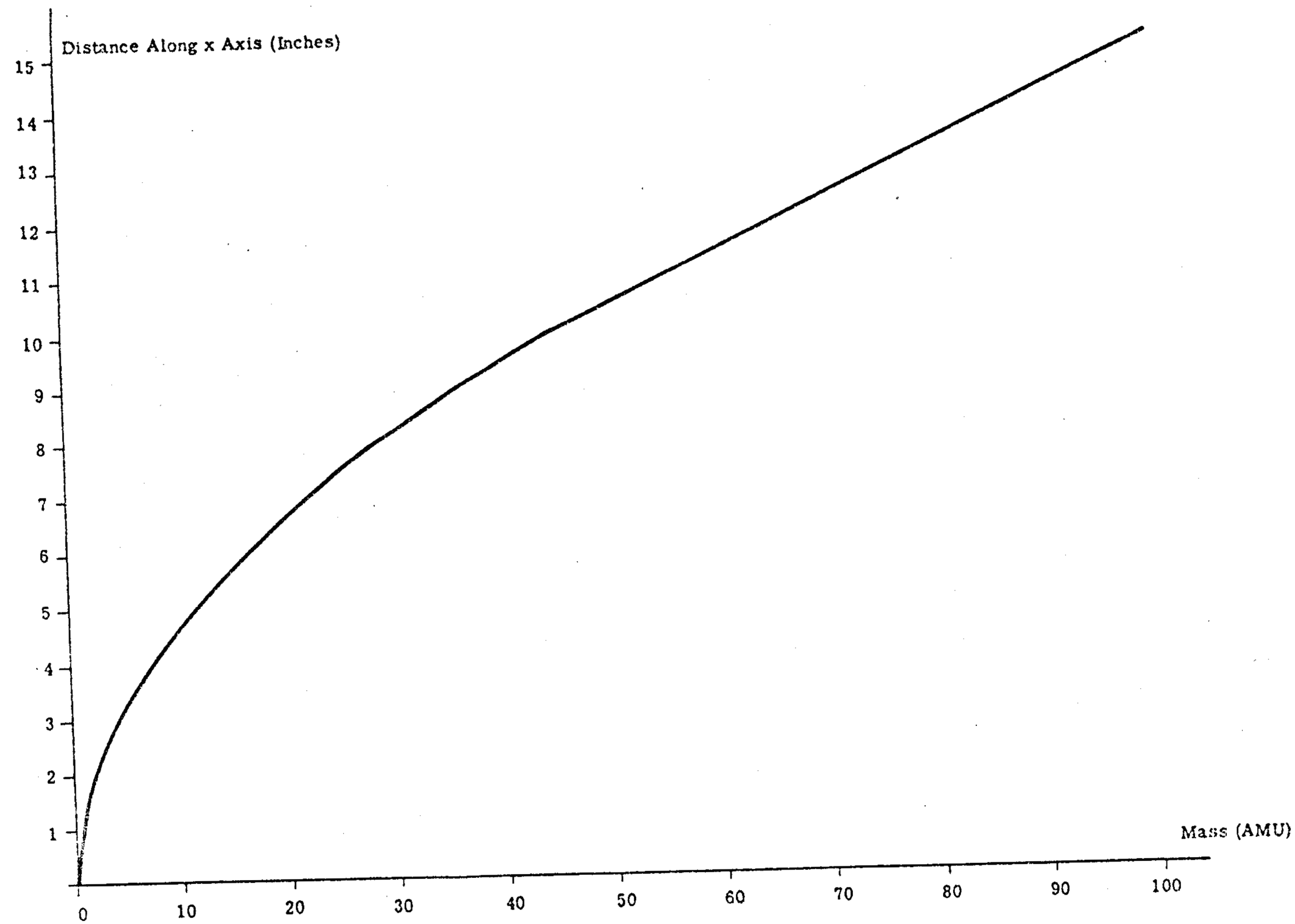

Figure 7 MASS PEAK CALIBRATION

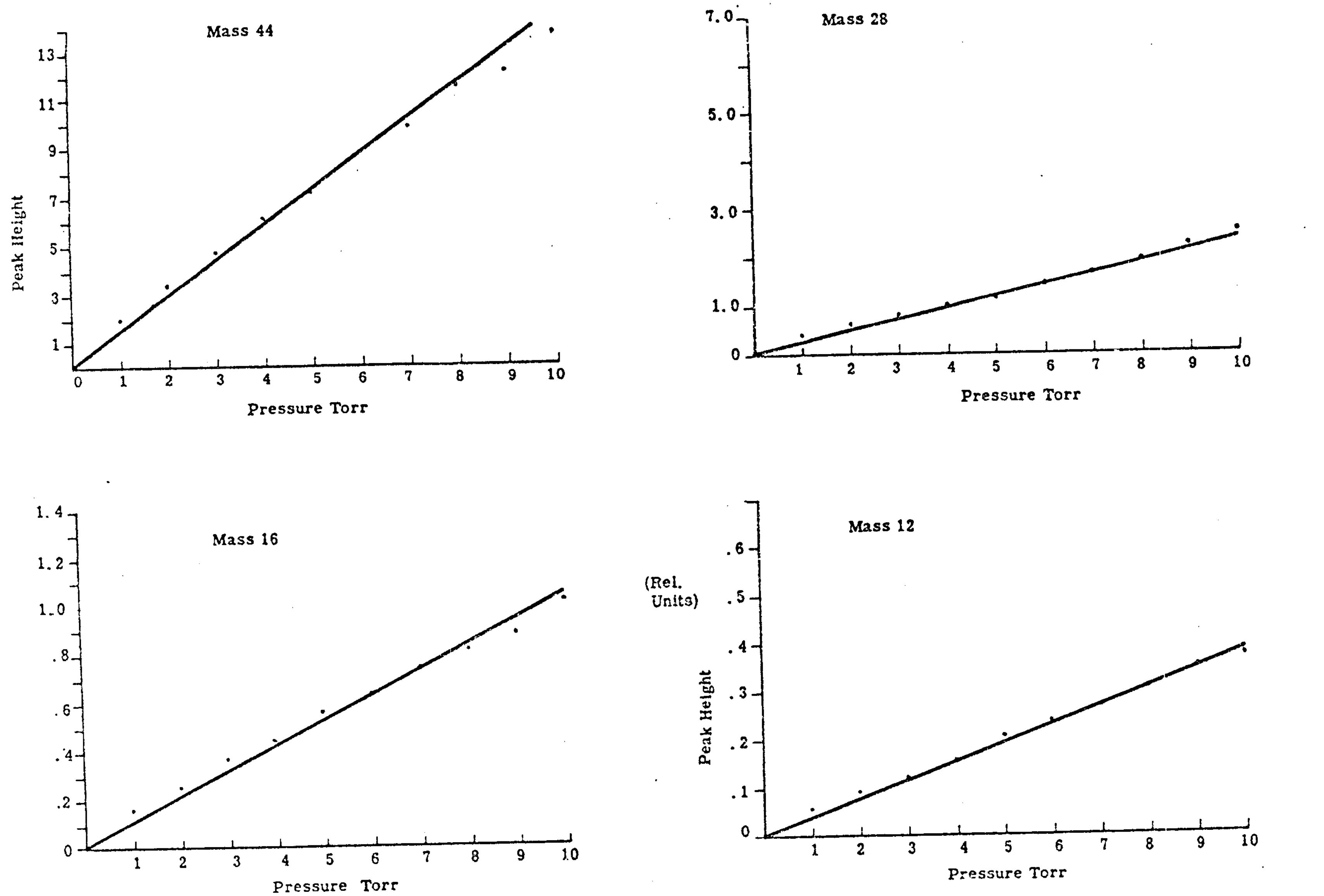

Figure 8 SAMPLE PARTIAL PRESSURE CALIBRATION

SECTION 5
RESULTS

Detailed results are presented for nine combinations of gas mixture and electrode material. The gases are pure CO_2, CO_2 with H_2O, and CO_2 with Xe. The electrode materials are aluminum, nickel, and nickel-coated iron. The Fe-Ni electrodes were neon sign electrodes without the ceramic sputtering-collar or the usual emissive coating.

<u>Pure CO_2, Al. (Figure 9)</u>

During the first 3-1/2 hours of this run, CO pressure increased and CO_2 decreased rapidly. While only 1.5 Torr of CO_2 disappeared, 5.3 Torr of CO appeared; an excess of 3.8 Torr which cannot be accounted for by the dissociation process. In this case, since CO_2 pressure is down to 0.2 Torr at 3-1/2 hours, the excess CO must have evolved from the electrodes. During the next 20 hours, the CO cleaned up at an average rate of 0.25 Torr/hr and CO_2 cleaned up at 0.01 Torr/hr.

Significantly, no oxygen was found during this run, even in the earliest period where dissociation of CO_2 into CO and O_2 would have been a significant factor.

<u>Pure CO_2, FE-Ni (Figure 10)</u>

In this run, an initial rapid change of partial pressures is observed during the first hour. Although we cannot at any time

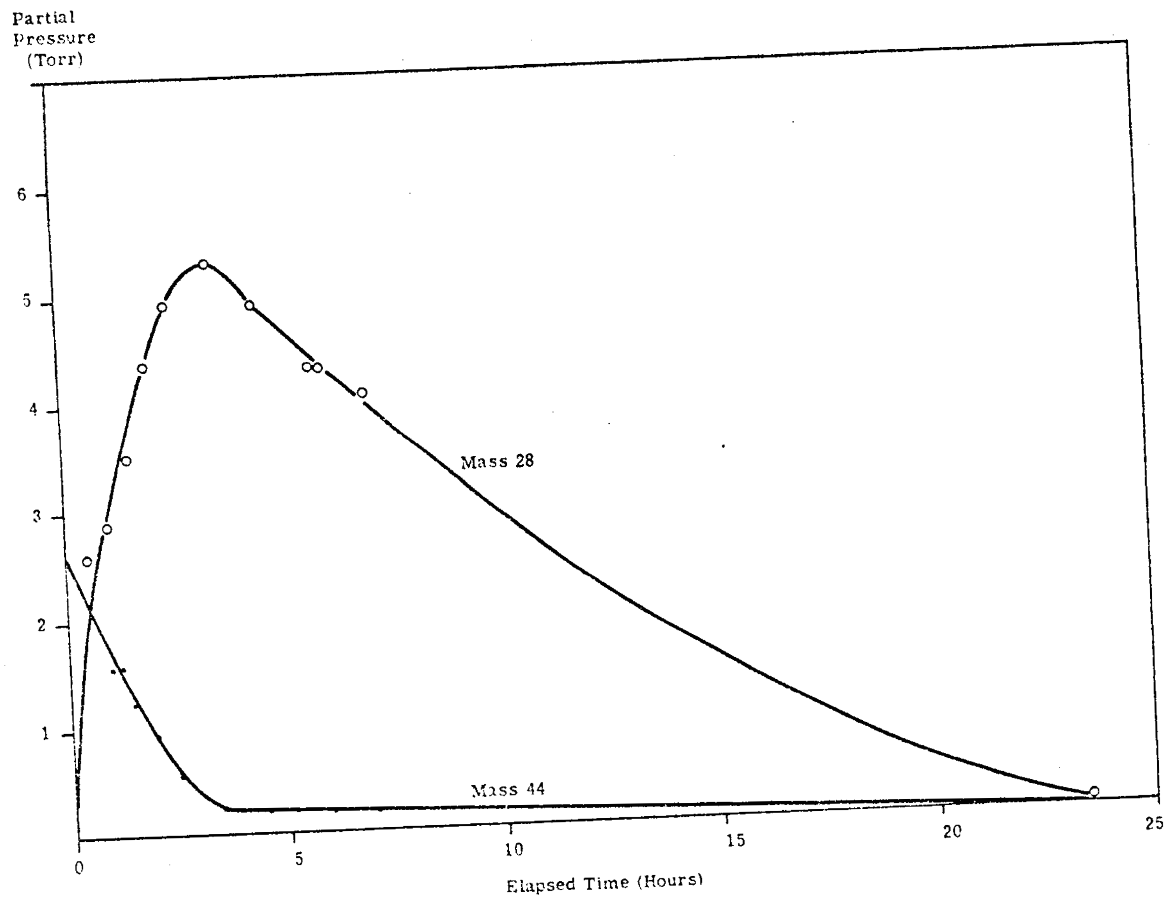

Figure 9 3 TORR CO_2, Al ELECTRODES

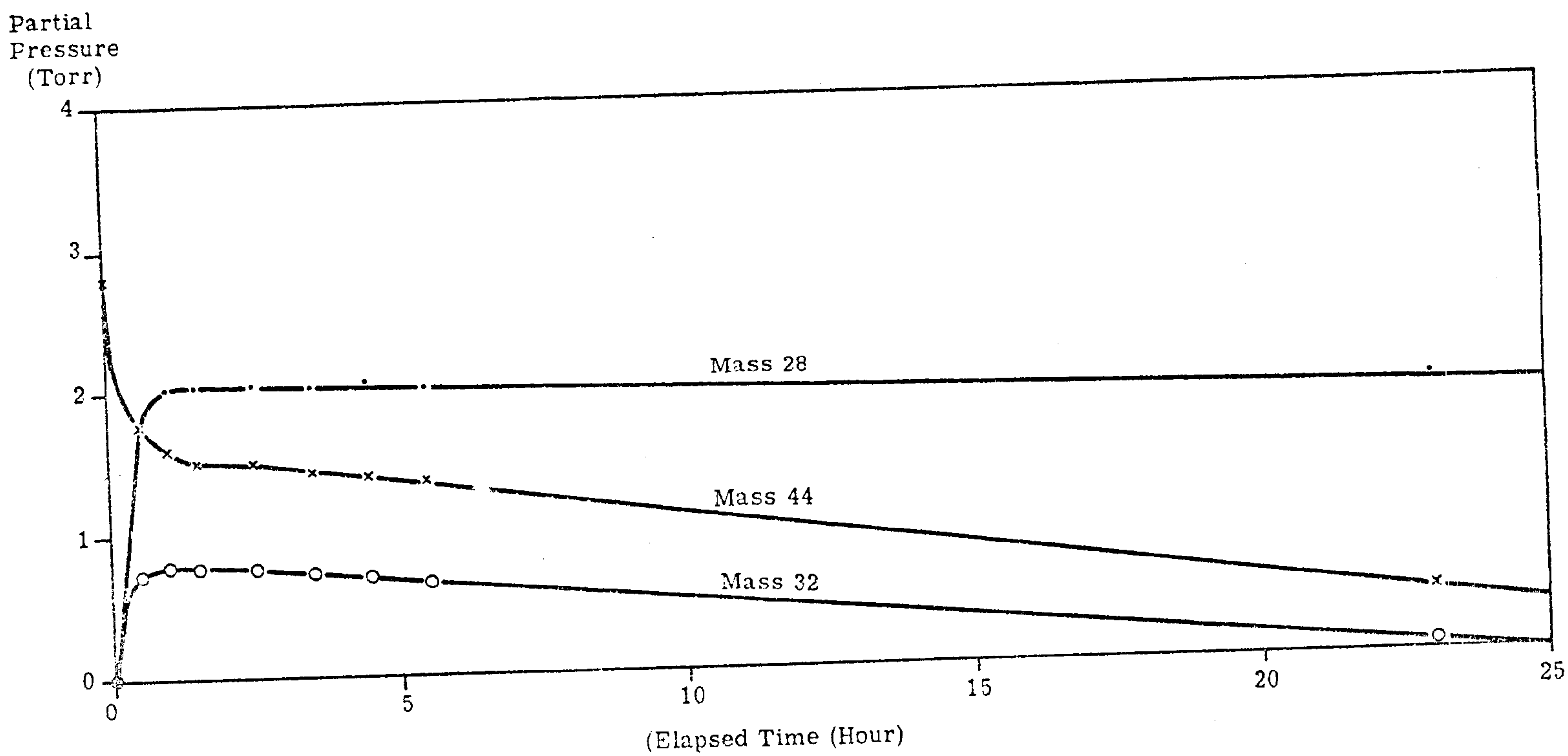

Figure 10 3 TORR CO_2 Fe-Ni ELECTRODES during this run see only the $2CO_2 \rightarrow 2CO + O_2$ reaction, the curves imply that it was the predominant process during the first hour. The CO_2 pressure decreased by 1.05 Torr while CO and O_2 increased by 1.75 Torr and 0.75 Torr, respectively. Thus, the discharge produced an excess 0.70 Torr of CO and 0.23 Torr of O_2.

After the first hour, all three gases cleaned up at constant rates.

CO_2	0.055 Torr/hr
CO	0.010 Torr/hr
O_2	0.035 Torr/hr

<u>Pure CO_2, Ni (Figure 11)</u>

There is a pronounced scatter in data points on this run, the reason for which is not clear.

Initially, excess CO and CO_2 appeared in this run, probably by evolution from the cathode. The electrodes were not processed prior to this run, so the initial pressure increase is not unreasonable. At 17 hours, the CO_2 pressure has decreased by 1.3 Torr while CO has increased by 1.2 Torr from the pressures at one-half hour. Beyond 18 hours, the CO clean-up rate is zero, or at least less than the uncertainty due to scatter of the data points. The clean-up rate for CO_2, after 18 hours, is on the order of 0.04 Torr/hr and appears to be zero at the very end of

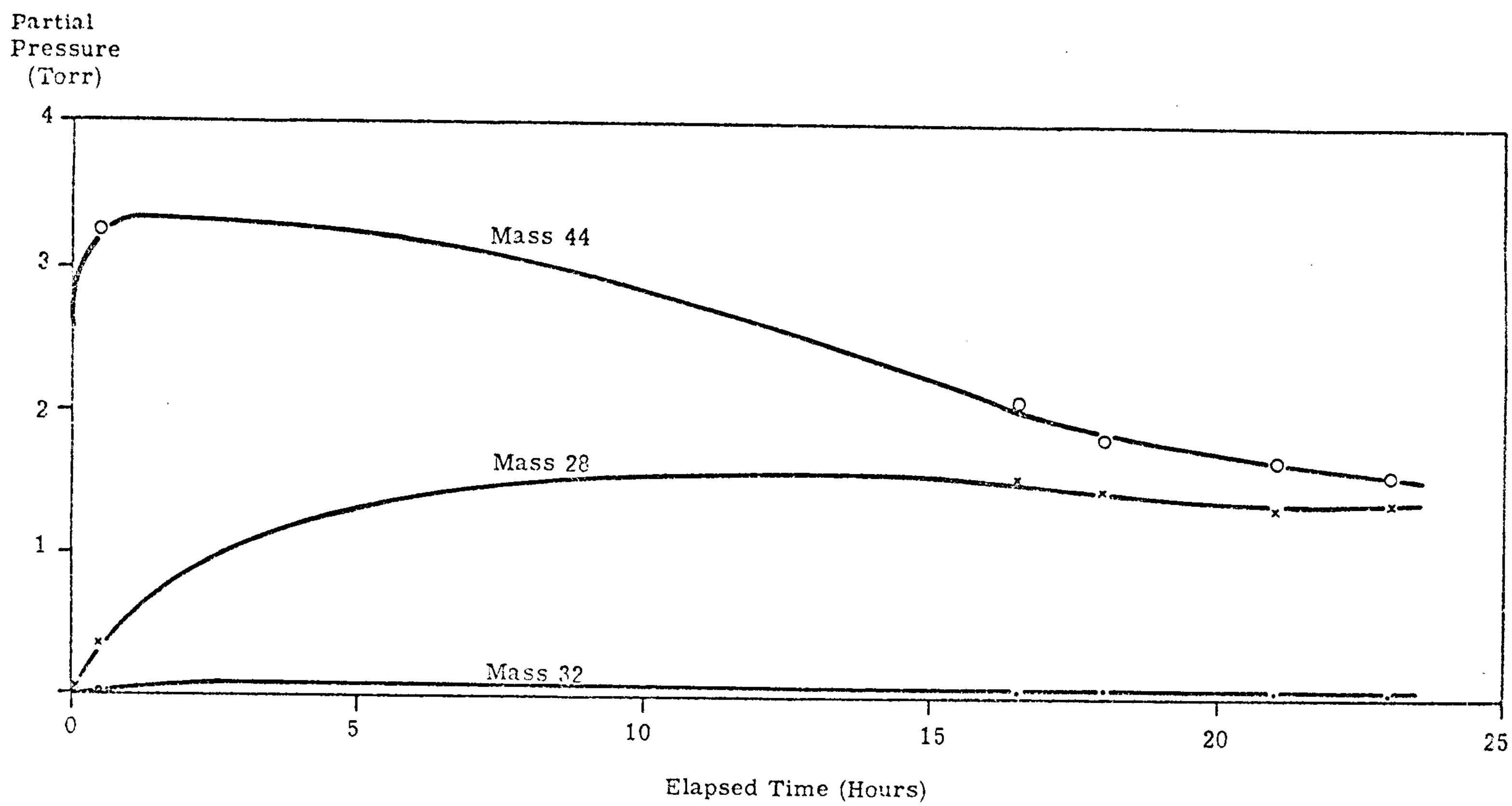

Figure 11 3 TORR CO_2, Ni ELECTRODES

the run. The O_2 pressure also appears constant at the end of the run, but is far less than that which would be produced by dissociation. The dissociation of 1.2 Torr of CO_2 would produce 1.2 Torr of CO and 0.6 Torr of O_2. It is very likely that dissociation was the primary process during the first 18 hours of this run, with the O_2 being cleaned up at the cathode.

<u>$CO_2 + H_2O$, Al (Figure 12)</u>

During the first nine hours of this run, more CO appears than can be accounted for by the disappearance of CO_2, assuming dissociation. Thus, either CO, CO_2, or both are released by the discharge. There is no measurable O_2 pressure at any time. The slopes of the curves during the early part of the run indicate that the dissociation rate is much less than it was in a pure CO_2 discharge. After nine or ten hours, clean-up is predominant and the pressure of each gas component is decreasing.

<u>$CO_2 + H_2O$, Fe-Ni (Figure 13)</u>

During the first one-half hour of this run, both CO_2 and CO were released. After this the CO_2 pressure decreased, and CO pressure increased, at constant rates. This strongly implies that clean-up and dissociation are taking place at constant rates. The net rates of change of partial pressure are:

CO_2	- 0.10	± 0.03 Torr/hr
CO	+ 0.08	± 0.03 Torr/hr

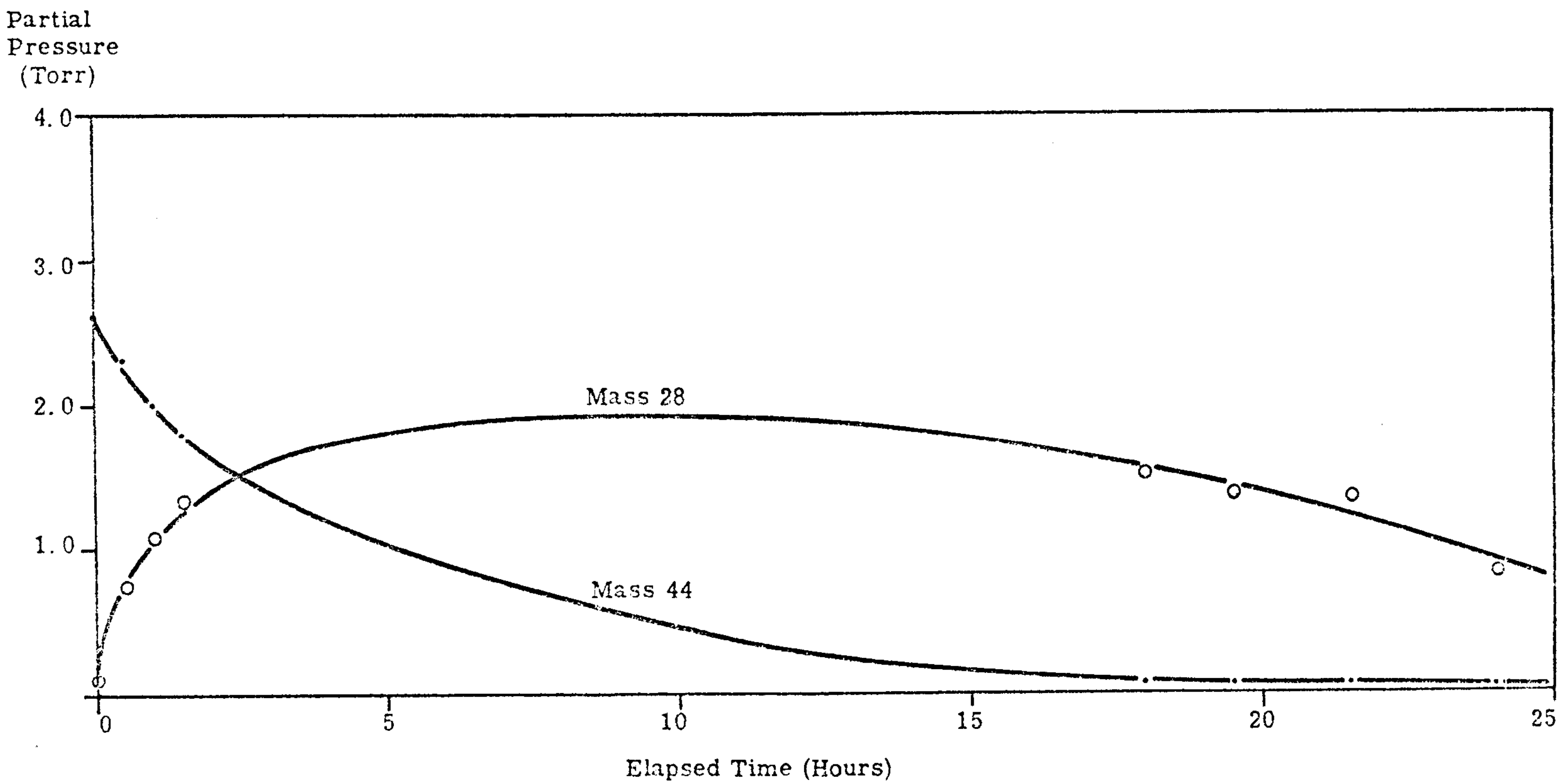

Figure 12 3 TORR CO_2, 0.1 TORR H_2O Al ELECTRODES

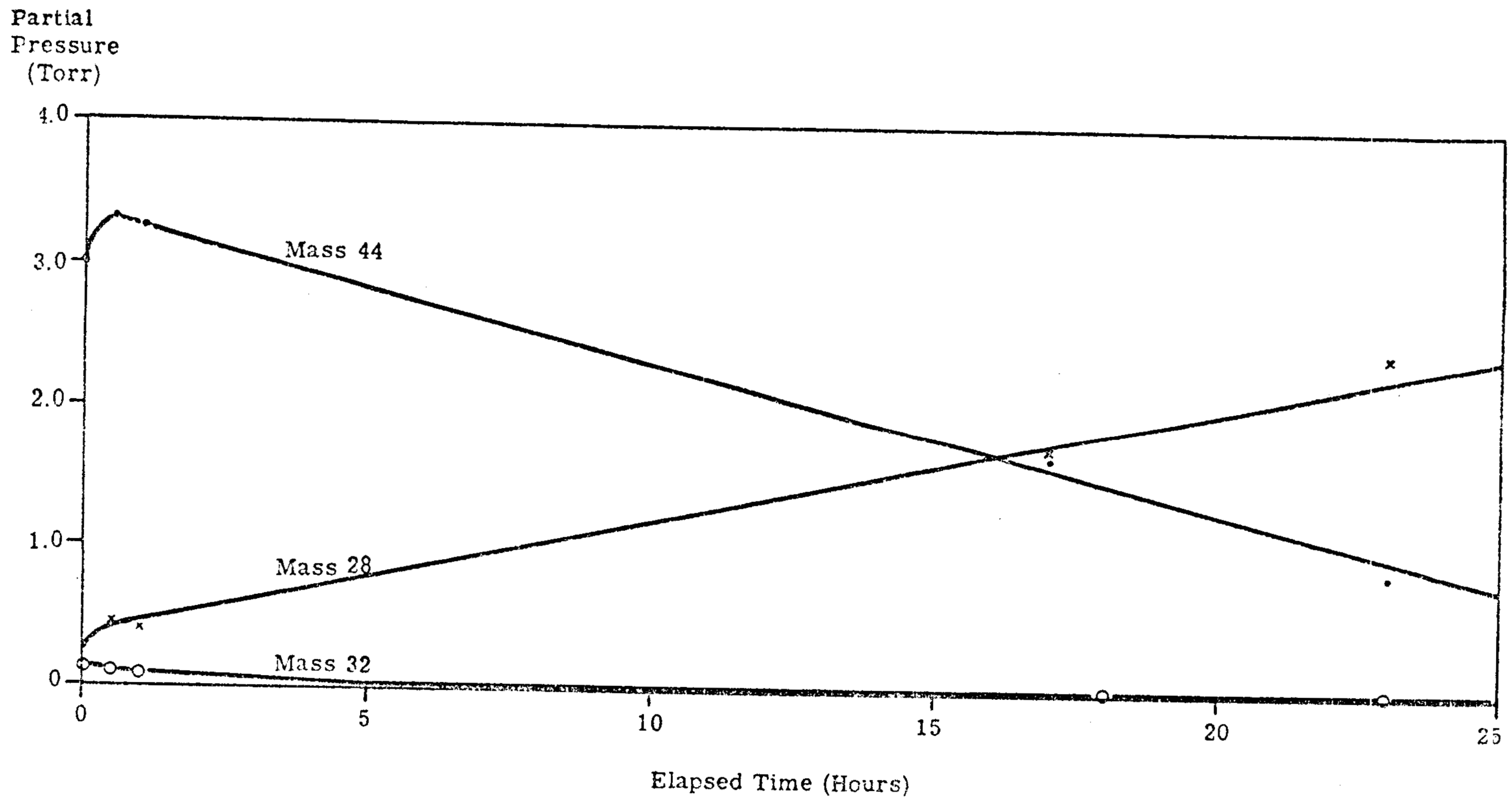

Figure 13 3 TORR CO_2, 0.1 TORR H_2O Fe-Ni ELECTRODES

Any constant dissociation rate 0.08 and 0.10 Torr/hr could, with the correct clean-up rates, explain this data. If a dissociation rate not in the range 0.08 - 0.10 Torr/hr is assumed, the data can still be explained if either CO or CO_2 is released at a constant rate (e.g., evolved from a cathode or etc). Since no evidence for long-term release of excess CO_2 or CO has been observed in any part of this program, it is reasonably safe to say the dissociation rate was in the range $0.05 < \text{rate} < 0.13$ Torr/hr.

$CO_2 + H_2O$, Ni (Figure 14)

Although O_2 pressure showed a slight rise during the early part of this run, it never exceeded 0.1 Torr. The partial pressures of CO_2 and CO showed constant rates of change during the entire run. These rates were:

CO_2	- 0.016
CO	+ 0.018

In this case, a constant balance is again implied between dissociation and clean up. However, the rates above are subject to uncertainties of ± 0.008 Torr/hr. Thus, the dissociation rate on this run was probably $0.010 < \text{rate} < 0.024$ Torr/hr.

CO_2 + Xe, Al (Figure 15)

The initial increase in CO pressure and rapid decrease in CO_2 occurs during the first five hours of this run. After this, both CO_2 and CO are slowly cleaned up. O_2 is not observed.

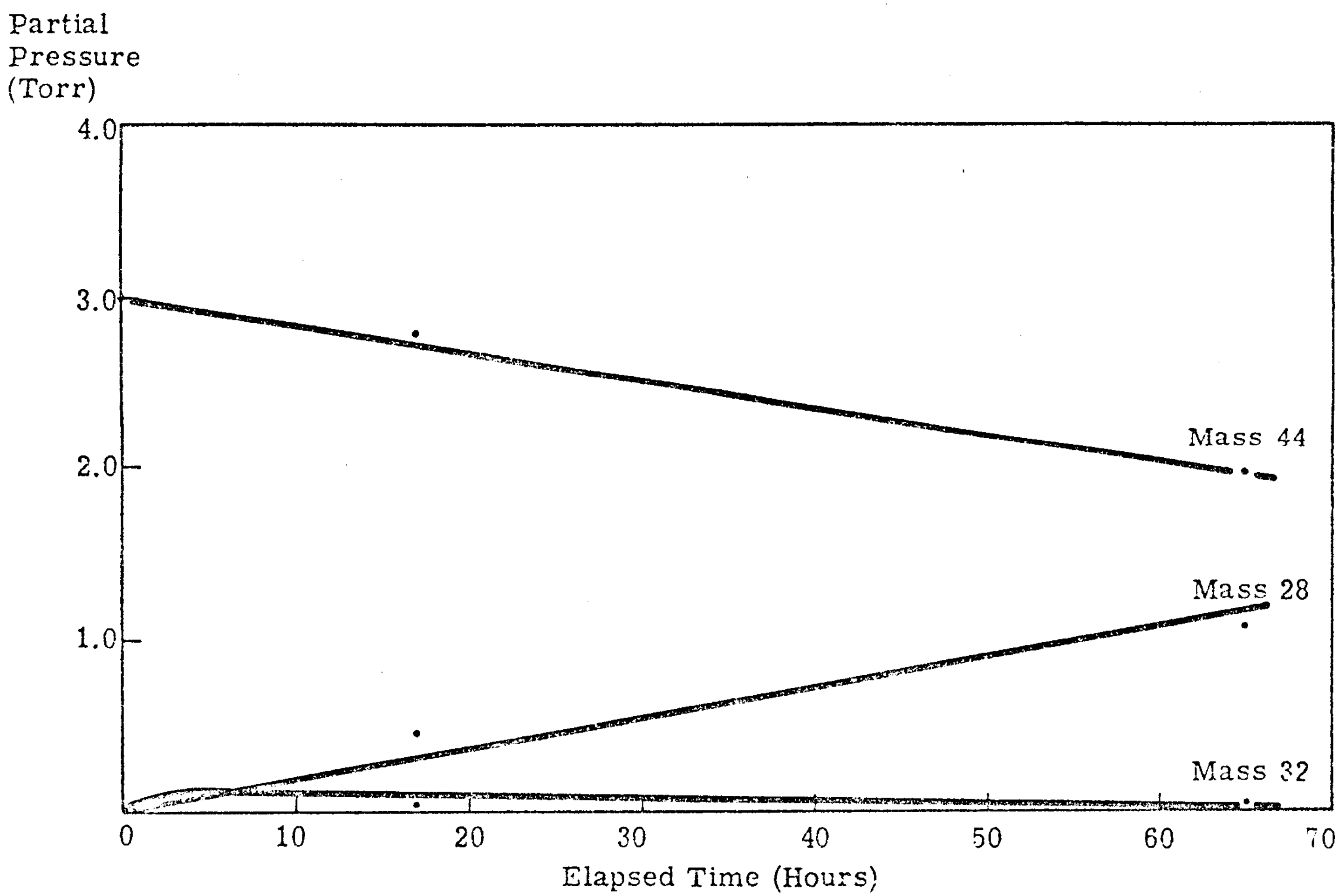

Figure 14 3 TORR CO_2 0.1 TORR H_2O Ni ELECTRODES

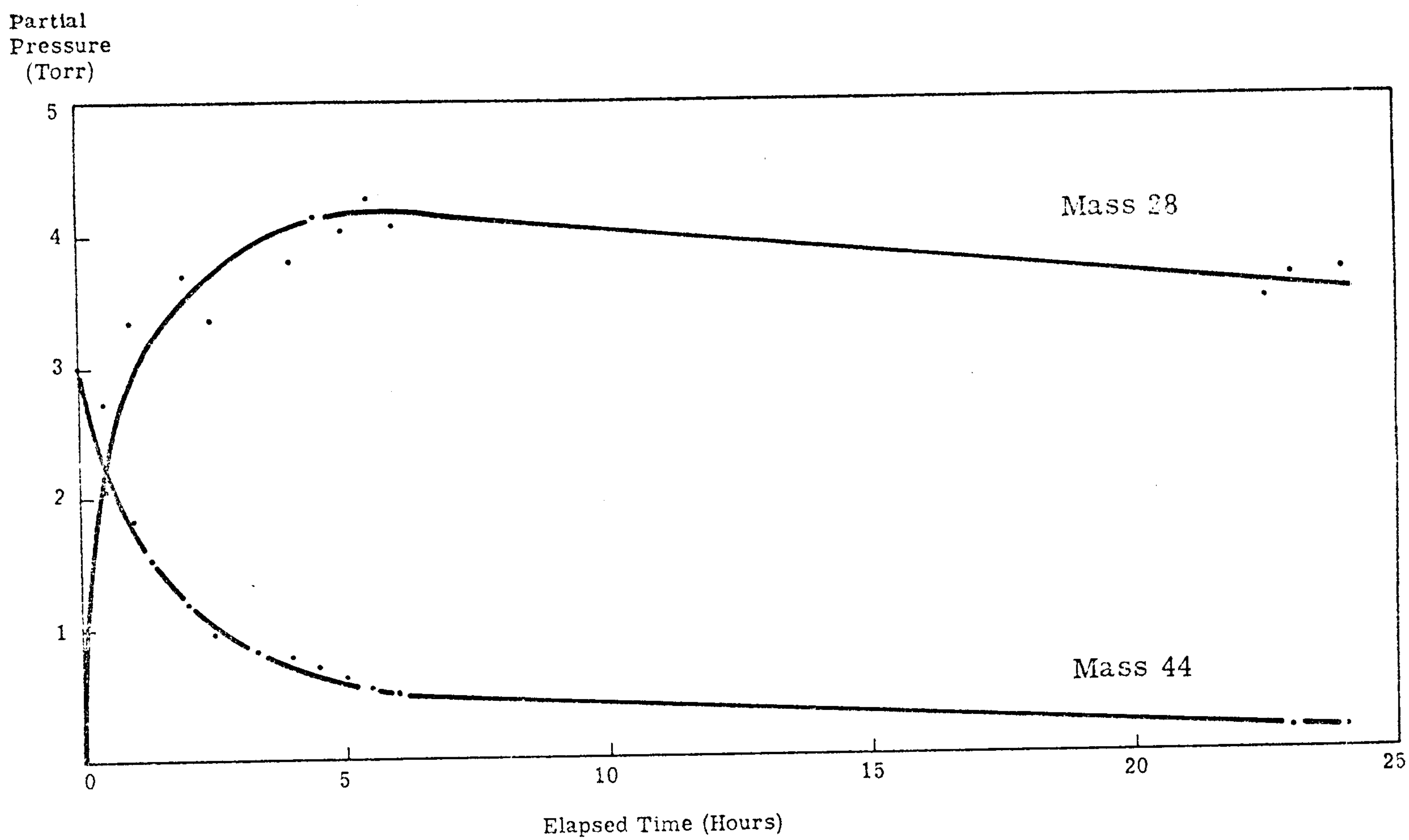

Figure 15 3 TORR CO_2, 1 TORR Xe, Al ELECTRODES

The only effect clearly evident is a reduction of the dissociation rate from that of pure CO_2. It appears that a rather large amount of CO was evolved from the electrodes during the first hour or one-half hour, and that dissociation was a predominant process during the next few hours. No O_2 was found in this run.

CO_2 + Xe, Fe-Ni (Figure 16)

Again, an excessive amount of CO appears and the dissociation rate is decreased. The production of O_2 and CO and reduction of CO_2 pressure imply that dissociation is a predominant factor from about the third to the tenth hour of the discharge.

CO_2 + Xe, Ni (Figure 17)

In this run, it appears that dissociation and production of CO are taking place during the first three hours. The CO_2, CO and O_2 then clean up at rates between 0.01 and 0.02 Torr/hr. After twenty hours, the curves behave as though dissociation again became the predominant effect.

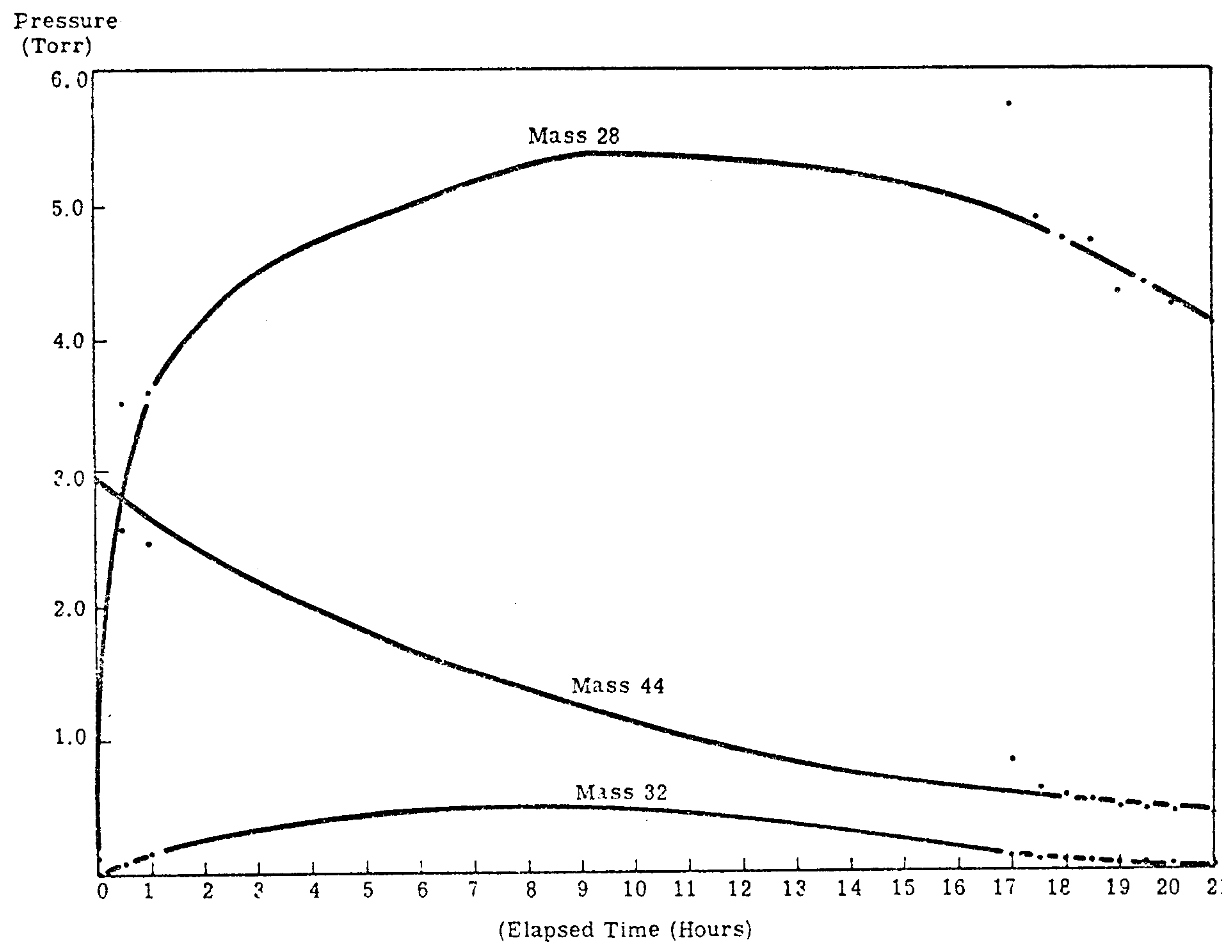

Figure 16 3.0 TORR CO_2, 0.5 TORR Xe, Fe-Ni ELECTRODES

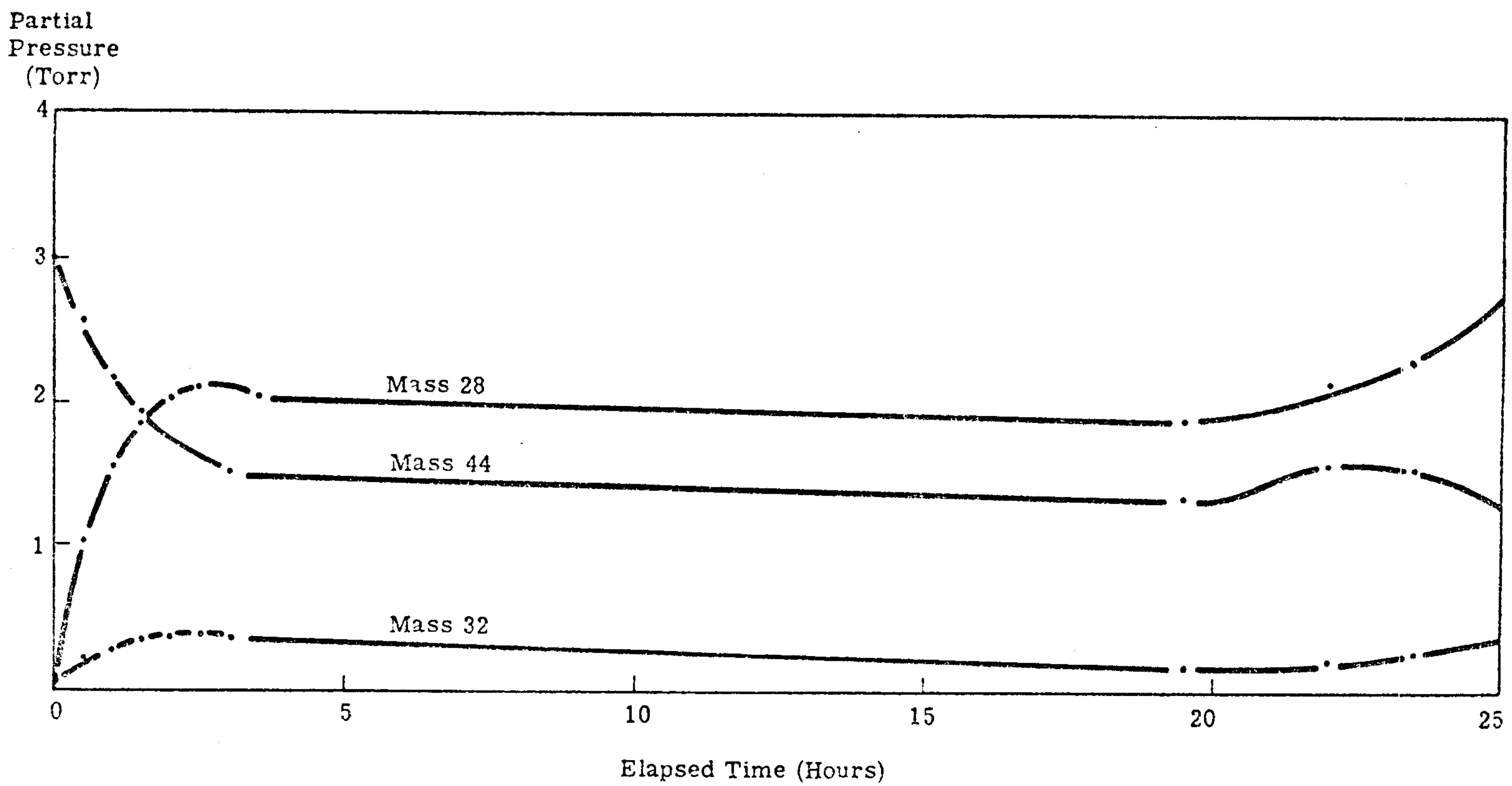

Figure 17 3 TORR CO_2, 1 TORR Xe, Ni ELECTRODES

SECTION 6
QUALITATIVE EXPERIMENTS

During the contract period, several additional electrode materials were used and qualitative observations were made. The electrode materials are: Platinum, Niobium, and Molybdenum DiSilicide.

Platinum

Platinum electrode material 0.001 inch thick was formed into a hollow cylinder configuration 3/4" I.D. x 1" long. A pyrex tube was inserted into the top half of the cylinder to restrict the discharge to the inside surface of the electrode. Severe deterioration of the electrode, i.e., sputtering, was observed during a four-hour run. No significant reduction of CO_2 dissociation was measured.

Niobium

A niobium electrode in the form of a hollow cylinder, closed on one end, was used as in the platinum experiment, i.e., a pyrex insert at the top end. Ten Torr of pure oxygen was used as a fill gas for the discharge tube. The pressure dropped to less than 0.01 Torr in 15 minutes of discharge. It is suggested that this material would make an excellent oxygen getter, or perhaps an oxygen pump.

Molybdenum DiSilicide ($MoSi_2$)

Because of the hardness of this material, the electrode shape was that of a solid rod with one end ground to a large radius. In order to seal this rod into a glass bulb, it was necessary to silver solder the $MoSi_2$ rod onto a glass to metal seal. After five hours of discharge into pure CO_2, the rod broke away from the weld joint and the experiment was terminated. The data taken during this brief operation indicate that $MoSi_2$ does not reduce dissociation of CO_2.

SECTION 7

CONCLUSIONS

(1) Dissociation according to $2CO_2 \rightarrow 2CO + O_2$ seems to be predominant during the early hours of discharge, but clean up becomes the limiting process. For example, consider the data of Sections 5.5 and 5.6, where constant rates of change are observed for both CO_2 and CO partial pressures. With Fe-Ni electrodes, the dissociation rate is $0.05 < \text{rate} < 0.13$ Torr/hr. With Ni electrodes, the data suggests $0.010 < \text{rate} < 0.024$ Torr/hr. This rate, of course, is the net dissociation rate for the system being studied. In an ideal situation, the rate would become zero with some equilibrium concentration of CO_2, CO and O_2.

(2) The dissociation rate is strongly influenced by the addition of H_2O or Xe. This is evident from a comparison of the earliest hours of the runs, when dissociation is still a controlling factor.

(3) The clean-up rate is determined by electrode material. The Fe-Ni and Ni electrodes showed distinctly better performance than the other electrodes tested. Pure Ni seems to be best.

(4) The best system tested, in regard to total performance, was CO_2 with H_2O added, using Ni electrodes.

APPENDIX A

NEW TECHNOLOGY

"After a diligent review of the work performed under this contract, no new innovation, discovery, improvement or invention were made."