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ON THE ABILITY OF FREON C-318 TO TRAP HYDROGEN ON A 77°K CRYOSURFACE

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ARO, Inc.

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FOREWORD

The research presented herein was sponsored by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, Tennessee, under Program Element 64719F.

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ABSTRACT

Studies of the trapping of hydrogen and helium by condensing Freon® C-318 (C_4F_8) on a 77°K surface have indicated that no pumping of the gases occurred. Freon was added to a predominately hydrogen atmosphere at rates from 1.52×10^{-3} to 0.73 torr-liters/sec with no change recorded in the partial pressure of hydrogen. A similar experiment was made with helium and no pumping was noted. It was observed that the mass spectrometer indicated a significant reduction in the partial pressure of hydrogen when the total pressure in the chamber increased to the 10^{-4} to 10^{-3} torr range. It was shown that this was not due to hydrogen pumping but to internal scattering and resulting nonlinearity of the mass spectrometer in this pressure range.

CONTENTS

APPENDIX
ILLUSTRATIONS

SECTION I
INTRODUCTION

Cryopumping is the most promising process for producing clean vacuum, and it offers high pumping speeds. Many times it is not economically feasible to consider cryopumping techniques for the removal of hydrogen (H_2) and helium (He) because of the low temperatures required (4.2°K for cryopumping H_2 and cryosorption of He). Hydrogen is a primary gas in rocket plume testing. With a need to fire large rockets at simulated high altitudes for long periods of time, a more economical method than liquid-helium (LHe)-cooled cryo-arrays would be highly desirable.

Hydrogen may be cryopumped directly if LHe-cooled panels are available since it has a vapor pressure of about 3×10^{-7} torr at 4.2°K. The vapor pressure of H_2 is 5×10^{-5} torr at 5.2°K. This is the critical temperature of LHe and thus represents the upper limit for LHe cooling (Ref. 1). In many instances, however, LHe is not available, or is not economically feasible to use, in the quantities required to pump large systems. In the past decade it has been shown (Refs. 2 to 7) that hydrogen can be successfully pumped by sorption on cryodeposited frost formed by condensing certain gases such as carbon dioxide (CO_2), water (H_2O) vapor, etc., on surfaces at temperatures between 10 and 20°K.

As a matter of good economics, the highest cryogenic temperature that will produce an acceptable base pressure should be used. At 77°K, only CO_2, ammonia (NH_3), and H_2O, of the major constituents of plume gases, are easily cryopumped. Dawbarn indicated in Ref. 5 that no H_2 sorption occurred on a CO_2 cryodeposit above 25°K. The introduction of high molecular weight gases into the vacuum chamber that would condense directly on the 77°K cryosurface and possibly act as a trapping agent has been discussed for some time. In Ref. 8, Daggerhart and Smetana report on the selection and investigation of such a gas, Freon® C-318 (octofluorocyclobutane (C_4F_8)), for the cryoentrainment of helium. The experiments reported herein were conducted to evaluate the entrapment method of Daggerhart and Smetana. They postulate that their observed pumping of He was a result of entrapment and subsequent burial of the noncondensible gas by the condensing Freon C-318. It is intuitively expected that, if He can be pumped in this fashion, then H_2 and nitrogen (N_2) can also be pumped. The primary goal of these experiments was, therefore, to determine if Freon C-318 condensing on a 77°K cryosurface would trap H_2 or N_2. Because any measurement of observed pumping in a gas mixture is no better than the accuracy of

the mass spectrometer calibration, the secondary objective was to carefully calibrate the mass spectrometer before and after each set of data and note any changes in its sensitivity.

SECTION II
APPARATUS

2.1 VACUUM CHAMBER

This work was performed in the 2- by 3-ft Research Ultrahigh Vacuum Chamber described in detail in Ref. 9 and shown in Fig. 1. After deducting the space taken by the cylindrical cryopump and the radiation shrouds, it has a free volume of 300 liters. The radiation baffles are vented to allow free passage of gas molecules, yet they are optically tight between the outer chamber walls and the cylindrical pump. The chamber is rough pumped by a 6-in. diffusion pump with an LN_2 cold trap. This system can be valved off with a 6-in. gate valve. A 2-in.-diam, thin-walled orifice installed between the chamber and the diffusion pump is used as a secondary calibration standard for checking gage sensitivities during test sequences.

2.2 CYLINDRICAL CRYOPUMP

The cylindrical cryopump (Fig. 2) is the lower half of a 10-in.-diam by 10-in.-high stainless steel cylinder. The cylinder is mounted to a low heat leak fill tube, and the upper half is surrounded by a radiation shield. This shield also serves to limit the pumping to the lower half of the cylinder. The cylinder will hold 13 liters of cryogenic fluid with the upper half of the cylinder being considered as the reservoir. The calculated pumping speed for 300°K Freon is 3000 l/sec.

2.3 GAS ADDITION SYSTEMS

Associated with the chamber are two gas addition systems. Different gases may be metered into the chamber, either separately or simultaneously, at various rates. These systems use a set of sintered steel leaks which have been calibrated in situ. Details of these systems may be found in Ref. 5. Both gas systems enter the chamber and end outside the shroud. Gas added thus has to diffuse through the open shroud before reaching the pump surface.

2.4 INSTRUMENTATION

Pressures in the vacuum chamber were monitored by a mass spectrometer connected to a tube which penetrated the shroud and thus sampled a gas flux similar to that "seen" by the pump surface. An ion gage was used to measure the total pressure in the chamber.

SECTION III
CALIBRATION

3.1 LEAKS

Each leak in the gas addition systems was calibrated for the gases used. The method consisted of monitoring the rate of pressure drop in the reservoir of known volume as the gas flowed from this volume, through the leak, and into the vacuum chamber. Pressures in the reservoir were in the 5- to 800-mm range and were recorded by instruments calibrated against mercury manometer standards. Full details of this procedure and analysis of the method are included in Ref. 5.

3.2 GAGE CALIBRATION

The ion gage and mass spectrometer were calibrated in situ before and after each experimental run. All calibrations were made with the shroud at room temperature, and thus no thermal transpiration correction terms were required. The method used was to compare the measured rate of rise of pressure in the vacuum chamber with a known rate of gas being admitted via the calibrated leak system and no pumps operating. This method is outlined in detail in Ref. 9. Once the gages were calibrated, they were used to determine the pumping speed of the 2-in.-diam, thin-walled orifice located between the chamber and the diffusion pump. This provided a second check on the gage calibration, since the pumping speed of the orifice should be approximately equal to the calculable rate of strike. Once the pumping speed of the orifice was determined, it provided a quick and reliable reference for checking the gage sensitivity at the end of each run and also for comparing gage and mass spectrometer sensitivities from day to day.

SECTION IV
EXPERIMENTAL PROCEDURES

After completing the calibrations described in Section III, liquid nitrogen was transferred to the cryopump, and the reservoir was filled. The base pressure in the chamber at this point was about 5×10^{-8} torr. The diffusion pumping system was valved off using the 6-in. gate valve, and H_2 was admitted to the chamber from the gas addition system. Sufficient H_2 was added to raise the chamber pressure to about 2×10^{-5} torr. Freon C-318 was then added to the system at various rates. During these additions, the H_2 partial pressure was monitored by the mass spectrometer. The total chamber pressure was recorded by the ion gage. After each Freon flow, the chamber was allowed time to recover from the gas addition.

At the end of a pumping sequence, the gate valve to the diffusion pump was opened, and the chamber pumped to its base pressure. The reservoir and cryopump were then allowed to warm up slowly. After the Freon had evaporated and been removed from the chamber, the mass spectrometer and ion gage were recalibrated in situ to determine if any changes in sensitivity had occurred.

Similar tests were conducted where the chamber was backfilled with He and then Freon C-318 added. During these tests, the He peak was monitored with the mass spectrometer.

A third series of experiments was made, repeating the previous procedures, but using N_2 as the sorbate.

Since there was no evidence of significant pumping in any of these tests, a series of runs was made wherein the chamber pressures were raised above the point where the mass spectrometer is designed to operate.

The first test was conducted in an attempt to reproduce the conditions reported in Ref. 8, in which the authors had reported trapping of He by Freon C-318. The chamber was backfilled to a pressure of 5.5×10^{-6} torr with He. The LN_2 pump was filled and Freon C-318 was introduced via the leak system. In these tests the Freon addition rate was adjusted to raise the total chamber pressure above 1×10^{-4} torr. At total chamber pressures above 1×10^{-4} torr, the mass spectrometer indicated an apparent drop in the He partial pressure.

The final test consisted of valving off the diffusion pumps and then starting a slow inbleed of H_2 into the chamber. This resulted in a slow rate of pressure rise which was monitored by the mass spectrometer. When the chamber pressure reached 4×10^{-5} torr, the valve to the second leak system was opened and a slow inbleed of N_2 was also started. The total chamber pressure was recorded by the ion gage. When the total chamber pressure reached 1×10^{-4} torr, the mass spectrometer indicated that the H_2 partial pressure started to drop even though H_2 was still being added to the chamber. In this experiment, there were no LN_2-cooled surfaces and thus no pumping for any of the gases in the chamber.

SECTION V
RESULTS AND DISCUSSION

The mass spectrometer used in these experiments is a particularly rugged instrument. While it is not as sensitive as some and its usable mass range is limited to 50 amu, it is very stable and shows minimal changes in sensitivity even under adverse conditions. Figure 3 shows the sensitivity factors (β) determined for H_2 from each day's runs. It should be noted that there was a slow decrease in sensitivity from day to day over the duration of these experiments. However, it was found that calibrations made in situ before and after each experimental run indicated very little, if any, change in the sensitivity. The data can thus be interpreted quantitatively.

Figure 4 shows a typical H_2 partial pressure history as recorded by the mass spectrometer during a Freon C-318 addition. The initial H_2 addition ensured that it was the predominate species in the chamber before Freon was added. The total pressure as recorded by the ion gage is shown in the upper plot and the H_2 partial pressure in the lower plot. From these data, it is obvious that there is no observable trapping or pumping of H_2 since the H_2 partial pressure was unaffected by addition of the Freon.

The second set of Freon additions in Fig. 5 is interesting in that a pocket of Freon gas was inadvertently trapped between two valves in the gas addition line. When these valves were opened, there was a temporary pressure rise which drove the ion gage off scale. It should be noted that, during this burst, the mass spectrometer shows a sharp decrease in the indicated H_2 partial pressure.

A similar test with He backfilled in the chamber is shown in Fig. 6. Again there is no observable pumping or trapping of the He.

The third test with N_2 backfilled in the chamber (Fig. 7) indicates that there was possibly some trapping or sorption of the N_2 by the Freon but that the efficiency of such a system is too low to be of any practical use in plume cryopumping.

The final two tests were conducted primarily to confirm the growing suspicion that the pumping reported by Daggerhart and Smetana was only an "apparent pumping." The partial pressure histories of the He and H_2 are shown in Figs. 8 and 9. These traces are taken directly from the mass spectrometer readout and if taken at face value indicate that during the test runs the He and H_2 are being pumped or trapped. Since in the case of the last H_2 experiment there were no pumping surfaces in the test cell, it is obvious that the change in the mass spectrometer reading does not represent a decrease in the H_2 partial pressure but rather a gross change in the mass spectrometer sensitivity.

The sensitivity of a mass spectrometer is a function of both the design and the condition of the operating elements. By assuming that the instrument has been properly aligned and that all the electronics associated with the mass spectrometer are stable, changes in sensitivity can usually be attributed to one or more of the following causes:

1. Deterioration of the electron producing element in the ionization section. -- Most mass spectrometers use a heated filament to produce electrons. In many instruments, this filament is coated with a compound which has a low electron work function. Over a period of time, the electron emission will decrease because of evaporation of the coating or contamination of the coating by residual gases in the vacuum chamber.

2. Decrease in sensitivity of the ion detector. -- Many mass spectrometers use electron multipliers to amplify the small ion currents which pass through the mass filter section. These detectors rely on a cascade of secondary electrons being produced by the initial ion impact on the first dynode of the detector. In time, the dynode surfaces become contaminated, and the electron emissions are attenuated.

3. Overpressure in the mass spectrometer. -- There is a practical upper limit to the pressures at which a mass spectrometer may operate. In most cases, the ultimate limit is set by the high voltages. At pressures in the 10^{-4} to 10^{-3} torr range, glow discharges occur, initiating arc-over between elements and catastrophic failure of the instrument. However, before this point is reached, the sensitivity of the instrument is affected by the high pressure. Mass spectrometers operate on the principle that ions are produced at one point in the instrument; these ions are extracted from the ionization region and travel a well-defined path to the detector. During the travel, those ions with the proper e/m ratio (charge to mass ratio) are assumed to suffer no molecular collisions. Depending on the particular instrument, but usually starting at pressures of 10^{-5} torr, this is no longer a good assumption. Ion-background molecule collisions can result in two different symptoms. This first is a loss in sensitivity. This is caused by direct scattering of the ion beam and a resulting attenuation of the output current from the detector. The second possibility leads to an apparent increase in sensitivity. This is due to ion-molecule collisions which result in secondary ionization. This process can avalanche throughout the flight distance, thus providing an increase in the number of ions reaching the detector. Since it is possible for either or both of these conditions to occur within the mass spectrometer, care should be taken to avoid operating the instrument in this pressure range, especially if quantitative interpretation of the data is to be attempted.

SECTION VI
CONCLUDING REMARKS

The data taken in the experimental runs during these tests with pressures in the 10^{-4} torr regime provide adequate evidence of a signal attenuation due to scattering. The instrument used by Daggerhart and Smetana is similar in design to the one used in this work, and while no total chamber pressures are reported in their paper, it is suspected that operation of their mass spectrometer in too high a pressure regime led to their conclusion that Freon was acting as a trapping agent.

REFERENCES

1. Borouik, E. S., Grishin, S. F., and Grishina, E. Ya. "The Vapor Pressure of Nitrogen and Hydrogen at Low Pressures." Soviet Physics - Technical Physics, Vol. 5, No. 5, November 1960, pp 506-511.

2. Brackmann, R. T. and Fite, W. L. "Condensation of Atomic and Molecular Hydrogen at Low Temperatures." Journal of Chemical Physics, Vol. 34, No. 5, May 1961, pp 1572-1579.

3. Hunt, A. L., Taylor, C. E., and Omohundro, J. E. "Adsorption of Hydrogen on Solidified-Gas Films." Advances in Cryogenic Engineering, Vol. 8, Plenum Press. 1963, pp 100-109.

4. Southerlan, R. E. "10 to 20°K Cryosorption of Helium on Molecular Sieve 5A and Hydrogen on Condensed Vapors." AEDC-TR-65-49 (AD463339), May 1965.

5. Dawbarn, R. "Cryosorption of Hydrogen by 12-20°K Carbon Dioxide Cryodeposits." AEDC-TR-67-125 (AD655067), July 1967.

6. Yuferov, V. B. and Busol, F. E. "Sorption of Hydrogen and Neon by Layers of Solids Formed by Vapor Condensation." Soviet Physics - Technical Physics, Vol. 11, No. 11, May 1967, pp 1518-1524.

7. Muller, E. "Adsorption Isotherms on Solid Carbon Dioxide." Cryogenics, Vol. 6, August 1966, pp 242, 243.

8. Daggerhart, James A., Jr. and Smetana, Frederick O. "The Entrainment and Trapping of Helium by a Condensing Gas Stream." Presented at the Seventh International Symposium on Rarefied Gas Dynamics, Pisa, Italy, June 30 to July 3, 1970.

9. Haygood, J. D. and Dawbarn, R. "Helium Pumping by 4.2°K Cryodeposits." AEDC-TR-66-204 (AD645511), January 1967.

APPENDIX
ILLUSTRATIONS

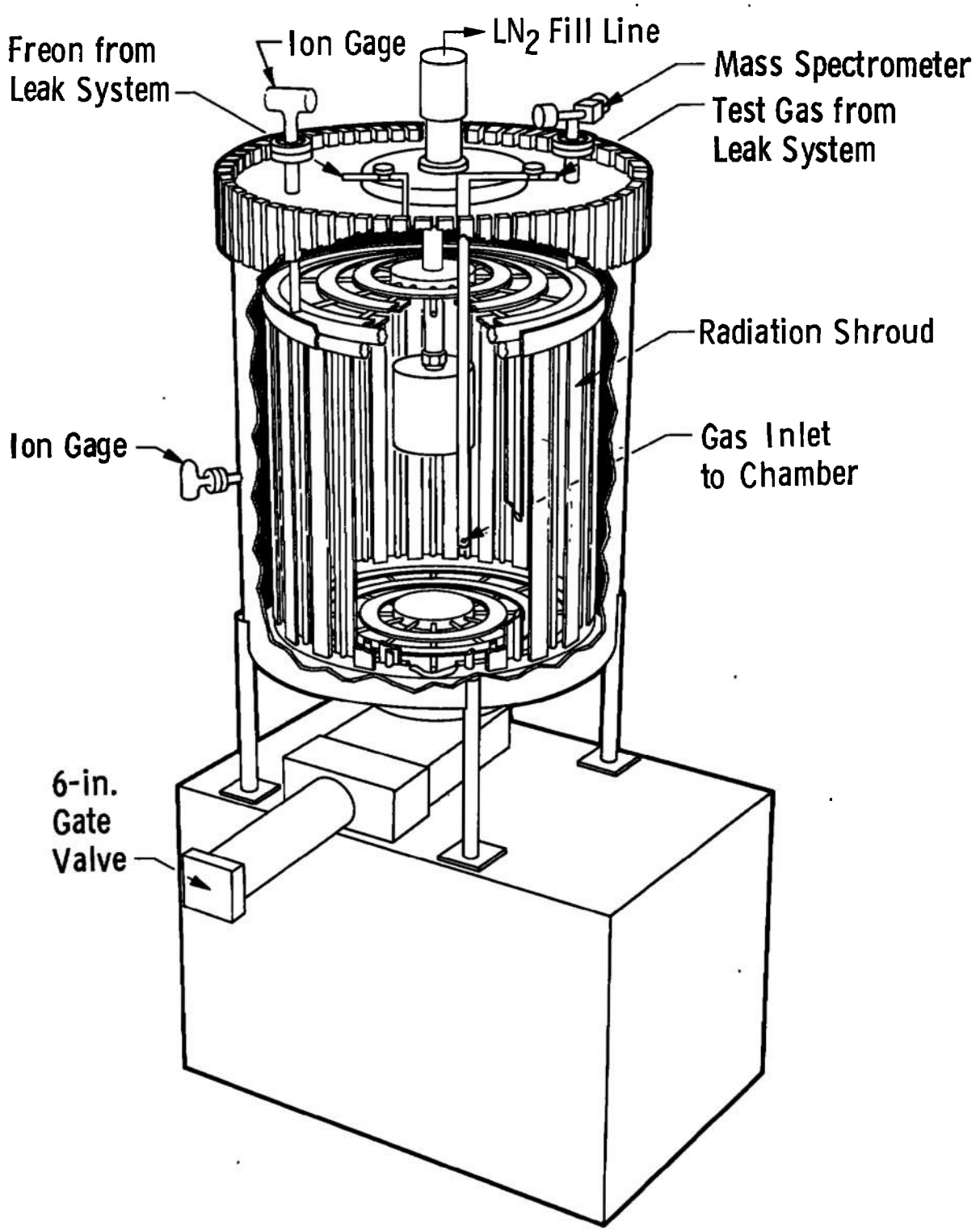

Fig. 1 Schematic of Pumping Research Chamber

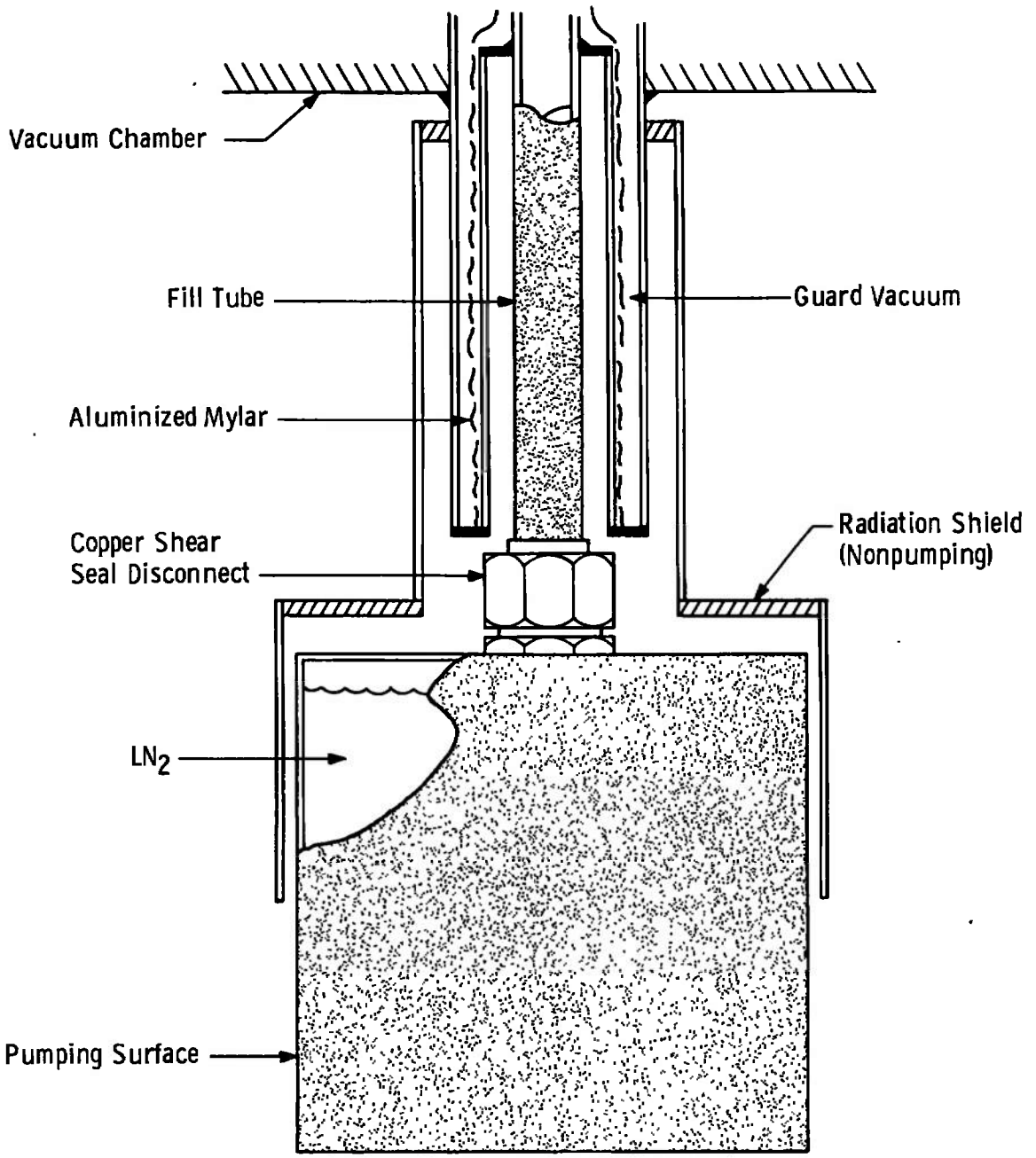

Fig. 2 View of Cryopump

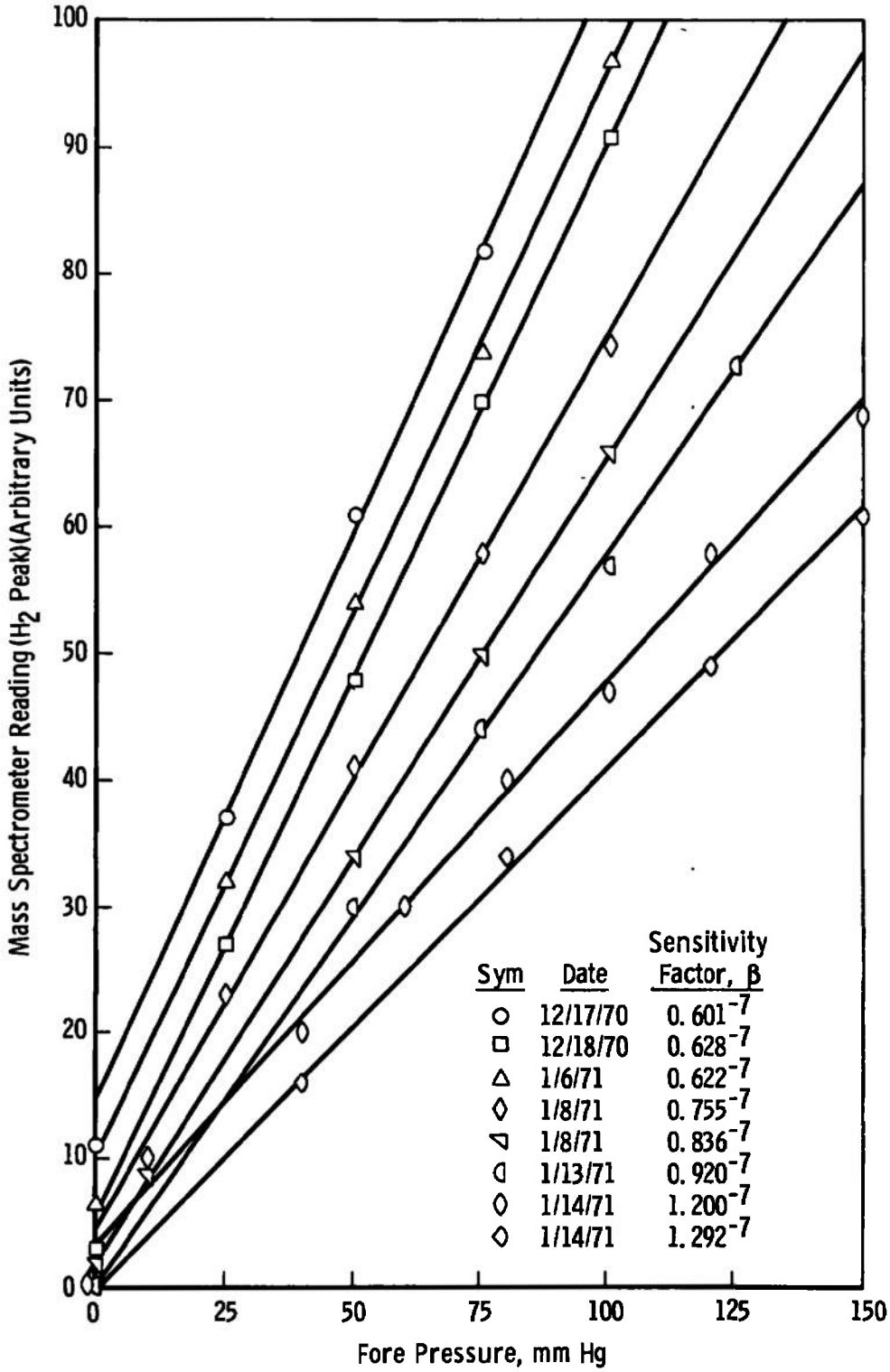

Fig. 3 Daily Variations in Mass Spectrometer Sensitivity

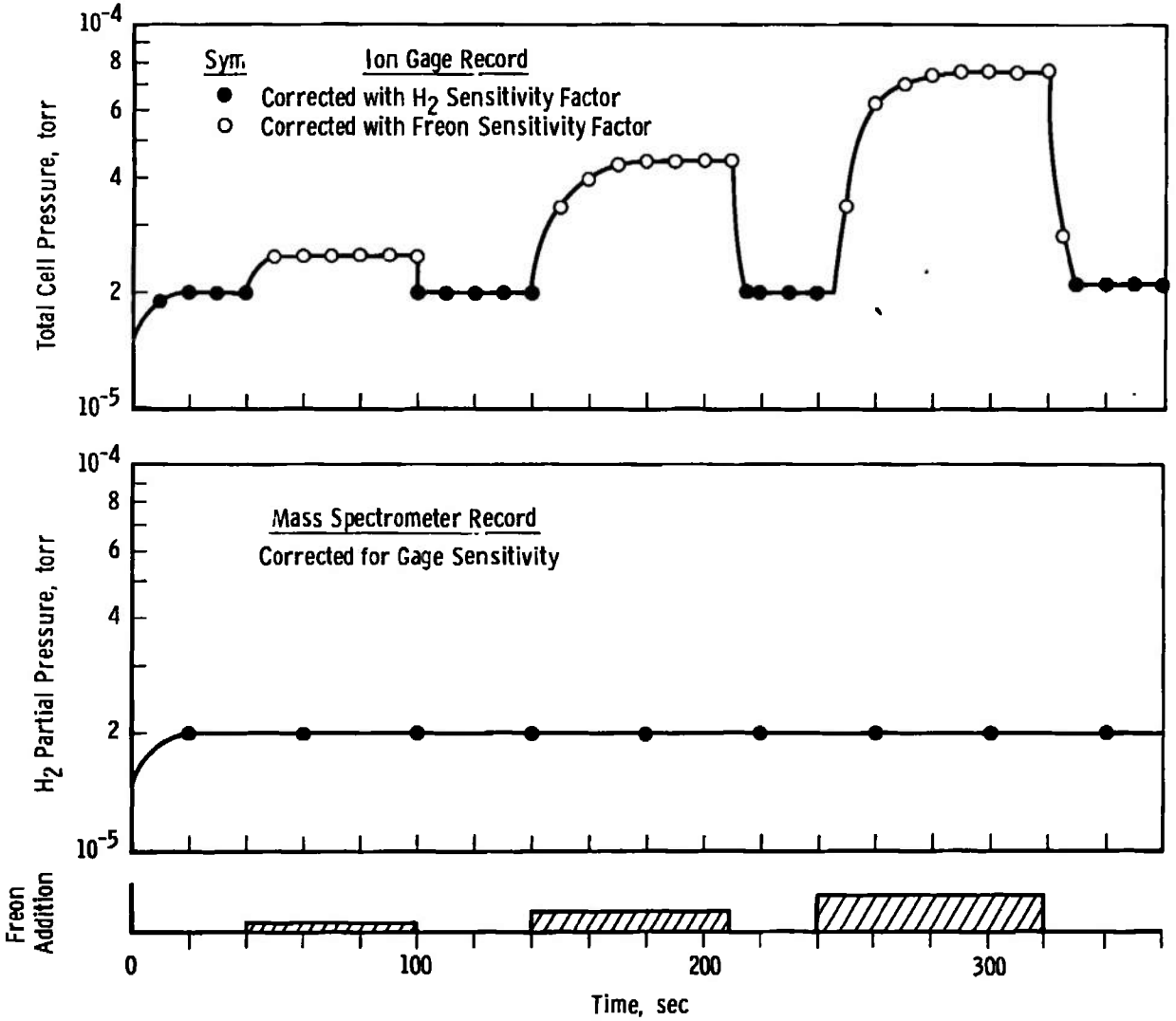

Fig. 4 Typical Chamber Pressure History

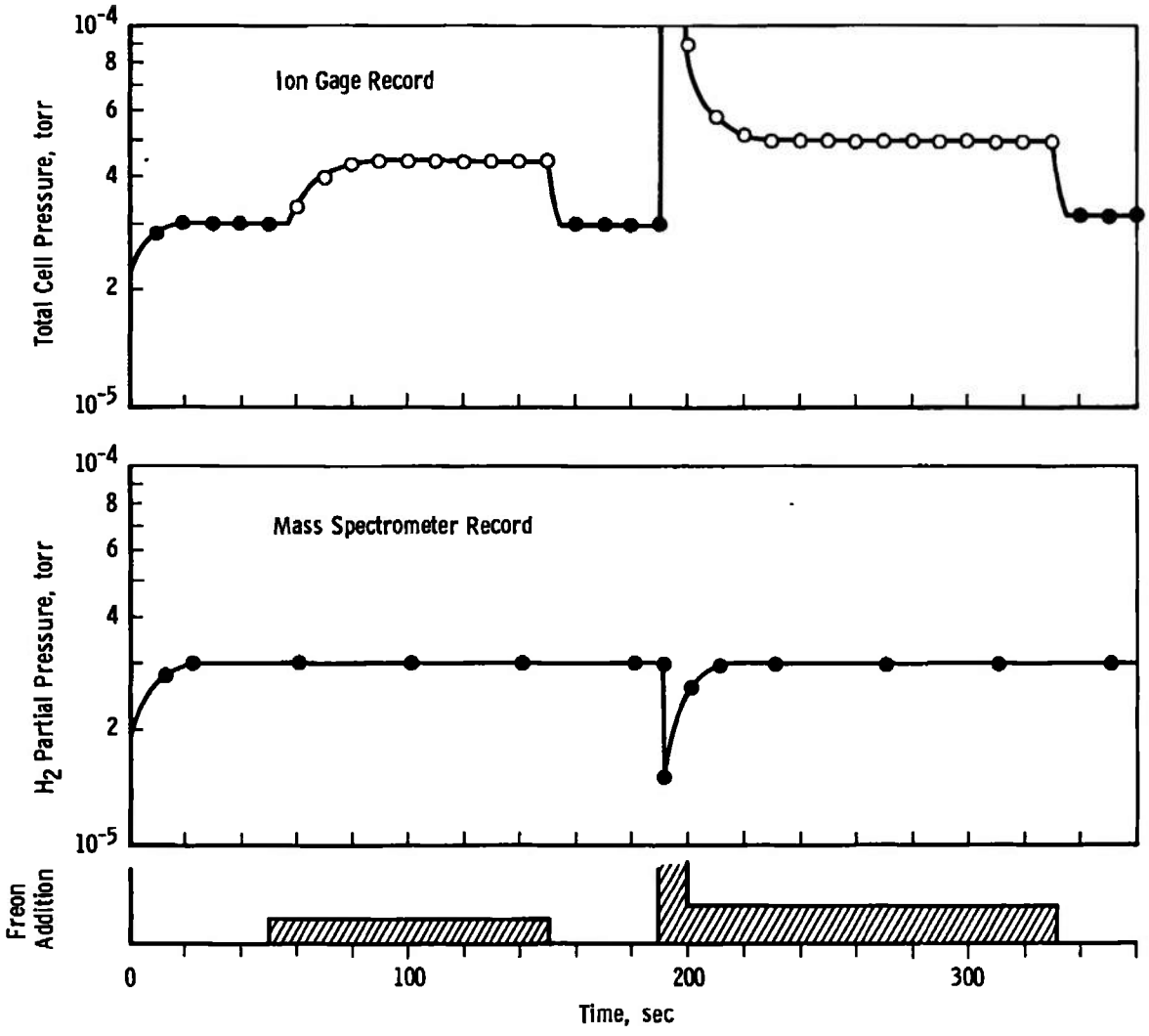

Fig. 5 Pressure History with H_2 as Test Gas

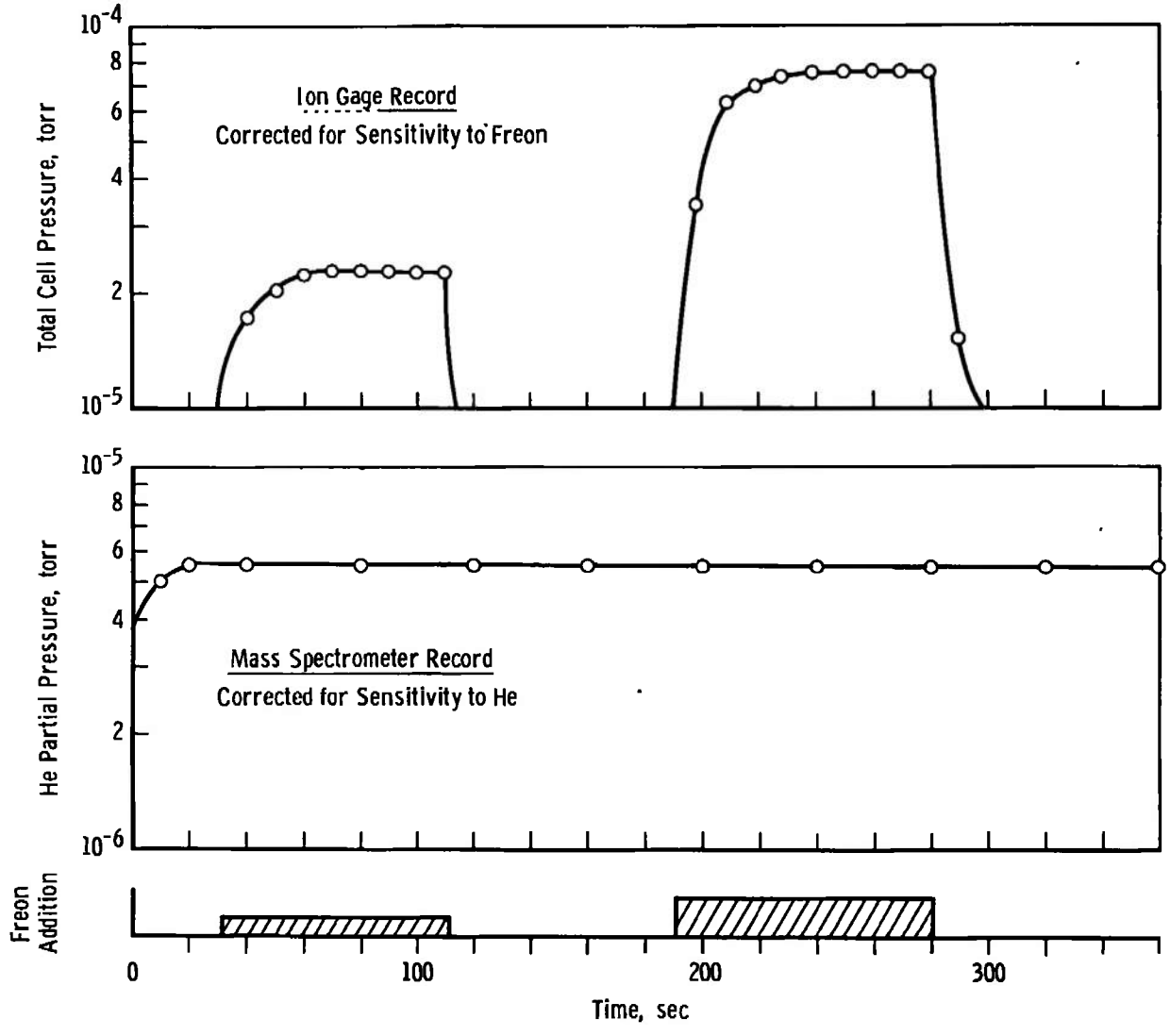

Fig. 6 Pressure History with He as Test Gas

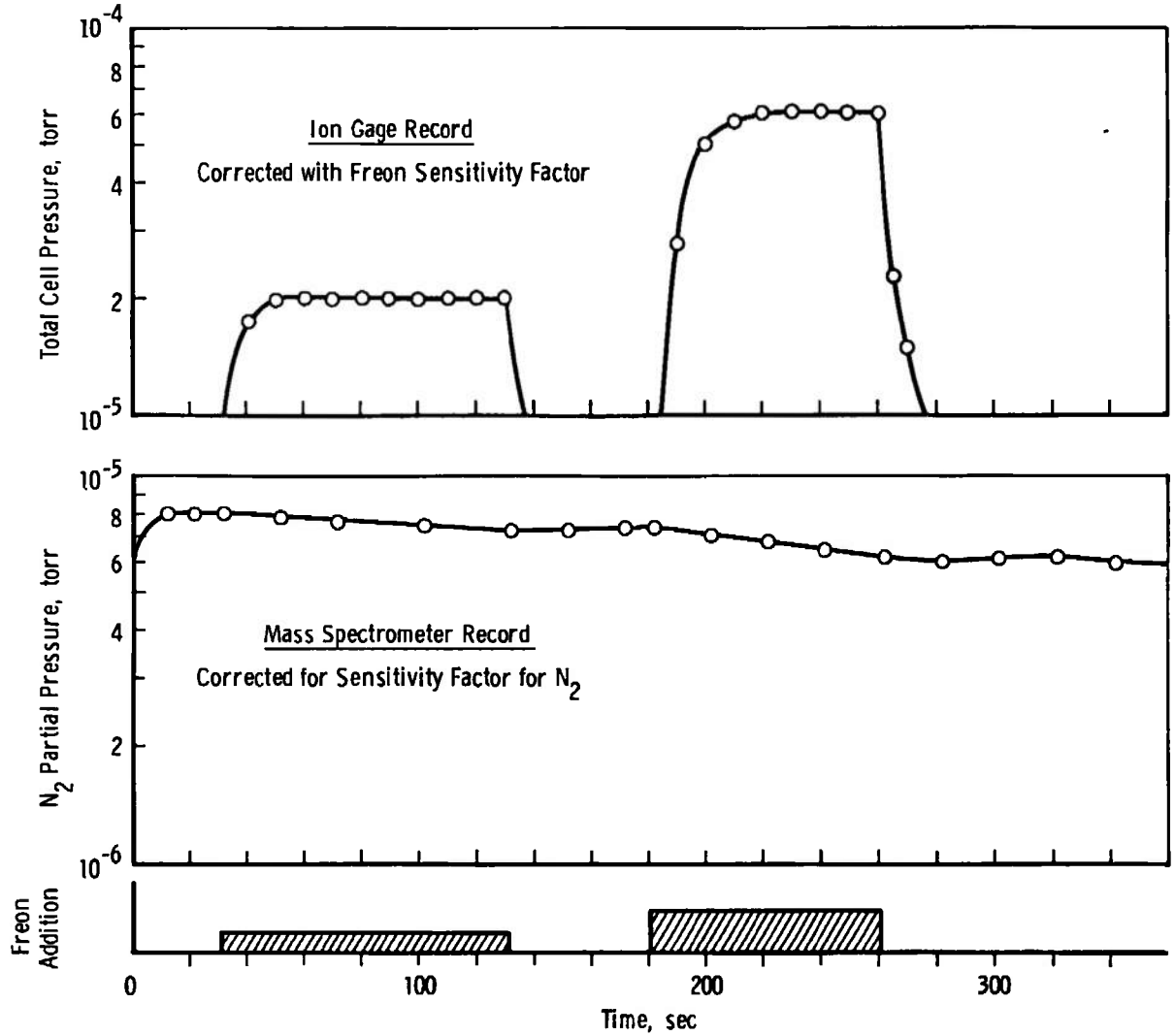

Fig. 7 Pressure History with N_2 as Test Gas

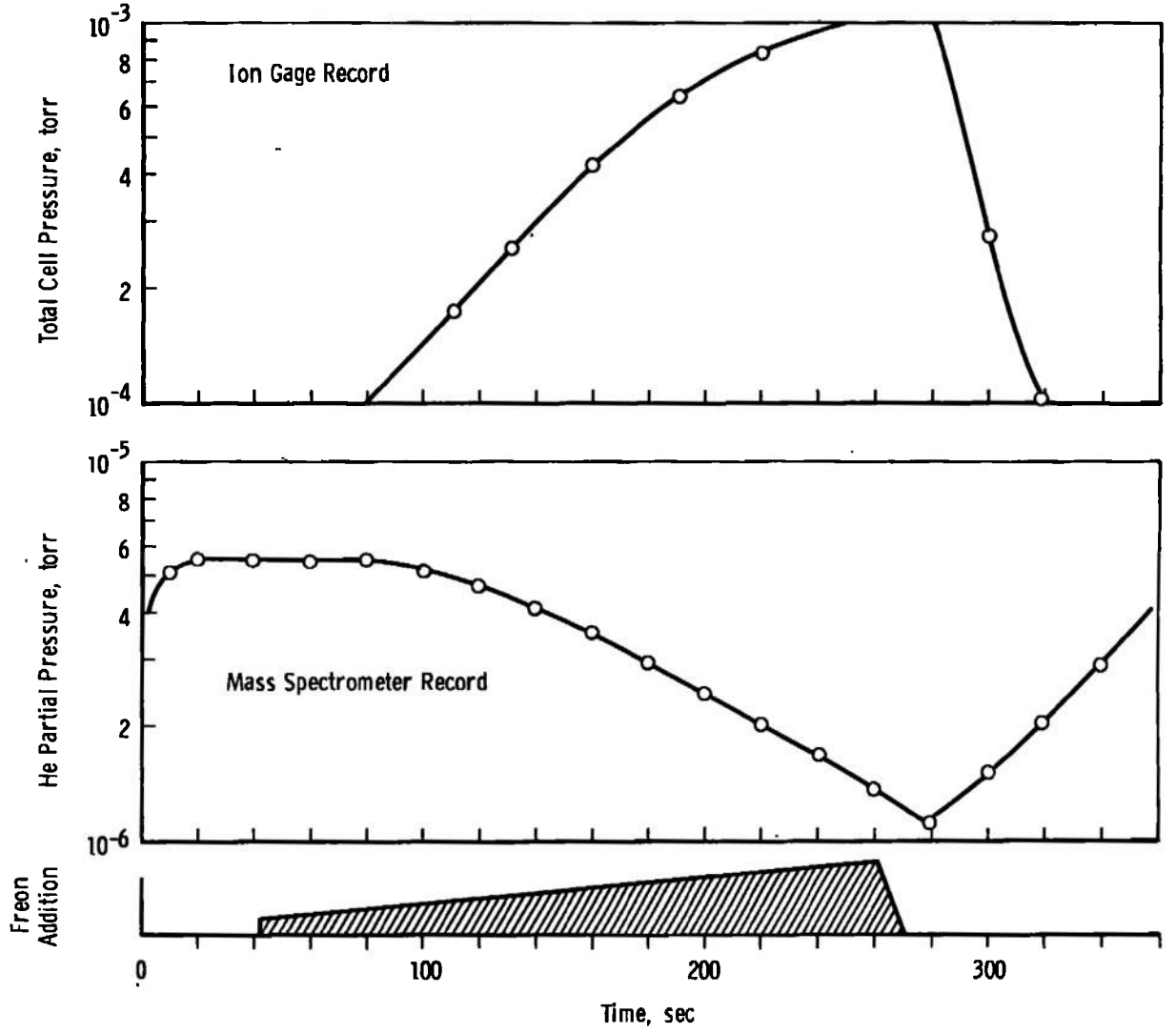

Fig. 8 Pressure History showing Apparent He Pumping

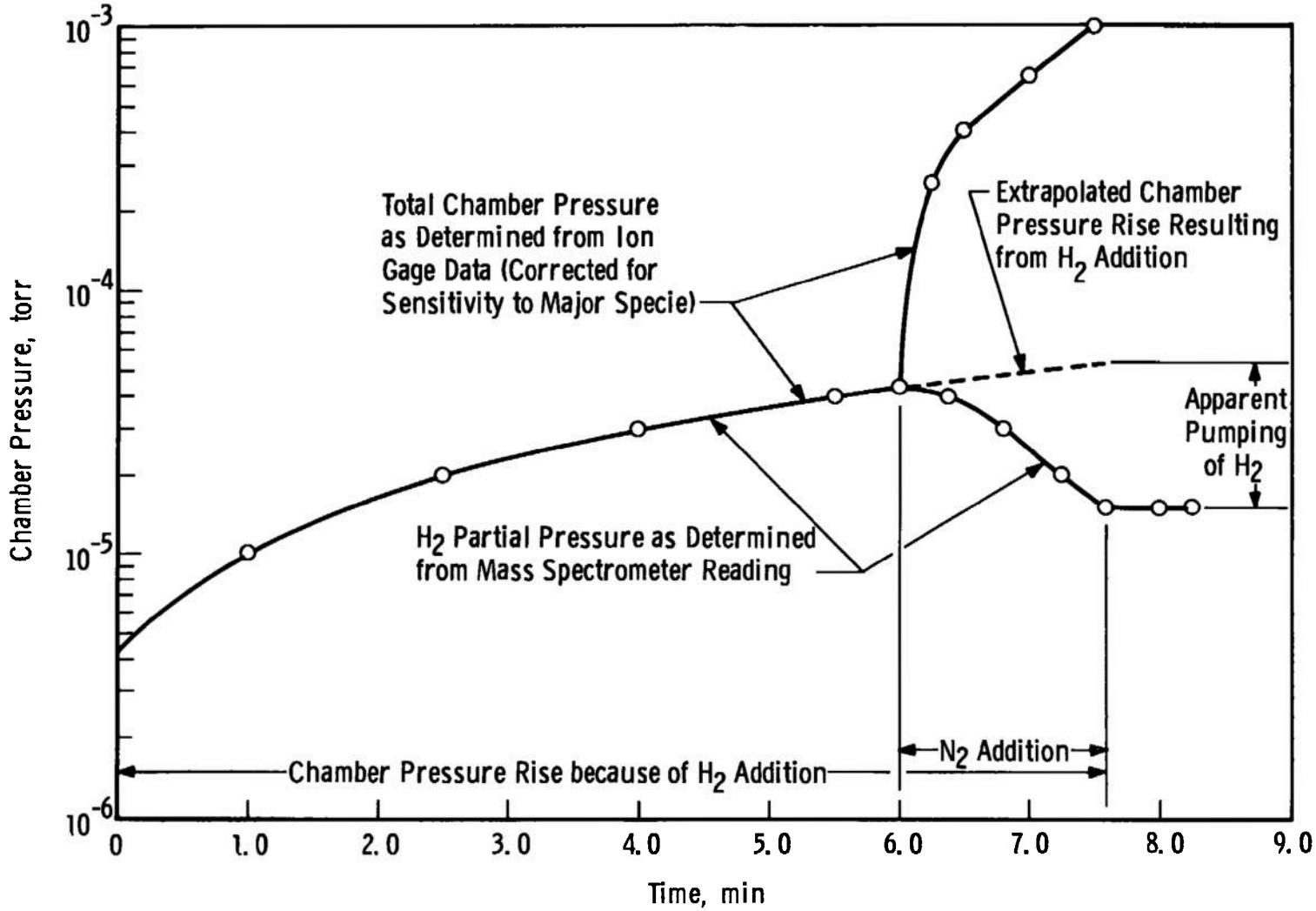

Fig. 9 Pressure History showing Apparent H_2 Pumping

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13. ABSTRACT

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