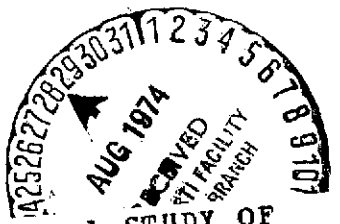

A STUDY OF STRATOSPHERIC GASES CATALYTICALLY REACTING ON ALUMINA

A FINAL TECHNICAL REPORT

By

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INTRODUCTION

Small particles of solid matter which enter the atmosphere, for example from rocket engine exhausts, may constitute an important source of pollution in the upper atmosphere. Their importance stems from the fact that even in small concentrations, they can provide large surface areas on which atmospheric gases can be chemically adsorbed. The nature of the bonding between an adsorbate molecule and the adsorbent particle may be such as to cause dissociation of one species of adsorbed molecule or may allow two different species of adsorbed molecules to react on the surface [1]. Since the adsorbent surface is unaltered in these processes, it acts essentially as a catalyst for reactions among the atmospheric gases.

One region of the atmosphere in which such an effect could have important consequences is the stratosphere, which lies approximately between altitudes of 17 and 50 kilometers. Although ozone (O_3) is a minor constituent of the total atmosphere, it is relatively abundant in the stratosphere where it is responsible for the absorption of ultraviolet radiation in the 2000 to 3000 Å wavelength region of the solar spectrum [2]. Since the nature of life on the surface of the Earth is dependent on this absorption of ultraviolet radiation, it is necessary to know how the concentration of ozone in the stratosphere is influenced by the introduction of particulate contaminants.

Among the exhaust emissions which need to be more fully characterized

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in this connection is alumina or aluminium oxide (Al_2O_3). Of particular interest is its catalytic action in the presence of HCl, SO_2, and O_3 (ozone).

Briefly, the experimental procedure originally proposed for this study is to expose alumina which has been thoroughly cleaned in ultrahigh vacuum to gases of interest and to detect atoms and/or molecules produced by catalytic action of the alumina with a mass spectrometer. The present report describes an experimental system which has been constructed and which may be used to conduct studies of this kind.

EXPERIMENTAL SYSTEM

A schematic diagram of the experimental vacuum system is shown in Figure 1. The system can be divided conveniently into a main vacuum chamber and a fore-line assembly. Except for portions of the fore-line assembly, the system is bakeable to a temperature of 450° C.

The main vacuum chamber is shown in Figure 1a. It is pumped by a 60 liter/sec noble ion pump and by a titanium sublimation pump with a pumping speed of approximately 100 liters/sec. Ions and electrons formed in the ion pump are prevented from streaming into the experimental area by the application of appropriate electric potentials to two grids which are located between the ion pump and sublimation pump.

The cross-shaped part of the chamber immediately above the sublimation pump is the target or experimental area where a sample of material such as alumina can be mounted for study. The sample can be mounted from the target flange, and a mass spectrometer can be connected to the flange opposite the target flange.* Two sapphire windows located on an axis perpendicular to the sample-analyser axis allow observation and irradiation of the sample.

System pressure is measured by a Nottingham gauge which is located in the tee section at the top of the system. A fine meter valve which is also

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* A Vanderslice mass spectrometer which was to be supplied for this purpose has been modified in design in order to improve its sensitivity. Substantial progress has been made in incorporating these design changes in the instrument, but it has not been incorporated into the system.

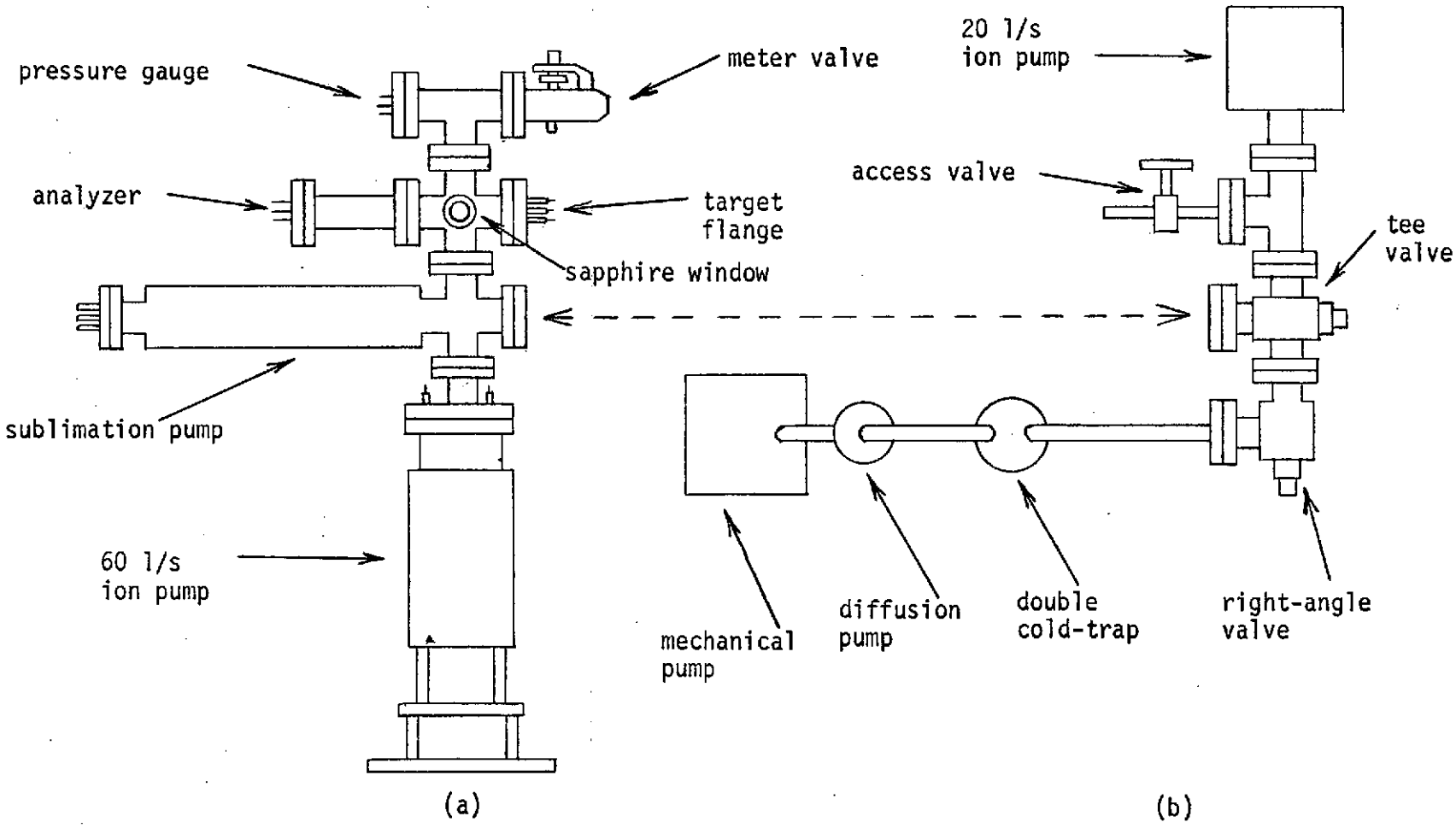

Figure 1. (a)the main vacuum chamber (b)the fore-line assembly

connected to this tee section can be used to admit gases of interest into the main chamber.

The fore-line assembly is shown in Figure 1b. It is connected to the main vacuum chamber at the tee valve which is used to isolate the main vacuum chamber from the fore-line assembly after system bake-out has been completed.

The fore-line assembly consists of two branches, one to either side of the right-angle valve. The branch which contains the mechanical pump, oil diffusion pump, and liquid nitrogen double cold trap (branch 1) is used to evacuate the system from atmospheric pressure to pressures on the order of 10^{-7} torr and is also used during the initial stages of system bake-out. The right angle valve is used to isolate branch 1 from branch 2. (Branch 2 contains the tee valve, access valve, and 20 liter/sec noble ion pump). After the initial stages of system bake-out have been completed, pumping during the remaining stages of this procedure is provided by the ion pump in branch 2. In order to keep them as clean as possible, the vacuum pumps on the main chamber are not normally operated, except for outgasing purposes, until system bake-out has been completed and the tee valve has been closed.

An additional function of the fore-line assembly is its use in cleaning the gas inlet from a gas supply cylinder to the meter valve on the main chamber. For this purpose, a connection is made from the inlet line to the access valve of the fore-line assembly. The inlet line can then be cleaned by opening the access valve and evacuating it to ultrahigh vacuum pressures. The access valve is then closed, leaving a clean inlet line through which gases can be admitted to the main chamber without being substantially contaminated.

Since alumina is an insulator, it is difficult to clean by methods commonly used to clean conductors under vacuum conditions. It was proposed, however, that a possible means of cleaning it is to irradiate it with a high power laser beam. A ruby laser which operates in a pulsed mode has been mounted so that it can be fired through the sapphire windows of the main chamber to irradiate the sample. It can produce power densities on the order of 100 megawatts/cm^2 when it is not focused and much higher power densities when it is focused on the target.

SYSTEM PERFORMANCE

The vacuum system is presently operating at a pressure on the order of 3×10^{-12} torr.* This is a pressure range which is more than adequate for purposes of establishing the cleanliness of the alumina sample.

Considerable experience has been gained in firing the high power laser into the system. It has been established that it can be fired through the sapphire windows without damage to them. If care is taken to properly position the focal point of a lens relative to the position of these windows, the laser beam can be focused on the sample in order to increase the energy density incident on the sample.

Experience gained with tungsten and sapphire targets indicates that gases are easily desorbed by high power laser irradiation and that surface temperatures of these materials can be raised to their melting points with little difficulty. It appears, therefore, that this method of cleaning the surfaces of samples, particularly when the sample is an insulator, is feasible.

The experimental study of catalytic reactions of the indicated gases on alumina could not be completed during the initial grant period primarily because the mass spectrometer which was to be supplied for this work was not available in time. It will not be possible to continue this work in the future because funds for this purpose are no longer available.

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* An ion current corresponding to this pressure was measured even though the normal x-ray limit of the gauge used is approximately 2×10^{-11} torr. However, the effective x-ray limit of a gauge of this type has been observed to be more than an order of magnitude lower than the normal limit when the gauge is operated inside a close-fitting metal sleeve [3], as is the case in this system.

REFERENCES

1. Condon, E.U. and H. Odishaw, Handbook of Physics, (McGraw-Hill Book Co., Inc., New York) p. 5-112.

2. Kondratyev, K. Ya., Radiation in the Atmosphere, (Academic Press, New York), p. 132.

3. Hayward, W.H., et al., Tenth National Vacuum Symposium, American Vacuum Society, Transactions, p. 228 (1963).