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STUDY OF ADSORPTION OF GASES ON SOLIDS IN THE HIGH VACUUM RANGE

FIRST SCIENTIFIC REPORT

JANUARY 1, 1962 ——— MARCH 31, 1962

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PREPARED FOR

AIR FORCE CAMBRIDGE RESEARCH LABORATORIES
OFFICE OF AEROSPACE RESEARCH
LAURENCE G. HANSCOM FIELD
BEDFORD, MASSACHUSETTS

GENERAL TELEPHONE & ELECTRONICS LABORATORIES
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ABSTRACT

An ultra-high vacuum system is described which was designed to perform surface adsorption studies in the region of extremely low pressures. Provision has been made for the controllable, contamination-free admission of gases into the system, and for the measurement of the composition and amount of gas present with an omegatron mass spectrometer.

Construction of the system has been initiated and all concomitant instrumentation has been ordered.

1. OBJECTIVE

To establish the laws governing adsorption of gases in the very low pressure range.

2. BACKGROUND

Theoretical and experimental investigations of surface phenomena are very difficult problems. Theoretical treatments of surface problems, i.e. physical adsorption, chemisorption, photoelectric and thermionic work functions, reflection of electrons at surfaces, etc. are receiving new impetus owing to the progressive development of more refined quantum mechanical models of the surface and the availability of computing facilities. Experimentally, investigations of surfaces are very exacting; ultra-high vacuum techniques must be used and the condition of the samples must be carefully investigated as to surface conditions. It is only very recently that advances in experimental techniques have reached a point where meaningful, i.e. reproducible, experiments on surfaces can be obtained.

In the field of physical adsorption and chemisorption of gases on surfaces the vast majority of the experimental data were obtained at fairly high pressures (about 10^{-5} Torr and above), and the conditions of the surfaces were not well defined. In many cases, powders or amorphous materials were used. In cases where low-pressure gas adsorption was investigated, uncertainties relating to the gas composition used in the experiments cannot be eliminated.

In these Laboratories high-vacuum instrumentation and techniques were developed permitting us to measure dynamically and continuously the gas composition in high-vacuum ambients in the pressure range 10^{-10} to 10^{-5} Torr.

These techniques are based on the study of the omegatron mass spectrometer as a tool for measuring partial pressures of gases in vacuum systems. The operating characteristics of omegatrons were investigated extensively and the capability of this instrument to measure in detail the composition of the vacuum ambient in the 10^{-5} to 10^{-10} Torr range was demonstrated.[1] It was also shown that any pressure-measuring instrument, including the omegatron, will change the vacuum ambient; however, it was also shown that the omegatron will contribute less to changes in vacuum ambient than any ionization gauge owing to its inherently lower ionizing current requirements. The importance of this characteristic of the omegatron of requiring an ionization current of only one microampere for full sensitivity cannot be over-emphasized. This small ionizing current entails a small pumping speed. The very small power required for the filament reduces outgassing and gas reaction phenomena. While the ionizing current of one microampere for full sensitivity cannot easily be reduced, the power input to the filament can probably be reduced by at least a factor of 10 by design improvements. Such a reduction in power would reduce further reactions at the filament. In many cases where measuring instruments using filaments with large power input and high ionizing currents are employed, the instrument itself may hopelessly alter the vacuum situation.

Additional important characteristics of the omegatron are extreme simplicity of construction, employment of very few materials, and ease of high-temperature processing.

It was noted during our investigations that the gas ambient is strongly dependent on the history of the vacuum system, i.e., the gases

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1. "Operational Data on the Omegatron as a Vacuum Analyzer," W. R. Watson, R. A. Wallace and J. M. Lech, 1960, Seventh Symposium on Vacuum Technology Transactions.

to which it has been exposed. It was noted for instance, that when N_2 is admitted to a system previously evacuated to 10^{-9} Torr, the analyzing instrument will show for a considerable length of time that there is an increase in the pressure of argon displaced from the wall by the other gas admitted. Any heating of materials, closing or opening of a valve, mechanical movement inside the vacuum system, etc. will alter the gas composition inside the system in a practically unforeseeable manner unless a partial-pressure analyzer is used. Measurements of adsorption of gases on well characterized and cleaned surfaces will be undertaken in the little-explored range of 10^{-10} to 10^{-5} Torr; these investigations will be performed while the gas composition in this range of pressure is constantly analyzed by means of the omegatron techniques mentioned above. The increased availability of large-size single crystals of various metals such as W, Mo and Ta may enable one to measure the adsorption of gases on selected crystal planes.

The data obtainable by these investigations will be specifically suited for comparison with theory and therefore will be of importance in advancing knowledge of surfaces.

The understanding of vacuum ambients and of surfaces is becoming progressively more important in several fields such as plasma physics, space physics and generally in many problems of experimental physics. From an application point of view, advances in both solid-state and vacuum electron devices require further understanding of surface properties.

3. TECHNICAL APPROACH

3.1 VACUUM SYSTEM

A block diagram of the ultra-high vacuum system designed to perform surface adsorption studies is shown in Fig. 1.

R1 is the sample chamber whose temperature can be regulated by appropriate means. Separate means are provided for cleaning and heating the sample. R1 is in communication with an omegatron, an ionization gauge (IG1), an ion pump (IP1) through an expendable "harp" HV1, and with reservoir R2 through a bakable high-vacuum valve V1. R2 is in communication with an ionization gauge IG2, an ion pump IP2 through "harp" HV2, and through a bakable high-vacuum valve with gas reservoir R3. R3 is in communication with the gas sample ampoules and, through harp valve HV3, with an oil diffusion pump trapped with two Biondi molecular sieve traps in series.

The entire system above the oil diffusion pump can be baked at temperatures up to 450°C for prolonged periods as required to obtain ultimate vacua well below 10^{-10} Torr. The harp mentioned above is shown schematically in Fig. 2. Its purpose is to provide either communication between pumps and systems through the capillary tubing, or isolation by being sealed off. Provision is made for re-establishing communication by opening a break seal and using a second capillary. In principle, as many alternative paths as desired may be provided.

3.2 PRESSURE MEASUREMENTS

Pressure measurements in the system will generally be made with the omegatron using existing calibration data whenever available; additional calibration data may be required. Since the present omegatron has a partial-pressure sensitivity limit of about 10^{-10} Torr, and ionization gauges usually have a lower limit for total pressure in the neighborhood of 10^{-11} Torr, lower pressures than these will be measured by

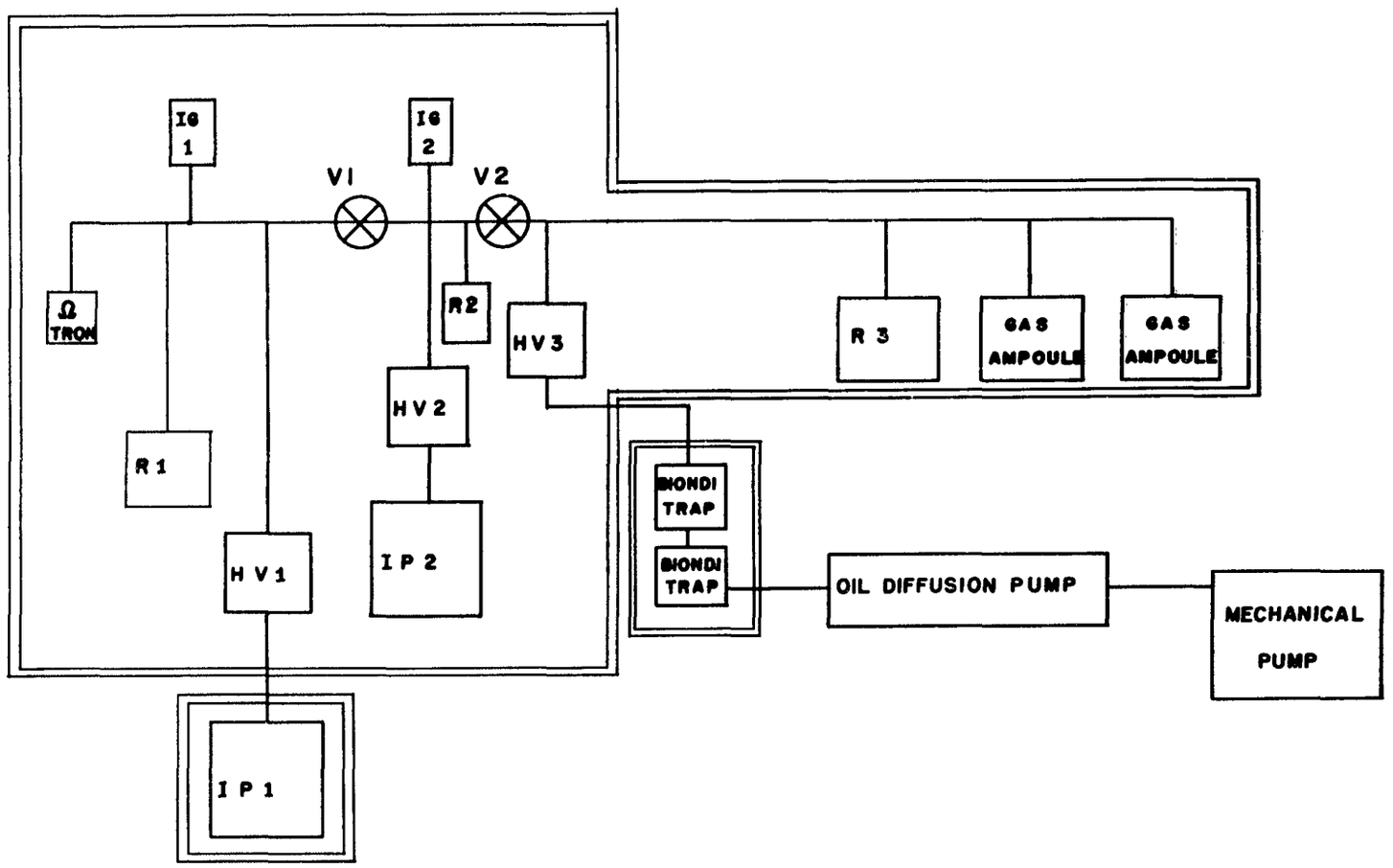

Fig. 1. Block diagram of ultra-high vacuum system.

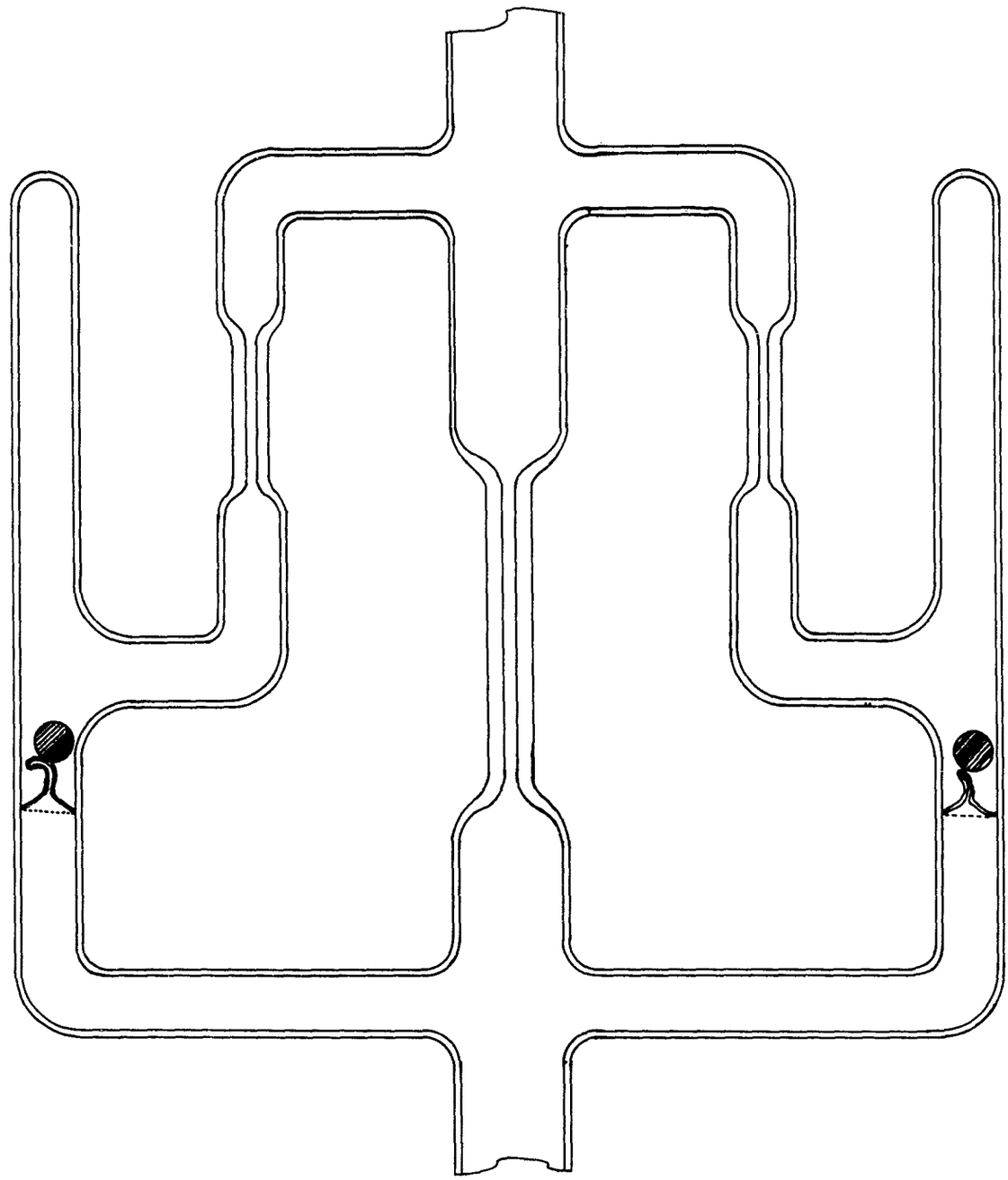

Fig. 2. Schematic of glass harp.

means of the "flash filament" techniques. This consists of: (1) flashing a tungsten filament to a high temperature so that all desorbs from it, (2) exposing the cold clean filament for an interval of time to the ambient gases, and (3) flashing the filament and measuring the burst of gas with a ballistic circuit. This technique will be improved upon in our experiments by determining the composition of the "flashed" off gases by means of the omegatron. It is apparent that by choosing progressively longer times for collecting gases on the filament, ultimate vacua and their composition can be estimated many orders of magnitude below the ultimate sensitivity of the omegatron or of ionization gauges.

3.3 SAMPLE TREATMENT

Samples to be investigated will generally be metals; however, insulators, particularly glasses, may also be investigated. The problems connected with sample cleaning and sample surface characteristics will vary according to the type of material used. Initial studies should preferably be performed on W and Mo, which can be cleaned by high-temperature flashing of ribbons of these materials. In other cases, special cleaning techniques will be investigated, e.g. electron bombardment, ion bombardment, etc. Surface conditions will be investigated by electron diffraction techniques and other appropriate analytical techniques. In cases where the cleaning of the surfaces is doubtful, as may be the case for instance with relatively low-melting-point materials such as Pt or Ni, it may become necessary to develop special methods for testing surface reproducibility. A possible method is to measure the work function of the material using it as an electron collector; this method is relatively simple and is very sensitive to surface changes.

The sample after cleaning must be brought to the temperature at which the adsorption isotherm is measured. This will be done by

immersion of the sample chamber R1 in appropriate constant-temperature baths. Since liquid helium is available in our Laboratory, adsorption isotherms can be measured at appropriate temperature intervals from 4.2°K to the highest temperatures compatible with the materials.

4. MEASUREMENTS

4.1 PRELIMINARY MEASUREMENT

The basic study will consist of measuring the adsorption isotherms described below. A number of preliminary measurements will be required such as:

a. The relative sensitivities of the ion gauges used in the course of our work.

b. Calibration of selected ion gauges.

c. Measurement of the surface adsorption properties of the glass sample chamber.

d. The effect on the gaseous ambient of the omegatron and ion gauges.

4.2 ADSORPTION ISOTHERMS

The basic measurement will consist in determining the low-pressure adsorption isotherms as a function of temperature. Schematically, this measurement will be performed as follows: with all valves open, the system is pumped and baked until a vacuum below 10^{-10} Torr is obtained. Degassing of sample, omegatron and I.G. filaments, etc. are part of this phase of the operation. To obtain the desired vacuum, the system will be isolated by valve HV3 from traps and pumps and the

ion pumps IP1 and IP2 used which later will be isolated from the system. During these operations the sample is periodically flashed at very high temperature or otherwise cleaned. When the desired high vacuum is obtained the test gas is admitted to the reservoir system between valves V1 and V2. Valve V1 is opened to admit a given amount of gas into the sample chamber, and a state of equilibrium is reached with the test chamber at the test temperature. Subsequently the sample is allowed to reach temperature equilibrium with the walls. During this time, adsorption takes place and the pressure of the gas decreases, at which time valve V1 is opened. The time t required to re-establish equilibrium at the test pressure is then measured. The product $Q = t \times P_{R2} \times s$, where P_{R2} is the pressure in R2 and s is the conductance of the valve V2, gives the quantity of gas adsorbed on the filament. A knowledge of the area of the filament then gives atoms adsorbed per unit area. During the entire process the detailed gas composition is monitored with the omegatron.

In principle, the ideal experimental condition is obtained when the only change in the system in which adsorption takes place is: filament hot (and clean) $\longrightarrow$ filament cold (and initially clean). In practice, some slight temperature variation of the walls of the vessel may take place. Corrections for this effect will be sought, if necessary, by estimating the possible temperature rise of the inside walls and the consequent effects. A measurement or determination of this wall effect will permit one to deduce from the time rate of pressure decreases, in the experiment of 4.2, the sticking probabilities of the atoms on the surface as a function of surface coverage and temperature. Studies must also be made of the pumping speed of the omegatron for the gas system under investigation and of possible sources of contaminations, and appropriate corrections introduced.

4.3 LIFETIME OF ADSORBED ATOMS

A second type of experiment consists of flashing the sample filament after adsorption has taken place and measuring the desorbed amount of gas by following the time rate of increase of pressure in the vessel. An objection to such a measurement may be raised owing to the fact that the temporary increase in concentration of the gas will affect the amount of gas adsorbed on the walls of the container and therefore this measurement is not a true indication of gas desorbed from the sample. One may argue, however, that the walls of the container are certainly covered already with a monolayer of the test gas (owing to the method of experimentation) and that, therefore, it is very likely that any addition of gas to the walls will take time which is long in comparison to the response time of the measuring instrument, which is limited only by the electronic circuitry. This question can be settled, however, by comparing the quantitites of gas desorbed from the sample with the quantities adsorbed on the sample and determined in the measurement of 4.2. If the desorption is quantitative and representative, this type of measurement will be performed and thus permit one to determine lifetimes of atoms on a surface as a function of surface coverage and temperature.

4.4 MIXED ADSORPTION

In the experiments of 4.2 and 4.3, a partial-pressure measuring instrument (the omegatron) is used, in addition to high vacuum techniques, to determine adsorption isotherms in a relatively little explored range of pressures. The presence of the omegatron permits one to check continuously the gas composition, thus eliminating errors of identification almost impossible to avoid as our experience in high vacuum work with an omegatron has demonstrated. Presence of foreign gases in such experiments is particularly objectionable in the low-pressure range, since it may falsify completely the phenomena studied.

The availability of an appropriate mass spectrometric tool such as the omegatron permits one, however, to perform more complicated and extremely interesting experiments with a plurality of gases.

Using an appropriate combination of the techniques of 4.2 and 4.3 one can study the effect on the adsorption characteristics of one gas owing to partial coverage of the surface with a second gas. Similarly, one can investigate the desorption of a monolayer of one gas as a consequence of bombarding the surface with another gas. An interesting sequence might be, for example, He, Ne, Ar, Xe or He, H_2, N_2, CO_2, CO, etc. For the study of such phenomena it is imperative that an appropriate mass spectrometer be employed. The variety of such mixed adsorption phenomena which can be studied with the technique here suggested requires a very careful selection of the systems to be investigated.

Selection of adsorbent-adsorbate system will follow a critical study of pertinent literature. The experimental data obtained from these measurements will be critically evaluated for their validity and a comparison of experiments with theory will follow.

5. FUTURE WORK

An ultra-high vacuum system adapted to measure adsorption rates of gases on cleaned surfaces of solids in the pressure range 10^{-10} to 10^{-5} Torr will be placed in operation. The composition of the gas ambient will be monitored with an omegatron mass spectrometer; the vacuum system will generally conform to the schematic diagram of Fig. 1.

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