OAK RIDGE NATIONAL LABORATORY

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EXTERNAL TRANSMITTAL
AUTHORIZED
ORNL
CENTRAL FILES NUMBER

58-9-937

DATE: June 30, 1959

COPY NO. 70

SUBJECT: METHODS FOR THE STUDY OF GAS-METAL REACTIONS
IN ULTRA-HIGH VACUUM

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ABSTRACT

A critical review of the methods reported in the literature for the study of gas-metal reactions in high and ultra-high vacuum systems is given. Experimental apparatus and techniques based on volumetric, gravimetric, magnetic, and other properties of the metals including work function, accommodation coefficient, resistivity, and others have been used. A volumetric method, based on a determination of rate-of-reaction, was selected as most readily applicable to the proposed investigation.

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METHODS FOR THE STUDY OF GAS-METAL REACTIONS IN ULTRA-HIGH VACUUM

PREFACE

In order to study the ionic beams and plasmas of interest to certain phases of thermonuclear research, it must first be possible to produce and maintain an ultra-high vacuum in the containing system. Materials used as components of such a system must not act as virtual leaks for gas into the vacuum. Wherever possible, component materials should remove gas from the vacuum. A method suitable for comparative evaluation of a great number of materials as sources and sinks for gas in ultra-high vacuum systems is required. The apparatus and procedure for such an investigation must be adaptable to widely varying test materials and test gases and must be as accurate in the study of desorption as adsorption. It also must be readily demountable and adaptable so that several combinations of materials and gases might be studied in succession. A critical review of the methods which have been used for the study of gas-metal reactions at very low pressures was conducted to select a method which could be used, or adapted for use, in such an investigation.

INTRODUCTION

There are a number of problems attendant to the use of commercial metals and ceramic materials in vacuum systems. When these materials are used without special preparation, either as containers or components for vacuum systems, difficulty arises because they frequently contain large amounts of dissolved, adsorbed, and occluded gases. Some materials also have appreciable vapor pressures at relatively low temperatures. Some metal oxides and nitrides, and many metal hydrides, have dissociation pressures of the same order of magnitude as the pressure desired in the vacuum system. When the pressure of gas over these materials is lowered, particularly at elevated temperatures, these gases may be evolved. The eventual equilibrium between gas desorption and evacuation rate of the vacuum pumps often sets a practical lower limit on the vacuum attainable at about 10^{-7} mm Hg. For a number of vacuum applications, notably the study of catalysis and the production and maintenance of ionic and atomic beams, pressures of the order of 10^{-7} mm Hg are sufficiently high to mask or destroy the effects being studied. This

collation has been conducted to summarize the methods which have been used to observe metal-gas reactions across a wide range of temperatures at pressures from nearly atmospheric to the low limit of experimental accuracy. It is hoped that this study will facilitate the choice of a suitable method for investigation of metal and ceramic materials as sources and sinks for gas in vacuum systems.

DISCUSSION:

A clean, metal surface is very difficult to obtain. Ashworth¹ has shown that even at a partial pressure of oxygen of 10^{-7} mm Hg a clean surface of tungsten will be covered with a single layer of oxygen in about 6 sec. Metal surfaces may be thought of as being electrically unbalanced since metal atoms on the surface experience the forces of surrounding metal atoms only on one side. Gas atoms striking the surface may be held by Van der Waals forces due to this. The surface free energy of the metal is reduced by such an adsorption, and the entropy of the gas is reduced because a two-dimensional gas layer is formed at the surface. From the relation $\Delta F = \Delta H - T\Delta S$, it may be seen that gas adsorption at a metal surface is spontaneous and exothermic. Physical adsorption of this type occurs in all metals at low temperatures and pressures and even takes place with the noble gases. The forces involved in physical adsorption are relatively short range and easily saturated; the total amount of gas adsorbed rarely amounts to more than the equivalent of one atomic layer of gas covering the surface, for example, a monolayer.

Physical adsorption as described above is reversible and temperature dependent. The heat of adsorption is of the same order of magnitude as the heat of evaporation of the gas. Vaporization of the gas and desorption of the gas from the metal surface are quite analogous and frequently, though not necessarily, proceed at nearly the same temperatures.

Metals also react chemically with gases impinging on the surface. This form of adsorption is termed chemisorption. This is apparently similar to chemical bonding without diffusion of metal or gas through the adsorbed layer. In this case, the heat of adsorption is of the same order of magnitude as the heat of formation of metal-gas compounds, and desorption is frequently

¹F. Ashworth, "Field Emission Microscopy," Advances in Electronics 3, 1 - 41 (1951).

incomplete up to temperatures of the same order as the dissociation temperature of the compound. In the tungsten-oxygen system, for instance, complete desorption on heating does not take place until above 2300°K. The two forms of adsorption are frequently observed simultaneously, several layers of adsorbate being chemically bonded to the absorbent and one or more additional layers being physically adsorbed as extreme outer layers. Differentiation between the two forms is difficult as there is considerable similarity between them. It is not the purpose of this paper to attempt such differentiation.

Complete thermodynamic discussions of the processes of adsorption and desorption have been reported by Guthrie and Wakerling,² Trapnell,³ and Dushman.⁴

The presence of an electric discharge influences the ability of a metal to adsorb and absorb gases.^{5,6} An intense discharge can drive adsorbed gas from the metal surface, while less strong discharges can markedly increase adsorption and absorption. Such discharges can dissociate some molecular gases, such as O₂, CO, CO₂, and H₂O, producing atoms which have a greater affinity for the sorbing material, and can excite the molecules of some other gases such as N₂ and H₂ increasing their chemical activity. Low and Taylor⁷ contend that there is an additional activation of absorbent materials which is independent of the gas to be collected. This activation has been related to the creation of large numbers of new adsorption sites by a form of surface chain reaction.

As a consequence of the enhancement of adsorption and absorption due to an electric discharge, some metals have found widespread use in the vacuum tube industry as gas sinks (getters) where they have been used to reduce the pressure in sealed containers and maintain it at very low values for the life of the tube. These getter materials have been studied frequently to evaluate their ability to absorb and hold gases. These studies yield much of the existing data on metal-gas reactions at very low pressures.

²A. Guthrie and R. K. Wakerling, Vacuum Equipment and Techniques, Div. 1 Vol. 1, National Nuclear Engineering Series, McGraw-Hill, New York, 1949.

³B. M. W. Trapnell, Chemisorption, Academic Press, New York, 1955.

⁴S. Dushman, Scientific Foundations of Vacuum Technique, John Wiley and Sons, New York, 1949.

⁵S. Wagener, "The Production of Very High Vacua by the Use of Getters," Proc. Inst. Elec. Engrs. 99(III), 135 - 147 (1952).

⁶S. Wagener, "Efficiency and Mechanism of Barium Getters at Low Pressures," Brit. J. Appl. Phys. 2, 132 - 138 (1951).

⁷M. J. D. Low and H. A. Taylor, "Enhanced Surface Reactions," J. Electrochem. Soc. 104, 439 - 442 (1957).

The ability of a metal to absorb and adsorb gases and the enhancing effect of an electric discharge have been combined in another way in the fabrication of the evapor-ion vacuum pump.^{8,9} In these pumps, the getter material is vaporized in the presence of an electric field and allowed to condense on the walls of the container or pump. While the metal is a vapor, it can occlude and dissolve considerable amounts of gases, and these are carried to the pump walls with the metal. Since vaporization and condensation are continuous, the deposited metal constantly presents a clean surface to the gases in the pump chamber and adsorption is therefore also continuous. The electric field ensures that any gaseous ions formed will be driven from the electrode region into the getter material on the wall and trapped in it. Neutral atoms and molecules striking the getter are adsorbed to the same extent as in vacuum tube getters. Solution of reactive gases sometimes occurs, and even noble and nonreacting gases may be physically trapped and held. Studies of evapor-ion pumps form the second major source of information about metal-gas reactions.

Molecules adsorbed on metal surfaces frequently dissociate into atoms and/or ions which are comparatively weakly bonded to the surface. It has been proposed that these adsorbed layers, because of the reduced energy associated with them, have appreciably lower activation energy for a number of chemical reactions than corresponding free molecules.¹⁰ Thus, metal surfaces may act to catalyze chemical reactions. Investigations of this theory of catalysis form the third principal source of data on metal-gas reactions.

In all the above cases, the adsorption has been of principal interest, and desorption has been considered only in order to secure clean surfaces, to activate catalysts, and to increase the capacity of adsorbent getters. Recent sorption studies have been performed quantitatively almost exclusively with

⁸R. H. David and A. S. Divatia, "Design and Operation of Evapor-Ion Pumps," Rev. Inst. 25, 1193 - 1197 (1954).

⁹I. Alexeff and E. C. Peterson, "Evapor-Ion Pump Performance with Noble Gases," Vacuum Symposium Transactions, pp 87 - 90, American Vacuum Society Committee on Vacuum Techniques, 1955.

¹⁰B. M. W. Tapnell, "Adsorption on Evaporated Tungsten Films, II; Chemisorption of Hydrogen and Catalytic Parahydrogen Conversion," Proc. Roy. Soc. (London) 206A, 39 - 50 (1951).

pure gases on otherwise clean metals. One field of interest in the present investigation is the determination of quantity and analyses of gases evolved from metals which have been surface-contaminated by atmospheric exposure. This will be considered in the recommendation for further experiments, but as very little parallel work has been done, the discussion of experiments to follow will be concerned with sorption experiments. Their applicability to desorption measurements will be noted only briefly.

This paper will attempt to review and evaluate some of the principal methods of measuring gas sorption and desorption at low pressures and to contrast the applicability of the several methods for the study of metal and ceramic materials as sinks or sources for gas in ultra-high vacuum systems.

EXPERIMENTAL TECHNIQUES

One of the earliest and most generally used methods for studying gas-metal reactions at reduced pressures is attributed to Sieverts. This method is described as follows: A measured pressure of gas is admitted into a container of known volume which is separated from the test sample by a valve. The region containing the test sample is evacuated, and any special preparation steps such as outgassing or activation of the sample are performed in the separated region. Then the valve separating the test sample from the gas is opened, and the pressure of the gas remaining in the system is measured. The volume of gas adsorbed on the sample can be directly calculated if the total volume of the system and the final pressure are known. The pressure range suitable for study with this apparatus is from 10^{-6} to 10 mm Hg.

Some particular difficulties are involved in pressure volume and flow determinations in this range of pressure. At pressures below about 10^{-5} mm Hg, Knudsen's laws of molecular motion apply to the dynamic vacuum system, while at pressures above about 0.1 mm Hg the conventional gas laws apply. In the intermediate region of pressure, no simple relationship between pressure, conductance, and flow exists. Experiments involving a study of adsorption as a function of temperature also must be calibrated to avoid errors due to thermal transpiration. It is necessary to determine the relationships existing in the experimental system across the entire range of pressures and temperatures of interest prior to the experiment. This type of apparatus is not readily adaptable for studies of out-gassing at low pressures.

In 1939, Orr¹¹ devised an apparatus to determine the differential adsorption of several gases on ionic salts in the range of pressure of 10^{-3} to 60 mm Hg. His method was developed and extended to pressures of 10^{-6} mm Hg by Frankenburg¹² who in 1946 used an experimental apparatus similar to that diagrammed in Fig. 1 for the study of metal powders. The adsorption vessel, AV, was surrounded by a resistance-wound vacuum furnace, VF, which was evacuated to minimize any chance of outside contamination of the reaction vessel. The reaction vessel was further protected from contamination by the cold traps T_1 and T_2 . The adsorbent was reduced using pure hydrogen prepared by diffusion through a palladium thimble. This purified hydrogen was then passed over the heated adsorbent and removed by pumping. The three manometers A, B, and C covered a wide range of pressure. In measuring sorbed volumes, known amounts of gas were admitted and their pressure was measured before and after sorption. The difficulties in the application of pressure-volume relationships in the pressure range 10^{-1} to 10^{-5} mm Hg where thermal transpiration and other effects may be important were a source of experimental difficulty in this experiment. This system is equally accurate for study of sorption or evolution; heating and cooling are direct, simple, and immediate; but the procedure is subject to too many errors in execution and evaluation, and the pressure range it can best study does not coincide with the range of maximum interest in the present study.

In 1954, Selwood¹³ utilized a self-recording device to evaluate gas pickup on finely divided ferromagnetic materials by measuring the effect of surface contamination on magnetic permeability. Nickel particles precipitated by partial reduction of nickel-kieselguhr catalyst materials were found to have a particle-size distribution of 10 - 50 Å. The surface-to-volume ratio of these particles is quite large. It may be assumed that nickel has 0.6 electron vacancies per d-band. When molecules of a gas are chemisorbed on the nickel, the sorption is accompanied by electron transfer from or to the nickel. When electrons are transferred to the nickel as in the sorption of hydrogen, they fill the vacancies in the d-band and thus reduce the atomic

¹¹W. J. C. Orr, "The Adsorption of Non-Polar Gases on Alkali Halide Crystals," Proc. Roy. Soc. (London) 173A, 349 - 367 (1939).

¹²W. G. Frankenburg, "The Adsorption of Hydrogen on Tungsten," J. Am. Chem. Soc. 66, 1827 - 1837 and 1838 - 1847 (1944).

¹³P. W. Selwood, T. R. Phillips, and S. Adler, "Some Magnetic Consequences of Chemisorption on Supported Nickel Catalysts," J. Am. Chem. Soc. 76, 2281 - 2282 (1954).

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Fig.1. Volumetric Measurement of Adsorption on Powders Ref: R.T. Davis, Jr., "The Activated Adsorption of Nitrogen on a Finely Divided Tungsten Powder," J. Am. Chem. Soc. 68, 1395 (1946).

magnetic moment and the bulk magnetic permeability of the nickel. Because of the high surface-to-volume ratio of small particles, a 20 Å cube of nickel, which adsorbs a monolayer of hydrogen molecules, will completely lose its ferromagnetism assuming each gas molecule donates one electron to the metal bulk. Similarly, adsorbed gases which take electrons from the nickel can increase the magnetic permeability. The change in ferromagnetism may be measured and used to determine the amount of gas adsorbed on small particles of ferromagnetic materials. The apparatus based on this principle is diagrammed in Fig. 2.

The apparatus is essentially a transformer with a primary winding of 3100 turns operating at about 1 amp and 230 v. There are two secondaries of 50 turns each which are connected in series as shown. One coil surrounds an air gap or a carefully degassed dummy sample sealed in glass. The other surrounds 5 - 10 g of sample catalyst pellets on which adsorption is to be measured. Although the entire assembly can be enclosed in the vacuum chamber, Selwood chose to evacuate only the test sample itself. This in no way reduces the accuracy of results and makes the experimental procedure less difficult. After adsorption by allowing gas at a known, small pressure to surround the sample, the change in magnetic permeability relative to the clean control sample can be determined on a voltmeter as shown. The full-scale sensitivity of the voltmeter was 1 mv, and voltage differences of about 0.5 mv were usually observed. Within limits, the volume of gas adsorbed could be calculated directly from this potential difference.

Two particular kinds of response were seen in the operation of this device. Chemisorbed gases, such as hydrogen and ethylene, which acted as electron donors resulted in marked loss in magnetic permeability by the mechanism described above. The chemisorption of gases, such as nitrogen and oxygen, which accepted electrons resulted in a gain in magnetic permeability, presumably by taking electrons from the d-band of the nickel and thus increasing its magnetic moment. Typical magnetization vs temperature curves showing the response of a clean, nickel sample and the response of typical samples containing adsorbed gases, which act either as electron donors or acceptors, are presented in Fig. 3.

The system was calibrated by allowing a known amount of adsorption to take place and measuring the difference in magnetization produced. The volume

Fig. 2. Induction Apparatus for Measuring Magnetization. Ref: P.W. Selwood, "Mechanism of Chemisorption: Hydrogen on Nickel. I," J. Am. Chem. Soc. **78**, 3893 (1956).

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Fig. 3. Thermomagnetic Curves for (1) Massive Nickel, (2) Reduced Nickel-Silica Catalyst With Chemisorbed Nitrogen, (3) Reduced Nickel-Silica Catalyst in Helium or Vacuum, and (4) Reduced Nickel-Silica Catalyst With Chemisorbed Hydrogen. Ref: P.W. Selwood, T.R. Phillips, and S. Adler, "Some Magnetic Consequences of Chemisorption on Supported Nickel Catalysts," J. Am. Chem. Soc. 76, 2282 (1954).

of gas adsorbed was initially determined using the techniques developed by Sieverts and described above. Subsequently, adsorbed volumes could be determined by comparing the magnetization of the adsorbent with the calibration curves thus constructed.

A number of advantages of this system are immediately obvious. Large assembly tolerances are possible, the system is readily demountable, and there are no volatile components in the system. The apparatus can be heated for test purposes or for bakeout without extreme precautions, and it gives reproducible results at any temperature up to 631°K, the Curie temperature of nickel. As it measures gas present at the surface directly, it is equally adaptable for study of adsorption or desorption. There are two principal drawbacks, however. Because the method is effective only for extremely small particles, the actual surface area of the particles cannot be accurately determined, and the responses measured might be as much dependent on the particle-size distribution as on the amount of gas adsorbed. Even discounting this, the method is applicable only to ferromagnetic materials and gases chemisorbed on them.

In 1950, S. Wagener¹⁴ investigated sorption and desorption of gases using the apparatus diagrammed schematically in Fig. 4. The test apparatus consisted principally of two ionization gages, P and S, connected by a capillary tube with a conductance of about 20 cm³/sec for air, and a gas source connected to the system through a controllable leak valve. This apparatus measured directly the rate of adsorption or desorption on a metal surface in gage S. The relationship, derived from Knudsen's law of molecular gases, considering the sample to be adsorbing gas, is

$$G = F \frac{p_p - p_s}{p_s}$$

in which G is the gettering rate, F is the conductance of the capillary, p_p is the pressure at the gage P containing the gas leak, and p_s is the pressure at the sample. For most determinations p_s was much smaller than p_p , and the equation reduced to

$$G = F \frac{p_p}{p_s}$$

¹⁴S. Wagener, "A Method for Measuring the Efficiency of Getters at Low Pressures," Brit. J. Appl. Phys. 1, 225 - 231 (1950).

Fig. 4. Experimental Arrangement for Measuring Gas Evolution and Gettering Rates.

When an adsorbent was placed in gage S, it was found experimentally that the ratio in pressures between gage S and gage P was independent of the initial pressure in gage P. From the equation above, it may be seen that F was, therefore, also independent of p_p to a first approximation. Residual gas not adsorbed by the getter surface produced deviations in the results at low pressures, but it was possible to determine the partial pressure of this gas and subtract it from the total pressure to obtain the pressure of reactive gas over the adsorbent.

For refractory metals and ceramic materials, the tube may be equipped, as shown, with tungsten or molybdenum filaments coated with powders of the test material. It also may be easily adapted to test refractory-metal filament ribbons directly, or in the case of comparatively high vapor pressure materials such as Ba, Ti, and others, a filament may be placed in the tube from which the metal may be evaporated onto the tube wall. This has the advantage of assuring a clean metal surface for adsorption in all cases where it is desired. The system is sensitive to variations of 0.001 monolayer of adsorbed gas at 10^{-6} mm Hg, is easily built, and can be adapted for either intermittent or continuous reading.

The total amount of adsorbed gas could not be determined directly in this experiment. The adsorbed volume was determined by an equation of the form:

$$Q = \int_0^t p_s G(t) dt$$

where Q is the total gas adsorbed and G(t) is the observed gettering rate as a function of time t. In practice, this integral cannot be accurately evaluated for t approaching infinity (total capacity of the sample), because the gettering rate at long times approaches zero asymptotically, and the ion pumping rate of the ionization gage is then of the same order of magnitude as the gettering rate. Wagener, therefore, quotes adsorption volumes as Q_{50} and Q_5 , the amount adsorbed before the adsorption rate fell to 50 and 5 cm³/sec, respectively. The accuracy of this determination is within 10% for physisorbed gases and slightly greater for chemisorbed gases.

The errors induced by ion-gage pumping and gas adsorption by surfaces other than the getter surface were corrected from measurements of the vacuum

factor K of the ionization gage.¹⁵ The ratio of collector (positive-ion) current to the anode (electron) current is K and it relates the sensitivity of the gage to the gas pressure in the gage at all pressures.

A principal disadvantage of Wagener's method is that it requires complete dismantling of gage S to change test samples and subsequent rebaking of the system. It will be seen that this disadvantage is common to all methods used to date. Desorption rates may be studied using the same apparatus and sample by closing the leak and considering gage S the source and gage P the sink.

There is an additional significant source of error inherent in all systems using ionization-gage determination of pressure. Ionization gages are sensitive to both the amount and the kind of gas which they are measuring; for example, they indicate different pressures depending on the nature of the gas they are measuring. Hot-cathode ionization gages actually operate at a different pressure than the system to which they are connected, because according to Knudsen's laws, the pressure in a hot region is greater than the pressure in a cold region to which it is connected. Additional sources of error are the pumping action of the ionization gage, the inability of any ionization gage to determine accurately the pressure of condensable gases, and variation of the sensitivity of the gage with duration of operation.¹⁶

The errors introduced by ion-gage pumping may be accounted for by determining the vacuum factor K of the gage as outlined above. Other errors cannot be accounted for as the gage cannot be calibrated at low pressures against any absolute pressure determination and must be considered to contribute to inaccuracies in the final results of all work in which ion-gage pressure determinations are used. Preliminary work with commercial, ultra-high vacuum gages indicates consistency and reproducibility of pressure indications to be no more accurate than $\pm 15\%$ at nominal pressures of 5×10^{-7} mm Hg.

In 1955, Becker described an apparatus similar to that of Wagener which allowed slightly greater control over the experimental procedure (See Fig. 5).

¹⁵G. H. Metson, "Vacuum Factor of Oxide-Coated Valve," Brit. J. Appl. Phys. 1, 73 - 77 (1950).

¹⁶J. H. Leck, "Pressure Measurement in Vacuum Systems," Inst. Physics (London), 1957.

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Fig. 5. Schematic Diagram of Experimental System Used to Study the Adsorption of Nitrogen on Tungsten. Ref: J. A. Becker, "Advances in Catalysis," Adsorption on Metal Surfaces, VII, Academy Press, New York, 161 (1955).

Instead of a vapor-deposited film, he used filament ribbons exclusively. In place of a capillary, he used tilting glass plate which presented a variable area to the gas and, therefore, had moderately variable conductance, and he shielded the adsorbent from the ionization gage with an electrostatic shield. Here again, the rate of adsorption was determined continuously, but in addition, the filament could be flashed intermittently to determine the total gas adsorbed without calculation. The analogous expression to the one derived by Wagener is

$$S = \frac{a_p}{a_f} \left(\frac{p_o - p}{p_o} \right)$$

where S is the sticking probability (proportional to the pumping rate of the ribbon), a_p is the area of the aperture, a_f is the area of the adsorbent ribbon, p is the pressure at the ribbon, and p_o is the pressure in the admitting system beyond the aperture. The flashing technique is obviously limited to low vapor-pressure materials and tacitly assumes complete desorption. While this assumption is reasonable at 2400°K for tungsten, it is open to debate at lower temperatures and for many less refractory materials. In every other respect, this apparatus seems as versatile, and possibly more accurate, than the apparatus described by Wagener. It is, of course, subject to the same difficulties with respect to demounting and the same inaccuracies as a result of ionization-gage pressure determination.

In 1953, Dillon and Farnsworth¹⁷ studied the adsorption of CO₂ on single crystals of nickel with the use of radioactive tracers. The adsorbate contained 5.8 at. % C¹⁴, and the volume of gas adsorbed was calculated by the activity of the sample as determined by a Geiger counter fused into the vacuum system and separated from the sample by a thin mica window. This method is also quite sensitive to distribution of the gas on the metal surface. One possible source of trouble in this apparatus is the fact that physical adsorption may be sensitive to the presence of isotopes of the gas.

In 1955, Becker and Brandes¹⁸ described a method for watching the adsorption of gases on tungsten surfaces at pressures in the range of 10⁻¹⁰ to 10⁻⁷ mm Hg through the use of the Field Emission Microscope (FEM). The apparatus they

¹⁷J. A. Dillon, Jr. and H. E. Farnsworth, "Adsorption of Carbon Dioxide on Nickel Single Crystal Surfaces Using a Radioactive Tracer," J. Chem. Phys. **22**, 1601 - 1605 (1954).

¹⁸J. A. Becker and R. G. Brandes, "On the Adsorption of Oxygen on Tungsten as Revealed in the Field Emission Microscope," J. Chem. Phys. **23**, 1323 - 1330 (1955).

used is diagrammed in Fig. 6. In the microscope, a point with a radius of about 2×10^{-5} cm is maintained at a potential of several thousand volts negative with respect to a spherical screen of 5 - 25 cm dia. The resulting potential gradient is sufficient to pull electrons from the point and carry them along straight lines to the screen. The magnification of the FEM is on the order of 10^7 X and the theoretical resolution limit, based on Heisenberg's uncertainty principle, is about 2.2 Å. A practical low limit on resolution is about 7.5 Å if resolution is thought of as the ability to detect a point disturbance, but occasionally particles as small as 3 Å have been observed.¹⁹

The light intensity on the screen is directly proportional to the number of incident electrons, which in turn are proportional to the work function of the emitting surface. A number of interesting consequences of these facts have been observed.

The point radius is sufficiently small that only a single crystal is visible in the microscope. Particular crystallographic planes have different work functions, depending in part on the relative strength of the interatomic band. Adsorbed gas atoms greatly influence the work function of a particular crystallographic plane and at elevated temperatures, promote the growth of particular planes at the expense of others. It has been proposed that the planes which grow are those which form the strongest metal-to-gas bonds. All these effects are visible in the FEM, and semiquantitative results for adsorption energies, saturation values, surface-diffusion and diffusion-activation energies, physical- and chemical-bond strength, and similar quantities may be calculated. This method appears to promise great utility in the study of the fundamental mechanisms of gas-metal surface reactions, catalysis, and sorption processes. It is not, however, ideally suited at this time to a quantitative study of sorption, either with respect to rate, total quantity, or to saturation and sorption of several gases simultaneously such as with air-metal reactions. It is theoretically applicable to any metallic body, as the emission is not thermally dependent. Two practical difficulties limit its applicability. First, as mentioned previously, it is quite difficult to obtain or maintain a clean metal surface; many metals cannot be cleaned of surface gases even at their melting point in the best obtainable vacua. Second, it is difficult to obtain the potential gradients necessary to obtain field emission without introducing electrostatic stresses in the test point which

¹⁹F. Ashworth, loc. cit.

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Fig. 6. Schematic of Experimental System Used to Study Oxygen on Tungsten With a Field Emission Microscope. Ref: J. A. Becker, "Advances in Catalysis," Adsorption on Metal Surfaces, VII, Academy Press, New York, 178 (1955).

are large enough to produce excessive coarsening and sometimes rupture in soft materials or materials at elevated temperatures. Until recently, the only satisfactory field emission results have been obtained from the refractory metals, but recent work by Gomer²⁰ indicates the possibility of extending field emission investigations to low melting point metals. He obtained reproducible field emission patterns from mercury whiskers grown and maintained at -40 to -78°C.

As early as 1927, Davisson and Germer²¹ discovered that gases adsorbed on metal surfaces could be studied by electron-diffraction techniques. They showed that electrons incident upon nickel single crystals were diffracted from the nickel lattice as expected. They also found that at low incident angles, low-energy electrons were diffracted by the crystal surface. Further investigation showed that this diffraction was due to a film of chemisorbed oxygen only a few atomic layers thick. Prior to this investigation, there was considerable debate as to whether gases adsorbed on metal surfaces behaved as a two-dimensional liquid or were bound to lattice sites. The observed layers had the same crystal structure and twice the lattice spacing as the nickel-base metal, thus apparently simultaneously verifying Langmuir's concept of adsorption at fixed-energy sites on the surface and introducing a new tool for the investigation of adsorption on metals. Recent work with electron diffraction has been confined to use in the determination of the structure of adsorbed gases in conjunction with other methods for determination of their volume. Electron diffraction is well suited to the study of multi-layer adsorption, mobility of adsorbed atoms, stability of films, etc. It is not sensitive, however, to kind and quantity of gas adsorbed, and, therefore, is not suitable by itself to the investigation of gas sorption and evolution on a quantitative basis. Also, experimental difficulties with electron-diffraction techniques are prohibitive and do not recommend them to investigations such as the one proposed here.

Combinations of the above techniques were used by Beeck, Smith, and Wheeler²² in 1941 for the study of vapor-deposited metal films. They found

²⁰R. Gomer, "Field Emission from Mercury Whiskers," J. Chem. Phys. 28, 457 - 464 (1958).

²¹C. Davisson and L. H. Germer, "Diffraction of Electrons by a Single Crystal of Nickel," Phys. Rev. 30, 705 - 735 (1927).

²²O. Beeck, A. E. Smith, and A. Wheeler, "Catalytic Activity, Crystal Structure and Adsorptive Properties of Evaporated Metal Films," Proc. Roy. Soc. (London) 177A, 62 - 89 (1940 - 1941).

that the films deposited in vacuo were randomly oriented, but films deposited in 1 mm Hg, nitrogen, or argon pressure were strongly oriented and adsorbed 5 - 30 times more gas. Although the area for adsorption of the films deposited in gas was higher, the increased activity of the films could not be attributed solely to that fact. The surface areas of films deposited by both techniques were determined, and the films deposited in gas were found to have only twice the surface area of the films deposited in vacuum.

The increased activity of the oriented films was explained in two ways. First, the planes of orientation were planes of lowest atomic density of the principal planes in the respective systems; (110) in fcc metals and (111) in bcc metals. The low metal-metal bond strength between atoms in these planes allows strong bonding between the metal atom and the adsorbed gas atom. Second, during crystal growth, additional metal-crystal layers tend to nucleate in the center of metal-crystal plane faces and then grow toward the crystal edge. A number of planes of the 110 form in the fcc system nucleating in rapid succession could lead to plane surfaces of much higher indices inclined at small angles to the (110) plane. These planes of higher indices have even lower metal-atom density and, therefore, could adsorb even greater amounts of gases. This viewpoint has been supported by more recent work with the Field Emission Microscope. A volumetric determination of adsorbed gases was made using the Sieverts technique, and the film orientation was determined using electron-diffraction techniques.

Adsorption has also been studied by the variation of thermionic emission of the adsorbent under the influence of the adsorbate. This work was initiated by Brattain and Becker²³ in 1933. Here the average work function across the surface was determined by measuring the electron current emitted from a filament before and after exposing it to the adsorbate gas. Fringe effects in the emission were minimized by including two shield cathodes on either side of the collector at which the current was measured. This method finds special applicability to the study of metal-metal adsorption and was used by the authors to investigate the system of cesium on tungsten.

Many other methods have been used to study metal-gas reactions at metal surfaces. Many of the approaches involve unnecessarily complex experimental

²³W. H. Brattain and J. A. Becker, "Thermionic and Adsorption Characteristics of Thorium on Tungsten," Phys. Rev. 43, 428-450 (1933).

procedures; many appear to be overly susceptible to variation in properties other than the properties under study; many apparently contain built-in errors which can neither be accounted for nor eliminated; and many are simply not adaptable to the type and scope of investigation for which this review is the prelude. For these reasons, a representative sampling of the methods might now be mentioned without additional comment. The concentration of the adsorbate has been determined by the variation in the accommodation coefficient of the adsorbent for neon after adsorption.²⁴ Variations in the resistivity of vapor-deposited films have been found to be directly dependent on the amount of adsorbed gas in the film.²⁵ Methods based on calorimetry,²⁶ weight gain per unit time,²⁷ and photoelectric emission²⁸ have been used. Diffusion, as well as sorption, has been studied using the permeation rate of gases through thin sheets.²⁹

Much of the data which have been presented for adsorption has unwittingly been determined upon contaminated surfaces with the use of impure gases and therefore is inaccurate. The data listed below are those which appear to be the most accurate or the most current. The reader is referred to the source material for the techniques used in their determination.

The presence of volatile or dissociable materials in a vacuum is one source of vapor. Giler has presented the vapor pressure vs temperature curves for a number of metals in Fig. 7 and the dissociation pressure vs temperature curves for a number of metal oxides in Fig. 8. The physical properties of a number of metals and refractories which are significant in vacuum practice have been tabulated by H. B. Micaelson and are presented in Tables I and II.

²⁴A. B. Van Cleave, "Adsorption of Nitrogen and Oxygen on Tungsten," Trans. Faraday Soc. 34, 1174 - 1177 (1938).

²⁵J. H. Singleton, "Hydrogen Sorption and the Parahydrogen Conversion on Evaporated Nickel Films," J. Phys. Chem. 60, 1606 - 1611 (1956).

²⁶R. A. Beebe et al., "Heats of Adsorption on Carbon Black. I," J. Am. Chem. Soc. 69, 95 - 101 (1947).

²⁷E. A. Gulbransen, "A Vacuum Microbalance for the Study of Chemical Reactions on Metals," Rev. Sci. Inst. 15, 201 - 204 (1944).

²⁸R. C. L. Bosworth, "The Mobility of Sodium on Tungsten," Proc. Roy. Soc. (London) 150A, 58 - 76 (1935).

²⁹D. Alpert and R. S. Buritz, "Ultra-High Vacuum. II; Limiting Factors on the Attainment of Very Low Pressures," J. Appl. Phys. 25, 202 - 209 (1954).

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Fig. 7. Vapor Pressure of Metals. Ref: R. R. Giler, "Vacuum Heat Treating," Symposium on Vacuum Tech. Trans., American Vacuum Society, Pergamon Press, Los Angeles, (December, 1957). p. 163

Fig. 8. Dissociation Pressure of Metal Oxides. Ref: R. R. Giler, "Vacuum Heat Treating," Symposium on Vacuum Tech. Trans., American Vacuum Society, Pergamon Press, Los Angeles, (December, 1957), p 162.

TABLE I

PROPERTIES OF METALS AND ALLOYS^a

Materials	Melting Point, °F	Coefficient of Thermal Expansion per °F	Thermal Conductivity Btu/hr/sq.ft./ft/°F	Brinell Hardness	Outgassing Temp., °F	Vaporization Rate at 7.6 mm Hg		Creep Strength (stress for 1% creep in 10,000 hr)	
						Temp. °F	g/cm ² /sec	psi	Temp. °F
Oxygen-free copper	1981	9.3×10^{-6}	224	100, ^b 42 ^c	925 - 1475	1735	1.33×10^{-7}		
Hastelloy C	2320 - 2380	6.3×10^{-6}	7.2	195, ^d 185 ^c	1650				
Iron, ingot	2795	6.8×10^{-6}	39	96, ^d 67 ^c	1800	2000	1.29×10^{-7}		
Inconel (wrought)	2540 - 2600	6.4×10^{-6}	8.7	150, ^c 180 ^d	1650			22,000	900
Inconel X	2540 - 2600	7.6×10^{-6}	8.5	200, ^b 260 ^b	1650			600	1800
Nickel	2650	7.4×10^{-6}	48	100 - 200 ^c	1400 - 1740	2115	1.18×10^{-7}	18,000	1500
Nicrhrome V	2550	9.8×10^{-6}	7.8	85 - 90 ^c	1700 - 3200			10,000	750
Molybdenum	4757	2.8×10^{-6}	84	200 - 230 ^b		3490	1.29×10^{-7}	350 ^g	2000
Stainless steel (310)	2540 - 2650	8.0×10^{-6}	7.8	165 ^c				970 ⁱ 900 ⁱ	1635 1760
Stainless steel (316)	2500 - 2540	8.9×10^{-6}	9.4	165, ^c 275 ^b				4,500	1500
Stainless steel (347)	2540 - 2600	9.3×10^{-6}	9.3	160, ^c 300 ^b				1,000	2000
Tantalum	5425	3.6×10^{-6}	31	55, ^c 125 ^b	3300 - 3600	4365	1.55×10^{-7}	24,000	1000
Tungsten	6152	2.2×10^{-6}	92	350, ^j	3300 - 4200	4630	1.47×10^{-7}	2,000	1500

^aH. B. Michaelson, "High Temperature Materials for Vacuum Service," Matls. and Methods 38, 113 (Dec., 1953).^bcold rolled, ^cannealed, ^dcast, ^erolled, ^fhot rolled, ^g1000 hr, ^hforged, ⁱ100 hr, and ^jswaged

TABLE II

PROPERTIES OF NONMETALLIC MATERIALS^a (ALL PROPERTIES DEPEND ON IMPURITIES AND FABRICATION METHOD)

Material	Melting Point, °F	Maximum Operating Temperature in High Vacuum, °F	Coefficient of Thermal Expansion per °F	Thermal Conductivity Btu/Hr/Sq. ft/ft/°F	Thermal Shock Resistance	Hardness Mohs' Scale	Vapor Pressure mm of Hg Temp. °F		Electrical Resistivity at 2200°F, ohm-cm	Load Bearing at 2200°F
Alumina, fused	3722	3270	4.5×10^{-6} (68 - 2300)	0.4 - 0.5	Excellent	9	0.35	3720	10^4	Good
Beryllia, fused	4568	3630	$5.1 - 5.2 \times 10^{-6}$	1.1 - 2.1	Excellent	9	1.8×10^{-3}	3775	10^{12}	Good
Graphite		4530	4.3×10^{-6}	4.4 - 14.4	Excellent	0.5 - 1.0	10^{-6}	3630	7.9×10^{-4}	Excellent
Magnesia	5072	2910	$7.9 - 8.3 \times 10^{-6}$ (68 - 3100)	0.4 - 0.8	Poor	6	High	>3630	5×10^{-11}	Fused, good, sintered, poor
Mullite	3250-3335	2730-3090	$5.5 - 2.9 \times 10^{-6}$ (68 - 2600)	0.2 - 0.3	Good	6				Excellent
Sillimanite	2950 ^b	2500-2730			Good	6 - 7				Good
Silica, fused	3110 ^c	2010 ^c	0.3×10^{-6} (68 - 2280)	0.3 - 0.35	Excellent	5 - 7	9.9×10^{-6}	1830	5×10^{-5}	Fair
Thoria, fused	5486	4900	$5.3 - 5.3 \times 10^{-6}$ (68 - 2550)	Very low	Poor	7	1×10^{-2}	4710	10^{-10}	
Zircon	4622	3090 ^d	$2.0 - 3.7 \times 10^{-6}$ (68 - 1475)	0.2 - 0.3	Good	8			10^4	Good
Zirconia, Stabilized	4600-4700	3990	$2.8 - 6.0 \times 10^{-6}$ (68 - 2275)	0.36	Fair to good	8.5				Good

TABLE II (Continued)

Material	Melting Point, °F	Maximum Operating Temperature in High Vacuum, °F	Coefficient of Thermal Expansion per °F	Thermal Conductivity Btu/Hr/Sq. ft/ft/°F	Thermal Shock Resistance	Hardness Mohs' Scale	Vapor Pressure mm of Hg Temp. °F	Electrical Resistivity at 2200°F, ohm-cm	Load Bearing at 2200°F
Silicon Carbide	>4900	3990 ^d	2.5 - 2.6 x 10 ⁻⁶ (32 - 3090)	1.1 - 2.4	Good	9 - 10		2.5	Excellent
Lava, fired		2190-2280	5.8 - 6.4 x 10 ⁻⁶ (77 - 2900)			6		10 ⁴	Good

^aH. B. Michaelson, "High Temperature Materials for Vacuum Service," Matls. and Methods 38, 112 (December, 1953).

^bdecomposes, ^cdevitrifies, ^ddissociates

The initial gas adsorption rate and the total gas capacity, as reported by Wagener³⁰ and Espe et al.,³¹ are presented for a wide variety of metal-gas systems in Table III. It can be noted that the actual adsorption area of vapor-deposited films is several times the apparent area and that it varies linearly with film weight. Trapnell has tabulated engineering data on the metal-gas systems in which chemisorption will or will not take place, and this is presented in Table IV. Current data on the use of materials as getters have been tabulated by Espe et al., and are presented in Table V.

Recent studies of gas desorption by metals are much less extensive. The best summary of the results of desorption determinations made prior to 1949 is given by Dushman,³² who refers to most of the common metals and many of the getter materials. These data, together with some of the more recent work by Tobin et al.,³³ are presented in Table VI.

CONCLUSIONS AND RECOMMENDATIONS

The experimental procedure to be adapted for the study of metal-gas reactions in ultra-high vacuum must possess both accuracy and flexibility. It must be adaptable to widely varying test materials and gases, and it must be as accurate in the study of evolution as of sorption. The apparatus and the procedure should be kept simple and direct to minimize calculation and experimental errors, and provision should be made for studying vapor-deposited films, metal filaments, and bulk and powder samples. On these bases and because the apparatus has been used successively in a number of significant investigations to date, it is recommended that a slightly modified form of the apparatus described by Wagener be used for the proposed study. In essence, this apparatus consists of two ionization gages separated by a tube of known, small conductance; one of the gages measuring the pressure in a reaction chamber and the other measuring the pressure produced by a controlled small leak. The principal modifications suggested are separation of the ion gage from the reaction chamber and suitable provision for demounting the reaction chamber for changing or modifying test materials.

³⁰S. Wagener, "Adsorption Measurements at Very Low Pressures (I and II)," I, J. Phys. Chem. 60, 567 - 573 (1956); II, J. Phys. Chem. 61, 267 - 271 (1957).

³¹W. Espe, M. Knoll, and M. P. Wilder, "Getter Materials for Electron Tubes," Electronics 23, 80 - 86 (October, 1950).

³²S. Dushman, loc. cit.

³³J. C. Tobin and M. J. Sinnott, "Gas Desorption of Copper Powders," Trans. AIME 212, 167 - 171 (1958).

TABLE III
ADSORPTION RATE AND GAS CAPACITY OF SEVERAL METALS

Material	Appli- cation	Gas	Initial Rate cm ³ /sec	Capacity ^a l-μ/cm ²	Op. Temp. °K	Comments
Barium	Flash deposit	O ₂	330	0.20	300-350	
		CO	1250	0.20	300-350	
		CO ₂	3000	0.052	300-350	
		H ₂ O	2300	--	300-350	
		N ₂	80	0.10	300-350	
		H ₂	250	0.87	300-350	Getters during flashing only
Magnesium	Flash deposit	O ₂	150	0.20	300-350	Adsorbs nothing else
Zirconium	Coating	O ₂	(large)	0.365	1075	
		CO	--	0.365	1075	
		CO ₂	--	0.304	1075	
		N ₂	--	0.146	1075	
		H ₂	--	1.333	625	H ₂ evolves at 1675°K
Thorium	Coating	O ₂	1400	0.50	950	Powders
		CO	2400	--	950	Very pyrophoric
		CO ₂	3000	--	950	
		H ₂ O	350	--	950	
		N ₂	35	--	950	
		H ₂	50	0.02	700	H ₂ evolves above 700°K
Titanium	Flash deposit	CO	12,000	0.154	300	
		N ₂	3,000	0.063	300	
		CO ₂	4,300	0.130	300	
Molybdenum	Foil	CO	3,500	0.140	300	
		N ₂	2,700	0.055	300	
Nickel	Flash deposit	CO	4,500	0.040	300	

TABLE III (Continued)

Material	Appli- cation	Gas	Initial Rate cm ³ /sec	Capacity l-μ/cm ²	Op. Temp. °K	Comments
Aluminum	Flash deposit	O ₂	0.075	----	900	Getters during flashing only
		N ₂ , H ₂ , CO ₂				No adsorption
Uranium	-----	O ₂	0.105			
		H ₂	0.089			
Misch metal	Flash deposit	O ₂	0.212	----	3300	H ₂ evolution Alloy of rare earths
		H ₂	0.461	----	300	
		N ₂	0.032	----	3300	
		CO ₂	0.022	----	300	

^a Gettering capacity has been converted where necessary to l-μ/cm² on the arbitrary assumption that bright deposits average 100 cm² of real surface area per gram. Dashed lines indicate no data.

TABLE IV
THE ACTIVITIES OF THE METALS IN CHEMISORPTION*

GROUP	METALS	N ₂	H ₂	CO	C ₂ H ₄	C ₂ H ₂	O ₂
A	W, Ta, Mo, Ti, Zr, U, Th, Fe, Ca, Ba	+	+	+	+	+	+
B	Ni, Pd, Rh, Pt	-	+	+	+	+	+
C	Cu, Al	-	+	+	+	+	++
D	K	-	-	-	-	+	+
E	Zn, Cd, In, Sn, Mg	-	-	-	-	-	+
F	Au	-	-	+	+	+	-

NOTES: + gas chemisorbed; - gas not chemisorbed

* B. M. W. Trapnell, "The Activities of Evaporated Metal Films in Gas Chemisorption," Proc. Roy. Soc. (London) 218A, 569 (1953).

TABLE V
OUTGASSING, FLASHING, AND OPERATING TEMPERATURES OF TYPICAL GETTERS*

Material	Ta	Cb	Zr	Th	CeO ₂	Mg	Al-Mg	Ba and Ba Compounds	Bato	Reaction-Type Getters		Phosphorus
										Batalum	Berylliate	
Form of application	Bulk coating	Bulk	Bulk coating	Coating	Coating	Flash	Flash	Flash	Flash	Flash	Flash	Flash
Form of getter	Sheet Powder	Pellets	Sheet Wire Powder	Powder	Powder	Ribbon Wire	Powder Paint	Metal-clad wire Pellets	Ni-clad pellets	BaCO ₃ paint on Ta	BaBeO ₂ paint on Ta	Powder suspension
Outgassing preheating temperature (deg C)	1600-2000	1650	700-1300 (up to 1700 in compound wires)	For metal base 800-1000, for graphite 1500-1600	800-1200	400	400	600-700	No ref	800-1100	900-1000	No ref
Flashing temperature (deg C)	--	--	--	--	--	500	No ref	900-1300	750-800 (900)	1200-1300	1300	>200
Operating temperature (deg C)	700-1200	500	800 (up to 1600 in compound wires)	400-500	200-500	Absorbs gases only during flashing		20-200 (max)	20-200	20-200	20-200	100-200
Applications**	D,E,M	D,E	C,D,E,F,I, K,L,M,N	C,D	P	I,K	A,F	A,B,D,F,G, H,I,(L)N	D,M	A,F	A,F	

*W. Espe, M. Knoll, and M. P. Wilder, "Getter Materials for Electron Tubes," *Electronics* 23, 85 (October 1950).

**A - Small receiving tubes,
B - Miniature tubes,
C - UHF tubes,
D - Medium-size transmitting tubes,
E - High-power transmitting tubes,
F - Oxide coated tubes,
G - Cathode-ray tubes,
H - Phototubes,

I - Gaseous-discharge tubes,
K - Hg-vapor tubes,
L - X-ray tubes,
M - High-power vacuum tubes,
N - Tubes with thoriated cathodes,
O - Incandescent lamps,
P - Vacuum tubes in which neither flashing getters nor the high temperatures necessary for Ta and Zr may be used.

TABLE VI
GAS DESORPTION FROM METALS

Metal	Vol. Desorbed (STP) mm ³	Analysis in vol %						
		O ₂	CO	CO ₂	H ₂	N ₂	H ₂ O	Others
Tungsten	(1500°C) 300	--	70-80	10	bal	--	--	--
Nickel	(1000°C) 5-15	--	75-90	20-10	bal	--	--	--
Monel	() 3-20	--	75-90	20-10	bal	--	--	--
Copper	(750°C) ca. 5	--	30	60	--	bal	8	--
Bess.	(1000) 6600	2.4	48.9	1.08	21.16	26.46	--	--
Steel	(1250)ca 6600	3.07	56.1	0.62	15.08	25.13	--	--
	(1500) 6600	4.28	18.75	0.00	4.20	72.77	--	--
	(1675) 6600	6.25	8.42	0.00	1.10	84.23	--	--
Molybdenum	(1760) 8-20	--	15-36	3-6	0-17	50-80	--	--
Aluminum	(1200) 6	--	15.4	2.56	71.7	10.4	--	--
Copper	(1000) 60	--	--	15.0	2.5	--	60.0	(SO ₂) 2.0

Note: All metals tested in the as-received condition. Dashed lines indicate no analysis.

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