Fifty years of vacuum science

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A selection is presented of problems in the physics and chemistry of vacuum systems and devices which has attracted considerable research during the past 50 years. These include examples where the limiting gas sources are water vapor, hydrogen, or helium. Also considered are self-sustained crossed-field discharges and the interaction of molecules, electrons, ions, and photons with the ''technical'' surfaces found in most vacuum systems.   © *2003 American Vacuum Society.*
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I. INTRODUCTION

Vacuum science is defined as that body of physical and chemical knowledge needed to explain, create, or measure any sub-atmospheric pressure. In 1950 the lower limit of pressure measurements was 10^{-6} Torr, 10^{-8} Torr in special cases, with some even lower unmeasured pressures. At 10^{-6} Torr it takes but a second to cover an already clean surface with a monolayer of gas, if all the impinging molecules stick. Thus few measurements had been done with ''clean surfaces.'' In 1950 the Bayard–Alpert gage[1] was announced, which reduced the lower limit to some 10^{-11} Torr, making possible many new measurements, including those with ''clean surfaces.'' There followed a worldwide synergistic expansion of studies in surface science, space science, particle accelerators, and a little later in fusion technology, and semiconductor technology, all based on vacuum science and technology, mainly at ultrahigh vacuum [(UHV), $p < 7.5 \times 10^{-10}$ Torr]. The surface studies discussed in the following are mainly concerned with ''technical'' surfaces, rarely with clean and pure single crystals, which are the primary domain of surface science.

II. LIMITING SOURCES OF GAS IN VACUUM SYSTEMS

A. Water vapor

Soon after pumping starts the limiting source of gas in almost all vacuum systems is water vapor originating from the original atmosphere ($\sim$20 Torr), which desorbs from all internal surfaces. The pressure follows a time dependence proportional to t^{-n}, where t is the time since pumping started and n is a constant between 0.5 (plastics and elastomers) and 1 (metals and metal oxides). In practical terms this is a very slow pump-down and much effort has been expended to speed it up. Dylla and associates[2,3] in particular, have tested various surface pretreatments of stainless steel and aluminum (e.g., electropolishing, vacuum remelting, and discharge cleaning), and found that glow discharge cleaning of stainless steel in He was the most effective, reducing subsequent outgassing of water by a factor of 13. This desorption process has been modeled by Li and Dylla[4] and others[5–8] assuming two sources of water: diffusion of water through the bulk solid and also the surface oxide layer, these

two sources are responsible for the desorption of many equivalent monolayers of water. The two-source model gave satisfactory agreement with experiment. Water vapor desorption has also been modeled as direct desorption from an adsorbed layer[9–11] at 300 K. Redhead,[9] in particular, examines the desorption from reversibly adsorbed multilayers, which are pumped in seconds, and monolayers, pumped much more slowly. Using an extended Temkin isotherm for the latter with reasonable energy values he obtained a pump-down following t^{-1}. Tuzi and colleagues[12] used a pulse of water vapor generated by a laser and measured the resulting time-dependence of the mass 18 peak in a residual gas analyzer in a stainless steel chamber to obtain the sticking probability (about 0.1). The conclusions were that water vapor is chemisorbed in two forms, strongly with dissociation and weakly molecularly, as well as weakly physically.

B. Hydrogen

The gas limiting the lowest pressure in metal UHV systems is frequently hydrogen which is initially dissolved in the metal during its production. The hydrogen efflux into vacuum has been conventionally treated as a diffusion process[6] with surface concentration on the downstream side taken as zero. Calder and Lewin[6] measured, for intensively heated stainless steel, an outgassing rate of 10^{-14} Torr$\,$l$\,$s$^{-1}\,$cm^{-2} (H$_2$ at 300 K). Moore[13] has recently revisited this subject concentrating on the modification in outgassing produced by assuming that recombination of H atoms on the downstream face was the rate limiting step, and drew two conclusions: (1) the conventional estimates for the permeation of atmospheric H$_2$ (4×10^{-4} Torr) through the walls of a stainless steel vacuum chamber may be too high by a factor 100; (2) former calculations of outgassing without recombination[6] are too low. In summary he proposed the building of stainless steel vacuum chambers of much thinner material to the limit of structural integrity, which would be easier to outgas to acceptable levels. Nemanič *et al.*[14] have verified Moore's main conclusions by constructing a variety of thin-walled stainless steel systems giving outgassing rates down to about 10^{-15} Torr$\,$l$\,$s$^{-1}\,$cm^{-2}. By heating their samples above 800 °C they found total quantities of hydro-

gen given off as high as 9×10^{19} atoms cm^{-3}, the previously accepted solubility of H_2 in stainless steel being about an order of magnitude less than this.

C. Helium

A recent problem is found in large accelerators and storage rings which use superconducting magnets, cooled by liquid helium, to control the particle beams. Even small helium leaks into the cold-bore vacuum can have very harmful results. Following the semi-quantitative observations of Edwards and Limon,[15] Hobson and Welch[16] developed a time-dependent model of how small leaks of helium (and hydrogen) spread in the Relativistic Heavy Ion Collider (RHIC) at Brookhaven. The central conclusion was that physical adsorption of helium on the cold-bore walls would cause major delays (even years) before the effects of a leak were observed on downstream gages. The model was tested experimentally by Wallén[17] at CERN and by Hseuh and Wallén[18] at RHIC and found to be quantitatively correct.

III. CROSSED FIELD DISCHARGES AT LOW PRESSURE

The basic theory of crossed-field gages (Penning, magnetron, and inverted magnetron gages) and the sputter ion pump, all of which depend on a self-sustained discharge, remains incomplete, despite 50 years of effort. Somerville,[19] Haefer,[20] and Redhead[21] calculated the striking characteristics of a crossed-field discharge without space charge; Smirnitskaya and Ti[22] added space charge. Reasonable agreement with experiment was obtained. Kendall[23] has reviewed data on the time delay before a steady state discharge is established after application of the appropriate voltages. The calculation of the steady state discharge current[24–27] is difficult, none of the models predicts the precise nonlinear relationship between ion current and pressure ($I^+ = kP^n$ with $n > 1$), nor the sudden break in this characteristic, with n increasing, found experimentally below 10^{-9} Torr. All crossed-field gages exhibit minor instabilities.[28]

IV. PARTICLE–SURFACE INTERACTIONS IN VACUUM SYSTEMS

Possibly the greatest single impact of UHV has been in the field of surface science. In 1969 the Surface Science Division of AVS was formed, accelerating the synergism between vacuum science and surface science. In the following we examine some examples of the interactions of molecules, electrons, ions, and photons with the engineering or technical surfaces of vacuum systems.

A. Desorption and adsorption of molecules at surfaces

1. Desorption

The desorption process has been reviewed by Comsa and David.[29] They focus, in particular, on the cosine law of desorption, almost universally assumed in vacuum texts, and show that while this law is widespread, it is not universally
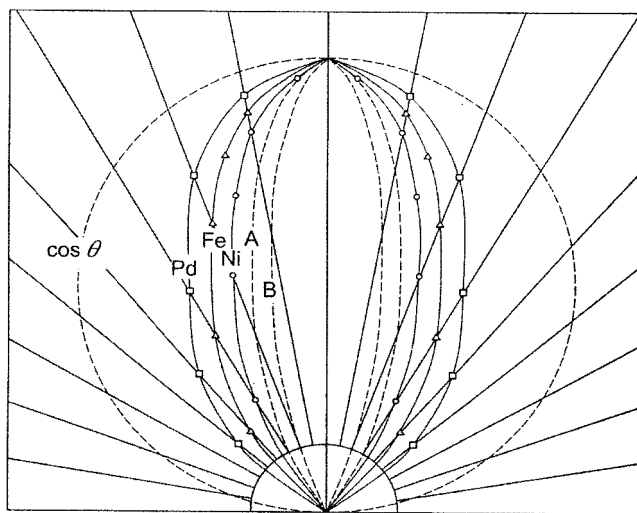

FIG. 1. Angular distribution of desorbing H_2 molecules, following permeation through thin foils of Pd, Fe, and Ni at 900 K. A and B are theoretical curves from van Willegen's model of associative desorption (Ref. 30).

true as indicated by the experiments of van Willigen,[30] shown in Fig. 1, where the cosine law is replaced by $\cos^n$, with $n > 1$. Similar deviations from the classic kinetic theory of gases have been found for the velocity distribution of desorbing molecules, and for the internal energy distributions of vibrating and rotating molecules.[29]

2. Physical adsorption

The situation at pressures in the UHV range is shown in Fig. 2, which shows measured data (points) for the physical adsorption isotherms of Xe, Kr, and Ar on porous silver at 77.4 K over 13 orders of magnitude in pressure,[31] and analyzed with the Brunauer, Emmett, Teller (BET) equation[32] (lines). The BET equation at low values of coverage increasingly predicts pressures many orders of magnitude above those measured. This means that cryosorption pumps are much more effective than was considered likely before 1950, and is a reasonable explanation of the extremely low (but
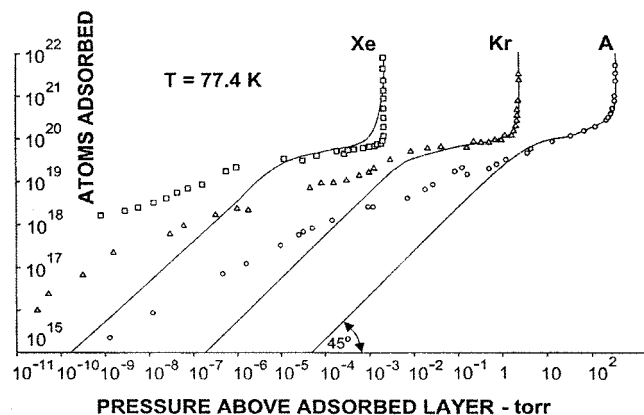

FIG. 2. Physical adsorption isotherms of Xe, Kr, and Ar on porous silver at 77.4 K. The points are experimental (Refs. 31 and 36) covering 13 orders of magnitude in pressure. The lines are the BET equation fitted conventionally for $0.01 < P/P_0 < 0.3$, P_0 being the vapor pressure.

unmeasured) pressures achieved by Anderson[33] in 1935. Gomer[34] achieved UHV in his glass field-emission and field-ion microscopes by immersing the entire microscope in liquid hydrogen or helium. Assuming reasonable values for the helium pressure in these microscopes before immersion and using the calculated helium adsorption isotherms[35] at 4.2 K one concludes that Gomer probably achieved background pressures about 10^{-30} Torr, i.e., no molecules in the gas phase most of the time.

All the experimental data of Fig. 2 were successfully fitted by Hobson[36] by joining an isotherm equation of Singleton and Halsey[37] at high pressures to one of Dubinin and Radushkevich[38] (DR) below a monolayer. Many adsorption isotherms have been found to follow the DR isotherm at low pressures,[39] which also predicts the observed temperature dependence.[35] No compelling explanation has been given for the widespread appearance of the DR equation. The isotherms of He and H_2 at liquid helium temperatures[40] are of central interest in cold bore accelerators. Low H_2 pressures are particularly difficult to measure with hot cathode ionization gages. Only recently have isotherms of mixtures of gases been measured.[41] Reviews of cryopumping have been published by Haefer[42] and Welch.[43]

3. Moving surfaces

In the turbomolecular pump (TMP) the pumping action depends on the gas molecule adsorbing momentarily on a rapidly moving surface (blade) acquiring at least some of its velocity and being desorbed in a desired direction[44-46] according to the cosine law. Typically in a TMP the most probable velocity of a gas molecule is of the same order as the highest blade velocity. The models are accurate for the compression ratio and pumping speed to about ±10%.

The action of the spinning rotor gage (SRG) is not unlike that of the TMP in that the tangential momentum given up by a magnetically suspended spinning steel ball to an impinging gas molecule slows down the ball, whose deceleration provides the measure of pressure.[47-49] A crucial physical parameter is the coefficient of tangential momentum transfer given by

$$\sigma = \left\langle \frac{c_{ti} - c_{tf}}{c_{ti}} \right\rangle_{av} ,$$

where c is the mean velocity of the gas molecules impinging on the ball surface, the subscript t refers to tangential, and i and f to initial and final, respectively. The remarkable result about the SRG is that for many surfaces, in particular for a shiny steel ball, σ is very stable and close to unity for many gases. This allows the SRG to be used as a secondary pressure standard around the world, where only the ball need be transferred with few special precautions. The pressure range of the SRG is $10^{-7} - 10^{-1}$ Torr.

4. Surfaces of different texture and temperature

The accommodation pump was announced by Hobson[50] in 1970. The principle of the pump is illustrated in Fig. 3(a) for a single stage pump made of Pyrex™ glass. It is in the
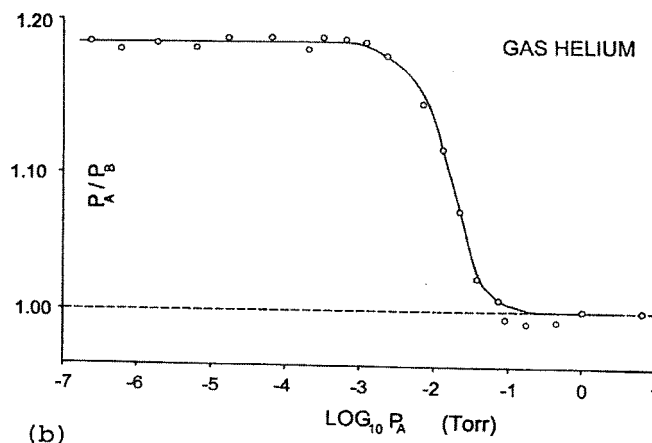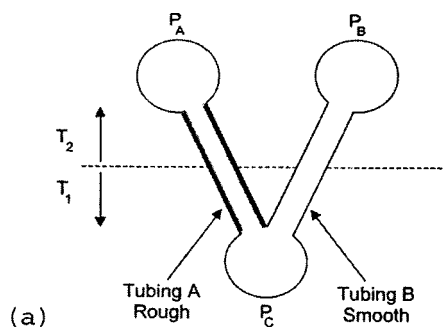

FIG. 3. (a) Schematic diagram of a single-stage accommodation pump in Pyrex glass (Ref. 50). Tube A is leached (100 h at 100 °C in 0.05N HCl) and is atomically rough, tube B is smooth (fire polished) Pyrex. The dashed horizontal line is a sudden temperature transition between T_2 (hot) and T_1 (cold). (b) Static performance of pump of (a) with inner tube diameters 22 mm, gas He, $T_2 = 295$ K, $T_1 = 77.4$ K (liquid nitrogen).

static mode, i.e., no flow. The roughened arm is leached (at 100 °C in 0.05 N HCl for 100 h) whereas the smooth arm is fire-polished. The central result for He gas with temperature $T_1 = 300$ K, $T_2 = 77.4$ K is shown in Fig. 3(b). A pressure differential develops when the mean free path is greater than the inner diameter of the tubes (here assumed equal), there is no apparent low pressure limit to this pressure differential. The proposed mechanism is speculative,[50] but does involve noncosine scattering. The pumping action is greatest for helium and declines with increasing molecular weight of the gas. Single stage pumps can be joined in series to increase the compression ratio P_A/P_B, or in parallel to increase the conductance or pumping speed. The highest compression ratio achieved to date has been 100 with a 10-stage Pyrex pump.[51] The accommodation pump has not seen commercial development, but shows some promise in a miniaturized form.[52] Like all thermal molecular pumps it has no moving parts and is noiseless.

B. Electron stimulated desorption (ESD)

A special problem arises at the grid of ionization gages and residual gas analyzers, when the ionizing electrons strike the grid causing desorption of positive (and sometimes nega-
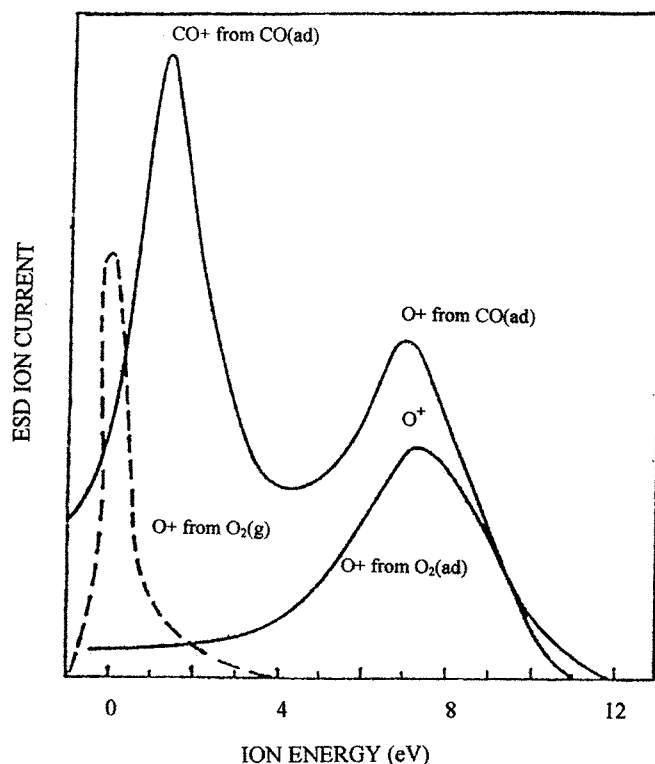
FIG. 4. Ion energy distribution for ESD ions (Ref. 53), at 300 K and electron energy of 100 eV, of O^+ from O_2 in gas phase (dotted line), O^+ from O_2 on polycrystalline Mo, and CO^+ and O^+ from CO on polycrystalline W.

tive) ions as well as neutral molecules from adsorbed layers. The positive ions, which are ejected with a substantial initial kinetic energy[53] as shown in Fig. 4, can be mistaken for ions created in the gas phase, leading to an overestimate of the true gas pressure. Methods, mainly based on the kinetic energy of the desorbed ions, have been devised to reduce the contribution to the measured pressure.[54] Menzel and Gomer,[55] studying the ESD of H_2, O_2, CO, and Ba from W in a field emission microscope, independently arrived at a model for the process which was quite similar to that of Redhead[54] and which became known as the Menzel–Gomer–Redhead model of ESD, a modern update may be found in a paper by Madey.[56] UHV mass spectra, particularly those measured by magnetic sector mass spectrometers,[57,58] frequently show ions originating from the grid of the ion source at masses 1, 16, 17, 19, 35, 36, and 39.

C. Ions on surfaces

The bombardment of a surface by ions is a constant process in gages, ion pumps, and in the sputtering of thin films. In general, many more ions strike the envelope of a gage than its collector. Grant and Carter[59] reviewed this work for glass ionization gages. Ion pumps produce a complex mix of ions created in a crossed-field discharge (see Sec. III above), which can be neutralized and are trapped upon impact at high energies (several thousand electron volts) with a surface, often titanium. They also sputter or eject atoms of titanium to a location elsewhere in the pump where they pump

chemically active molecules by chemisorption. Inert gases are least readily pumped by ion pumps and can be released by subsequent pumping. Thus ion pumps can have the undesirable property of being possible sources of gas previously pumped. These mechanisms are reviewed in Ref. 35. Kornelsen and Sinha[60,61] have made an extensive study of the binding energies of trapped ions by measuring the thermal desorption spectra of Ne and Ar atoms which originated as Ne and Ar ions, between 100 and 5000 eV, striking and being entrapped in single crystals of tungsten and also polycrystalline tungsten. There is considerable structure in these spectra which differ for all crystal surfaces. Wehner[62] and Behrisch[63] placed the study of sputtering on a very solid basis.

D. Photon stimulated desorption (PSD)

While PSD of molecules is commonplace in many vacuum devices it becomes the central problem in accelerators and storage rings where synchrotron radiation from the circulating beam is the source of the photons.[64–67] Consider the Large Hadron Collider (LHC), currently under construction at CERN, which will use two counter-rotating proton storage rings with colliding beams of $7+7$ TeV energy.[67] After clean-up, the dominant PSD gas load is likely to be hydrogen at an estimated adsorbing rate of 100 monolayers/yr on the inner surface of the cold-bore tube. While a monolayer time of 3.5 days may be adequate for many experiments, it is insufficient for the LHC where the circulating beam must be stored for several days, and the H_2 vapor pressure at 4.2 K is some 4×10^{-7} Torr. For this and other reasons[67] the cold bore will be operated at 1.9 K where the vapor pressure even of H_2 is extremely low and of all other gases, save He, even lower. Even with the cold bore at 1.9 K a three day monolayer time of He would be disastrous (vapor pressure 10 Torr). This places a tremendous burden on leak-testing for the LHC,[68] which must be flawless.

V. THE FUTURE OF VACUUM SCIENCE

At the beginning of the 21st century the routine lower limit of creation and measurement of vacuum stands at 10^{-13}–10^{-12} Torr. Methods for reaching controlled and measured pressures below this are available but do not appear to be widely needed. Advances may be expected in the basic theory of sticking coefficients, of low pressure discharges, and of the processes of water vapor desorption. Miniaturized vacuum systems, using the fabrication techniques of the semi-conductor industry (Micro-Electronic-Mechanical-Systems) seem highly likely, particularly for special missions like space probes. It is possible that thin walled UHV stainless steel vacuum systems will become widespread (see Sec. II B); that UHV/XHV systems with nonevaporable getters coated on the interior walls will be used for special purposes.

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