

Lesson 4. Experimental Surface Science

Gas-surface interaction

The development of surface science is strongly connected to technological advances that made possible to perform experiments under well-controlled conditions. Because surfaces are the boundaries between condensed matter and a gas or liquid phase, their structure and composition is determined by the interaction between atoms and molecules in both phases. Gas phase and solution species will, in equilibrium, form a layer of adsorbates of certain thickness on the surface. Thus in principle, one should not describe a surface without at the same time describing the environmental gases or liquids in equilibrium with it.

Rapid progress in fundamental studies of surfaces started approximately in the 60's as a result of the commercial development of Ultra-High Vacuum (UHV) techniques and of electron, photon and ion based spectroscopies to monitor surface composition and structure. Electrons and ions interact strongly with matter and can only propagate undisturbed in highly rarefied media, i.e. vacuum.

This chapter is devoted to present the basic technical aspects of surfaces in UHV, including preparation techniques and analysis. The structure of surfaces immersed in gases at atmospheric pressure or in liquids is also very important from both practical and fundamental points of view.

They require different techniques, particularly on the analysis side, since the traditional spectroscopies based on electrons and ions are no longer applicable in a straightforward fashion. Catalysis, environmental and atmospheric sciences are examples of the importance of high gas pressure-surface systems.

Electrochemistry is a vast field of great technological importance dealing with the solid- liquid interfaces, of capital importance in today's emerging technologies of solar photovoltaic cells, photocatalysis, film growth, corrosion, and energy storage (batteries). We will treat them in separate chapters.

Units of pressure

1 Pa (Pascal) = 1 N/m² (The SI unit)

1 Bar = 10⁵ N/m² = 100 kPa ≈ 1 atm

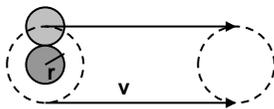
1 Tor = 1 mm Hg = 133.3 Pa

1 atm = 101.3 kPa = 760 mm Hg

Vacuum

Let's first review the motion of atomic particles (atoms, ions, electrons) in a gas at a certain pressure P . The particles move in response to applied forces from electric, magnetic or gravitational fields, following the laws of mechanics and electromagnetism. In the absence of fields the motion trajectory is a straight line, uninterrupted until the particle comes close to another atom or molecule in the gas phase and undergoes elastic or inelastic scattering. The distance of approach to the gas molecule where the interaction becomes appreciable defines the cross-section, σ . For neutral gas molecules this distance is of the order of magnitude of atomic radii, i.e., a few angstroms. The average distance between scattering events or collisions, is the mean free path λ . To calculate λ for an atom or molecule moving in its own gas, let's consider the schematic below.

Since the distance of closest approach is 2 times the molecular radius r , we need to consider the volume swept by a disc of radius $2r$ in one second. If v is the average molecular velocity, this volume is $\pi(2r)^2v = \sigma v$. The number of collisions is equal to the



number of intercepted gas phase molecules, i.e., $\pi(2r)^2vn$, where n is the gas density. Using the mean square velocity for v , as given by the kinetic theory of gases: $v = (3kT/m)^{1/2}$, and the gas

density for a perfect gas: $n = kT/P$ (k = Boltzman constant), the number of collision per unit time is: $z = \sigma P / (mkT/3)^{1/2}$

The average time between collisions τ is $1/z$, and the mean free path is then $\lambda = v\tau = 1/(\sigma n)$. These formulas are also valid for collisions of ions and electrons with gas phase molecules, with the appropriate changes in the cross-section values, which are still of the same order.

The following table gives values of z , τ , n and λ at room temperature and as a function of pressure, for a molecule of mass 28 atomic units (N_2 , CO).

P(torr)	760	1	10^{-1}	10^{-3}	10^{-6}	10^{-10}
$z(\text{s}^{-1})$	1.6×10^9	2×10^6	2×10^5	2×10^3	2	2×10^{-4}
τ (s)	6×10^{-10}	5×10^{-7}	5×10^{-6}	5×10^{-4}	0.5	5000
n (cm^{-3})	2×10^{19}	3×10^{16}	3×10^{15}	3×10^{13}	3×10^{10}	3×10^6
λ (cm)	3×10^{-5}	2×10^{-2}	2×10^{-1}	2×10^1	2×10^4	2×10^8

It is clear from the table that if the atoms, electrons or ions have to travel distances of several cm to reach undisturbed a target sample or a detector, the gas pressure has to be 10^{-4} torr or below. Other limitations on the pressure arise from the fact that many instruments use hot filaments for electron emission. The presence of O_2 at partial pressures of 10^{-6} torr and above rapidly reduces the life of the filaments, as they burn producing volatile metal oxides.

Gas collisions with surfaces

If vacuum is necessary for the operation of electron and ion based spectroscopies, it is equally important to control and maintain the surface cleanliness. This can be understood easily by considering the rate of molecular collisions per unit surface area. From gas kinetic theory this number is:

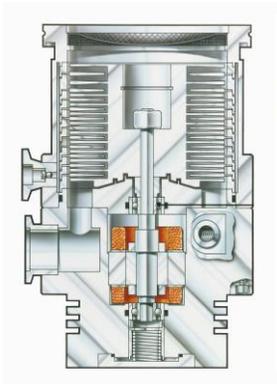
$$Z = P/(2\pi mkT)^{1/2}$$

For molecules of mass 28 a.u. at room temperature, Z is $2.88 \times 10^{22} \times P$ (Pascal)/ m^2/s , or $3.8 \times 10^{20} \times P(\text{torr})/\text{cm}^2/\text{s}$. Since the typical atomic density of a surface is $\sim 10^{15}$ atoms/ cm^2 , we find that at 10^{-6} torr, each surface atoms will be hit by a collision from gas phase atoms or molecules approximately every second on average. If every atom that hits the surface were to stick to it, a clean surface would be covered by a monolayer of adsorbed molecules in one second. Since performing an experiment might require one hour or more, we conclude that gas pressures of the order of 10^{-10} torr are necessary for surface studies. Ultra High Vacuum refers to pressures that satisfy this condition. Since the sticking probability is not always 100%, UHV conditions can be satisfied at 10^{-8} torr and below.

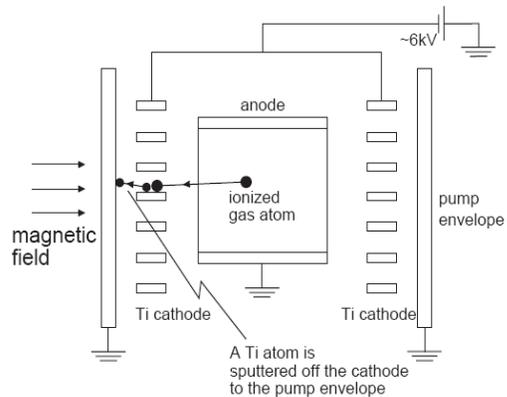
Exercise: calculate the impurity molarity of a solution so that the electrolyte concentration (= # molecules per unit volume) is comparable to that at UHV (10^{-9} Torr) pressure

Pumping systems

There are many types of pumps that are used to reach low pressures, below 10^{-6} torr and down to the UHV regime of 10^{-10} torr. Pumping is usually done in stages, each one using a particular type of pump. From the atmosphere down to 10^{-3} torr, oil-free



Turbo mechanical Pump



Schematic of an Ion pump

mechanical pumps and cryopumps based on high surface area materials cooled to liquid nitrogen temperatures are commonly used.

Below 10^{-3} torr, turbomechanical pumps, diffusion pumps and ion pumps are used.

Turbomechanical pumps are the pumps of choice today due to their wide operation range and low residual back-streaming. They are based on a turbomotor that rotates at frequencies above 10^{3-4} rpm. The tilted blades rotating at high speed impart a downward momentum to the gas molecules they collide with, thus creating a flow of gas to the end part of the chamber, with compression rates of several orders of magnitude. The high pressure exhaust side is pumped by another pump, mechanical or even another turbopump.

Surface cleanliness

Cleanliness is of paramount importance in UHV chambers, particularly in what concerns hydrocarbons that stick and decompose on metal surfaces to leave C deposits. For that reason, thoroughly degreased materials are used in the fabrication of chambers and instruments. Stainless steel is widely used for this purpose. The vapor pressure of metals gives an indication of their usefulness in UHV applications.

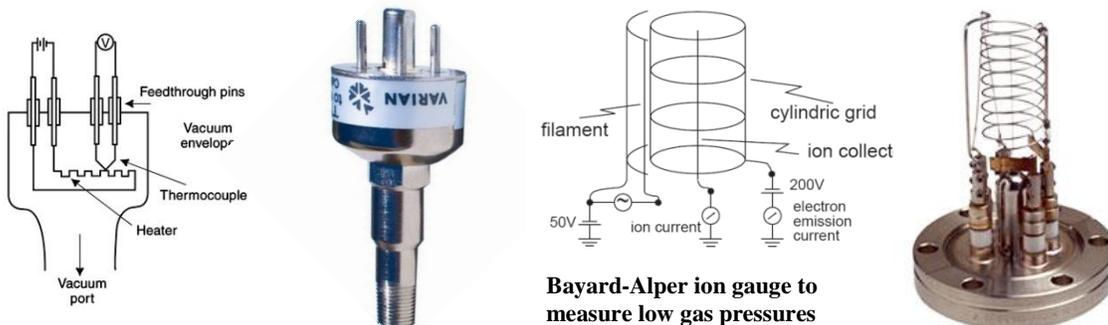
	10^{-10} mbar	10^{-6} mbar
Na	310K	400K
Zn	355K	450K
Cd	310K	390K
Hg	150K	230K
Mg	405K	505K
Al	860K	1100K
Fe	1000K	1300K
W	2160K	2680K

Temperatures at which the vapor pressure of metals reaches the pressures shown in the columns

Pressure measurement

Measuring the pressure is the first thing that a surface science experimentalist needs to do. During initial pumping, between one atmosphere and a few Torr, the pressure is measured by means of capacitance gauges (ex. Baratron).

In the pressure regime between 10 Torr and 10^{-3} Torr a common pressure gauge is the so-called Pirani thermocouple gauge. It is based on the fact that the temperature of a heated wire depends on the pressure of the gas surrounding it, which cools it through molecular collisions with the wire. The schematic below shows the measurement of the wire resistance with a thermocouple, and the picture a commercial gauge.



Bayard-Alper ion gauge to measure low gas pressures

At pressures in the range of 10^{-4} to 10^{-11} Torr the Bayard-Alper ion gauge is the most common device. A filament produces a beam of electrons that are accelerated into a

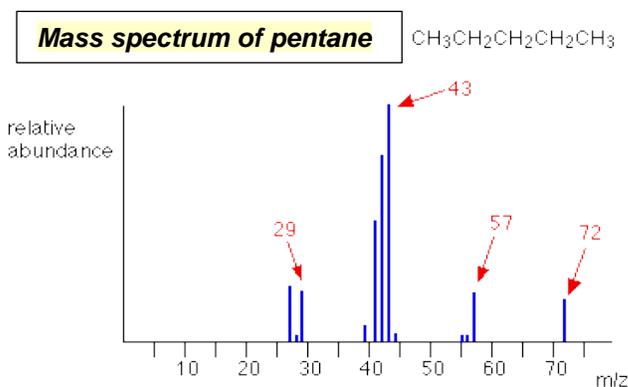
cavity surrounded by a biased grid. A collector wire at the center attracts and collects positive ions from the residual gas created by the electrons. The ion current is proportional to the pressure. After calibration, which depends on the gas composition, the gauge gives the pressure over an extended pressure range, down to the low 10^{-11} Torr regime.

Analysis of residual gas composition

Various instruments have been developed to determine the composition of the residual gas in a chamber, based on various types of mass spectrometer. To separate atoms according to their masses the spectrometer first ionizes the atoms or molecules. The ions enter then a region with electric or magnetic fields that deflect their trajectories in directions and distances that depend on their mass and charge, and thus can be detected separately.

Ionizers can use electrons with $V >$ ionization potential of atoms and molecules, typically around 10 eV. Because ionization cross sections have a maximum at an energy around twice that value, and because emission of electrons from hot filaments is more efficient at high extraction voltages, electron energies of up to several tens of eV are used. This often results in double ionization. Since the deflection of ions by applied electric fields in the analyzer depend of the ratio of mass and charge, doubly ionized species appear as having a mass half the value of the single ionized species.

Another ionization scheme also utilized is by photoionization. Photons have the advantage that they are less effective in damaging the molecules. On the other hand the advantage of electron ionizers is that the source is easy and cheap to build, and can be miniaturized easily. Its disadvantage is that electrons with energies of several tens of eV



are very effective in dissociating the molecules into fragments, often with higher yield than the ion of the parent species. Hydrocarbon molecules for example can fragment into a variety of species which are the same in many different

hydrocarbons, thus greatly complicating the analysis.

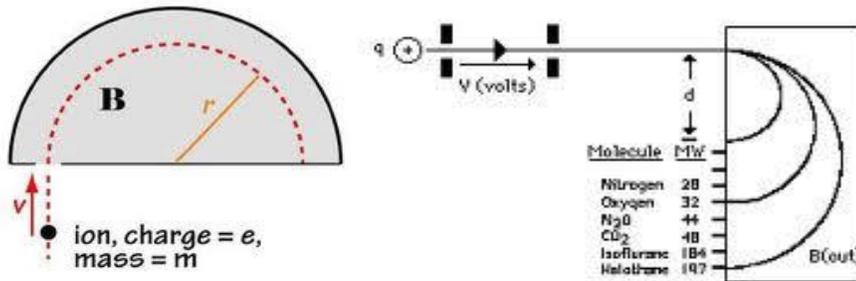
The first instruments were based on electric or magnetic fields that deflect the charged particles. In reference to the figure we have:

Acceleration by electric field: $eV = \frac{1}{2} mv^2$

Circular path in a magnetic field B due to centripetal Lorentz force: $mv^2/r = Bev$

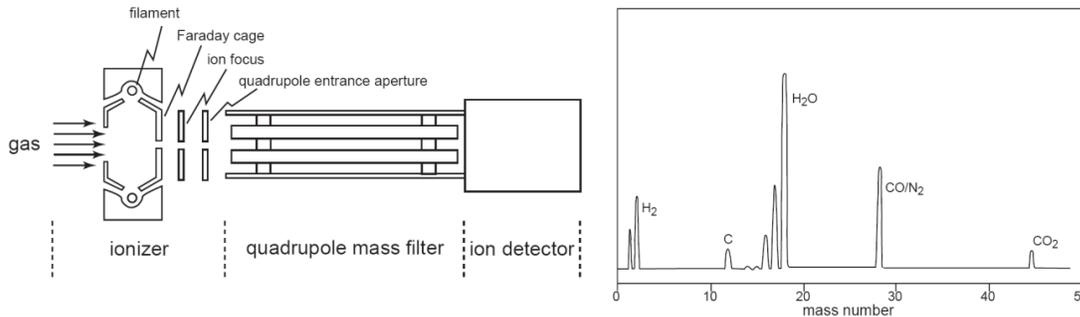
The radius of curvature of the ion path: $r = mv/eB = \frac{1}{B} \sqrt{2Vm/e}$

Often there is a combination of electric and magnetic filters. These are still in use today



and can produce very high mass resolutions.

One of the most common instruments is the Quadrupole Mass Spectrometer or QMS. The ions are injected into a quadrupole electric field produced by 4 cylindrical electrodes. The voltage there is the sum of a DC and a radiofrequency AC field with amplitudes that increase linearly with time. Only molecules with a given mass to charge ratio can move through the electrodes in a “contained” sinusoidal trajectory to the exit aperture and be detected by an electron multiplier.



Other instruments measure the mass by the time of flight of the ions traveling on a straight line from the ionization point to the detector. Ionization by an electric pulse triggers the timer for the detector. An ion at thermal velocities will travel one meter in milliseconds.