Creating a Vacuum on Earth

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What is a "vacuum"?

The term "vacuum" is no stranger to humans who live on planet Earth. A vacuum cleaner is not at all strange in the everyday life of most people around the world. Most of us have of course been curious enough to place our palm at the end of the vacuum line and felt the effect of "sucking-in". For scientists, "vacuum" is a very familiar terminology in the laboratory set up. We have seen and worked with vacuum lines, vacuum pumps etc. and at the very least, we have all performed vacuum filtrations in chemistry laboratory experiments. However, if someone asks you the question: "What exactly is a vacuum?" how would you explain it? For the non-scientist, you might refer to a vacuum cleaner, and for the scientist, you might refer to a vacuum pump. Or else, you might take a very realistic example and refer them to the atmosphere of the Moon. We all know that the Moon has "no atmosphere" and we refer to it as a "vacuum". Then, the question arises into the naturally curious mind; "Do we have the same conditions in a laboratory vacuum line as we find on the Moon?". The answer is simply "No".

Pressure regimes in vacuum technology

Although we refer to all of it very simply as "vacuum", it is important to know that there are different subdivisions of vacuum, called rough, medium, high and ultra-high vacuum. These different divisions of vacuum are based on the pressure regimes as shown in Table 1. Furthermore, in a vacuum system, there still remain certain gases although in very low quantities.

When we discuss about the value of atmospheric pressure on Earth, we all are aware of the fact that this number arises as a result of the gases that make up the Earth's atmosphere. The different pressure regimes in vacuum technology also describe to the pressure of gases in that given environment, be it on the Moon or in a vacuum line in the laboratory. As the pressure changes, the behavior and characteristics such as the nature of gas flow also change. By defining a pressure regime in vacuum technology, what we actually refer to is the nature of flow and its characteristics. For example, in the rough vacuum region, gas flows like a viscous fluid, i.e. viscous flow regime, where the mutual interaction of the gas molecules with each other determines the character of the flow. In contrast to this, in high and ultra-high vacuum regions molecular flow of gas molecules dominates, where the individual molecules can move freely.

Uses of vacuum technology

By the time you reach this paragraph of the article, you might be wondering why we are describing vacuum, pressure regimes and flow types and might also be wondering what this ultra-high vacuum regime is. Vacuum technology is a separate field of study in advanced chemistry and chemical engineering applications. One such area of study is catalysis. We come across a wide range of catalysts when studying synthetic reactions in organic chemistry. We take the liberty of writing reactions catalyzed by a variety of catalysts, explaining their reaction mechanisms, but never have we stopped for a second and thought how anyone has come up with these mechanisms. Most, if not all, have been studied by doing surface science experiments, mostly

Table 1: The pressure regimes of vacuum technology

Subdivision	Pressure (torr)	Mean free path (cm)	Monolayer formation time (s)	Major gases present
Rough vacuum	10^{-3}	5.1	2.2×10^{-3}	Water vapour (75% - 85%)
Medium vacuum	10^{-6}	5.1×10^{3}	2.2	H_2O, CO
High vacuum	10^{-9}	5.1×10^{6}	2.2×10^{3} (37 min)	H_2O, CO, N_2, H_2
Ultra-high vacuum	$<10^{-9}$	5.1×10^{9} at 10^{-12} torr	2.2×10^{6} at 10^{-12} torr (25.5 days)	CO, H_2 at 10^{-10} torr H_2 at 10^{-11} torr

heterogeneous catalysis in ultra-high vacuum (UHV) conditions. A regular surface science experiment would be to mount a well-defined catalyst surface in a UHV chamber (Figure 1) and perform the chemical reaction over the catalyst. Although the industrial heterogeneous catalysis would most likely use supported catalysts under ambient conditions, the basic surface science studies done in UHV conditions give very important information about the reaction mechanisms, reaction conditions, intermediates formed, rate of the reaction, yield, stability data and the characteristics of the ideal catalyst. This very basic information is used as the starting point to engineer the industrial catalytic processes.

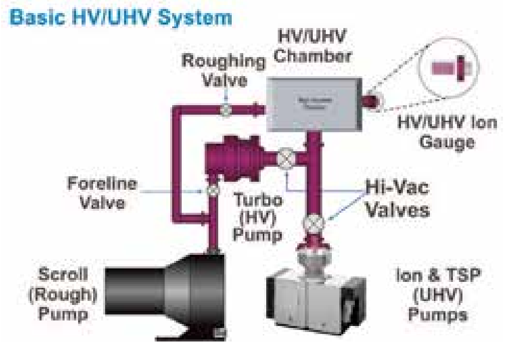


Figure 1: A basic HV/UHV chamber (Photo source: Agilent technologies Seminar Handbook 2011)

Ultra-high vacuum (UHV)

Why use UHV and not just a rough vacuum which can very easily be achieved by using a simple roughing pump (mechanical pump)? The answer lies in Table 1. Compare the pressure ranges corresponding to different subdivisions of vacuum. Imagine you have a well-defined catalyst surface which is clean and ready to be used in a surface science experiment. Let us take a platinum single crystal as an example. Assume that it is ready to be used in studying the hydrogenation of ethylene. In fact, platinum is a superior catalyst for hydrogenation reactions and there are many surface science studies in UHV to study this heterogeneous catalytic reaction.[2–10] What if you place this catalyst in a chamber which is in the rough vacuum regime in which the pressure is relatively high? What would happen to the catalyst surface? The inherent nature of any surface is to adsorb material onto its surface due to the presence of unsatisfied valence.[11] Therefore, by the time you start the catalytic reaction, your catalyst surface will be dirty, due to adsorption of the gas molecules from its surroundings and there will not be any catalytic site left for the adsorption of the incoming reaction molecules. A key feature in heterogeneous catalysis is the adsorption of the adsorbate(s) onto the catalyst (adsorbent) surface (Figure 2).

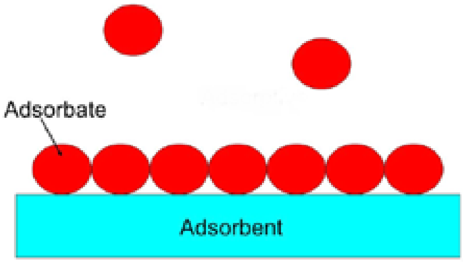


Figure 2: The process of adsorption.

If it is still unclear, think about yourself. In the morning before you go to work or school, you definitely wash your body. After returning home in the afternoon, you take a wash again. Why? To remove dirt particles which are adsorbed onto your skin. It is the 'adsorption' of material onto surfaces we are referring to, and not the 'absorption' as when a liquid is soaked into a tissue paper. Since the surface of our skin is exposed to the outside atmosphere filled with particles, it gets dirty and we need to remove the dirt particles by washing. In the same manner, if a catalyst surface is exposed to high pressure of gas, the gas molecules will readily get adsorbed onto its surface and it will be "dirty" in no time. Therefore, a rule of thumb in surface science studies is to have a clean surface and the only feasible way to achieve it is by maintaining UHV conditions inside the reaction chamber where the catalyst is mounted.

Creating ultra-high vacuum conditions

Creating and maintaining UHV conditions are the two most critical jobs of any surface scientist. It is a nightmare to lose the UHV conditions in a vacuum chamber because to get it back, it may take a long time. We can create UHV conditions by pumping down the gas molecules in the chamber. However, we cannot use any pump for this purpose. We have to seek the help of UHV pumps. There are different types of vacuum pumps available, such as roughing (mechanical) pumps, turbomolecular pumps, cryo pumps and diffusion pumps (Figure 3). The latter three types are specifically known as UHV pumps.

However, for a UHV pump to start working, pressure in the chamber to be evacuated by that pump should be much less than the atmospheric pressure. These UHV pumps will not start (in fact they may breakdown), at atmospheric and higher pressures. Only when the pressure reaches at least to the level down to 10^{-3} torr, we can start using some of the UHV pumps. It is the roughing pumps which are also called the backing pumps that help to lower the pressure down to the desired level. By definition, they back the UHV pumps. Different vacuum pumps have different pumping mechanisms. For example, a turbomolecular pump has a number of blades around a spinning rotor and the impulse from the rotor is transmitted to the gas particles which help in getting them expelled out of the vacuum chamber.

Figure 3: Different types of pumps used in UHV systems; (a) – roughing pump; (b) – turbomolecular pump; (c) – cryo pump; (d) – diffusion pump

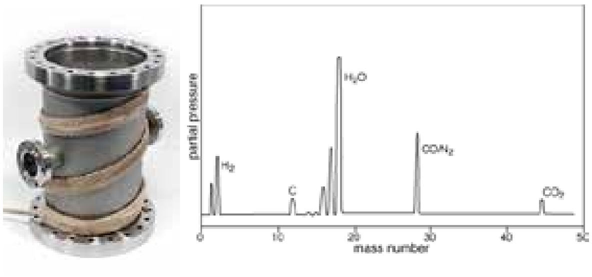
On the other hand, a cryo pump has a cryo surface (a cold surface) which gets all the molecules adsorbed onto it and thereby cleaning the chamber of gas molecules. This pump needs regeneration from time to time, in order to get rid of the adsorbed molecules. They fall into the category of sorption or entrapment pumps.

An interesting feature that changes from one pressure regime to another is the so called mean free path (λ) of gas molecules (Table 1). Atkins et al12, in their Physical Chemistry textbook have defined the mean free path as the average distance travelled by a gas molecule between collisions. In other words, it is the distance travelled by a gas molecule in the vacuum chamber, before it collides with another gas molecule. In rough vacuum regime, the mean free path of gas molecules is smaller than the diameter of the chamber and there are frequent collisions between gas molecules. In fact, the collisions between gas molecules are much more frequent than their collision with the chamber wall. In UHV, mean free path is greater than the diameter of the vacuum chamber.[1]

When comparing high vacuum and ultra-high vacuum regimes, another important parameter is the monolayer time (τ) as shown in Table 1.1 It is defined as the time taken to form a single molecular or atomic layer (a monolayer), on a gas free surface in the vacuum. This parameter also indicates how long the surface can be kept clean before it gets covered with gas molecules. In summary, it is crucial for the surface science experiments to maintain UHV conditions for the duration of the experiment.

The tedious process of pumping down a vacuum chamber

From the time of exposure of the reaction chamber to atmospheric pressure, up to the time you read a UHV pressure on the pressure gauge, there is a series of steps to be undertaken. (i.e. Pressure gauges are used to measure the approximate pressure inside the chamber). Suppose you had to open up your chamber for a repair or for installing a new catalyst surface, which means, breaking of the UHV. After the repair or reinstallation is over, the surface scientist will put everything together and close-up the chamber. However, since it was exposed to atmosphere, the inside of the chamber is now at atmospheric pressure, and need to be pumped down using vacuum pumps. After the chamber is closed, it will first be pumped down using a backing pump and once the chamber pressure is low enough, then, the UHV pumps will take over the process. However, even if you pump down for days, you may not be able to reach the UHV pressure that you were originally having before the repair, and this is due to the presence of a lot of water molecules adsorbed onto the inner surface of the stainless steel chamber. These water molecules will very slowly desorb and fill the space inside the chamber and it is usually very difficult for the UHV pumps to pump down water vapour. Moreover, desorption of water under normal conditions off the walls of the chamber is an extremely slow process. In order to accelerate this desorption, usually, the chamber walls are heated. This is the so called "baking-out" of a vacuum chamber. The chamber will be wrapped with heating tapes (Figure 4A) which are connected to an external power source through a variable transformer (Variac) and the temperature of the surface of the chamber is monitored by thermocouples attached onto it. The surface is heated to a temperature greater than the boiling point of water and throughout the bake-out, the system will be pumped down. After carrying this out for several days and when the pressure drops down to a significantly low value, the heating is turned off and it will be allowed to cool down before checking the mass spectrum of the gas phase inside the chamber (Figure 4B). If the percentage of water has significantly dropped and at a desired level, the chamber is ready to use. If not, another round of bake-out has to be done and this procedure is repeated until the desired gas composition is obtained.



(a) (b)

Figure 4: (a) - Heating tape wrapped around a port that connects to a UHV chamber ; (b) - Mass spectrum before bakeout of the chamber

It is important to know that even under UHV conditions, in a vacuum chamber, certain gases exist. The common gases that are present are nitrogen, carbon monoxide, water vapour (small amount) and hydrogen. The respective ratios of these gases vary when going from one pressure regime to another. A typical UHV chamber has a lot of probes connected to it. These probes are connected to the available ports on the chamber. Typically, the open end of the chamber port and the probe being attached to it have components called flanges. These two flanges are connected using nuts and bolts, and the sealing is ensured by placing a gasket (usually oxygen-free copper gasket) in-between the two conflat flanges (Figure 5).

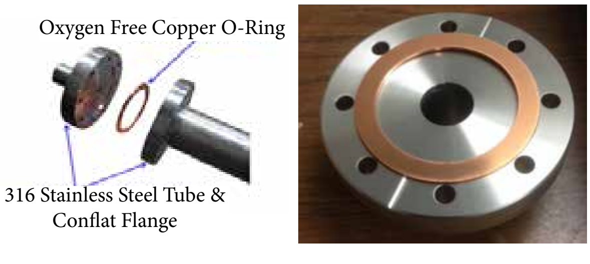
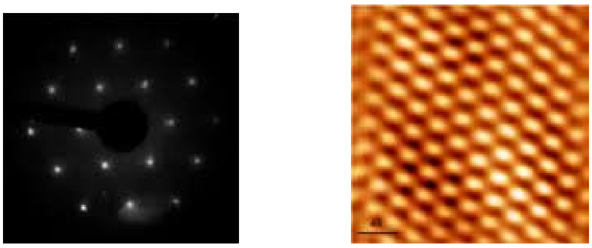


Figure 5: Placement of copper gaskets on the flanges to make the sealing

If there is a leak in the vacuum connections, even a very tiny leak, mass spectrum will detect the presence of molecular oxygen (at m/z = 32), molecular nitrogen (m/z = 28) and a huge peak at m/z = 18 corresponding to water. However, if the leak is significant, the pressure gauge will read a value higher than normal, and the mass spectrometer should not be turned on under such conditions as that can destroy its filament. If the leak is a considerably large one and the outside air is leaking into the chamber, the pressure gauges will not start up. Sometimes the backing pumps can back stream the hydrocarbon oils into the vacuum chamber. This can also be detected by recording a mass spectrum because it will be indicated by the presence of hydrocarbon peaks appearing at higher masses. While mass spectral analysis can reveal tiny leaks there are specific leak detection methods for identifying major leaks and the position of the chamber that is leaking.

In principle, vacuum technology goes hand-in-hand with surface chemistry. It is more difficult to maintain the UHV than to do a surface reaction and get the results. As mentioned earlier, a surface scientist plays a key role when it comes to understanding reaction mechanisms and identifying suitable catalysts for a given reaction. Although it seems like this is not being recognized by the scientific community, I should also mention that there are many Nobel Laureates who worked in different areas of surface chemistry, inventing and reinventing reactions, mechanisms, devices and equipment. They were recognized for their contribution to science, the most recent being awarded to Prof. Gerhard Ertl for his studies of chemical processes on solid surfaces in 2007.

Once the UHV is achieved, marvelous experiments can be done in surface science research. There are many surface analytical techniques which produce interesting results. Some of these are reflection absorption infrared spectroscopy (RAIRS), scanning tunneling microscopy (STM), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), electron energy loss spectroscopy (EELS), and low energy electron diffraction (LEED). In XPS, high voltages are used and to avoid electrical discharges, it needs to be performed in UHV. On the other hand, techniques such as LEED use electron beams focused on the reactive surface and unless UHV conditions are maintained, these electron beams will be scattered off the desired pathway. Discharges may also happen if a vacuum is not maintained. While XPS is usually used for elemental analysis, LEED can be used to check the cleanliness of the surface and also to obtain the diffraction pattern of the bare and adsorbed surfaces (Figure 6a). Scanning tunneling microscopy (STM) uses a very fine, atomically sharp metal or alloy tip to raster across the surface. This produces a topographical image (Figure 6b) with atomic resolution, of the catalyst surface and it can further be manipulated to move atoms across the surface (Figure 7).



(a) (b)

Figure 6: (a) LEED pattern of a clean single crystal graphite[13]; (b) STM image of a Cu(111) surface

Even though one goes through all the trouble to maintain UHV to ensure that a clean catalyst surface is available for experiments, due to the presence of some gases in the chamber, the surface will get dirty over the time. Therefore, before each experiment, it has to be cleaned using argon sputtering to remove the adsorbed particles, followed by oxidation of the surface and annealing to high temperatures.

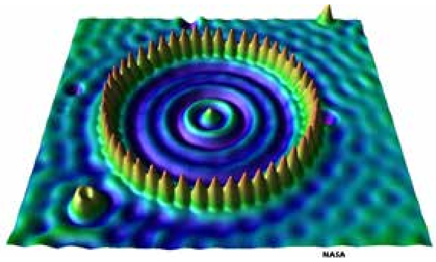


Figure 7: STM image of a quantum corral; an artificial structure created from 48 iron atoms (the sharp peaks) on a copper surface. Image source: https://warwick.ac.uk

To end this article, I would like to bring your attention back to the pressure regimes mentioned in Table 1. UHV is around 10-9 torr or below, while the atmospheric pressure on Earth is 760 torr. The surface pressure at night on the Moon is about 10-13 torr. Getting back to my original question once again, what exactly is meant by a "vacuum"?

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