

Surface Contamination Under Ambient Pressure

We learned in today's class that surface science experiments often require ultra-high vacuum (UHV) conditions to ensure that the surface under study remains clean and uncontaminated. Let's do some problems to understand why UHV is essential for obtaining clean surfaces.

Useful equations:

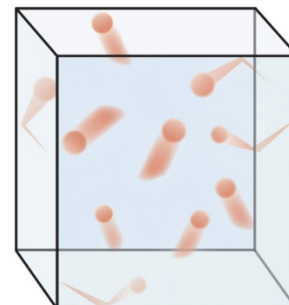
Average molecular velocity of gas molecules, v :

$$v = \sqrt{\frac{8k_B T}{\pi m}}$$

k_B is the Boltzmann constant = 1.38×10^{-23} J/K

T is the temperature in Kelvin = 25°C

m is the molecular mass (for $\text{N}_2 = 28$ g/mol, main component)



Ideal gas law:

$$PV = Nk_B T$$

P is the pressure = $1 \text{ atm} = 1.01 \times 10^5 \text{ Pa}$

V is the volume

N is the total number of molecules

Molecular flux:

$$\Phi = \frac{1}{4} n v$$

n is the number density of molecules

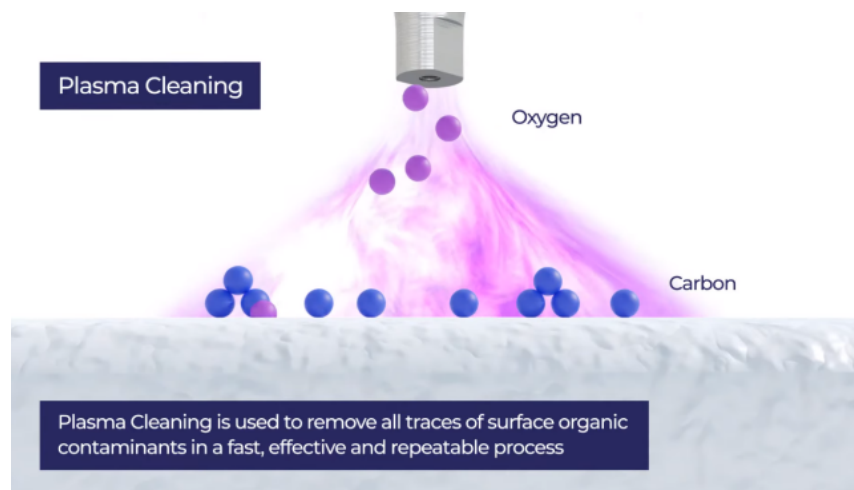
v is the average molecular velocity of gas molecules

1. Assume a surface in a laboratory environment at standard atmospheric pressure (1 atm) and room temperature (25°C). The laboratory air contains nitrogen (78%), oxygen (21%), and trace amounts of water vapor and other gases. Using the kinetic theory of gases, calculate the number of gas molecules that strike a 1 cm^2 surface each second under these conditions.

2. If each molecule (we can assume N_2 again as the main component) occupies an area of 0.1 nm^2 , estimate how long it would take for a monolayer of contaminants to form on this 1 cm^2 surface?

3. Now consider the same scenario under UHV conditions ($10^{-10} \text{ Torr} = 1.33 \times 10^{-8} \text{ Pa}$) and repeat the calculation of the monolayer formation time. Compare the results – can you see why UHV is critical for surface studies?

A solution to clean dirty surfaces is by using plasma cleaning, a surface treatment process that removes contaminants like dirt, oils, and organic residues using a low-pressure, high-energy plasma environment. Plasma, an ionized gas, consists of a mix of ions, radicals, electrons, and neutral species that interact with and break down contaminants on a surface.



A surface contaminated with hydrocarbon molecules C_xH_y is cleaned using an oxygen plasma. The plasma generates reactive oxygen species (ROS) such as O_2^+ , O^+ , and O (atomic oxygen), which react with the hydrocarbon molecules, converting them into gaseous CO_2 and H_2O , which are removed under vacuum.

4. Assume the surface area is 1 cm^2 and the plasma density is $1 \times 10^{16} \text{ ions m}^{-3}$. The plasma bombards the surface at a rate of $1 \times 10^{18} \text{ ions m}^{-2} \text{ s}^{-1}$. How long does it take for the plasma to bombard every hydrocarbon molecule on the surface if it is covered by a monolayer of contaminants?

Here are some assumptions:

- Contaminants form a uniform monolayer on the surface.
- Plasma ions react perfectly with no loss or inefficiencies.
- Area of one molecule: $0.1 \text{ nm}^2 = 1 \times 10^{-19} \text{ m}^2$

5. How would this time required to remove the layer of contaminants change if the plasma density was increased by a factor of 10?

Key Takeaways from this Exercise:

- The importance of cleaning surfaces for experiments
- Contaminants in the air can form monolayers immediately on surfaces
- The role of UHV in significantly reducing contamination rates
- Plasma cleaning is an efficient method to ensure clean surfaces

Solution:**Problem 1:****Step 1: Calculate the average molecular velocity:**

$$k_B = 1.38 \times 10^{-23} \text{ J/K}$$

$$T = 298 \text{ K}$$

$$m = 28 \text{ g/mol} = 28 \times 10^{-3} \text{ kg/mol} \rightarrow \text{use Avogadro's number} = 6.022 \times 10^{23} \text{ molecules/mol}$$

$$\text{Mass of one } N_2 \text{ molecule} = \frac{28 \times 10^{-3}}{6.022 \times 10^{23}} \text{ kg}$$

$$\text{Mass of one } N_2 \text{ molecule} = 4.65 \times 10^{-26} \text{ kg}$$

Plug all the values in to get the average molecular velocity:

$$v = \sqrt{\frac{8 \times 1.38 \times 10^{-23} \times 298}{\pi \times 4.65 \times 10^{-26}}} = \sqrt{\frac{3.29 \times 10^{-20}}{1.46 \times 10^{-25}}} = 4.78 \times 10^2 \text{ m/s}$$

Step 2: Calculate the number density of molecules ($n = N/V$):

$$PV = Nk_B T \rightarrow n = \frac{P}{k_B T}$$

$$n = \frac{1.01 \times 10^5}{1.38 \times 10^{-23} \times 298} = 2.45 \times 10^{25} \text{ molecules/m}^3$$

*Note how the units cancel out:

$$1 \text{ Pa} = \frac{N}{m^2} = \frac{kg}{ms^2}$$

$$1 \text{ N} = kg \frac{m}{s^2}$$

Step 3: Calculate the flux of molecules striking the surface:

$$\Phi = \frac{1}{4}nv$$

$$\Phi = \frac{2.45 \times 10^{25} \times 4.78 \times 10^2}{4} = 2.93 \times 10^{27} \text{ molecules/m}^2 \cdot \text{s}$$

For a 1 cm² surface:

$$\Phi = 2.93 \times 10^{27} \times 10^{-4} = 2.93 \times 10^{23} \text{ molecules/s}$$

Comparison point: Astronomers estimate that there are about 10^{22} stars in the observable universe. Every second, the number of particles hitting this surface exceeds the total number of stars in the observable universe!

Problem 2:**Step 1: Calculate the number of molecules needed to form a monolayer on the surface.**If each molecule occupies $0.1 \text{ nm}^2 = 1 \times 10^{-20} \text{ m}^2$ On a total surface area of $1 \text{ cm}^2 = 10^{-4} \text{ m}^2$

$$\text{Number of molecules for a monolayer} = \frac{\text{Total surface area}}{\text{Area per molecule}} = \frac{1 \times 10^{-4}}{1 \times 10^{-19}} = 1 \times 10^{15} \text{ molecules}$$

Step 2: Time to form a monolayer

$$t = \frac{\text{Number of molecules for monolayer}}{\Phi}$$

$$t = \frac{1 \times 10^{15}}{2.93 \times 10^{23}} = 3.41 \times 10^{-9} \text{ s}$$

At atmospheric pressure, a monolayer will form in 3.4 nanoseconds – rapid contamination!

Problem 3:**Step 1: New number density under UHV conditions:**

$$n = \frac{P}{k_B T} = \frac{1.33 \times 10^{-8}}{1.38 \times 10^{-23} \times 298} = 3.22 \times 10^{14} \text{ molecules/m}^3$$

Step 2: New molecular flux under UHV conditions:

$$\Phi = \frac{nv}{4} = \frac{3.22 \times 10^{14} \times 4.78 \times 10^2}{4} = 3.85 \times 10^{16} \text{ molecules/m}^2 \cdot \text{s}$$

For a 1 cm^2 surface:

$$\Phi = 3.85 \times 10^{16} \times 10^{-4} = 3.85 \times 10^{12} \text{ molecules/s}$$

Step 3: New monolayer formation time:

$$t = \frac{1 \times 10^{15}}{3.85 \times 10^{12}} = 260 \text{ s}$$

In UHV, a monolayer forms in 260 seconds (approx. 4 minutes) demonstrating the effectiveness of UHV in preserving clean surfaces for longer periods of time.

Problem 4:**Step 1: Calculate the number of hydrocarbon molecules on the surface (1 cm^2 area):**

$$\text{Number of molecules} = \frac{\text{Surface area}}{\text{Area per molecule}} = \frac{1 \times 10^{-4} \text{ m}^2}{1 \times 10^{-19} \text{ m}^2} = 1 \times 10^{15} \text{ molecules}$$

Step 2: Calculate the ion bombardment rate of the plasma:

The plasma bombards the surface at a rate of 1×10^{18} ions/m²·s. This means that for every second, 1×10^{18} ions impact each square meter of surface.

For a surface area of 1×10^{-4} m², the number of ions bombarding the surface per second is:

$$\text{Ions per second} = (1 \times 10^{18} \text{ ions/m}^2 \cdot \text{s}) \times (1 \times 10^{-4} \text{ m}^2) = 1 \times 10^{14} \text{ ions/s}$$

Step 3: Calculate the time required to remove contaminant molecules:

Since each ion removes one hydrocarbon molecule (assumption), the time required to remove all 1×10^{15} molecules is:

$$\text{Time} = \frac{\text{Number of molecules}}{\text{Ions per second}} = \frac{1 \times 10^{15}}{1 \times 10^{14}} = 10 \text{ seconds}$$

Thus, it will take 10 seconds to remove the monolayer of contaminants using plasma cleaning.

Problem 5:

If the plasma density is increased by a factor of 10, the number of ions bombarding the surface per second would be:

$$\text{New ion bombardment rate} = 10 \times 1 \times 10^{14} = 1 \times 10^{15} \text{ ions/s}$$

Time required to remove all molecules on the surface:

$$\text{New Time} = \frac{1 \times 10^{15}}{1 \times 10^{15}} = 1 \text{ second}$$

So, by increasing the plasma density by a factor 10, the time required to clean the surface also decreases by a factor 10 to 1 second. Typical oxygen plasma cleaning of surfaces in a lab ranges from 30 seconds to 2 minutes depending on the plasma density.