

Methods of Experimental Physics

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Recommend Texts

1. Chambers, A. (2004), Modern vacuum physics (1st ed.). London: CRC Press.
2. Fraden, J. (2010), A handbook of modern sensors: Physics, design and applications (4th ed.). New York: Springer.

Chapter1-Introduction to Vacuum

1.1 What is Vacuum

From the practical point of view, a vacuum is defined as a space in which the pressure of gas is low compared with normal or atmospheric pressure.

This definition correctly allows a rather broad interpretation because the vacuums encountered cover a wide range of pressure values.

1.2 Unit of Vacuum measurement

Vacuum is measured in terms of pressure. The SI unit of pressure is the Pascal (Pa) or N/m^2 . Other units of pressure are Torr, mmHg and mbar.

$$\text{Standard Atmospheric Pressure} = 101325 \text{ Pa} = 760 \text{ torr} = 760 \text{ mmHg} = 1013 \text{ mbar}$$

$$1 \text{ mbar} = 100 \text{ Pa} = 0.75 \text{ torr}$$

The lowest laboratory-made vacuum achieved thus far, under very specialized conditions, corresponds to n being of the order 10^8

1.3 The Ranges of Vacuum

The range of vacuum presently explored and utilized covers a range of about 15 orders of magnitude below atmospheric pressure. This corresponds therefore to pressures from 1000 mbar down to 10^{-12} mbar. This range is subdivided into smaller ranges as defined below.

Low (rough) vacuum	Atmospheric pressure (1000 mbar) to 1 mbar
Medium vacuum	1 to 10^{-3} mbar
High vacuum (HV)	10^{-3} to 10^{-8} mbar
Ultrahigh vacuum (UHV)	10^{-8} to 10^{-12} mbar
Extreme high vacuum (XHV)	Less than 10^{-12} mbar

Vacuum from 1000 or 10^3 mbar to 10^{-3} mbar also called **Primary Vacuum**, from 10^{-3} mbar to 10^{-8} mbar **Secondary Vacuum** and from 10^{-8} mbar to 10^{-12} mbar **Ultra High Vacuum (UHV)**.

Under standard conditions of temperature and pressure ($T = 0^\circ\text{C} = 273\text{ K}$ and atmospheric pressure $p = 101.3\text{ kPa} = 1000\text{ mbar}$), a cubic meter of gas contains molecules, $n = 2.5 \times 10^{25}/\text{m}^3$, where n is called molecular number density.

The lowest laboratory-made vacuum achieved thus far, under very specialized conditions, corresponds to n being of the order 10^7 molecules per m^3 and pressure or vacuum of the order of 10^{-15} mbar .

At altitudes of about 800 km where observational earth satellites typically orbit in a virtually friction-free atmosphere, vacuum is approximately 10^{-7} mbar ($n = 2.5 \times 10^{15}$ molecules/ m^3)

In interplanetary space n is about $10^7/\text{m}^3$, vacuum is approximately 10^{-10} mbar due mainly to the solar wind. In the space between galaxies there is thought to be on average less than one atom of hydrogen per cubic meter.

1.4 Applications of Vacuum

Primary Vacuum Applications

Many applications in the low-vacuum region exploit the force created by the pressure difference with atmospheric pressure for example, in vacuum molding and mechanical handling or lifting heavy luggage or things using suction pads. Also, oils may be degassed to rid them of dissolved air.

Applications in the medium vacuum range include vacuum and freeze-drying in the pharmaceutical industries in which vacuums have to be sufficiently low to permit relatively free evaporation from surfaces, and sputtering and chemical vapor deposition processes, to coat ultrathin films of thickness in nanometer range.

Secondary Vacuum Applications

High vacuum has a very large number of applications that include the manufacture of television tubes; the deposition of thin film coatings by evaporation of materials from the bulk, as in lens blooming; and semiconductor technology in which there is an additional strict requirement for “clean” vacuum, free of critical impurities.

Instruments such as electron microscopes and mass spectrometers for chemical and forensic analysis operate in this region.

A significant property of the high vacuum is that it is sufficiently rarefied to allow free passage of particles e.g, atoms, molecules, or electrons from one place to another within it.

Ultrahigh Vacuum Applications

Ultrahigh vacuum is widely used in research applications where it is important that surfaces are subject to minimal contamination by capture of molecules of the residual gas. Surface science was one of the early driving forces that stimulated progress in this field.

Such vacuums are also a prerequisite in thermonuclear fusion experiments, prior to their back-filling with ultrapure gases for fusion studies, and vacua of 10^{-12} mbar are necessary in order that charged particle beams can be accelerated to very high energies and stored for reasonable times with acceptable rates of attenuation due to scattering, as in the large hadron collider, the LHC, at the CERN laboratories.

As is pointed out by O'Hanlon (2003), manufacturing processes for some sophisticated semiconductor and optoelectronic devices now necessitate the ultraclean conditions of the UHV environment, a trend that will continue.

Chapter2 - The Molecular description of Gases

2.1 Introduction

The molecular-kinetic description of matter recognizes that the constituent atoms or molecules of a substance are in ceaseless motion, with a kinetic energy that increases with increase of temperature. The cohesive intermolecular forces that hold molecules close together in the condensed state are opposed by this thermal agitation. In the solid state of a substance, its molecules vibrate about average positions of a fixed array, which is ordered if the material is crystalline, disordered if it is not.

At higher temperatures, in the liquid state rigidity is lost and molecules move more freely but are still held together in close proximity by cohesive forces. Thus, volume changes when a solid melts are very small.

However, at the boiling temperature of a liquid, the intermolecular bonds are broken and the energy of the gas becomes kinetic energy of free translation of its molecules, now occupying a much greater space than they did as a liquid. Thus the average distance of a molecule from its neighbors in the gaseous state at atmospheric pressure is about 10 times the molecular diameter.

Freed from the bonding of the condensed state, the energy of a simple **Monatomic** gas is purely kinetic energy of translation, and its molecules travel with speeds of typically several hundreds of meters per second. **Diatomic** molecules have similar speeds but rotational energies in addition.

2.2 The Maxwell–Boltzmann Distribution of Molecular Speeds

The density of molecules in gases is such that frequent collisions are inevitable, and so they travel in straight “free paths” between the successive collisions that cause their directions and speeds to be changed. Because of the enormous number of molecules involved, we must expect that there will be a range of molecular speeds and of the free paths traveled between collisions.

Most probable speed (V_w):

The speed with which maximum number of molecules move

$$v_w = \sqrt{\frac{2kT}{m}}$$

Mean or Average speed:

$$\bar{v} = \sqrt{\frac{8kT}{\pi m}}$$

Mean Square Speed:

$$\overline{v^2} = \frac{\int v^2 n(v) dv}{n} = \frac{3kT}{m}$$

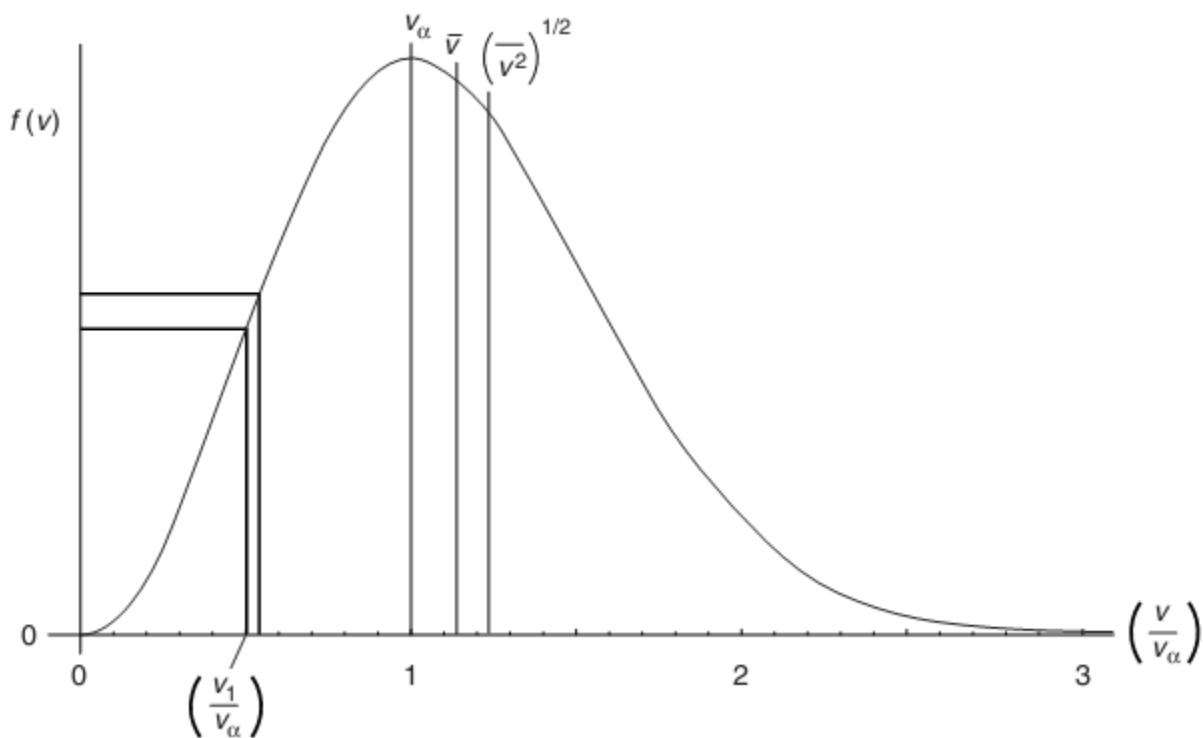


Fig. Maxwell - Boltzmann distribution of Molecular speeds

2.3 Molecular Impingement Rate, J

It is defined as “Total number of molecules striking the surface from all directions and with all speeds” and given by

$$J = \frac{n\bar{v}}{4} \quad \text{or} \quad J = \frac{p}{\sqrt{2\pi mkT}}$$

Where 'n' is molecular number density.

It is extremely important and can be used to calculate numerous other quantities such as condensation and evaporation rates, monolayer adsorption times, and flow properties of gases.

2.4 Pressure and Molecular Number Density, n

The pressure exerted on the surface by the impact of molecules having number density 'n' at temperature T is given by

$$p = nkT$$

where k is Boltzmann constant.

It shows that the pressure exerted by an ideal gas is directly proportional to its absolute temperature and the number density of molecules. This is very reasonable because we have seen that n directly determines the rate of molecular impacts, and that T determines the energy.

2.5 Molecular Collisions and Mean Free Path, λ

The mean free path λ is defined as "The average distance traveled by a molecule between successive collisions". The mean free path is thus the distance traveled in one second divided by the number of collisions per second.

$$\lambda = \frac{1}{\sqrt{2}n\sigma} = \frac{1}{\sqrt{2}n\pi d^2}$$

Notice that λ depends on n and σ , the collisional cross section $\sigma = \pi d^2$

The probability that a molecule will have a free path equal to or greater than x is given by

$$s(x) = \exp(-x/\lambda)$$

The total number of molecules which will have free paths of x or longer is given by

$$N = N_0 \exp(-x/\lambda)$$

The familiar exponential curve of above equation is plotted below showing fraction of molecules having free path equal or greater than x.

Remembering that $\exp(-1) = 0.37$, we may deduce that 63% of free paths are shorter than λ . Since $e^3 = 20$ to a very good approximation, 95% are shorter than 3λ ; only 1 in 22,000 is greater than 10λ

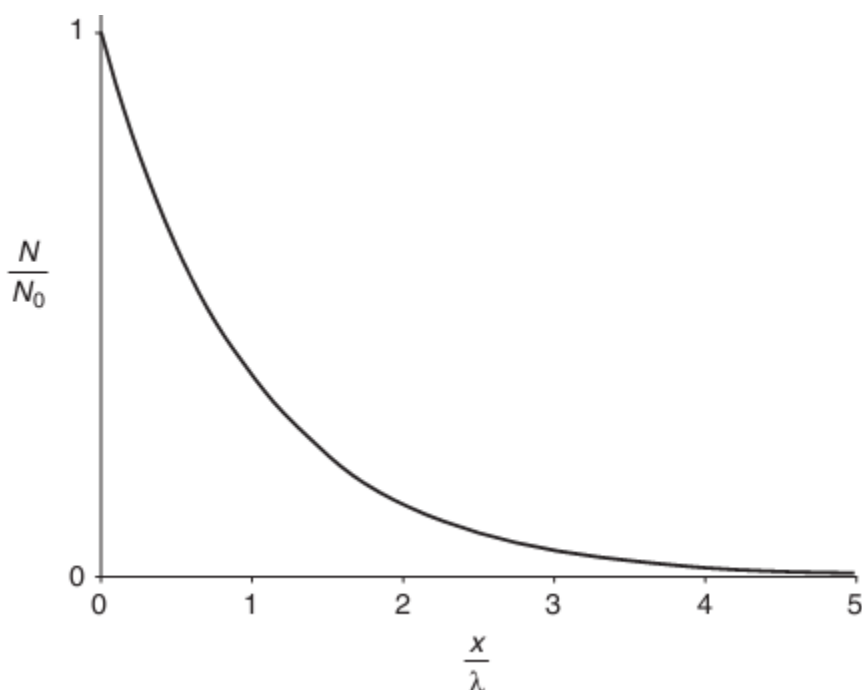


Fig. Fraction of molecules having free paths longer than x

n , λ , and J at various p for N_2 at 295 K

p mbar	n (m^{-3})	λ	J ($cm^{-2} s^{-1}$)
$10^3 = 1$ atm	2.5×10^{25}	64 nm	2.9×10^{23}
1	2.5×10^{22}	64 $\mu m = 0.064$ mm	2.9×10^{20}
10^{-3}	2.5×10^{19}	64 mm	2.9×10^{17}
10^{-6} , HV	2.5×10^{16}	64 m	2.9×10^{14}
10^{-10} , UHV	2.5×10^{12}	640 km	2.9×10^{10}

2.6 Knudsen Number: Continuum and Molecular States of Gas

The molecule–molecule collisions is the characteristic process that determines gas behavior. In other words, the mean free path λ in the gas at atmospheric pressure is very much less than the characteristic dimension of its container. For a cubical box, that would be the length of a side, or for a pipe, its diameter. But from above Table it is evident that at low pressures, mean free path will become comparable with or greater than a container’s characteristic dimension. Molecule–surface collisions will now dominate gas behavior and molecule–molecule collisions become quite rare.

It is useful to have a criterion for distinguishing between the fluid (or what is better called the continuum state) and the molecular state. This is provided by the Knudsen Number Kn defined as $Kn = \lambda / D$, where λ is the mean free path and D is a characteristic dimension. There is, of course, in the nature of things, no sharp change between the continuum and molecular states, but rather a gradual transition between them. These states, or regimes as they are sometimes called, are conventionally taken to be

$$Kn < 0.01: \text{CONTINUUM}$$

$$Kn > 1: \text{MOLECULAR}$$

and in between, $0.01 < Kn < 1: \text{TRANSITIONAL}$

Kn is a useful dimensionless number because it automatically incorporates information about the gas condition in relation to the container size.

For example, at a pressure such that λ is 5 cm, the gas in a 1-cm cube would be in a molecular state, but in a large vacuum tank of dimension 3 m at the same pressure, conditions would be more nearly continuum.

Chapter-3 Surface Processes and Outgassing

3.1 Introduction

Although an obvious and important role of surfaces in vacuum practice is that of the inner wall of the vessel in providing the boundary of the vacuum within, there are a number of processes occurring between gases and surfaces, both inside the vacuum and at its boundary wall, that make the role of surfaces more important than their mere mechanical presence.

There are few circumstances in which surfaces play a strictly neutral role. For example, as we shall see shortly, the rebound or scattering of gas molecules from surfaces is not as simple as it is modeled to be in the kinetic theory, though the results of that theory are correct.

In addition to scattering molecules in non-simple ways, surfaces may, depending on a number of factors, trap molecules in bound states, a process called **adsorption**. The reverse process, the release of molecules from trapped states, is called **desorption**. Adsorption finds applications in pumping, while, less benignly, desorption is the principal feature of the process of outgassing, a property of fundamental importance and characteristic of all surfaces in vacuum. It describes the prolonged desorption of gas molecules from a surface, some of which reach it from subsurface regions in which they have been earlier stored by exposure to the atmosphere and other mechanisms.

Thus, after the air in a vacuum vessel has been pumped away, pumping is still needed to remove the continual outgassing load from surfaces exposed to the vacuum. These matters, together with sputtering, which is the removal of surface atoms due to energetic particle bombardment, are to be discussed in this chapter.

3.2 The Scattering of Molecules by a Surface

There are three possible outcomes to collision of molecule with the surface.

1. An elastic rebound without energy loss, in which the angle of incidence made with the normal to the surface at the point of impact equals that of reflection, with the directions of incidence, reflection, and the normal all being in the same plane. In this “specular” reflection, the molecule’s linear momentum parallel to the surface is unchanged. Perpendicular to it, the momentum is unchanged in magnitude but reversed in direction, as shown in figure (a) below.

2. Although the rebound of the molecule to the gas phase is more or less immediate, some energy is either lost to the surface or gained from it (for example, by exchange of energy with vibrations of the surface atoms), in which case the collision is described as inelastic as shown in fig. (b) below.

3. The molecule may lose sufficient kinetic energy that it becomes bonded to the surface in an adsorbed state. Its stay in this trapped state will not be permanent. A molecule that has lost sufficient energy to bring it into equilibrium with the host surface at the prevailing temperature will nevertheless have kinetic energy of vibrational motion under the restraints imposed by its bonding to the surface and will eventually, by statistical chance, acquire enough energy from favorable collisions with its neighbors to break free.

Depending on the identities of the molecule and the surface atoms, its stay may be brief or long. When the molecule does leave the surface, its direction of departure will be random and unrelated to its direction of arrival, because its initial momentum parallel to the surface, like the perpendicular component, will have been dissipated in the collisions that led to its capture. Thus, whereas elastic and inelastic rebounds off the surface will occur with either complete or partial preservation of the parallel component of momentum in the plane of incidence, the direction of release from a trapped state can be anywhere into the three-dimensional solid angle of 2π above the surface, as suggested in fig. (c) below.

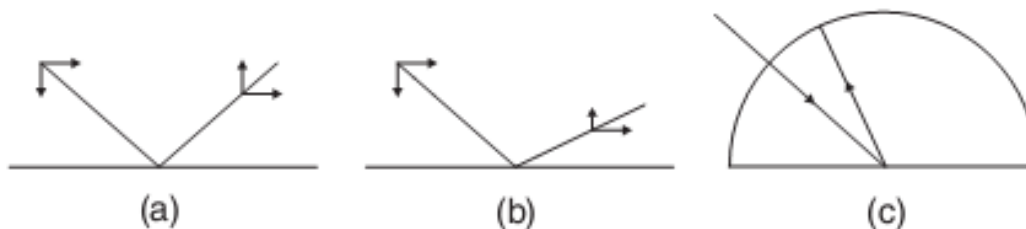


Fig. Rebound of a molecule from a surface. (a) Specular, (b) inelastic, (c) via a trapped state.

In the context of molecules losing energy to a surface, one may define an energy accommodation coefficient α_E by the equation

$$\alpha_E = \frac{E_1 - E_2}{E_1 - E_S}$$

in which E_1 and E_2 are the energy of the incident molecule before and after scattering, respectively, and E_S the energy associated with equilibrium at the surface.

Thus, for elastic reflection $E_1 = E_2$ and $\alpha_E = 0$, and No adsorption

While if $E_2 = E_S$, the other extreme, $\alpha_E = 1$ and accommodation is complete.

In non equilibrium situations for example, if a gas is hotter than a surface on which it impinges the energies E_1 and E_2 can represent the mean kinetic energies of translation associated with the fluxes of arriving and scattered molecules.

Because the mean kinetic energy of translation is $3kT/2$, above equation may then also be expressed as

$$\alpha_E = \frac{T_1 - T_2}{T_1 - T_S}$$

For diatomic and polyatomic molecules like N_2 , CO , and H_2O , for example, there are vibrational and rotational kinetic energies in addition to that of translation, although these may not be excited at 300 K. Potentially, however, the complexity of the scattering process is greater than for monatomic species such as argon, and accommodation coefficients appropriate to different aspects of the scattering process need to be defined.

3.3 Adsorption and Desorption

Adsorption

Adsorption is the process of adhesion of molecules of liquid or gases onto the surface of a solid particle. While absorption is a bulk phenomenon where molecules of absorbate enter into the absorbent.

The character of the adsorbed state in which a molecule may be trapped on a surface will depend, of course, on the identity of the partners. For example, one would expect that the interaction between an inert gas such as argon and a glass surface would differ from that of a chemically active gas, such as oxygen, and a metal.

The bonds established between a molecule and a surface are not intrinsically different in nature from those existing within molecules and in bulk phases.

Physical Adsorption:

If molecule adsorbs on a surface via van der Waals forces, which arise from the attraction between fluctuating dipole moments such adsorption is called physical adsorption. Van der Waals forces are responsible for the condensation of gas to liquid, and are the source of the attractive force between a molecule and a surface.

It is the weakest form of adsorption and this type of bonding leaves the structure of the molecule essentially unchanged and is purely physical in origin. Physical adsorption, sometimes shortened to “Physisorption”.

Heats of adsorption in physical adsorption, referred to one mole, are in the range of 6–40 kJ per mole. For nitrogen on various surfaces, it is about 15 kJ mol⁻¹

Chemical Adsorption:

In contrast, in Chemical adsorption bonding involves electron transfer or sharing between the molecule and atoms of the surface.

Bonding in chemisorption is generally much stronger. It can be thought of more as a chemical reaction between the two. Chemical adsorption sometimes shortened to “Chemisorption”

In many cases it alters a molecule’s structure and occurs with dissociation of the molecule into its constituent atoms. In others, the molecular identity is retained. For example, when adsorbing at room temperature on nickel, hydrogen dissociates, whereas carbon monoxide on nickel does not.

Heats of adsorption in chemical adsorption, referred to one mole, are in the range of, from about 40 up to 1000 kJ per mole.

Molecular Stay or Adsorption Time

For a molecule that becomes adsorbed at $t = 0$, the average time it stays adsorbed τ_a , may be evaluated as follows.

$$\tau_a = 1/\sigma = 10^{-13} \exp\{+q/kT\}$$

Evidently, this equation makes the sensible predictions that the stronger the binding to a surface and the lower the temperature, the greater is the average time of stay.

Variably, τ_a is called the mean stay time, or the adsorption time. Because of the exponential factor, the variation of τ_a with binding energy is quite dramatic, as Table below shows for species adsorbed at room temperature. The ratio of binding energy to the thermal energy is critical. For molar rather than molecular specifications of q , kT is, of course, replaced by R_0T .

Notice the enormous range of times, from small fractions of a nanosecond in physisorption for the first two entries, through micro and millisecond times in weak chemisorption to seconds, days, and years, with progressively stronger chemisorption. But, as well as that of q , the effect of temperature is profound.

Consider physisorption at 15 kJ mol^{-1} at room temperature $\sim 300\text{K}$. Lowering the surface temperature to that of liquid nitrogen 77 K will give a roughly fourfold increase in q/T and raise the stay time from $5 \times 10^{-11}\text{s}$ to that of the fourth entry in the table, $5.5 \times 10^{-3}\text{s}$, i.e., increase it by a factor ~ 108 . Such is the behavior of thermally activated processes.

The strong effect of temperature is also evident in table below showing effect of temperature on stay time, which shows the stay time at 77 , 295 , and 600 K for a q value of 80 kJ mol^{-1} ($\sim 0.8 \text{ eV}$ per molecule) which is approximately the binding energy of water on many surfaces.

Dependence of Stay Time on Binding Energy at Room Temperature

q in kJ mol^{-1}	τ_s
6	$1.2 \times 10^{-12} \text{ s}$
15	$5 \times 10^{-11} \text{ s}$
40	$1.2 \times 10^{-6} \text{ s}$
60	$5.5 \times 10^{-3} \text{ s}$
80	15 s
90	15 min
95	2 h
100	$8 \times 10^4 \text{ s} \sim 1 \text{ d}$
120	$2 \times 10^8 \text{ s} \sim 10 \text{ years}$
150	$7 \times 10^{13} \text{ s} \sim 20,000 \text{ years}$

Effect of Temperature on Stay Time for $q = 80 \text{ kJmol}^{-1}$

$T \text{ K}$	τ_s
77	$10^{41} \text{ s} !$
295	15 s
600	$1 \mu\text{s}$

Fractional Coverage (θ)

It is the fraction or part of atoms adsorbed on a unit surface area of total number of atoms that can be adsorbed on that surface area forming a single monolayer of atoms. It is given by

$$\theta = n_a/N_0$$

Where n_a is number of molecules adsorbed per unit surface area and N_0 total number of molecules that can adsorbed on unit surface area forming a monolayer.

Sticking Coefficient

The sticking coefficient $s = s(\theta)$ is defined as the probability that, on striking the surface already having coverage θ , a molecule becomes adsorbed.

Whatever its initial value, one would expect it to change with coverage, becoming less as the number of available sites is reduced. Measurements show that for chemisorption at room temperature, initial sticking coefficients $s(0)$ on fresh surfaces are usually between 0.1 and 1 and that they start to decrease at $\theta \sim 0.5$, falling to very low values as θ approaches complete coverage.

Analytical Model for Population of Adsorbed Molecules on a Surface

Provided we restrict ourselves to dilute adsorbed layers, $\theta \ll 1$, consistently with our earlier assumption for the desorption process, it is possible to create a simple model for the equilibrium state as follows. The rate of adsorption at coverage θ will be

$$\frac{dn_a}{dt} = s(\theta) \times J$$

The rate of desorption will be

$$\left(\frac{dn_a}{dt}\right)_{des} = -n_a \sigma = -\frac{n_a}{\tau_a}$$

At equilibrium the rates balance and so

$$n_{a,eq} = s_{eq} J \tau_a$$

Where n_a is required population of adsorbed molecules at equilibrium state.

3.4 Outgassing (Desorption)

Why it is difficult to create Vacuum

Surfaces facing a vacuum release gas. If they did not, practical vacuum technology would be much simpler. The inner wall of a vacuum container would serve simply as a clean and inert barrier to gaseous molecules, and by the selection of a suitable pump all the air and vapor initially contained could be rapidly removed and very high vacuum attained quickly. In practice this is not so. Gas is continuously released, albeit at relatively small rates, but they prove to be a limitation on the attainable vacuum. Even with careful preparatory cleaning of surfaces, the steady release of gas, principally water vapor, limits the degree of vacuum achievable in reasonable times to values $\sim 10^{-6}$ mbar or a little less, the conventional high vacuum. If vacua substantially lower than this are to be achieved, special procedures to reduce out-gassing are necessary. Thus, boundary surfaces play an active role in the attainment of vacuum.

Origins of Outgassing

It is molecules desorbing from bound states at vacuum-facing surfaces that constitute the outgassing flux. Although their point of departure into the vacuum space is at the surface, they have various origins as follows

1. A surface that has been exposed to normal air at atmospheric pressure for some time will be in equilibrium with it and covered by an adsorbed phase, dominantly of water molecules from atmospheric water vapor, which adsorb more strongly than other atmospheric species. If the pressure of the adjacent gas and vapor to which it has been exposed is now lowered by the action of pumping, this equilibrium is upset and molecules desorb into the vacuum space.
2. Exposure to atmosphere will also have caused diffusion of gases into the near-surface region of the bulk material, assisted perhaps by the presence of rough, microcracked surface structure.
3. Metals frequently have an oxidized surface layer, the passivation layer, typically a few nanometers thick, that absorbs gases by their inward diffusion following initial adsorption. From this near-surface region it will tend to diffuse back to the surface and desorb under low-pressure conditions.
4. The material of the boundary wall of the vacuum, typically stainless steel and several millimeters or more in thickness, will also contain gas that was trapped inside it at the time of its manufacture. Under certain conditions its slow diffusion to the vacuum interface and desorption can be significant. Dissolved hydrogen, occurring as interstitial H atoms rather than H₂, is present in this way and is particularly important.

- Although, at very small rate, gas adsorbed on the outer wall of the container may permeate the wall to arrive by similar diffusive processes at the inner wall, prior to desorption. Permeation through the relatively small areas associated with elastomer seals that join metallic components can be a significant contribution to outgassing even when, as is usually the case, permeation through bulk walls is not.

Thus, the desorption of gas, its diffusion out of near-surface regions and the bulk, and its permeation through bulk solid material are matters of concern.

Analytical Modeling of Outgassing Process

Outgassing due to desorption of gassing adsorbed on the surface

Measurements show that under the action of pumping, the outgassing of surfaces diminishes with time approximately according to the relationship

$$q_G = \frac{q_1}{t^\alpha}$$

In this equation, q_G is the rate of release of gas per cm^2 , referred to as the specific gassing rate, and q_1 its value after 1 h of pumping. The quantity t is the dimensionless ratio of the time in hours to 1 h, and α is an exponent that is frequently about 1 for gassing from metallic surfaces, and nearer 0.5 for elastomers. This dependence is followed for tens of hours and then evolves exponentially into a sensibly constant value.

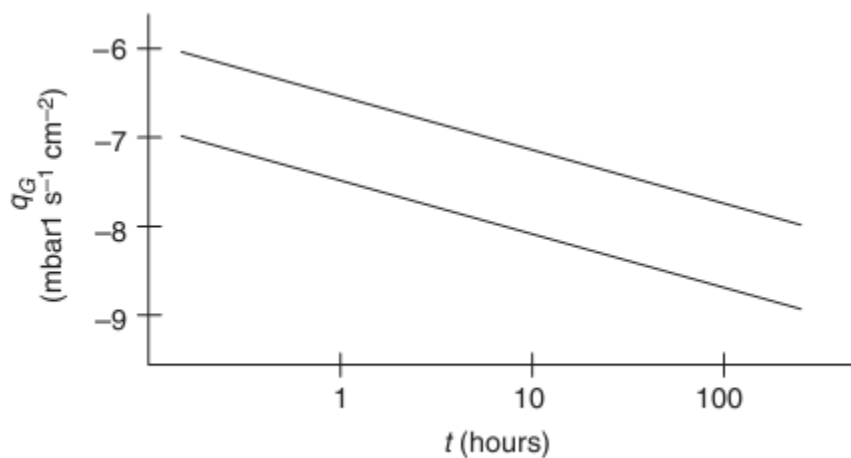


Fig. Typical outgassing rates of adsorbed species on the surface as a function of time.

Outgassing due to desorption of gassing diffused from outside of chamber walls

Evidently, gas that is adsorbed relatively weakly, with q less than 60 kJ mol^{-1} , is quickly pumped away consistent with the discussion above. Strongly adsorbed gas, with adsorption energy 100 kJ mol^{-1} or greater, des-orbs at such a slow rate that its contribution to the pressure, though prolonged, is negligibly small. But gas adsorbed with q between these values, and particularly at about 80 kJ mol^{-1} , has a sizeable contribution and is long lasting. This is approximately the energy with which the water molecule binds to many surfaces.

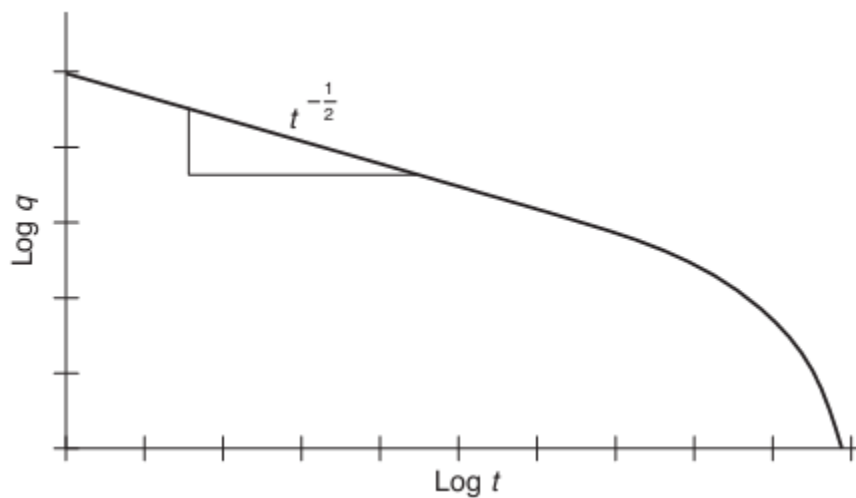


Fig. Outgassing rates of diffused species from outside chamber walls as a function of time

This $1/t^{1/2}$ dependence changes at later times into a faster exponential fall $\exp(-\alpha Dt)$ as the quantity of dissolved gas becomes substantially depleted. Initially, the slope is $-1/2$, changing eventually to a steeper linear portion. It describes the hydrogen outgassing of well-baked stainless steel at long times and after all near- surface adsorbed gases have been pumped away.

$$q = C_0 \left(\frac{D}{t} \right)^{1/2}$$

Where C_0 is initial uniform concentration of diffused gas and D is diffusion coefficient.

Outgassing due to desorption of permeated gases from outside of chamber walls

Permeation is the diffusive flow of gas through a vacuum wall of thickness t driven by the pressure difference P across it. For monatomic gases and those that do not dissociate on diffusing into the solid, the outgassing flux is described by the equation (O'Hanlon, 2003)

$$q_{perm} = \frac{KP}{t}$$

where K is the permeation constant with unit m^2s^{-1} , q_{perm} expressed in Pa ms^{-1} , P in Pa, and t in m.

When vacuum systems are vented back up to atmospheric pressure, direct adsorption from the gas phase leads to the adsorption and absorption into the near-surface of atmospheric gases, principally water vapor in relatively large amounts. It is prudent to try to minimize water vapor adsorption by venting to dry nitrogen.

In pumping down from atmospheric pressure, most of the free gas in the pumped volume is soon removed, and in typical systems, sub-millibar pressures of 10^{-2} mbar or better are achieved in times of order of minutes.

Desorbing gas starts to contribute to the gas load below about 10^{-1} mbar, and as the pressure continues to fall into the region below 10^{-4} mbar the gas load (assuming no leaks) becomes increasingly due to outgassing. Of the molecules that desorb, a number will find the entrance to the pump and be removed immediately. But others, a majority in vacuum chambers of typical proportions, will traverse the chamber to another part of the vacuum wall and further surface interactions before being pumped away. It is this traffic of molecules in transit to and fro across the chamber, fed by desorption and diminished by pumping, that constitutes the number density n of molecules in the vacuum and determines the pressure achieved.

Gas that is loosely bound on internal surfaces is pumped away quickly. Gas that is tightly bound desorbs at a very slow rate and does not contribute a significant load. But water vapor, which has an appreciable probability of desorption, has been stored in large amounts during exposure to the atmosphere. The result is that there is protracted gassing of water vapor from structural materials such as stainless steel and glass. The outgassing rate does decrease, but only slowly, and desorbing water vapor accounts for the dominant gas load for times of order tens of hours, unless bakeout procedures are used. In circumstances in which pump performance did not limit the vacuum achieved, outgassing would be observed to diminish as time progressed, with the contribution to it of the small amount of diffusion of hydrogen from the interior becoming more important, and eventually, after very long times, becoming the dominant contribution. Beyond that, if all the gas stored initially in the wall were removed by diffusion, the ultimate source of gas would be permeation.

Effect of temperature on Outgassing (Baking)

Because the desorption of gases is a thermally activated process whose rate increases dramatically with temperature, it is possible by raising surface temperatures to greatly accelerate the desorption process and, indeed, other thermally activated processes such as diffusion that occurs within the bulk of the vacuum wall. This process is called “baking” and consists of heating vacuum systems, walls, and contents, to temperatures of 150–250 °C for times of order 10 h, with continual pumping.

Surface adsorbed gas is removed at a much greater rate than at room temperature, and gas absorbed in the bulk diffuses at a much greater rate to the interior surface where it desorbs and is pumped away. Both the surface and its hinterland in the vacuum wall are therefore depleted of gas molecules, and on cooling back to room temperature the outgassing rate is dramatically reduced by factors $\sim 10^3$ or more, consistent with the attainment of ultrahigh vacuum.