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Molecular Flux Provides Process Understanding

One of the major impediments in the full understanding of the behavior of vacuum systems stems, ironically, from the most basic vacuum relationship. This relationship is the basic formula written as Q (Gas Load) = S (Pumping Speed) x Pressure (torr). This means, for example, that if the gas load increases due to a leak, the pressure will rise. Conversely, fixing the leak will reduce the gas load, and the pressure will drop. The impediment that arises is due to the qualification that the system must be in equilibrium. Although the acceptance and understanding of the Q=SP relationship is key to working with vacuum technology, a deeper and more practical understanding needs to be based on the fact that a system is never in a condition of true equilibrium. Various phenomena such as variable outgassing loads or regurgitation of gases from pumps are among the seemingly endless list of subtle conditions that can and will continually place the system into a state of non-equilibrium. The best we can achieve or expect. in a practical system, is a state of quasi-equilibrium where these infinitesimal changes are just too small to be observed.

The prime indicator of performance is usually taken to be pressure. This could be readings of either total pressure from a gauge or partial pressures of specific gases from a residual gas analyzer (RGA). Since pressure readings, in either case, are based on statistical averages of molecules that enter the sensor, it is extremely difficult to detect small changes in pressure that might occur elsewhere in the system. If an apparently steady pressure reading is observed, it is usually assumed that the system is in equilibrium and that going beyond the simple Q=SP relationship isn’t necessary. The practical truth, though, is often otherwise.

Process specifications are usually established in terms of a target total pressure or partial pressures of specific problem gases before the process is initiated. Applying the operative question “what are you trying to do?” in terms of achieved pressures can be misleading. In almost every practical process, the reason for using vacuum is to prevent the interaction of residual gases with the process. A good example would be a thin film process that depends upon thermally evaporating a material onto a substrate where the evaporated material condenses to form a thin film. In this case, the idea is to prevent residual gases from reacting with the material being evaporated either in the thermal evaporation source, in flight, or as it condenses on the substrate.

One of the most effective ways of looking at the residual gases as they affect the process is not in terms of pressure but of impacts of gas molecules with surfaces. Assuming true system equilibrium, as in the Q=SP relationship, it is easy to calculate the number of molecular impacts per unit time per specific surface area. The equation for air at room temperature is stated as $(4 \times 10^{20}) \times \text{torr} = \text{impacts/sec./cm}^2$. This is a useful calculation to make under any circumstances because it can allow you to make assessments of the practicality of the process specifications in terms of such things as stoichiometrical calculations of gas/surface reactions. More importantly, though, it opens your thinking to the concept of molecular flux.

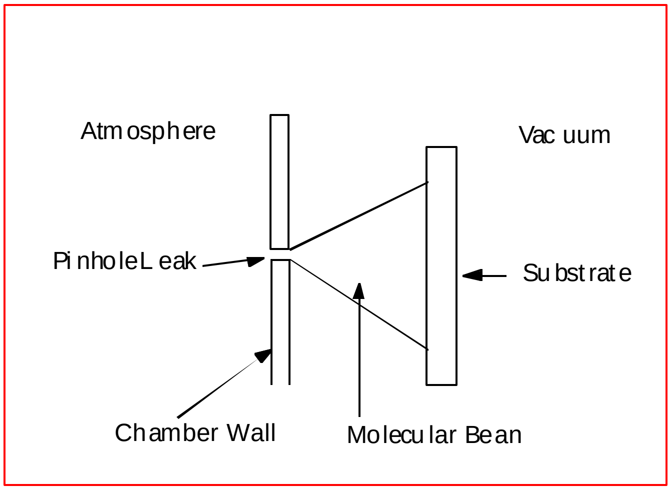
Molecular flux thinking can open a number of windows of understanding beyond the more simplistic thinking of pressure alone. The small changes in real total or partial pressures that are hidden within gauge and RGA readouts that are statistical averages of the gas concentration within a chamber can be analyzed to some extent. It allows us to think about what happens to a gas molecule before it is pumped away. For example, water vapor is usually considered to be a process killer and that makes it work looking at in some detail. In a working high vacuum system, the residual gas within the chamber will almost certainly be, at least, 95% water vapor.

If we take the thermal evaporation system mentioned earlier as an example and think of the flux of water molecules within the chamber, we can begin to widen our understanding. In terms of evaporation rates, we are really thinking of molecular flux in that we are evaporating a flux of the evaporant that is dependent upon the evaporant's surface area, temperature, molecular weight, and vapor pressure. We can easily calculate the evaporation rate with the formula $Q = 0.058 \times P_v \times (M/T)^{1/2}$, where Q= evaporation rate in $\text{gm./cm}^2\text{/sec.}$, P_v = vapor pressure in torr at the evaporation temperature in ^{o}K, M= molecular weight, and T = ^{o}K. From this calculation we can know the evaporation rate and then determine the rate of condensed film growth. We also know where the evaporated flux is going and where it's condensing. The behavior of the other gases in the system can be looked at in much the same way. With this concept in place, we can think about what's happening to the water vapor we mentioned earlier.

The water vapor that's being measured by either the total pressure gauge or RGA is only a statistical average of what enters the sensor, but the desorbing water molecules are passing continually through the chamber. The source of the water molecules is desorption from the chamber's internal surfaces and from elastomer O-rings. Since the water molecules don't just desorb and are pumped away, we have to think further. The molecules will desorb, impact another surface, and resorb with only a portion of the desorbing molecules entering the pump. During this continual sorb/desorb cycle, they will pass through the chamber and might or might not impact and interact with the process during each cycle. This is pretty complex behavior since a single desorbing molecule will then have many chances of encountering the process, but we can. at least, begin to make a quantitative assessment.

If the pressure specification of the example process is 1 x 10^{-7} torr, we can assume, for the sake of simplicity, that the only residual gas is water vapor. Since the number of impacts per area per second is a function of the molecular weight of the gas in question, the formula will differ from the one given earlier for air. The formula (4.8 x 10^{20}) x torr = number of impacts of water molecules/sec./cm^2 at room temperature. At 1 x 10^{-7} torr, we calculate 4.8 x 10^{13} impacts/sec./cm^2. If the process has already been proven to withstand this level of impacts, what will effect will a leak have? Well, if we introduce a leak that raises the total pressure in the chamber from 1.0 x 10^{-7} to 1.1 x 10^{-7}, the number of impacts /sec./cm^2 will only rise from 4.8 x 10^{13} to 5.28 x 10^{13}. This isn't much difference, and would usually be considered to be within the limits of acceptability for the process. In fact, the total pressure reading difference probably wouldn't even be noticed since the difference would be within the normal scatter encountered from run-to-run. What we would have here is a "no problem" operational situation if we look at as a simple Q=SP equilibrium picture. Molecular flux thinking, though, can offer a vastly different picture.

A typical system of the type under consideration would probably have an effective pumping speed of 1,000 Liters/sec. A Q=SP calculation would be as follows: Q torr Liters/sec. = 1,000 liters/sec. x (1 x 10^{-7} torr) where Q = 1 x $10^{-}4$ torr Liters/sec. at 1 x 10^{-7} torr and 1.1 x 10^{-4} torr Liters/sec. at 1.1 x 10^{-7} torr. This would mean that we had a gas load difference of 1 x 10^{-5} torr Liters/sec. This would be a leak rate that would be easily detected with a helium leak detector, but, based on the above calculations. it wouldn't be enough of a leak to produce a major process problem. If, however, the leak was located in a position where it formed a molecular beam that directed the incoming gas directly onto a part of the process such as the substrate being coated, the situation changes dramatically. Multiplying the leak rate in torr Liters/sec. by 3.54 x 10^{19} gives us a total of 3.5 x 10^{14} molecules/sec. entering through the leak. If the leak is a pinhole, the molecules will form an expanding cone within the chamber, and if that the entire cone impacts 10 cm^2 of substrate, we have a potential process problem. The residual gas molecules at 1 x 10^{-7} torr will already be bombarding the substrate at a rate of 4.8 x 10^{13}/sec./cm^2, and we now add an impact rate of 3.5 x 10^{13} impacts/sec./cm^2 due to the leak. This gives us a total of 8.3 x 10^{13} impacts/sec./cm^2, and this would be equivalent to the impact rate that would occur if the total pressure was actually 2.1 x 10^{-7} torr. A pressure reading difference between 1.0 x 10^{-7} torr and 2.1 x 10^{-7} torr would be noted, but in this scenario, it would probably pass unnoticed until it was found that the process was producing out-of-spec product. Thus, molecular flux thinking goes beyond Q=SP thinking in that it takes into account where the gas originates and where it goes within the chamber instead of being merely looked at in an equilibrium sense. Although the effects of a leak can show, as in this example, a dramatic practical process example, molecular flux considerations apply to a wide range of vacuum system parameters.



A leak that's too small to notice can destroy a process. The molecules entering through the leak can play directly across a substrate and provide many more molecular impacts than would be expected at the equilibrium pressure.

The physical location of a gas source can have important effects upon the performance of a system. If, for example, a process gas is deliberately introduced into a chamber the location of the leak valve is important. If the leak is located directly across the chamber from the pump inlet, a large portion of the gas will stream directly into the pump and the pressure sensor monitoring the gas level will not be able to detect all the gas although all of that gas will pass through the chamber and probably interact with the process. Conversely, the location might allow most of the gas to stream into the sensor and provide a non-equilibrium reading. This is why many practical working systems have methods such as diffusers or baffles placed on process gas inlets. Internal virtual leaks also provide a useful example in that pockets of active gas can result in gas-process reactions that are never detected by the gauges. Virtual leaks in sputtering cathodes can cause reactions across the face of active metal targets that cause insulating films to form that can charge up and arc out during the sputtering process. These are only a few of the possible problems that need to be considered in light of molecular flux thinking.

The power of using the Q=SP relationship is obvious to practitioners of vacuum technology, and thinking in terms of molecular flux is only a deeper layer to apply to either a process or system. It also helps build a mental picture of what is occurring within the system that goes far beyond merely accepting what equilibrium conditions can tell us. In all, the more you understand about what's happening within the system and process, the better you can protect or fine tune the process.

Formulae for molecular flux calculations

Make molecular calculations to help solve vacuum process problems with these simple formulae.

MOLECULE/SURFACE COLLISIONS AT EQUILIBRIUM

Air at room temperature
$(3.95 \times 10^{20}) \times \text{torr} = \text{Collisions/sec./cm}^2$

Water vapor at room temperature
$(4.8 \times 10^{20}) \times \text{torr} = \text{Collisions/sec./cm}^2$

Other Gas Molecules
$(3.51 \times 10^{22}) \times \text{torr}/ (TM)^{1/2} = \text{Collisions/sec./cm}^2$

MASS FLOW

$\text{torr Liters/sec.} \times (3.54 \times 10^{19}) = \text{Molecules/sec.}$

EVAPORATION RATE

$0.058 \times P_v(M/T)^{1/2} = \text{gm/sec./cm}^2$ evaporation rate

T = Temperature in ^{o}K
M = Molecular Weight
P_v = Vapor Pressure at T in ^{o}K

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