

## Pumping Speed in the Drydown Zone

*The extended pumpdown time through the water vapor-dominated drydown zone is a complex process that can be dissected to show that it is only partially dependent upon pumping speed.*

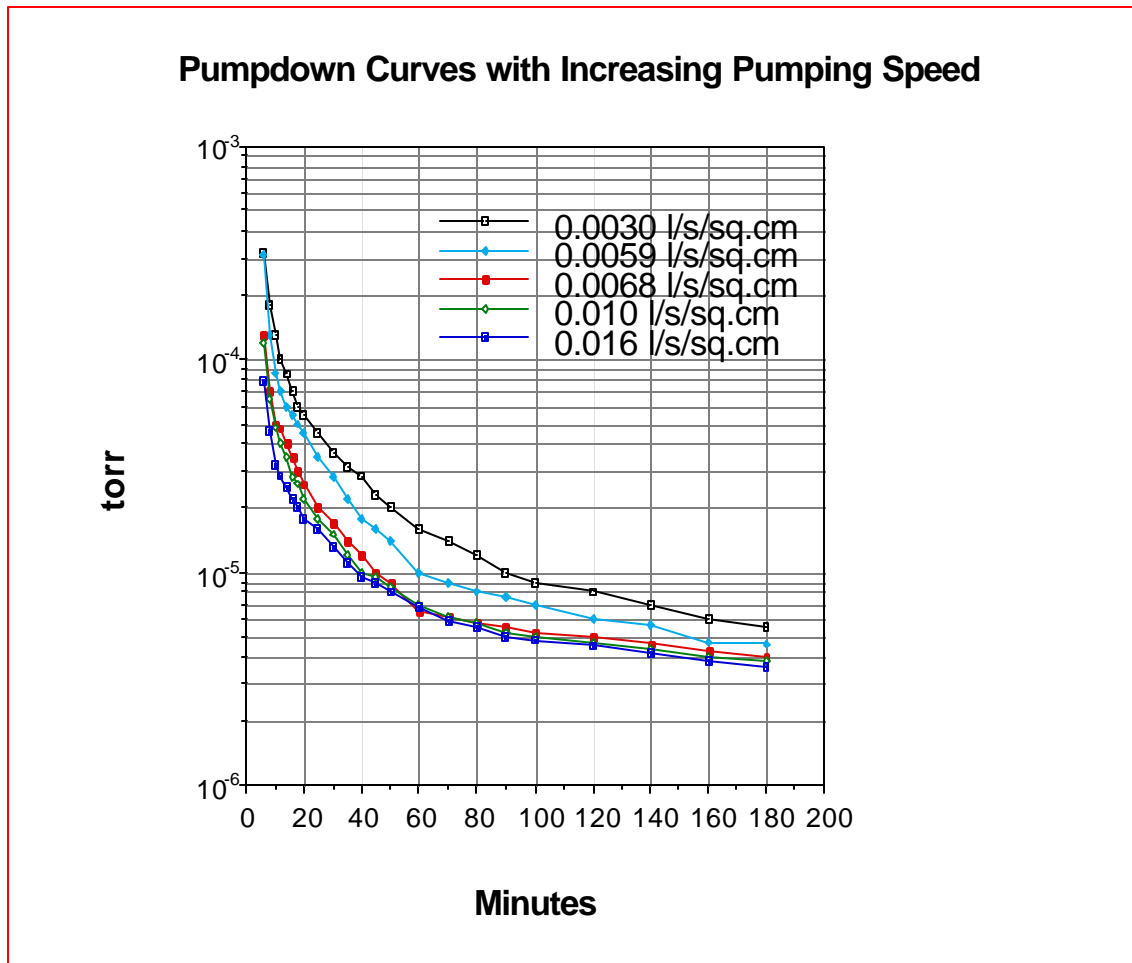
Every vacuum practitioner has seen the phenomenon and felt the frustration. During a pumpdown, the pressure drops fairly quickly to  $10^{-3}$  torr or so and the rate of reduction starts to slow down and just keeps getting slower until, finally, the pressure reaches the level specified for the process. This painfully drawn out portion of the total pumpdown curve is often called the drydown zone, and an apt term it is, since either all or almost all of the residual gas in the chamber is water vapor. If you're quick enough to turn on a residual gas analyzer (RGA) as the pressure drops past  $10^{-3}$  torr, you'll see nitrogen and oxygen peaks appear and disappear in an eyeblink while leaving only the signature water vapor peaks at 17 and 18 amu behind with any other peaks hidden down in the noise level. Since the drydown zone of the pumpdown is, by far, the most time consuming, it's worth understanding just what's going on in the chamber.

### The Source

When a chamber is open to air, prior to pumpdown, it's exposed to continual collisions between water vapor molecules in the ambient air and the chamber's internal surfaces. At room temperature, only a few percent of these molecules will stick to the surface, but a surface can easily be coated with several hundred adsorbed monolayers at the onset of pumping. The thickness of this bed of molecules will be proportional to the number of collisions which will be, in turn, proportional to the exposure time and the amount of water vapor (humidity) in the air. The subsequent pumpdown curve will reflect the total thickness in that the thicker the bed, the longer it will take to reach a given pressure. During the roughing cycle portion of the pumpdown curve, almost all of the thick bed will desorb and be pumped away, but enough water molecules will be left behind on the chamber's surfaces to slowly desorb and make up the residual gas throughout the drydown zone. This is the point where we need to take a closer look at the sorbed molecules and the chamber's surface area to understand the water vapor's persistence throughout the drydown zone.

## Binding Energy and Sojourn Time

Water vapor, being a polar molecule, will form bonds both with surfaces and with itself. Water vapor will bond to metal surfaces with a strength of about 23 kcal/mole while water vapor will bond to itself with a strength of about 10 kcal/mole. The layers closest to the first one will have energies somewhere in between. To put these bond energies into perspective, most gases will physisorb at much lower strengths and desorb immediately on pumpdown and chemical bonds are much higher and won't



*Changes in either the number of collisions or the total time a desorbing water molecule remains in the chamber before being pumped away decline beyond 0.01 Liters/sec./cm.<sup>2</sup>*

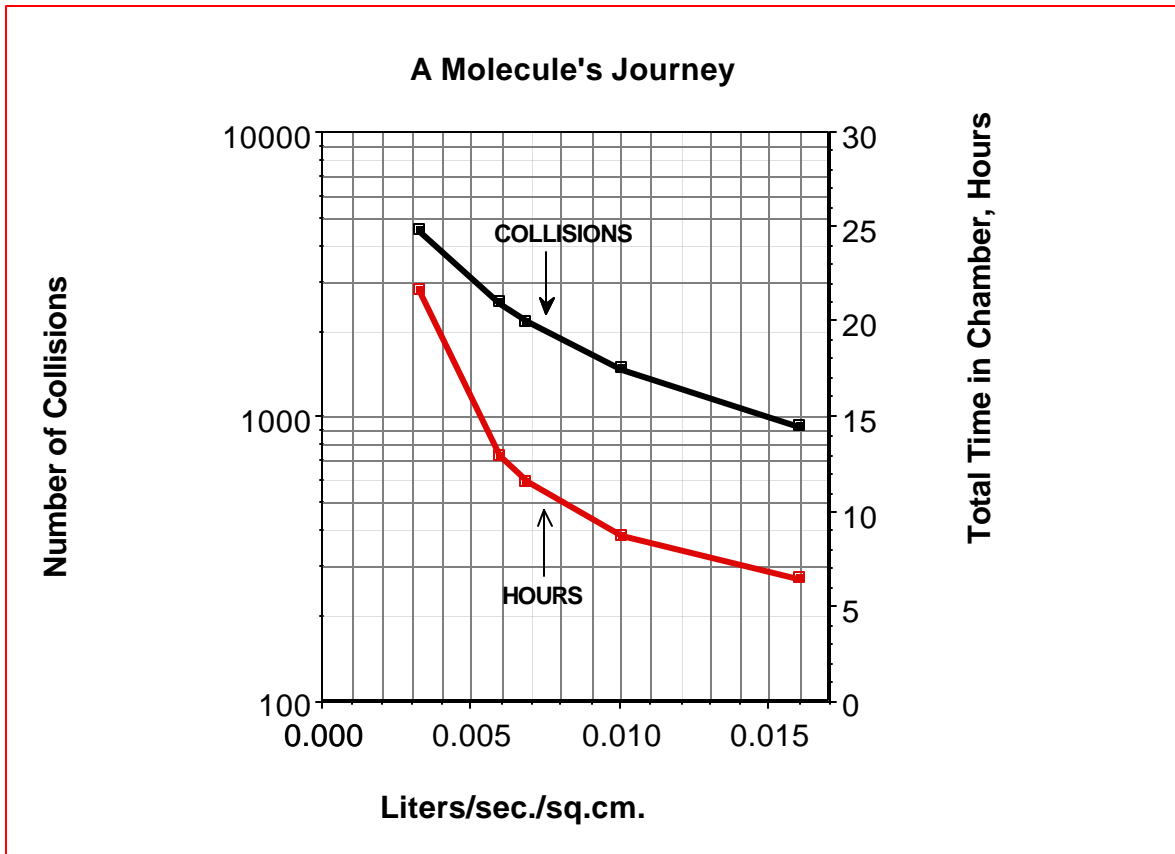
desorb at all. It's the in-between bonds that are the problem.

At a given temperature, and here we only consider room temperature, the amount of time that a sorbed molecule remains in place before desorbing is called the sojourn time, and the sojourn time depends on the bond strength. In our case, a water molecule bonded to a metal surface has a sojourn time of about 25 hours while the sojourn time of water molecule bonded to another water molecule is measured in

microseconds. Looking at these numbers, it would seem that the water molecules, with the obvious exception of those bonded to metal surfaces, would desorb almost immediately and be pumped away. Just as obviously, based on the shape and duration of a pumpdown curve in the drydown zone, this doesn't seem to happen. The reason for this is that a desorbing molecule doesn't desorb and enter a pump in one stage. Instead, it has a long journey ahead of it.

### A Molecule's Journey

When an adsorbed water molecule acquires enough internal energy to overcome its bond and desorb, it will either pass into the chamber or migrate along the surface to a site where it can form a stronger bond. If it passes into the chamber, it might leave at any angle relative to the surface. Since the drydown zone exists in molecular flow conditions, the desorbing molecule will proceed in a straight line until it collides with another surface without impacting another molecule on its way.



*A series of pumpdown curves with increasing pumping speed shows that performance does not appreciably increase beyond 0.01 Liters/sec./cm.<sup>2</sup>*

It's fairly easy to see, then, that a molecule will only be pumped if its trajectory lets it enter a pumping port, and this result will only reflect a tiny portion of the possible trajectories a desorbing molecule might take. Instead, it will most likely impact

another surface where it might resorb or it might not. The possibility of the molecule resorbing, called the sticking coefficient, will depend upon the condition of the surface in terms of the availability of a sorption site and the energy level of the surface. Across most of the drydown zone, the sticking coefficient will be about 0.01 which means that about 1% of the impacting molecules will resorb. Nonetheless, it will leave the colliding surface, again in any direction, and so on and so on, until its random final trajectory enters the pumping port and it's removed from the system at last. The total length of a molecule's journey has an important impact on the practical need to traverse the drydown zone far enough to reduce the total desorption rate to a point where a process pressure is achieved.

## Pumping Speed and Desorption Rate

When encountering a gas load such as a desorption rate, the intuitive answer for dealing with the gas load faster is to add pumping speed. The overall vacuum relationship of  $Q$  (gas load) =  $S$  (pumping speed)  $\times$   $P$  (pressure) would seem to show that clearly. In the case of a water molecule's journey from surface to pump, there's a problem. There are two ways of stating a desorption rate: intrinsic and net. The intrinsic desorption rate considers only the molecules that leave a surface with no recognition of resorbing molecules. Net desorption, though, considers the total rate of removal from a surface in terms of molecules pumped away, and this is the rate we need to look at in a practical system.

Again, intuition tells us a faster pump will remove more water molecules. True enough, but a series of pumpdown experiments reveals a problem. If pumping speed is increased incrementally, significant improvement in time-to-pressure curves will result until a speed of about 0.01 Liters/sec/cm<sup>2</sup> is reached. Further incremental increases in pumping speed show improvement, but that improvement is too small to be practical. Thus, 0.01 Liters/sec./cm<sup>2</sup> can be called the critical pumping speed since further increases produce significantly diminishing returns. To put this into perspective, consider a 40 cm X 80 cm. cylindrical chamber of 100 Liters with a total surface area of 13,000 cm.<sup>2</sup> A pumping speed of 0.01 Liters/sec./cm<sup>2</sup> would have an effective speed of 130 Liters/sec, while a speed of 0.016 Liters/sec./cm<sup>2</sup> would have an effective speed of 200 liters/sec. This translates as moving up to the next fastest pump in a given product line. This non-intuitive phenomenon is explained by a molecule's journey.

The total number of surface impacts of a desorbing molecule before it is pumped away can be calculated as a function of the ratio of pumping speed to surface area. The total number of impacts will decrease as more pumping speed is added, but will begin to tail off at a ratio of about 0.01 Liters/sec./cm.<sup>2</sup> This is also borne out by calculating the total amount of time a desorbing molecule spends in the chamber before being pumped where the time reduction tails off the same way. What's happening is that incremental increases in pumping speed don't make all that big a change in the diameter, and proportional conductance, of the pumping port. This

means that the statistical chances of a molecule entering the pumping port don't increase all that much.

### Putting It Together

The only practical way, then, for increased pumping speed to have much effect on the net desorption rate is to provide a massive increase in pumping speed. Since a pumping port large enough would probably be bigger than the chamber wall it would have to penetrate, an internally arrayed capture pump would be required. This could be met with either a cryosurface or a getter panel. Such an installation would shorten the traverse of the drydown zone slightly, but would have little effect on the intrinsic desorption rate. If, though, energy is provided to the sorbed water molecules by heat or low wavelength UV photon bombardment, the intrinsic desorption rate can be greatly increased while energy is being transferred and cause a temporary rise in pressure. Although a molecule's journey will be just as long, the sticking coefficient will drop and the desorbed molecule's time in the chamber will be greatly decreased. Increased desorption, coupled with adequate pumping speed, will then result in a much greater reduction in the traverse of the drydown zone to whatever level your process requires.

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