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Understanding Water Desorption

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Water vapor desorption is usually accepted as one of the major problems confronting the vacuum practitioner in that the process chamber's pumpdown time is usually controlled by the desorption rate of the water vapor molecules sorbed on the inner surfaces of the chamber. With a potential problem of this magnitude, it is useful to gain a more complete understanding of the mechanism that is occurring during the pumpdown. Let's start with the source of the molecules within the chamber: the bed of sorbed water.

THE BED

When the chamber is let up-to-air, a bed of sorbed water is formed from the water vapor in the air. The mechanism and amount of sorption¹ is dependent upon relative humidity and duration of exposure. The portion of the bed that forms first is closest to the chamber's surface and is the most ordered part of the bed. As sorption continues, the bed becomes more and more disordered. The strongest water-to-water bonds are found in the most ordered portion of the bed and the weakest in the least ordered portion.

Figure 1 shows the desorption rate of water vapor with time. As you can see, the desorption rate is highest at the beginning and then declines with time. This change in rate is due to the increasing bond strength as the bed erodes to expose molecules of higher and higher bond strength.

The second curve on Figure 1 shows the relative bond strength of the sorbed bed that is exposed for desorption as the bed erodes. We can see that the relative bond strength is inversely proportional to the desorption rate.

THE OVERSIMPLIFIED MENTAL PICTURE

If you look at Figure 1 and try to build a mental picture, you can easily fall into an erroneous oversimplified picture. That picture starts with a single molecule leaving a surface and being pumped away, then another, and another, etc. It's not at all like that in a system.

The nice, neat picture that springs from Figure 1 is useful in thinking about a sample of material in a system where each and every molecule is removed by the pump following desorption. In a real chamber, however, we have a condition where large numbers of molecules are

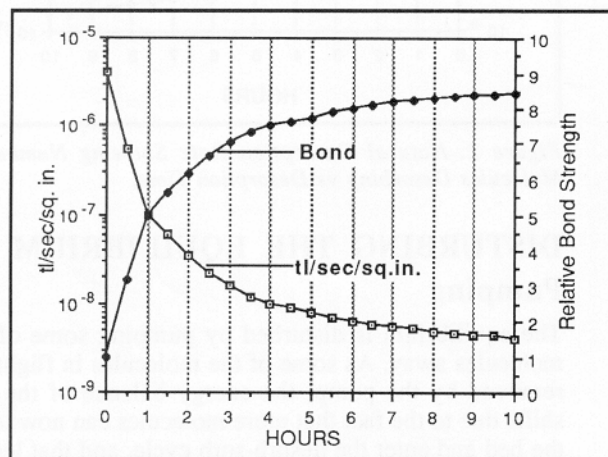


Figure 1. Desorption Rate and Relative Bond Strength.

in constant motion between surfaces where the numbers of molecules desorbing are equal or close to equal with the numbers of molecules arriving to be re-sorbed.

THE REAL PICTURE

A Single Molecule Desorbing

We can picture a single water vapor molecule on the surface of a bed of other molecules that has been slowly absorbing energy until it's almost to the energy level where its energy is slightly greater than the energy binding it to the other molecules in the bed. It continues to absorb energy: thermal through the bed or from other impacting molecules. As its energy rises, it finally breaks loose from its place on the bed and wanders across the chamber in a straight line at whatever angle it departed from. That's right, a straight line since we're at molecular flow where the odds are that it'll hit a wall before hitting another molecule in flight.

When it impacts the sorbed bed on the wall, it will probably lose its energy to one or several other molecules. At its new low energy state, the bond energy of the molecules in the bed will probably capture it. Depending upon its energy level versus the bed, it might stay for awhile atop the bed or its sojourn might be so short it can be safely termed a bounce.

What we have here is a condition where the molecules leaving a surface, passing through the chamber, and impacting another surface are in a sort of quasi-equilibrium. The process goes on and is wholly dependent upon the energy level of the bed as to how many molecules are in flight at any one time. Figure 2 shows the desorption rate again, but this time adds the number of molecules desorbing. This process goes on until the equilibrium is disturbed.

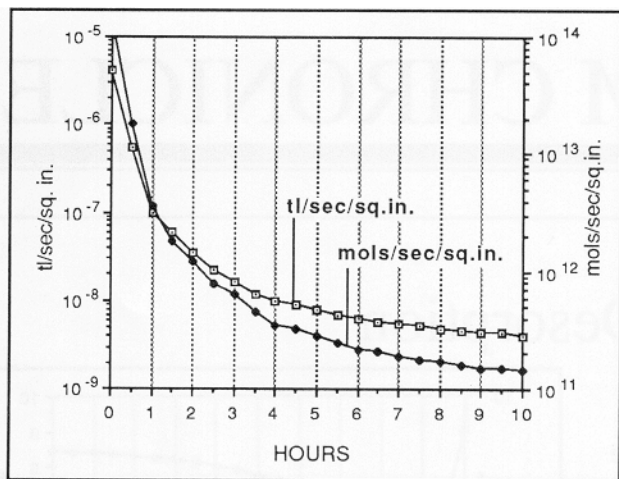


Figure 2. Natural Desorption Rate Showing Number of Molecules Desorbing vs Desorption Time.

DISTURBING THE EQUILIBRIUM

Pumping

The equilibrium is disturbed by pumping some of the molecules away. As some of the molecules in flight are removed by the pump, the energy balance of the bed shifts due to the fact that more molecules can now leave the bed and enter the desorb-sorb cycle, and that leaves fewer molecules in the bed. As the equilibrium is disturbed by removing molecules from play, the pressure (number of molecules) will slowly drop because more and more energy is required to remove a single molecule from the bed as the bonds become stronger and require more energy to overcome them.

What we have at this point is a statistical process where a molecule just happens to randomly enter a pump and is removed from the quasi-equilibrium population in the chamber. At any pressure and at any time period in the pumpdown cycle, only a percentage of the available molecules will statistically enter the pump. We can truthfully say that the pump is altering the desorption rate, but it can still only remove a statistical percentage of the molecules within the quasi-equilibrium.² Additional pumping speed will alter the equilibrium to some extent, but it is still a slave to the statistics and dependent upon the number of molecules available to be pumped.

Adding Energy

The equilibrium can also be disturbed by adding energy to the picture. Heating the system is one common way of doing this in that thermal energy is passed from the chamber walls into the bed of sorbed water molecules. This new energy is absorbed by the molecules at the sur-

face of the bed and gives them enough energy to desorb and enter the quasi-equilibrium. Radiation of UV energy from a Phototron is another common way of adding energy to the bed.³ In this case the UV is of the proper wavelength to directly couple with the water molecule.

As the desorption rate rises, more and more molecules become available to be pumped since the statistics still allow a percentage of the molecules in play to be pumped. This, then, means that the pressure goes up a little, but more molecules are pumped away so the pressure drops a little. Then more molecules gain enough energy to escape, and so on and so on as the pressure continues to drop.

Still the quasi-equilibrium condition of desorb/sorb goes on with only a portion of the molecules in play being removed by the pump. Using a Phototron as an energy pump has a distinct advantage because the molecules in play continue to be energized in flight and this causes even more energy transfer as they impact another wall or surface. Still, we're playing the energy balance game.

THE BED LAYERS

At this point we can look at the bed itself in that we have two distinct layers. We have the original bed of, so far, un-desorbed water vapor molecules and another bed of transient molecules that are part of the on again, off again quasi-equilibrium. The transient bed contains most of the energy added to the system so that when the heat of UV is removed, this energy level must play out through a series of continual collisions until the original bed has levelled out in its energy level and the chamber reaches a new and lower desorption rate.

CONCLUSIONS

As we look at the mental picture we've developed here, we can begin to see that the actual system desorption rate is a function of the "normal" desorption rate to some extent. It is also a function of a given system in that the pumping speed and physical layout and dimensions of the chamber's walls come into play as the desorbed molecules go their random way. A system's actual desorption rate can only be worked out by experimentation and experience on that given system, but the graphs shown in Figures 1 and 2 can be used as an indicator.

References

- ¹ "Sources of Water Vapor in Vacuum Systems," *The Vacuum Chronicles*, Vol 4, No. 8
- ² "The Molecular Method for Understanding Vacuum Technology," *The Vacuum Chronicles*, Special Edition, 1996
- ³ "How the Phototron Works," *The Vacuum Chronicles*, Vol. 4, No. 10