Vacuum Technology III

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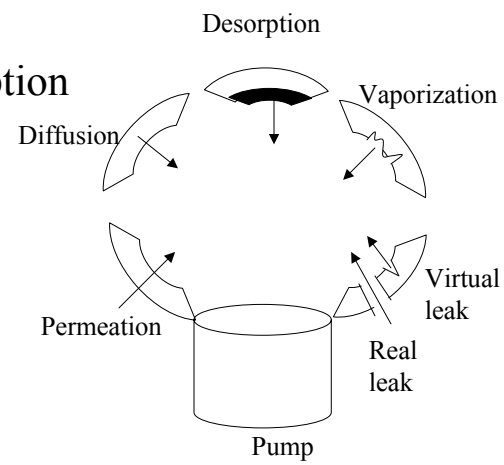
Gas Sources in a Vacuum

- Vaporization
- Thermal Desorption
- Diffusion
- Permeation
- Backstreaming
- Leaks
  - Real
  - Virtual



Vaporization

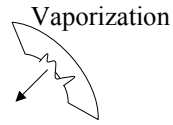
- Particle Flux (Γ) (from before)

$$\Gamma = n\left(\frac{kT}{2\pi m}\right)^{1/2}$$

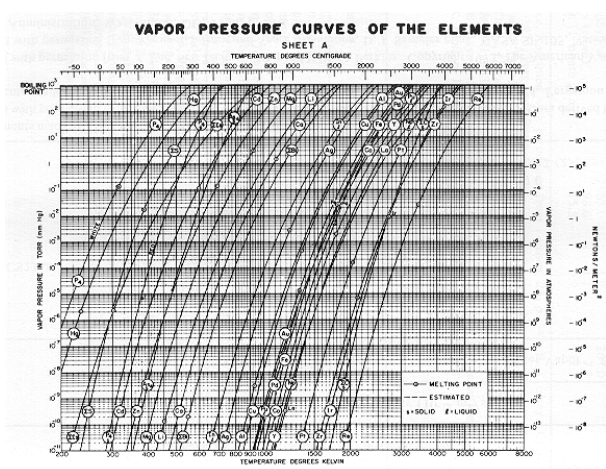
- Similarly for Vaporization of a solid source (or evaporation)

$$\Gamma(molecules/\sec) = 2.63\times10^{24}\times\frac{PA}{(MT)^{1/2}}$$

where:
P = Vapor Pressure
A = Surface Area
M = Molecular weight
T = Temperature



Vapor Pressure Curves



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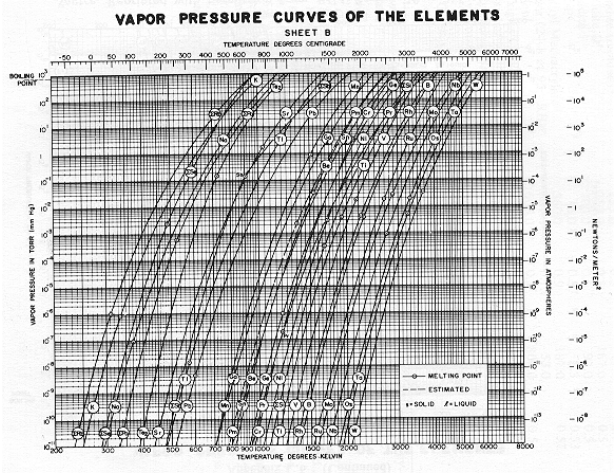

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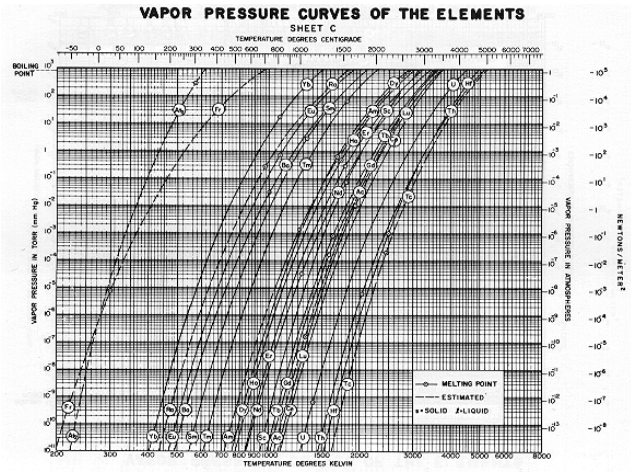
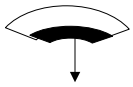


Thermal Desorption

- Heat stimulated release of gases or vapors previously adsorbed on the surface of the chamber walls
  - Function of:
    - Molecular binding energy
    - Temperature of the surface
    - Number of monolayers formed on the surface

Desorption



Thermal Desorption

- First Order Desorption
  - Atoms or molecules that do not dissociate prior to desorption

$$\frac{dC(t)}{dt} = -K_1 C(t) = -\frac{\exp^{-E_D/N_0 kT}}{\tau_0} C(t)$$

where:

$\frac{dC(t)}{dt}$ = desorption rate (concentration as a function of time)

K_1 = rate constant

E_D = desorption energy

τ_0 = 1/vibrational frequency ($\sim 10^{-12}$ sec)

$$\frac{1}{K_1} = \frac{1}{\tau_0} \exp^{-E_D/N_0 kT}$$

$$\tau_R = \tau_0 \exp^{-E_D/N_0 kT}$$

where:

τ_R = average residence time a molecule spends on a surface

Integration

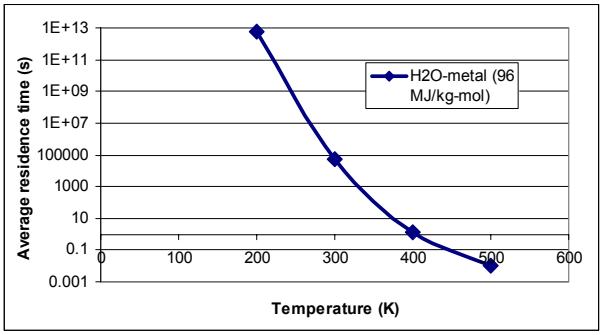
$$\frac{dC(t)}{dt} = K_1 C_0 \exp(-K_1 t) = C_0 K_1 \exp(-t/\tau_R)$$

where:

C_0 = concentration at t = 0

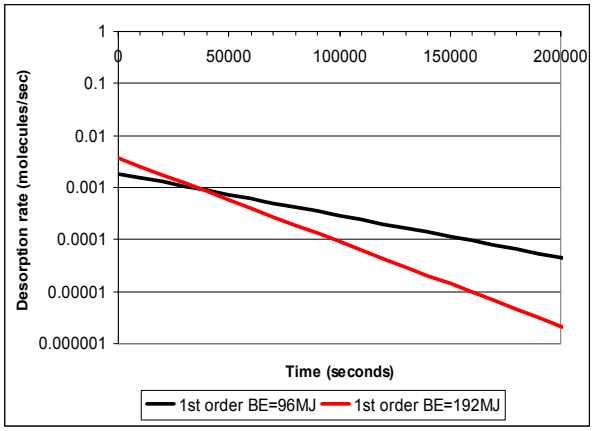
Thermal Desorption

- Temperature dependence of average residence time (τ_R)



First Order Desorption

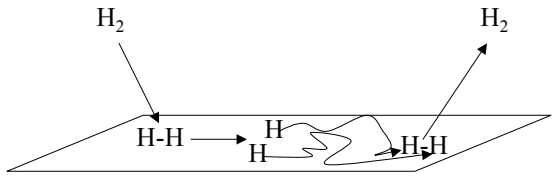
- Desorption Rate vs Time



Second Order Desorption

- Atoms Dissociate upon adsorption and must recombine to be desorbed
  - Example H_2 on steel

H_2 (adsorption) $\rightarrow$ H + H (dissociation) $\rightarrow$ H_2 (recombination) $\rightarrow$ H_2 (desorption)



Second Order Desorption

$$\frac{dC(t)}{dt} = -K_2 C(t)^2$$

where:

$\frac{dC(t)}{dt}$ = desorption rate (concentration as a function of time)

K_2 = second order rate constant

$$\frac{1}{K_1} = \frac{1}{\tau_0} \exp^{-E_D / N_0 kT}$$

$$\tau_R = \tau_0 \exp^{-E_D / N_0 kT}$$

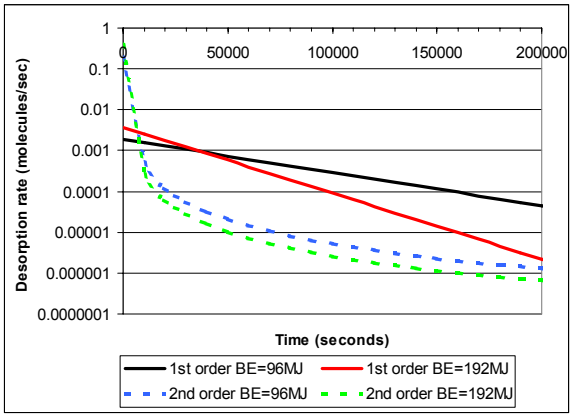
where:

τ_R = average residence time a molecule spends on a surface

$$\boxed{\frac{dC(t)}{dt} = \frac{-K_2 C_0^{\,2}}{(1 + C_0 K_2 t)^2}}$$

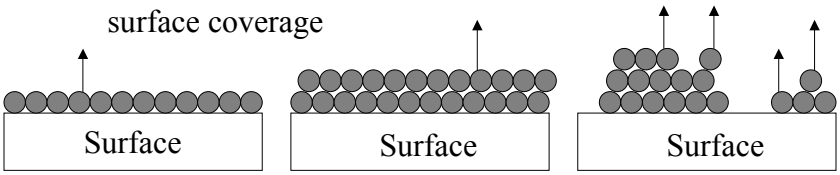
First and Second Order Desorption Rate

- Desorption rate vs Time



Real Surfaces

- Must consider multiple binding energies
  - Particle - surface BE
  - Particle - particle BE (for > 1 monolayer)
  - Particle - particle BE changes as a function of the surface coverage

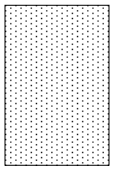


Most systems: outgassing rate $\propto 1/t$

Diffusion

- Diffusion of gas particles inside chamber wall to the interior of the chamber
  - 2 step process
    - Diffusion of gas to the interior of chamber surface
    - Desorption of diffused species
  - Diffusion << slower than desorption, therefore diffusion is the rate limiting step

External Surface P >> Co



Internal Surface P < Co

Diffusion

- Outgassing rate (q) [Pressure-volume/sec)/surface area] ie {(Torr-liters/s)/m^2]

$$q = C_0\left(\frac{D}{t}\right)^{1/2}\left[1+2\sum_{n=o}^{n=\infty}(-1)^n \exp\left(\frac{-nd^2}{Dt}\right)\right]$$

where:

C_0 = initial concentration of gas in solid wall

D = diffusion coefficient

d = thickness of the wall

Diffusion

Short times

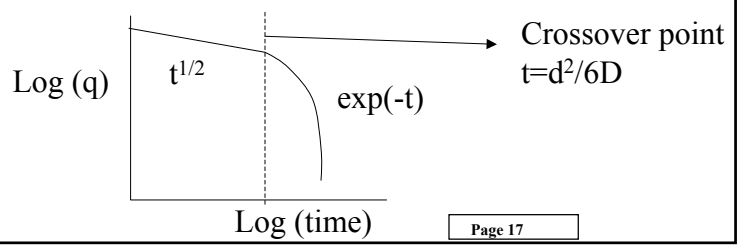
$$q = C_0\left(\frac{D}{t}\right)^{1/2}$$

$$q \sim \frac{1}{t^{\frac{1}{2}}}$$

Long times (infinite series solution

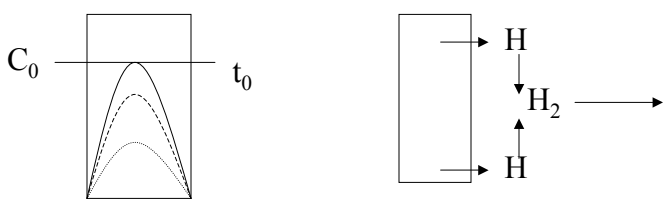
$$q = \frac{2DC_0}{d}\exp\left(\frac{-\pi^2 Dt}{2d^2}\right)$$

$$q \sim \exp(-t)$$



Diffusion

- Diffusion in Stainless steel
  - H2 is a common diffuser gas in stainless steel

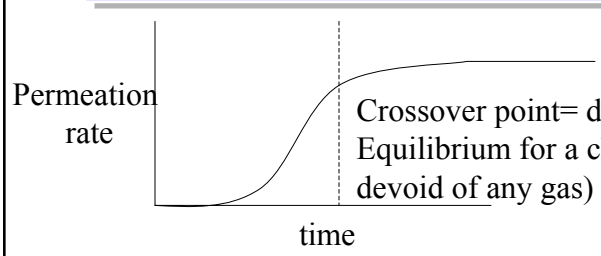


  - Vacuum Bake Stainless Steel chambers
    - D=Doexp(-Ed/kT) increase T, increase D, remove H2 fr,p stainless steels and decrease q(diff)

Permeation

- Three step process
  - Gas adsorbs onto outer wall of vacuum chamber
  - Gas diffuses through chamber wall
  - Gas desorbs from interior of chamber wall
- Permeability of a wall (K_P)
  - $K_P = DS'$ where:
    - D = diffusion coefficient
    - S' is the solid solubility of the gas in the chamber material

Permeation



Crossover point= $d^2/6D$ (time to reach Equilibrium for a chamber wall initially devoid of any gas)

Permeation Rate

$$q = \frac{K_P P}{d}$$

where:

Kp = permeation of the wall

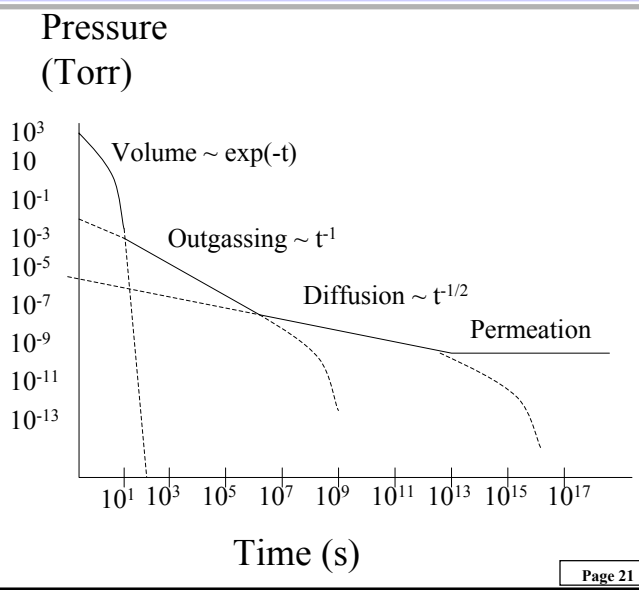
P = pressure drop across chamber wall

d = chamber wall thickness

Stainless Steel – H_2

Glass -- Helium

Big Picture


Pressure
(Torr)
10^3
10
10^{-1}
10^{-3}
10^{-5}
10^{-7}
10^{-9}
10^{-11}
10^{-13}
Volume ~ exp(-t)
Outgassing ~ t^{-1}
Diffusion ~ $t^{-1/2}$
Permeation
10^1 10^3 10^5 10^7 10^9 10^{11} 10^{13} 10^{15} 10^{17}
Time (s)