

Thin Films and Coating Techniques

By:Dr.Modhaffar A.Al-Asadi/Lectures for 4th class students-Branch of Materials science

REFERENCE

1. Vacuum Technology, Thin Films, and Sputtering, R. V. STUART, ACADEMI PRESS, INC.,Orlando, Florida 32887, 1983.
2. Vacuum Technology, A. Roth, Elsevier Science, 1990.
3. K. L. Chopra, "Thin Film Phenomena" Mc Grow-Hill Book Company, New-York, (1969).
4. K. L. Chopra, I. Kaur, "Thin Devices Application", Plenum Press, New-York, (1983).
5. G. Hodes, "Chemical Solution Deposition of Semiconductor Films", Marcel Dekker (2003).
6. Vacuum Technology, Theory and Laboratory Exercises, Biltoft, Benapfl and Swain, Las Positas College, 2002.
7. John L. Vossen "Materials Science of Thin Films" Second Edition, Elsevier Elsevier Inc., 2002.

1- Gas Theory for Vacuum Technology:

- 1.1 Physical State of Matter.
- 1.2 Perfect and Real Gas Laws.
- 1.3 Motion of Molecules in rarefied Gases.
- 1.4 Pressure and Mean Free Path.
- 1.5 Transport Phenomena in Viscous State.
- 1.6 Transport Phenomena in Molecular State.
- 1.7 Thermal Diffusion and Energy Transport.
- 1.8 Conduction and Impedance in V.Tubes.

2- Production of Low Pressures – Vacuum Pumps:

- 2.1 Mechanical Pumps:
 - (a) Mechanical Molecular Oil-Sealed Pumps.
 - (b) Roots Pumps.
 - (c) Mechanical Molecular Pumps.
- 2.2 Vapor Pumps.
- 2.3 Chemical Pumps.
 - (a) Sputter Ion Pumps.
 - (b) Titanium Sublimation Pumps.
 - (c) Other Chemical Pumps.
- 2.4 Sorption Pumps.
- 2.5 Cryo-Pumps.

3- Measurement of Pressure:

- 3.1 Introduction
- 3.2 Survey of Types of Gauge Measuring Total Pressure.
- 3.3 The Mcload Gauge.
- 3.4 Thermal Conductivity Gauges.
- 3.5 Hot – Cathode Ionization Gauges.

- 3.6 Cold – Cathode Ionization Gauges.
- 3.7 The Knudsen Ionization Gauge.
- 3.8 The Viscosity Gauge.
- 3.9 Gauge calibration.
- 3.10 Thermal transpiration and pressure measurement.
- 3.11 The determination of partial pressure.

4- Physical Vapor Deposition (PVD):

- 4.1 Evaporation Process.
- 4.2 Sputtering Process.
- 4.3 Ion Plating and Ion Implantation.

5- Chemical Vapor Deposition (CVD):

- 5.1 The CVD process.
- 5.2 CVD reactor.
- 5.3 The fundamentals of CVD.
- 5.4 CVD reaction.
- 5.5 CVD products and process routes.
- 5.6 Plasma assisted CVD, Plasma enhanced CVD.
- 5.7 Laser CVD.

6- Coating:

- 6.1 The Pack Coating.
- 6.2 Slurry Coating Technique.
- 6.3 The Sol – Gel Coating Technique.
- 6.4 Hot – Dip Coating Process Technique.
- 6.5 Electrochemical and Chemical Coating Methods.

7- Coating by Laser Surface Treatment Rapid Solidification Processing, Spraying Welding, Cladding and Diffusion Method.

- 7.1 Laser Coating Technology.
- 7.2 Rapid Solidification Processing.
- 7.3 Droplet Transfer Coating by Spraying.
- 7.4 Coating by Plasma Spraying.
- 7.5 Clad Surfacing.
- 7.6 Diffusion Bonding.

8- Thickness Measurements:

- 8.1 Optical Interference Techniques.
- 8.2 Optical Interference Technique for Transparent Films.

1- Gas Theory for Vacuum Technology

Vacuum:

From a practical sense, vacuum may be defined as the condition of a gas under less than atmospheric pressure.

Vacuum rang

Vacuum Description	Range
Low vacuum	25 to 760 Torr
Medium vacuum	10^{-3} to 25 Torr
High vacuum	10^{-6} to 10^{-3} Torr
Very high vacuum	10^{-9} to 10^{-6} Torr
Ultrahigh vacuum	10^{-12} to 10^{-9} Torr
Extreme Ultrahigh vacuum	Below 10^{-12} Torr

Vacuum technology is based upon the creation of an environment in which a process (thin film deposition, electron beam welding, etc.) can be carried out. This normally implies that one remove air from a system to some acceptable sub atmospheric pressure by the use of some type of vacuum pumping equipment.

Atmosphere:

The blanket of gases that surrounds the surface of the earth and extends outward to a distance of about 25 miles is referred to as "air" or "the atmosphere". This mixture of gases exerts a pressure that presses uniformly on all objects on the surface of the earth. This pressure is about 15 pounds per square inch at sea level.

Composition of Dry Air

Gas	Partial Pressure [Torr]	Percent [by volume]
nitrogen	593	78.1
oxygen	159	20.9
argon	7.1	0.934
carbon dioxide	0.25	0.033
neon	1.4×10^{-2}	0.0018
helium	4.0×10^{-3}	0.00053
methane	1.5×10^{-3}	0.0002
krypton	8.6×10^{-4}	0.00013
hydrogen	3.8×10^{-4}	0.00005
nitrous oxide	3.8×10^{-4}	0.00005
xenon	6.6×10^{-5}	0.0000087

Properties of Systems Under Vacuum

If we remove some amount of atmospheric gas from a leak-free vessel we will have created an environment that is drastically different in many respects: mechanically, chemically and physically.

Mechanical Effects of Vacuum:

Have you ever placed a half full 2 liter plastic soft drink container that is at room temperature into a refrigerator, and noticed later after it has cooled that its sides are distorted and pulled inwards? What you have inadvertently done is create a condition in which the internal pressure of the plastic container was reduced, causing its surface to buckle. Vacuum engineers are acutely aware of this phenomenon, and design vacuum vessels to be sturdy enough to withstand the external atmospheric pressure of 14.7 pounds per square inch (at sea level) in the absence of compensating internal pressure. Structures and components that are particularly susceptible to distortion under vacuum conditions include flat, unsupported surfaces, thin sections, and flexible lines or bellows.

Problem:

Calculate the approximate total force that will be exerted on a 4" diameter glass view port used in a vessel under high vacuum conditions.

Chemical Effects of Vacuum:

The removal of gases from a container will reduce the number of gas atoms that are available to interact with materials in the container. For this reason many materials that are hygroscopic (have a tendency to absorb water from the atmosphere) are stored under vacuum. Materials that readily oxidize are also often stored either under high vacuum, or in an inert atmosphere (nitrogen or argon gas) after the air has been removed from the storage vessel.

Problem:

List as many reactive elements or compounds that you know of which you would consider storing under vacuum or inert gas conditions.

Physical Effects of Vacuum:

Many of the physical properties of gases are strongly affected by the pressure of the gas. Thermal conductivity, electrical conductivity, propagation of sound, optical transmission, optical absorption are just a few. In addition to the effect of reduced pressure on the physical properties of gases, under vacuum solids and liquids also show markedly different behavior. Liquids, such as water, can be made to boil in a vacuum vessel without the application of heat. This occurs as soon as the vapor pressure of the water exceeds that of the vacuum environment.

Similarly, atoms of solid material under vacuum conditions will spontaneously leave the surface of the solid. The rate at which materials vaporize under vacuum is a function of the pressure in the system and the vapor pressure of the material. A more in-depth discussion of vapor pressure will be presented later.

Problem:

We have suggested that physical changes in the thermal and electrical conduction of gases are brought about by a decrease in pressure. What are the trends you would expect in these two physical characteristics as pressure is decreased from atmospheric? (Increase or decrease?)

Gas Laws

Gases are composed of independent, randomly moving atoms or molecules that spontaneously expand to fill any container. The collective behavior of these atoms or molecules in a contained volume can be described when one knows any three of the four following quantities:

1. Pressure:

The force per unit area a gas exerts on its surroundings. (in our calculations we will use primarily Torr or atmospheres).

- 1 atm = 1.01325 bars = 1.01325×10^5 pa = 1.01325 dyne/cm²

- The torr is defined as 1/760 of a standard atmosphere, hence

1 torr = 1mmHg

1 torr = 1.333×10^3 (dyne/cm²) = 133.32 (N/m²)

1atom = 760 mmHg

1 bar = 750.06 mmHg

2. Volume:

The internal capacity of a container, or vessel. (Liters)

3. Temperature:

The temperature of a gas is a function of its kinetic energy, that is, how vigorously the gas atoms are vibrating. Temperature must be specified in terms of an absolute temperature scale. We will use the Kelvin scale ($K = ^\circ C + 273$).

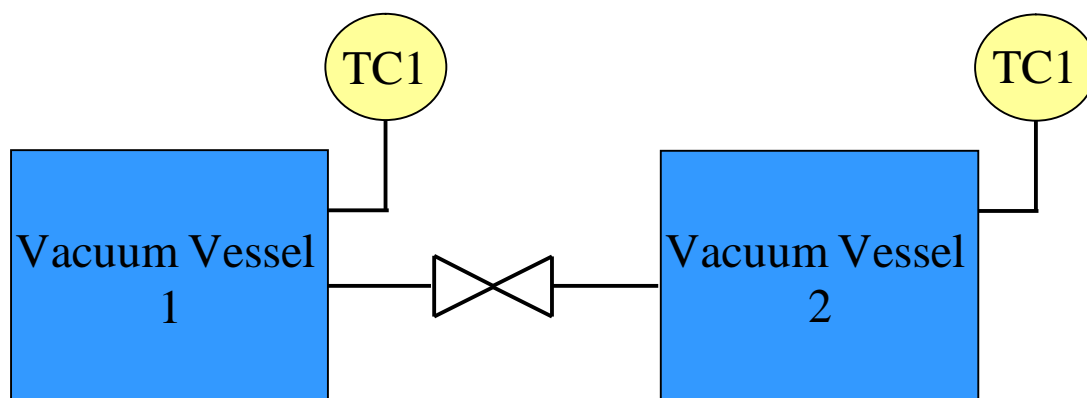
4. Amount: The number of gas atoms in a volume (can be in terms of atoms or moles). {A mole of material is 6.02×10^{23} particles}.

Boyle's Law

Under conditions of constant temperature, Boyle's Law gives the relationship between volume and pressure for a fixed quantity of gas.

$$P_1 \times V_1 = P_2 \times V_2$$

Let's do a thought experiment to demonstrate Boyle's Law. Imagine a system of two leak-free vessels as shown below.



Assuming that the temperature is constant everywhere in our system, and that we can accurately measure the pressure in both vessels, we should be able to apply Boyle's law to calculate the volume of vacuum vessel 2.

If we know that at the beginning of our experiment the volume of vessel 1 is 120 liters, and the pressure of gas inside vessel 1 is 760 Torr, and that vacuum vessel 2 has been rough pumped to about 10 m Torr we can write:

$$P_1 = 760 \text{ Torr}$$

$$V_1 = 120 \text{ Liters}$$

Now, if we open the valve between vessels 1 and 2, and allow sufficient time for the system to equilibrate, we read pressures at TC1 and TC2 to be 500 Torr.

$$(760 \text{ Torr})(120 \text{ Liters}) = (500 \text{ Torr})(V_2 + 120 \text{ Liters})$$

Solving for V_2 we find the second vessel has a volume of 62 liters (note that we include the tabulation to the right of the valve as part of the volume of vessel V_2).

Problem:

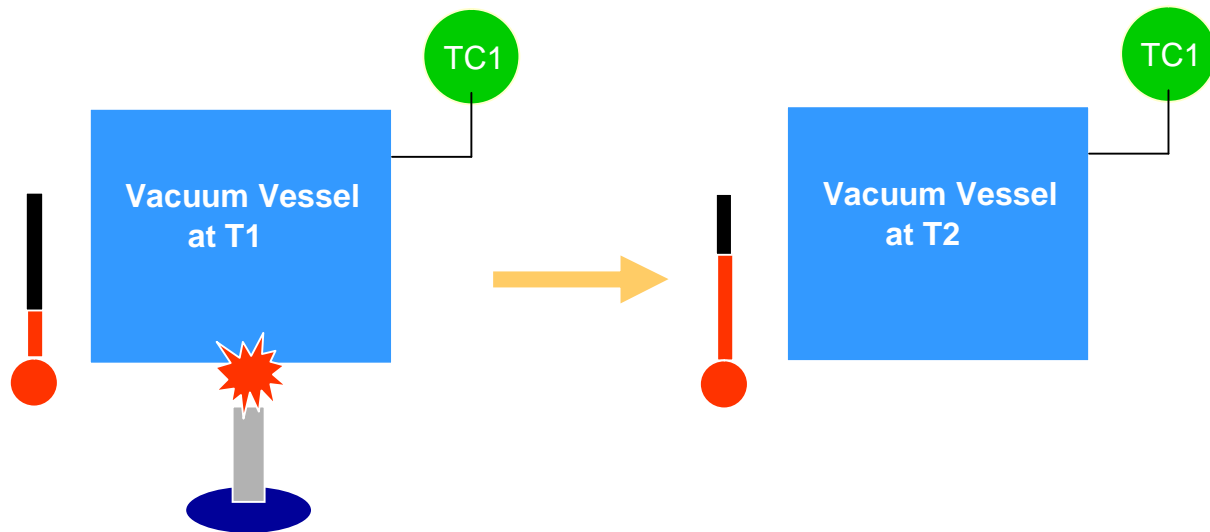
What would be the volume of vessel 2 in figure 3.1 if the final pressure read on TC1 and TC2 was 350 Torr rather than 500 Torr?

Charles' Law:

Under conditions of fixed volume and amount of gas, Charles' Law describes the relationship between the temperature and pressure of a gas.

$$P_1/T_1 = P_2/T_2$$

If we raise the temperature in a closed leak-free vessel containing a gas initially at pressure P_1 the pressure will rise to P_2 , following Charles' Law.



Problem:

If the initial pressure and temperature of the leak-free vessel in figure were 50 mTorr and 25 °C respectively, and the vessel was heated uniformly to 100 °C what would be the new pressure reading?

The Ideal Gas Law

The relationship between pressure, volume, amount of gas and temperature of gas for "ideal" gases is given by the ideal gas law. Fortunately, most gases behave "ideally" under subatmospheric conditions.

$$PV = nRT$$

P= pressure [Atmospheres]

V=volume [Liters]

n=moles of gas [moles]

R=ideal gas law constant (0.08206 L-atm/K-mole)

T=absolute temperature [Kelvin]

Problem:

If a 100 liter vessel at room temperature is evacuated to a pressure of 50 mTorr, how many moles of gas are in the vessel? How many molecules is this? How many molecules per cubic centimeter is this?

Kinetic Description of the Behavior of Gases:

As the name may suggest, the kinetic theory of gases has to do with describing how gases behave under the influence of external forces that induce motion. There are four basic assumptions that provide the foundation of the kinetic theory of gases:

- 1) Gases are comprised of a large number of extremely small particles (atoms or molecules).
- 2) These gas molecules are in constant, rapid motion in a chaotic manner.
- 3) The distances between individual gas molecules are large compared with the diameter of the molecules.
- 4) The molecules exert no force on one another, or on the walls of a container except during collisions.

Velocity of Gas Molecules:

The speed at which gas molecules travel is independent of pressure, but is a function of the temperature and molecular weight of the gas.

$$v = 1.455 \times 10^4 \sqrt{\frac{T}{M}} \left[\frac{cm}{sec} \right]$$

V = average molecular velocity [cm/sec]

T = absolute temperature [K]

M = molecular weight of gas [grams/mol]

Problem:

Calculate the velocity of a nitrogen molecule at 100 °C.

Mean Free Path:

The distance a gas molecule can travel (on the average) is a function of total pressure and the diameter of the gas molecules.

$$L(cm) = \frac{1}{\sqrt{2}PNd^2}$$

L = mean free path [cm]

P = pressure, Torr

d = molecular diameter [cm]

N = number density of particles [cm⁻³]

Problem:

For a vacuum system at room temperature having a volume of 50 liters, and containing nitrogen gas at a pressure of 5×10^{-6} Torr, find the number density, N , and the mean free path, L {the molecular diameter of N_2 is 3.8\AA or 3.8×10^{-8} cm}

For most clean vacuum systems the majority of the gas load may be assumed to be nitrogen, and at room temperature the following approximation may be used to calculate the mean free path for N_2 molecules:

$$L = \frac{5.0 \times 10^{-3}}{P}$$

L = mean free path [cm]

P = pressure [Torr]

Collisions of Gaseous Species

Gas molecules travel in straight lines between collisions and tend to strike all exposed internal surfaces of the vessel in which they are contained. Pressures that we measure using various types of gauges are the result of the collective impacts of these gas molecules on the inner surfaces of the containing vessel. The rate of impact (or impingement rate) of gas molecules per second per square centimeter of surface area is a function of the speed of the molecules and the gas density:

$$I = Nv/4 \quad (1/\text{cm}^2 - \text{sec})$$

N = molecular density, [cm^{-3}]

V = molecular velocity [cm/sec]

I = impingement rate [$\text{cm}^{-2}\text{-sec}^{-1}$]

Usually, the quantities that we can easily measure are pressure and temperature, so, the same equation expressed in terms of these units is:

$$I = 3.5 \times 10^{22} \frac{P}{\sqrt{W_m T}} \quad (1/\text{cm}^2\text{-sec})$$

Problem:

What is the impingement rate for nitrogen molecules on the inner surface of a vacuum vessel having a pressure of 5×10^{-6} Torr and a temperature of 25°C ?

What am I for the same system at 5×10^{-9} Torr?

Flow of Gas Through an Orifice

The number of gas molecules leaving is:

$$I = Nv/4 \quad (1/\text{cm}^2 - \text{sec})$$

The volume of gas leaving may be calculated by dividing the number of gas molecules leaving by the number of molecules per unit volume (N).

The volumetric flow rate of gas through a hole is independent of the gas pressure; but depends on the gas velocity, v, which is a function of temperature and molecular weight.

For the situation in which the mean free path of gas molecules is greater than the diameter of the opening in the wall of the chamber, the volumetric flow rate (s) is given by:

$$S = \frac{v}{4} = 1.455 \times 10^4 \sqrt{\frac{T}{W_m}}$$

S= volumetric flow rate [L/s]

T= absolute temperature [K]

W_M = molecular weight [g/mole]

Modes of Gas Flow Under Various Vacuum Conditions

The three modes of gas flow that we will be interested in describing are:

1. turbulent (or viscous).
2. laminar (or transition) .
3. molecular flow.

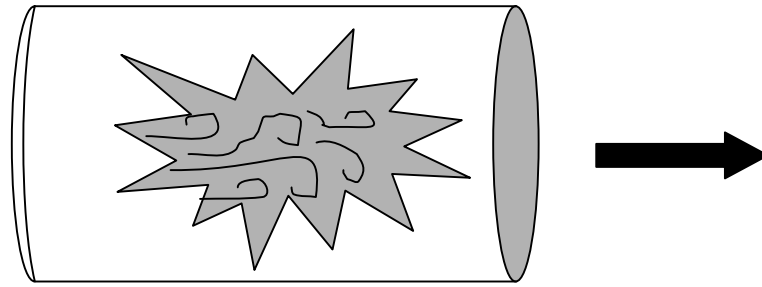
The flow regime created when air is induced to move through cylindrical tubes is a function of the tube diameter and the average pressure

$DP \geq 0.18$ (Viscous Flow)

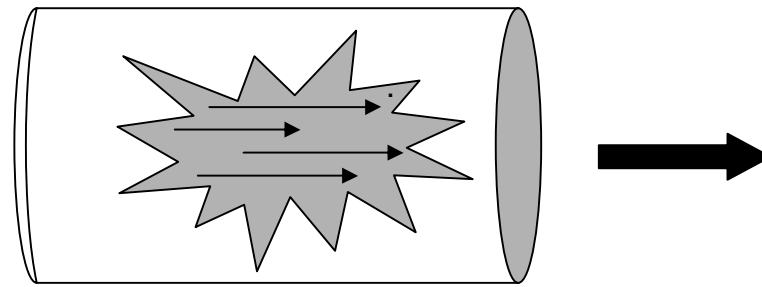
$DP \leq 0.004$ (Molecular Flow)

$0.004 \leq DP \leq 0.18$ (Transition Flow)

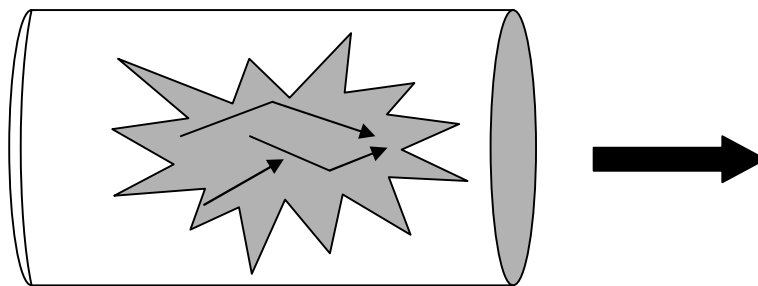
(D is the inside diameter, in inches, and P is the average pressure in Torr)



Viscous flow of gas molecules during pump down



Gas molecules in transition flow conditions. Mean free path is roughly equivalent to the pipe diameter.



Gas molecules in molecular flow conditions. Mean free path is greater than 1.5 times the pipe diameter.

Gas Flow Rates

Volumetric:

Flow rate (S) is the volume amount of gas that passes by a point per unit time (liters/second or cubic feet/ minute). The volumetric flow rate may be considered to be the pumping speed of a system at a specified point in the conductance path.

Quantitative:

Flow rate (Q) is the amount of gas that passes by a point per unit time.(Torr liters/second). The quantitative flow rate is also referred to as the throughput, or mass flow, and is constant everywhere in the vacuum system, unless gas is leaking or is being captured or condensed along the path.

$$Q = SP$$

Q= quantitative flow rate [torr-liters/sec.]

S= volumetric flow rate [liters/sec]

P= pressure [torr]

Conductance in a Vacuum System

Gases moving through conductance elements (pipes, tubes, vessels, and orifices) in a vacuum system encounter resistance to their motion. At higher pressures, this resistance is a function pressure difference and geometry of the conductance element.

$$Z = \frac{P_1 - P_2}{Q}$$

Z= resistance [sec/liter]

P= pressure [Torr]

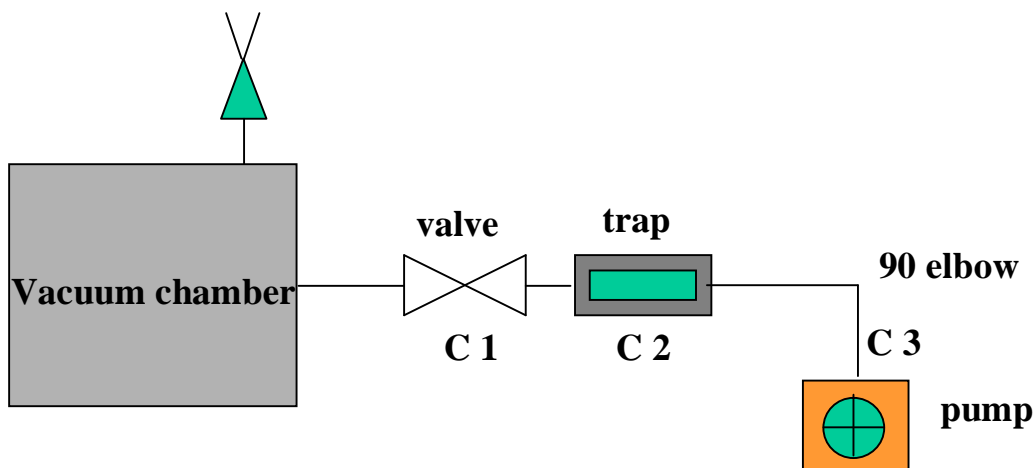
Q=flow rate [Torr-L/s]

Conductance is the inverse of resistance and therefore,

$$C = \frac{1}{Z} = \frac{Q}{P_1 - P_2}$$

C= conductance [liter/sec]

Conductance elements connected in series:



Conductance elements connected in Series

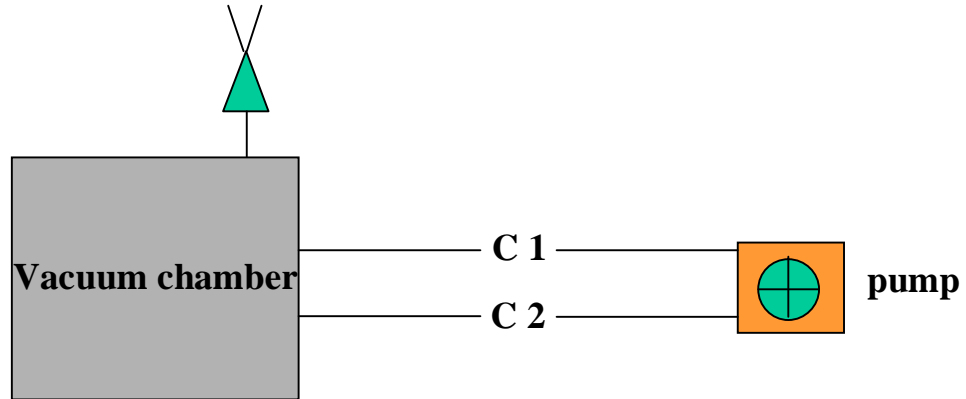
$$\frac{1}{C_T} = \frac{1}{C_1} + \frac{1}{C_2} + \frac{1}{C_3} + \dots$$

C_T = total conductance for elements $C_1, C_2, C_3 \dots$ that are connected in Series

Problems

For the vacuum system shown in figure, if $C_1 = 50$ L/s, $C_2 = 100$ L/s and $C_3 = 100$ L/s what is the total conductance of the three elements?

Conductance elements connected in parallel:



Conductance elements connected in parallel

$$C_T = C_1 + C_2 + C_3 + \dots$$

C_T = total conductance for elements C_1 , C_2 , etc. which are connected in Parallel

Problems

For the vacuum system shown in figure, if C_1 and C_2 , have the same values as in the previous problem, what is the net conductance of the assembly?

2- Production of Low Pressures – Vacuum Pumps

Kind of Vacuum Pump:

1. Gas Transfer Pumps.
2. Gas Capture Pumps.

Gas Transfer Pumps:

1. Mechanical positive displacement pumps.
2. Kinetic pumps.

Mechanical positive displacement pumps:

1. Reciprocating positive displacement pumps.
 - (a) Diaphragm Pump.
 - (b) Piston Pump.
2. Rotary positive displacement pumps.
 - (a) Liquid Ring Pump.
 - (b) Sliding Ring Pump.
 - (c) Roots Pump.
 - (d) Rotating-Plunger Pump.

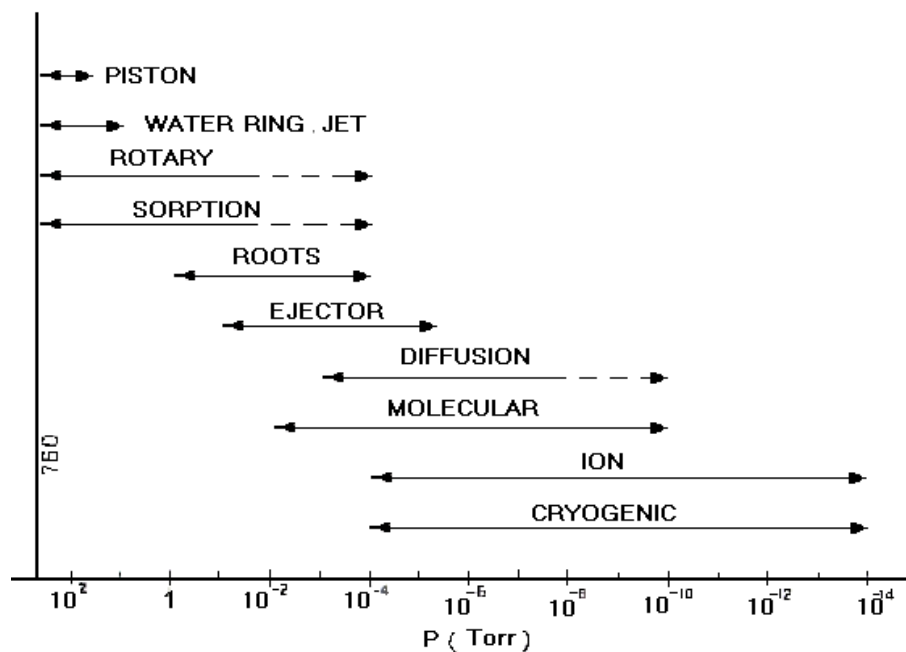
Kinetic Pumps:

- (a) Diffusion Pump.
- (b) Ejector Pump.

Gas Capture Pumps:

1. Ion-pumps.
2. Sorption pumps.
3. Cryo pump.
4. Getter pump.

Pressure ranges of vacuum pumps:



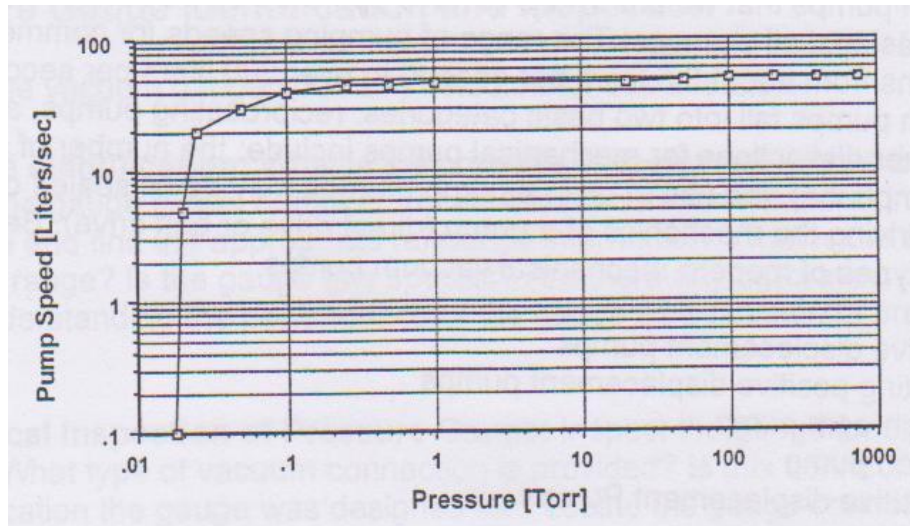
Mechanical Vacuum Pumps:

Theory of Operation:

Mechanical vacuum pumps work by the process of positive gas displacement, that is, during operation the pump periodically creates increasing and decreasing volumes to remove gases from the system, and exhaust them to the atmosphere. In most designs a motor driven rotor spins inside a cylindrical stator of larger diameter. The ratio of the exhaust pressure (atmospheric) to the base pressure (lowest pressure obtained at the vacuum pump inlet) is referred to as the **Compression Ratio** of the pump. For example, if a mechanical vacuum pump obtains a base pressure of 15 mTorr, its compression ratio is:

$$\frac{760\text{Torr}}{0.015\text{Torr}} = 51000$$

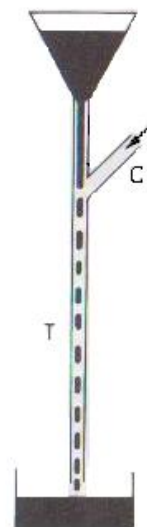
Another more common way to state this is to say that the pump has a compression ratio of 51,000:1. At pressures above 1 Torr, rotary mechanical pumps have a fairly constant pumping speed. The pumping speed decreases rapidly below this pressure, and approaches zero at the pump's base pressure. Most manufacturers of mechanical vacuum pumps will include in their product literature information on the pump's performance including a pump speed curve.



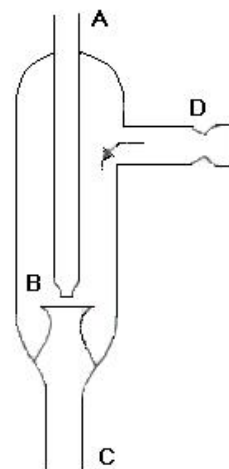
Liquid pumps:

1. Sprengel pump: this pump based on the principle shown in fig. the mercury drops introduced in the vertical capillary T, capture between them air bubbles. In this way the system evacuates air from the side tube C and exhausts it through the mercury at bottom, to atmosphere.

2. Water-jet pump: water supplied from a fast-running tap is fed into the nozzle at A. This water stream then emerges at high velocity from the converging jet B. the jet is surrounded by a cone to prevent splashing and also guide the water stream to waste at C. A side tube D is connected to the vessel to be evacuated.



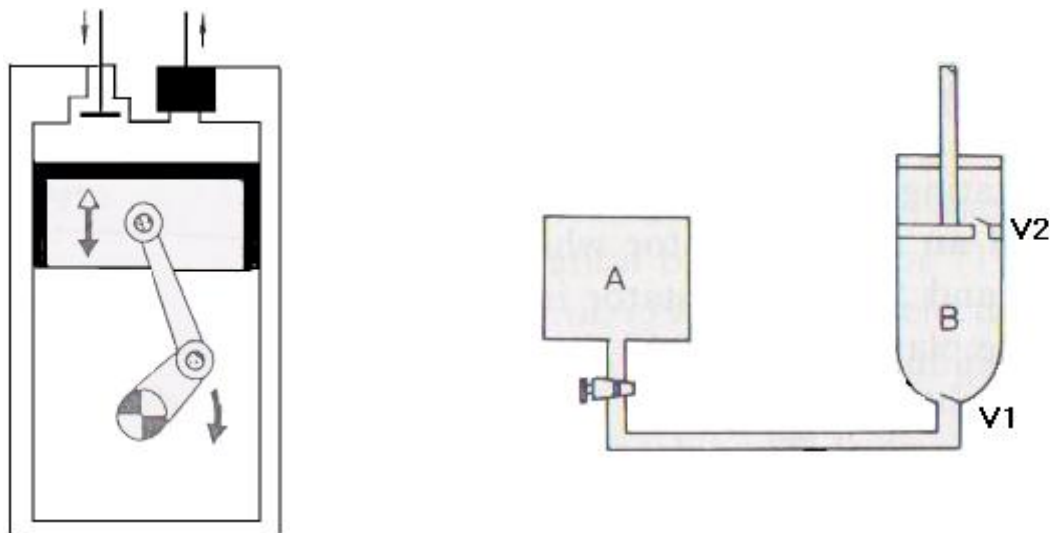
Sprengel pump



Water ejector pump

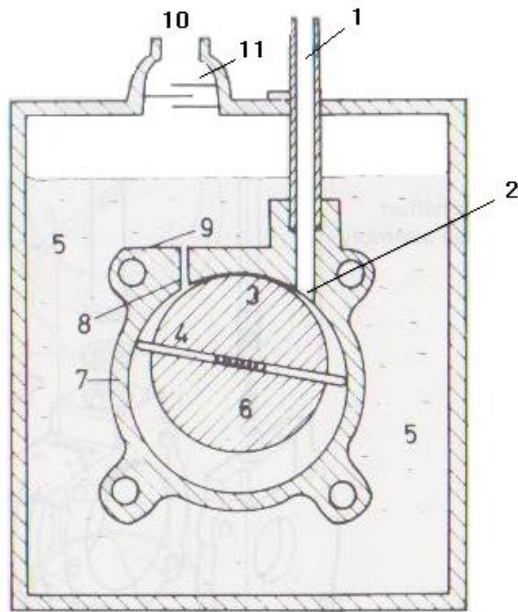
Piston pumps:

The piston pumps have valves so arranged that air is pumped out of vessel A. As the piston is raised from the lowest position, the valve V_2 closes, and the motion of the piston then reduces the pressure in B. The pressure difference between A and B will open valve V_1 and gas will pass from A to B. As the piston descends, the pressure in B increases, V_1 closes, V_2 opens and the gas in B escapes through V_2 .



Rotating-vane pumps:

Rotary vane pumps typically have an electric motor driven rotor (either belt or directly driven) which has one to three sliding vanes that maintain close contact with the inner wall of the cylindrical stator. The vanes are metal in oil sealed pumps, and carbon in dry pumps. Centripetal force acts upon the vanes in the spinning rotor so as to force them against the inner sealing surface of the stator. In some mechanical pumps springs are used to augment this action. Rotary vane pumps may be of the single or double stage design. Single stage pumps are simpler, having only one rotor and stator, and are less expensive. The base pressure one can expect from a good single stage mechanical pump is about 20 mTorr. In a two stage design, the exhaust port of the first stage is connected to the inlet port of the second stage which exhausts to atmospheric pressure. Two stage pumps may attain a base pressure of one to two millitorr, but are more expensive than single stage pumps.

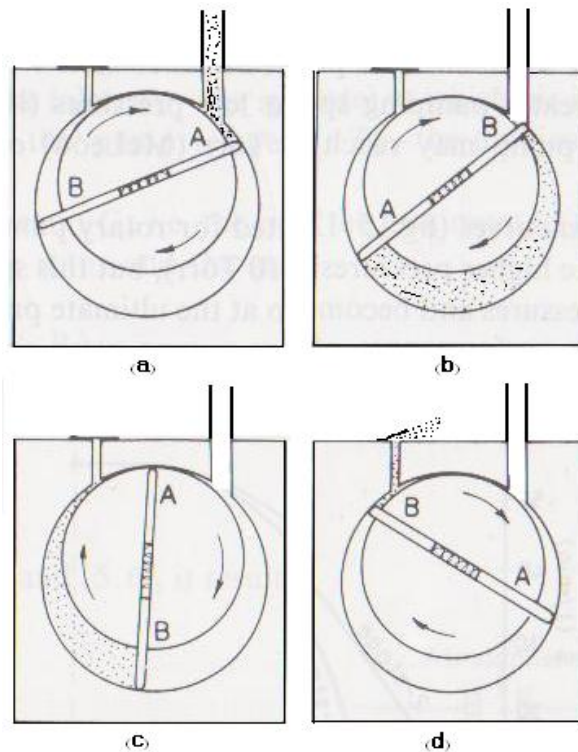


Cross section of a rotating –vane pump.

1. Inlet tube; 2. Inlet port; 3. Top seal; 4. Vanes; 5. Oil; 6. Rotor; 7. Stator; 8. Exhaust port; 9. Exhaust flap valve with backing plate; 10. Exhaust outlet; 11 .Oil splash baffles

The oil in an oil sealed pump serves three important functions:

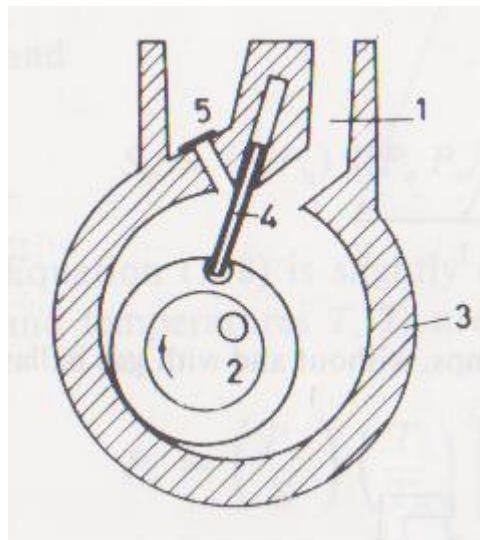
- A) providing a vacuum seal at the pump exhaust.
- B) as a lubricant and
- C) provides cooling for the pump.



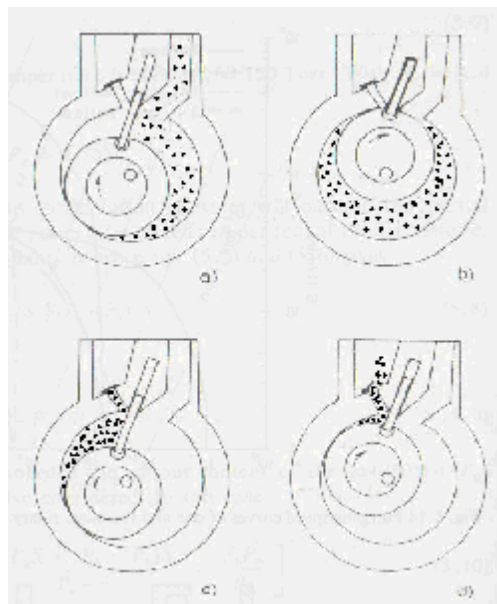
Action of the rotating-vane pump.

Sliding-vane pumps:

These pumps have a single vane which slides in a slot cut in the stator between the inlet and exhaust ports. In this type the vane is fixed by a bearing to the outer sleeve of the rotor. The rotor rotates eccentrically, which makes the vane slide in its slot in the casing. The whole assembly is submerged in oil which completes the vacuum seals and provides lubrication. The pumping cycle is shown in figure, the volume of gas wept around the pump at each rotation is that between the stator and the rotor at the instant when the rotor passes the vane slot.



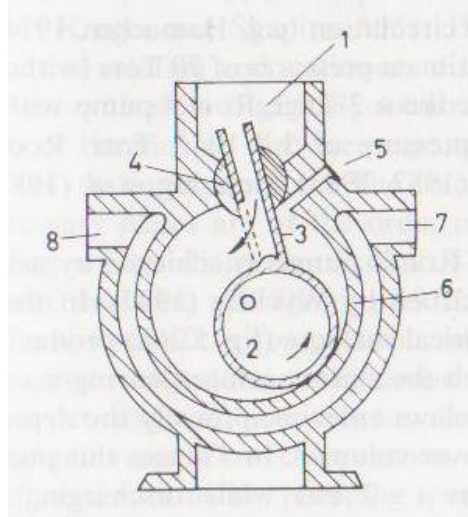
Sliding-vane pump, 1. Inlet port; 2. Rotor; 3. Stator; 4. Vane; 5. Exhaust.



Mode of action of a sliding-vane pump; (a) induction; (b) isolation; (c) compression; (d) exhaust.

Rotating-plunger pumps:

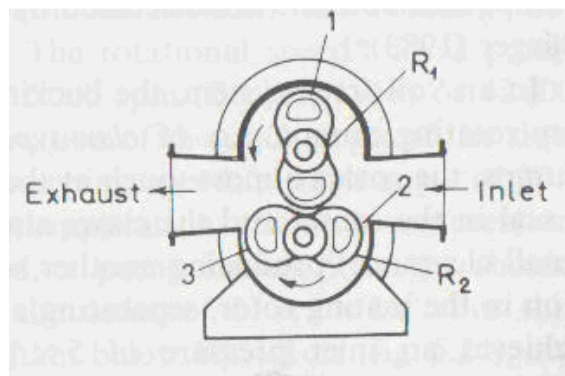
In this pump the sliding vane is replaced by a hollow tube which is rigidly attached to the outer sleeve of the rotor. The tube rolls and slides in a bearing, and an appropriate hole cut in the side of the tube allow gas to be drawn into the inlet side of the pump.



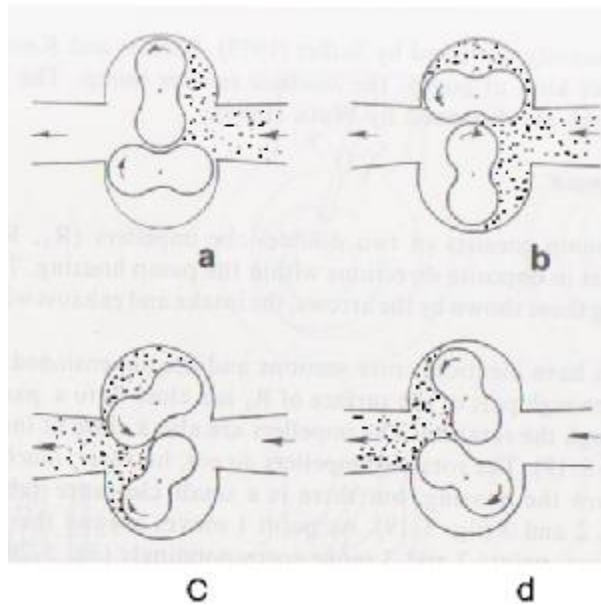
Rotating-plunger pump. 1. Intake; 2. Rotating-plunger; 3. Sliding tube; 4. Bearing; 5. Exhaust; 6. Stator; 7. Cooling water inlet; 8. Cooling water outlet.

Roots pumps:

The Roots pump consists of two double-lobe impellers (R_1 , R_2). These are rotated in opposite directions within the pump housing. The impellers have identical Cross sections and are dimensioned and arranged so that a large enough part of the surface of R_1 is a close fit to a part of the surface of R_2 through the rotation. The impellers are also a close fit inside the pump housing. The rotating impellers do not, however, touch one another, nor do they touch the housing, but there is a small clearance (about 0.1 mm) at the point 1, 2 and 3 .



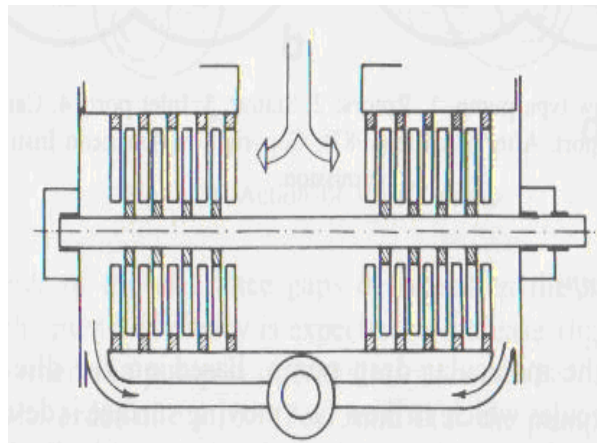
Roots pump



Action of Roots pump.

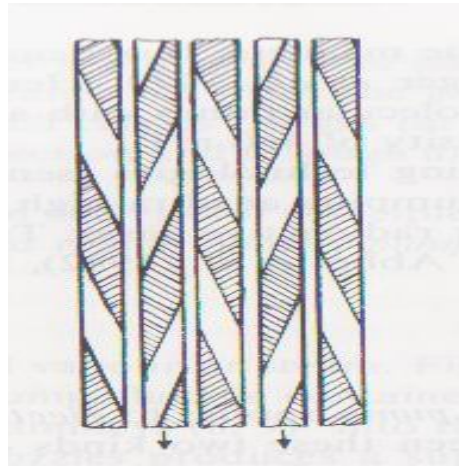
Molecular pumps:

The principle of the molecular pump, based on the directional velocity imparted to gas molecules which strike a fast moving surface. This principle is applied in modern turbomolecular pumps, which contain alternate axial stages of rotating and stationary discs and plates.



Molecular pump

The discs and plates are cut with slots set at an angle (20°) so that gas molecules caught in the slots of the moving disc are projected preferentially in the direction of the slots in the stationary plates. The running clearances between the rotating and stationary plates are of the order of 1 mm.



Details of the rotor and stator plates of the molecular pump