Lecture WS 2002/2003

Modern Methods in Heterogeneous Catalysis Research:
Theory and Experiment

Vacuum / electrons and ions

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vacuum regimes, pumps, pressure measurement, generation of electrons and ions, deflection, energy filtering and detection

Literature:

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Contents

1. Vacuum

1.1 Vacuum ranges, pressure, gas flow, materials

Pressure units:
1 Pa = 1 N/m^2;
1 bar = 10^5 Pa;
1 mbar = 1 hPa;
1 Torr = 1.333 mbar = 133.3 Pa.

Def.: Vacuum exists if the pressure is below atmospheric pressure.

Applications of vacuum:

Phenomenon	**Typical application**
Uniform and isotropic pressure of the atmosphere	Holding, lifting, transport (vacuum cleaner), forming, packing technology
Thermal insulation	Dewar
Evaporation at low vapor pressure	Drying, freeze-drying, vacuum destillation
Avoidance of light absorption	UV spectroscopy
Avoidance of impacts of particle beams with gas	Valves, accelerators, plating (evaporation, sputtering)
Avoidance of chemical reactions	Valves, plating (evaporation, sputtering), analytics, surface science

Vacuum ranges and characteristics:

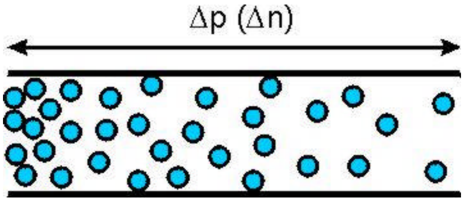
Vacuum range	**Pressure (Pa, *mbar*)**	**Mean free path l (m) (approx.)**	**Characteristics**
Grobvakuum *low vacuum*	10^5 - 10^2 *10^3 - 10^0*	10^{-7} – 10^{-4}	**continuum flow**, turbulent or viscous; range of mechanical force of atm. pressure; evaporation, drying, degassing, destillation
Feinvakuum *mean vacuum*	10^2 – 10^{-1} *10^0 – 10^{-3}*	10^{-4} – 10^{-1}	transition: **Knudsen flow**; evaporation, drying, degassing, destillation
Hochvakuum *high vacuum*	10^{-1} – 10^{-5} *10^{-3} – 10^{-7}*	10^{-1} - 10^3	**molecular flow**; avoidance of particle impart and chem. reactions with gas, thermal insulation
Ultrahochvakuum *ultrahigh vacuum*	10^{-5} – 10^{-9} *10^{-7} – 10^{-11}*	10^3 - 10^7	**molecular flow**; clean surfaces, accelerators

Important quantities		
Mean velocity of gas particles $c_{av} = 1.45\times10^{2}\,(T/M)^{1/2}$ m/s, **M in g/mol**	At 273 K: H_2 He N_2	m/s 1693 1201 454
Mean free path of gas particles $l_{av} = 2.44\times10^{-26}\,T/(s\,p)\,m$, s = cross section in m^2, p in mbar	At 273 K, N_2: 1000 mbar 1 mar 10^{-3} mbar 10^{-6} mbar 10^{-10} mbar	 5.9×10^{-8} m 5.9×10^{-5} m 5.9×10^{-2} m 5.9×10^{1} m 5.9×10^{5} m
Flux of molecules striking 1 m^2 of surface: $j_N = 2.63\times10^{26}\,p/(MT)^{1/2}\ m^{-2}\,s^{-1}$, p in mbar, M in g/mol. For comparison: Density of atoms on solid surfaces Pt(111): $1.5\times10^{19}\ m^{-2}$ Si (001): $6.8\times10^{18}\ m^{-2}$	N_2 at 273 K: 1000 mbar 1 mbar 10^{-3} mbar 10^{-6} mbar 10^{-10} mbar	 $3\times10^{27}\ m^{-2}\,s^{-1}$ $3\times10^{24}\ m^{-2}\,s^{-1}$ $3\times10^{21}\ m^{-2}\,s^{-1}$ $3\times10^{18}\ m^{-2}\,s^{-1}$ $3\times10^{14}\ m^{-2}\,s^{-1}$

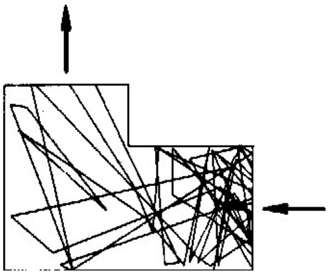
Flow

One distinguishes three flow regimes:

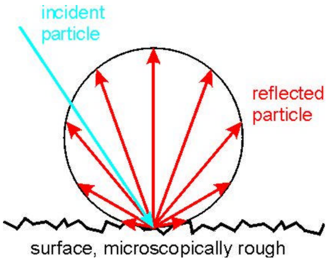
Continuum flow	$p > \sim 1$ mbar
Knudsen flow	1 mbar $> p > 10^{-3}$ mbar
molecular flow.	$p < 10^{-3}$ mbar



***Continuum flow**:*
Gas can be considered as continuum; driven by pressure difference = density difference, molecule-molecule impacts; Molecule-molecule impacts decisive, molecule-wall impacts negligible



***Molecular flow**:*
Molecule-molecule impacts negligible, molecule-wall impacts decisive.
Example: simulation of flow in an elbow, 15 in, 3 out, 12 back. (O'Hanlon, fig. 3.3)



*If accomodated to the surface or if scattered by a rough surface, molecules loose directional memory after an impact with the wall: **cosine distribution** of scattered molecules.*

According to the general gas law

$p\,V = n\,R\,T$, (n number of moles),

the product $p\,V$ (mbar l) at constant T indicates a certain amount of gas or matter. In vacuum technology, one uses this "$p\,V$-value".

The gas flow (amount of gaseous matter per s) or **throughput** (Saugleistung)is then given by

$q_{pV} = p\,V\,/\,\Delta t$ (mbar l s^{-1}).

Most pumps, however, can transport a certain volume per sec, often independent of p over large pressure ranges. This **volume flow rate** (Saugvermögen) S has the dimension (l s^{-1}). The same applies for the leak rate q_l and the conductance of a vacuum device (tube, valve etc.) L. Devices like tubes, valves or apertures between pump and chamber reduce the volume flow rate at the chamber to an effective volume flow rate (effektives Saugvermögen) S_{eff}:

$$\frac{1}{S_{eff}} = \frac{1}{S} + \frac{1}{L}$$

with

$$\frac{1}{L} = \frac{1}{L_1} + \frac{1}{L_2} + \ldots + \frac{1}{L_n}\,.$$

Conductance of tubes and orifices

Tubes ($l \geq 10$ d) , air, 293 K (Knudsen):

$$L = 135\frac{d^4}{l}\bar{p}_m + 12.1\frac{d^3}{l}\frac{1+192d\,p_m}{1+237d\,p_m} \quad (\mathrm{l\,s^{-1}}),\ \ d, l \text{ in cm},$$

$p_m = (p_1 + p_2)/2$.

Molecular flow limit:

$L = 12.1\ d^3/l \quad (\mathrm{l\,s^{-1}})$.

Orifices (Prandtl), air, 293 K:

$$L_{visc} = 76.6\mathrm{d}^{\,0.712}\sqrt{1-\mathrm{d}^{\,0.288}}\,\frac{A}{1-\mathrm{d}} \qquad (\mathrm{l\,s^{-1}}),\ A \text{ in cm}^2,$$

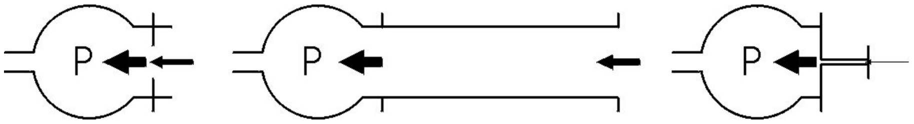
$\mathrm{d} = p_2/p_1 < 1$.
(for special cases see literature).

Molecular flow limit:
$L = 11.6\,A \quad (\mathrm{l\,s^{-1}})$.

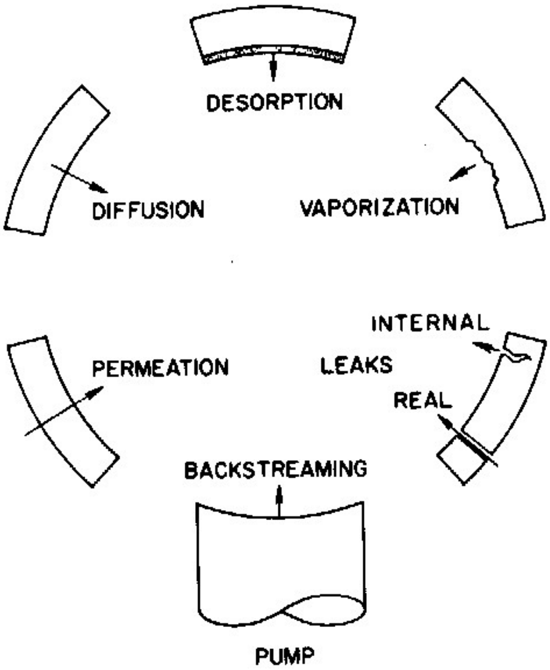
The conductances for other gases differ, mainly for He (molecular flow: multiply by 2.64) and H_2 (molecular flow: multiply by 3.77).

Examples (molecular flow regime):

Pump S=500 l s^{-1}, d=15 cm	+ reduction flange d=7 cm	+ tube d=15 cm l=50 cm	+ tube d=1 cm, l=10 cm	+ tube d=0.5 cm, l=10 cm
L (l s^{-1})	446	817	1.21	0.15
S_{eff} (l s^{-1})	236	310	1.21	0.15
S_{eff}/S	0.47	0.62	0.0024	0.0003



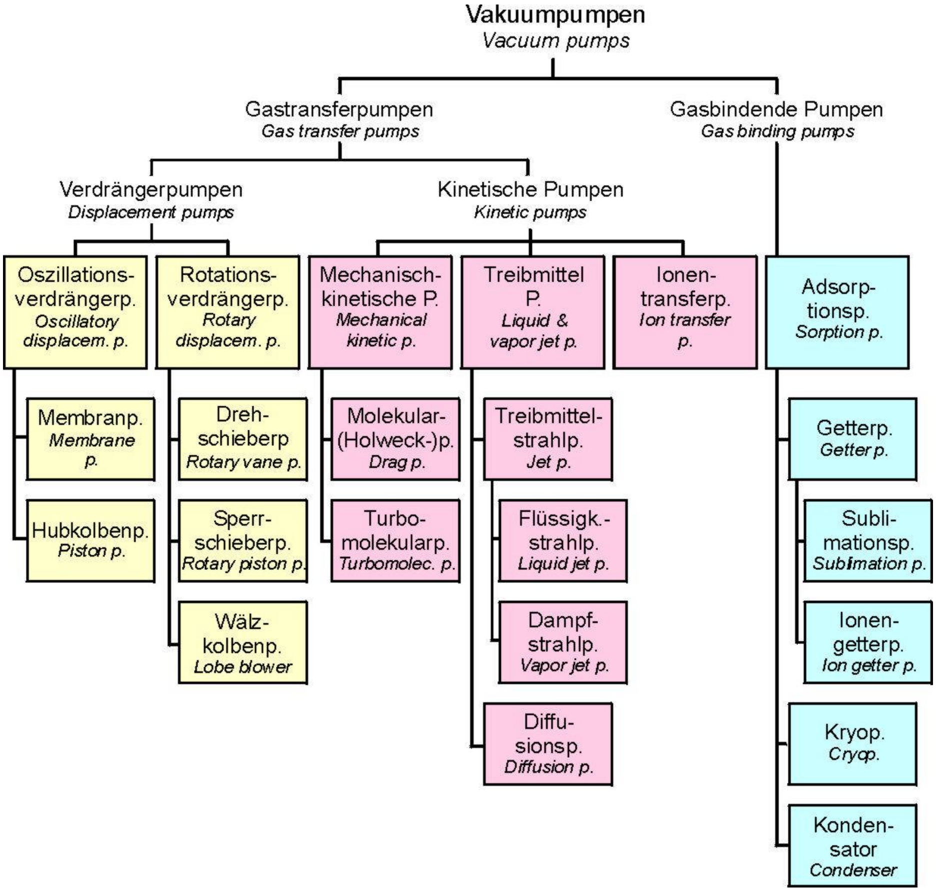
Gas sources



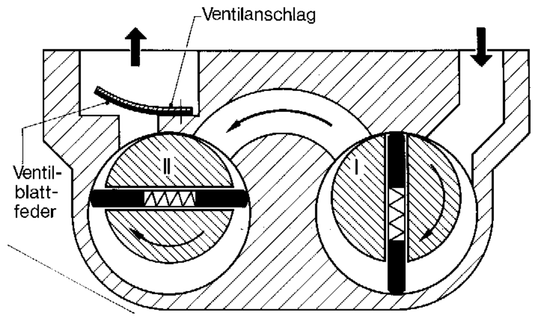
Sources of gas in a vacuum system
(O'Hanlon fig. 4.1)

Source	**Avoid by:**
Backstreaming	cold trap, right type of pump
Permeation, diffusion, desorption, vaporization	choose right materials for UHV: stainless steel, OHFC copper, glass, ceramics, aluminum, (W, Mo, Ta, Ni)
Internal leaks	correct construction and production (no tapped holes, right welding techniques. . .)
External leaks	undamaged sealing surfaces on flanges and valves experienced welding

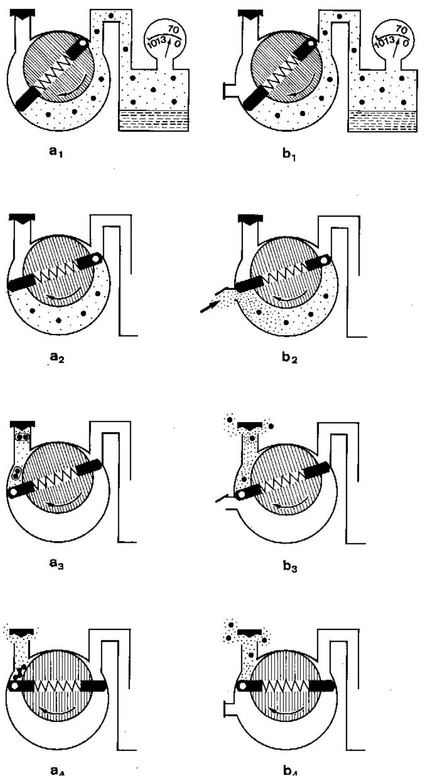
1.2 Pumps



Rotary vane pump
low and mean vacuum



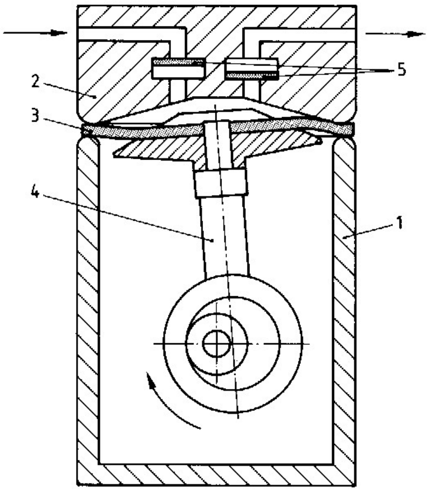
Schematics of a two-stage rotary vane pump



Right: Gas ballast
$a_1 - a_4$: without gas ballast. When a vapor is compressed beyond its equilibrium vapor pressure at the working temperature, it condenses, cannot be exhausted and may form an emulsion with the pump oil.
$b_1 - b_4$: with gas ballast. When air is admitted after the vacuum side is separated from the pumping volume (b_2), the partial pressure of the vapor is not increased during exhaust and condensation is avoided.

Advantage:
Robust, final pressure sufficiently low (p_{final} <10^{-2} mbar) for turbo and diffusion pumps
Disadvantage:
not oil-free, not resistant to many chemicals

Membrane pump
low vacuum

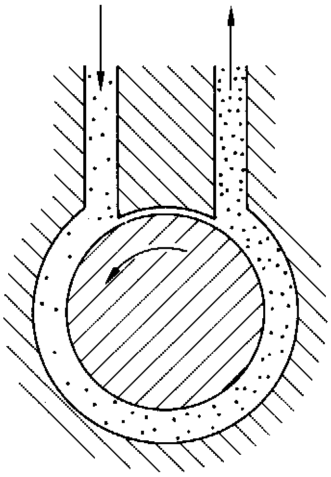


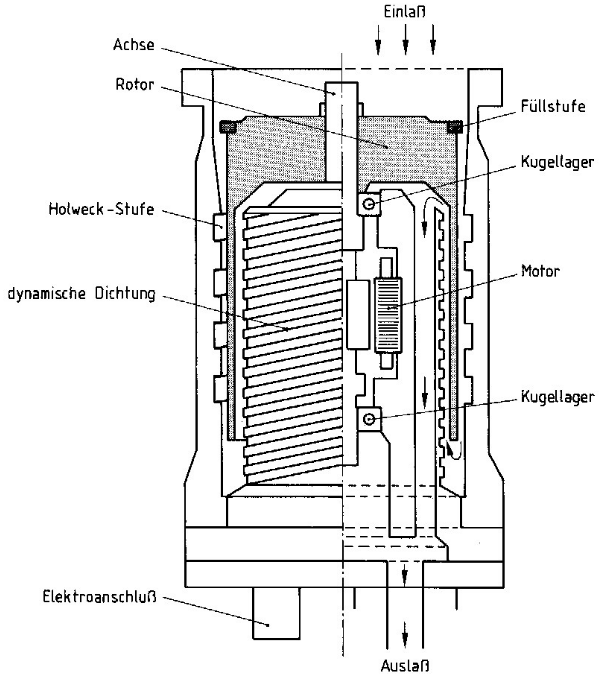
Membrane pump
1 housing
2 pump head
3 membrane
4 connecting rod
5 inlet and outlet valves

Stages	*final pressure (mbar)*
1	*80*
2	*9*
3	*2*
4	*0.7*

Advantage:
Robust, oil-free, resistant against aggressive chemicals possible
Disadvantage:
rel. high final pressure (p_{final} >1 mbar), regular membrane exchange necessary, loud, vibrations

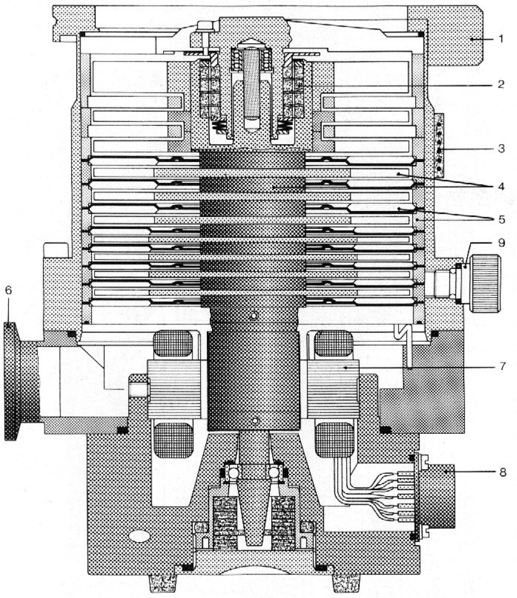
Molecular pumps
HV, UHV





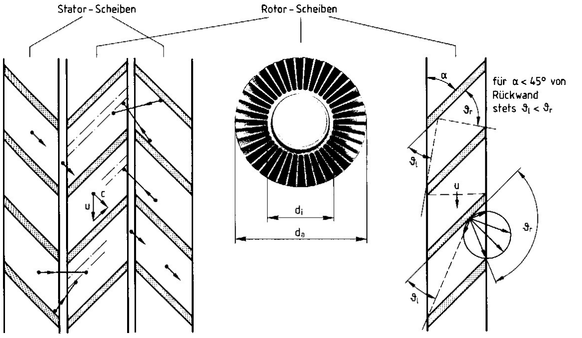
Principle of the molecular pump.

Holweck pump, p_{exit}»4 mbar
The gas is "screwed" out along a spiral-groove

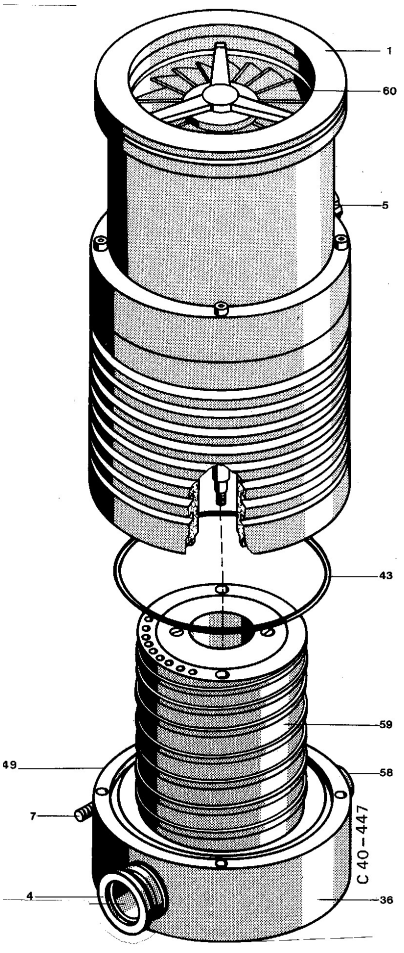


1 UHV-Anschluß
2 Lager
3 Heizung
4 Rotor/Rotorscheibe
5 Stator/Statorscheibe
6 Vorvakuumanschluß
7 Motor
8 Elektrischer Anschluß
9 Flutanschluß

Turbomolecular pump; $p_{exit}<10^{-2}$ *mbar*



Principle of the turbomolecular pump.
Left: stack of stator – rotor – stator disks. The upper gas particle will move freely through the downwards moving rotor. The lower gas particle will hit a rotor blade. Since it is oblique, desorption (cos-distribution, right), it will preferentially move towards the right.

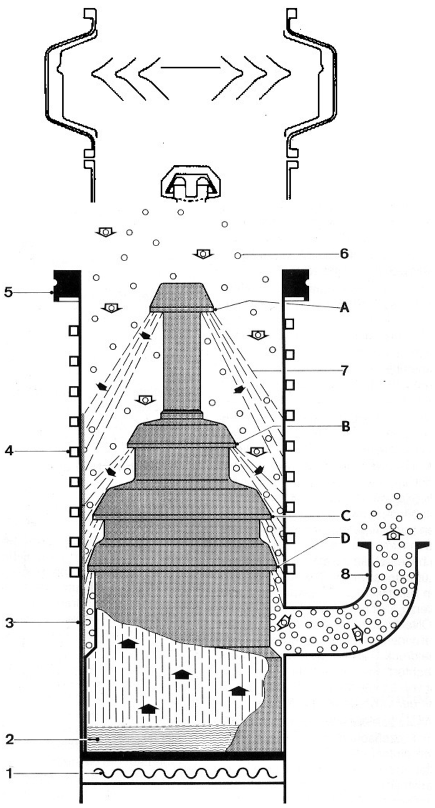


Combined turbomolecular and Holweck pump, sometimes called drag-pump. $p_{exit} \gg 4$ *mbar.*

Advantage:
Clean UHV, $p_{final}<10^{-10}$ mbar, no preferential pumping
Disadvantage:
not chem.-resistent, expensive, (bearings sensitive to shocks, vibrations)
Combination drag pump with magnetic bearings + membrane pump: completely oil-free

Diffusion pump

HV



Turbulence at the edge of the top jet stage is the main source of oil back-streaming.
A cold cap (Düsenhut) reduces it considerably.
Further reduction by a water-cooled baffle and (not shown) by a liquid N_2 cooled trap.

Oil diffusion pump.
1 heater
2 evaporating oil
3 housing, cooled
4 water cooling (also air possible) for oil condensation
5..high vacuum flange
6..gas to be pumped
7 oil vapor jet
8 exhaust
A – D pumping stages

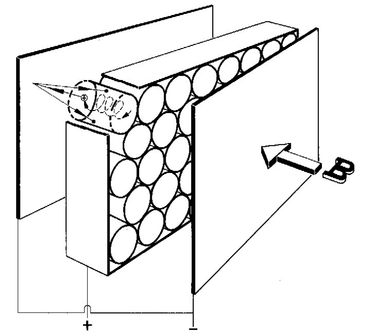
$p_{exit} < \sim 10^{-2}$ *mbar,*
suitable roughing pump:
e.g. rotary vane pump

Limitation of performance:
Oil back-streaming

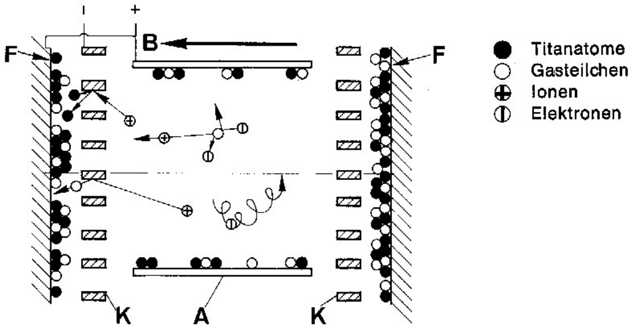
Advantage:
Cheap hifg-vacuum pump, $p_{final} < 10^{-6}$ mbar (10^{-10} mbar with cold trap), almost every size possible, no preferential pumping
Disadvantage:
Not oil-free, hot oil must not be exposed to air, not suitable for chemicals reacting with hot oil

Ion getter pump

(HV), UHV



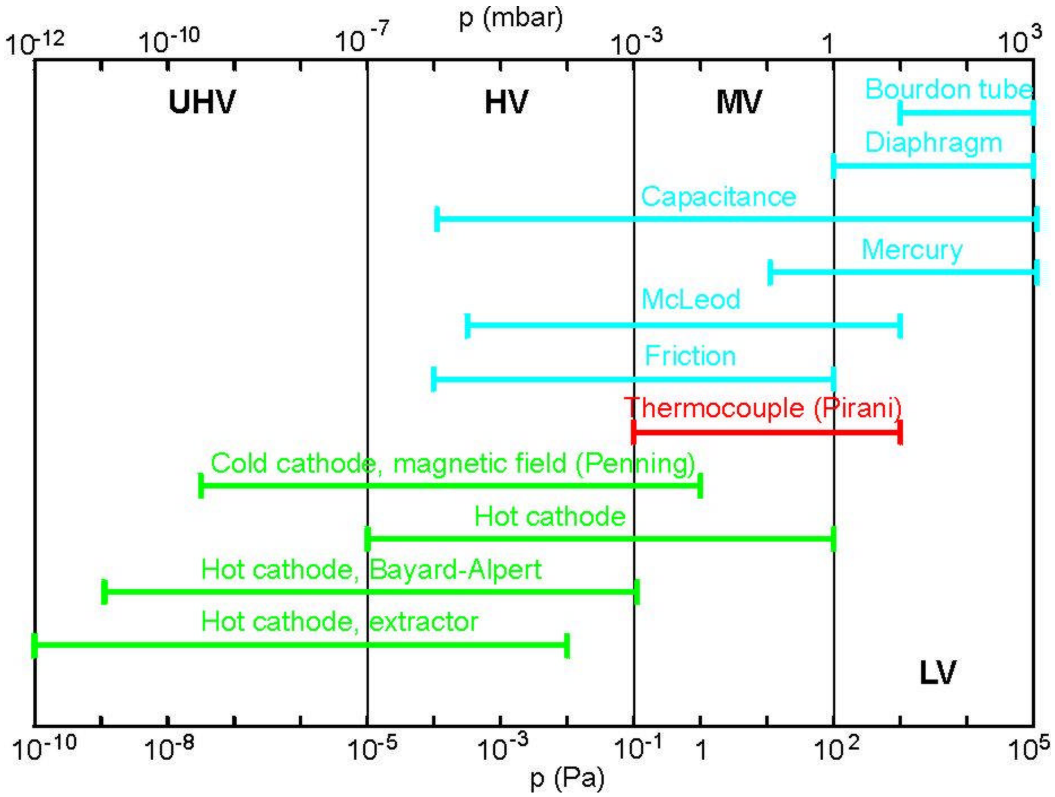
Principal arrangement of a diode pump. In the triode pump, a grid-like cathode is inserted between anode structure and wall.



Triode pump, principle. Electrons are forced by the magnetic field into long spiral trajectories. They ionize molecules which hit the cathode (K), sputter off Ti which deposits on the wall (F) and forms a chemisorption getter. Most ions are neutralized at the cathode, travel further, penetrate into the outer wall and are buried. This is the pumping mechanism for inert gases.

Advantage:
Cheap UHV-pump, p_{final}<10^{-10} mbar, oil-free, almost every size possible, no mech. parts, no noise
Disadvantage:
Usable only at p<10^{-6} mbar (shortly 10^{-4} mbar), gas-dependent pumping, difficulties with large amounts of inert gases

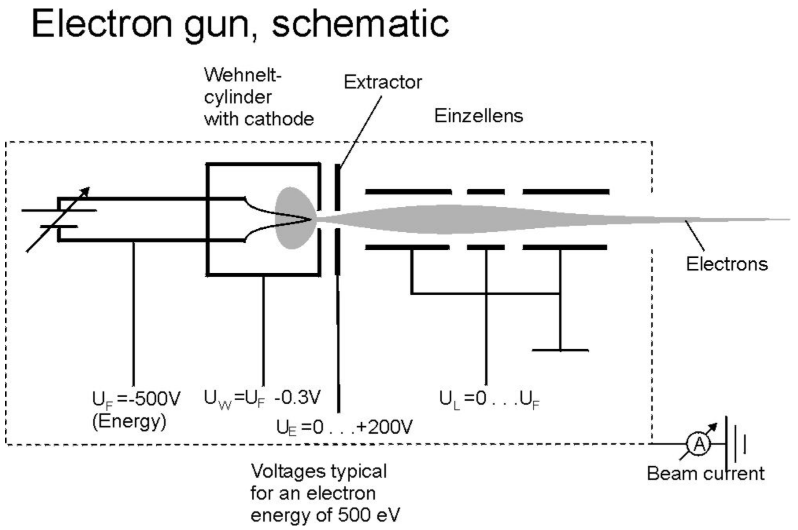
1.3 Pressure measurement



Pressure ranges for different vacuum gauges.
Blue: Direct measurement of force.
Red: Indirect, p-dependence of thermal conductivity.
Green: Indirect, p-dependence of ion current in electrical discharge.

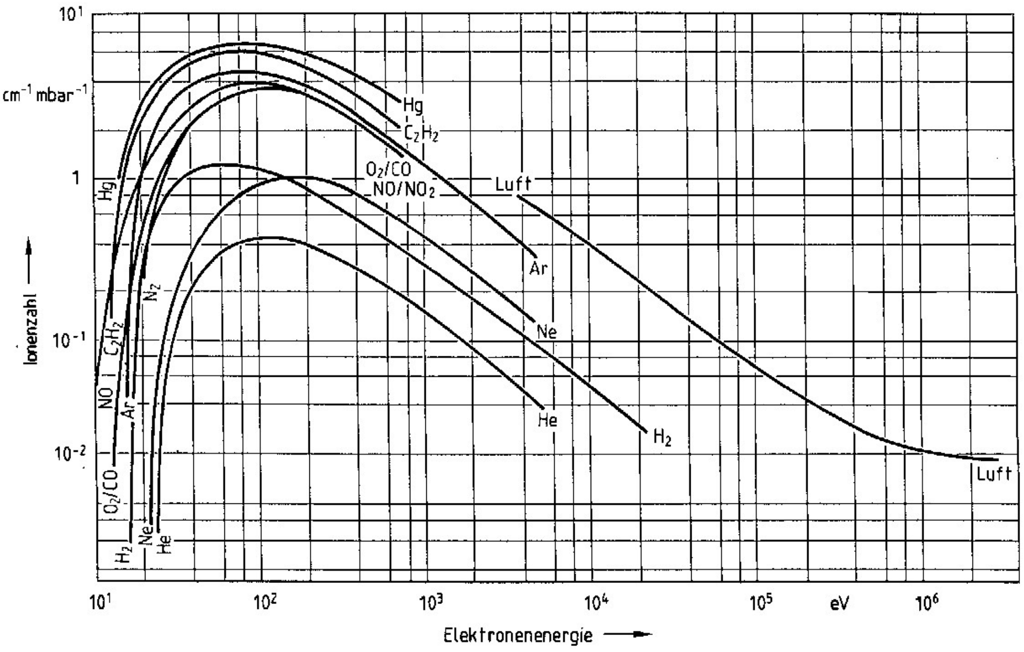
2. Electrons, ions

2.1 Electron beams

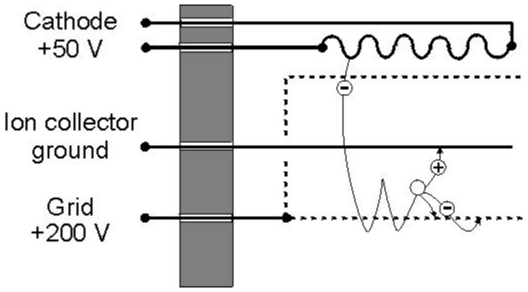


The Wehnelt voltage is slightly negative with respect to the cathode. In this way, a space charge cloud is formed. The extractor extracts only a small portion of the produced electrons through the hole of the Wehnelt. In this way, the beam current is almost independent of variations of the cathode emission and the effective size of the source gets smaller.

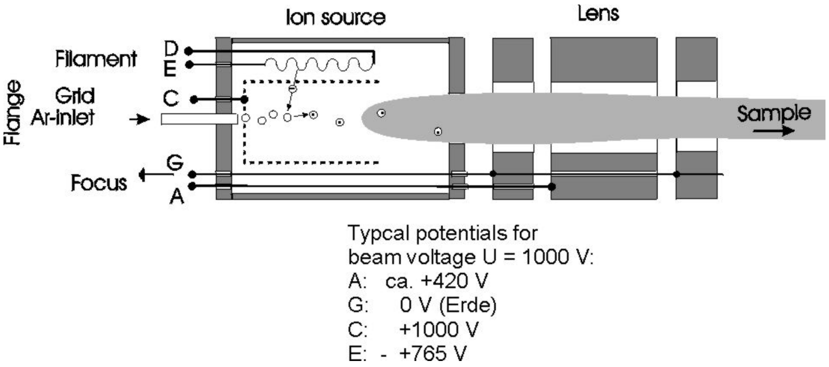
2.2. Ionization, ion beams



The energy needed for ionization depends on the kind of the gas and determines the onset of the curves. The maximum ionizability occurs for all gases at around 100 eV

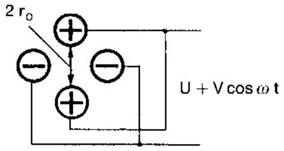


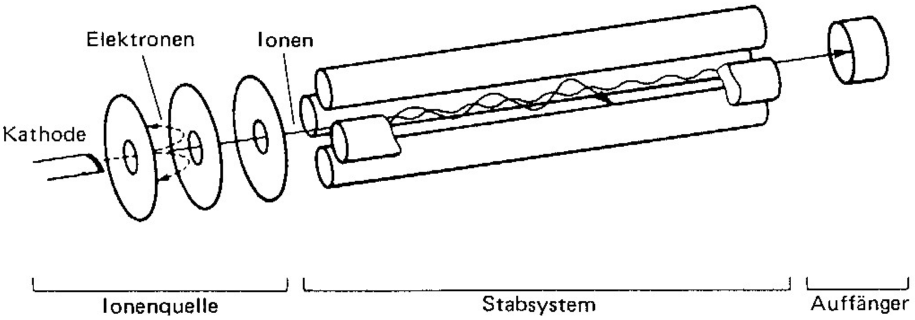
Bayard-Alpert type ionization gauge.
The hot cathode emits electrons (const. current) which pass the grid several times before they hit it. They ionize gas particles which are collected by a thin wire (collector). Potentials so that e^- cannot reach the collector.
X-ray limit: e^- generate X-rays when hitting the grid which generate a constant photoionization current from the collector. Its size limits the p-measurement.



Simple ion gun.
Ion source like in B-A-gauge, ions are extracted and focussed by an electrostatic lens.

QMS **Quadrupole mass spectrometer**



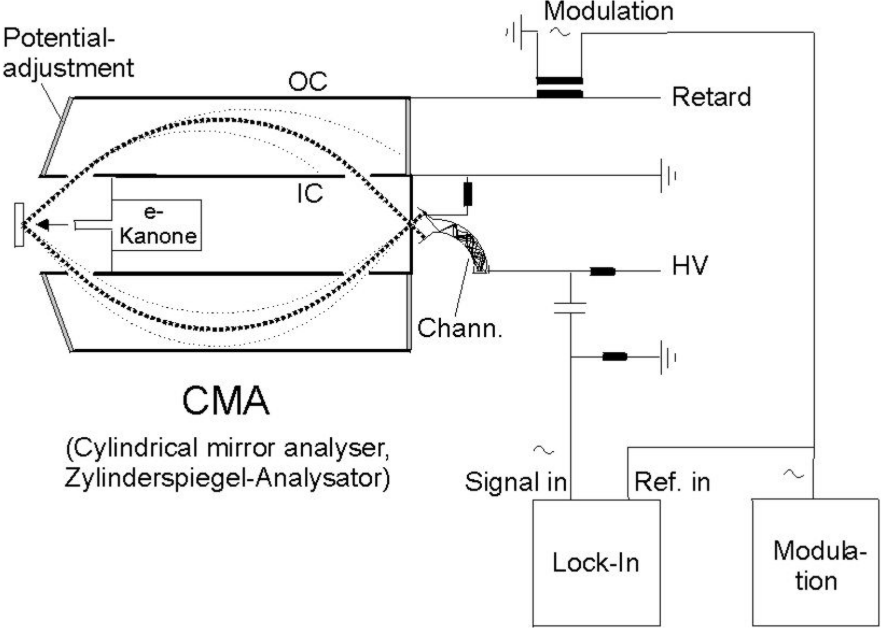


Quadrupole rod system, applied DC voltage U and AC voltage V cos Wt

Arrangement consisting of ionizer, mass separator (rod system) and collector (Faraday cup or multiplier).
Particles are excited to vibrations in the separator. For given values of U and V, the amplitude for a particle with certain m/e-ratio remains limited and the particle is transmitted. All others are in resonance, hit a rod and are neutralized. A m/e scan is achieved when scanning U and/or V.

2.3. Deflection, energy analysis

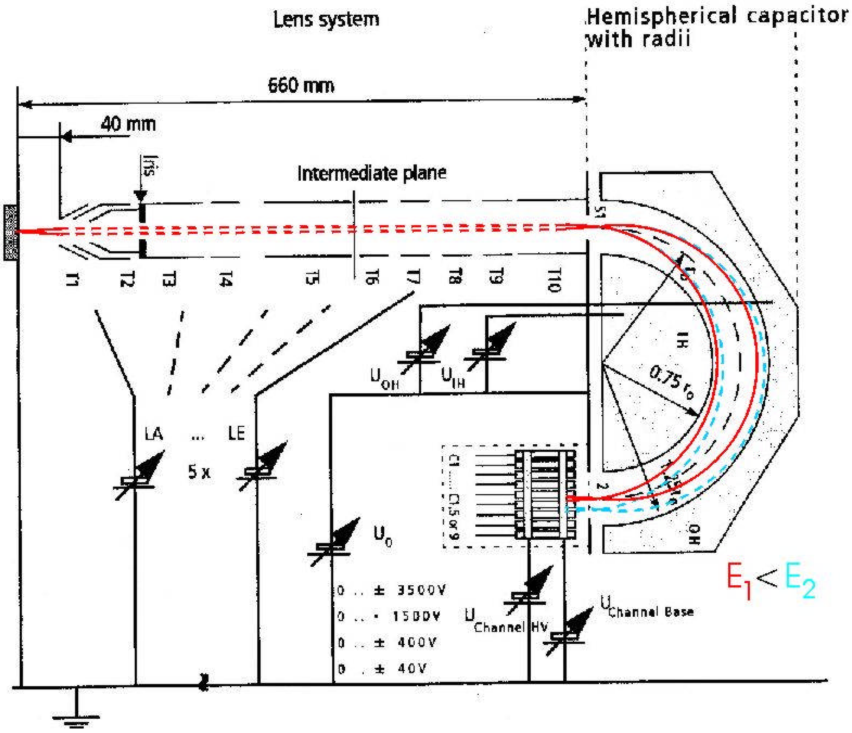
A cylindrical mirror analyser as used for Auger electron spectroscopy



Depending on the retard voltage, electrons of a certain energy from the focus point on the CMA axis are focussed on the exit aperture (lower trajectory). Electrons with other energies are not focussed or do not even pass the second annular slit (upper trajectories).

Large solid angle of acceptance (high sensitivity),
Averaging over large escape angle range.

Hemispherical energy analyser (SPECS company)



For a given U_{OH}-U_{IH}, electrons of different energies are focussed on different positions in the exit plane. Registration by one or several channeltrons or a channel plate. The long lens system allows to keep the space around the sample free and to vary the acceptance angle.

Small solid angle of acceptance,
Angle resolution possible.