Mass spectrometry: principles and applications

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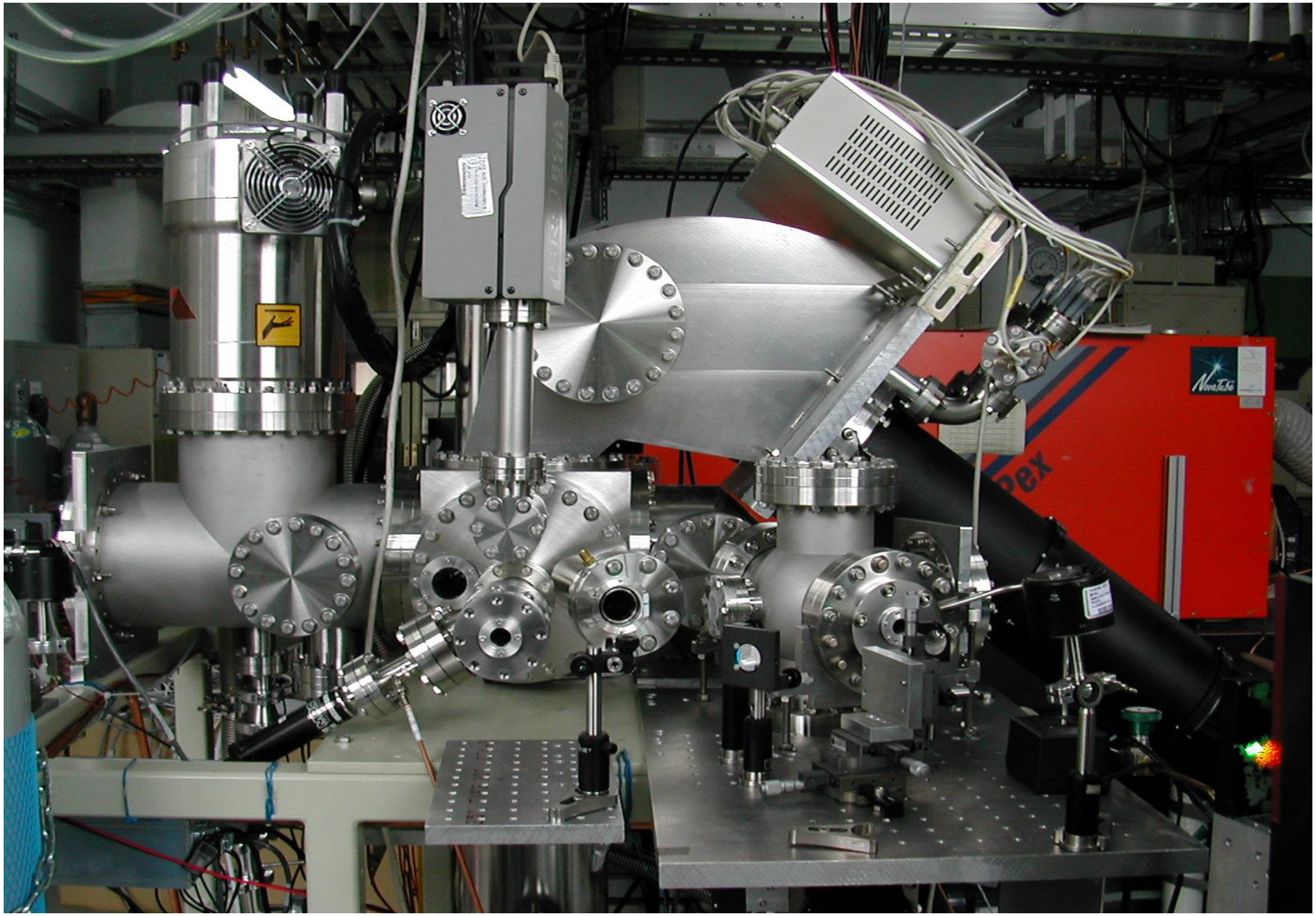
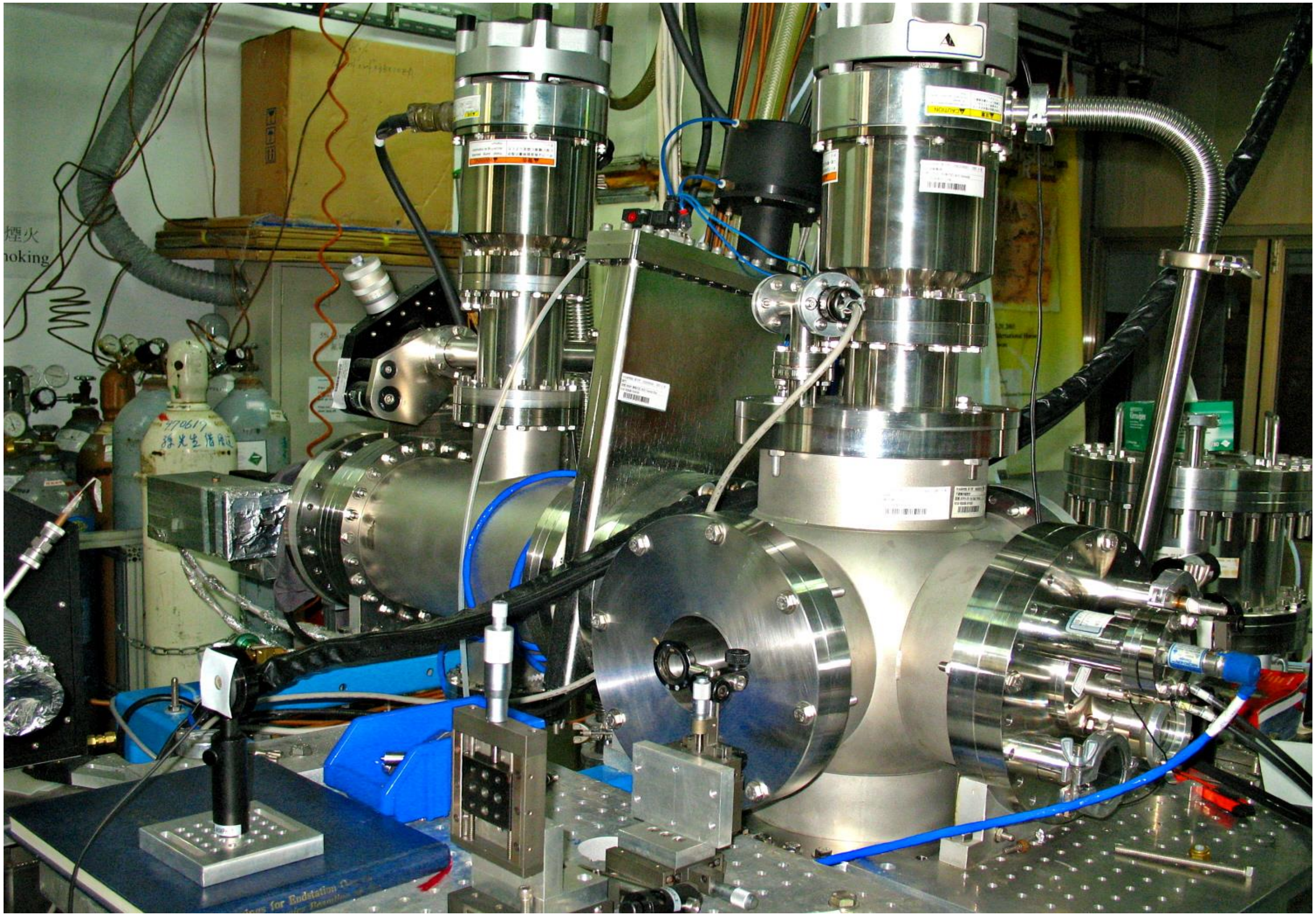




徵博士後、博士班、碩士班、研究助理

歡迎有理工、生化背景，對研究有興趣者應徵

研究主題:

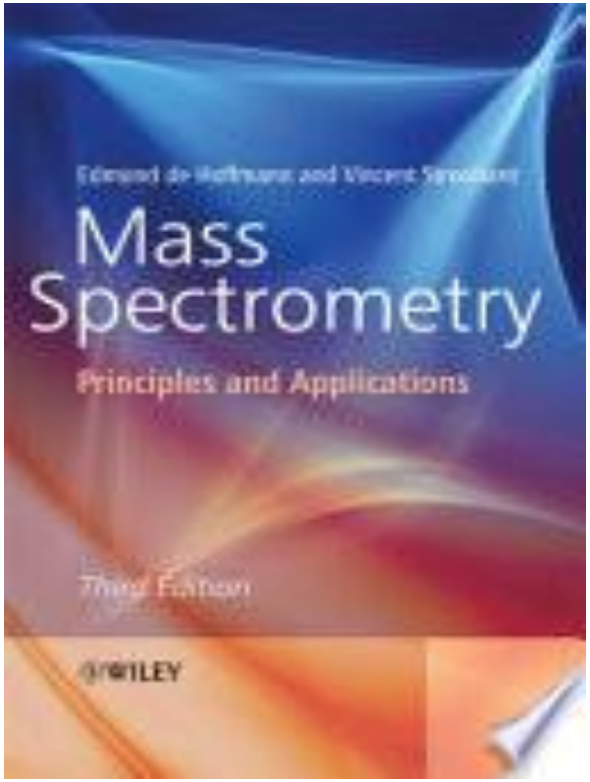
(1) 建造質譜儀（具機械、電子電路、真空技術背景者尤佳）

(2) 生物樣品萃取醣分子、質譜鑑定結構（具化學、生化背景者尤佳）

工作地點：中央研究院原子與分子科學研究所
（位於台北市臺灣大學校總區內）

Selected topics from textbook and my handout

Mass Spectrometry: Principles and Applications
Edmond de Hoffmann & Vincent Stroobant
John Wiley & Sons, 2007年10月29日 512 頁



Edmond de Hoffmann and Vincent Stroobant

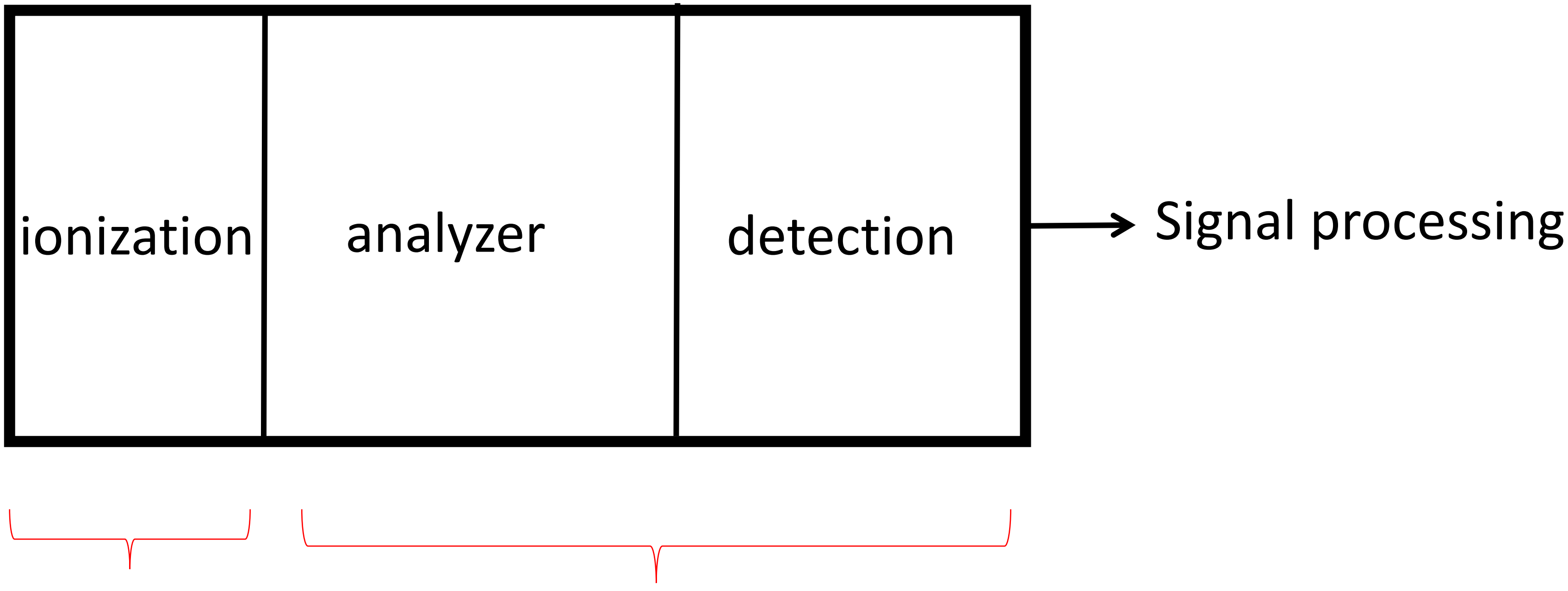
Mass Spectrometry

Principles and Applications

Third Edition

WILEY

Overview of mass spectrometers



ionization

analyzer

detection

Signal processing

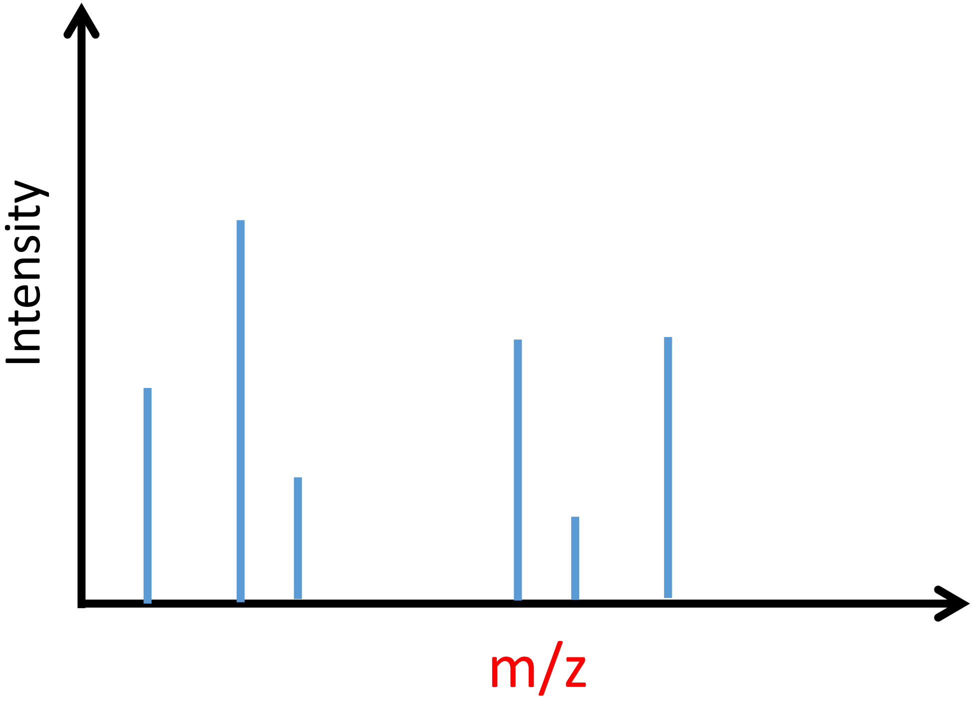
in vacuum
or
not in vacuum

Low vacuum or High vacuum

11/24	Maas spectra, vacuum technology
12/1	Ionization method
12/8	Mass analyzer, ion detection
12/15	Applications

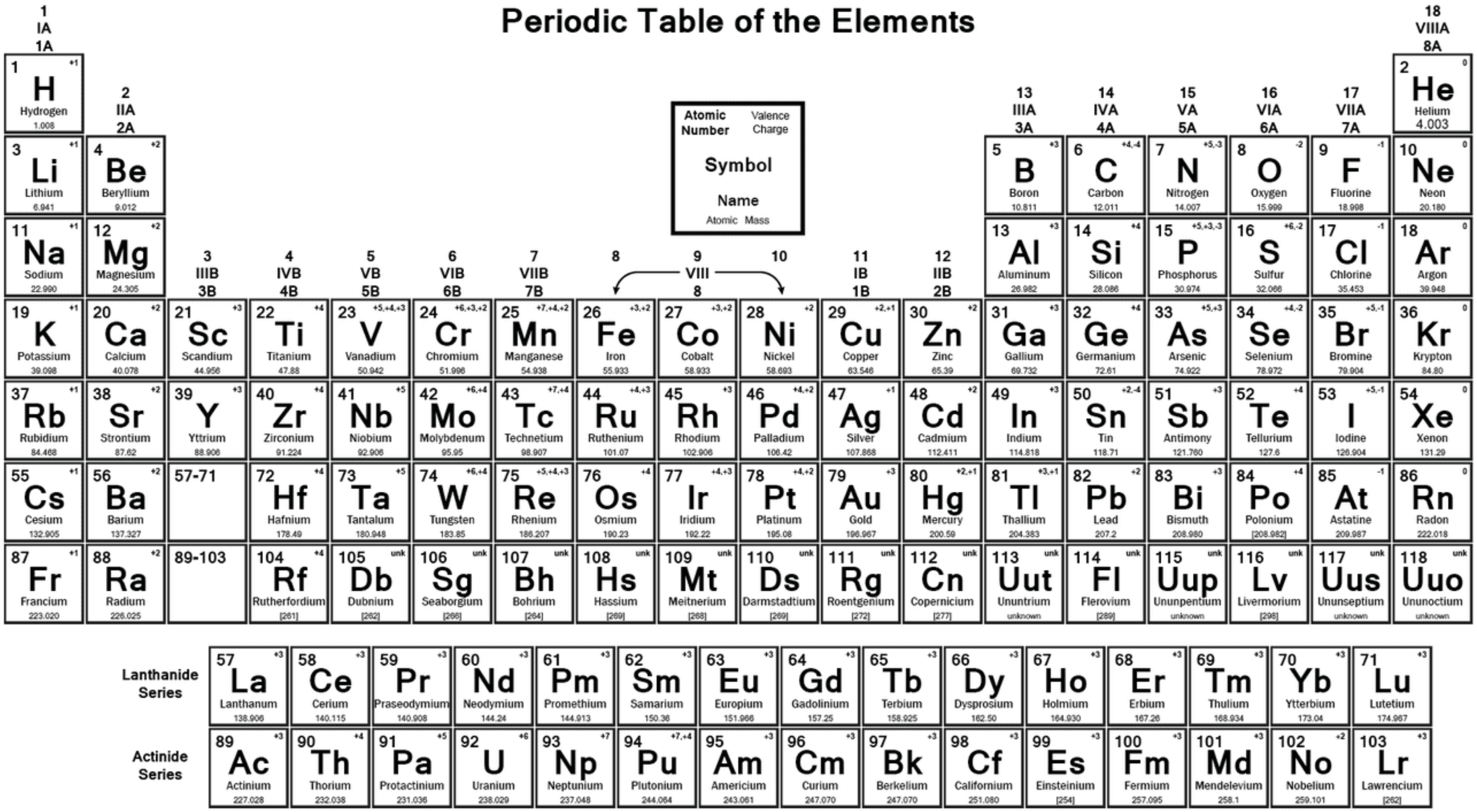
Evaluation: quiz, 20 min/close book in 12/1, 12/8, 12/15.

Mass spectrum



Mass spectra only provide information of m/z

- How to obtain molecular weight?
- How to obtain charge value?



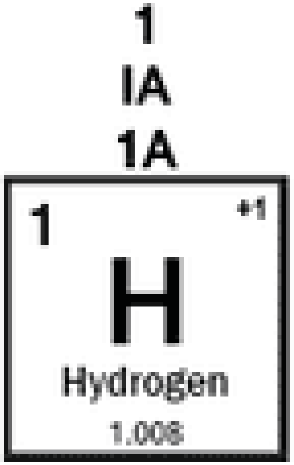
Periodic Table of the Elements

Atomic Number Valence Charge
Symbol
Name
Atomic Mass

1 IA 1A	2 IIA 2A	3 IIIB 3B	4 IVB 4B	5 VB 5B	6 VIB 6B	7 VIIB 7B	8	9 VIII 8	10	11 IB 1B	12 IIB 2B	13 IIIA 3A	14 IVA 4A	15 VA 5A	16 VIA 6A	17 VIIA 7A	18 VIIIA 8A
1 +1 H Hydrogen 1.008																	2 0 He Helium 4.003
3 +1 Li Lithium 6.941	4 +2 Be Beryllium 9.012											5 +3 B Boron 10.811	6 +4,-4 C Carbon 12.011	7 +5,-3 N Nitrogen 14.007	8 -2 O Oxygen 15.999	9 -1 F Fluorine 18.998	10 0 Ne Neon 20.180
11 +1 Na Sodium 22.990	12 +2 Mg Magnesium 24.305											13 +3 Al Aluminum 26.982	14 +4 Si Silicon 28.086	15 +5,+3,-3 P Phosphorus 30.974	16 +6,-2 S Sulfur 32.066	17 -1 Cl Chlorine 35.453	18 0 Ar Argon 39.948
19 +1 K Potassium 39.098	20 +2 Ca Calcium 40.078	21 +3 Sc Scandium 44.956	22 +4 Ti Titanium 47.88	23 +5,+4,+3 V Vanadium 50.942	24 +6,+3,+2 Cr Chromium 51.996	25 +7,+4,+2 Mn Manganese 54.938	26 +3,+2 Fe Iron 55.933	27 +3,+2 Co Cobalt 58.933	28 +2 Ni Nickel 58.693	29 +2,+1 Cu Copper 63.546	30 +2 Zn Zinc 65.39	31 +3 Ga Gallium 69.732	32 +4 Ge Germanium 72.61	33 +5,+3 As Arsenic 74.922	34 +4,-2 Se Selenium 78.972	35 +5,-1 Br Bromine 79.904	36 0 Kr Krypton 84.80
37 +1 Rb Rubidium 84.468	38 +2 Sr Strontium 87.62	39 +3 Y Yttrium 88.906	40 +4 Zr Zirconium 91.224	41 +5 Nb Niobium 92.906	42 +6,+4 Mo Molybdenum 95.95	43 +7,+4 Tc Technetium 98.907	44 +4,+3 Ru Ruthenium 101.07	45 +3 Rh Rhodium 102.906	46 +4,+2 Pd Palladium 106.42	47 +1 Ag Silver 107.868	48 +2 Cd Cadmium 112.411	49 +3 In Indium 114.818	50 +2,-4 Sn Tin 118.71	51 +3 Sb Antimony 121.760	52 +4 Te Tellurium 127.6	53 +5,-1 I Iodine 126.904	54 0 Xe Xenon 131.29
55 +1 Cs Cesium 132.905	56 +2 Ba Barium 137.327	57-71	72 +4 Hf Hafnium 178.49	73 +5 Ta Tantalum 180.948	74 +6,+4 W Tungsten 183.85	75 +5,+4,+3 Re Rhenium 186.207	76 +4 Os Osmium 190.23	77 +4,+3 Ir Iridium 192.22	78 +4,+2 Pt Platinum 195.08	79 +3 Au Gold 196.967	80 +2,+1 Hg Mercury 200.59	81 +3,+1 Tl Thallium 204.383	82 +2 Pb Lead 207.2	83 +3 Bi Bismuth 208.980	84 +4 Po Polonium [208.982]	85 -1 At Astatine 209.987	86 0 Rn Radon 222.018
87 +1 Fr Francium 223.020	88 +2 Ra Radium 226.025	89-103	104 +4 Rf Rutherfordium [261]	105 unk Db Dubnium [262]	106 unk Sg Seaborgium [266]	107 unk Bh Bohrium [264]	108 unk Hs Hassium [269]	109 unk Mt Meitnerium [268]	110 unk Ds Darmstadtium [269]	111 unk Rg Roentgenium [272]	112 unk Cn Copernicium [277]	113 unk Uut Ununtrium unknown	114 unk Fl Flerovium [289]	115 unk Uup Ununpentium unknown	116 unk Lv Livermorium [298]	117 unk Uus Ununseptium unknown	118 unk Uuo Ununoctium unknown

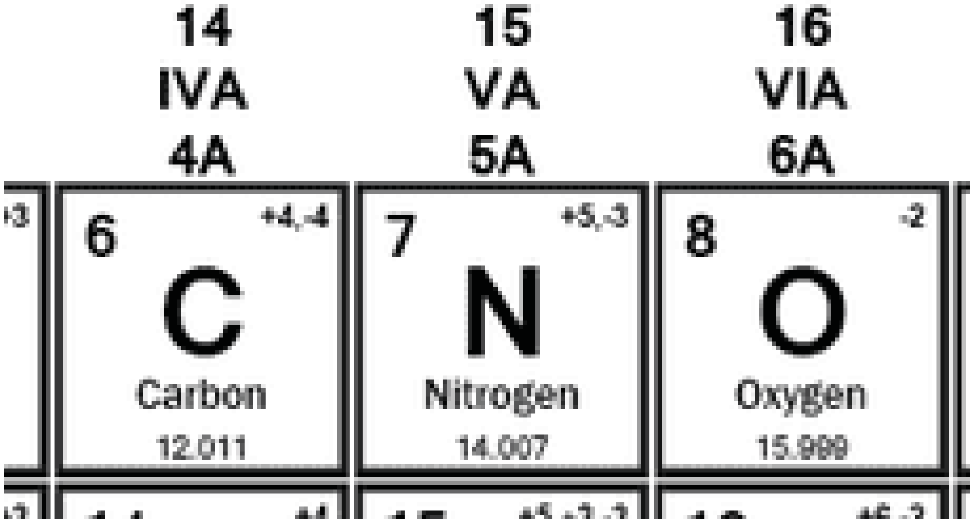
Lanthanide Series	57 +3 La Lanthanum 138.906	58 +3 Ce Cerium 140.115	59 +3 Pr Praseodymium 140.908	60 +3 Nd Neodymium 144.24	61 +3 Pm Promethium 144.913	62 +3 Sm Samarium 150.36	63 +3 Eu Europium 151.966	64 +3 Gd Gadolinium 157.25	65 +3 Tb Terbium 158.925	66 +3 Dy Dysprosium 162.50	67 +3 Ho Holmium 164.930	68 +3 Er Erbium 167.26	69 +3 Tm Thulium 168.934	70 +3 Yb Ytterbium 173.04	71 +3 Lu Lutetium 174.967
Actinide Series	89 +3 Ac Actinium 227.028	90 +4 Th Thorium 232.038	91 +5 Pa Protactinium 231.036	92 +6 U Uranium 238.029	93 +7 Np Neptunium 237.048	94 +7,+4 Pu Plutonium 244.064	95 +3 Am Americium 243.061	96 +3 Cm Curium 247.070	97 +3 Bk Berkelium 247.070	98 +3 Cf Californium 251.080	99 +3 Es Einsteinium [254]	100 +3 Fm Fermium 257.095	101 +3 Md Mendelevium 258.1	102 +2 No Nobelium 259.101	103 +3 Lr Lawrencium [262]

chemistry.about.com
sciencenotes.org

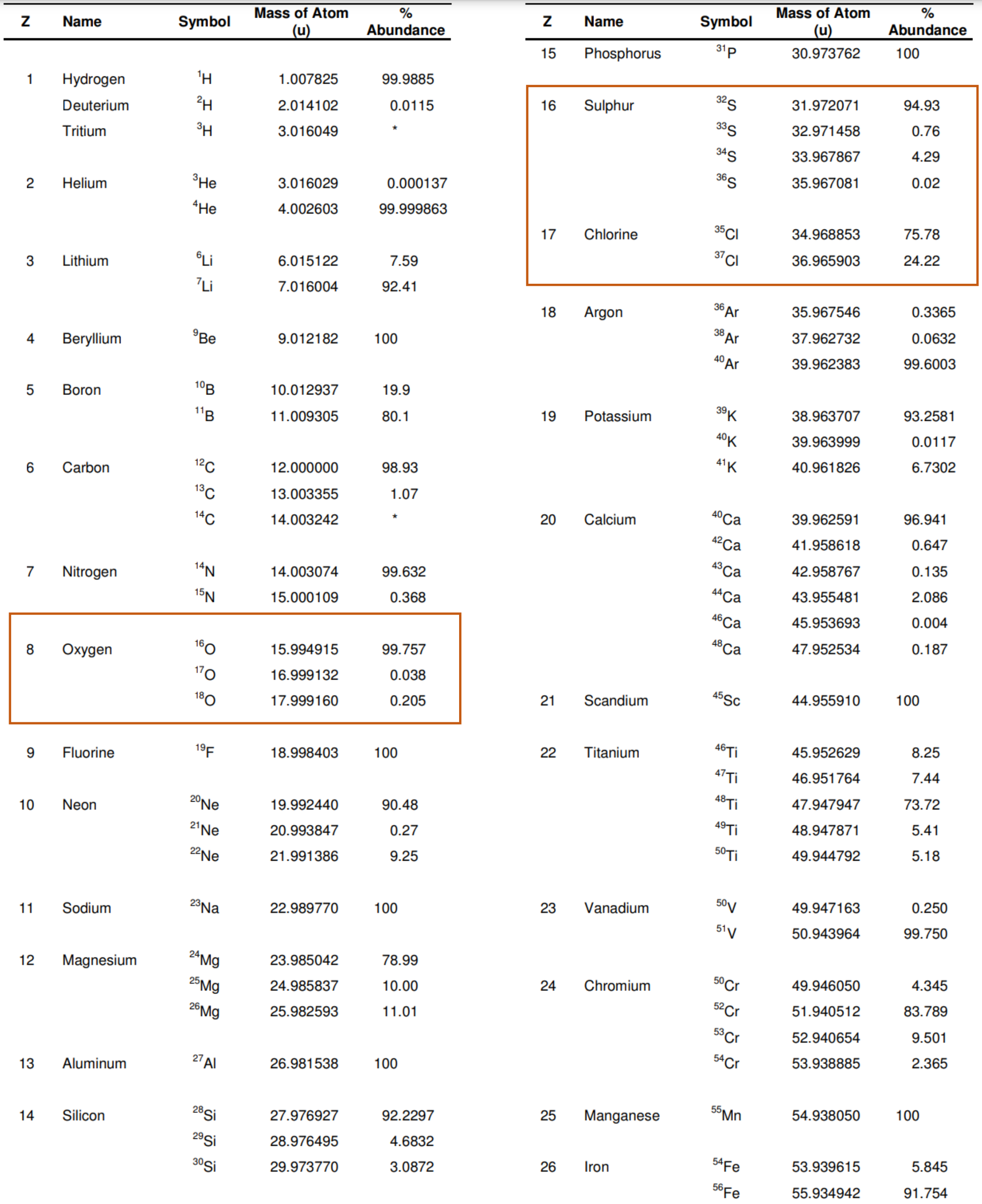


1
IA
1A

1	+1
H	
Hydrogen	
1.008	



14 IVA 4A	15 VA 5A	16 VIA 6A
6 +4,-4	7 +5,-3	8 -2
C	N	O
Carbon	Nitrogen	Oxygen
12.011	14.007	15.999



Z	Name	Symbol	Mass of Atom (u)	% Abundance
1	Hydrogen	^{1}H	1.007825	99.9885
	Deuterium	^{2}H	2.014102	0.0115
	Tritium	^{3}H	3.016049	*
2	Helium	^{3}He	3.016029	0.000137
		^{4}He	4.002603	99.999863
3	Lithium	^{6}Li	6.015122	7.59
		^{7}Li	7.016004	92.41
4	Beryllium	^{9}Be	9.012182	100
5	Boron	^{10}B	10.012937	19.9
		^{11}B	11.009305	80.1
6	Carbon	^{12}C	12.000000	98.93
		^{13}C	13.003355	1.07
		^{14}C	14.003242	*
7	Nitrogen	^{14}N	14.003074	99.632
		^{15}N	15.000109	0.368
8	Oxygen	^{16}O	15.994915	99.757
		^{17}O	16.999132	0.038
		^{18}O	17.999160	0.205
9	Fluorine	^{19}F	18.998403	100
10	Neon	^{20}Ne	19.992440	90.48
		^{21}Ne	20.993847	0.27
		^{22}Ne	21.991386	9.25
11	Sodium	^{23}Na	22.989770	100
12	Magnesium	^{24}Mg	23.985042	78.99
		^{25}Mg	24.985837	10.00
		^{26}Mg	25.982593	11.01
13	Aluminum	^{27}Al	26.981538	100
14	Silicon	^{28}Si	27.976927	92.2297
		^{29}Si	28.976495	4.6832
		^{30}Si	29.973770	3.0872
15	Phosphorus	^{31}P	30.973762	100
16	Sulphur	^{32}S	31.972071	94.93
		^{33}S	32.971458	0.76
		^{34}S	33.967867	4.29
		^{36}S	35.967081	0.02
17	Chlorine	^{35}Cl	34.968853	75.78
		^{37}Cl	36.965903	24.22
18	Argon	^{36}Ar	35.967546	0.3365
		^{38}Ar	37.962732	0.0632
		^{40}Ar	39.962383	99.6003
19	Potassium	^{39}K	38.963707	93.2581
		^{40}K	39.963999	0.0117
		^{41}K	40.961826	6.7302
20	Calcium	^{40}Ca	39.962591	96.941
		^{42}Ca	41.958618	0.647
		^{43}Ca	42.958767	0.135
		^{44}Ca	43.955481	2.086
		^{46}Ca	45.953693	0.004
		^{48}Ca	47.952534	0.187
21	Scandium	^{45}Sc	44.955910	100
22	Titanium	^{46}Ti	45.952629	8.25
		^{47}Ti	46.951764	7.44
		^{48}Ti	47.947947	73.72
		^{49}Ti	48.947871	5.41
		^{50}Ti	49.944792	5.18
23	Vanadium	^{50}V	49.947163	0.250
		^{51}V	50.943964	99.750
24	Chromium	^{50}Cr	49.946050	4.345
		^{52}Cr	51.940512	83.789
		^{53}Cr	52.940654	9.501
		^{54}Cr	53.938885	2.365
25	Manganese	^{55}Mn	54.938050	100
26	Iron	^{54}Fe	53.939615	5.845
		^{56}Fe	55.934942	91.754

Mass number 質量數

The mass number, also called the nucleon number, is the number of protons and neutrons in an atomic nucleus.

The mass number is unique for each isotope of an element and is written either after the element name or as a superscript to the left of an element's symbol.

For example, carbon-12 (^{12}C) has 6 protons and 6 neutrons.

Molecular mass

The molecular mass (abbreviated Mr) of a substance, formerly also called **molecular weight** and abbreviated as **MW**, is the mass of one molecule of that substance, relative to the unified atomic mass unit u (equal to 1/12 the mass of one atom of 12C).

The dalton or unified atomic mass unit (symbols: **Da** or **u**) is a non-SI unit of mass defined as 1/12 of the mass of an unbound neutral atom of carbon-12 in its nuclear and electronic ground state and at rest

Nominal mass

The nominal mass for an element: the mass number of its most abundant naturally occurring stable isotope.
The nominal mass for a molecule: sum of the nominal masses of the constituent atoms.

Carbon: has two stable isotopes 12C at 98.9% natural abundance and 13C at 1.1% natural abundance, thus the nominal mass of carbon is 12 Da.

The nominal mass is not always the lowest mass number, for example iron has isotopes 54Fe, 56Fe, 57Fe, and 58Fe with abundances 6%, 92%, 2%, and 0.3%, respectively, and a nominal mass of 56 Da.

Water H2O nominal mass: is 18 Da.

Average mass

The average mass of a molecule is obtained by summing the average atomic masses of the constituent elements.

For example, the average mass of natural water with formula H_2O is 1.00794 + 1.00794 + 15.9994 = 18.01528 Da.

Exact mass

The exact mass of an isotopic species is obtained by summing the masses of the individual isotopes of the molecule.

For example, the exact mass of water containing two hydrogen-1 (^1H) and one oxygen-16 (^{16}O) is 1.0078 + 1.0078 + 15.9949 = 18.0105 Da.

The exact mass of heavy water, containing two hydrogen-2 (deuterium or ^2H) and one oxygen-16 (^{16}O) is 2.0141 + 2.0141 + 15.9949 = 20.0229 Da.

Average mass

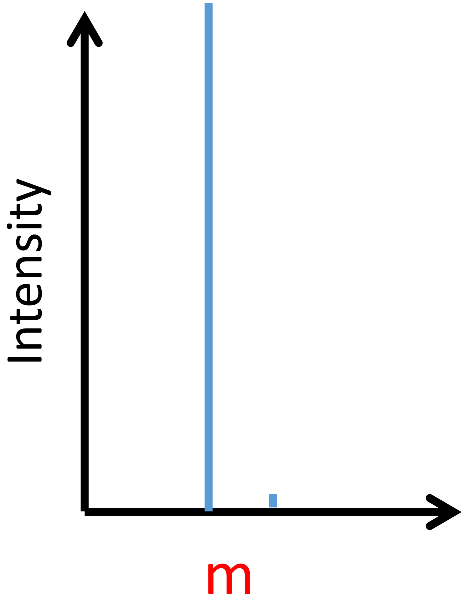
12.000x0.9893 + 13.003355x0.0107

= 12.0107

Exact mass

12.000, 13.003355

1 mole =12.0107g



Monoisotopic mass

The monoisotopic mass is the sum of the masses of the atoms in a molecule using the most abundant isotope for each element.

For typical organic compounds, where the monoisotopic mass is most commonly used, this also results in the lightest isotope being selected.

For some heavier atoms such as iron and argon the principal isotope is not the lightest isotope.

Most abundant mass

The mass of the molecule with the most highly represented isotope distribution, based on the natural abundance of the isotopes.

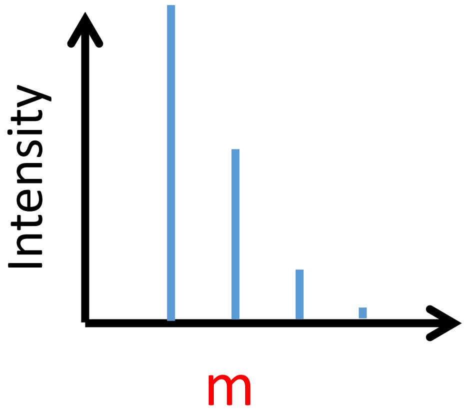
HCl

M. W.	Abundance
$^{1}H^{35}Cl$	(0.9999)x(0.7578) = 0.7577
$^{2}H^{35}Cl$	(0.0001)x(0.7578) = 0.00007
$^{1}H^{37}Cl$	(0.9999)x(0.2422) = 0.2421
$^{2}H^{37}Cl$	(0.0001)x(0.2422) = 0.00002

C_{60}

M. W.	Abundance
120	$(0.9893)^{60} = 0.5244$
121	$[(0.9893)^{59}x\ (0.01^{)1]}xC_1^{60} = 0.32$
122	$[(0.9893)^{58}x\ (0.01)^{2}]xC_2^{60} = 0.09$
123	$[(0.9893)^{57}x\ (0.01)^{3}]xC_3^{60} = 0.02$

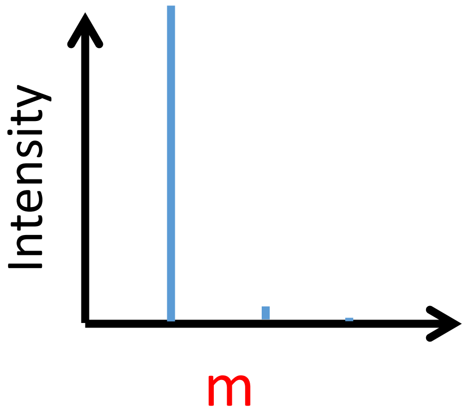
Mass spectrum

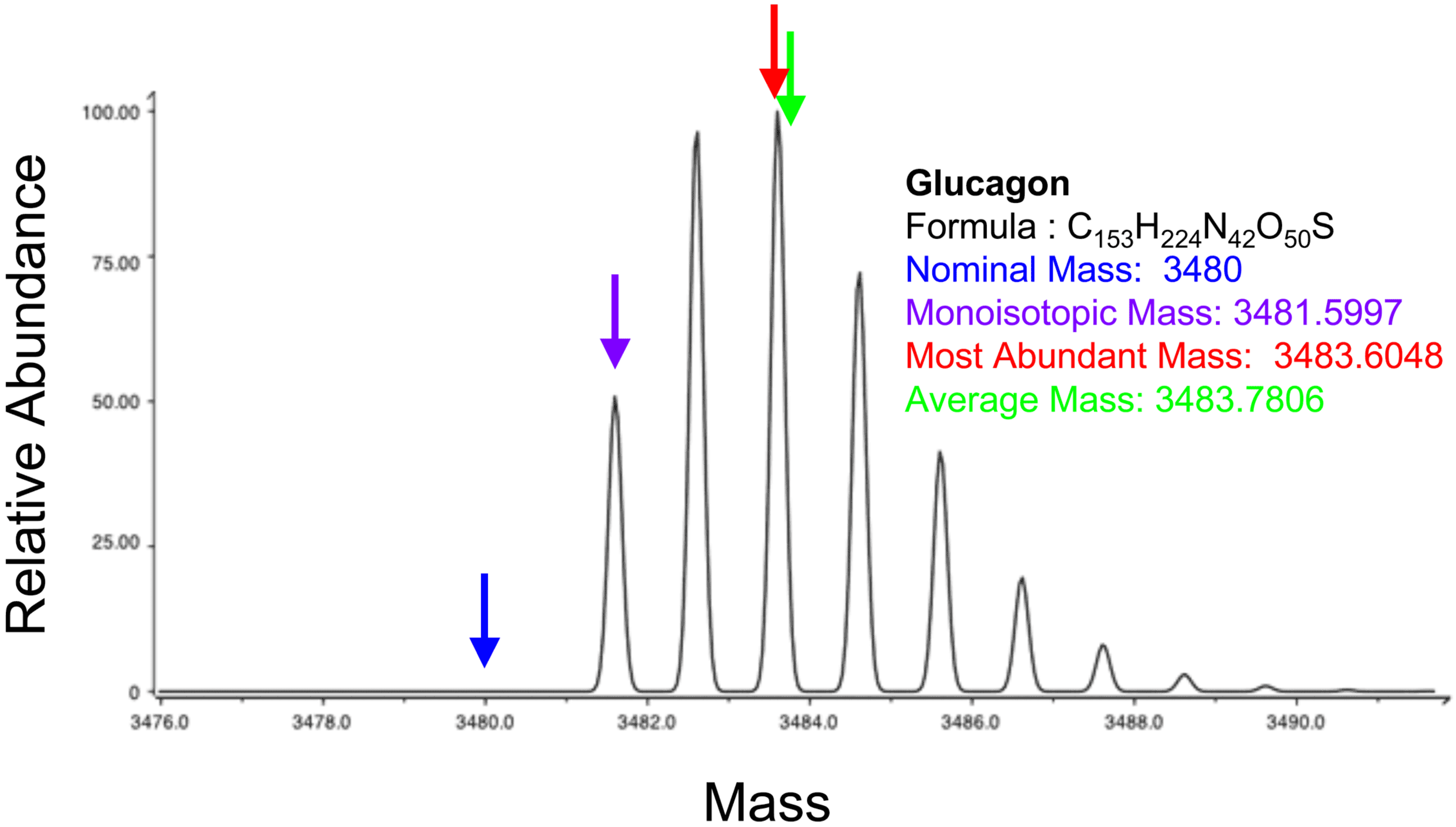


CO_2

M. W.	Abundance
$^{12}C+^{16}O+^{16}O$ $=12.00+15.995x2=43.99$	$[(0.9893)x(0.9975)x(0.9975)] = 0.98$
$^{13}C+^{16}O+^{16}O$ $=13.00+15.995x2=44.99$	$[(0.01)x(0.9975)x(0.9975)] = 0.01$
$^{12}C+^{16}O+^{18}O$ $=12.00+15.995+17.99=45.98$	$[(0.9893)x(0.9975)x(0.002)]xC_1^2 = 0.004$
$^{13}C+^{16}O+^{18}O$ $=13.00+15.995+17.99=46.99$	$[(0.01) x (0.9975)x(0.002)]xC_1^2 = 0.00004$

Mass spectrum





Glucagon

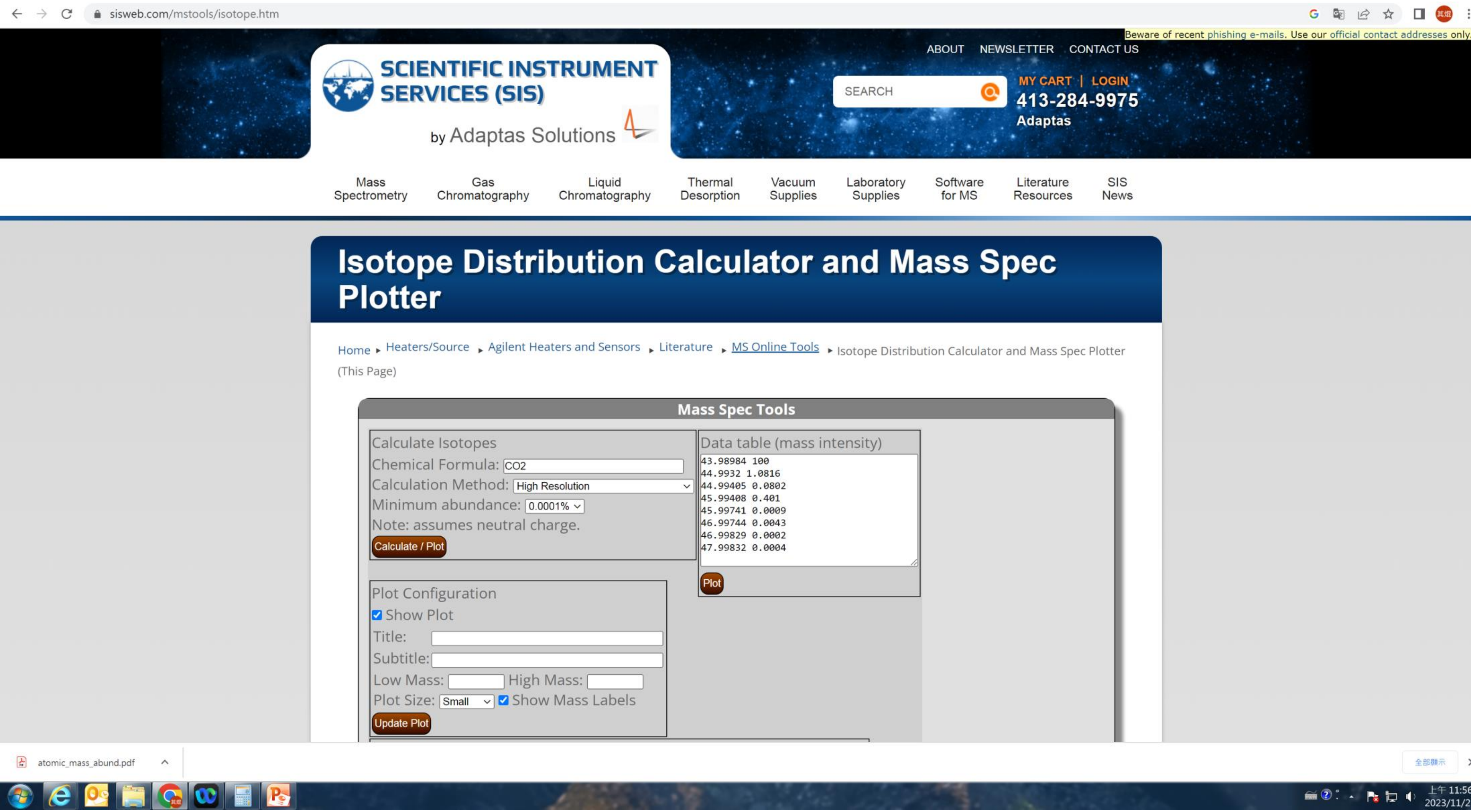
Formula : $C_{153}H_{224}N_{42}O_{50}S$

Nominal Mass: 3480

Monoisotopic Mass: 3481.5997

Most Abundant Mass: 3483.6048

Average Mass: 3483.7806



Isotope Distribution Calculator and Mass Spec Plotter

Home ▸ Heaters/Source ▸ Agilent Heaters and Sensors ▸ Literature ▸ MS Online Tools ▸ Isotope Distribution Calculator and Mass Spec Plotter (This Page)

Mass Spec Tools

Calculate Isotopes

Chemical Formula: CO2

Calculation Method: High Resolution

Minimum abundance: 0.0001%

Note: assumes neutral charge.

Calculate / Plot

Data table (mass intensity)

```
43.98984 100
44.9932 1.0816
44.99405 0.0802
45.99408 0.401
45.99741 0.0009
46.99744 0.0043
46.99829 0.0002
47.99832 0.0004
```

Plot

Plot Configuration

☑ Show Plot

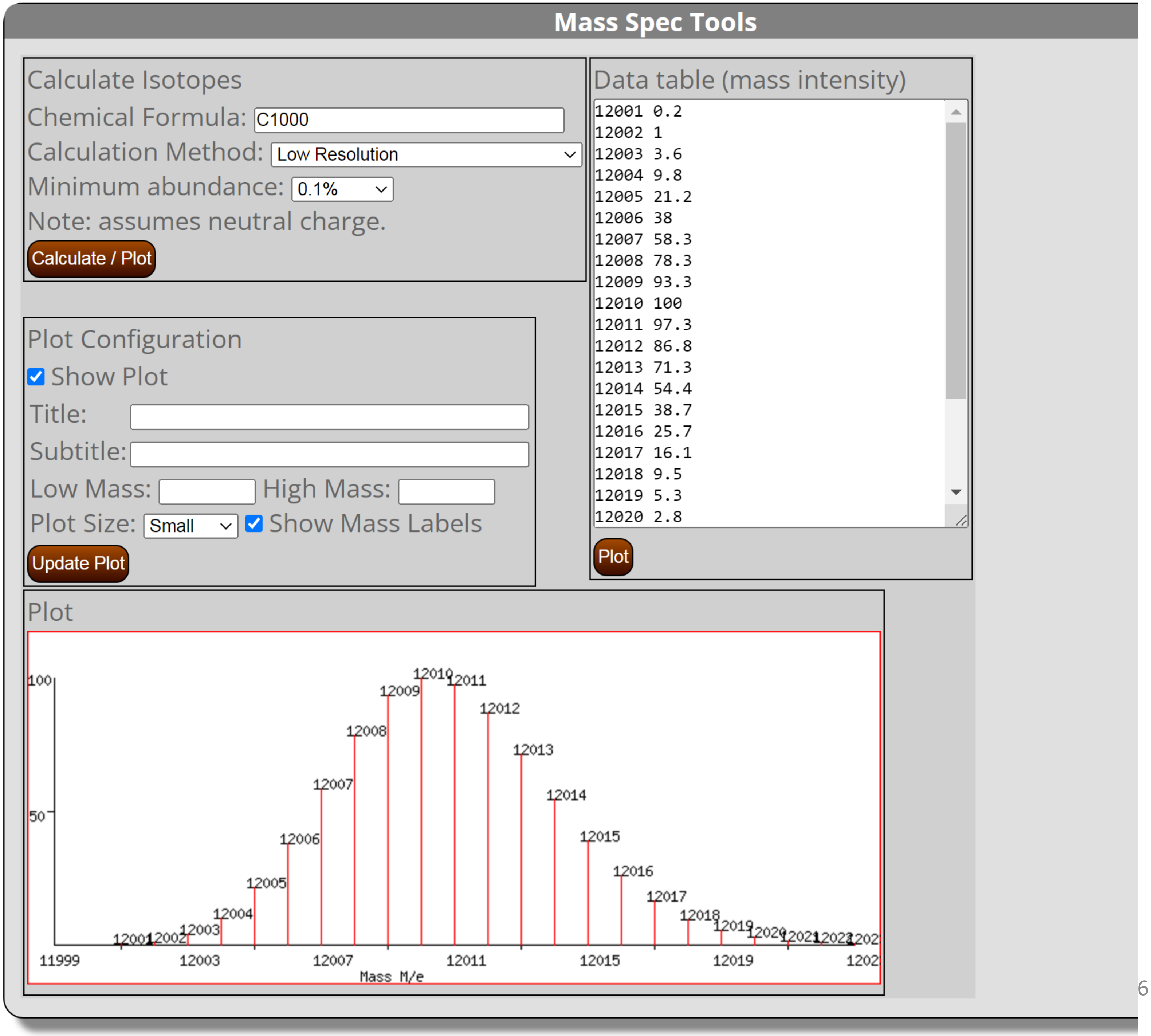
Title:

Subtitle:

Low Mass: High Mass:

Plot Size: Small ☑ Show Mass Labels

Update Plot



Calculate Isotopes

Chemical Formula: C1000

Calculation Method: Low Resolution

Minimum abundance: 0.1%

Note: assumes neutral charge.

Plot Configuration

☑ Show Plot

Title:

Subtitle:

Low Mass: High Mass:

Plot Size: Small ☑ Show Mass Labels

Data table (mass intensity)

```
12001 0.2
12002 1
12003 3.6
12004 9.8
12005 21.2
12006 38
12007 58.3
12008 78.3
12009 93.3
12010 100
12011 97.3
12012 86.8
12013 71.3
12014 54.4
12015 38.7
12016 25.7
12017 16.1
12018 9.5
12019 5.3
12020 2.8
```

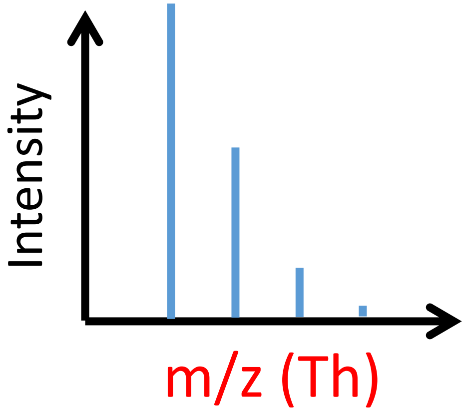
Plot

$1u = 1Da = 1.660540x10^{-27}$ kg

$1e = 1.6x10^{-19}$ C

1Th (Thomson) = 1 u/e $=1.036426x10^{-8}$ kg/C

Mass spectrum



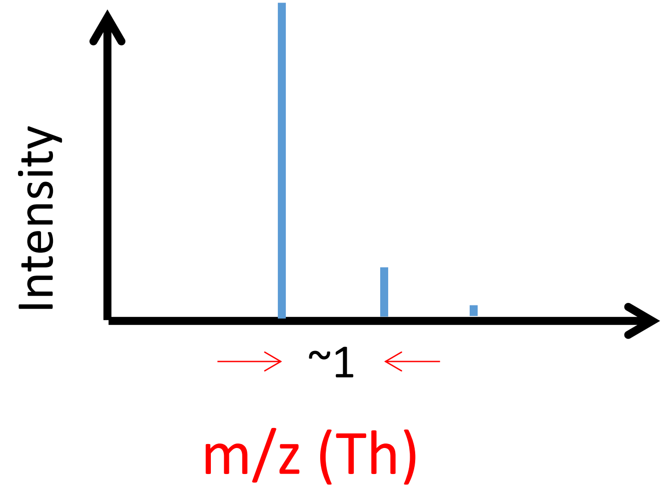
Mass spectra only provide information of m/z

- How to obtain molecular weight?
- How to obtain charge value?

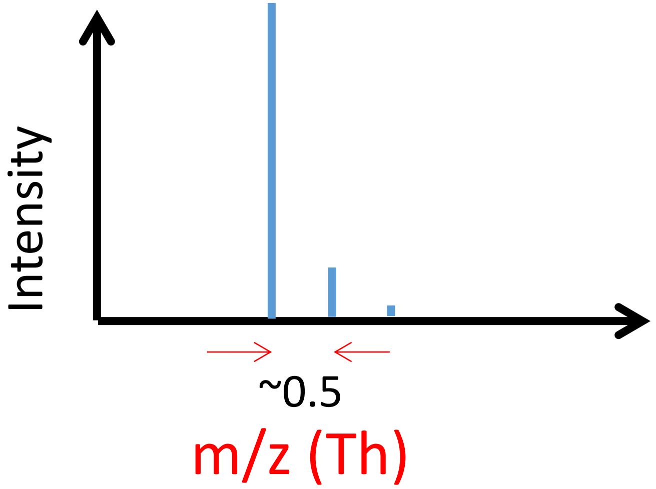
Mass spectrum

For most organic molecules

Singly charge

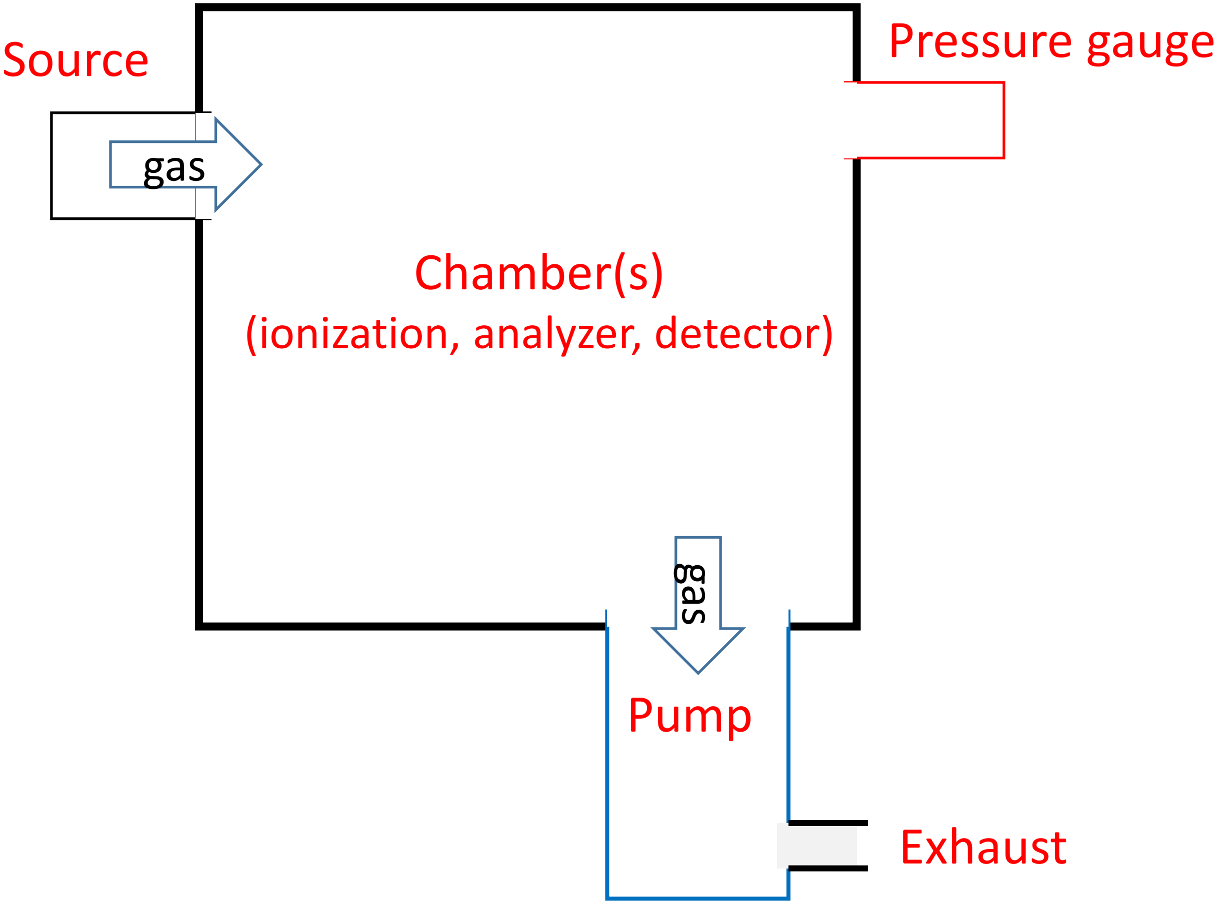


doubly charge



I. Vacuum technology

30


Source

gas

Pressure gauge

Chamber(s)

(ionization, analyzer, detector)

gas

Pump

Exhaust

- Collision frequency
- Mean free path
- Molecular flow vs viscosity flow

From gas kinetics

Velocity in three dimension

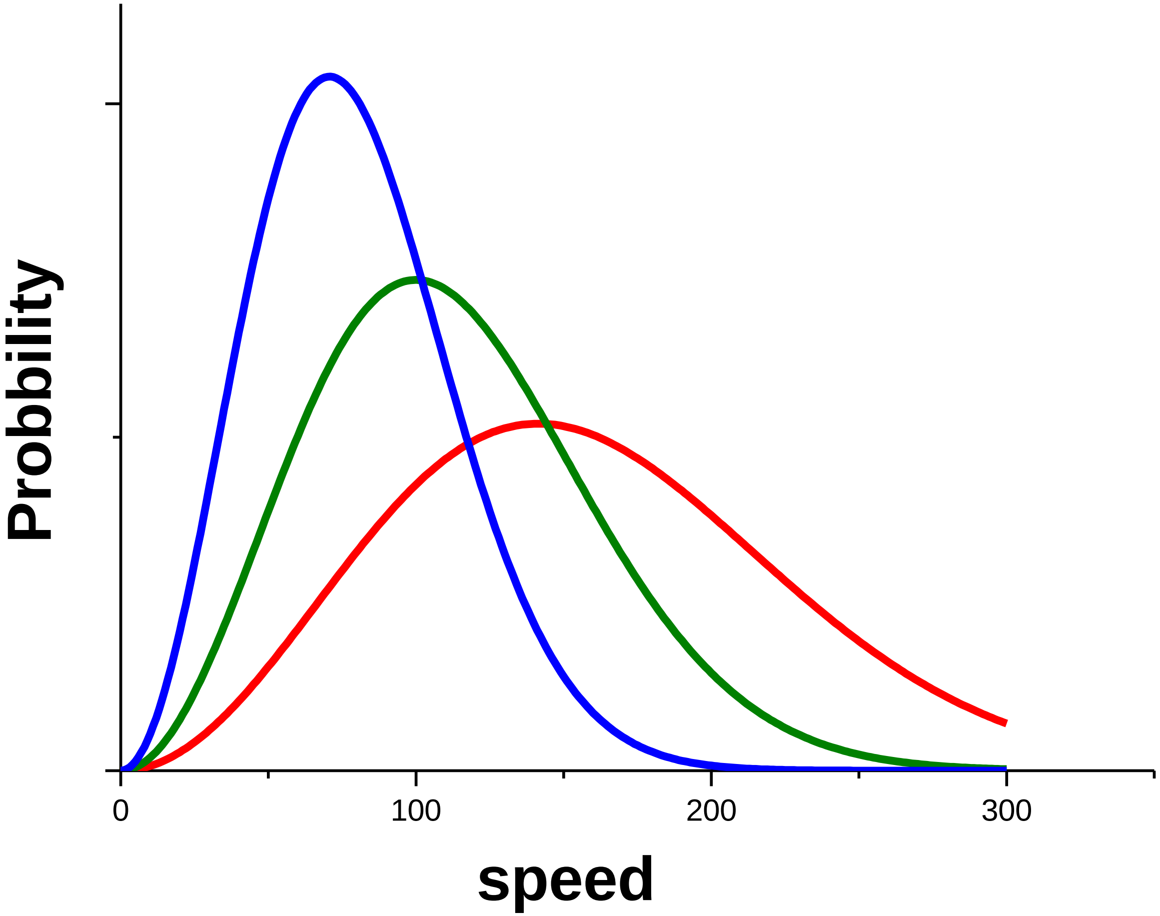
$$G(v)dv = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-mv^2}{2kT}} dvxdvydvz$$

Change from velocity to speed

$$F(v)dv = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{\frac{-mv^2}{2kT}} 4\pi v^2 dv$$

Note: velocity is a vector
speed is a scalar

For different temperatures



mean speed

$$\langle v \rangle = \int_0^\infty v \times F(v) dv$$

$$= \left(\frac{8kT}{\pi m} \right)^{\frac{1}{2}}$$

Mass dependence

At 300 K ,

H_2: 1780 m/s

He: 1258 m/s

H_2O: 593 m/s

O_2: 445 m/s

N_2: 475 m/s

Xe: 222 m/s

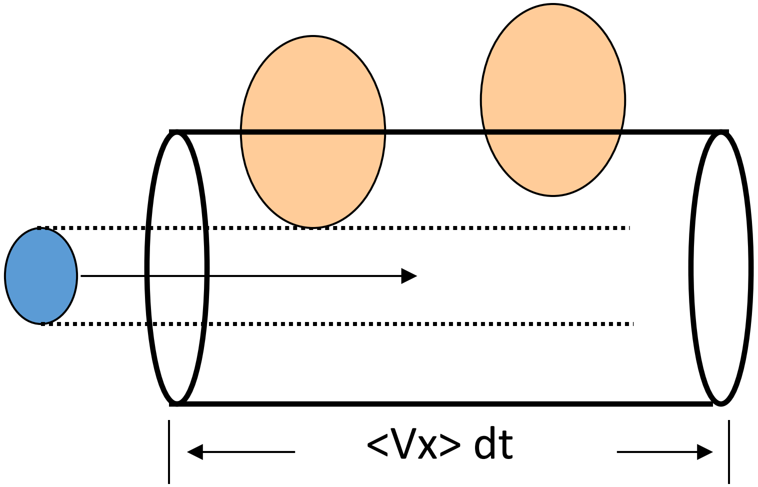
Same temperature ⇔ same kinetic energy ⇔ large mass has small velocity

Collisions between molecules:

For a particular particle 1

the volume it sweeps during *dt*:

$$V = \pi b^2 < V_x > dt$$



the number of n_2 in this volume:

$$N = \pi b^2 < V_x > dt \ n_2$$

the collision number during time *dt* (collision frequency):

$$Z_2 = \pi b^2{}_{\max} < Vr > n_2 \qquad b_{\max} = r_1 + r_2$$

$$Z_1 = \pi d^2 < Vr > n_1 \qquad d = r_1 + r_1 = 2r_1$$

Note: velocity has been changed to relative velocity

Relative velocity:

$$< V_r > = \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}}$$

$$\mu = \frac{m_1 \cdot m_2}{(m_1 + m_2)}$$

Example 1:

Calculate the collision frequency of N_2 (d=3.6 Å) at 1 atm (76o Torr)?

μ = [28x10^{-3} kg mol^{-1}/(6.02x10^{23}/mol)]x [28x10^{-3} kg mol^{-1}/(6.02x10^{23}/mol)]/
{[28x10^{-3} kg mol^{-1}/(6.02x10^{23}/mol)]+ [28x10^{-3} kg mol^{-1}/(6.02x10^{23}/mol)]}
= [(28x10^{-3}x28x10^{-3}/(28x10^{-3}+28x10^{-3})]/ 6.02x10^{23} kg
= 2.3x10^{-26} kg

Vr = $(8kT/ \pi \mu)^{1/2}$
= (8x1.38$\times$$10^{-23}$ m^2 kg s^{-2} K^{-1}x300 K/(3.14x2.3x10^{-26} kg) $^{1/2}$
= 670 m s^{-1}

n = 6.02X10^{23}/(22.4 L)x1000 L m^{-3} = 2.6x10^{25} m^{-3}

Z = π x d^2 x V_r x n
= 3.14 x (3.6x10^{-10}m$)^2$ x (670 ms^{-1})x2.6x10^{25} m^{-3}
= 7.1x10^9 s^{-1}

τ = 1/(7.1x10^9 s^{-1}) = 1.4x10^{-10} s = 0.14 ns

Average distance travel by molecules (mean free path) is:

$$\lambda = \frac{<V>t}{Z_1 \cdot t} = \frac{<V>}{Z_1}$$

$$= \frac{1}{\sqrt{2}\pi d^2 n_1}$$

Independent of velocity, temperature

For : N_2, 25°C, 1 atm

$\lambda = 475\ ms^{-1} \times 1.4\times10^{-10}\ s = 665$ Å

i> smaller than container

ii> larger than molecular dimension, molecules collide with each other, not wall.

For vacuum system, 0.76×10^{-7} Torr

λ=665 m

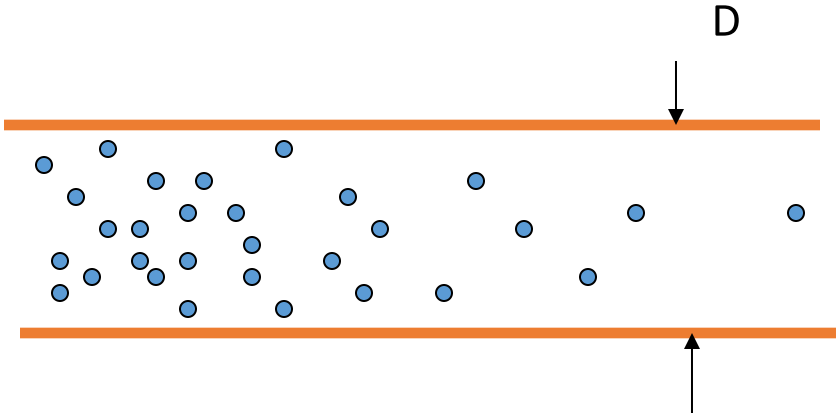
molecules collide with wall,

not with each other.

molecular flow: $\lambda > D$

viscosity flow: $\lambda / d < 0.01$

Transition region: $0.01 < \lambda / d < 1$



Example 2:

Calculate the collision frequency of protein (MW=2800 Da, d=50 Å) with He (d= 2.6Å) at 7.6 mTorr?

$\mu = [2800\text{x}10^{-3}\text{ kg mol}^{-1}/(6.02\text{x}10^{23}/\text{mol})]\text{x }[28\text{x}10^{-3}\text{ kg mol}^{-1}/(6.02\text{x}10^{23}/\text{mol})]/$
$\{[2800\text{x}10^{-3}\text{ kg mol}^{-1}/(6.02\text{x}10^{23}/\text{mol})]+[28\text{x}10^{-3}\text{ kg mol}^{-1}/(6.02\text{x}10^{23}/\text{mol})]\}$
$= [(2800\text{x}10^{-3}\text{x}28\text{x}10^{-3}/(2800\text{x}10^{-3}+28\text{x}10^{-3})]/6.02\text{x}10^{23}\text{ kg}$
$= 4.6\text{ x}10^{-26}\text{ kg}$

$Vr = (8kT/\pi\mu)^{1/2}$
$= (8\text{x}1.38\times10^{-23}\text{ m}^2\text{ kg s}^{-2}\text{ K}^{-1}\text{x}300\text{ K}/(3.14\text{x}4.6\text{x}10^{-26}\text{ kg})^{1/2}$
$= 335\text{ m s}^{-1}$

$n = 6.02\text{X}10^{23}/(22.4\text{ L})\text{x}1000\text{ L m}^{-3}\text{ x}7.6\text{ x}10^{-3}/760 = 2.6\text{x}10^{20}\text{ m}^{-3}$

$Z = \pi \text{ x } d^2 \text{ x } V_r \text{ x } n$
$= 3.14\text{ x }(50\text{x}10^{-10}\text{m})^2\text{ x }(335\text{ ms}^{-1})\text{x}2.6\text{x}10^{20}\text{ m}^{-3}$
$= 6.9\text{x}10^6\text{ s}^{-1}$

$\tau = 1/(6.9\text{x}10^6\text{ s}^{-1}) = 1.4\text{x}10^{-7}\text{ s} = 0.14\ \mu\text{s}$

Example 3:

If the protein is accelerated to 1000 m/s, how low the pressure of N_2 in vacuum has to be in order to have mean free path 1 m?

μ = [2800x10^{-3} kg mol^{-1}/(6.02x10^{23}/mol)]x [28x10^{-3} kg mol^{-1}/(6.02x10^{23}/mol)]/
{[2800x10^{-3} kg mol^{-1}/(6.02x10^{23}/mol)]+ [28x10^{-3} kg mol^{-1}/(6.02x10^{23}/mol)]}
= [(2800x10^{-3}x28x10^{-3}/(2800x10^{-3}+28x10^{-3})]/6.02x10^{23} kg
= 4.6 x10^{-26} kg

Vr $\approx$ (1000^2+475^2)$^{1/2}$
= 1107 m s^{-1}

τ = 1000 m s^{-1} x τ s > 1 m; τ > 10^{-3} s; Z < 10^3 s^{-1}

Z = π x d^2 x V_r x n
= 3.14 x (50x10^{-10}m)^2 x (1107 ms^{-1})x n m^{-3}
= 8.6x10^{-14} x n s^{-1} < 10^3 s^{-1}

n < 1/8.6 x 10^{17} m^{-3} = 1.1 x 10^{16} m^{-3} = 3.2 x10^{-7} Torr

- Pumping speed
- Throughput
- Conductance

- Constant volume per sweep per unit time
- As the pressure decreases, less molecules can be sweep (absorbed) per sweep (per unit time) than previous sweep

Pumping speed: Sweep volume per unit time

$S \equiv dV/dt$

- A property of a pump
- Depending on mechanical design

Throughput: number of molecules pumped per unit time

$Q(t) \equiv P(t) \mathrm{x} \frac{\Delta v}{\Delta t} = P(t)S$ (Q changes with time if P changes with time)

⇒ $S = Q/P$

Pumping speed:

$S \equiv dV/dt$

Pump down time:

Number of molecules pumped out per unit time

From :PV=nRT, we have

$$\frac{dn}{dt} \approx \frac{d(PV)}{dt} = -SP$$

$$\frac{dP}{dt} = -\frac{S}{V}P$$

$$P = P_0 e^{-t/\tau}$$

$$\tau = \frac{V}{S}$$

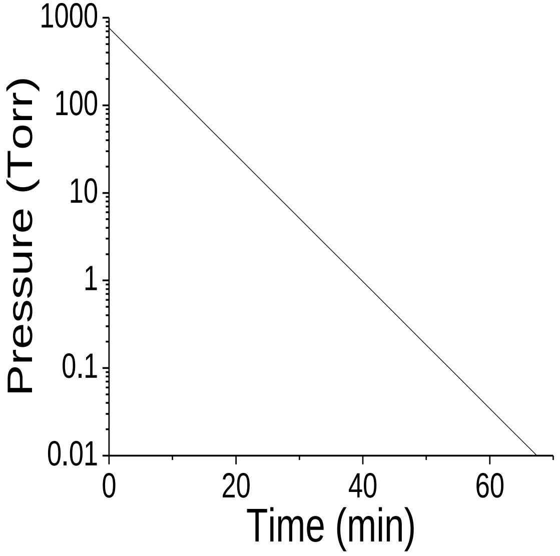
$$t = \frac{V}{S}\ln(\frac{P_0}{P})$$

Example:

Pump down time:

$V=1\ m^3$, $S=10\ m^3/h$

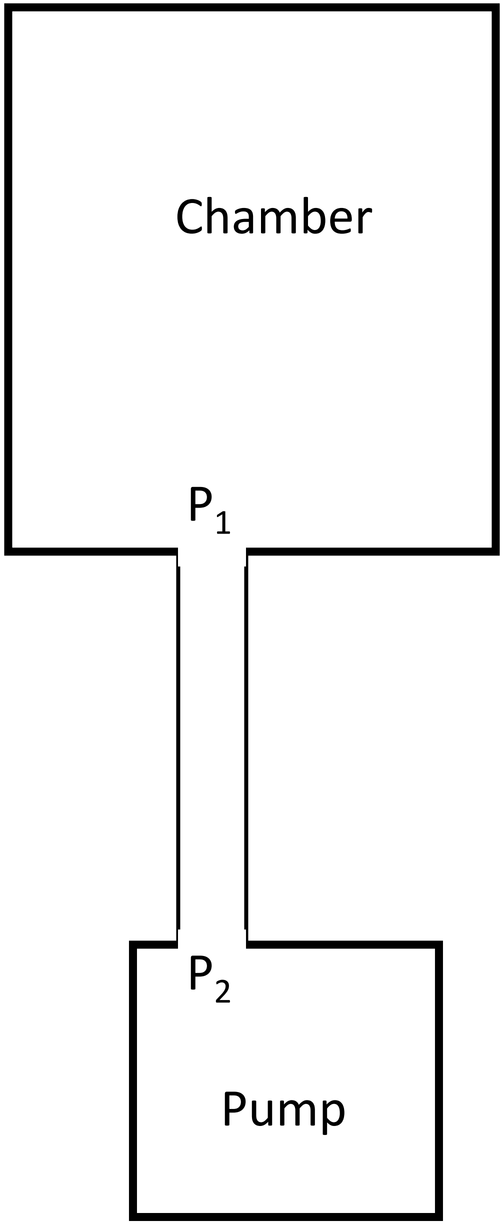
$P_0=101323.2$ Pa $=760$ Torr



Conductance:

A property of vacuum components
tube, aperture,…)

- How easy gas can flow through the component
- inverse of resistance to flow
- related to the shape of tube, aperture



$C \equiv Q/(P_1-P_2)$

$Q = C(P_1-P_2)$

Note: Q at every position is the same

C is pressure dependent

Continuum flow
(viscosity flow region)
Long round tube

$$C = 180 \frac{d^4}{L} P_{ave} \quad \text{liter/sec}$$

Pressure dependent
(d and L in cm, P in Torr)

Molecular flow
Long round tube

For air at 22 C

$$C = 12 \frac{d^3}{L} \quad \text{liter/sec}$$

Pressure independent
(d and L in cm, P in Torr)

Real pumping speed

Pumping speed:

$S \equiv Q_1/P_1$ (1)

$S_p \equiv Q_2/P_2$ (2)

Conductance:

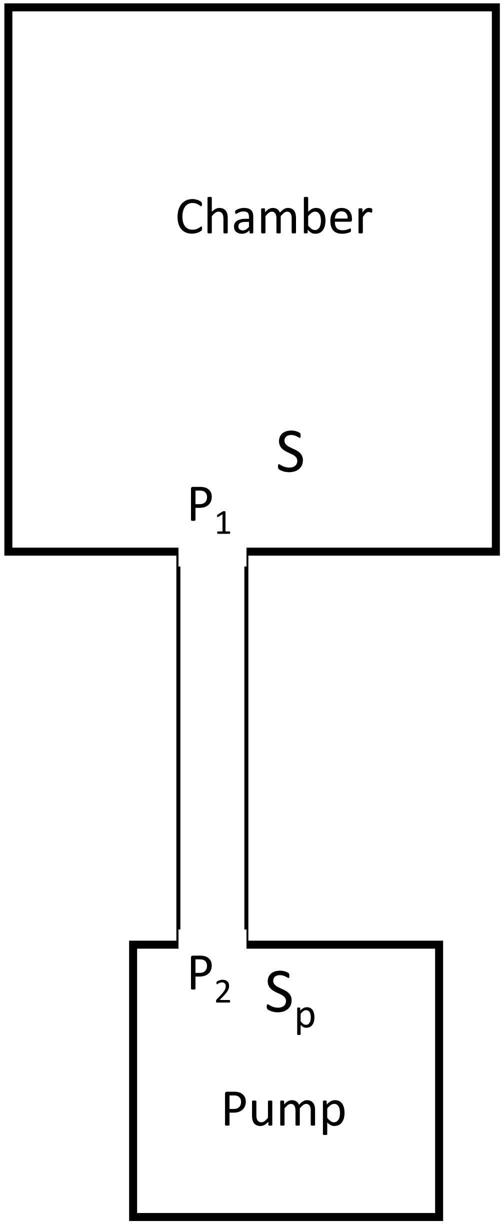
$C \equiv Q/(P_1\text{-}P_2)$ (3)

Because

$Q_1 = Q_2$ (If $T_1=T_2$) (4)

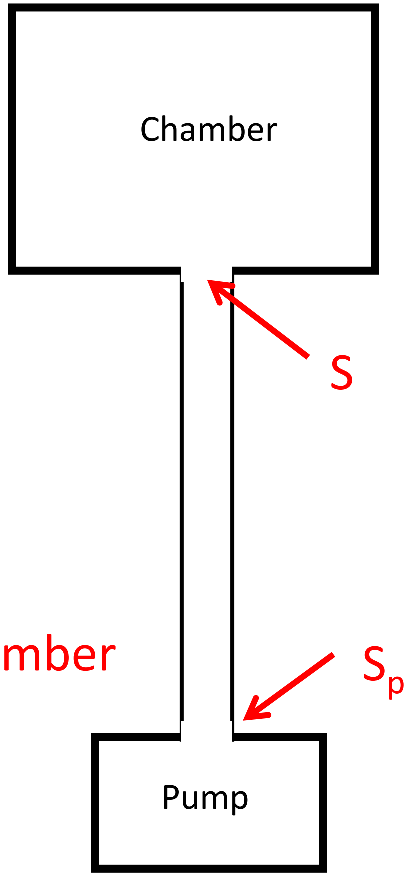
Feom (1)-(4), we have:

$1/S = 1/S_p + 1/C$



Example I : for a long round tube, *L*=1m, d=0.05 m,

in continuum flow (viscosity flow) region



$C = 180\frac{d^4}{L}P_{ave}$ d and L in cm, P in Torr

$=180\frac{5^4}{100}10^{-1}$ liter/sec

= 112 liter/sec

= 405 m^3/h

For a pump of pumping speed S_p=10 m^3/h connected to a chamber through the tube , the real pumping speed for chamger is

$1/S = 1/S_p + 1/C = 1/10 + 1/405$, $S=9.8m^3/h$

Example II: for a long round tube, *L*=1m, d=0.01 m, in continuum flow (viscosity flow) region

$$C = 180\frac{d^4}{L}P_{ave}$$ d and L in cm, P in Torr

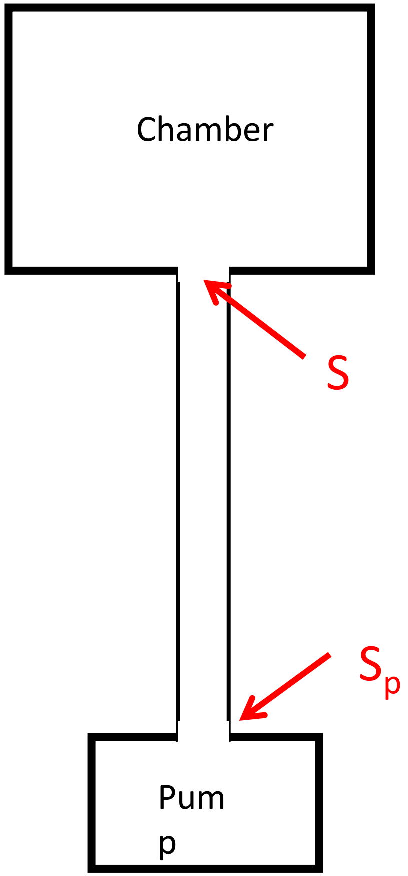
$=180\frac{1^4}{100}10^{-1}$ liter/sec

= 0.18 liter/sec

= 0.65 m^3/h

For a pump of pumping speed S_p=10 m^3/h connected to a chamber through the tube, the real pumping speed is:

$1/S = 1/S_p + 1/C = 1/10 + 1/0.65$, $S=0.63$ m^3/h (Waste of money)

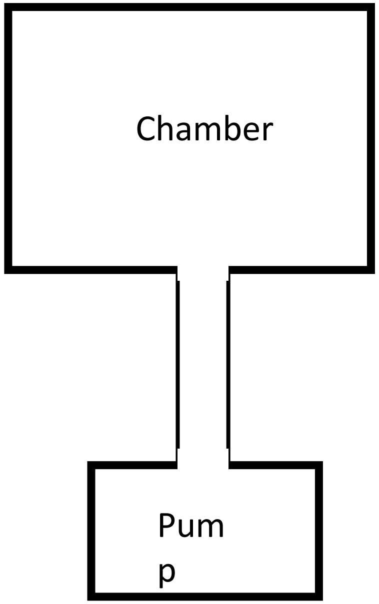


For L=1m, d=0.05 m, S_p=10 (m^3/h)

1/S = 1/10 + 1/405, S=9.8

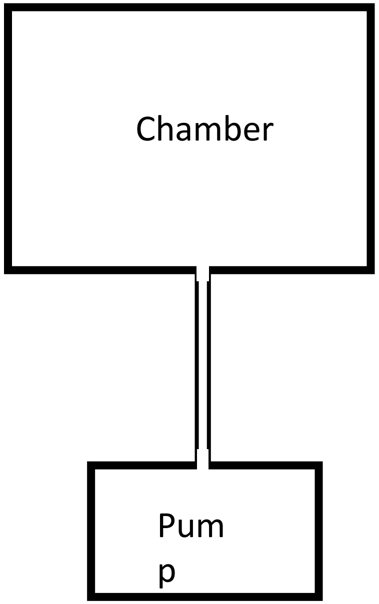
For l=1m, d=0.01 m, S_p=10 (m^3/h)

1/S = 1/10 + 1/0.65, S=0.63



Pump down time: t ~1/S

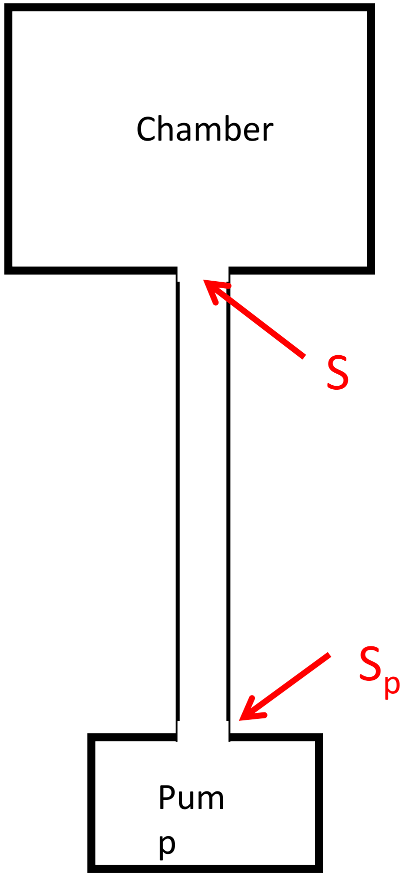
15 times difference.



Mechanical pumps should connected to mass spectrometer using tube with diameter > 4 cm, not longer than 2 m.

Example III: for a long round tube, L=1m, d=0.08 m,

in molecular flow region,



$C = 12\frac{d^3}{L}$ d and L in cm,

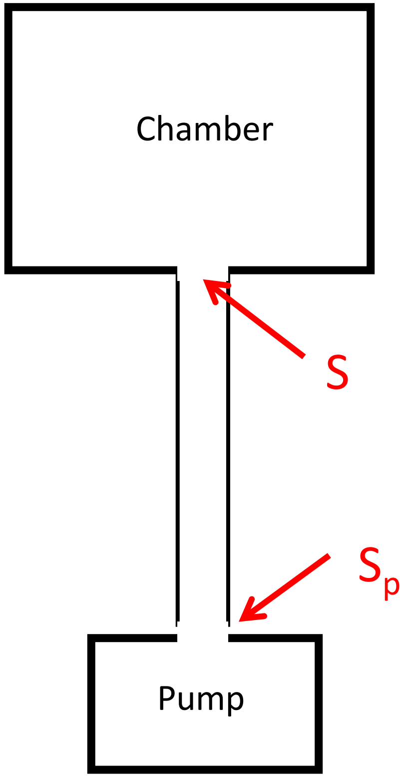
$=12\,\frac{8^3}{100}$ liter/sec

= 61.4 liter/sec

For a pump with pumping speed of S_p=300 liter/sec, connected to a chamber through the tube, the real pumping speed is:

$1/S = 1/S_p + 1/C$ =1/300 + 1/61.4, S=50 liter/sec (waste of money)

Example IV: for a long round tube, *L*=0.05 m, d=0.08 m, in molecular flow region,



$C = 12\frac{d^3}{L}$ d and L in cm

$=12\frac{8^3}{10}$ liter/sec

= 1228 liter/sec

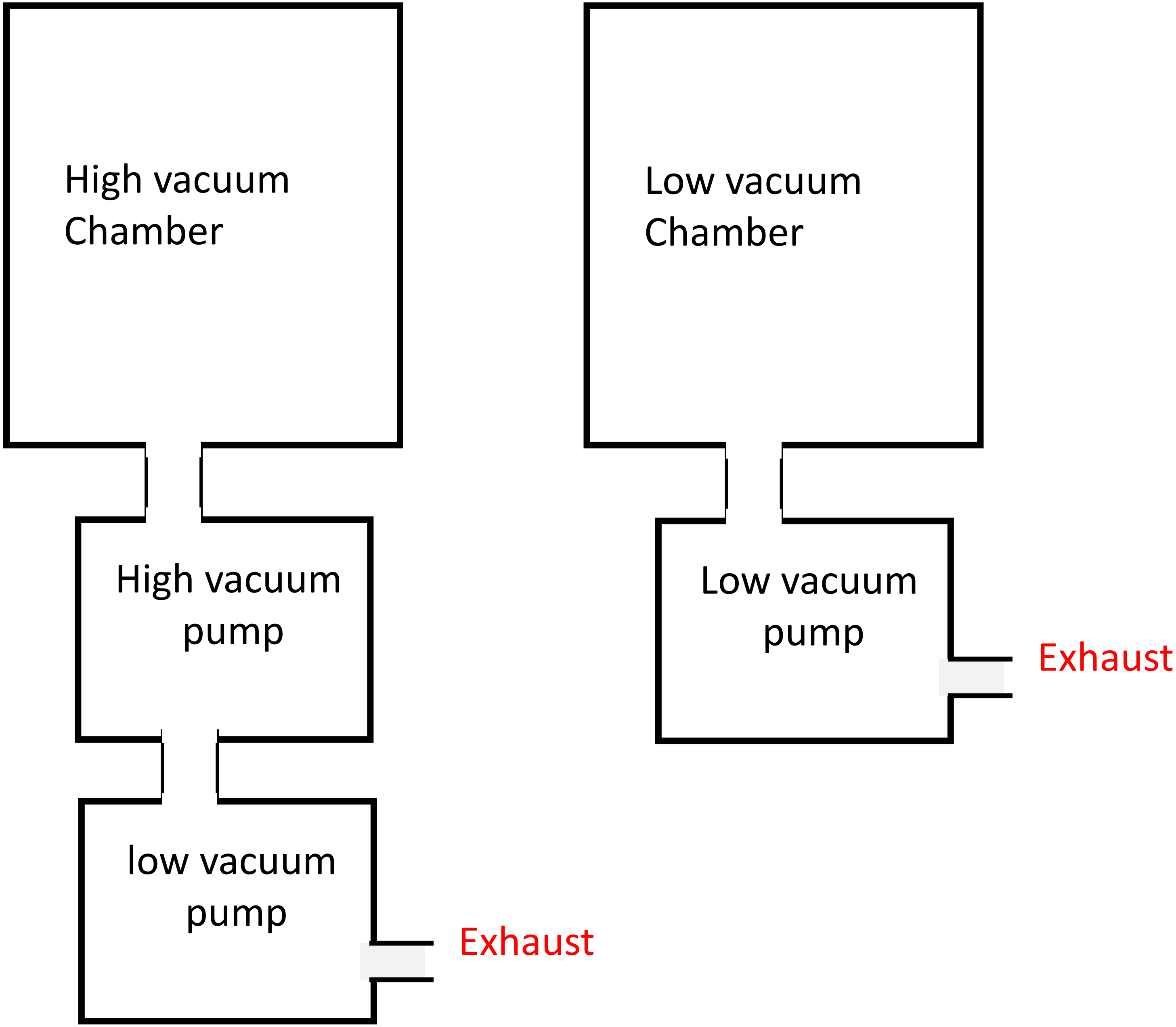
For a pump with pumping speed of S_p=300 liter/sec, connected to a chamber through the tube, the real pumping speed is:

$1/S = 1/S_p + 1/C = 1/300 + 1/1228$, S=241 liter/sec

(tube should be as short as possible, as large as possible, e.g., connected directly to chamber)

- High vacuum pumps
- Low (and medium) vacuum pumps

Degree of Vacuum	Pressure range	
Low	10^{5}-3.3×10^{3} Pa	760-25 Torr
Medium	3.3×10^{3}-10^{-1} Pa	25-7.6×10^{-4} Torr
High	10^{-1}-10^{-4} Pa	7.6×10^{-4}-7.6×10^{-7} Torr
Very high	10^{-4}-10^{-7} Pa	7.6×10^{-7}-7.6×10^{-10} Torr
Ultrahigh	10^{-7}-10^{-10} Pa	7.6×10^{-10}-7.6×10^{-13} Torr
Extreme ultrahigh	$< 10^{-10}$ Pa	$< 7.6 \times 10^{-13}$ Torr



High vacuum Chamber

High vacuum pump

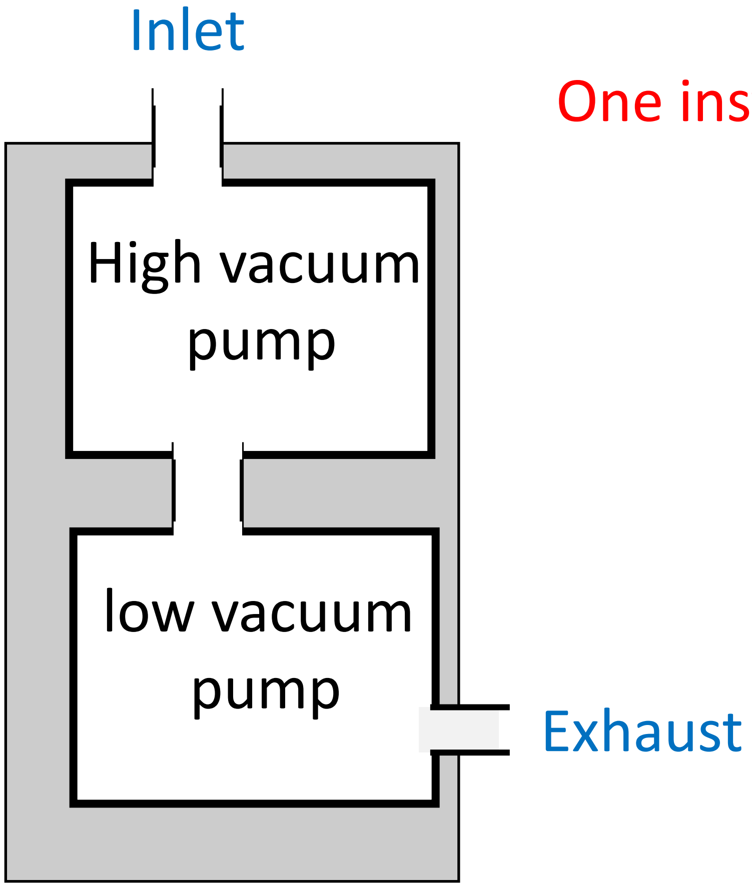
low vacuum pump

Exhaust

Low vacuum Chamber

Low vacuum pump

Exhaust

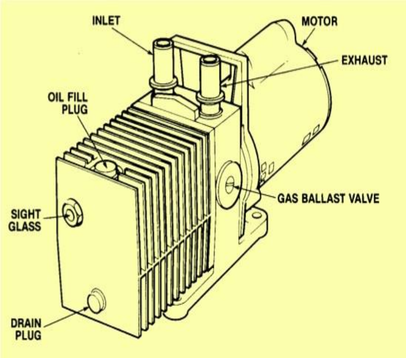


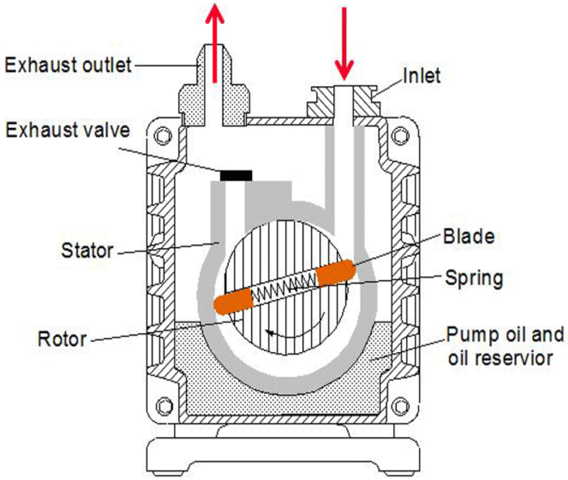
One instrument?

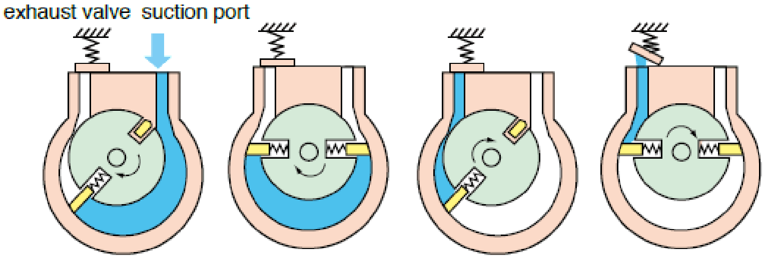
oil sealed low vacuum pump

Low vacuum pump

Rotary vane pump
Working principle



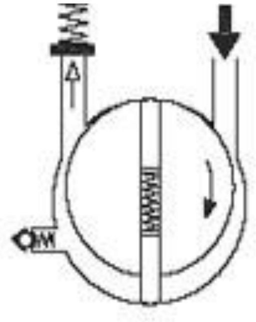




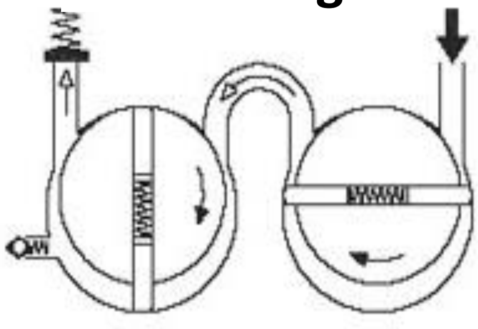
Suction Transport Compressio Exhaustion

Rotary vane pump
One-stage vs. Two-stage

One stage



Two stage



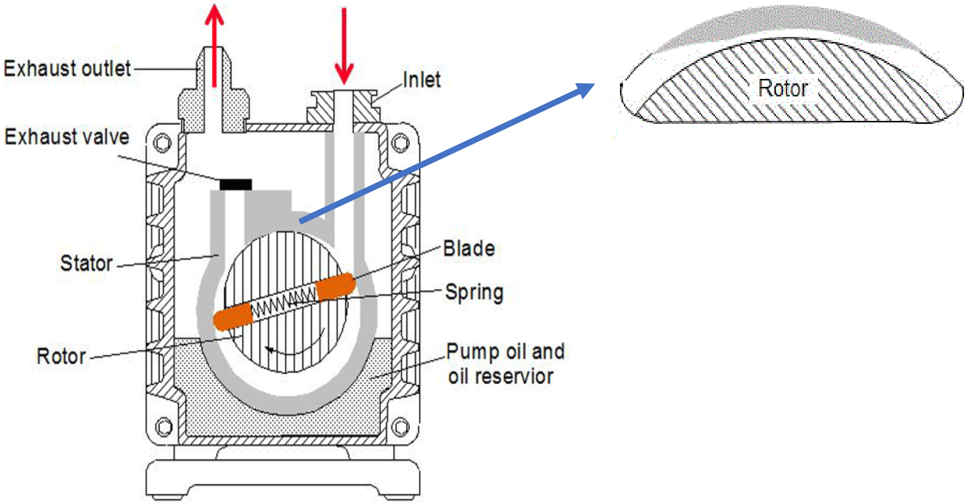
→ Reduce the ultimate pressure

	One stage	Two stage
Ultimate pressure (torr)	10^{-3}	**10^{-4}**
Price	**Cheap**	Expensive

Oil in rotary pump

- Oil functions:
  -Lubricant
  -Seal
  -Cooler

Low vapor pressure
Appropriate viscosity
Stability



- Pumping speed: 1-500 L · s^{-1}
- P_{min} (Ultimate pressure): 10^{-3}-10^{-4} Torr
- Typical pressure

  new pump: 5x 10^{-3} Torr

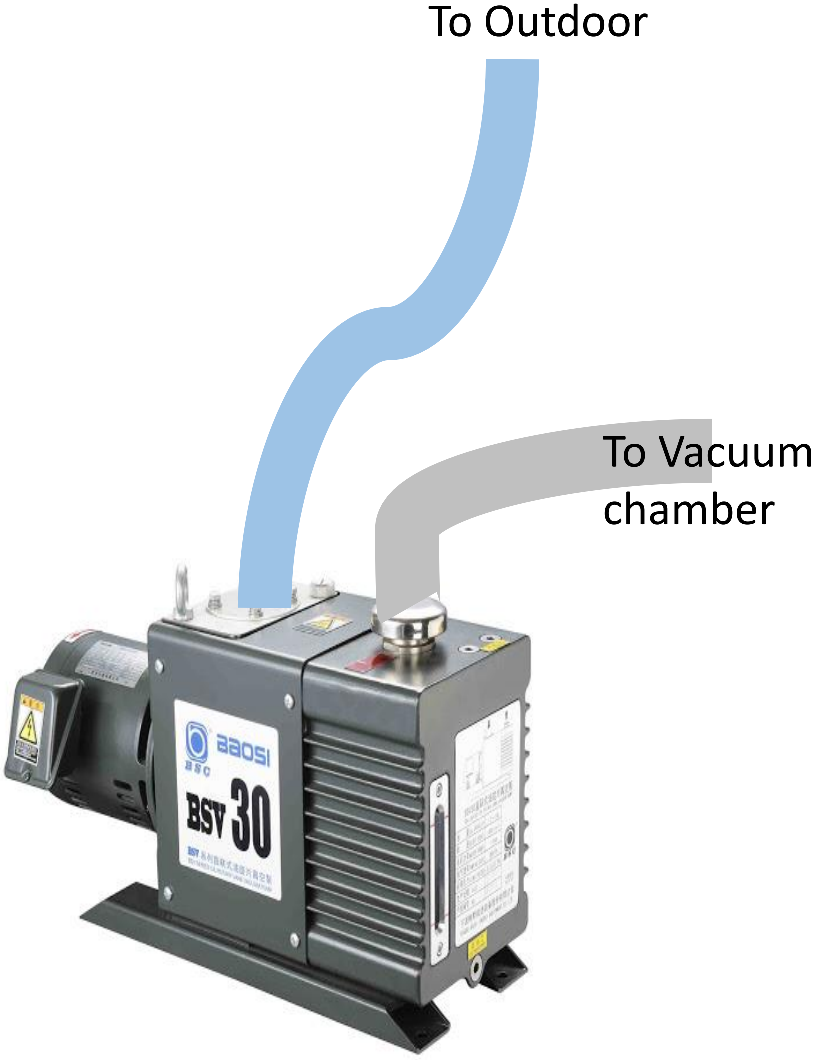
  old pump: 2x 10^{-2} Torr

  bad pump: 1x 10^{-1} Torr

Oil sealed low vacuum pump operation notes:

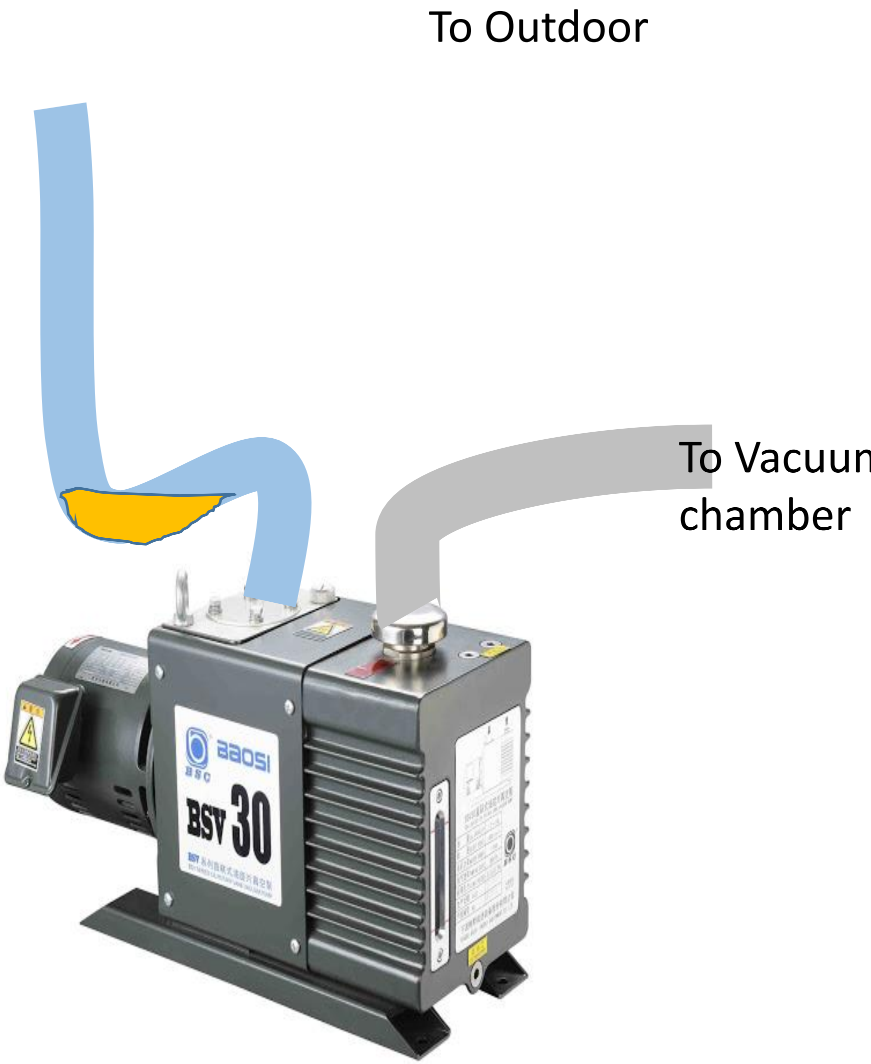
1.Oil level
2. Change oil when it is dirty
3. Change oil when it is hot
4. Pump oxygen?
5. Pump halogen?
6. Pump water vapor?

Oil sealed low vacuum pump operation notes:



To Outdoor

To Vacuum chamber



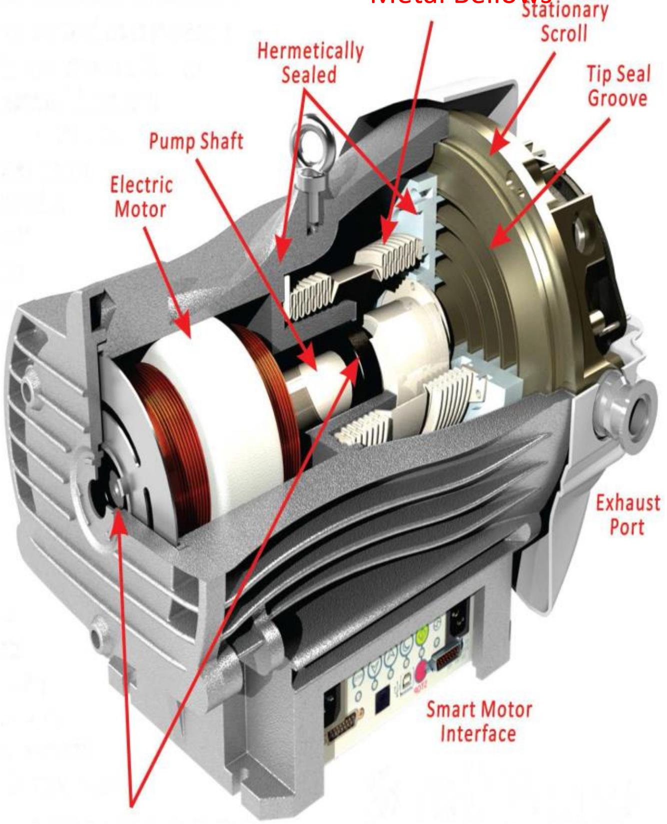
To Outdoor

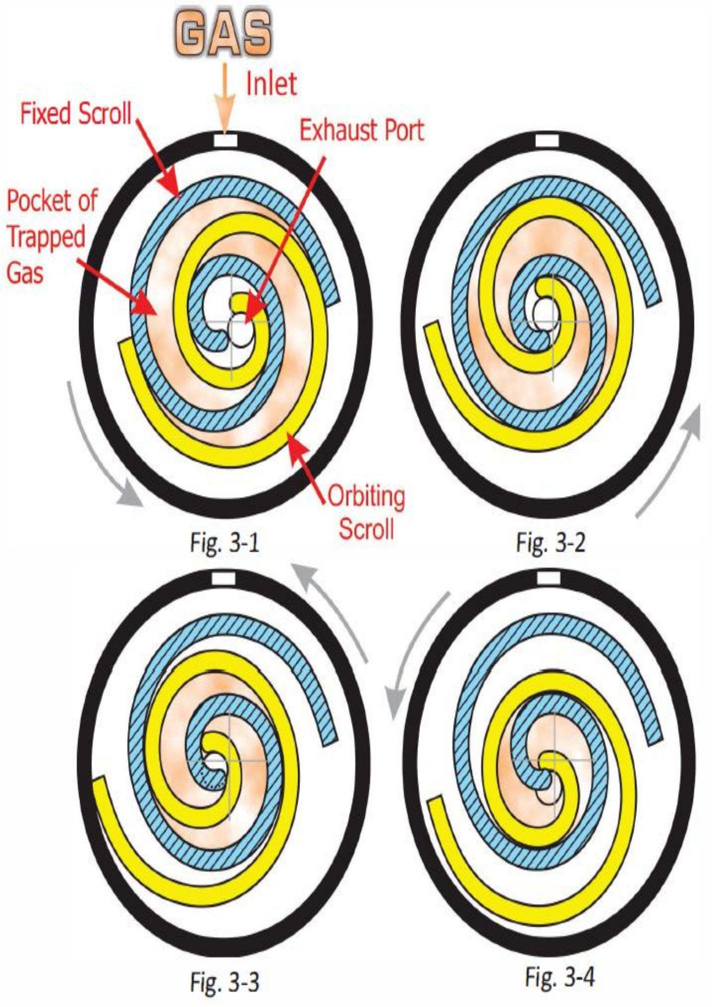
To Vacuu
chamber

oil free low vacuum pump

Low vacuum pump

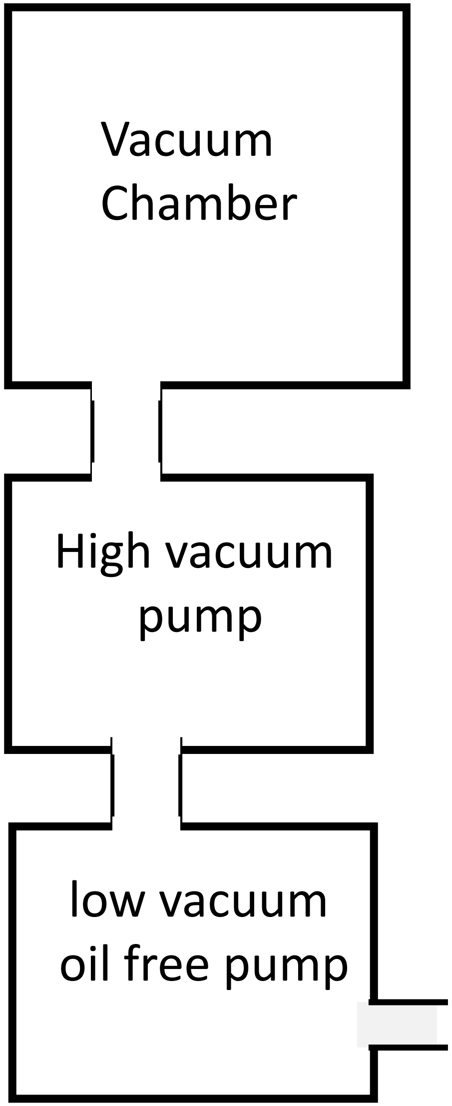
Scroll Pump
Working principle


Metal Bellows



Scroll pump operation notes:

- Change scroll on time



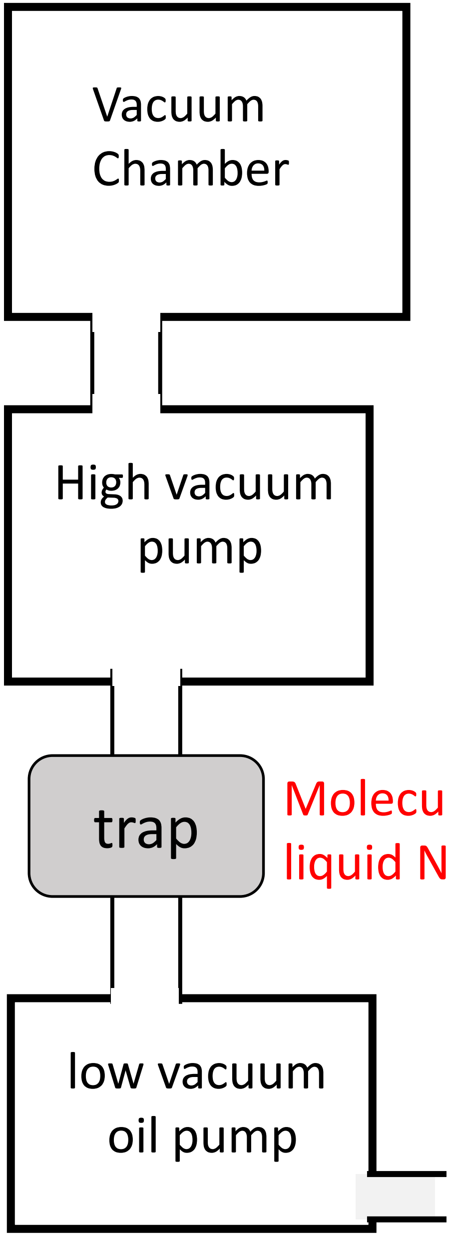
Vacuum Chamber

High vacuum pump

low vacuum oil free pump

Exhaust

Oil free low vacuum pump



Vacuum Chamber

High vacuum pump

trap

Molecular sieve or liquid N_2 trap

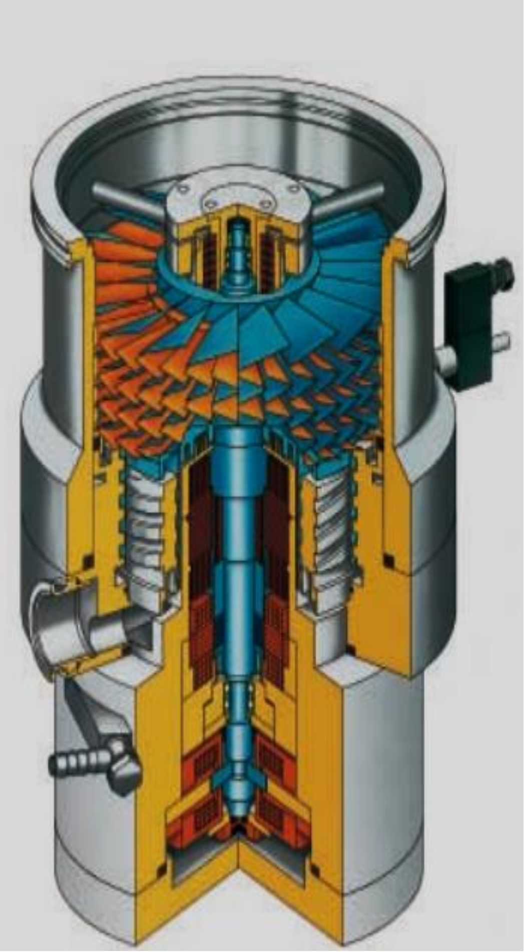
low vacuum oil pump

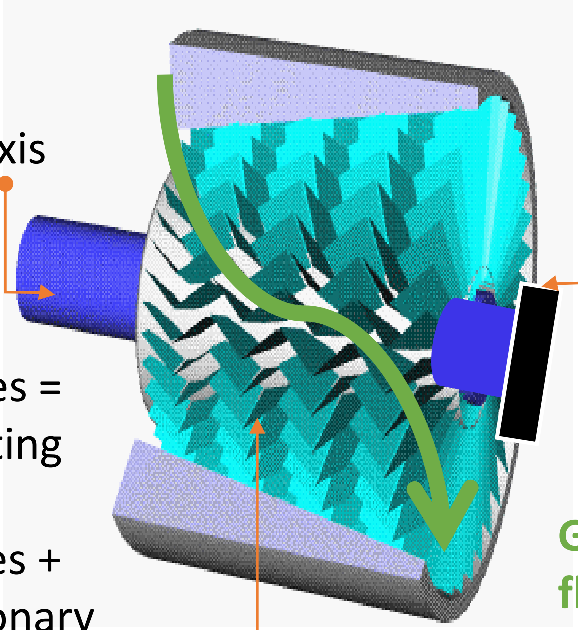
Exhaust

Oil sealed low vacuum pump

High vacuum pump

High vacuum pump: Turbo molecular pump



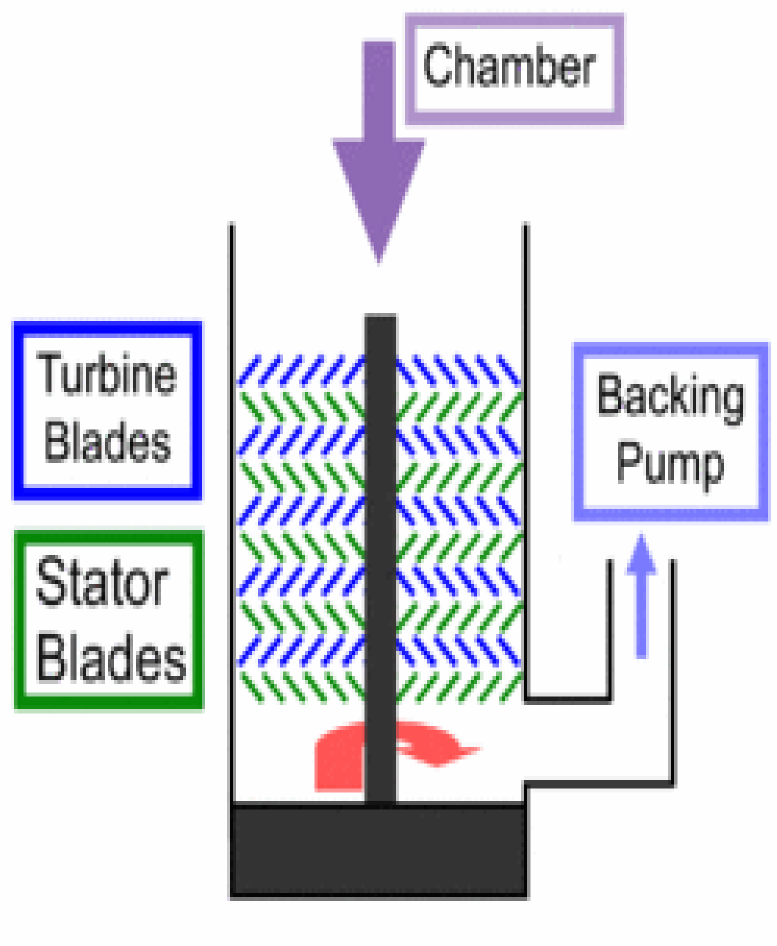


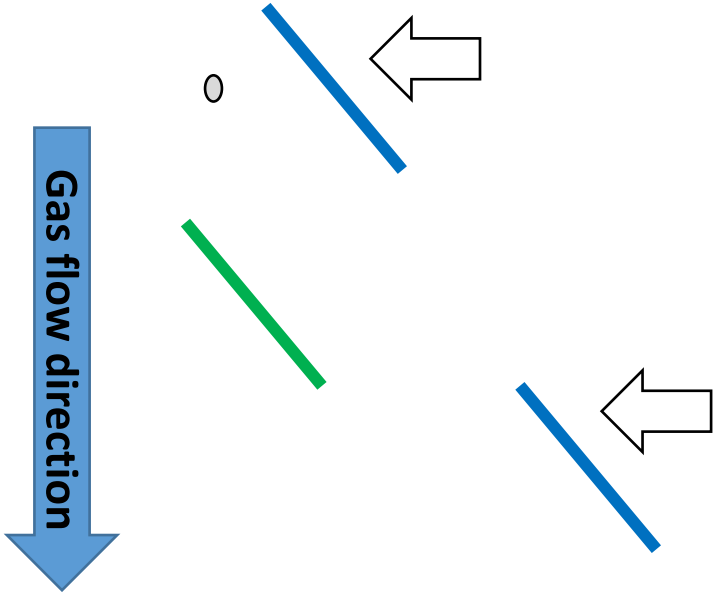
axis

bearing

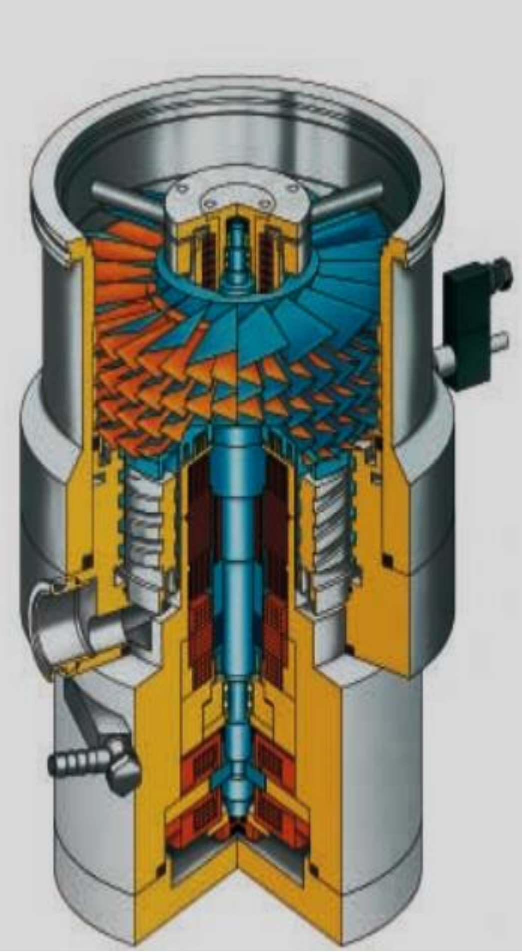
Blades = Rotating rotor blades + stationary stator blade

Gas flow


Chamber
Turbine Blades
Stator Blades
Backing Pump


Gas flow direction

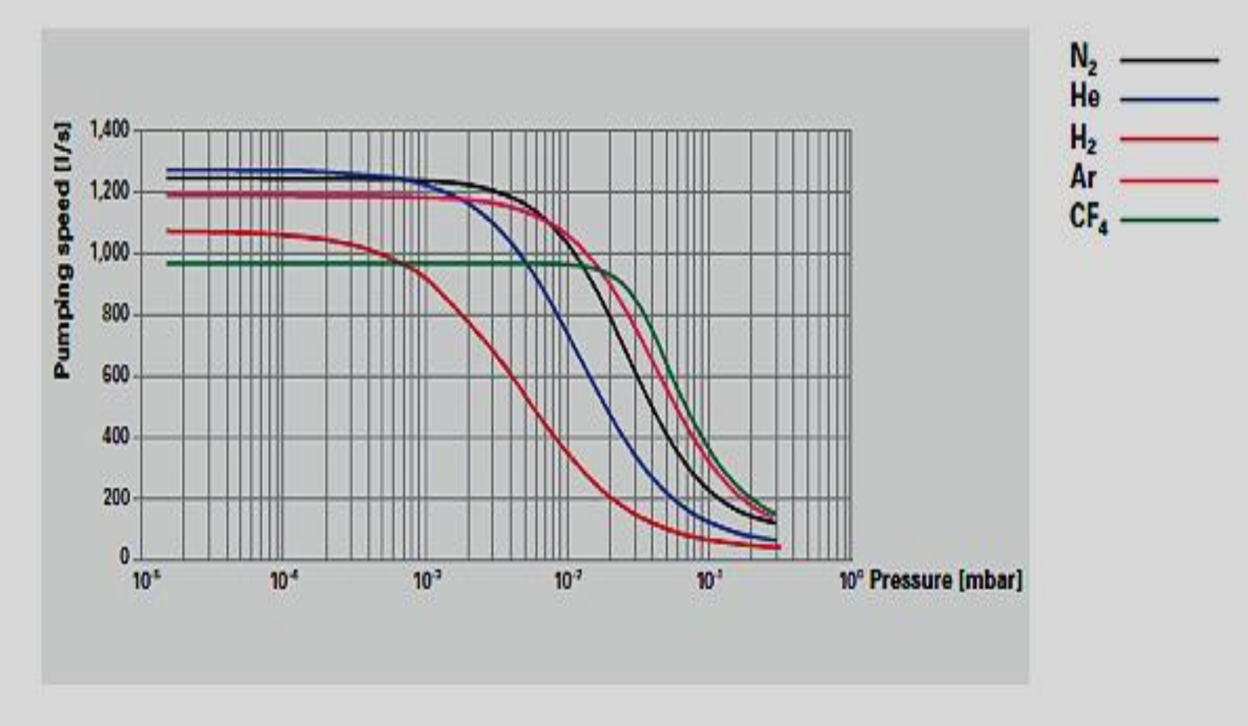
High vacuum pump: Turbo molecular pump



- Pumping speed is proportional to the inlet area A and the mean circumferential velocity of the blades v, i. e. rotational speed.
- Pumping range: 10^{-4} to 10^{-11} Torr
- Oil free, Low vibration & noise

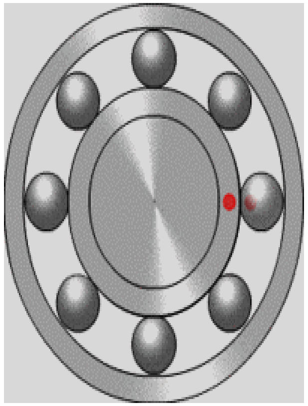
Pumping speed

- Different gases pump down at different rates
- Compression ratio varies exponentially with molecular weight of gases



Turbo molecular pump operation notes

1. A roughing pump is used to get the pressure down to ~10^{-3} Torr
2. Magnetic turbo (how many axis?)/non-magnetic turbo pump
3. Orientation (bearing/oil)
4. Particle drop in
5. Pressure raise
6. Electric power shutdown
7. Vibration (earthquake)



Ball bearing

Turbo-V
81 M

Turbo-V
81 T

Turbo-V 301
Navigator

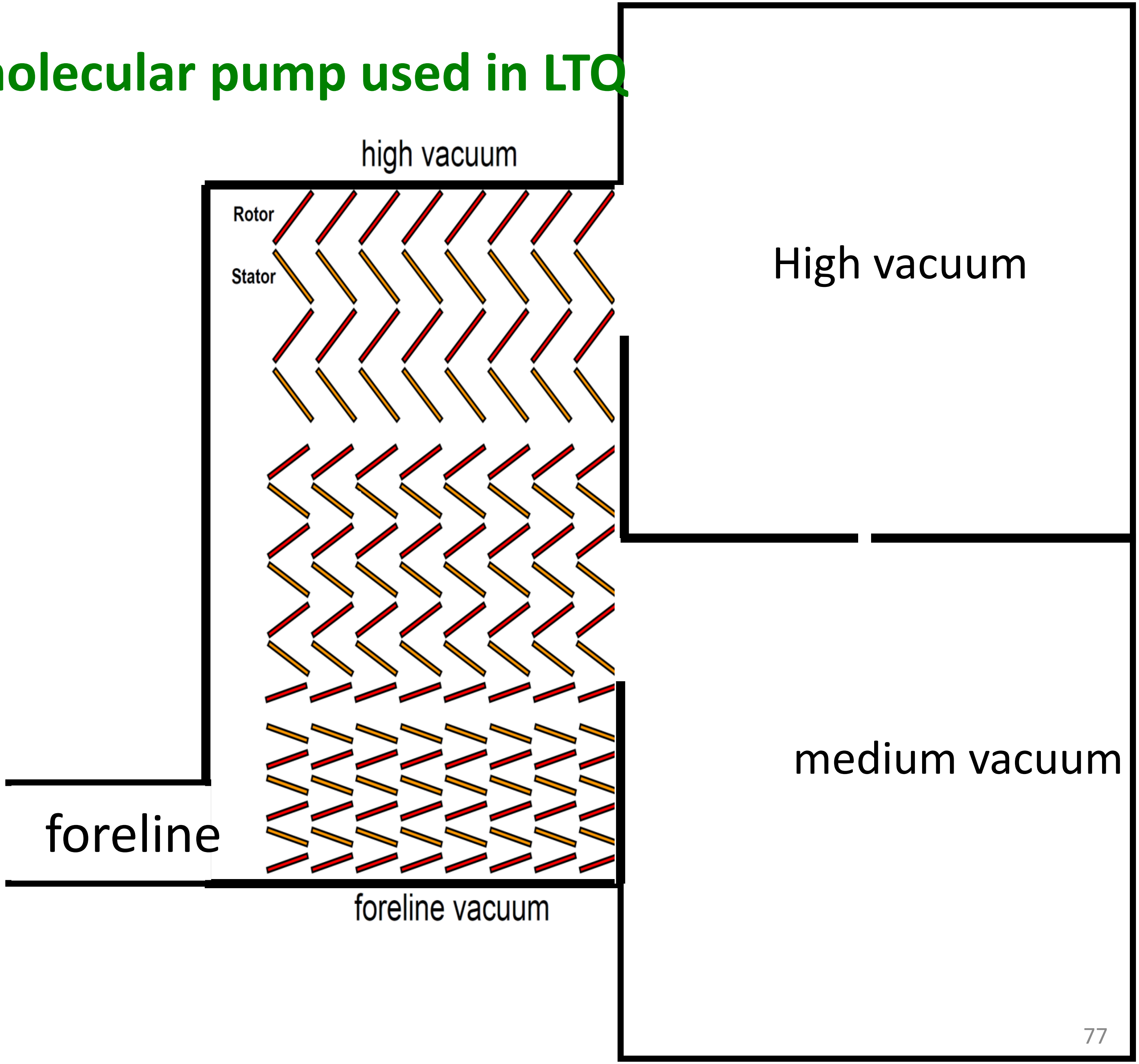
Turbo-V 551
Navigator

Turbo-V 701
Navigator

Turbo-V 1001
Navigator

Pump Model	Turbo-V 81 M	Turbo-V 81 T	Turbo-V 301 Navigator	Turbo-V 551 Navigator	Turbo-V 701 Navigator	Turbo-V 1001 Navigator
Pump Specification	DN 40	DN 63	DN 100	DN 160	DN 200	DN 250
Pumping Speed, l/s						
Nitrogen	50	77	250	550	690	1050
Helium	56	65	220	600	620	900
Hydrogen	46	50	200	510	510	920
Compression Ratio						
Nitrogen	5 x 10^{8}	7 x 10^{8}	7 x 10^{8}	> 1 x 10^{9}	1 x 10^{9}	1 x 10^{9}
Helium	8 x 10^{4}	3 x 10^{3}	1 x 10^{5}	1 x 10^{7}	1 x 10^{7}	1 x 10^{7}
Hydrogen	7 x 10^{3}	3 x 10^{2}	1 x 10^{4}	1 x 10^{6}	1 x 10^{6}	1 x 10^{6}
Base pressure, mbar						
with recommended mechanical pump	5 x 10^{-10}	5 x 10^{-9}	< 5 x 10^{-10}	< 1 x 10^{-10}	< 1 x 10^{-10}	< 1 x 10^{-10}
with recommended dry pump	5 x 10^{-9}	5 x 10^{-8}	< 5 x 10^{-9}	< 1 x 10^{-10}	< 1 x 10^{-10}	< 1 x 10^{-10}
Startup Time, min	< 1	< 1	2.5	< 5	< 5	< 4
Rotational Speed, rpm	80,000	80,000	56,000	42,000	42,000	38,000

Turbo molecular pump used in LTQ



Differential pumping

Molecular flow

aperture

For air at 22 C

C (L/s)=3.7 $(T/M)^{1/2}$ = 11.6 A (cm^2) (for air)

T: temperature in K, M: molecular weight

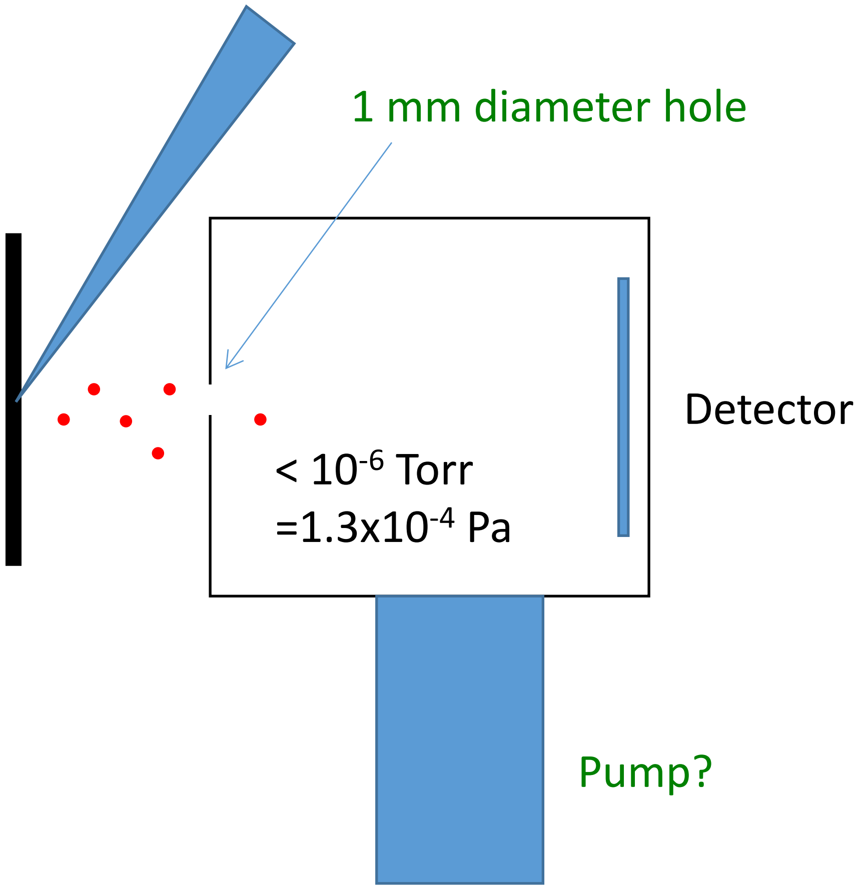
Continuum flow

aperture

Q(Pa-m^3/s)= 200PAC’

P in Pa, A in m^2, C’=0.85

Ambient ionization mass spectrometer



1 mm diameter hole

Detector

$< 10^{-6}$ Torr

$=1.3\text{x}10^{-4}$ Pa

Pump?

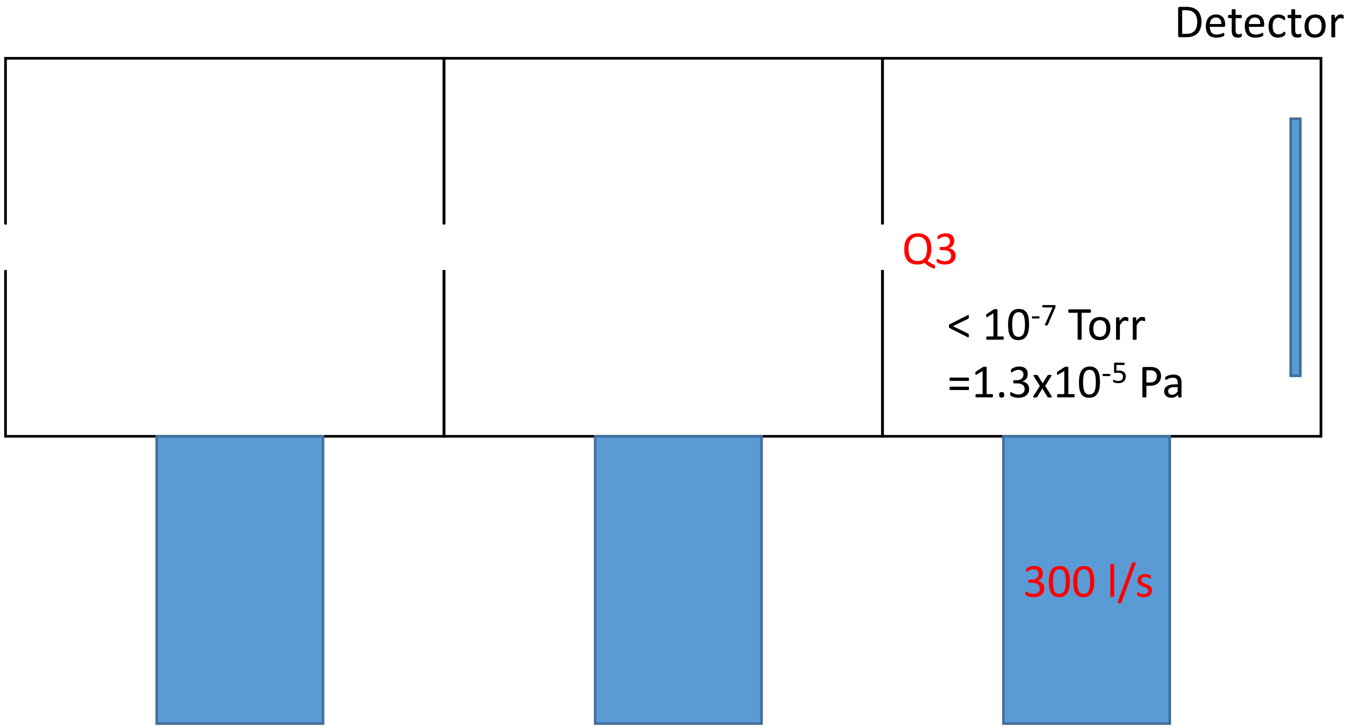
$Q(\text{Pa-m}^3/\text{s}) = 200PAC' = 200 \text{ x } 1\text{x}10^5 \text{ Pa x } 3.14 \text{ x } 0.25 \text{ x}10^{-6} \text{ m}^2 \text{ x}0.85 = 13$

$Q = P\text{x}S$; $13 = 1.3\text{x}10^{-4} \text{ x } S$

$S = 10^5 \text{ m}^3/\text{s} = 10^8 \text{ l/s}$

Differential pumping

$Q_3 = 1.3\text{x}10^{-5}$ x 300 L/s = $1.3\text{x}10^{-5}$ x 0.3 m^3/s = $3.9\text{x}10^{-6}$ Pa-m^3/s

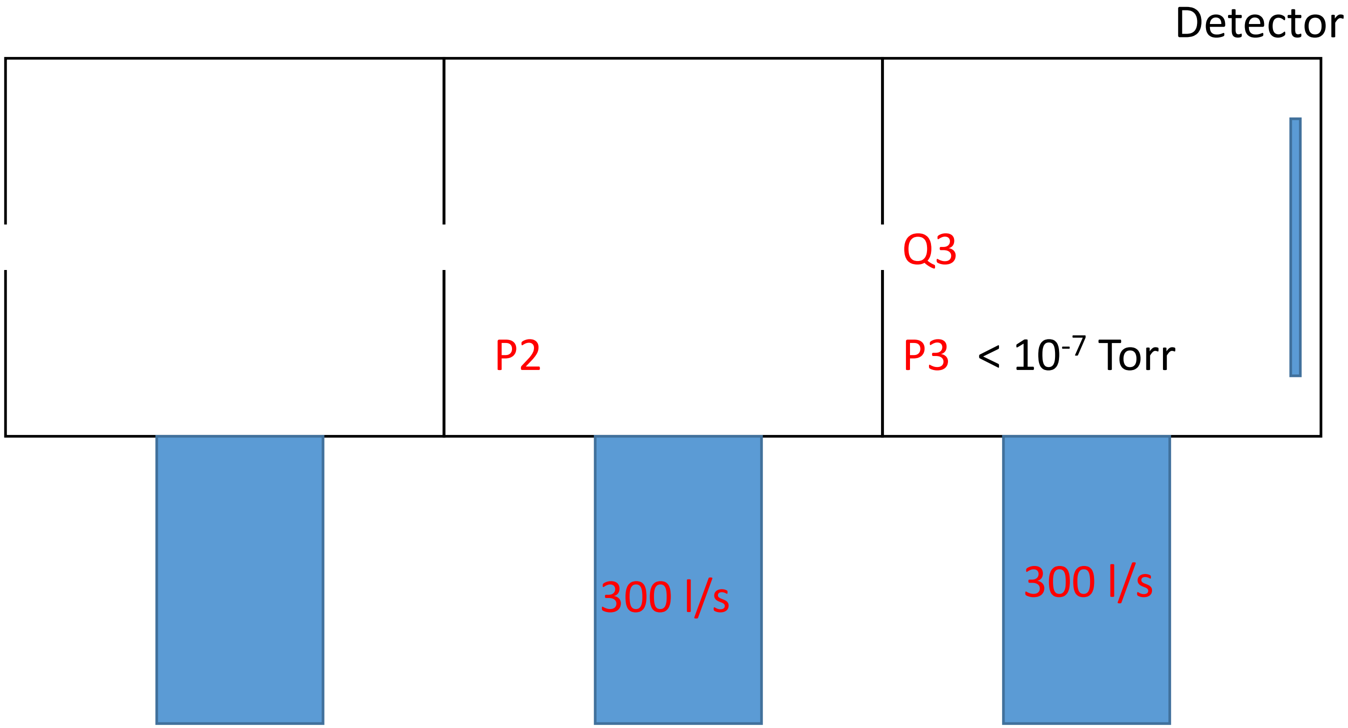


For air at 22 C $A = 3.14 \times 0.05 \times 0.05 = 7.8 \times 10^{-3}\ cm^2$

$C\ (L/s) = 11.6\ A\ (cm^2) = 0.09\ L/s = 9 \times 10^{-5}\ m^3/s$

$Q_3 = 3.9 \times 10^{-6}\ Pa\text{-}m^3/s = 9 \times 10^{-5}\ (P_2 - P_3) = 9 \times 10^{-5}\ P_2$

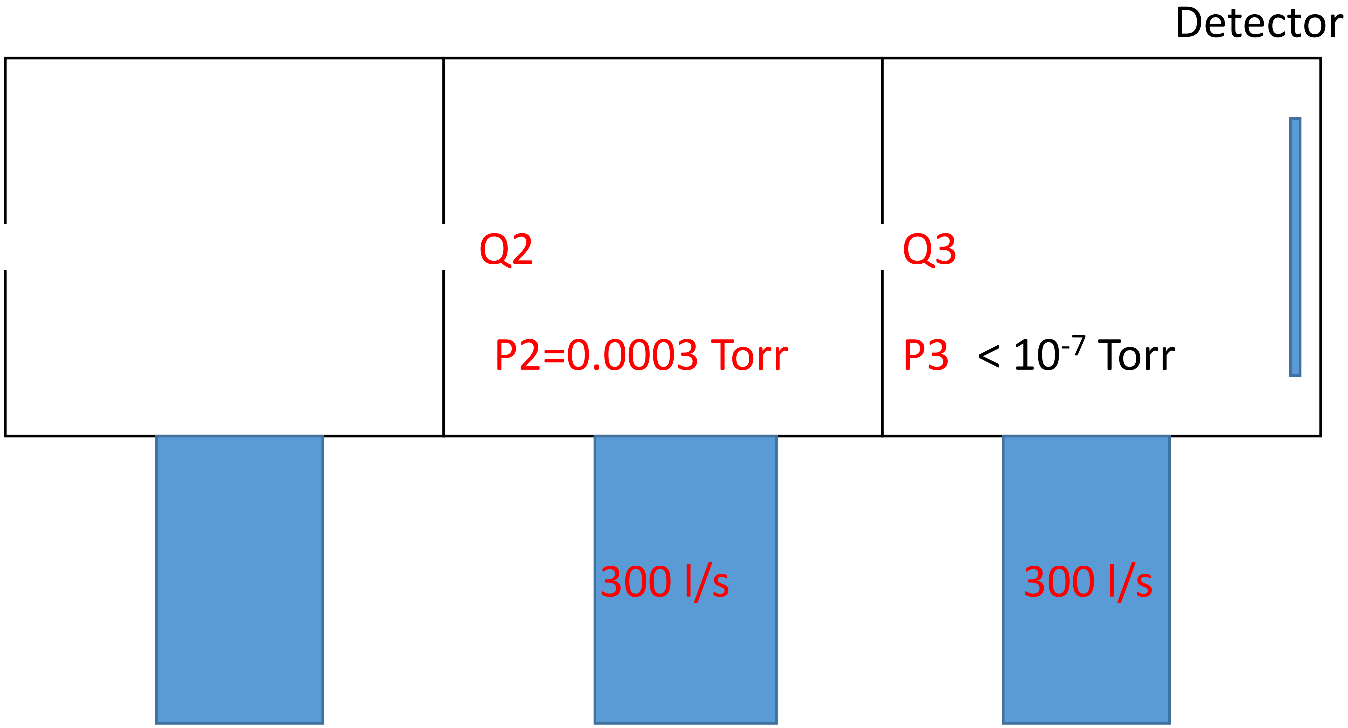
$P_2 = 4.2 \times 10^{-2}\ Pa = 3 \times 10^{-4}\ Torr$



To keep $P_2 = 4.2 \times 10^{-2}$ Pa = 3×10^{-4} Torr

Maximum of Q_2:

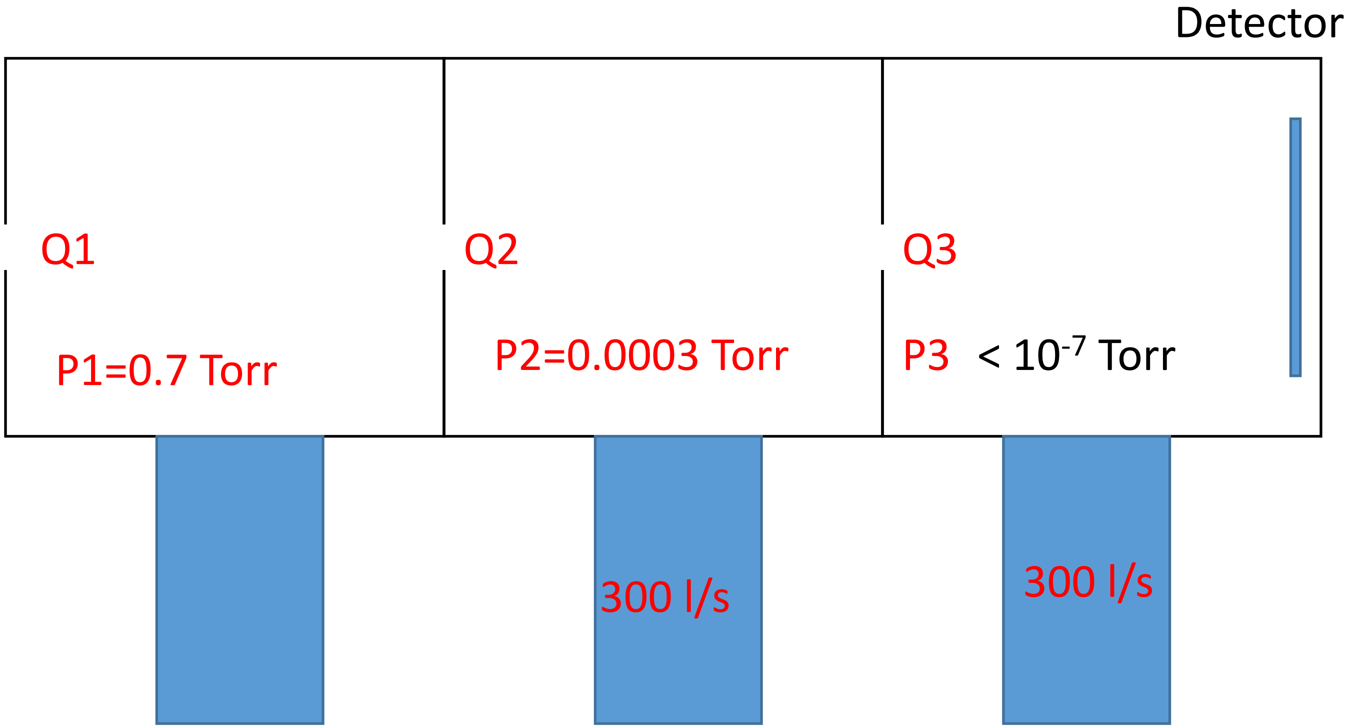
$Q_2 = 4.2 \times 10^{-2}$ Pa x 0.3 $m^3/s = 1.2 \times 10^{-2}$ Pa m^3/s



Q_2=0.012 = 200 P_1AC’ Pa-m^3/s = 1.3x$10^{-4}$$P_1$

A = 7.8 x10^{-7} m^2

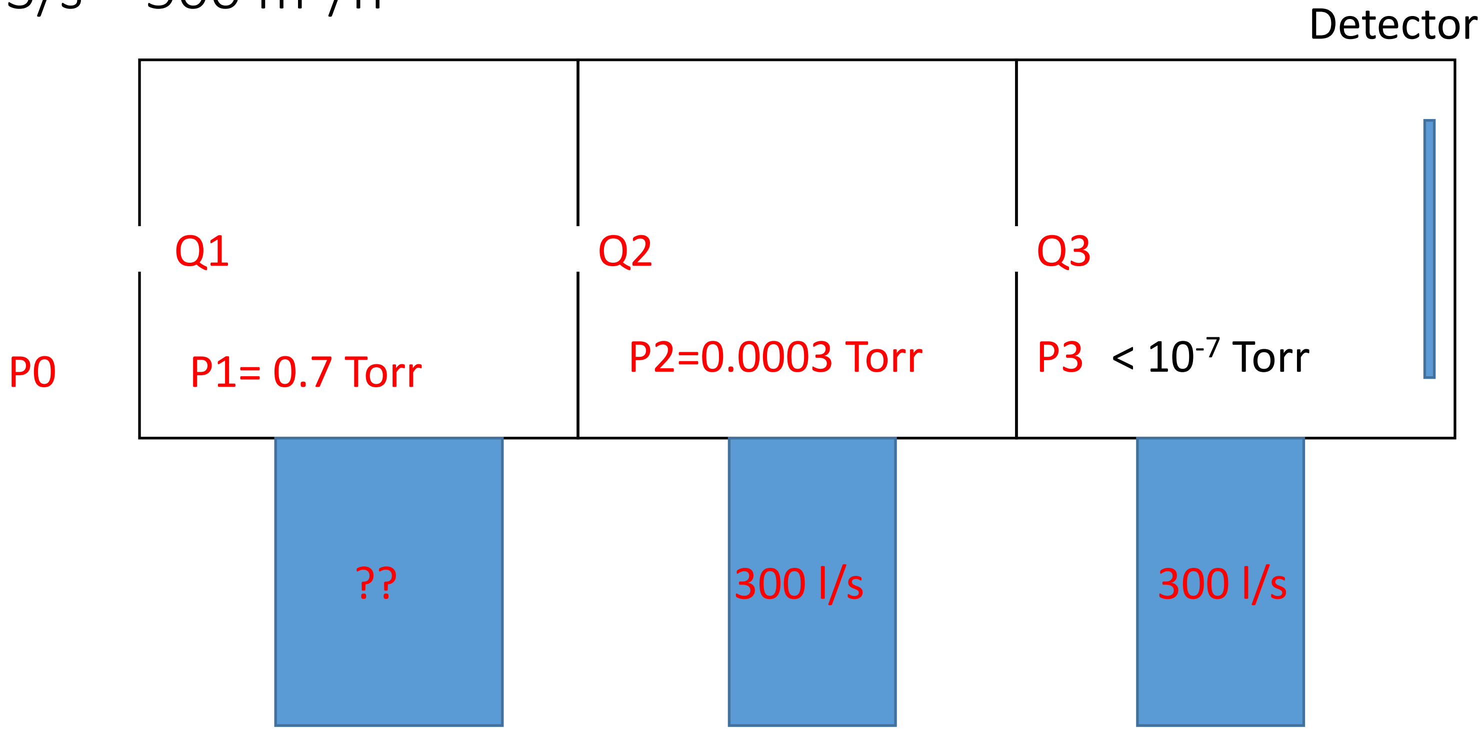
P_1= 92 Pa = 0.7 Torr



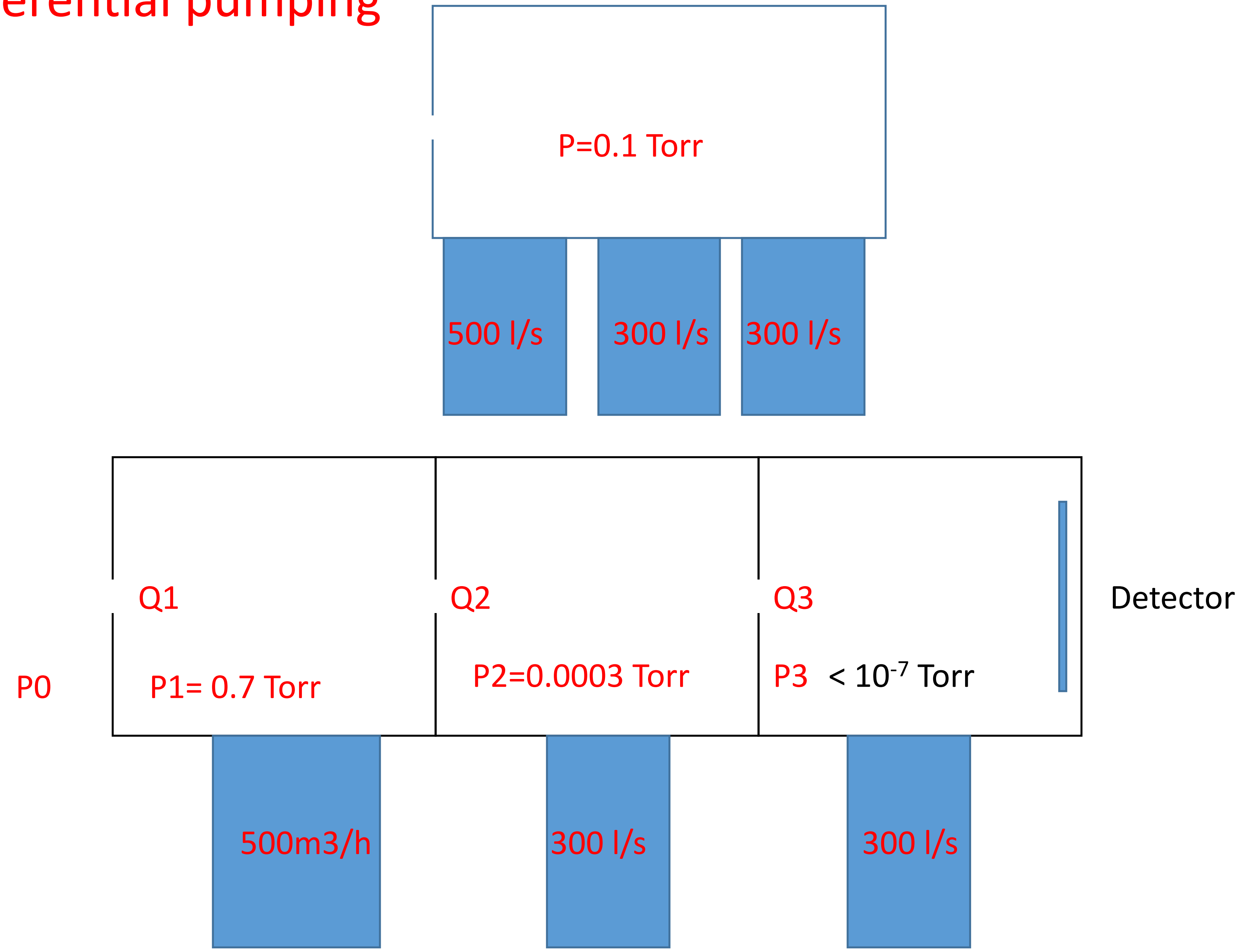
If P_0= 1 atm, to keep P_1 = 0. 7 Torr, what is the pumping speed of S1?

Q_1= 200 P_0AC’ Pa-m^3/s = 13 Pa m^3/s = 92 S_1

S1 = 0.14 m3/s = 500 m^3/h



Differential pumping



P=0.1 Torr

500 l/s

300 l/s

300 l/s

Q1

Q2

Q3

Detector

P0

P1= 0.7 Torr

P2=0.0003 Torr

P3 $< 10^{-7}$ Torr

500m3/h

300 l/s

300 l/s

Pressure detector (gauge)

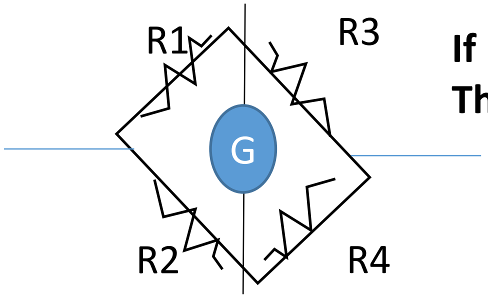
- Low vacuum: direct, indirect
- High vacuum: indirect

Thermal Conductivity Gauges

- Thermal conductivity gauges are a class of pressure-measuring instruments that operates by measuring in some way the rate of heat transfer between a heated wire and its surroundings.
- The heat transfer between a heated wire and a nearby wall is pressure dependent

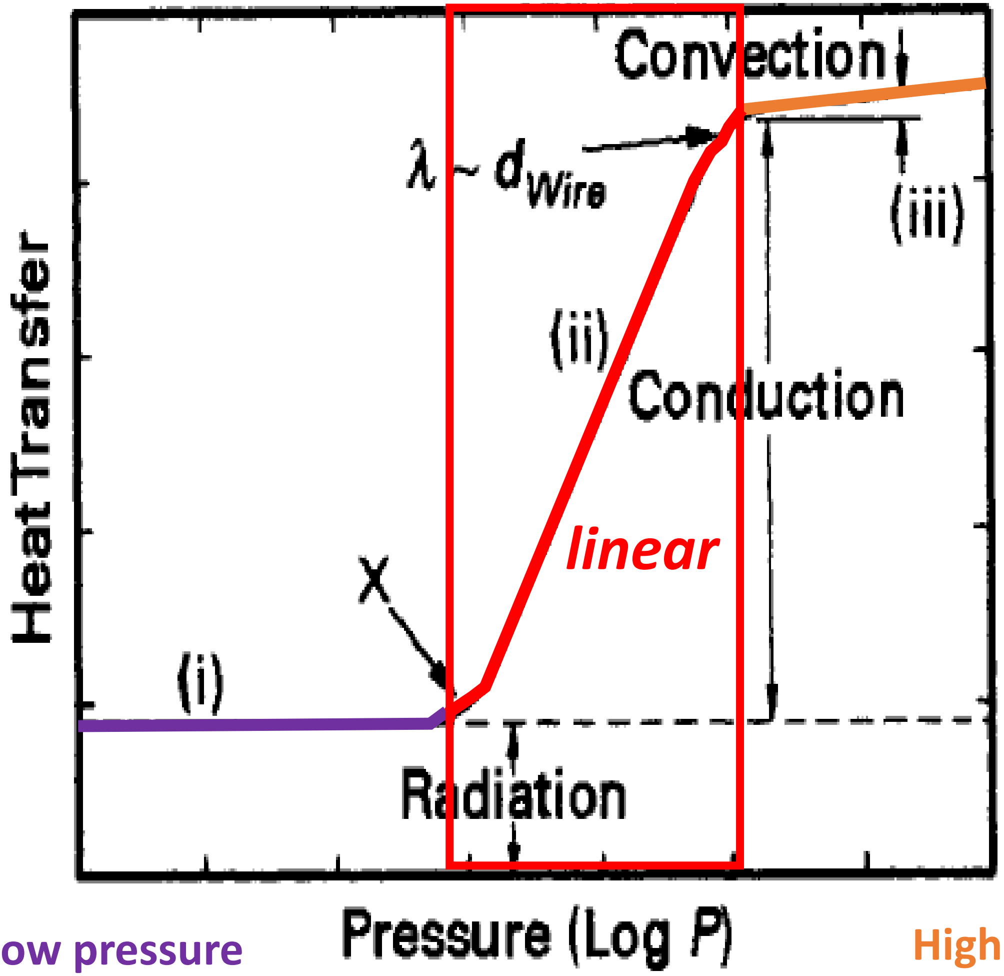
Types of thermal conductivity gauges

- Pirani guage:
  The change in temperature can be detected by monitoring the resistance of the heated wire, then a Wheatstone bridge circuit is used to measure the resistance change.
- Thermocouple gauge
  The change in temperature can be measured directly with a thermocouple.



If R1/R2 = R3/R4
Then G = 0

The heat flow under different pressure



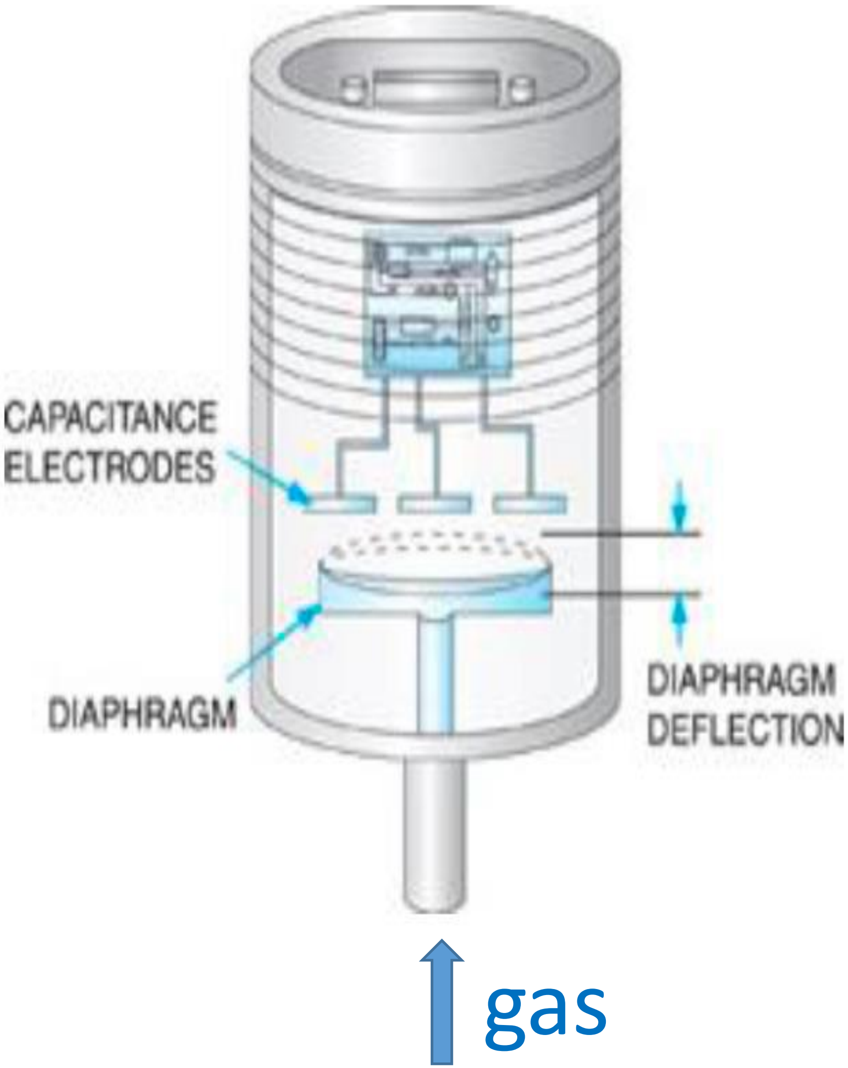
Low pressure

High pressure

Operation notes:

- Orientation
- Gas species

Capacitance manometer: gas species independent



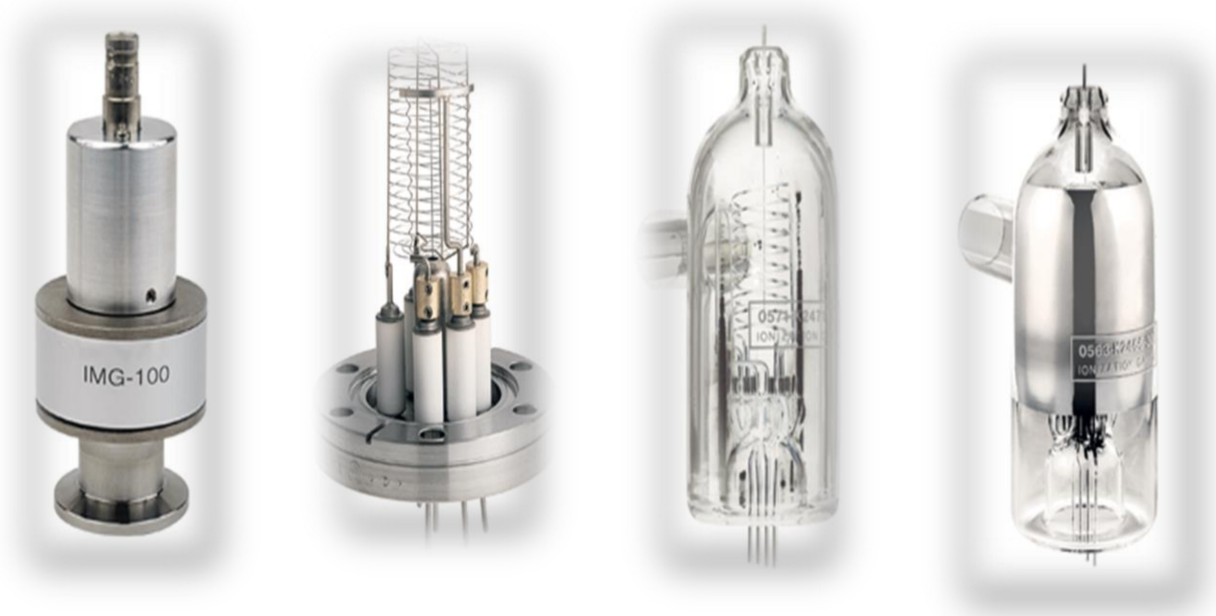
capacitance

$$C = \varepsilon_r \frac{A}{4\pi d} = \frac{Q}{V}$$

Operation notes:

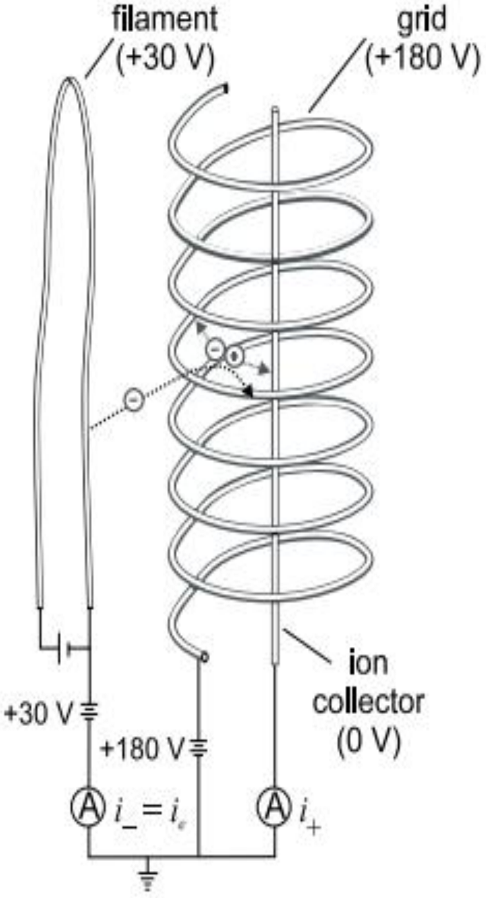
- Orientation
- Calibration

High vacuum gauge



Ionization Gauge for Pressure Measureme

Hot cathode gauge



Nude Bayard-Alpert Gauge
with thoria-coated iridium filament

Using the vacuum chamber makes nude gauge become a complete seal.

∗Gas correction factor

$P = [I_c / (S_g \cdot I_e)]$ where $S_g = S_{N_2} \cdot R_g$

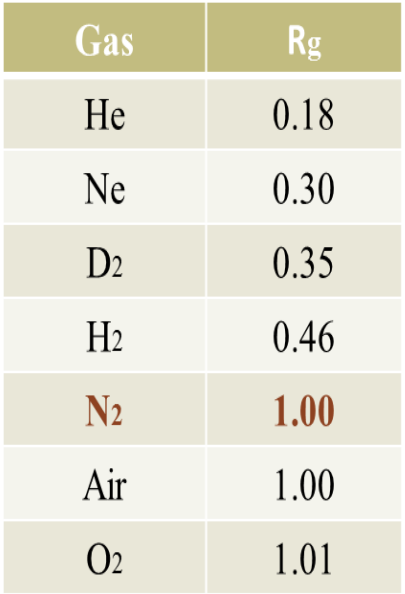
I_c is ionization current collected by ion collector. (amps)

I_e is electron emission current. (amps)

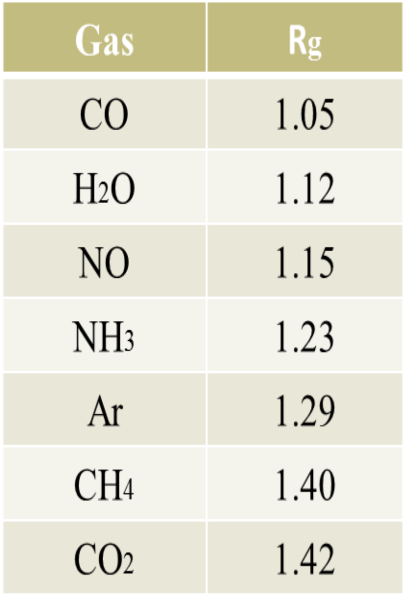
S_g is sensitivity factor for gas “g”. ($torr^{-1}$)

S_{N_2} is sensitivity factor for nitrogen, standard gas used by industry. (tor

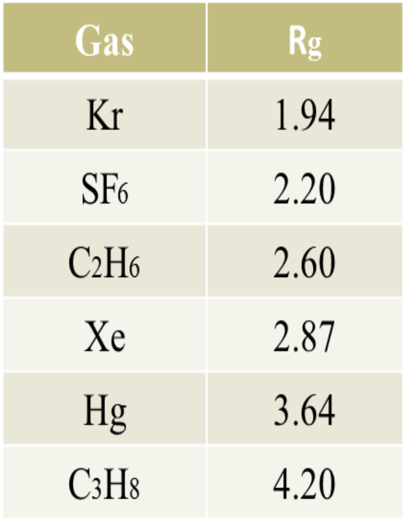
R_g is gas correction or relative sensitivity factor.



Gas	Rg
He	0.18
Ne	0.30
D_2	0.35
H_2	0.46
N_2	**1.00**
Air	1.00
O_2	1.01



Gas	Rg
CO	1.05
H_2O	1.12
NO	1.15
NH_3	1.23
Ar	1.29
CH_4	1.40
CO_2	1.42

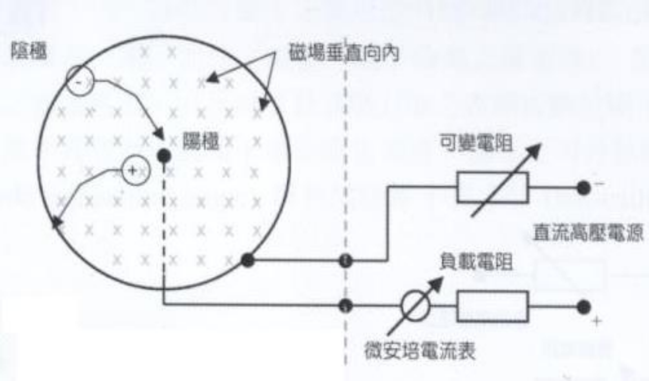


Gas	Rg
Kr	1.94
SF_6	2.20
C_2H_6	2.60
Xe	2.87
Hg	3.64
C_3H_8	4.20

Cold cathode gauge

∗ Working principle

Cold cathode gauge utilize crossed electric and magnetic fields to trap electrons.



Electric field	2000 – 6000 V
Magnetic field	1000 – 2000 G
Range	10^{-2} – 10^{-9} torr

Without fragile filament, cold cathode gauges are robust and economical, suffering only from the limited range of applicability.

Operation notes:

- Pressure
- Gas species

Full range pressure gauge

Combination of convention and ionization gauge