Interaction plasma/matter

S. Lucas,
University of Namur,
Physics Department
LARN Laboratory
61 Rue de Bruxelles,
B-5000 Namur,
Belgium

Stephane.lucas@fundp.ac.be

Table of content

If you want to apply the included formulas:

1ev->K	11600	K
Boltzman (J/K)	1,3806E-23	Bolt
Avogadro	6,0221E+23	Avo
amu (MeV)	931,49	Mev
Pi	3,14159265	pi
M proton (kg)	1,6726E-27	Mp
M électron (kg)	9,1094E-31	Me
amu (kg)	1,6605E-27	amu
µ0 (H/M)	1,25664E-06	mu0
ε0 (Φ/M)	8,8542E-12	eps0
Electron charge	1,6E-19	e

Chapter I: Gas

1.Introduction

Gas in a closed system

Gas and vapors in the vacuum range where cold plasma are carried out can be considered as ideal gases for all practical purposes. Therefore, It is necessary to understand the basics of gas-phase reactions and vacuum systems.

The kinetic theory of gases can be applied providing the following assumptions are met :

- Swarm of particules of mass m in a random motion,

- Negligible size (radius of gas atom < mean free path)

- Elastic collisions predominant

Those assumptions are nearly met for low pressure plasmas.

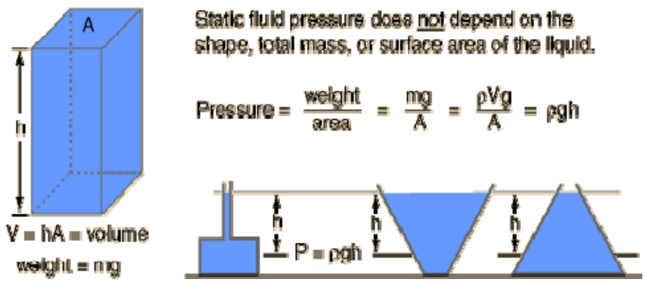
What can drive away from ideal gas ?

- Effect of E (Electric field)
- Inelastic collisions, ….

2.Pressure

$$P = \frac{F_\perp}{S} = \frac{F_\perp}{A} \quad (N/m^2)$$

When you deal with the pressure of a liquid at rest, the medium is treated as a continuous distribution of matter.

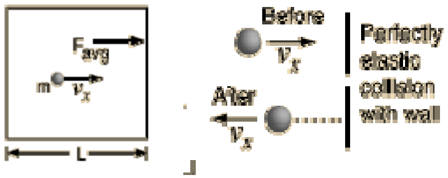


Pa	Torr, mmHg	Bar	Atm	mm water
101.300	760	1,013	1	$1,03x10^4$

But when you deal with a gas pressure, it must be approached as an average pressure from molecular collisions with the walls

3. Pressure of an ideal gas

- One mole of an ideal gas contains $6.02x10^{23}$ molecules (N_a).
- At the standard state of temperature (273K) and 1 atm pressure (760 Torr, 1 athm), it occupies 22.4 liters.



$$\Delta p = p_f - p_i$$
$$= m.\vec{V}_{xf} - m.(\vec{V}_{xi})$$
$$= 2.m.\vec{V}_x$$

But :

$$\Delta p = <\vec{F}>.\Delta t \quad \rightarrow \quad <\vec{F}> = \frac{\Delta p}{\Delta t}$$

$$<\vec{F}> = \frac{2.m.\vec{V}_x}{\frac{2.L}{\vec{V}_x}} = \frac{m.<\vec{V}_x>^2}{L}$$ for a round trip

3. Pressure of an ideal gas

For N molecules,

$$<\vec{F}> = \frac{m.N.<\vec{V}_x^2>}{L}$$

If random speed in all directions:

$$<\vec{V}^2> = <\vec{V}_x^2>+<\vec{V}_y^2>+<\vec{V}_z^2>$$

$$=3<\vec{V}_x^2>$$

The pressure is then;

$$P=\frac{<\vec{F}>}{A}=\frac{m.N.<\vec{V}^2>}{3.L.A}=\frac{m.N.<\vec{V}^2>}{3.V}$$

$$=\frac{m.<\vec{V}^2>}{3}.\tilde{N}$$

In terms of kinetic energy:

$$P = \frac{m.<\vec{V}^2>}{3}.\tilde{N} = \frac{2}{2}\frac{m.<\vec{V}^2>}{3}.\tilde{N}$$

$$P = \frac{2}{3}.E_c.\tilde{N} = \frac{2}{3}.E_c.\frac{N}{V} \qquad \text{(I.1)}$$

2. Pressure excerted by a ideal gas

If we use the ideal gas law :

$$P.V=n.R.T$$

R = k .N_a = 8.31 J/mole °K = k.N /n
= 6.24 10 $^{-4}$ Torr cm^3/mol °K
K = 1.38 10 $^{-23}$ J/°K = 8.617 10^{-5} eV/K

n: number of mole = mass of the material (in grams) equal to the molecular mass in amu
N : Number of molecules = n . Na

ex: 1 mole (n=1) of C = 12 gr = 6.02 10^{23} molecules

$$P.V=n.R.T \quad \text{and} \quad P.V = \frac{2}{3}.N.E_c$$

$$T=\frac{P.V}{n.R}=\frac{2}{3}.\frac{N}{n.R}.E_c \qquad \text{(I.2)}$$

There is a relashionship between E_c and T°: Gas have a T°

3. Pressure by an ideal gas

If we use the ideal gas law :

R = k .N_a = 8.31 J/mole °K = k.N /n
= 6.24 10 $^{-4}$ Torr cm^3/mol °K
K = 1.38 10 $^{-23}$ J/°K = 8.617 10^{-5} eV/K

$$T = \frac{P.V}{n.R} = \frac{2}{3}.\frac{N}{n.R}.E_c \quad \Rightarrow \quad E_c = \frac{3}{2}.\frac{n.R}{N}.T$$

$$\frac{m\vec{V}^2}{2} = \frac{3}{2}.k.T$$ Per molecules (I.3)

$$\frac{M\vec{V}^2}{2} = \frac{3}{2}.R.T$$ Per moles

Rem:

$$\tilde{N} = \frac{N}{V} = \frac{P}{k.T} = 9.65\,10^{18}\,\frac{P\ (\mathrm{Torr})}{T\ (°K)} \qquad (\mathrm{molec/cm^3})$$

(I.4)

!! Number of molecules/cm^3 independant of molecular weight of the gas (ethylene (M=28), styrene (M=104) : N/V equals,

3. Pressure by an ideal gas

Summary so far:

$$T = \frac{2}{3}.\frac{N}{n.R}.E_c$$

$$P = \frac{2}{3}.E_c.\tilde{N} = \frac{2}{3}.E_c.\frac{N}{V}$$

$$E_c = \frac{m\vec{V}^2}{2} = \frac{3}{2}.k.T$$

⇓

Everything relies on speed (V)

4. Molecular speeds

4.1 Mean values

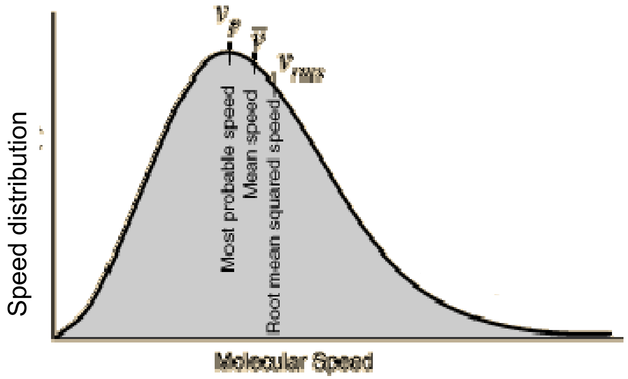
$$\text{From } E_c = \frac{3}{2}.k.T = \frac{m.\vec{V}^2}{2}$$

We find $$\vec{V}_{rms} = \sqrt{\frac{3.k.T}{m}} \quad (m:kg;T:K)$$

If 1 eV = 11600 K

$$Al\,,\ 1200°C \rightarrow V_{rms} = 0.19\ eV = 1166\ m/s$$
$$H_2,\ 1200°C \rightarrow V_{rms} = 0.19\ eV = 4286\ m/s$$

But, gas have a speed distribution



4. Molecular speeds

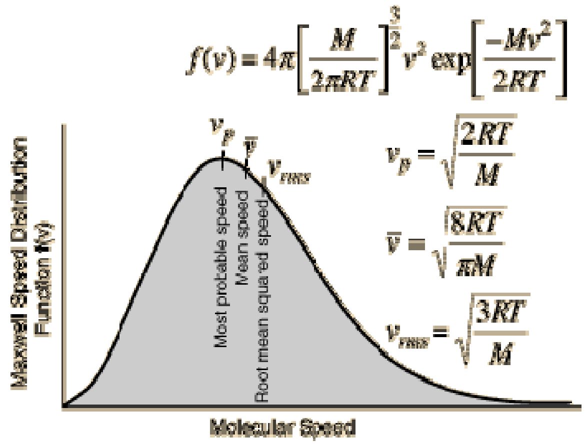
4.1 Distribution

The different molecules do not have exactly the same speed. Their speeds are distributed according to the Maxwell speed distributions

$$f(\vec{V}) = 4.\pi\left(\frac{m}{2.\pi.k.T}\right)^{3/2}.e^{-\left(\frac{m.\vec{V}^2}{2.k.T}\right)}.\vec{V}^2$$

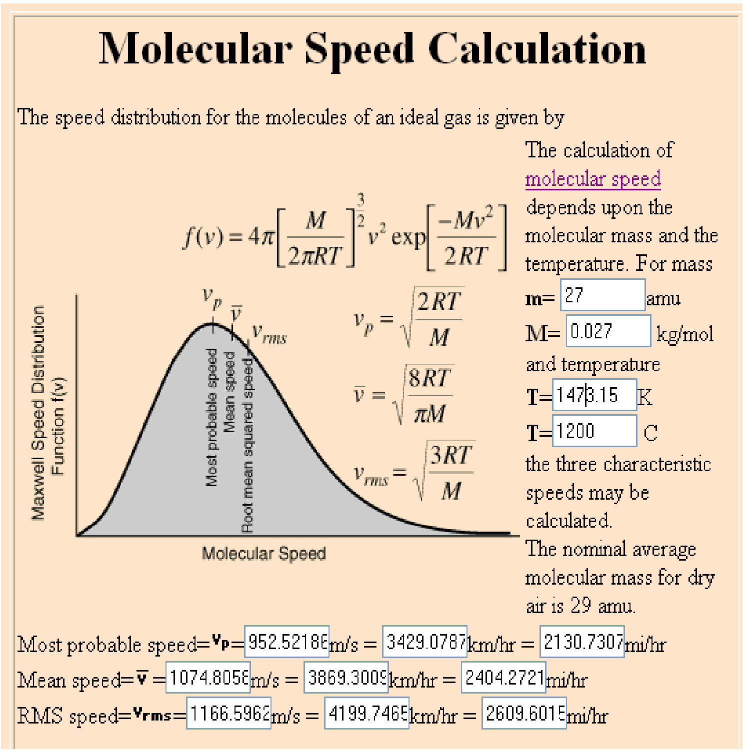
$$\vec{V}_{rms} = \sqrt{\frac{3.k.T}{m}}, \quad \vec{V}_{mp} = \sqrt{\frac{2.k.T}{m}}, \quad <\vec{V}> = \sqrt{\frac{8.k.T}{\pi.m}}$$

(I.5) (I.6) (I.7)



4. Molecular speeds

Example



Molecular Speed Calculation

The speed distribution for the molecules of an ideal gas is given by

$$f(v) = 4\pi\left[\frac{M}{2\pi RT}\right]^{\frac{3}{2}} v^2 \exp\left[\frac{-Mv^2}{2RT}\right]$$

$$v_p = \sqrt{\frac{2RT}{M}} \qquad \bar{v} = \sqrt{\frac{8RT}{\pi M}} \qquad v_{rms} = \sqrt{\frac{3RT}{M}}$$

The calculation of molecular speed depends upon the molecular mass and the temperature. For mass m= 27 amu M= 0.027 kg/mol and temperature T= 1473.15 K T= 1200 C the three characteristic speeds may be calculated. The nominal average molecular mass for dry air is 29 amu.

Most probable speed= v_p= 952.5218 m/s = 3429.0787 km/hr = 2130.7307 mi/hr

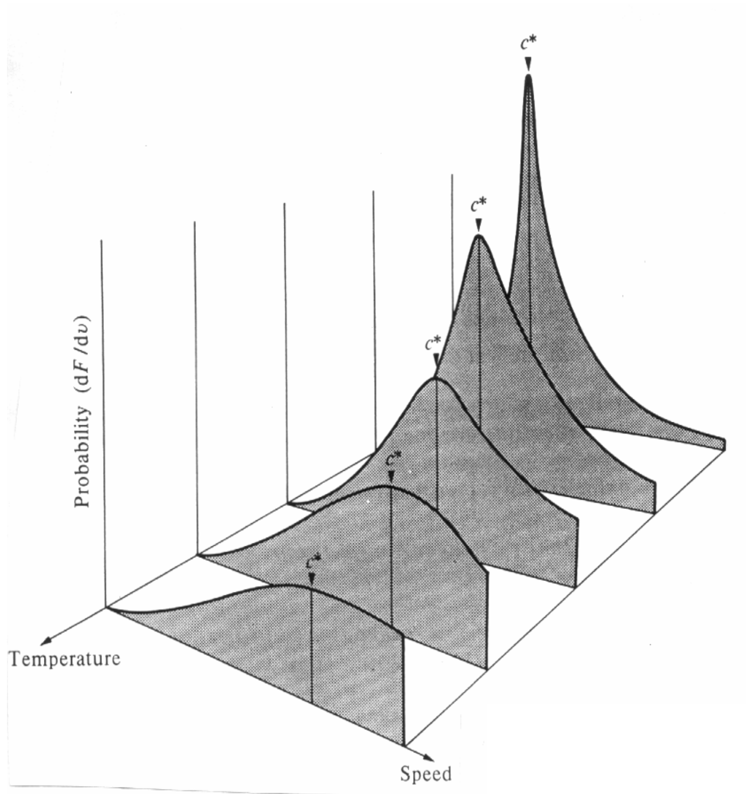
Mean speed= $\bar{v}$ = 1074.8058 m/s = 3869.3009 km/hr = 2404.2721 mi/hr

RMS speed= v_{rms}= 1166.5962 m/s = 4199.7465 km/hr = 2609.6015 mi/hr

http://hyperphysics.phy-astr.gsu.edu/hbase/kinetic/kintem.html

4. Molecular speeds

Effect of T°

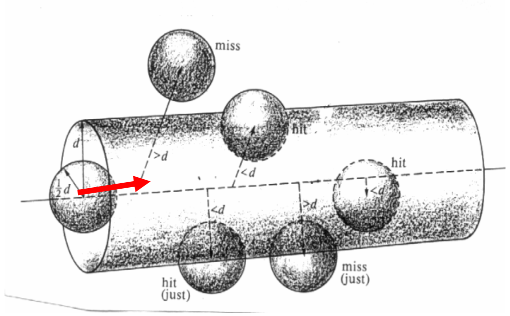


5. Collisions

5.1 Intermolecular

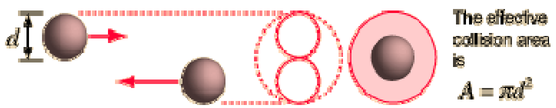
5.1.1 Reaction rate

- Molecules = hard spheres
- Position of all atoms (mol.) are frozen except the one of interest



Hit when centre of 2 molecules are within d = 2r

Effective collision area is s = $\pi.d^2$ = ***cross section*** = σ



- Molecule moving sweeps out a tube of area πd^2 and length $\langle V\rangle.\Delta t$
- All collisions are within that volume:

$$Volume = \sigma.\langle\vec{V}\rangle.\Delta t$$

5. Collisions

5.1 Intermolecular

5.1.1 Reaction rate

$$\text{If } \tilde{N} = \frac{N}{V} = \text{number of molecules in that volume}$$

$$\text{Number of collisions: } N_c = \tilde{N}.\sigma.\langle\vec{V}\rangle.\Delta t \qquad \text{(Coll)} \qquad (I.8)$$

$$\text{Collision frequency: } \nu_c = \tilde{N}.\sigma.\langle\vec{V}\rangle \qquad \text{(Coll/s)} \qquad (I.9)$$

$$\text{Reaction rate: } R = \nu_c.\frac{N}{V} = \sigma.\langle\vec{V}\rangle.\left(\frac{N}{V}\right)^2 \qquad (\text{Coll/cm}^3\text{.s}) \qquad (I.10)$$

$$\text{Rem.: } r_{Ar} \approx 3.56\text{x}10^{-10}\text{m}$$

$$\sigma(Ar \rightarrow Ar) = \pi.r^2 = 3.98 \quad 10^{-19}\text{m}^2$$

5. Collisions

5.1.2 Mean free path

$$\lambda = \frac{<V>}{\nu_c} = \frac{1}{\sigma.\tilde{N}} \qquad \text{(I.11)}$$

But N = n.Na and P.V = n.R.T

$$\lambda = \frac{1}{\sigma}\frac{kT}{p} \rightarrow \lambda \approx \frac{T}{p}$$

To be exhaustive, we must consider that target molecules in the swept cylinder are also moving, and therefore the mean free path and the frequency of collisions depend upon the average velocity of the randomly moving molecules.

$$<\vec{V}_{rel}> = \sqrt{2} <\vec{V}>$$

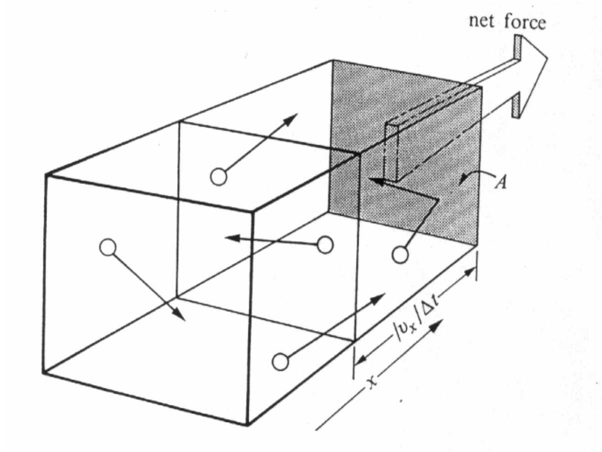
$$\lambda = \frac{1}{\sqrt{2}\sigma}\frac{k.T}{P} \quad (\text{P in Pa}) \qquad \text{(I.12)}$$

$$\lambda_{é} = 4.\sqrt{2}\lambda_{ions} \qquad \text{(I.13)}$$

5. Collisions

5.2 With walls

Suppose wall of area A perpendicular to x Axis and volume density of container N/V particules



All molecules in volume A. V_x.Δt will strike the wall at interval time Δt.

Intermolecular collisions showed that

$$N_c = \tilde{N}.\sigma.<\vec{V}>.\Delta t \qquad \text{(Coll)}$$

Wall area

Dist. MB

5. Collisions

$$N_c = \tilde{N}.A.\Delta t \int_0^{\infty} \vec{V}_x . f(x). d\vec{V}_x$$

$$N_c = \tilde{N}.A.\Delta t. \sqrt{\frac{k.T}{2.\pi.m}}$$

$$n_c = \frac{N_c}{A.\Delta t} = \tilde{N}. \sqrt{\frac{k.T}{2.\pi.m}} = \frac{\tilde{N}}{4}.<\vec{V}> \qquad \text{(I.13-b)}$$

(Coll/s.cm^2)

But

$$P.V = n.R.T$$

$$P.V = N.k.T$$

$$n_c = \frac{p}{k.T}. \sqrt{\frac{k.T}{2.\pi.m}} = \frac{p}{\sqrt{2.\pi.m.k.T}} \qquad \text{(I.14)}$$

6. Mono layer formation time

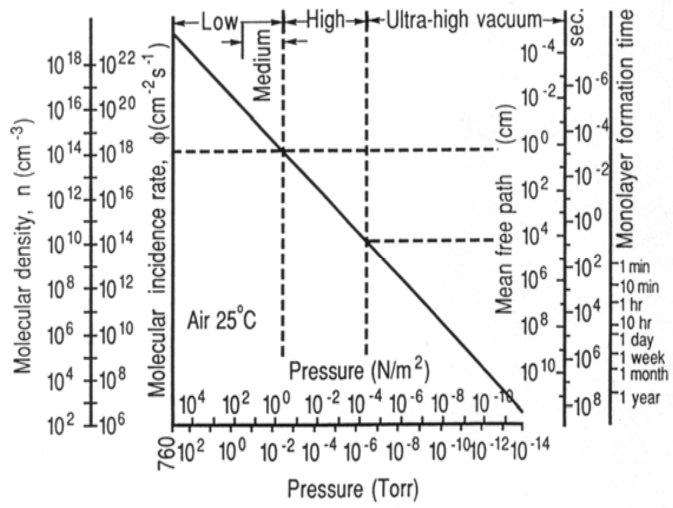
$$T_c \; (10^{15} \text{ at/cm}^2) = \frac{10^{15}}{n_c} = 7x10^5 \frac{\sqrt{m.T}}{P} \quad (s) \qquad \text{(I.15)}$$

m: kg, M: kg/Mol, P: Torr

$$= 2.85x10^{-8} \frac{\sqrt{M.T}}{P}$$

If all molecules stick

In air at 20°C; ≈ 3.5 10-9 sec,
At 10^{-10} T ≈ 7.3 h.



7. Gas flow

We've been so far talking about a fixed number of atoms in a sealed enclosure. Reality in plasma processing is that we have a steady state population of atoms being continuously fed by gas flow and pumped by a vacuum system. Depending on the plasma process, the gas inlet is either consumed or not:

•Plasma etching and deposition: gas inlet consummed,
•Plasma sputtering: no comsumption of the sputtering gas.

Type of gas flow:

☒ At high pressure, λ ↓↓↓, → lot of collisions.

☞ Atoms move by collisions with each others,

→ *VISCOUS FLOW* (laminar or turbulent)

☒ At low pressure, λ ↑↑↑, → no interactions except with walls of the vessel

→ *MOLECULAR FLOW*

☒ in between: → *KNUDSEN FLOW*

If d = ∅ of tube, p the pressure,

VISCOUS FLOW (rough vacuum):

$p.d. > 6\ 10^{-1}$ mbar cm

$\lambda < d / 100$

KNUDSEN FLOW (medium vacuum):

$6\ 10^{-1} > p.d > 1\text{-}3\ 10^{-2}$ mbar cm

$d / 100 < \lambda < d/2$

MOLECULAR FLOW (high and ultra high vacuum):

$p.d < 1\text{-}3\ 10^{-2}$ mbar cm

$\lambda > d / 2$

ressure ranges used in vacuum technology and their characteristic features

	Rough vacuum	Medium vacuum	High vacuum	Ultra-high vacuum
Pressure p in mbar	1,013 . . . 1	$1 \ldots 10^{-3}$	$10^{-3} \ldots 10^{-7}$	$< 10^{-7}$
Particle number density n in cm^{-3}	$10^{19} \ldots 10^{16}$	$10^{16} \ldots 10^{13}$	$10^{13} \ldots 10^{9}$	$< 10^{9}$
Mean free path $\bar{l}$ in cm	$< 10^{-2}$	$10^{-2} \ldots 10$	$10 \ldots 10^{5}$	$> 10^{5}$
Impingement rate Z_A in $cm^{-2} s^{-1}$	$10^{23} \ldots 10^{20}$	$10^{20} \ldots 10^{17}$	$10^{17} \ldots 10^{13}$	$< 10^{13}$
Collision rate Z_V in $cm^{-3} s^{-1}$	$10^{29} \ldots 10^{23}$	$10^{23} \ldots 10^{17}$	$10^{17} \ldots 10^{9}$	$< 10^{9}$
Monolayer time in s	$< 10^{-5}$	$10^{-5} \ldots 10^{-2}$	$10^{-2} \ldots 100$	> 100
Type of gas flow	Viscous flow	Knudsen flow	Molecular flow	Molecular flow
Some other features	Convection dependent on pressure	Marked change of the thermal conductivity of a gas	Marked reduction of the volume-related collision rate	Surface effects dominate

ote: All figures shown are round figures and related to air of 20 °C.

8. Pumping speed and residence time

8.1 Pumping speed

It is the process of removing gas molecules through action of pumps:

$$S = \frac{Q}{P} \qquad \text{(L/sec)} \qquad \text{(I.16)}$$

Q: Flow rate: Pressure x Volume per second (e.g. Torr L /sec or SCCM)

$$Q = C(P_1 - P_2) \qquad \text{(I.17)}$$

$$\text{C:conductance (L/sec)}$$

SCCM: Standard cm^3 per minute at 0°C, 1 atmosphere

$$1\,\text{SCCM} = \frac{6.02\ \text{x}10^{23}}{22414}\ \text{molecules per minutes} \qquad \text{(I.18)}$$

$$= 2.69\text{x}10^{19}\ \text{molecules per minutes}$$

1 Torr litre/sec = 79.05 sccm
= $2.13\text{x}10^{21}$ molecules per minutes

8. Pumping speed and residence time

8.2 Residence time

T: mean time a gas molecule remains in the process chamber before being pumped

Volume V, Pumping speed S:

$$T = \frac{V}{S} = \frac{p.V}{p.S} = \frac{p.V}{Q} \qquad \text{(I.19)}$$

Ex: Volume 200 l, p = 5 10^{-3} Torr, 100 sccm Ar: ☞ 0.79 sec.

9. Various stuffs

Table 5: Some fundamental constants relevant in vacuum technology

	Symbol	Value and Unit	Remarks
Atomic mass unit	u	1.6605×10^{-27} kg	
Avogadro constant	N_A	6.0225×10^{23} mol^{-1}	Number of particles per mol
Boltzmann constant	k	1.3805×10^{-23} J K^{-1} = $= 13.805 \times 10^{-23} \frac{\text{mbar ltr}}{\text{K}}$	
Electron rest mass	m_e	9.1091×10^{-31} kg	
Elementary charge	e	1.6021×10^{-19} A s	
Molar gas constant	R	8.314 J mol^{-1} K^{-1} = $= 83.14 \frac{\text{mbar ltr}}{\text{mol K}}$	$R = N_A\, k$
Molar volume of the ideal gas	V_m	22.414 m^3 k mol^{-1} = = 22.414 ltr mol^{-1}	$\vartheta = 0$ °C p = 1013 mbar
Standard acceleration of free fall	g_n	9.8066 m s^{-2}	
Planck constant	h	6.6256×10^{-34} J s	
Stefan-Boltzmann constant	σ	$5.670 \times 10^{-8} \frac{\text{W}}{\text{m}^2\,\text{K}^4}$	
(Negative) specific electron charge	$\frac{-e}{m_e}$	$-1.7588 \times 10^{11} \frac{\text{A s}}{\text{kg}}$	
Speed of light in vacuum	c	2.9979×10^8 m s^{-1}	
Standard reference density of a gas	ϱ_n	kg m^{-3}	at $\vartheta = 0$ °C and p_n = 1013 mbar
Standard reference pressure	p_n	101,325 Pa = 1,013 mbar	
Standard reference temperature	T_n	273.15 K or $\vartheta_n = 0$ °C	

Table 6: Conversion of pumping speed (volume flow rate) units

Unit	ltr s^{-1}	m^3 h^{-1}	cm^3 s^{-1}	c.f. min^{-1}
1 ltr s^{-1}	1	3.6	1,000	2.12
1 m^3 h^{-1}	0.2778	1	277.8	0.589
1 cm^3 s^{-1}	10^{-3}	3.6×10^{-3}	1	2.1×10^{-3}
1 c.f. min^{-1}	0.4719	1.699	471.95	1

Table 7: Conversion of throughput and mass flow rate units

Unit	mbar ltr s^{-1}	kg h^{-1} (air, 20 °C)	kg h^{-1} (air, 0 °C)	cm^3 (NTP) h^{-1}	cm^3 (NTP) s^{-1}
1 mbar ltr s^{-1}	1	4.29×10^{-3}	4.61×10^{-3}	3,560	0.95
1 kg h^{-1} (air, 20 °C)	233	1	1.073	8.29×10^5	230
1 kg h^{-1} (air, 0 °C)	217	0.933	1	7.75×10^5	215
1 cm^3 (NTP)[1]) h^{-1}	2.81×10^{-4}	1.21×10^{-6}	1.29×10^{-6}	1	2.78×10^{-4}
1 cm^3 (NTP) s^{-1}	1.05	4.33×10^{-3}	4.64×10^{-3}	3,600	1

[1]) The unit cm^3 (NTP) s^{-1} which is also used in practice corresponds to 1.05 mbar ltr s^{-1} or 1 mbar ltr s^{-1} = 0.95 cm^3 (NTP) s^{-1}. In most cases, however, the rounded off factor 1.00 can be used instead, so that: 1 cm^3 (NTP) s^{-1} ≙ 1 mbar ltr s^{-1}

9. Various stuffs