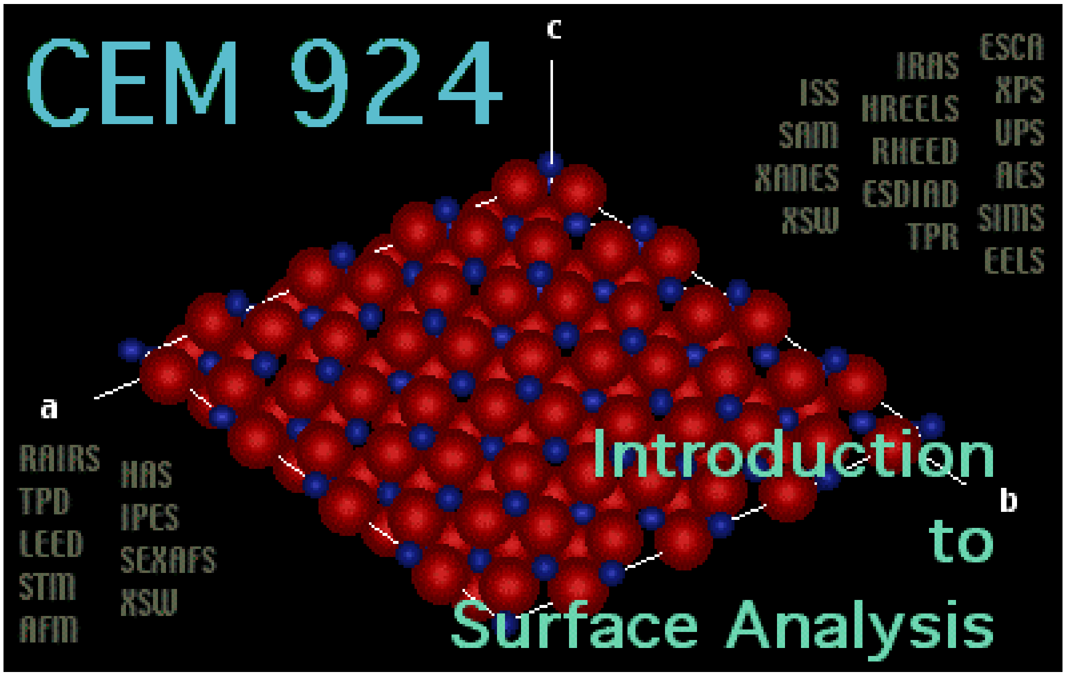
CEM 924 - Special Topics in Analytical Chemistry

Introduction to Surface Analysis



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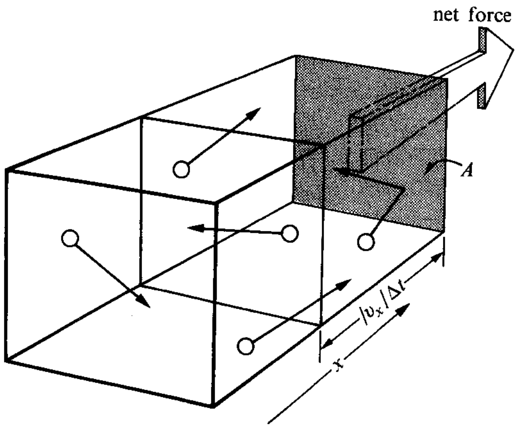
1. Introductory Material and Basics

1.1 Some Results from Kinetic Theory

Assumptions:

- Gas consists of large number of particles with random trajectories
- Particle diameter is much smaller than average interparticle separation
- Particles only interact through elastic collisions
- Pressure results from large number of collisions with wall producing a constant force per unit area

1.1.1 Pressure and Molecular Velocity



For molecules travelling with average velocity $\langle v_x \rangle$ the distance they can travel in time interval Δt is

$$\langle v_x \rangle \Delta t$$

If they move towards a wall of area A and the number density is *n* (= N/V), the number of molecules that strike the wall in time Δt is

$$n\ A\langle v_x\rangle \Delta t$$

But half molecules move towards, half away from surface

$$\frac{1}{2} n\ A\langle v_x\rangle \Delta t$$

When a molecule collides with surface, it's momentum changes from mv_x to -mv_x (total $2mv_x$) ($m = MW/N_A$)

Total momentum change is

$$= \text{number of collisions} \quad \times \text{momentum change per collision}$$

$$= \left(\frac{1}{2} n\ A\langle v_x\rangle \Delta t\right) \times \left(2m\langle v_x\rangle\right)$$

$$= n\ m\ A\left\langle v_x{}^2\right\rangle \Delta t$$

Force is rate of change of momentum

$$= n\ m\ A\left\langle v_x{}^2\right\rangle$$

Pressure is force per unit area

$$p = n\ m\ \left\langle v_x{}^2\right\rangle$$

Generalizing

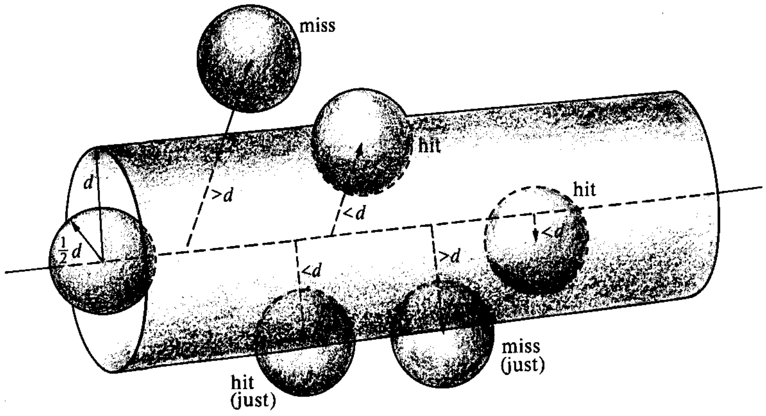
$$\left\langle v^2\right\rangle = \left\langle v_x{}^2\right\rangle + \left\langle v_y{}^2\right\rangle + \left\langle v_z{}^2\right\rangle$$

$$= 3\left\langle v_x{}^2\right\rangle$$

$$p = \frac{1}{3} n\ m\ \left\langle v^2\right\rangle$$

1 atm = 1013 mbar = 1.013 bar = 760 mmHg = 760 torr = 101,325 Pa (Nm^{-2})

1.1.2 Collision Frequency



A molecule of diameter d sweeps out a collision cylinder of cross-sectional area

$$\sigma = \pi d$$

and length

$$\langle v \rangle \Delta t$$

during period Δt.

For two colliding objects we must really take into account their relative speeds (not one fixed, one moving)

The collision frequency z (per unit time) per molecule is

$$z = \sqrt{2} \quad \sigma \langle v \rangle \; n$$

1.1.3 The Mean Free Path

The time a molecule spends between collisions is 1/z. The distance it has traveled in this time is called the mean free path, λ

$$\lambda = \frac{\langle v \rangle}{z} = \frac{1}{\sqrt{2}\quad \sigma n}$$

Using the Ideal Gas Law (pV = nRT) and n = N/V, this can be rewritten

$$\lambda = \left(\frac{1}{\sqrt{2}\quad}\right)\left(\frac{nRT}{N\ \ p}\right)$$

Since $N=n\cdot N_A$ and $k=R/N_A$

$$\lambda = \left(\frac{1}{\sqrt{2}\quad}\right)\left(\frac{kT}{p}\right)$$

Note: The product $\lambda \cdot p$ is constant for any gas at fixed T.

For N_2 at 300 K and 1 atm (σ=0.43 nm^2), λ=70 nm

Requirement for Experiment in Vacuum: Pathlength between surface and detector might be 1 m - p must be less than about 10^{-7} atm (7.6×10^{-5} torr).

1.1.4 Collisions with Surfaces

As above, the number of molecules crossing a plane per unit area A per unit time can be calculated the velocity and number density of the particles

$$\#\ \text{collisions} = n \int_0^\infty v_x\ f(v_x)\ dv_x$$

where $f(v_x)$ represents the velocity distribution of particles. This is given by the Maxwell-Boltzmann distribution of speeds

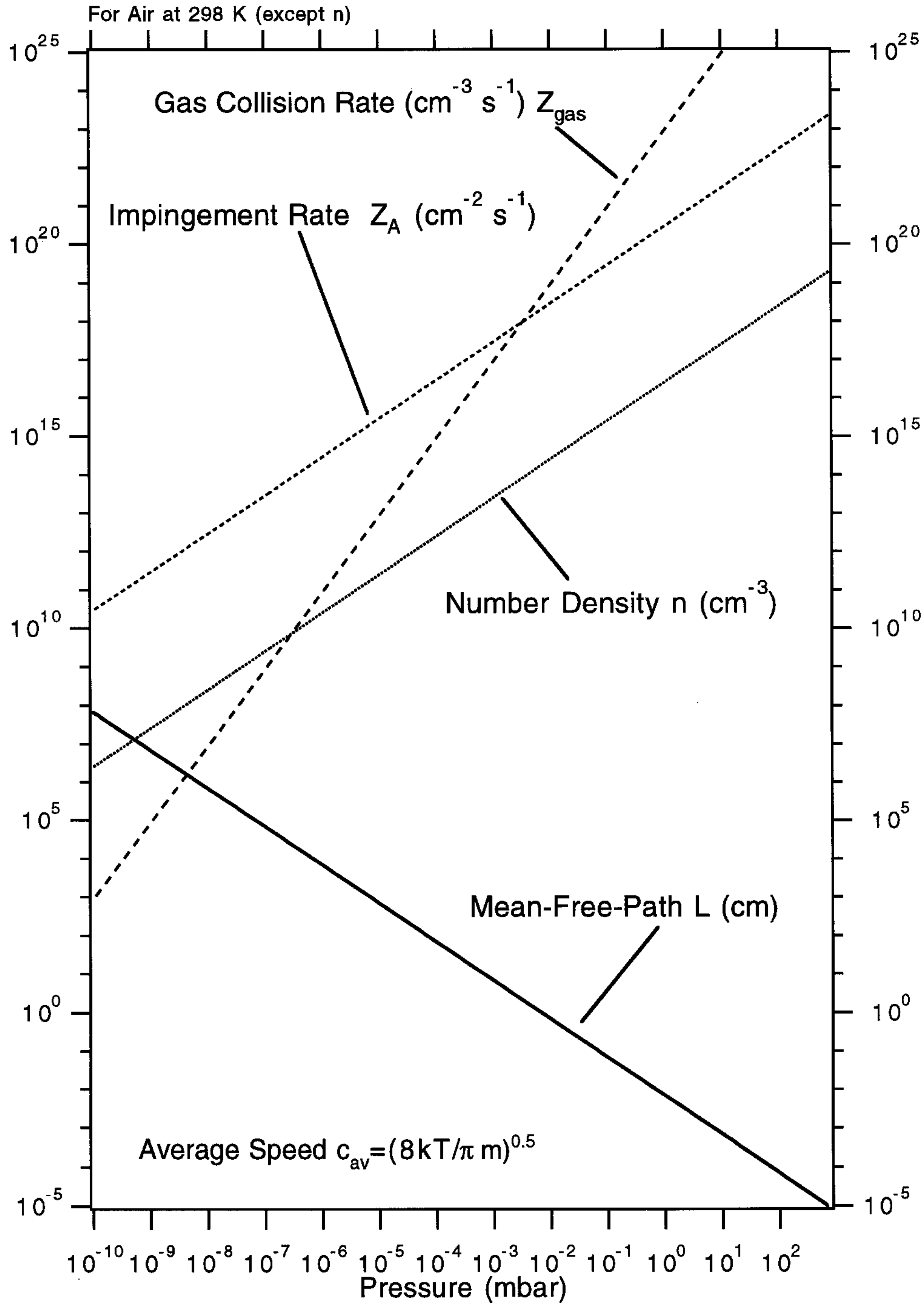
$$\int_0^\infty v_x\ f(v_x)\ dv_x = \left(kT/2\pi m\right)^{1/2}$$

so the collision frequency with the wall per unit area, Z_A, is (substituting n = N/V = p/kT)

$$Z_A = \frac{p}{(2\pi mkT)^{1/2}}$$

Hertz-Knudsen Eqn

At 300 K and 1 atm for N_2, Z_A is about $3\text{x}10^{23}$ s^{-1} cm^{-2}



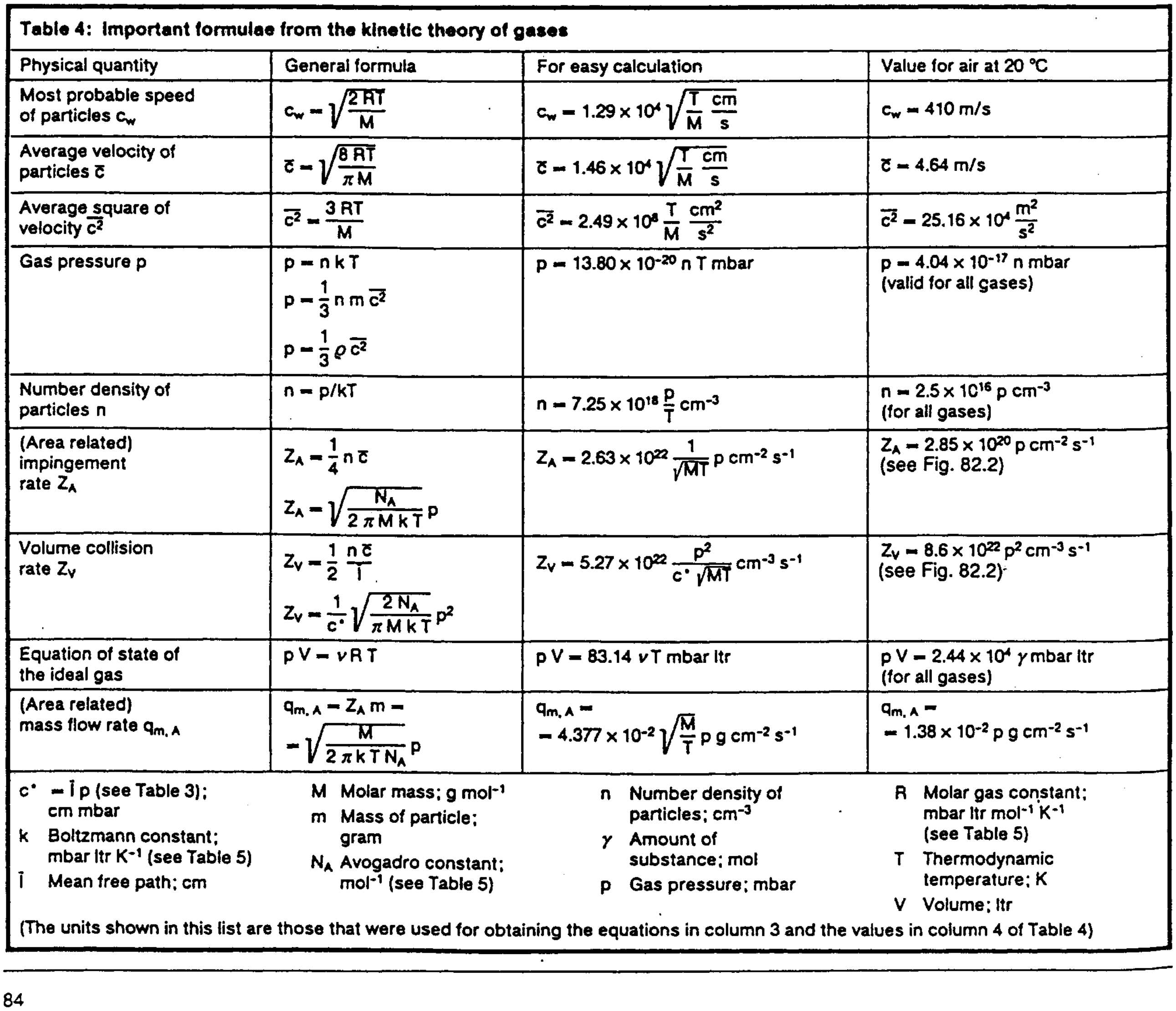


Table 4: Important formulae from the kinetic theory of gases

Physical quantity	General formula	For easy calculation	Value for air at 20 °C
Most probable speed of particles c_w	$c_w = \sqrt{\frac{2RT}{M}}$	$c_w = 1.29 \times 10^4 \sqrt{\frac{T}{M}} \frac{cm}{s}$	$c_w = 410$ m/s
Average velocity of particles $\bar{c}$	$\bar{c} = \sqrt{\frac{8RT}{\pi M}}$	$\bar{c} = 1.46 \times 10^4 \sqrt{\frac{T}{M}} \frac{cm}{s}$	$\bar{c} = 4.64$ m/s
Average square of velocity $\overline{c^2}$	$\overline{c^2} = \frac{3RT}{M}$	$\overline{c^2} = 2.49 \times 10^8 \frac{T}{M} \frac{cm^2}{s^2}$	$\overline{c^2} = 25.16 \times 10^4 \frac{m^2}{s^2}$
Gas pressure p	$p = nkT$ $p = \frac{1}{3} n m \overline{c^2}$ $p = \frac{1}{3} \varrho \overline{c^2}$	$p = 13.80 \times 10^{-20}\, n\, T$ mbar	$p = 4.04 \times 10^{-17}\, n$ mbar (valid for all gases)
Number density of particles n	$n = p/kT$	$n = 7.25 \times 10^{18} \frac{p}{T}$ cm^{-3}	$n = 2.5 \times 10^{16}\, p$ cm^{-3} (for all gases)
(Area related) impingement rate Z_A	$Z_A = \frac{1}{4} n \bar{c}$ $Z_A = \sqrt{\frac{N_A}{2 \pi M k T}}\, p$	$Z_A = 2.63 \times 10^{22} \frac{1}{\sqrt{MT}}\, p$ cm^{-2} s^{-1}	$Z_A = 2.85 \times 10^{20}\, p$ cm^{-2} s^{-1} (see Fig. 82.2)
Volume collision rate Z_V	$Z_V = \frac{1}{2} \frac{n \bar{c}}{\bar{l}}$ $Z_V = \frac{1}{c^*} \sqrt{\frac{2 N_A}{\pi M k T}}\, p^2$	$Z_V = 5.27 \times 10^{22} \frac{p^2}{c^* \sqrt{MT}}$ cm^{-3} s^{-1}	$Z_V = 8.6 \times 10^{22}\, p^2$ cm^{-3} s^{-1} (see Fig. 82.2)
Equation of state of the ideal gas	$pV = \nu R T$	$pV = 83.14\, \nu T$ mbar ltr	$pV = 2.44 \times 10^4\, \gamma$ mbar ltr (for all gases)
(Area related) mass flow rate $q_{m,A}$	$q_{m,A} = Z_A m =$ $= \sqrt{\frac{M}{2 \pi k T N_A}}\, p$	$q_{m,A} =$ $= 4.377 \times 10^{-2} \sqrt{\frac{M}{T}}\, p$ g cm^{-2} s^{-1}	$q_{m,A} =$ $= 1.38 \times 10^{-2}\, p$ g cm^{-2} s^{-1}

$c^* = \bar{l}\, p$ (see Table 3); cm mbar
k Boltzmann constant; mbar ltr K^{-1} (see Table 5)
$\bar{l}$ Mean free path; cm
M Molar mass; g mol^{-1}
m Mass of particle; gram
N_A Avogadro constant; mol^{-1} (see Table 5)
n Number density of particles; cm^{-3}
γ Amount of substance; mol
p Gas pressure; mbar
R Molar gas constant; mbar ltr mol^{-1} K^{-1} (see Table 5)
T Thermodynamic temperature; K
V Volume; ltr

(The units shown in this list are those that were used for obtaining the equations in column 3 and the values in column 4 of Table 4)

84

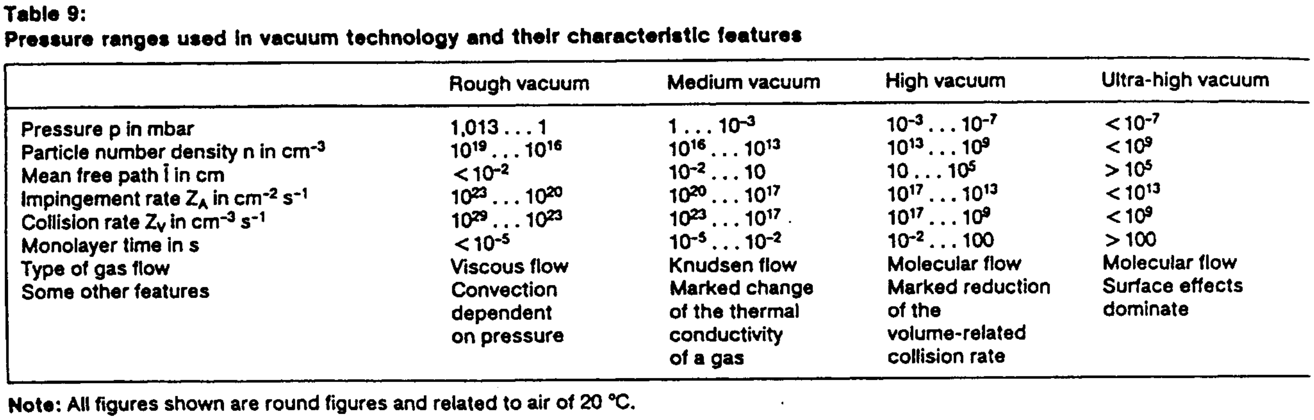


Table 9:
Pressure ranges used in vacuum technology and their characteristic features

	Rough vacuum	Medium vacuum	High vacuum	Ultra-high vacuum
Pressure p in mbar	1,013 . . . 1	1 . . . 10^{-3}	10^{-3} . . . 10^{-7}	$< 10^{-7}$
Particle number density n in cm^{-3}	10^{19} . . . 10^{16}	10^{16} . . . 10^{13}	10^{13} . . . 10^{9}	$< 10^{9}$
Mean free path $\bar{l}$ in cm	$< 10^{-2}$	10^{-2} . . . 10	10 . . . 10^{5}	$> 10^{5}$
Impingement rate Z_A in cm^{-2} s^{-1}	10^{23} . . . 10^{20}	10^{20} . . . 10^{17}	10^{17} . . . 10^{13}	$< 10^{13}$
Collision rate Z_V in cm^{-3} s^{-1}	10^{29} . . . 10^{23}	10^{23} . . . 10^{17}	10^{17} . . . 10^{9}	$< 10^{9}$
Monolayer time in s	$< 10^{-5}$	10^{-5} . . . 10^{-2}	10^{-2} . . . 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

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

1.1.5 Monolayer Formation Times

If we assume a typical interatomic distance for a solid surface of 3.1 Å, then

$$\#\ \text{surface atoms} = \left(\frac{1}{3.1\text{x}10^{-10}\ \text{m}}\right)^2$$

$$= 1\text{x}10^{19}\ \text{m}^{-2}$$

$$= 1\text{x}10^{15}\ \text{cm}^{-2}$$

At 300 K, if every N_2 molecule that strikes this surface remains adsorbed, a complete monolayer is formed in about t=3 ns.

If p=10^{-3} torr (1.3x10^{-6} atm), t=3x10^{-3} s

If p=10^{-6} torr (1.3x10^{-9} atm), t=3 s

If p=10^{-9} torr (1.3x10^{-12} atm), t=3000 s or 50 minutes

> *Requirement for Experiment in Vacuum*: Clean surface quickly becomes contaminated through molecular collision - p must be less than about 1.3x10^{-12} atm (10^{-9} torr).

10^{-10} to 10^{-11} torr (UHV - ultrahigh vacuum) is lowest pressure routinely available in vacuum chamber.

1.2 Pressure Measurement

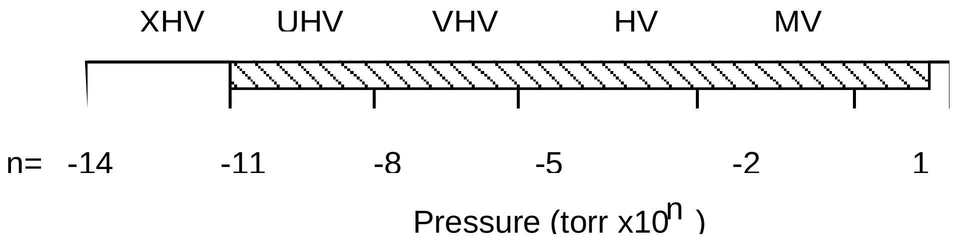
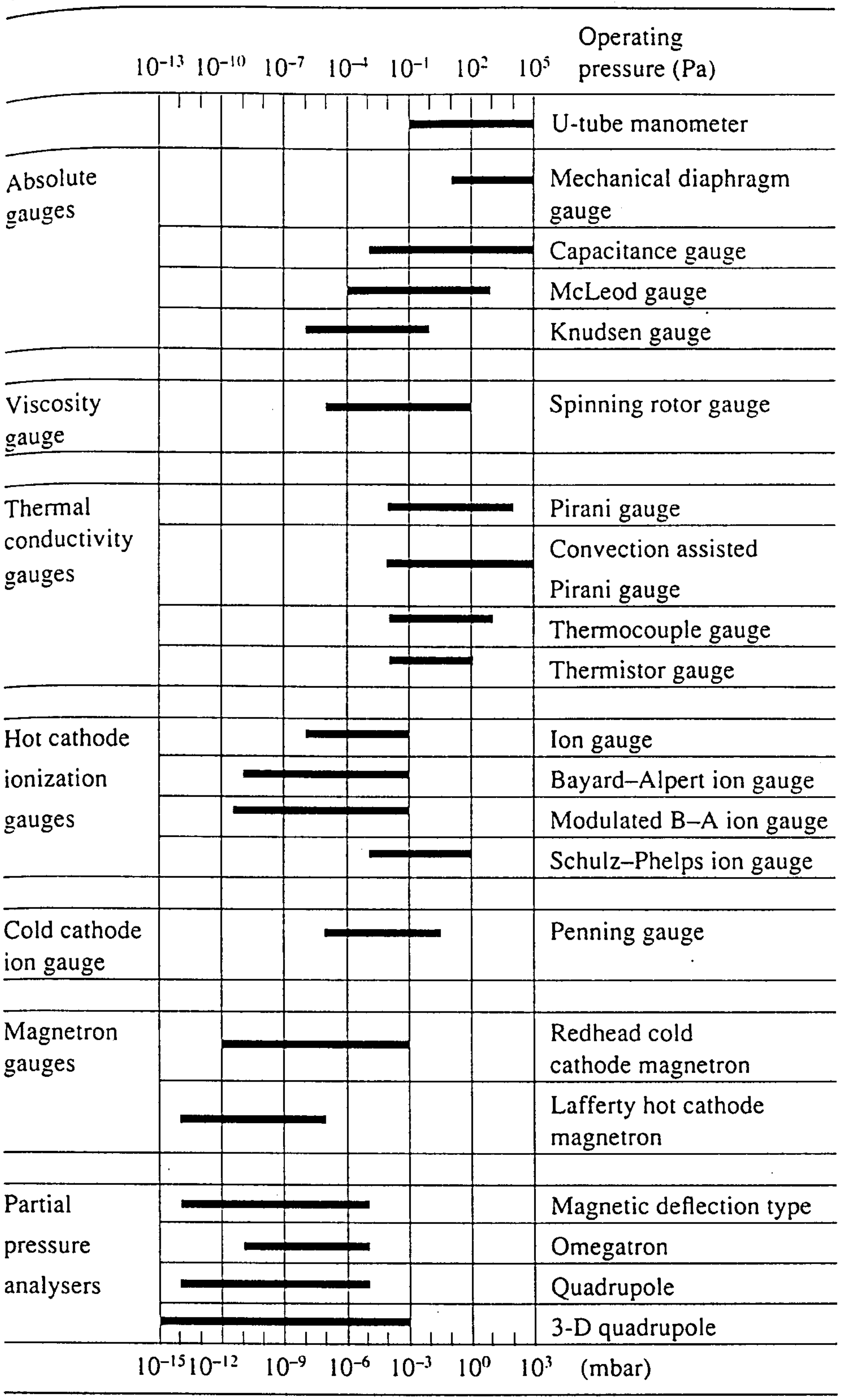


Table 5.1 Summary of vacuum gauge performance



1.2.1 Mercury Manometer

Simple Hg-filled U tube: one side evacuated, one side open

Absolute (*gas independent*) gauge

atm to 10^{-3} torr (10^{-3} mm Hg)

1.2.2 Diaphragm Gauge

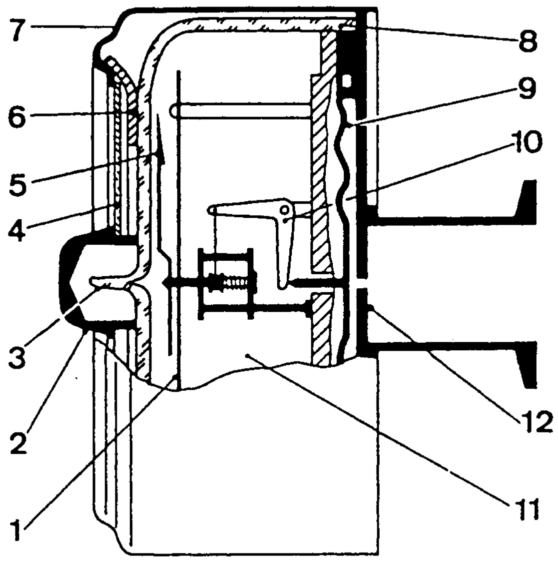


Figure 3-2. Section of a diaphragm vacuum gauge: 1) Reflecting cover plate; 2) Protective cap; 3) Seal-off point; 4) Plexiglass disk; 5) Pointer; 6) Scale; 7) Metal cover; 8) Glass chamber; 9) Diaphragm; 10) Lever system; 11) Reference vacuum; 12) Connecting flange

Absolute gauge

Mechanical connection between moving diaphragm and indicator (needle)

atm to 10^{-1} torr (>2 % accuracy)

Simple but sensitive to vibration

1.2.3 Capacitance Manometer

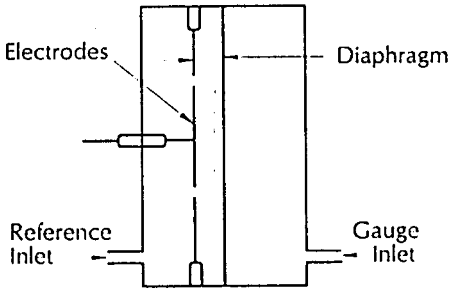


Fig. 5
Capacitance Manometer

Variation of diaphragm gauge but with electrical transducer

atm to 10^{-5} torr

Moderately complex, stable, accurate

1.2.4 Bourdon Gauge

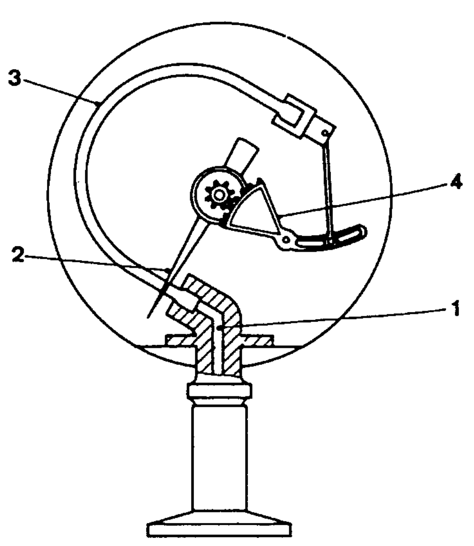


Figure 3-3. Section of a Bourdon gauge
1. Connection line to vessel; 2. Pointer;
3. Bourdon tube; 4. Lever mechanism

Bourdon: This is a curved, oval, cross-section, copper tube that is connected to the vacuum (Fig. 2). Atmospheric pressure outside the tube bends it to a greater or lesser degree depending on the internal pressure. The mechanical force moves an indicator needle through a geared linkage.

Bourdon gauges are used primarily in high-pressure measurement (regulators for gas cylinders), but variations that indicate pressures from 0" Hg to 30" Hg find use in rough vacuum measurement for freeze drying, 'house' vacuum systems, vacuum impregnation, etc., where the major concern is whether vacuum exists rather than its accurate measurement.

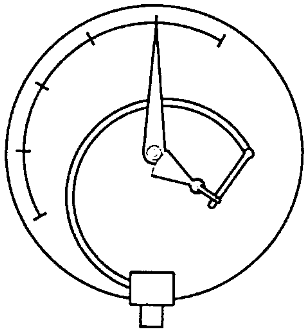


Fig. 2
Bourdon Gauge

Absolute gauge

atm to 1 torr

Simple, stable

1.2.5 Thermocouple Gauge

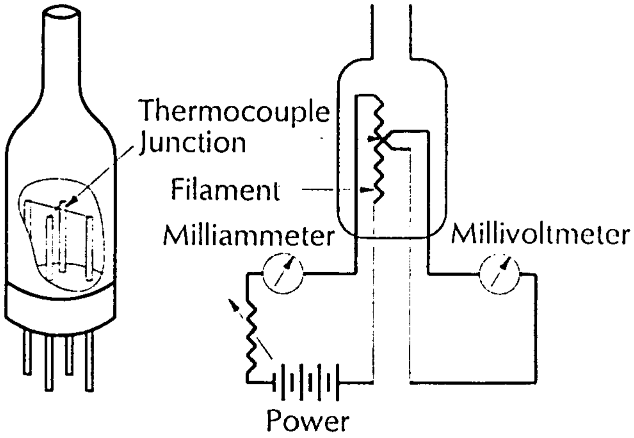


Fig. 3

Thermocouple Gauge

Constant current heats filament

Thermocouple attached to filament measure temperature

At high pressure, gas molecules collide and cool filament

Larger voltage need to drive filament to same temperature

Fast, simple, inexpensive

Gas sensitive

10 (convection) to 10^{-4} torr

1.2.6 Pirani Gauge

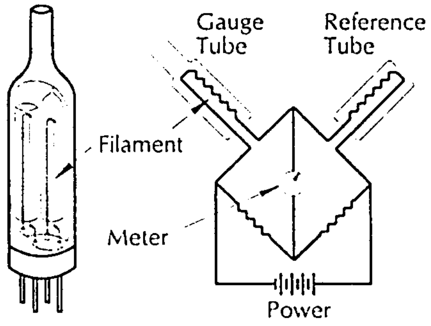


Fig. 4
Pirani Gauge

Two identical heated filaments; one sealed at HV, one exposed to system

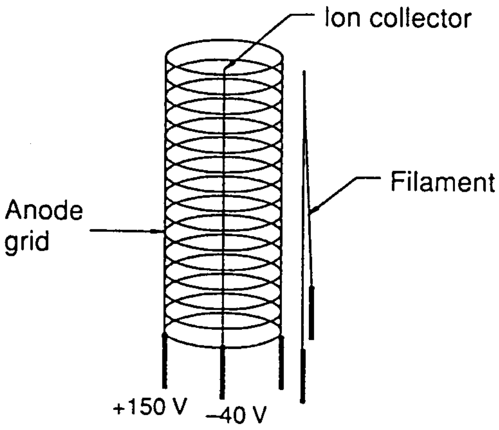
Current flows through Wheatstone bridge circuit

Pressure difference indicated by meter (non-linear)

10^{2} to 10^{-4} torr

Simple, reliable, inexpensive but gas dependant

1.2.7 Ionization Gauge (Bayard-Alpert)



Heated filament produces electrons via thermionic emission

Electrons accelerated towards anode grid

Many electrons pass through grid, enter center region and create +ve ions from gas molecules

Ions accelerated to collector wire

Measure current between anode and collector

10^{-3} (filament burnout, multiple ions per electron) to 10^{-11} (low current) torr

$i_p = S\ p\ i_e$ $\quad$ i_e = electron emission current

S = gauge sensitivity

Sensitive, high accuracy, widely used

Gas dependant, moderately complex

Hot filament chemically poisoned, can produce gases

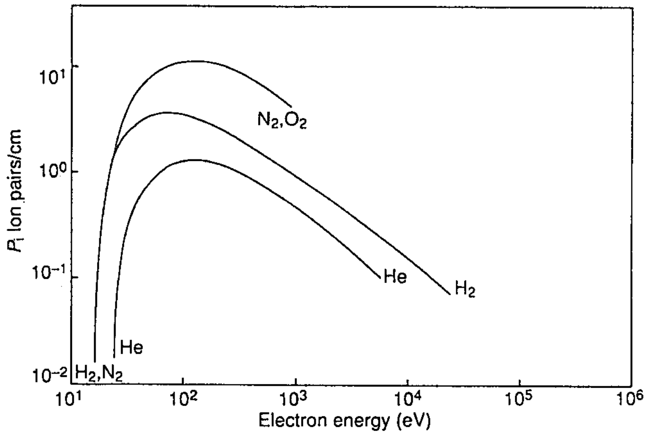


Fig. 5.13 Ionization probability versus electron energy for some common vacuum system gases.

Table 5.2 lists the usual gas calibration factors for a range of gases. These values must be viewed as approximate.

true pressure = meter reading × gas calibration factor

Table 5.2 Ion gauge calibration factors

Gas	Calibration factor*
Air	1.0
Ammonia	1.53
Argon	0.88
Carbon monoxide	0.90
Carbon dioxide	0.71
Neon	2.94
Nitrogen	1.0
Oxygen	0.94
Helium	7.7
Hydrogen	3.1
Methane	0.71

* The values given should be regarded as typical.

1.2.8 Mass Spectrometers

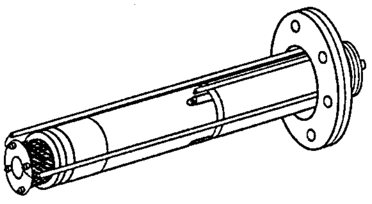


Fig. 8

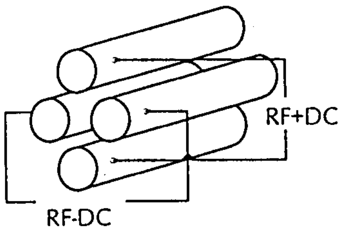


Fig. 9

Quadrupole mass spectrometer - RGA (residual gas analyzer)

10^{-4} to $<10^{-14}$ torr

Total pressure mode integrates all ion intensities

Partial pressure mode indicates residual vacuum composition

Highly accurate, precise

Complex, expensive, gas dependant

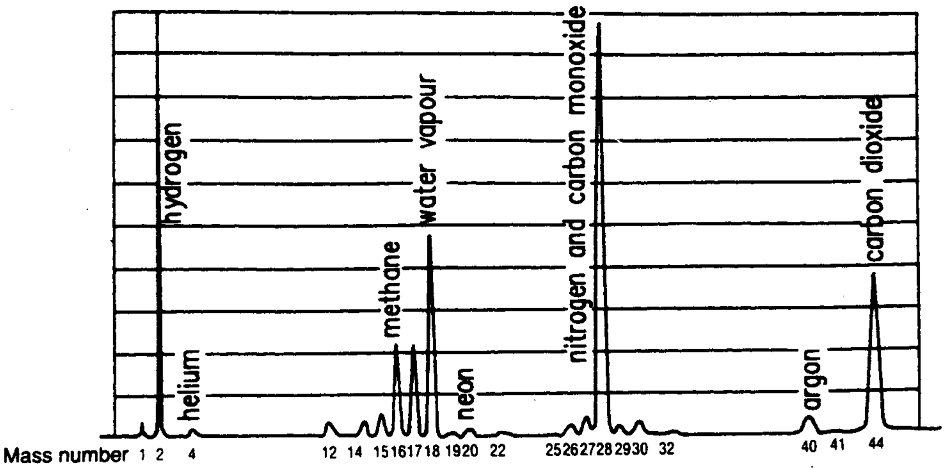


Fig. 8.1 Typical residual gas spectrum for an unbaked stainless steel vacuum system.