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SI Units

- basic SI units:

• Mass	- kg
• Length	- m
• Temp	- K
• Current	- Amp
• Luminous intensity	- Cd (candela)
• Time	- s
• Amount	- mol

Derived units:

- Temp in celcius (degree C = K - 273,15)
- Force = Newton (N) = kg.m.s⁻²
- Pressure = N.m⁻² = Pascal (Pa) (1 Bar = 1 atmosphere = 101,3 kPa)
- Energy = Joule (J) = N.m
- Power = watt = J.s⁻¹
- Frequency = Hertz (Hz) = s⁻¹
- Volume = m³ (= the official SI unit, liter is not an SI unit.)

Electrical units:

- Potential (volt): V = W.A⁻¹
- Resistance (Ohm): R = V.A⁻¹
- Charge (Coulomb); C = A.s (1 C = electrical charge of 6,24 x 10¹⁸ electrons)
- Capacitance (Farad): F = C.V⁻¹

Miscellaneous:

Pico = 10⁻¹²

Nano = 10⁻⁹

Micro = 10⁻⁶

Milli = 10⁻³

Kilo = 10³

Mega = 10⁶

Giga = 10⁹

Standard Temperature and Pressure (STP): = 273,15 K and 101,3 kPa

Gas Laws

1. Boyle's law: (the 1st perfect gas-law)

At a constant temperature, the **volume** of a gas is inversely proportional with the absolute **pressure**.

[Note: Boyle's law is applied in the Body plethysmograph... loved by registrars + examiners...]

$$V = \frac{1}{P}$$

Thus, $V \cdot P = k_1$

2. Charles law: (second perfect gas law)

At constant pressure, the **volume** of given gas is directly proportional to the absolute **temperature**.

$$V = T$$

Thus , $V/T = k_2$

3. Third perfect gas-law:

At a constant volume, the **pressure** of a given mass of gas varies directly with absolute **temperature**.

$$P = T$$

Thus, $P/T = k_3$

4. Dalton's law of partial pressures:

In a *mixture* of gases, the pressure exerted by each gas is the same as that which it would exert if it occupied the container *alone*.

Note: by applying Boyle's law + Dalton's law, the partial pressure of a gas in a mixture is obtained by multiplying the total pressure with the fractional concentration of the gas.

Miscellaneous:

Law of Mass action: *Rate of chemical reaction = proportional to the product of the concentrations of reactants.*

5. Avogadro's hypothesis:

Equal volumes of gases, at same temp + pressure, contain the same amount of molecules.

6. Avogadro's number: $= 6,022 \times 10^{23}$ = number of atoms in 12g Carbon 12 = ONE MOLE.

7. Mole: = the quantity of substance containing the same amount of particles or molecules as there are atoms in 12 g of carbon (C₁₂).

8. OsMole: = number of moles of a solute which contribute to the osmotic pressure of a solution

Note also: one mole of any gas at STP occupies a volume of 22,4 liter.

9. Universal Gas constant (R):

From $PV = k_1$, $V/T = k_2$, $P/T = k_3$: $\rightarrow PV/T = K$

For 1 mole of gas, $PV/T = R$ (R = universal gas constant)

$\rightarrow PV = nRT$ (where n = number of moles of the substance)

in practice P = directly proportional to n ($V, R + T$ kept constant)

9. Critical temperature:

That temperature, **above** which a substance cannot be liquefied, no matter how much pressure is applied.

\hookrightarrow ie becomes a gas

- Critical Pressure: = vapour pressure of a substance at its critical temp.
- Lines of pressure against volume at various temp's = isotherms
- The term "Gas" applies to a substance above its critical temp
- Term "vapour", to a substance below its critical temp.
- "Filling ratio" of a cylinder: = mass of gas in the cylinder divided by mass of H₂O which would fill it (~ internal volume of cylinder) = used to describe how much gas is used to fill a cylinder.

10. Pseudo-critical temperature:

In a *mixture* of gases, there is a specific critical temperature at which the mixture may *separate out into its constituents*. (Poynter Effect)

- Eg, **Entonox** (50% O₂ + 50% N₂O) = dependant on pressure + temperature.
 - ▶ Below -7 Celcius at 137 Bar \Rightarrow liquefaction of N₂O with gaseous O₂ at top \Rightarrow consumed 1st \Rightarrow pure N₂O hypoxic mixture to follow
 - ▶ \therefore Entonox cylinders must always be stored above -7 degrees.

11. Henry's law

At a given temp, the amount of a given gas dissolved in a given liquid, is directly proportional to the partial pressure of the gas in equilibrium with the liquid.

Eg: dissolved oxygen in blood (mlO₂/100ml blood) = 0.003 x PO₂

Note: At *equilibrium*, the tension of the dissolved gas is the same as the partial pressure of the gas above the surface of the liquid.

Other factors influencing the solubility of gases in liquids:

- **Temperature:** The higher the temp, the *less* soluble gases get in it. (Reason for bubbles in boiling water and bubble-formation in a heated ivi line)
- **Type of gas:** Different gases has different solubilities (eg N₂O > N₂)
- **Type of liquid:** eg water vs blood (eg N₂O has higher sol in blood vs H₂O)

12. Ostwald Solubility coefficient:

The volume of gas that dissolves in one unit volume of liquid at a given temperature.

Note: = independent of pressure

13. Partition coefficient:

The ratio of the amount of substance present in one phase compared with another, the two phases of equal volume and in equilibrium.

eg blood:gas coefficient N₂O 0.47 = 1ml blood contains 0.47 of the alveolar conc of gas @ 37deg

= similar to Ostwald, but:

- a. Relative order of phases must be specified, eg blood:gas
- b. Can be applied to two liquids (eg blood:oil)

Note: - At equilibrium, the **tension** of the gas in the two liquid phases must be equal.

- Tension is used instead of *partial pressure* for gases in solution.

- ∴ the tension of a gas in solution = the partial pressure of the gas which is in equilibrium with it.

Solubility + uptake of anaesthetics:

- The higher the Ostwald solubility, the more gas carried away by blood and the slower the build up of [] in the alveoli.
- The [] of anaesthetic in blood + brain are close to the alveolar concentration, → thus, faster onset with a less soluble agent eg desflurane.

Note: solubility is very relative, eg N₂O has low solubility c/f say sevoflurane, but high solubility compared to eg N₂.
↳ solubility = 20x O₂, 40x N₂

Practical implications:

- Second gas effect: During induction of anaesthesia with N₂O, at peak of inspiration, when alveolar pressure equalized with ambient pressure, there is a surplus of N₂ + O₂ (because of the more rapid uptake of N₂O). = augmented alveolar flow. Conversely, [N₂O] is increased in alveoli if given with halothane (more soluble).
- Diffusion hypoxia: = reverse of above, = faster excretion of N₂O into alveoli dilutes gases present there, eg O₂.

Oil solubility and anaesthetic potency:

The more oil soluble, the more potent, thus low MAC ~ high oil solubility.

Postulated reason: high oil-solubility ? related to affinity for long fatty acid chains within neurons / synapses in brain.

Attachment to FA chain molecules = relatively loose + readily reversible Van der Waals type bonds.

Pressure

Conversion of units for pressure:

SI unit = N/m² , and 1 N/m² = 1 Pa.

1 kPa ~ 7,5 mmHg

1 kPa ~ 10 cmH₂O

1 kPa ~ 10⁴ dyne.cm²

1 Bar (1 atmosphere) = 101,3 kPa

Gauge vs absolute pressure:

- **Gauge** pressure: pressure above or below atmospheric pressure.
- **Absolute** pressure: gauge pressure + atmospheric pressure.

Eg:

- Gauge pressure of a full cylinder O₂ reads 140 Bar (14 180 kPa) → t
- absolute pressure is 141 Bar (14 283 kPa)
↳ ∴ the absolute pressure of an **empty** cylinder at sea level = 1 Bar (101.3 kPa)

Pressure Gauges

- classification:
 - ▶ liquid manometers
 - ▶ anaeroid gauges: bourdon, bellows
 - ▶ diaphragm type

Liquid Type

- water, alcohol, mercury
- principle:
 - ▶ pressure exerted by column of liquid depends on force of gravity on the mass of liquid in the column
 - ▶ mercury x13.6 more dense than water
 - ▶ meniscus:
 - water manometer - see concave meniscus: adhesive forces of water to glass > waters cohesive forces
 - mercury manometer - see convex meniscus: cohesive forces > adhesive force to glass
↳ should take reading from centre of tube irrespective
 - ▶ capillarity:
 - adhesiveness of water ⇒ capillarity
 - dip tube into reservoir, water will draw itself up tube until gravity overcomes the adhesive forces
 - see opposite with mercury
 - result
 - water manometer will over-read by 4.5mm in 6mm diameter tube
 - mercury manometer will under-read by 1.5mm in 6mm tube

- example:
 - ▶ mercury sphygmanometer = end must be open to air because gauge pressure is measured
 - ▶ mercury barometer = end sealed

Anaeroid Gauges

- anaeroid = no liquid

- Bourdon gauge
 - = used for cylinder pressure
 - mechanism:
 - coiled tube:
 - one end connected to pressure source
 - other end closed
 - ↑ pressure \Rightarrow tube to uncoil which moves pointer on a calibrated scale

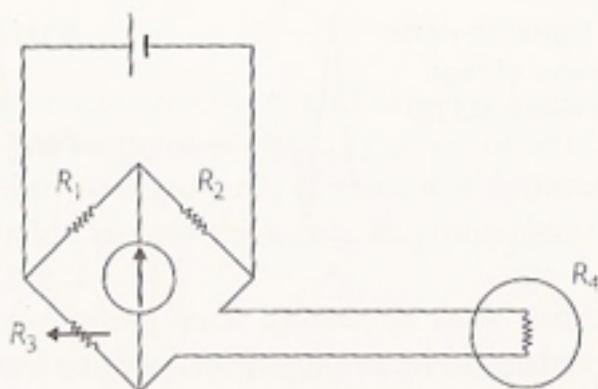
Diaphragm

- pressure change \Rightarrow movement of flexible diaphragm
- movement sensed & transduced via:
 - wire strain gauge =
 - wire stretched or compressed \Rightarrow electrical resistance to change
 - usually incorporated into a wheatstone bridge
 - eg A line transducer
 - optical =
 - reflection of light off the moving diaphragm changes the amount detected by a photoelectric cell
 - eg some fibre optic cardiac catheters
 - capacitance =
 - diaphragm = one plate of capacitor
 - distance from other plate varies with movmt of diaphragm
 - inductance =
 - diaphragm attached to a magnet which is moved between coils as diaphragm bulges \Rightarrow potential proportionately

Wheatstone Bridge

- = special circuit used to measure changes in resistance
- usually coupled with a strain gauge
- it is used to ↑ sensitivity/gain of a measuring circuit
- this is done by constantly resetting reference range to zero
- original form includes:
 - 4 resistors
 - battery - source of electrical potential
 - galvanometer

Figure 14.14 Wheatstone bridge circuit; R_4 is a strain gauge transducer or resistance thermometer and R_3 is a variable resistance which is adjusted until there is a null deflection on the galvanometer



- theoretical arrangement:
 - R_4 = strain gauge transducer ie measuring resistor
 - R_3 = variable resistor
 - this is changed by the circuit so that $R_1 + R_2 = R_3 + R_4$ ie zero

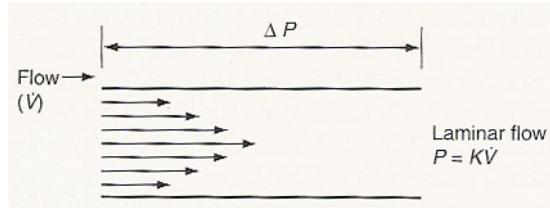
- \therefore galvanometer in middle should read zero
- = a null deflection system
- this is how \uparrow sensitivity is created:
 - change of measurement from zero $\Rightarrow 1 = 100\%$
 - change of measurement from 100 $\Rightarrow 101 = \text{only } 1\%$
- practical arrangement:
 - pressure transducer contains 4 strain gauges which form 4 resistors in Wheatstone bridge:
 - 2 gauges are on either side of the strain:
 - 2 gauges \uparrow pressure
 - 2 \downarrow gauges \downarrow pressure
 - this gives amplified potential change at the galvanometer

Flow

Ohm's law: $Q = \frac{\Delta P}{R}$

Flow (liquids or gases) can be: **laminar**, **turbulent** or **transitional**

Laminar Flow



- $P = kv$
- occurs in concentric cylinders of fluid/gas sliding over each other
- movement is steady, without eddies
- greatest velocity in centre ($\times 2$ mean flow) \Rightarrow falling to zero at walls

Hagen poiseulle equation:

$$Q = \frac{P \pi r^4}{8 \eta L}$$

L = length of a smooth-walled tube

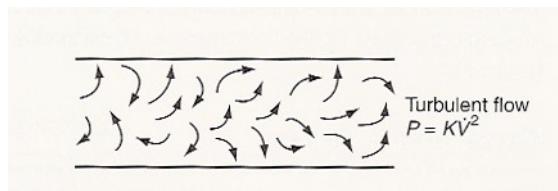
η = viscosity of fluid / gas (= shear stress/shear rate)

r = radius of tube

- equation can be altered using Ohm's law ($Q = P/R$) to express resistance to laminar flow:

$$R = \frac{8 \eta L}{\pi r^4}$$

Turbulent Flow



- $P = kv^2$
- in turbulent flow in a tube
 - with a rough surface: density is the important factor
 - with a smooth surface: density & viscosity is impt
- resistance defined by:

$$R = \frac{dl}{\pi r^5}$$

Reynolds number

- =dimensionless number which predicts whether flow will be laminar or turbulent

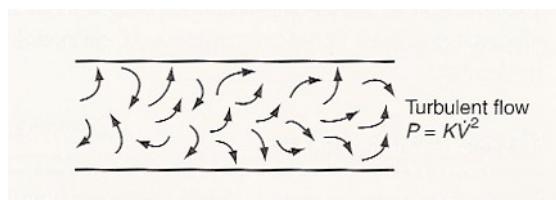
$$\frac{2rvD}{\eta}$$

Reynold's no = $\frac{2rvD}{\eta}$

Where r = radius, v = velocity, D = diameter, η = viscosity

- ∴ if viscosity, density, diameter remain constant \Rightarrow velocity = determining factor
- Re number $> 2000 \approx$ turbulent
- critical flow
 - = flow at which transition takes place between laminar & turbulent
 - for typical anaesthetic gas value \sim same numerical value as internal diameter of airway concerned in mm
↳ ie 9L/min for size 9 ETT
- critical velocity = velocity above which all flow = turbulent

Transitional Flow



- $P = KV + KV^2$
- combination of turbulent & laminar
- majority of flow in airway

Misc Flows

Venturi

- = where flow occurs in a tube with a constriction in which cross section \downarrow s and then \uparrow s

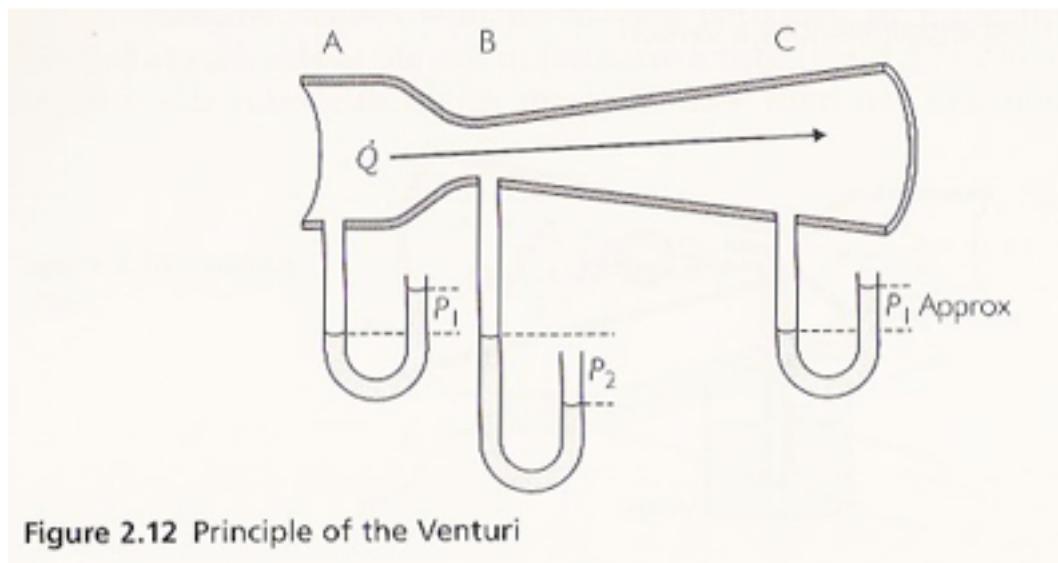


Figure 2.12 Principle of the Venturi

Bernoulli effect

- =fall in pressure during flow at a constriction in a tube
- caused by:
 - flowing fluid/gas contain energy in 2 forms:

- kinetic = associated with flow
- potential energy = assoc with pressure
- at a narrowing see ↑velocity (ie ↑kinetic energy) but total energy remains constant ∴ must be a ↓potential energy (ie ↓pressure)

Entrainment

- air or fluid can get entrained through a side tube at a venturi because of this drop in pressure as described by Bernoulli
- this principle used in
 - nebulisers
 - venturi masks
 - injectors

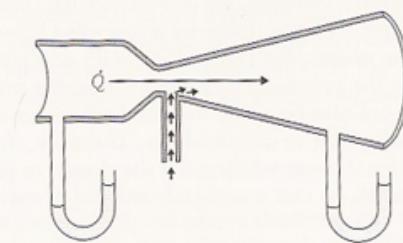


Figure 2.13 Fluid entrainment by a Venturi

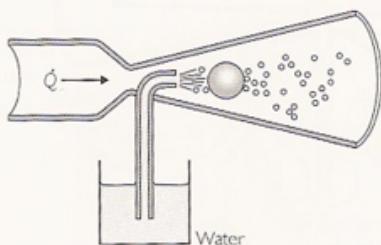
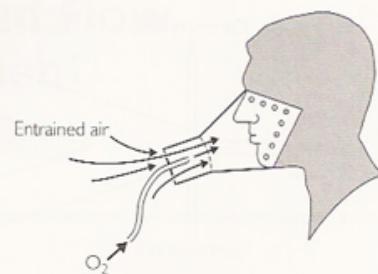


Figure 2.14 Principle of a nebulizer

Figure 2.15 Venturi oxygen mask



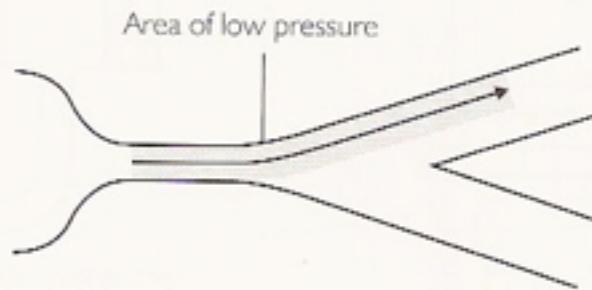
$$\text{Entrainment ratio} = \frac{\text{Entrained flow}}{\text{Driving flow}}$$

- jet entrainment = friction between gas at high speed ⇒ air pulls more air along with flow
- entrainment ratio = entrained flow / driving flow

Coanda Effect

- = behaviour of fluid/gas to follow only 1 limb of a Y junction after a narrowing in a tube
- due to development of lower pressure area between jet from a nozzle & an adjacent surface
- jet can be switched in direction by signal jets across nozzle
- this effect implicated in uneven ventilation of alveoli due to bronchi constriction

Figure 2.16 Coanda effect



Measurement of Gas Volumes & Flow

Volumes

- benedict spirometer
- vitalograph
- dry gas meter
- wright respirometer
- electronic volume monitor
- pneumotachograph

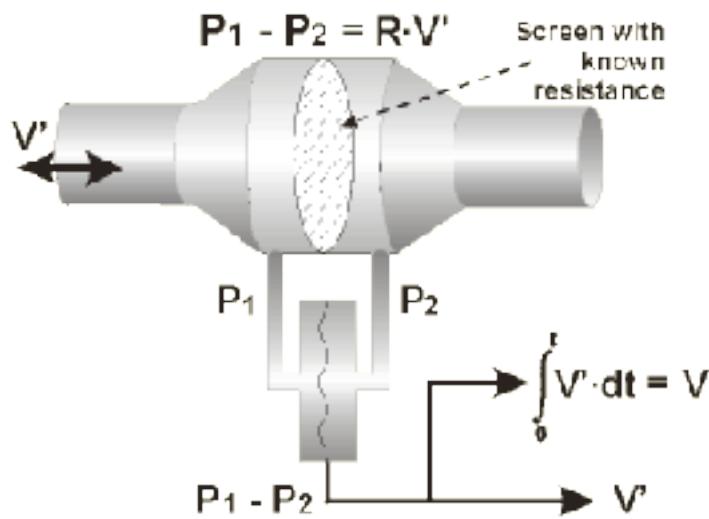
Gas Flow

- Variable orifice flow meters aka rotameters
- wright peak flow meter
- bubble flowmeter
- pneumotachograph

Variable Orifice Flow Meters

- consists of tapered glass tube with free floating bobbin inside
- bobbin has vanes so that it can rotate & not stick to glass due to static
- tapered tube ⇒
 - variable orifice around bobbin
 - depending on gas flow ⇒ constant pressure across bobbin
- ∵ pressure in equilibrium with gravity ∵ bobbin remains at constant level in tube for a given flow
- both laminar & turbulent flow are measured
 - ↳ ∵ viscosity & density of gas impt ⇒ need careful calibration of gauge to specific gas
- conductive strip or clear conductive coating is applied to tube to prevent electrostatic charge build up

Pneumotachograph



- principle: $Q = \frac{P_1 - P_2}{R}$ ie is Ohms law: $F = P/R$

- need measuring head with a gauze screen of
 - known resistance
 - large diameter \Rightarrow to ensure laminar flow
 - \hookrightarrow \uparrow diameter \Rightarrow $\downarrow \downarrow \downarrow \downarrow$ velocity \Rightarrow Reynolds defines \uparrow chance laminar flow
- adv:
 - continuous flow recorder
 - rapid changes can be measured
 - can also measure volume by integration of the flow through it electronically
 - very accurate
- disadv:
 - laminar flow dependant on viscosity; turbulent flow on density
 - \hookrightarrow \therefore diff gas used changes accuracy
 - temp changes effects viscosity & density \therefore calibration
 - \hookrightarrow to counter this usually contains a heating element to keep at constant temp
 - water condensation on the gauze screen can cause change in resistance
 - \hookrightarrow also prevented by heating

Temperature

see physiology section on thermoregulation

Gas Analysis

- O₂
- CO₂
- volatiles
- (pH electrode)

Oxygen Analysis

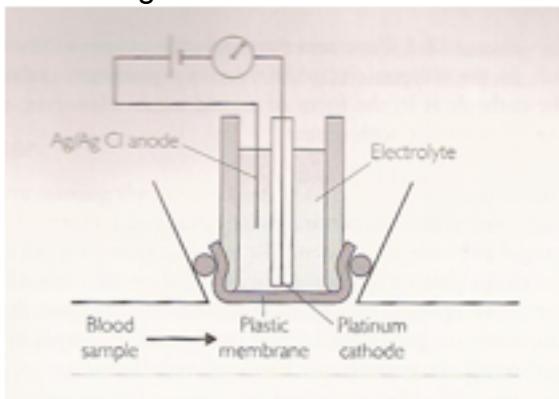
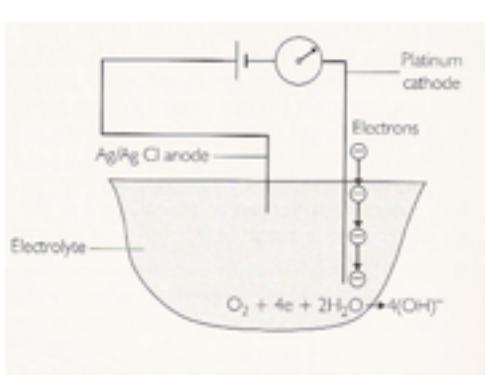
- variables to measure:
 - partial pressure (PO₂)
 - O₂ content (CaO₂)
 - O₂ saturation (SpO₂)

Partial Pressure Measurement

- diff methods:
 - polarographic method
 - fuel cell
 - paramagnetic method
 - mass spectometry
 - raman scattering
 - other:
 - US
 - UV
 - gas chromatography
 - magnetic acoustic spectometry
 - fluorescence

Polarographic

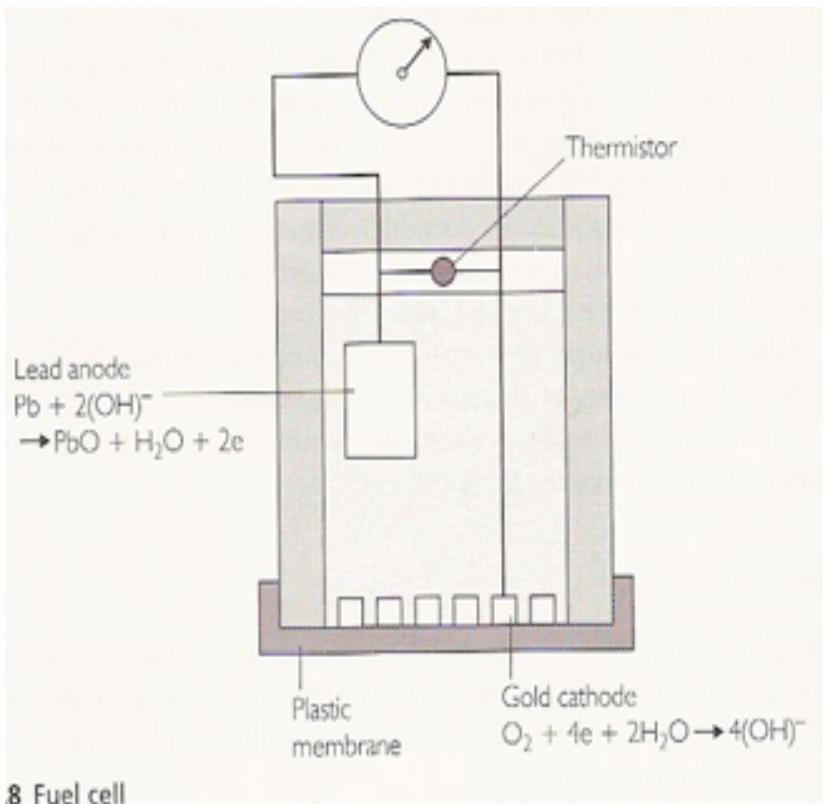
- aka Clark electrode = can measure PO₂ in gas mixtures as well as from blood samples:



- O₂ from either a gas or blood sample crosses a plastic membrane into an electrolyte solution (KCl)
 - ↳ plastic membrane prevents electrode direct contact with blood as would lead to protein deposits & error
- O₂ then participates in an electro-reduction reaction at a platinum cathode
- electrons are available for this reaction at the cathode due to 0.6v battery in circuit
- circuit completed by silver/silver-chloride anode (which also placed in electrolyte solution)
- result:
 - more O₂ available at platinum cathode \Rightarrow more electrons taken up at cathode \Rightarrow greater current flow
 - ↳ current flow = linear & proportional to PO₂

- reactions at electrodes:
 - cathode (reduction of O₂): O₂ + 4 electrons + 2H₂O \Rightarrow 4(OH⁻)
 - anode (oxidation of Ag): Ag + Cl (from KCl) \Rightarrow AgCl + electron
 - ↳ for every molecule of O₂ reduced \Rightarrow 4e⁻ supplied to electrical circuit
- role of 0.6v battery:
 - ensures linear response for current vs O₂
 - ↓s interference from reduction of other gases
- temp must also be controlled carefully at 37C

Fuel Cell



8 Fuel cell

- = very similar to Clark electrode but:
 - no battery needed ie no polarising current needed
 - cathode = gold mesh
 - anode = lead
 - electrolyte = KOH
 - reaction at cathode: O₂ + 4 e⁻ + 2H₂O \Rightarrow 4(OH⁻) ie same as Clark!
 - reaction at anode: Pb + 2(OH⁻) \Rightarrow PbO + H₂O + 2 e⁻
- current flow \sim PO₂
- used in some modern anaesthetic machines eg some Draegars

Paramagnetic

- used in some modern anaesthetic machine eg Datex Ohmeda
- principle: O₂ is paramagnetic ie can be drawn into a magnetic field

Figure 18.9 Paramagnetic property of oxygen

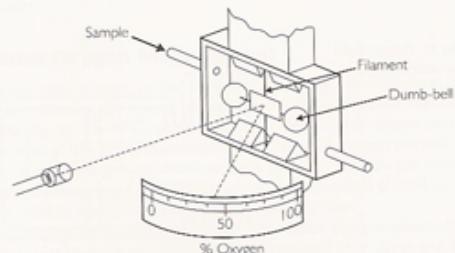
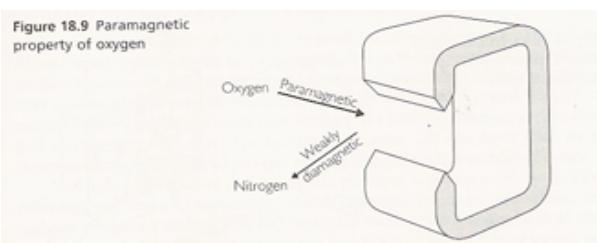
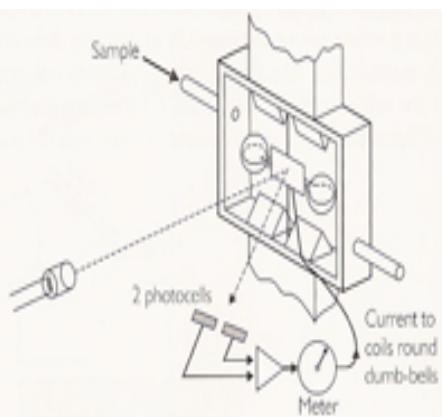


Figure 18.10 Simple paramagnetic oxygen analyser

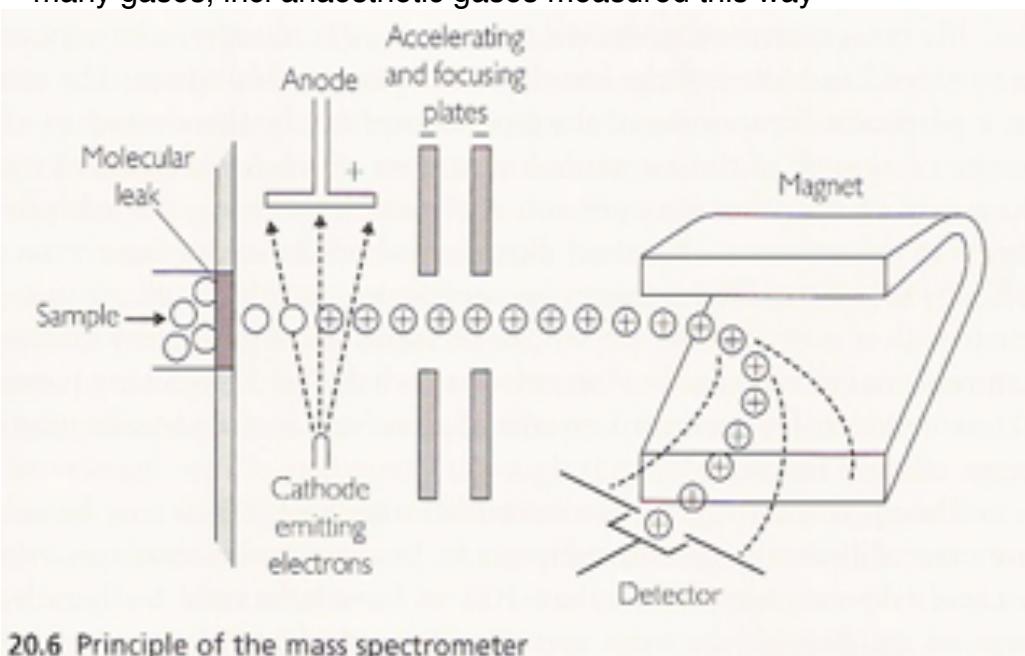
Figure 18.11 Null-deflection type of paramagnetic oxygen analyser



- in most simple form:
 - O_2 drawn into magnetic field \Rightarrow displacement of nitrogen (which is contained in glass spheres at ends of rod - looks like dumbbells)
 - N_2 is weakly diamagnetic (tend to move out of magnetic field)
 - deflection of dumbbells is registered by reflected light from a LED source & displayed
- adv:
 - can be set as a null-deflection system ie $\uparrow\uparrow$ sensitivity + gain
 - fast
- disadv:
 - must be calibrated with 100% O_2 & 100% nitrogen
 - affected by water vapour \therefore gases must be dried over eg silica gel before entering
- more modern devices have \uparrow ed sophistication

Mass Spectrometry

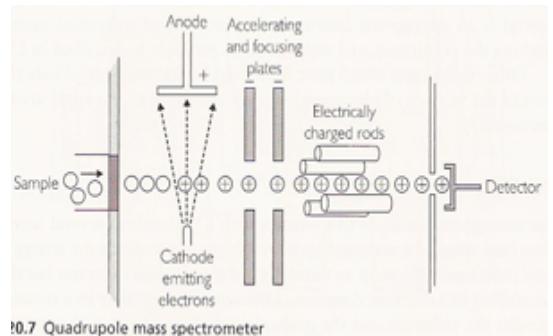
- many gases, incl anaesthetic gases measured this way



20.6 Principle of the mass spectrometer

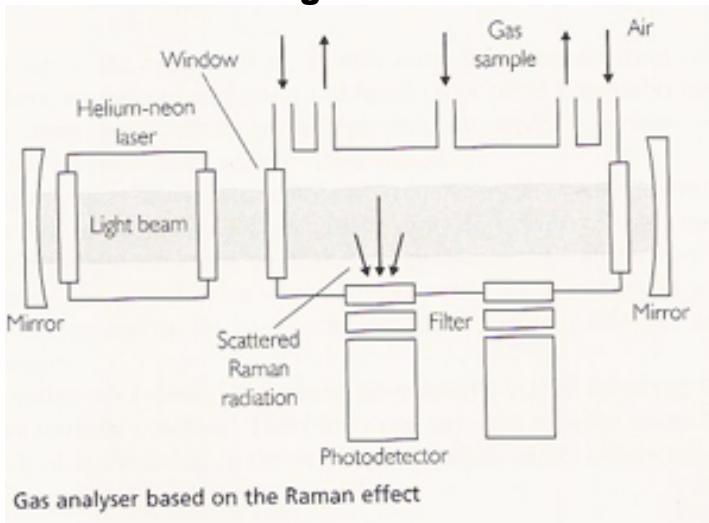
- sample is drawn through a tube into a the sample chamber by a pump
- molecular leak permits a few molecules of sample substance to diffuse into an ionisation chamber
- in chamber they are bombarded by beam of electrodes passing from a hot cathode to anode

- when electrons collides with gas molecules \Rightarrow some become charged ions \Rightarrow then accelerated out of chamber in narrow beam by accelerating & focusing plates
- stream of ions then pass through strong magnetic field \Rightarrow deflects them in an arc
- the deflection is picked up by a detector
- deflection:
 - = proportional to the amount of O₂ = as identified by its mass
 - lighter ions \Rightarrow deflected most
 - \therefore different gases form different streams
- \therefore mass spectrometers identify compounds by their mass numbers
- different streams can be identified & isolated by single mass spectrometer eg quadrupole mass spectrometer



- disadv of mass spectrometer:
 - problems with some gases eg CO₂ - breaks up into CO & O \Rightarrow both detected
 - CO₂ & N₂O both have same mw (44)
 - \hookrightarrow solution is to measure NO (breakdown product from N₂O) & use it as an index for N₂O
 - large machine
 - expensive
 - sampling delay

Raman Scattering



- raman effect:
 - light interacts with a gas molecule & changes the rotational or vibrational energy of the molecule
 - resulting transfer of energy from or to the light, changes its wavelength by amounts that are specific to molecule concerned
 - \therefore monochromatic (1 wavelength) radiation is changed, when passing through gas, into a spectrum of different wavelengths (= scattering)
 - \hookrightarrow this depends on the structure of individual molecules
- the type & concentration of molecules in a gas mixture can be determined by this principle
- advs:
 - accuracy - similar to mass spectrometer
 - breath by breath analysis
 - identify different types of gases

Ultrasound

- velocity of sound varies with the concentration of the gas it travels through
- US transducer emits a signal that is reflected & picked up
- delay in pick up varies with O₂ concentration

Fluorescence

- fluorescent light from certain dyes can be quenched by O₂
- this dye is incorporated in fiberoptic catheters
- dye is excited by light at 385nm \Rightarrow producing emitted light at 515nm
- the \downarrow in light emitted is directly proportional to O₂ tension

Oxygen Content Measurement

Direct Measurement

- Van Slyke apparatus:
 - = gold standard
 - blood is haemolysed (by lactate)
 - Hb converted to MetHb (by adding saponin & potassium ferricyanide)
 - \therefore O₂ is released \Rightarrow collected in closed apparatus
 - amount of O₂ is measured via manometric method:
 - measure pressure changes in constant gas volume (PV = nRT)
 - disadv:
 - needs large sample + slow process
 - doesn't measure dissolved amount of O₂
 - high degree of operator skill required
- Lex-O₂-Con:
 - blood haemolysed (by distilled water)
 - O₂ enters carrier gas bubbles \Rightarrow transported to a fuel cell
 - in fuel cell:
 - reaction O₂ + 4e⁻ + H₂O \Rightarrow 4(OH⁻) at cathode
 - current produced by electrons = proportional to total number of O₂ molecules

Calculated

- ie from PO₂, Hb, SaO₂

$$\text{CaO}_2 = [\text{Hb} \times \text{SaO}_2 \times 1.39] + (\text{PaO}_2 \times 0.003) = \text{ml O}_2 / 100 \text{ ml blood}$$

- errors via this method:
 - SaO₂ - oximetry sources of error
 - Huffner's number -
 - predicted number is 1.39
 - actual number is 1.3 - 1.36
 - due to non-functional Hb eg COHb, or metHb
 - foetal HbF

Oxygen Saturation measurement

- spectrophotometry:
 - oximeter (SaO₂)
 - pulse oximeter (SpO₂)

↳ see monitoring

Carbon Dioxide Measurement

- from gas sample:
 - infrared absorption
 - mass spectrometry
 - raman scattering
 - chemical colorimetric
 - gas chromatography
- from blood sample:
 - Severinghaus CO₂ - electrode

Infrared Absorption

- principle method = absorption of infrared radiation
 - IR radiation shines through sampling & reference chambers
 - detector measures the difference in absorption between the two
- this technique used for CO₂ detection & volatile sampling
- NB only gases with 2 or more different atoms in the molecule can be measured this way
 - ie O₂ cannot be
- to differentiate between CO₂ & eg volatile agent: analyser must look at different wavelengths:
 - volatiles = 3.3 um
 - CO₂ = 4.3um
 - N₂O = 3.9
 - wavelength correlates to where gas has strong absorption
- monochromatic analyser = unable to differentiate between diff volatiles
- polychromatic analyser = adds additional wavelengths to determine which agent responsible for 3.3um absorption
 - ∴ can differentiate diff volatiles

Gas Chromatography

- used for:
 - a mixture of gases
 - blood samples - it vaporises the sample at the injection port with heat
- components:
 - stationary phase = silica alumina & silicon oil coating
 - mobile phase = carrier gas (eg N₂) + sample gas
- detectors:
 - flame ionisation - for detecting organics
 - thermal conductivity - for inorganics
 - electron capture detector - for halogenated substances

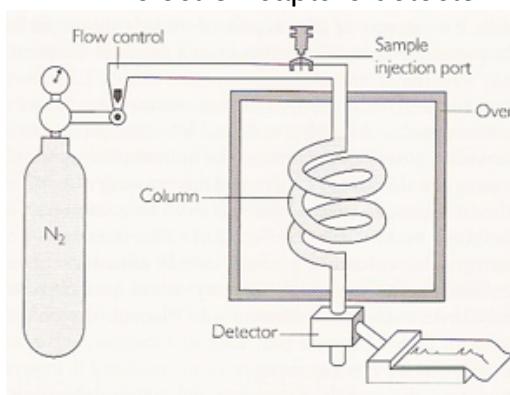
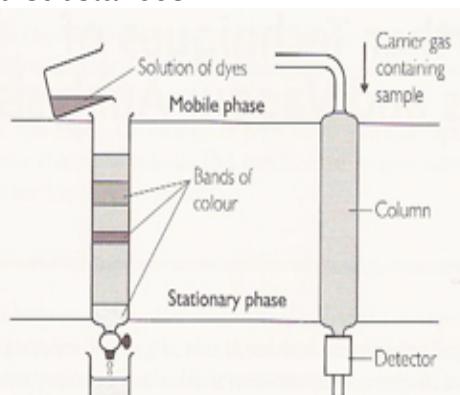
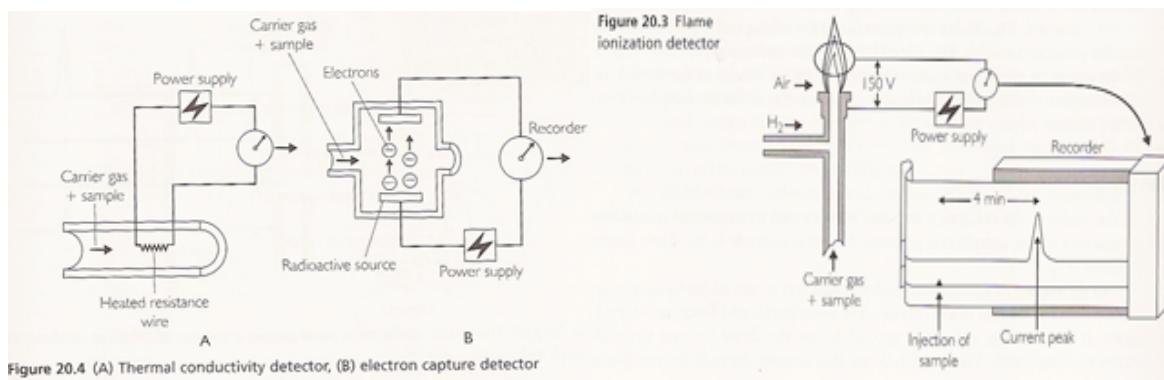


Figure 20.1 Principle of liquid chromatography (left) and gas chromatography (right)

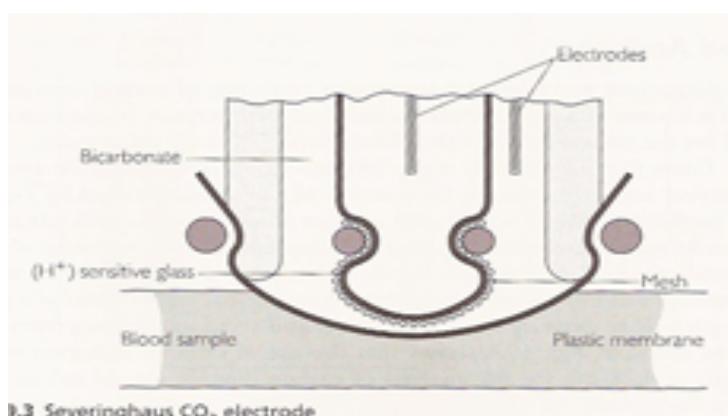




- principle of chromatography:
 - components of sample gas pass through column (stationary phase)
 - speed through this phase dependant on their differential solubility between 2 phases
 - appearance of components detected at outlet then detected by diff detectors as outlined above
- ∵ each substances progress has its own characteristic rate
 - time between injection & appearance at detector used to identify it
 - ↳ = retention time

Severinghaus CO₂ Electrode

- used to measure CO₂ directly from blood sample
- principle:
 - to measure CO₂ from liquids eg blood sample
 - methods based on H⁺ measurement:
 - CO₂ + H₂O \Rightarrow H₂CO₃ \Rightarrow H⁺ + HCO₃⁻
 - ↳ CO₂ tension ∵ directly proportional to H⁺ concentration
- electrode equipment:
 - apparatus incorporates hydrogen ion sensitive glass with electrodes either side of it
 - H sensitive glass in contact with a thin film of NaHCO₃ solution (acts as a buffer) in a nylon mesh
 - mesh is fixed over the glass tip with an o-ring
 - liquid to be tested is separated from the nylon mesh & bicarb by a plastic membrane
 - plastic membrane is permeable to CO₂ and is also attached by o-ring
 - at tip of electrode:
 - CO₂ diffuses thru plastic into the mesh impregnated with NaHCO₃ solution \Rightarrow
 - CO₂ combines with water present \Rightarrow H₂CO₃ \Rightarrow H⁺ + HCO₃⁻
 - electrode potential depends on the conc of H ions
 - ↳ ∵ proportional to voltage measured in circuit
- must be kept at 37deg
- must be calibrated with known mixtures of Co₂/O₂ before use



Volatile Agent Measurement

- infrared absorption - monochromatic or polychromatic analysers (Datex AS/3)
- piezo-electric crystal resonance technique (Siemens, Engstrom)
- photo-acoustic analysers (hewlit Packard)
- Raman scattering (Ohmeda Rasca)
- mass spectrometry
- refractometry
- gas-liquid chromatography
- other: laser analysers, UV, solubility, density

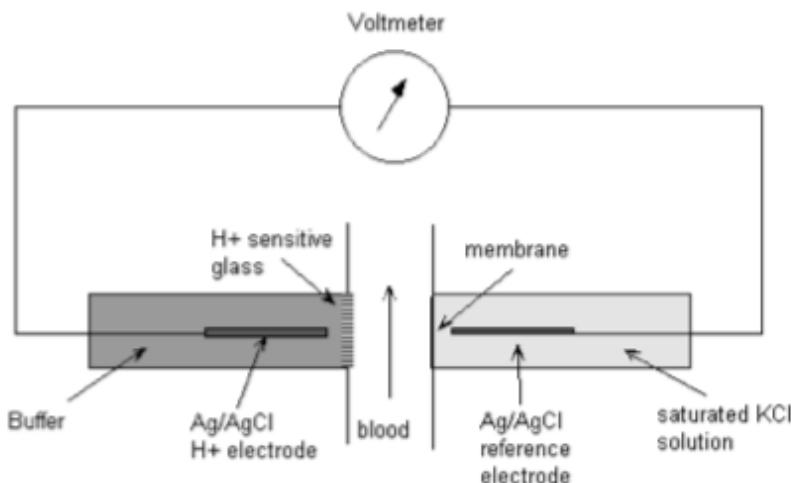
Piezo-electric crystal resonance

- when electrical potential applied across a quartz crystal \Rightarrow contracts
- if specific AC current applies \Rightarrow crystal oscillate at resonant frequency
- crystal coated with silicon oil:
 - volatile will dissolve in according to specific oil:gas partition coefficient
 - \Rightarrow change in resonant frequency \Rightarrow detected
- an uncoated crystal is incorporated as a reference
- problems:
 - does not distinguish which volatile
 - interference from water vapour (remove by heating)
 - CO₂, O₂, N₂O are not measured

Raman Scattering

- as per previously
- monochromatic laser light absorbed by substance in question
- light emitted at different wavelengths + frequencies
- adv:
 - can measure O₂, CO₂, N₂O, N₂ & volatiles
 - breath by breath analysis
 - accuracy \sim mass spectrometer
 - can identify diff volatiles

pH Electrode



(similar to Severinghaus electrode in CO₂ measurement)

- H⁺ electrode = ion selective electrode dependant on H ion sensitive glass at its tip
- potential develops across glass that is dependant on difference of H⁺ across it
- H⁺ within H⁺ electrode kept constant by buffer solution ∴ potential across glass is dependant on H⁺ in blood sample
- reference electrode used to complete circuit which has a membrane at tip to avoid contamination
- both electrodes are silver in contact with its chloride which is in turn in contact with a solution of chloride ions
 - H⁺ electrode - surrounded by buffer
 - reference electrode - surrounded by KCl
- potential difference between the electrodes is measured & converted into a direct reading of H⁺ or pH
- only variable in circuit is difference in pH between the inner buffer of the H⁺ electrode & that of sample
 - ↳ this difference creates the potential difference which is measured on volt meter
- temp control in imp - 37deg

Misc Laws, Definitions, Terminologies

Ficks Law of Diffusion

- not to be confused with Fick's principle!!
- The rate of diffusion of a substance across a unit area is proportional to its concentration gradient.
↳ (This applies to a homogenous phase)

$$J_s = D \cdot A \cdot \frac{\Delta c}{\Delta x}$$

J_s = rate of diffusion,

A = surface area,

Δc = concentration gradient,

Δx = thickness of membrane

D = a constant = \sim solubility / $\sqrt{m_w}$

Grahams Law

- The rate of diffusion of a gas is inversely proportional to the square root of its molecular weight (mw).
↳ this law only applies in certain cases when dealing with membranes and can also be applied to liquids

Osmosis

Osmosis:

Movement of *solvent* molecules across a semipermeable membrane into a region with higher conc of solute, so to equalise conc on both sides

Osmotic pressure:

The hydrostatic pressure required to *prevent* movement of *solvent* molecules by osmosis across a *semipermeable* membrane.

$$\text{predicted with } P = \frac{nRT}{V}$$

Molality:

Is the number of moles of solute per **kg** solvent. Molality represents the **number** of particles of the particular substance present.

Osmolality:

- Is the no of osmoles of solute per **kg** solvent. One osmole = 6×10^{23} particles
- NB **no** distinction is made about the type of particle present

↳ many different particles may be present.

- NB: it is *independent of temperature* or volume of solvent
- Units = mosmoles / kg

Osmolarity:

- Is the no of osmoles of solute per liter of solvent.
- altered by:
 - ▶ changes in temperature
 - ▶ volume of the solvents.
- Units = mosmoles / l

Tonicity:

- Is the *effective* osmolality of a solution (c/f to eg plasma, ECF, ICF etc).
- ∴ a measure of *only those particles effective at exerting an osmotic force across a membrane*.
- ∴ tonicity = Total osmolality minus ineffective osmolality.

“Effective” osmoles: = most solutes = those that does not cross membranes easily and are thus effective at exerting an osmotic force across the membrane in question.

“Ineffective osmoles”: Some solutes cross cell membranes, eg urea + glucose*. Thus, they are not effective at exerting an osmotic force across the membrane, but they do contribute to the *total* osmolality.

*Note: - **glucose** moves via facilitated diffusion across fat + muscle cells via action of Insulin. Thus, in diabetes, it becomes an effective osmole as fat + muscle cells form ~ 80% of cells in the body.

- **urea** is an effective osmole at the BBB, which it crosses very slowly compared to H₂O. Thus “hypertonic” urea (and also manitol) is hypertonic in relation to the BBB, and therefore effective in the Rx of cerebral oedema.

Colligative Properties

= *those properties of a solution that depend only on the particle concentration, ie the number of particles per volume.*

- They are:
 - ▶ *SVP depression*,
 - ▶ *boiling point elevation*,
 - ▶ *freezing point depression*
 - ▶ osmotic P.
- An example of where this is NB is glucose which is stored as glycogen.
 - ▶ Many glucose molecules combine to form one glycogen molecule.
 - ▶ One glucose molecule exert exactly the same osmotic pressure over a semipermeable membrane than does one glycogen molecule.
 - ▶ Put another way, all the glucose molecules which make up a glycogen molecule would have exerted an immense osmotic pressure if they were individual (non-combined) molecules.