

CHEM1031 Study Notes

Assumed Knowledge

Acid - proton donor

Base - proton acceptor

Acidic oxides (non-metals) react with water to make acids or bases to form salts (CO_2). Basic oxides (metals) react with acids to form salts but do not react with alkaline solutions (CuO , Fe_2O_3). Amphoteric oxides (Al , Zn , Pb , Sn) react with acids or bases to form salts. Neutral oxides (CO , N_2O) don't react.

acid + metal \rightarrow H_2 + salt

acid + carbonate \rightarrow CO_2 + H_2O + salt

Gases

Distinguishing properties of gases:

- very compressible
- flow rapidly
- take shape of and fill a container (liquids only take shape)
- expand and contract with temperature changes (more so than liquids, solids is near negligible)
- infinitely expandable (unlike liquids, solids)
- low density

Gas variables:

- Pressure (Pa)

=force/area. Due to particles in motion, colliding with momentum into each other and walls. $1\text{Pa} = 1\text{N}/\text{m}^2 = 1\text{J}/\text{m}^3$ ($1\text{N} = 1\text{kgm}/\text{s}^2$)

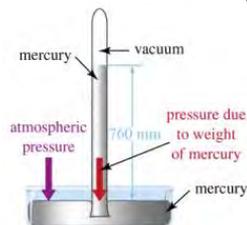
$1\text{atm} = 760\text{mmHg}/\text{Torr}$

= 101325Pa

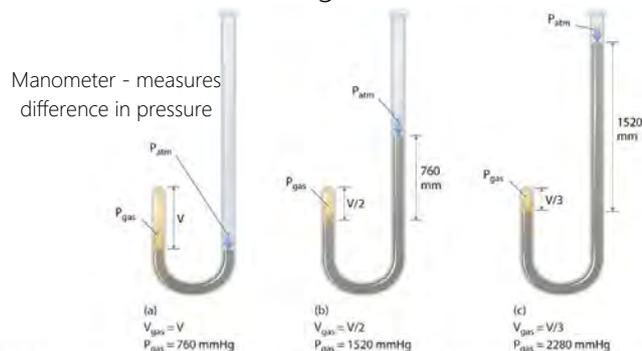
= 101.325kPa

= 1.01325bar

= 14.7psi



Barometer - measures atmospheric pressure



- Manometer - measures difference in pressure
- (a) Initially the gas is at a pressure of 1 atm = 760 mmHg (the mercury is at the same height in both the arm containing the sample and the arm open to the atmosphere); its volume is V .
 (b) If enough mercury is added to the right side to give a difference in height of 760 mmHg between the two arms, the pressure of the gas is 760 mmHg (atmospheric pressure) + 760 mmHg = 1520 mmHg and the volume is $V/2$.
 (c) If an additional 760 mmHg is added to the column on the right, the total pressure on the gas increases to 2280 mmHg, and the volume of the gas decreases to $V/3$.

- Volume (m^3 - 10^3L)
- number/Amount (mass - kg, moles)
- Temperature (always in Kelvin; absolute temperature)

These are dependent upon each other in the three Empirical Gas Laws:

- **Boyle's Law** - $V \propto \frac{1}{P}$ (or $P_1V_1 = P_2V_2$) - as pressure increases, volume decreases

- **Charles' Law** - $V \propto T$ (or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$) - as temperature increases, volume increases
- **Avogadro's Law** (also Gay-Lussac's - found when gases reacted volumetric ratios were small whole numbers - a stoichiometric ratio) - $V \propto n$ (or $\frac{V_1}{n_1} = \frac{V_2}{n_2}$) - as the number of moles increases, so does the volume

Combining Boyle's and Charles' Law: $PV \propto T$ or $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

Combining all three forms the **Ideal Gas Law**: $PV \propto nT$

or $PV = nRT$ where $R = \text{Universal Gas Constant}$
 $= 8.3145 \text{ J mol}^{-1} \text{ K}^{-1} \text{ (SI)}$
 $= 0.082057 \text{ L atm K}^{-1} \text{ mol}^{-1}$

Standard Temperature and Pressure (STP): 0°C (273.15K) and 1 bar ($1.00 \times 10^5 \text{ Pa}$ or 0.98atm). 1 mole of gas at STP is 22.7L. We can also sub in $n=m/M$ and density (ρ - rho) = m/V to integrate other values.

Dalton's Law of Partial Pressures - in a mixture of gases, total pressure is the sum of the pressure each gas would exert if alone under the same conditions (assuming the gases are independent and do not react):

$$P_T = P_a + P_b + P_c + \dots$$

Mole Fraction - for each component A in a mixture, the mole fraction is (a value between 0 and 1 - not percentage - to express the "percentage" of moles of that substance in a mixture):

$$X_A = \frac{n_A}{n_T}$$

Partial Pressure of A $P_A = X_A P_T$

Each gas also obeys the Ideal Gas Law independently as if they took up all the volume, and hence were $P_T = P_A + P_B$, $P_A V = nRT$ and $P_B V = nRT$. However these conclusions in the 17th-19th century, and it wasn't until the 19th-20th century that a theory of atoms began to form, so these laws all looked at macroscopic ideas, influenced by what we know to be properties of microscopic atoms.

Kinetic Theory of Gases:

- molecule size is negligible compared to distance between them
- molecules move randomly in straight lines in all directions at various speeds
- forces of attraction/repulsion are negligible (because they are very weak) except in collisions
- gas particle collisions are perfectly elastic
- $E_{k,av} \propto$ absolute temperature

This explains Boyle's Law as less space means more **frequent** collisions, and hence higher pressure (as collisions result in a force applied), and Charles' Law as increasing temperature, kinetic energy (molecule speed) increases, so collisions become more **frequent** and with **greater force**.

Kinetic theory states $E_{k\ av}$ is only dependent on temperature, not gas type, and difference gases at the same temperature have the same average kinetic energy. As $\bar{E}_k = m\bar{u}^2/2$, heavier gases will travel more slowly with the same energy.

It can be found that (don't need to know derivation):

$$\bar{E}_k = \frac{3RT}{2N_A}$$

N_A is Avogadro's number. Remember this is per molecule, so to find per mole multiply by Avogadro's number. Combining this with our other formula for \bar{E}_k :

Rate of Gas Movement:
$$\bar{u}_{rms} = \sqrt{\frac{3RT}{M}}$$

Root-mean-square (rms) simply means we have square-rooted the mean value.

Effusion - escape of molecules through a hole of molecular dimensions (assuming no collisions between molecules)

Diffusion - mixing of gases until the mixture is homogeneous

Using the above rate and these ideas (in diffusion it could be two gases reacting and producing a colour located at a particular point and speeds) we can determine molecular mass.

Graham's Law - The rates of effusion (and diffusion) of two gases at the same temperature and pressure are inversely proportional to the square roots of their densities (note time is inversely proportional to rate):

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{\sqrt{\rho_1}}{\sqrt{\rho_2}}$$

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{\sqrt{M_2}}{\sqrt{M_1}}$$

$$\frac{\text{time}_1}{\text{time}_2} = \frac{\sqrt{M_1}}{\sqrt{M_2}}$$

All gases are actually non-ideal:

- all particles do have volume - becomes significant at high pressure (real volume > ideal volume as ideal volume hits zero)
- they have attractive forces - significant at low temperatures (real volume < ideal volume as particles are brought together; gases with low interatomic dispersion forces like He do not experience this)
- particles do interact - negligible at high temperature (enough energy to keep bonds apart), but significant at other temperatures (real pressure < ideal gas pressure as there are less molecules - chemically bonded together - and hence less collisions)

All known life depends upon the atmosphere, however the atmosphere doesn't have a definite end, with 99% within 30km, "outer space" at ~10,000km.

Atomic Structure

Only valence electrons determine chemical properties, and hence isotopes have nearly identical chemical properties. Light is electromagnetic radiation (a self-sustaining oscillation of electric and magnetic fields), and is characterised by its frequency (ν - nu; Hz or sec^{-1}) or wavelength (λ ; m or angstrom= $\text{\AA}=10^{-10}\text{m}$), which are related by $c=\nu\lambda$, with visible light being $3.9\text{--}7.0 \times 10^{-7}\text{m}$, whilst gamma rays are around 10^{-12}m and long radio waves 10^4 .

Monochromatic Radiation - a selection of one frequency (in practicality, a narrow band of frequencies) for various scientific measurements

Polychromatic Radiation - consisting of many frequencies

Light has typical wave-like properties (refraction, diffraction and interference), however also exhibits the photoelectric effect, discovered in 1887 by Hertz who found light could eject electrons from the surface of a metal, and a current could flow to another electrode in a vacuum. He also found it required a threshold frequency that was dependent on the type of metal used which was independent of the intensity, however once above the threshold frequency the intensity increased current size, and the energy of the electrons emitted depended on the frequency. In 1905, Einstein realised light comes in packets or quanta (got Noble Prize in 1921), where each quantum of energy is proportional to frequency:

$$E = h\nu$$

where h = Planck's constant = $6.626 \times 10^{-34}\text{Js}$

A photon with enough energy could be absorbed and eject an electron, producing a current, and only one with enough energy could overcome the attraction of the atom, the remainder energy being converted to kinetic ($E_k = h\nu - W$). The energy of a particular orbital can be found by the Rydberg Equation:

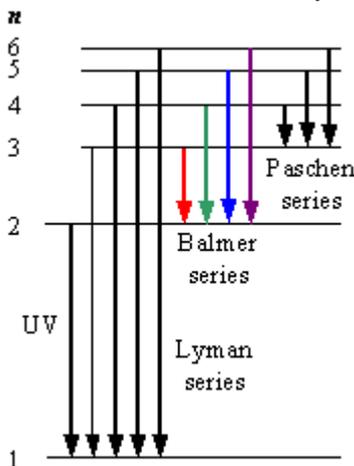
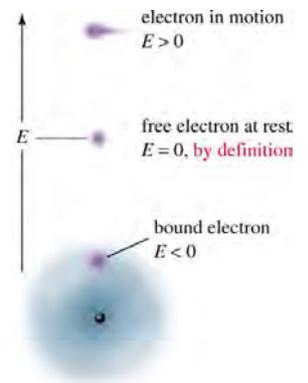
$$\frac{1}{\lambda} = R_H \left(\frac{1}{n_1^2} - \frac{1}{n_2^2} \right)$$

where R_H = Rydberg constant for H (on data sheet)

n_1 = lower shell

n_2 = upper shell

For hydrogen the shell is a good indicator of electron energy: $E = -R_H/n^2$



White (polychromatic) light passing through a gas composed of single atoms gas lines (or specific frequencies) removed, forming an **absorption spectrum** (the release of the photons once electrons fall is in all directions, and hence much weaker at the detecting screen; a prism can be used to distinguish between colours). When heating a gas by electrical discharge, it produces these series of lines in an **emission spectrum**. This is because electrons occupy discrete energy states that they move up or down. The spectra vary with the gas used and pressure (proximity alters energy of shells).

Lyman = UV

Balmer = visible light

Paschen = IR