PROPERTIES OF GASES

[MH5; Ch 5, 5.1 - 5.5 (only)]

FEATURES OF A GAS

- Molecules in a gas are a long way apart (under "normal" conditions).
- Molecules in a gas are in rapid motion in all directions.
- The forces between molecules in a gas are small.
- The molecules in a gas make frequent collisions with each other, and with the walls of the container.
- The collisions of molecules with the walls of the container result in pressure (force per unit area).
- A gas expands to fill all of, and takes the shape of, the available space.

MEASUREMENTS ON GASES [MH5; 5.1]

- A complete description of a gas requires several measurements.....
- We need to know the amount of gas, (usually expressed as the • number of moles of gas) the volume, the temperature and the pressure of the gas.

VOLUME

Volume of a gas may be expressed in L, cubic centimetres or cubic 1000 mL = 1Lmetres.

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lm^{3} = 1000 L lcm^{3} = 100 = lmL
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TEMPERATURE

While the temperature of a gas is usually measured in degrees Celsius, anytime a calculation is involved requires a conversion to degrees Kelvin (or absolute temperature).

UNITS OF PRESSURE

- The SI unit is the **Pascal** (**Pa**; a force of one Newton m $^{-2}$).
- The Pascal is very small so we usually use kiloPascals (kPa).
- Another unit of pressure is the Atmosphere (atm);

Standard Atmospheric Pressure

1 atm = 760 torr = 760 mm Hg = 101.325 kPa

• We also use: 1 Bar = 100 kPa; note that 1 Bar < 1 atm

THE IDEAL GAS LAW [MH5; 5.2]

Volume is directly proportional to amount of gas present.

• Assuming that pressure and temperature are kept constant.





These three equations can be combined into a single equation......

$$V = k_{a}T$$
 $V = \frac{k_{3}}{P}$
 $k_{1} \times k_{a} \times k_{3}$
 $V = constant \times m \times T$
 P

Avogadro's Hypothesis (or Principle):

- Equal volumes of all gases contain the same number of molecules (under the same conditions of P and T).
- The product PV depends on the number of molecules (or moles) of gas present and not on their mass or compositions.
- So, in the equation:

$$PV = n \times constant \times T$$

the value of the constant is the **SAME** for all gases!

• In the Ideal Gas Equation, we use the symbol **R** for this gas constant.....

 The units of R, the gas constant, depend on the units of pressure, P:

• PV = nRT so $R = PV mol^{-1} K^{-1}$

- Be very careful to always use a numerical value for **R** which has units consistent with the units of **P**.
- Notice that Volume is always in <u>L.</u>
- An "ideal" gas obeys the equation PV = nRT exactly !!!
- Real gases show small departures from the Ideal Gas Law, called "non-ideal behaviour".
- Departures from the equation are greatest for:
 - 1) high pressures (molecules close together)
 - 2) low temperatures (molecules move slower)
 - 3) gases of higher boiling-point, which have stronger intermolecular forces.
- Departures from ideal behaviour are due to attractive forces between molecules.
- In the (hypothetical) "ideal gas" there are NO forces (attractive or repulsive) between molecules.

Rearrangements of the Ideal Gas Law

- There are five (5) variables in the Ideal Gas Equation, so there are lots of ways to rearrange this equation.....
- Sometimes, we may make minor substitutions that will give us other useful variables.
- So let's rearrange PV = n R T...... and introduce the mass of gas.

Number of moles:
$$n = \frac{PV}{RT}$$

Mass of gas present:
so: $\frac{mass}{MM} = \frac{PV}{RT}$ $\Rightarrow mass = \frac{PV}{RT} \times MM$
Gas density, d, is always expressed in gL^{-1}

$$d = \frac{mass}{Val} = \frac{\frac{1}{RT} \times MM}{Val} = \frac{\frac{1}{RT}}{RT}$$

MN

= <u>ma</u>

mass

Ja55

Molar Mass, MM, from mass of gas present:

$$MM = \frac{d RT}{P}$$

DON'T memorize each of these equations!!

Instead, use:

PV = nRT = (m/MM)RTto obtain the relationship you need in each problem.

Notes:

- 1) All gases always mix together in all proportions.
- 2) A gaseous mixture behaves like a single gas and obeys the same laws.

So.....

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In any gas mixture, the average $MM = MM_{avg}$ and $MM_{Avg} = X_AMM_A + X_BMM_B + X_CMM_C$ (3 gases)

(same as avg atomic mass of mixture of isotopes)

For just 2 gases, $X_A + X_B = 1$

so.....
$$X_{\mathcal{A}} = I - X_{\mathcal{B}}$$

 $X_{\mathcal{B}} = I - X_{\mathcal{A}}$

EXAMPLE 1:
$$R = 8.314 L kPa mol^{-1} K^{-1}$$

What is the mass of 5.60 L of O_2 gas at 100°C and 50.0 kPa pressure?
 $PV = TRT$ \Rightarrow $T = \frac{PV}{RT}$
 $T = \frac{(50.0 kPa)(5.60k)}{(8.314 k kPa)(100°C + 273.15)K}$
 $= 0.0903 m0l$
 $Mass = 0.09030 mol \times 32.00 g mol^{-1}$
 $= 2.89 g$
EXAMPLE 2:
What is the density of SO_2 gas at 47°C and 82.5 kPa pressure?
 $MT = \frac{dRT}{P} \Rightarrow d = \frac{PMM}{RT}$
 $d = \frac{(82.5 kPa)(64.07 g mot^{-1})}{(8.314 L kPa)(64.07 g mot^{-1})}$
 $(8.314 L kPa)(64.07 g mot^{-1})$
 $= 1.987 g L^{-1} = 1.99 g L^{-1}$

EXAMPLE 3:

At what temperature in K will the density of gaseous CO_2 be 2.00 g L⁻¹ at 100 kPa pressure ?

$$MM = \frac{dRT}{P}$$

$$T = \frac{MM \times P}{OR}$$

= $(44.01 \text{ prod}^{-1})(100 \text{ Ra})$
 $(2.00 \text{ g} \text{ }^{-1})(8.314 \times \text{ Ra})$
 $\frac{1}{MOH}$

Changes in Conditions [MH5; 5.3]

 Often a given amount of a gas changes from an initial to a final state - by changing the pressure, temperature or volume (or any or all of these conditions!)

EXAMPLE 1:

A 500.0 mL sample of gas at $25^{\circ}C$ and 100 kPa is heated to $100^{\circ}C$. The volume increases to 550.0 mL What is the new pressure ?



EXAMPLE 2:

A 2.50 L flask contains CO_2 gas at 100° C. The pressure of the gas is measured at 85.0 kPa. The flask is cooled to 25° C. What is the pressure of the cooled gas ?

$\frac{\overline{7, \sqrt{1}}}{\overline{7, 7}} = \frac{\overline{P_2 \sqrt{2}}}{\overline{7_2}}$	V remains constant at 2.50L
$S_0 \dots \frac{P_i}{T_i} = \frac{P_a}{T_a}$	
Subotitut: 85.0 kPa 373 K	$= \frac{P_2}{298 \text{ K}}$
$P_a = 67.9 LPa$	
of Temperature rema	ains constant
\Rightarrow $P, V, = P_{a} V_{a}$	

DALTON'S LAW OF PARTIAL PRESSURES [MH5;5.5]

- In a gas mixture, the total pressure equals the sum of the partial pressures of the components.
- The **partial pressure** of each component is the pressure that component would exert if it were present **alone** in the <u>container</u>.
- for n_A moles of component 'A': $\mathcal{PP}_{\mathcal{D}}$ =
- In a gaseous mixture, R, T and V are constant, so total P is given by:

$$P_{total} = PP_A + PP_B + PP_C \quad and \quad n_{total} = (n_A + n_B + n_C) \quad so....$$

$$P_{tot} = \underbrace{n_{tot}}_{V} P_{T}$$

- Dalton's Law of Partial Pressures **means**: the Ideal Gas Equation can be applied to individual components **and** to the whole mixture......
- So.....if we keep R, T and V constant:

 $P_{total} \propto n_{total}$ and $PP_A \propto n_A$

• If we divide one into the other (keeping R, T and V constant allows us to make these relationships equalities):

$$\frac{n_{H}}{n_{total}} = X_{H} = \frac{P_{H}}{P_{total}}$$

$$\frac{n_{H}}{2} ways to calculate Mole Fraction:$$

EXAMPLE 1:

Two vessels, A (volume 4.0 L) and B (volume 6.0 L), are connected by a stopcock.

Initially, the stopcock is closed, the temperature is 300 K, and A contains $N_2(g)$ at a pressure of 50 kPa, while B contains $O_2(g)$ at a pressure of 80 kPa.

i) What is the final pressure (still at 300 K) after the stopcock is opened? PV = TT

ii) What is the mole fraction of each gas in the final mixture?iii) What is the average molar mass of the final mixture?

i)
$$\mathcal{N}_{N_{a}} = \frac{\mathcal{P}V}{\mathcal{R}T} = \frac{50 \times 4.0}{8.314 \times 300} = 0.0802 \text{ mol.}$$

 $\mathcal{N}_{a} = \frac{\mathcal{P}V}{\mathcal{R}T} = \frac{80 \times 6.0}{8.314 \times 300} = 0.1924 \text{ mol.}$
 $\mathcal{N}_{total} = 0.0602 \text{ mol} + 0.1924 \text{ mol.}$
 $= 0.2726 \text{ mol.}$
 $\mathcal{P}_{total} = \frac{\mathcal{N}_{total}}{V_{total}} = \frac{0.2726 \times 8.314 \times 300}{10.0}$
 $= 68.0 \text{ kPa}$

) Second Approach :
$$P_{1}V_{1} = P_{2}V_{2}$$

 $N_{3}: P_{1} = 50k^{2}V_{2} = 4.0L$
 $P_{2} = ? V_{2} = 10.0L$
 $P_{3} = Q_{1} \circ k^{2}R = 10.0L$
 $P_{3} = 20.0 k^{2}R - PP of N_{3}$
 $O_{3}: P_{1} = 80k^{2}R = V_{1} = 6.0L$
 $P_{3} = ? V_{2} = 10.0L$
 $P_{4} = ? V_{2} = 10.0L$
 $P_{3} = 48.k^{2}R - PP of Q_{3}$
 $P_{40}f = PP_{N_{3}} + PP_{0} = 20.0k^{2}R + 48.0k^{2}R$
 $i) N_{n} = \frac{7N_{2}}{7164} = \frac{0.0802}{0.2726} = 0.294$
 $i) N_{n} = \frac{7N_{2}}{7164} = \frac{20.0}{68.0} = 0.294$
 $N_{a} = \frac{7N_{a}}{P164} = \frac{20.0}{68.0} = 0.294$
 $N_{a} = \frac{1-0.294}{27166} = 0.706$
 $MM_{a}v_{g} = [MM_{N_{2}}X_{N_{3}}] + [MM_{0}X_{0}]$
 $= (28 \times 0.294) + (32 \times 0.706)$
 $g^{mol^{-1}}$
 $= 30.8 g^{mol^{-1}}$

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EXAMPLE 2:

A mixture of ethane, C_2H_6 , and oxygen, O_2 , has the correct stoichiometric composition for combustion to CO_2 and H_2O .

 $2 C_2 H_6 + 7 O_2 \rightarrow 4 CO_2 + 6 H_2 O$ of each gas ole fraction of each gas before the

- a) What is the mole fraction of each gas before the reaction ?
- b) If the total pressure of the mixture is 80 kPa, what is the partial pressure, in kPa, of each gas before the reaction?
- a) Initial mixture contains 2 mol C, H6 and 7 mol Os Total moles of gas = 9 $X_{C_{a}H_{6}} = \frac{d}{q} = 0.322$ $X_{\partial_{a}} = \frac{7}{q} = 0.778$ b) $80.0 \, \text{LPa} = P_{C_3} H_6 + P_{O_3}$ $Pan \Rightarrow X_{e_a}H_6 = \frac{P_{e_a}H_6}{P_{total}}$ PCAHE = XCAHE X Ptotal = 0.222 × 80 kPa

$$P_{0} = P_{+0+} - P_{c_{3}}H_{6} \quad OR \quad P_{0} = 0.778$$

= 80 - 18
= 62 kPa -90 - = 62 kPa

= 18.0 kPa

EXAMPLE 3:

A gas mixture contains ethane, $C_2H_{6_1}$ at 70.0 kPa and propane, C_3H_8 , at a pressure of 45.0 kPa.

What is the average molar mass of the gas mixture?

$$MM_{avg} = \left[MM_{e_{a}H_{b}}^{2} X_{e_{a}H_{b}}^{2} \right] + \left[MM_{e_{a}H_{b}}^{2} X_{e_{a}H_{b}}^{2} \right]$$

$$- uce partial pressures of each gas
to find mole fraction $P \propto n$
 $X_{e_{a}H_{b}}^{2} = \frac{70 \cdot 0 \, \text{kPa}}{(70 \cdot 0 + 45 \cdot 0) \, \text{kPa}} = 0 \cdot 609$
 $X_{e_{a}H_{b}}^{2} = 1 - 0 \cdot 609 = 0.391$
 $MM_{avg}^{2} = \left(30.0 \, \text{gmol}^{-1} \times 0.609 \right)$
 $+ \left(44.0 \, \text{gmol}^{-1} \times 0.391 \right)$
 $= 35.5 \, \text{gmol}^{-1}$$$

$$MM = \frac{d}{RT}$$

$$\frac{EXAMPLE 4: 38}{A \text{ mixture of } N_2(g) \text{ and } Cl_2(g) \text{ has density } 1.58 \text{ g} \text{ L}^{-1} \text{ at } 25 \, ^\circ \text{C} \text{ and}}$$

$$100 \text{ kPa pressure. What is the partial pressure of } N_2?$$

$$MM_{avg} = \frac{dRT}{P} = \frac{1.58 \times 8 \cdot 314 \times 298}{100}$$

$$= 39 \cdot 2 \text{ gmol}^{-1}$$

$$Mm_{avg} = \left[MM_{N_3} \times_{N_3}\right] + \left[MM_{elg} \times_{elg}\right]$$

$$det \times_{N_3} \text{ be } \chi \qquad \therefore \quad \chi_{elg} = 1 - \chi$$

$$Sub: 39.2 = (28 \times) + [711(1-\pi)]$$

$$39.2 = 28 \times + 711 - 711 \times$$

$$39.2 - 71 = 28 \times - 71 \times$$

$$+ 31.8 = + 43 \times$$

$$\therefore \times = 0.74 = X_{N_2}$$

$$\chi_{N_3} = \frac{PP_{N_3}}{P_{tot}} \Rightarrow 0.74 = \frac{PP_{N_3}}{100 \text{ kPa}}$$

$$\therefore PP_{N_3} = 74 \text{ LPa}$$

EXAMPLE 5:

A container with a fixed volume of 10.0 L contains 5.60 grams of N₂ (g) at 10° C. Then 5.00 L of CO_2 (g) at a pressure of 75.0 kPa and 15°C are added. The gases mix and the temperature equilibrates at 12° C. What is the final pressure of the gas mixture ?

STOICHIOMETRY OF GASEOUS REACTIONS [MH5; 5.4]

 From Avogadro's Hypothesis, it follows that, at constant T and P, gases react in simple whole-number ratios by volume (Gay-Lussac's Law).....

2 H ₂ (g) +	• O ₂ (g)	\rightarrow 2 H ₂ O(g))	
2 mol	1 mol	2 mol		OR
2 volumes	1 volume	2 volumes		OR
20 kPa	10 kPa	20 kPa		
C ₃ H ₈ (g) +	5 O₂(g) →	3 CO2(g) +	4 H ₂ O(g)	
1 mol	5 mol	3 mol	4 mol	OR
1 vol	5 vol	3 vol	4 vol	OR
10 kPa	50 kPa	30 kPa	40 kPa	

- If temperature and pressure are kept constant, the volumes of each gas could be used instead of moles to do stoichiometry calculations.
- If volume and temperature are kept constant, the pressures of the gases may be used in place of moles for stoichiometric calculations.
- If using moles of gases in a mixture, remember that the pressure of the gas mixture is due to the total number of moles of gas present!!

EXAMPLE 1:

A 2.00 L vessel contains 14.0 kPa of propane, C_3H_8 . Exactly enough O_2 is added to react completely, giving CO_2 and H_2O . What is the initial pressure in kPa, before reaction, at 300 K? The combustion heats the product gases. What is the final pressure at 650 K?

RXN:	(3 Hg +	$50_{2} \rightarrow$	3 CO2	+ 4 H ₂ O	
1 mo	$I C_3 H_8$	reacts	with ?	5 <i>0</i> 2 "	
Pan: 14 1H	Kra (3Hg		_ 70 kł	Da Oz	
T			TO kPa	0	
P _{tot} =	14 kła o 84 kła.		10 014	2	
		,		7	/
after:	6 mol _ 84 kPa	ula(tants	yield	x kPa "	[.
84	= ~	\Rightarrow \checkmark	$=\frac{84}{b}x$	$7 = 98 \text{L}^2$) a
6	7		at	300 K	
$\frac{P_{1}V_{1}}{T_{1}}$	$= \frac{P_{a} \chi_{a}}{T_{a}}$	\Rightarrow	78 kPa 300 K	$=\frac{P_a}{650}$	(
		- 95 - P	$a^2 = a_1 a$	kPa	

EXAMPLE 2:

What is the formula of gas X, given the following volume relationships at constant T and P?

X(g) + 0.21 L	O₂(g) → CC 1.36 L → 0.	₽₂(g) + H₂O(g 84 L 1.05 L)
Of consta	ant Pand	T: Va	n
Valunds	are in a	some fixe	a ratio 4 coefficients
(proportio	mal to me	(45) - Will	
X	0,	CO2	HD
0.91	1.36	0.84	1.05
0.21	0.21	0.9)	0.91
=	= 6.5	= 4	= 5
So X Does Dr	+ 6.50 _a cygen bala	$\rightarrow 400_{a}$ nce? ye	$+ 5H_2O$
:. X con	tains only	(1 and 1	7
$\Rightarrow C_{+}$	H ₁₀		

Pan - ul	P instead of moles
EXAMPLE 3: to do	oto; chionday
A mixture contains 55 kPa pressure	of methane, CH ₄ , and 80 kPa
pressure of O_2 . A spark produces a	n explosion.
What pressures of CO. (a) and H.O.	(a) are produced (measured at the
original temperature) 2 000/1002	so change in volume
What are now aird ware acted 2. What	
what gas remains unreacted ? who	t is the total pressure after the
reaction is complete?	$\rightarrow 10 + 2HD$
RXN: CH_ + ~C	$\gamma \rightarrow c c \gamma $
7	
\mathcal{D} = 55 k Pa	$P_0 = 80 k t_a$, $r c_{191}$
$r_{CH_4} = 33$ ~~~	à
NO 7 AU 1 55 -5	
dh i i i i i i i i i i i i i i i i i i i	
	d
ХD	
	\rightarrow co ± 24 O
	0 0
154. 33 60	
01' 55 - 50 0	40 \$0
a a	00
= 15	

 $\begin{array}{l} P_{CO_{a}} = 40 \ \text{kPa.} \\ P_{H_{a}O} = 80 \ \text{kPa} \\ P_{H_{a}O} = 80 \ \text{kPa} \\ P_{CH_{4}}(xs) = 15 \ \text{kPa}. \end{array} \begin{array}{l} P_{total} = 40 + 80 \\ + 15 \\ = 135 \ \text{kPa} \\ = 135 \ \text{kPa} \\ \end{array}$

Liquid-Vapour Equilibrium

 A volatile liquid (or solid) in a closed container will reach equilibrium when molecules enter the liquid (or solid) [i.e. condense] and leave the liquid or liquid [i.e. evaporate] at the same rate.



- This is a dynamic process.
- The pressure (or, in a mixture, the partial pressure) of this component in the gas phase is the **Equilibrium Vapour Pressure** of that substance.
- Its value depends on:
- 1) The nature of the liquid (solid). Those with lower boiling-points (sublimation points, for solids) will have higher vapour pressures. They are volatile, e.g. (diethyl) ether, bp. 35 °C; hexane, bp. 69 °C. Substances with higher bp.'s (sublimation points) have lower vapour pressures and are less volatile e.g. H_2SO_4 , bp. 336 °C and Hg(I), bp 351 °C, have very low volatilities at room temperature.
- 2) **The Temperature**. As the temperature increases, the vapourpressure increases because heating gives extra energy to the liquid molecules. However, the increase in vp is not linear with temperature so long as liquid (solid) is present.

As the temperature is increased, eventually the vapour-pressure will reach 1 atmosphere at the Normal Boiling Point of the liquid (Normal Sublimation Point, for solids).

- If the atmospheric pressure is low, e.g. on a mountain-top, liquids boil at lower temperatures.
- Whenever there is liquid water, there is also water vapour present; if this liquid water is in a closed container, there will be a liquid vapour equilibrium.
- As another gas (besides water vapour) may be present as well, the total pressure of the gas mixture will be due to the gas and the water vapour.
- So..... the equilibrium vapour-pressure of water is very important!

°C	0	20	24	100
kPa	0.61	2.4	2.9	101.3

EXAMPLE 1:

Suppose O_2 (g) is in equilibrium with liquid water at 24°C. The **total** gas pressure is 100 kPa.

$$P_{total} = P_{0,y} + P_{H_{a}O(y)}$$
This is a gaseous mixture; it contains $O_{2}(g)$ and $H_{2}O(g)$.
 $a + a + C$; $P_{H_{a}O} = a \cdot g \cdot Ba$.
 $\therefore P_{0,a} = P_{total} - P_{H_{a}O}$
 $= 100 - a \cdot g$
 $= 97.1 k Pa$

EXAMPLE 2:

Suppose carbon dioxide gas is collected over water at 20°C. The volume is 265 mL and the total pressure 98.0 Kpa. What mass of dry CO_2 is present? P_{H_2O} at 20°C = 2.4 kPa

Ptotal = Pco, + PH,0 . PCO2 = Ptotal - PH20 = 98.0 - 2.4= 95.6 kPa $PV = \pi RT =) \pi cog = Pcog V$ $m_{co_{a}} = 95.6^{k_{a}} 0.265L$ 8.314 LkPa x 293 K = 0.0104 mal $Mass = 0.0104 \text{ mol} \times 44 \text{ gmol}^{-1}$ = 0.458g