Physical behavior of gases

Kinetic theory

This is useful in accounting for the known properties of gases, liquids and solids. The ideas underlying the kinetic theory, may be summarized as follows:

(a) Matter is made up of atoms/small particles/molecules
(b) The particles in a gas are in continuous rapid random motion in straight line in every direction and them colliding with each other and with the walls of the container. The pressure exerted by the gas on the container wall is due to bombardment by moving particles.
(c) The particles in a gas are separated from each other by distances which are large compared to the size of the particles (particles in a gas are very far apart and they are very small)
(d) Collision of gas particles are regarded as being perfectly elastic (such that there is no loss in kinetic energy)

Gas laws

The following laws were formulated from results of the experimental observation in the behavior of gases.

Gay Lussac's law of combining volumes

States that "when gases combine together at a given temperature and pressure, the do so in volumes which bear a simple ratio to each other and to the volume of the product if it is a gas

Example 1

40 cm^3 of oxygen was added to 30 cm^3 of carbon monoxide and the mixture ignited. What is the volume and composition of the resulting mixture? (All volumes measured at the same temperature and pressure).

$2CO (g) + O_2 (g) \rightarrow 2CO_2 (g)$

2 mole 1 mole 2 moles

2 vol. 1 vol. 2 vol. (Gay-Lussac's Law)

30 cm^3 15 cm^3 30 cm^3 (volume ratio)

The volume of CO_2 produced is the same as that of CO used up, i.e. 30 cm^3 of CO_2 are produced.

15 cm^3 of the 40 cm^3 of oxygen are used up in the reaction, i.e. 25 cm^3 of oxygen remain un reacted

30 cm^3 of carbon dioxide produced and 25cm^3 of un reacted oxygen give total volume is 55 cm^3.

Trial 1

10 cm^3 of a gaseous hydrocarbon were mixed with 90 cm^3 of oxygen and sparked. The resulting volume at r.t.p. was 70 cm^3, which reduced to 30 cm^3 on shaking with sodium hydroxide. Find the empirical formula of the hydrocarbon.

The physical behavior of gases is described by four gas laws which include

1. Boyles' law
2. Charles law
3. Daltons law of partial pressures
4. Graham's law of diffusion

Boyles' law

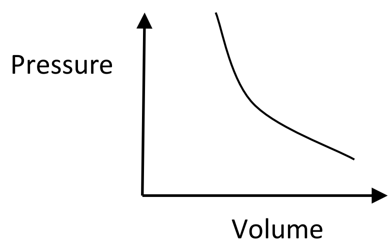
It state that the volume of a given mass of a gas is inversely proportional to its pressure at constant temperature

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

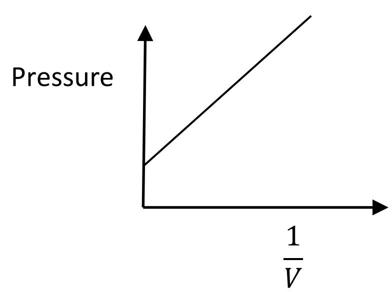
PV =K or PV = constant.

It follows that $P_1V_1 = P_2V_2$

A graph of pressure versus volume



A graph of pressure against inverse of volume gives a straight line



Charles' Law

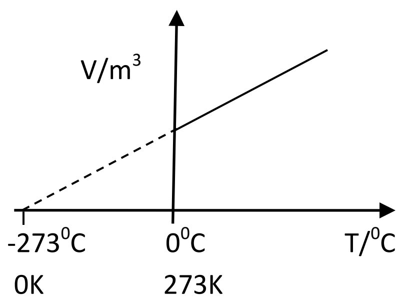
It states that the volume of a given mass of a gas is directly proportion to its temperature at constant pressure.

V$\propto T$

V =KT or $\frac{V}{T}$ = constant.

It follows that $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Graphically



NB: The units of temperature in all gas laws are Kelvin. However, units of pressure and volume vary, although must be the same in a given situation.

Pressure law

It is a modified version of Charles law. it states that pressure of a given mass of a gas is directly proportional to its temperature at constant volume.

P$\propto T$

P =KT or $\frac{P}{T}$ = constant.

It follows that $\frac{P_1}{T_1} = \frac{P_2}{T_2}$

The Ideal gas equation

Boyle's law and Charles' laws can be combined to give a single equation which represents the relationship between, volume, pressure and temperature of a given mass of a gas.

That is, $\frac{PV}{T}$= constant

When the quantity of the gas is 1 mole, the constant K is referred to as a molar gas constant, represented as R

For 1 mole of a gas PV = RT

For n moles of a gas

PV = nRT (the ideal gas equation)

Conditions at “standard temperature and pressure (s.t.p)

Temperature = 273K or 0^0C

Pressure = 760mmHg or 1 atmosphere or 101325 Pascal

Molar volume of a gas (volume occupied by 1 mole of a gas) = 22.4dm^3 or 22400cm^3

Conditions at “room temperature and pressure (r.t.p)

Temperature = 278K or 25^0C

Pressure = 760mmHg or 1 atmosphere or 101325 atmospheres

Molar volume of a gas (volume occupied by 1 mole of a gas) = 24dm^3 or 24000cm^3

NB. When using ideal gas equation PV =nRT, pressure, and volume must be changed to Pascal and m^3 while the unit of temperature must be in Kelvin.

Example 2

A certain mass of a gas occupies a volume of 24dm^3 at 18^0C and a pressure of 100.4kPa. Calculate the volume of a gas at s.t.p.

From $\frac{PV}{T}$ = constant

$$\frac{24\ x\ 100400}{(273+18)} = \frac{V\ x\ 101325}{(273)}$$

V = 22.31dm^3

Example 3

1.18g of a compound on vaporization occupied 300cm^3 at s.t.p.

(a) Calculate the relative molecular mass of P.

300cm^3 weigh 1.18g

22400cm^3 weigh $\frac{1.18\ x\ 22400}{300}$ =88

Trial 2

0.13g of P occupies 112 cm^3 at s.t.p

Calculate the formula mass of P

Trial 3

When 0.225g of T was vaporized at 127^0C and 760mmH, it occupied 119.11cm^3. (Molar volume at s.t.p is 22.4dm^3).

(i) calculate the molecular mass of T

Trial 4

When vaporized 0.1g of a compound A occupied 54.5cm^3 at 208^0C and 98.3kPa; determine the molecular formula of A

Deviation from Ideality

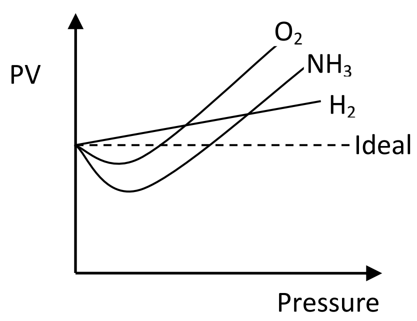
Ideal gases are those that obey ideal gas equation. These gases are not common and most gases tend to deviate from ideality. A gas is said to be ideal (perfect) if

(i) occupies a negligible volume
(ii) when there is no forces of attraction between its molecules.

Real gases

These do not obey the ideal gas law exactly because at high pressure and low temperature the volume occupied by gas molecules and the forces of attraction between the molecules is not negligible.

Plot of PV against pressure give a graph below:



NB. The higher the intermolecular forces the higher the deviation, e.g. in NH_3.

Correction of volume and Pressure for the real gas **to account for intermolecular forces and volume**

To account for molecular volume and intermolecular forces J.H. Vander Waal proposed that

(i) The volume of gas molecules reduces the actual volume of the container the molecules are left to move i.e. the volume of the container is not the volume in which molecules can move. The actual volume open to them is less than that of the container. For this reason Van der Waal wrote the volume of the gas as (V-nb) where n is the number of moles of a gas and b is the volume the volume that is no longer available to each mole.

(ii) Intermolecular attraction reduces the pressure the gas exerts. Therefore, if the real pressure is less than the ideal, this correction is added to the real pressure to give a value closer to ideal figure. Van der Waal wrote the corrected pressure as $(P+\frac{an^2}{V^2})$

Putting the volume and pressure in Ideal gas equation give Van der Waal equation

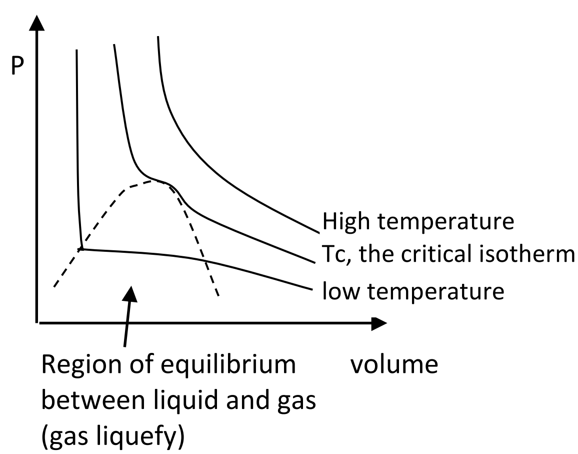
$(P+\frac{an^2}{V^2})(V-nb) = nRT$

For 1mole,

$(P+\frac{a}{V^2})(V-b) = RT$

Where a and b are constant.

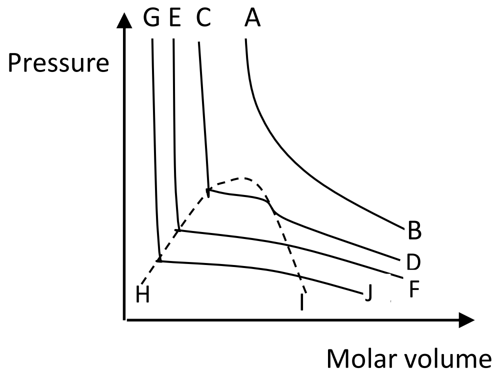
A plot of a graph of pressure versus volume at different temperatures give lines called isotherms shown below.



NB. The critical isotherm marks the border between gases and liquids. The temperature of critical isotherm is called critical temperature, T_c. Above; T_c a gas will not liquefied no matter how high the pressure. Each gas has its own critical temperature because the strength of the intermolecular forces in each gas are different. Below the critical temperature a gas will be liquefied when the pressure is high enough.

Trial 5

The curves below show a plot of pressure against molar volume at different temperatures of carbon dioxide



(a) State the curve which represent the highest temperature (1mark)

(b) What do the following lines represent

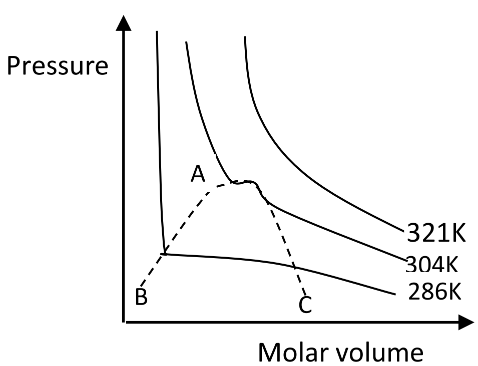
(i) HI (ii) GH

(c) Explain what is meant by the term critical temperature

(ii) Draw a sketch on the graph a line that represent isotherm of critical temperature.

Trial 6

(a) The diagram in figure 1 shows isotherms of a gas.



(i) What is the critical temperature

(ii) Which isotherm almost represent the behavior of an Ideal gas

(iii) What does the region ABC represent

(b) State one condition necessary for liquefying a gas.

Graham's Law of gaseous diffusion and effusion

Diffusion is the movement of particles from a region of high concentration to a region of low concentration.

Graham's Law of diffusion of gases state that the relative rates of diffusion of gases, under the same conditions, are inversely proportional to the square roots of their densities.

Comparing the rate of diffusion of gases A and B

$$\frac{rA}{rB} = \sqrt{\frac{\rho B}{\rho A}}$$

where r = rate of diffusion, ρ = density

or $\frac{rA}{rB} = \sqrt{\frac{MB}{MA}}$

where, M = molar mass and $\rho = \frac{M}{V_m}$,

V_m= molar volume

Graham' Law also applies to gaseous effusion. Effusion is the passage of a gas through a very small hole into a vacuum.

Example 4

50cm^3 of a gas A effuse through a tiny aperture in 146s and the same volume of carbon dioxide effuse under the same condition in 115s.Calculate the molar mass of A.

solution

$$\frac{Rate(CO_2)}{Rate\ A} = \frac{50/_{115}}{50/_{146}} = \sqrt{\frac{M_A}{M_{CO_2}}}$$

$$(1.27)^2 = \frac{M_A}{44}$$

the molar **mass of A, M_A =71**

(ii) A gaseous Alkane diffuses through a porous partition at a rate of 2.56cm3s-1. Helium diffuses through the same partition under the same conditions at a rate of 8.49cm3s-1. What is the molar mass of Alkane? What is the its molecular formula a

$$\frac{Rate\ alkane}{Rate\ Helium} = \sqrt{\frac{M_{Hellium}}{M_{alkane}}} = \sqrt{\frac{4}{M_{alkane}}}$$

The molar mass of alkane = 44

C_nH_{2n+2} = 44

n =3

∴ molecular formula of alkane = C_3H_8

Trial 7

(a) (i) State Graham's Law. (2marks)

(ii) Oxygen diffuses through a small hole 0.935 times faster than gas X. Calculate the relative molecular mass of X (4marks)

Trial 8

(a) A gaseous compound contains 44.4% carbon, 51.9% nitrogen and hydrogen. Determine empirical formula of X.

(b) 50ml of X diffuses through a porous plug in 25 second. Under similar conditions, the same volume of hydrogen gas diffuses in 6.8 seconds. Calculate

(i) the molecular mass of X

(ii) The molecular formula of X

Dalton's Law of partial Pressure

The total pressure exerted by a mixture of gases that do not react chemically is the sum of the pressure that the individual gases would exert if they were to occupy the same volume alone.

In symbols, for a mixture of gases A and B, the total pressure (P_t) is given by

$$P_t = P_A + P_B$$

The mole fraction of a gas A, in the mixture is given by

$$X_A = \frac{P_A}{P_t}$$

Example 5

4.0dm^3 of oxygen at a pressure of 400kPa and 1dm^3 of nitrogen at 200kP were introduced into a 2.00dm^3 vessel. What is the total pressure in the vessel?

Solution

When oxygen contracts from 4.00dm^3 to 2.00dm^3 the pressure increases to

$$400 \times \frac{4.0}{2.0} = 800\text{kPa}$$

The partial pressure of oxygen = 800kPa

When nitrogen expand from 1.0dm3 to 2.0dm3, the pressure decreases from 200kPa to

$$200 \times \frac{1.00}{2.00} = 100\text{kPa}$$

The partial pressure of nitrogen = 100kPa

Total pressure = $P_{(O_2)} + P_{(NH_3)}$

= 800+ 100 = 900kPa

∴ the total pressure = 900kPa.

Trial 9

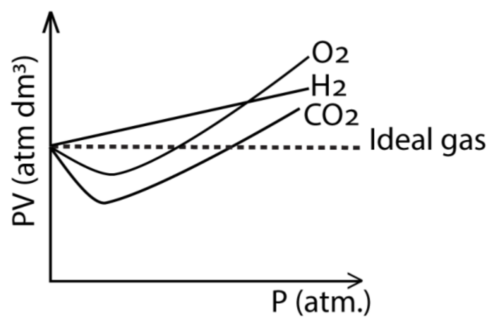
(a) State what is meant by the term an ideal gas. (01 mark)

(b) Explain how liquefaction of a gas can be affected by

(i) Pressure (2 ½ marks)

(ii) Temperature (2 ½ marks)

(c) The curve below shows deviation of some gases from ideal behaviours.



(i) State why hydrogen shows a small deviation from ideal behavior compared to other gases (1 ½ marks)

(ii) Compared to deviations of oxygen and carbon dioxide from ideal behavior. (2 ½ marks)

Solutions to trials in chapter 1

Trial 1

Volume of excess oxygen = 30cm^3. i.e. the volume that remained un absorbed by KOH

Volume of oxygen that reacted = 90-30 = 60cm^3

Volume of CO_2 = volume absorbed by KOH

= (70-30) = 40cm^3

Reaction equation

$$C_xH_y\ (g) + (x+\frac{y}{4})\ O_2 \rightarrow XCO2(g) + \frac{y}{2}H_2O\ (l)$$

volumes 10cm^3 60cm^3 40cm^3

Volume ratio 1 6 4

- ⇨ x= 4
- ⇨ $(x+\frac{y}{4})$ =6; y= 8
- ⇨ Empirical formula of Hydrocarbon = C_4H_8

Trial 3

Formula mass of P = 26

Trial 1.3 (2000/1/13b)

Volume at s.t.p

$$\frac{119\ x\ 760}{(273+127)} = \frac{760\ x\ V}{273}$$

V = 81.3 cm^3

Molecular mass of T

81.3cm^3 weighs 0.225g

∴ 22400cm^3 weigh $\frac{22400\ x\ 0.225}{81.3}$

= 62

∴ molecular mass of T = 62

Trial 4

Formula mass = 74.6

Trial 5

(a) AB

(b) HI: equilibrium between a gas and a liquid (change in volume at constant pressure)

(ii) GH: represents a line of change in pressure at constant volume

Trial 6

(a)(i) 304^0C

(ii) 321^0C

(iii) Equilibrium between liquid and vapour

(c) – Increasing temperature

- Decreasing temperature

Trial 7 :28

Trial 8:28

Trial 9

(a)(i) HCN

(ii) 27

(iii) HCN

Trial 10:

(a) An ideal gas is one that obeys ideal gas equation.

(b) (i) Increasing pressure reduces intermolecular distance which increase intermolecular forces leading liquefaction

(ii) when the temperature reduces, the molecules lose kinetic energy to an extent that they cannot overcome intermolecular forces

(c) (i) has low molecular mass and low intermolecular force

(iii) CO_2 deviates more than oxygen because has high molecular mass and stronger intermolecular force.