15 Gas Laws

Gas laws

A number of laws have been developed to account for and predict the changes in gases when the temperature, pressure or volume changes.

Boyle's law

Boyle's law was named after Robert Boyle (1627-1691), an Irish physicist, chemist, inventor and philosopher who described the relationship between the **pressure and volume** of a gas.

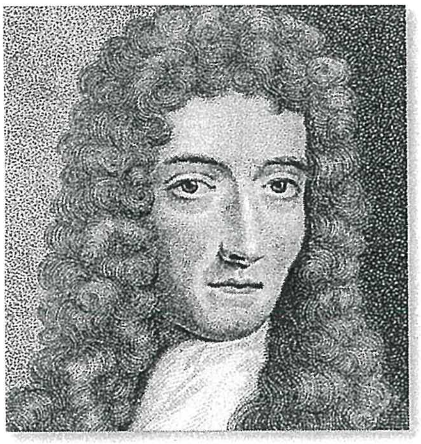


Figure 15.1 Robert Boyle.

Boyle's law states that, for a given mass of gas at a constant temperature, the pressure is inversely proportional to the volume. $P \propto 1/V$

If the pressure on a gas is doubled, then its volume will be halved.

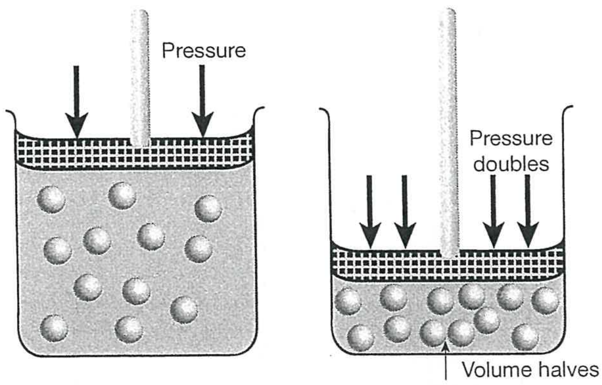


Figure 15.2 When pressure doubles, the volume halves.

An application of Boyle's law is that when deep-sea fish are brought to the surface they die. As they ascend, the pressure reduces, so the volume of gases in their bodies increases and can pop their swim bladders and other organs.

Charles' law

Charles' law was based on the work of a Frenchman, Jacques Charles (1746-1823), who was involved in the development of the first hydrogen balloons.

Figure 15.3 Jacques Charles.

Charles' law explains and predicts the relationship between **temperature and volume** of a gas. It describes how gases expand and contract when they are heated and cooled. For a given amount of gas, its volume is proportional to its temperature in kelvins. $V \propto T$

If the temperature of a gas is doubled, (measured in kelvins) then its volume will also double.

The gas equation

Boyle's and Charles' laws are combined into a relationship called the **gas equation** which says that PV/T is a constant relationship. This is written as follows.

$$PV/T = k$$

Applications of the gas laws

If you look around you will find many applications of the gas laws in everyday life, e.g. using a syringe and a football shrinking on a very cold day.

When you go up or down a mountain, or change altitude in a plane, the pressure on each side of your eardrum must be equalised to avoid pain. Chewing or swallowing can open up the tube to your middle ear (the Eustachian tube) and allow the air on each side of your eardrum to become the same pressure.

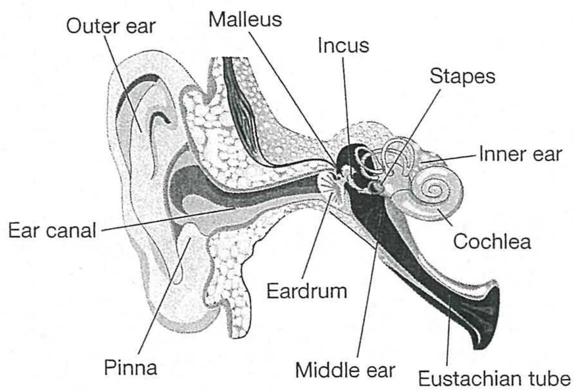


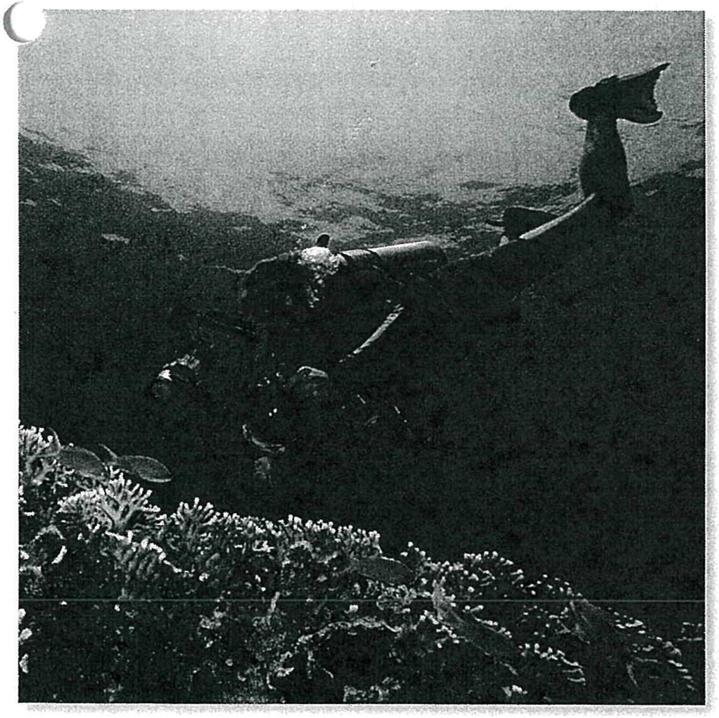
Figure 15.4 The ear.

If you have tried scuba diving you will be very aware of the effect of pressure on gases. Water is more dense than air, so it exerts more pressure than air. The deeper you go in water, the more water there is above you, so the greater the pressure.

This pressure will compress the air, in the diver's body, into a smaller volume. When the diver ascends again the air will expand. Scuba divers must breathe continuously and never hold their breath. If they hold their breath while ascending, the air in the lungs expands and causes damage. The air for a diver flows from a tank through a regulator. This makes sure that the diver receives air at the correct pressure to counteract the pressure of the surrounding water.

Guidelines and regulations for scuba divers are designed to avoid harm to the body due to these pressure changes. If these are not followed, the diver may develop **barotraumas**. These are pressure related injuries, e.g. a ruptured ear drum or lung tissue (pulmonary barotrauma) and other medical problems such as **decompression sickness**.

Decompression sickness occurs because gases such as nitrogen (that makes up approximately 80% of air) become more soluble when under pressure. At increased pressure, more atmospheric nitrogen dissolves in the blood, where it can act like an anaesthetic (nitrogen narcosis), reducing manual dexterity and cognitive ability and can even cause death. When the diver starts to rise to the surface, this must be a very slow process to allow the blood time to release all the nitrogen back into the lungs so it can be breathed out. If a diver ascends too rapidly, nitrogen comes out of solution in tiny blood vessels. Tiny gas bubbles form and these can block blood flow, and accumulate in tissues, causing extreme pain and even death.



Measuring temperature

The **temperature** of an object is defined as the average kinetic energy of its moving particles.

When an object is cooled, its temperature drops as its particles slow down. In theory, at some point, the particles should become so slow that they stop moving altogether and the volume of the gas should drop to zero. This temperature is called **absolute zero**, and its value is theorised to be −273°C. Nobody has been able to achieve a temperature of absolute zero, although some scientists have managed to get very close – down to less than a billionth of a kelvin.

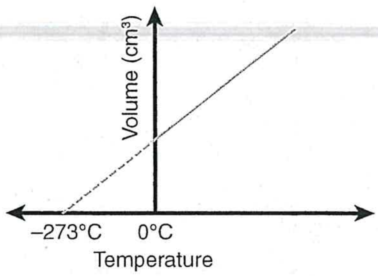


Figure 15.5 Absolute zero.

Kelvin temperature scale

The Celsius scale is the one used in Australia today to measure temperature. In some other parts of the world, such as the United States of America, the Fahhrenheit scale is still used.

There is a third temperature scale which is frequently used by scientists – the Kelvin scale. The Kelvin scale was designed so that 0 K is absolute zero and nothing can be colder than this.

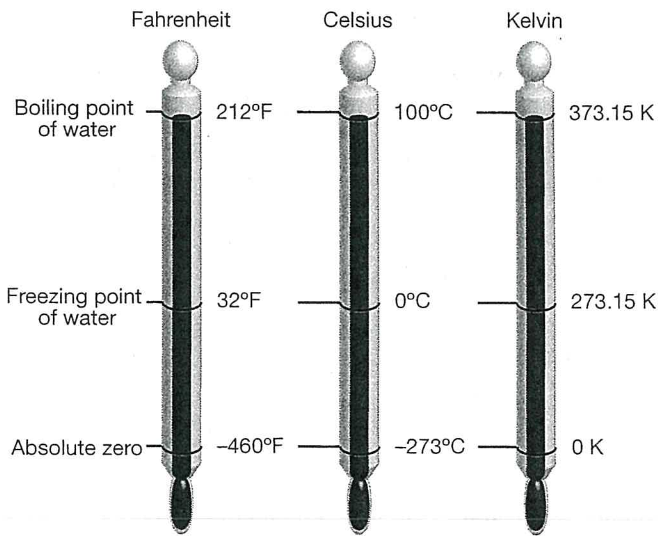
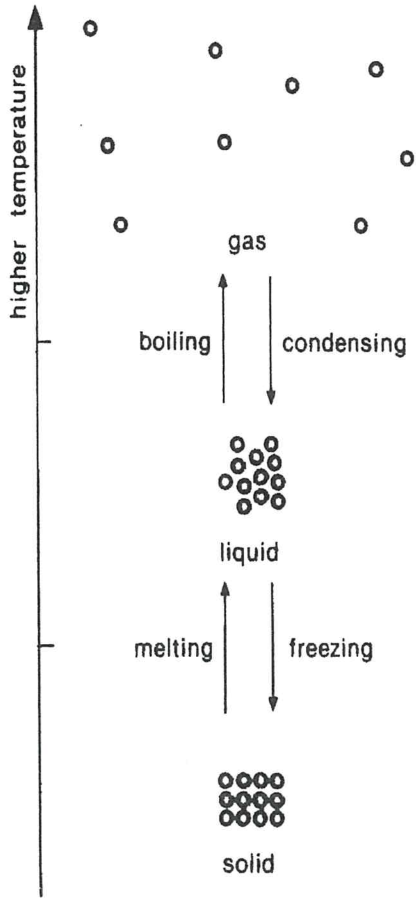


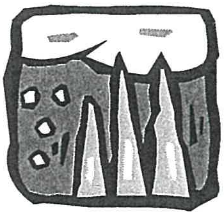
Figure 15.6 Three temperature scales.

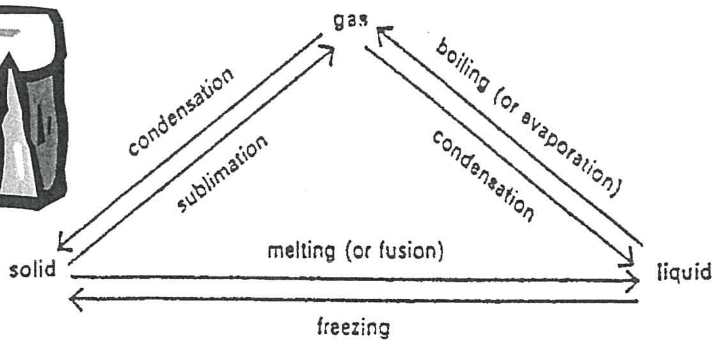
Kinetic Theory and Ideal Gas Behaviour

Solids, Liquids and Gases

- A **solid** has definite shape due to the forces that holed the particles together and generally on heating melts to form liquids. Some by-pass the liquid phase at atmospheric pressure and **sublime** (change from solid to gas). Eg: Iodine.
- Solids **cannot flow** as their particles are in **fixed positions**, held by the variety of forces that bond materials. They have a **fixed volume** as their particles cannot spread out and move freely they are only capable of **vibrating** about a fixed position. As solids are heated their particles do move slightly further apart as the solid **expands slightly** with heating but the volume is a fixed value for each temperature.
- A **liquid** has a definite volume, but no definite shape. On further heating, a liquid forms a gas.
- The particles in a liquid are more spread than those in the solid and may **move more freely** which allows them to **flow** and **take the shape of their container** but there are still forces of attraction that prevent the particles moving farther apart hence the volume is fixed and they will always flow to the lowest level in any container. Most liquids will **expand slightly** as they are heated but their volume is fixed for each value of temperature. The flow rate or **viscosity** of every liquid is different due to **differences in bonding forces** and different for every **temperature.** Generally a liquid will flow better as it is heated as the particles have more kinetic or movement energy.
- A **gas** has no definite shape or definite volume.
- The particles of a gas have little attractive forces holding them together; their kinetic energy is such that they have great freedom of motion. The freedom of motion allows the particles to **spread out in all directions** and to fill a container with an even distribution or concentration.
- Solids and liquids are said to **cohere** (cling together), whereas gases have no significant cohesion.







Energy and

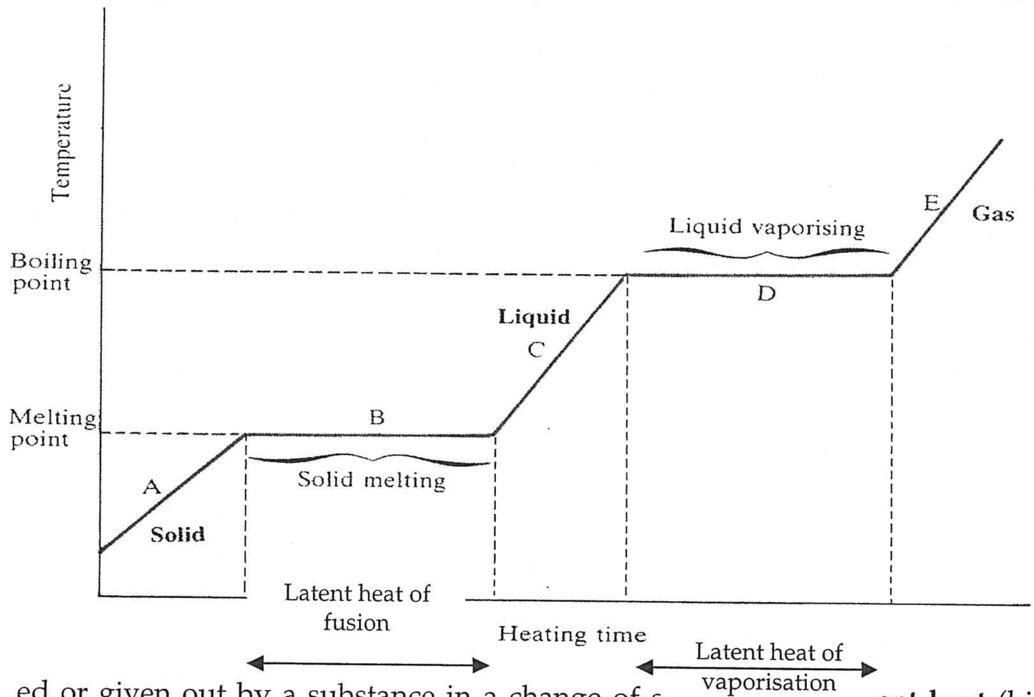
Changes of State

- Near **absolute zero** (-273°C) all substances are solids. If energy flows into a solid (heating) the atoms vibrate more energetically and therefore take up more space, so the solid expands.

- At its melting point, the thermal vibration overcomes the forces of attraction that hold the solid in rigid form, and the solid begins to **fuse** (melt). The melting point of a material depends on the strength of its bonding.

- Energy needs to be **taken in** to overcome the attractive forces that hold particles together in a solid or liquid. Processes that take in energy from the surroundings are said to be *ENDOTHERMIC*.

- Energy is **given out** in the reverse changes from gas to liquid and from liquid to solid. Processes that give out energy to the surroundings are termed *EXOTHERMIC*.



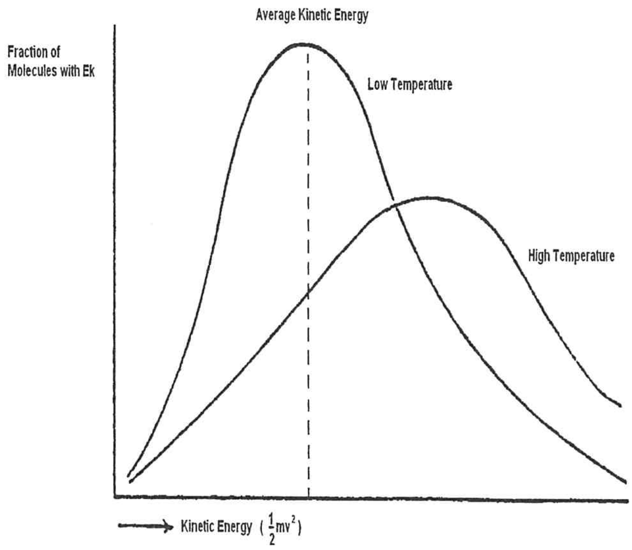
- The heat energy absorbed or given out by a substance in a change of s ent heat (hidden heat). Heat will be need to be **absorbed** when changing from **solid to liquid** and in turn **to gas** and heat will be given out in the reverse transitions. Energy that is absorbed is used to increase the **potential energy** or separation of the particles without necessarily changing their kinetic or movement energy. Energy given out has come from the loss of potential energy as particles condense back together and get closer as their phase changes.

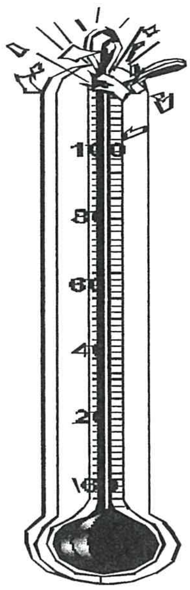
- **Latent Heat** refers to the input of heat **without a change of temperature**. As temperature only measures kinetic or movement energy it is clear to see why phase change is not accompanied by temperature rise.

- The heat for one mole is called the **Molar Heat Of Fusion** (melting) or the **Molar Heat Of Vaporisation**. Molar heats are dependent on the cohesive forces that hold particles together.

Molecules in Motion

- Our ideas about the behaviour of gases and liquids are based on the **Kinetic Theory Of Matter**, the theory that the molecules are in continual motion.
- The pressure of a gas in a container is the result of the ceaseless motion of the molecules and their continual battering against the wall of the container.
- The **greater the temperature** of the gas in a container the **faster** the particles are **moving**, and the more often and more forcefully they hit the walls, hence the pressure rises.
- All the molecules are not moving at the same speed within the gas but the **Average Kinetic Energy** of the molecules of all gases is the **same** at a particular temperature. (Temperature = Measure of the average kinetic energy of the molecules of a gas, liquid or solid.)





Temperature Scales

- In Chemistry, two scales of temperature are used, **Celsius** degrees for everyday work and **Kelvin** for more fundamental science work.
- On the Celsius scale, 0°C is the freezing point of water and 100°C is the boiling point of water at 101.3 kPa (1 atmosphere).
- One Kelvin is equal to one Celsius degree, but the Kelvin scale starts from **absolute zero** temperature, which is 0 K or -273°C. Thus 0°C is the same as 273 K.

$$\therefore \ T\ (K) = (t - 273)\ °C$$

S.T.P. = Standard Temperature and Pressure

T	= 0°C, 273 K
P	= 101.3 kPa = 1 atm= 760 mm of Hg

Ideal Gas and Behaviour

- In gases the molecules behave as though they are almost **completely independent** of each other. There is much more space between molecules and, for similar conditions of pressure, temperature, and volume, the space occupied by a given number of molecules of ANY gas is much the same.

- This property of gases was suggested by AVOGADRO in his HYPOTHESIS which is now so well accepted that it is known as AVOGADRO'S LAW :

  "Equal volumes of *ALL* gases, under the same conditions of temperature and pressure contain the *SAME* number of molecules."

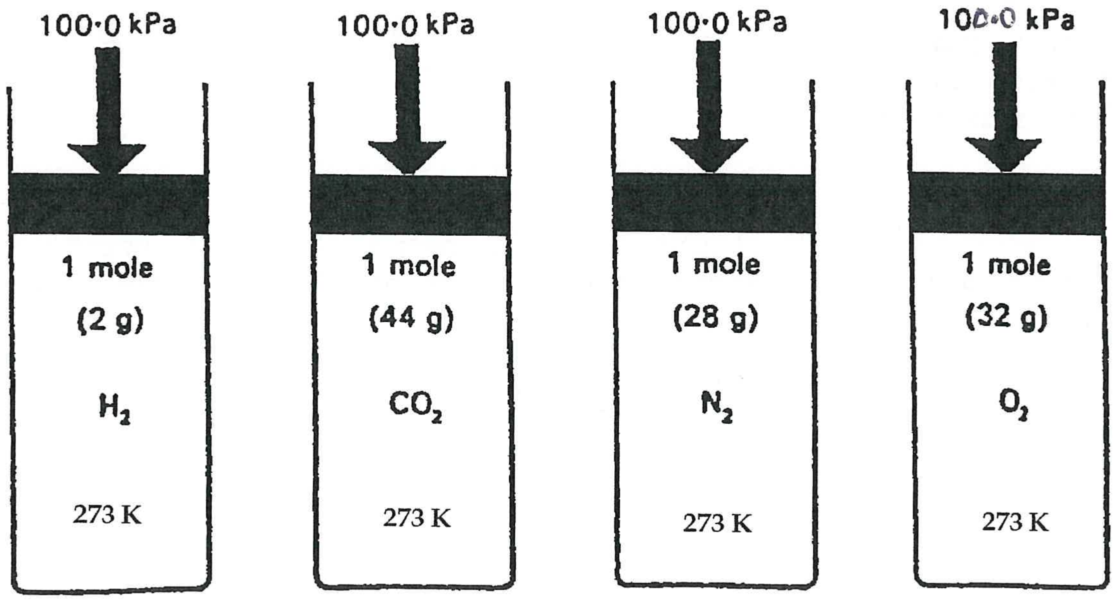
- A gas that closely approximates this total independence of particles is known as an **IDEAL GAS** and will behave accordingly. In reality as the temperature of a gas becomes lower its particles are not moving as fast and their intermolecular forces will become more effective and start to influence each other's motion leading to non-ideal behaviour.

- As the pressure of a gas increases the particles are also closer together and this can also lead to some non-ideal behaviour.

- For convenience in comparing measurements on gases, it is customary to make measurements under standard conditions, **S.T.P.** (Standard, Temperature and Pressure).

- S.T.P. is normal atmospheric pressure **100Kpa** (1 atm) and **273 K** (0^0C).

- Under S.T.P. conditions it is found that 1 mole of any gas occupies a volume of **22.7** LITRES and is known as its MOLAR VOLUME.



Pressure and Volume Relationship

- The relationship between the pressure and volume of a gas, called **BOYLE'S LAW** : "At constant temperature, the volume of a given mass of gas is **INVERSELY** proportional to its pressure."

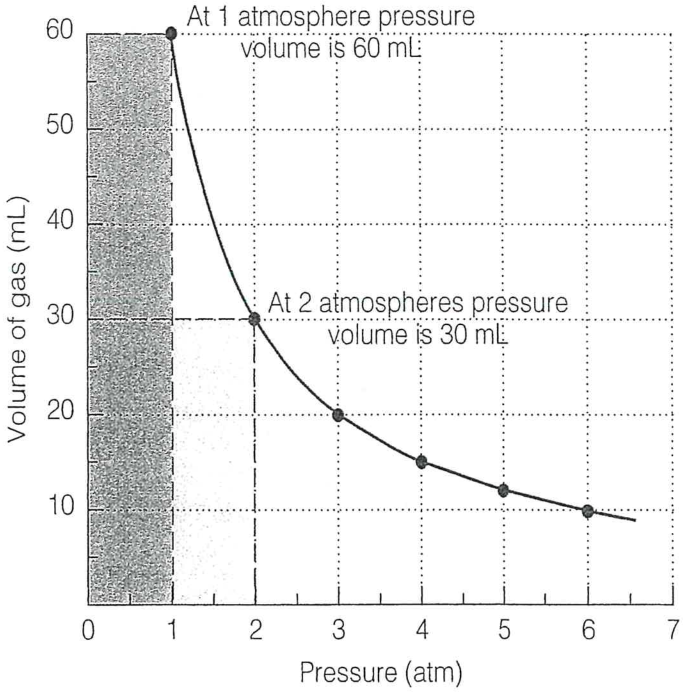
* PV = CONSTANT

$$P_1V_1 = P_2V_2$$

*$P_1 + V_1$ = INITIAL CONDITIONS
*$P_2 + V_2$ = NEW CONDITIONS

V ⇧ P ⇩

V ⇩ P ⇧



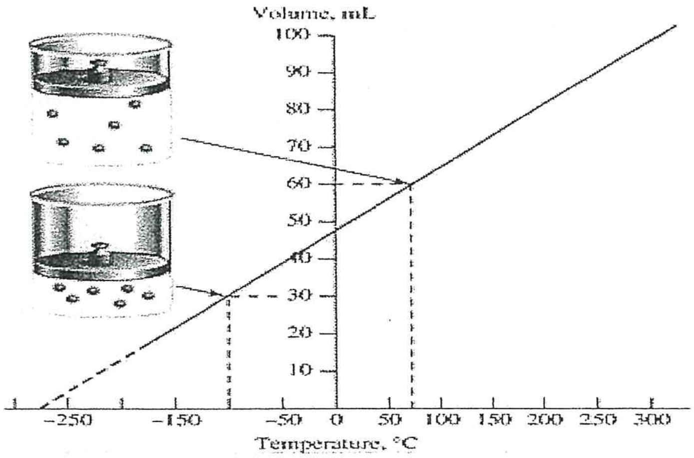
Temperature and Volume Relationship

- The relationship between pressure and volume called **CHARLES' LAW** : "At **constant pressure**, the volume of a given mass of gas is **DIRECTLY** proportional to its temperature."

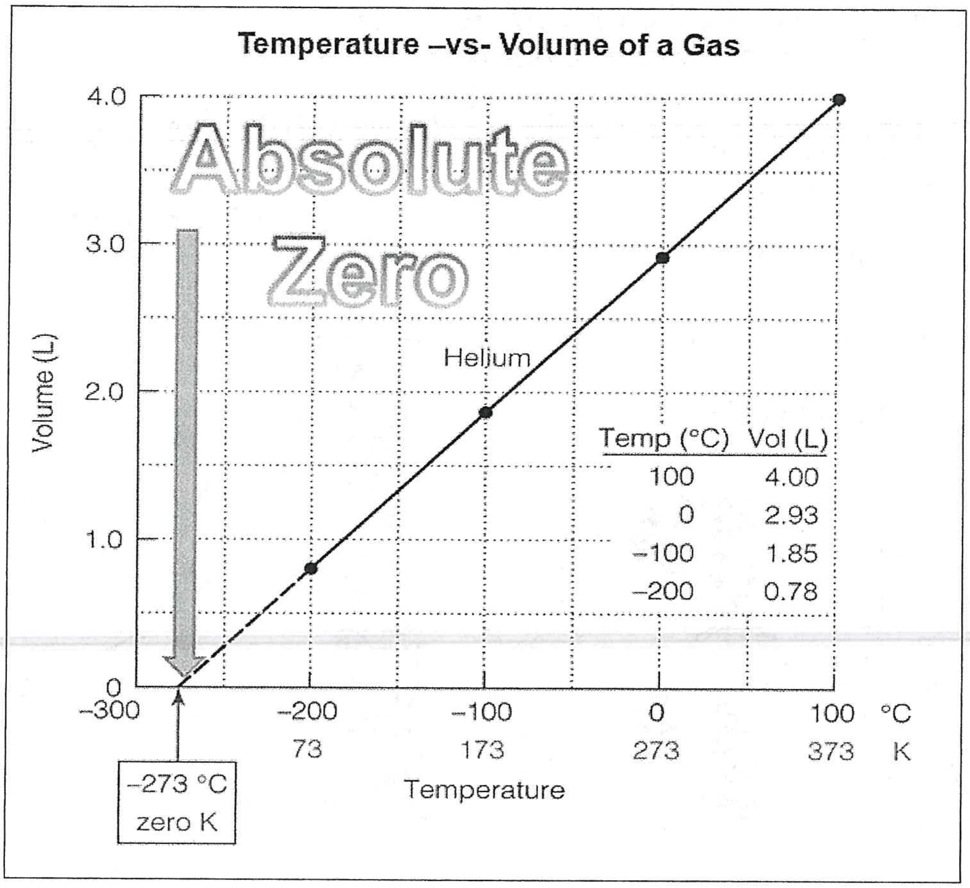
* V = kT or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

T ⇧ V ⇧

T ⇩ V ⇩

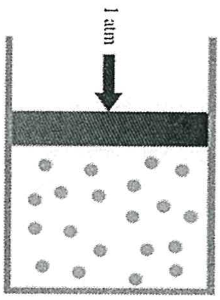


- Raising the temperature of a gas increases the **speed** and therefore the **average kinetic energy** of its molecules. Both the *frequency* and the *force* of their impacts on one unit of area of the container wall increases. If the volume is constant the rise in temperature causes the pressure to increase. If the pressure is not to change, then the volume must increase to compensate for the extra motion of the particles.



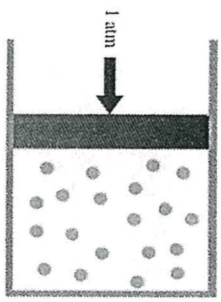
►The pressure and volume of a gas are also affected by the number of moles that are present.

► A new equation that takes this into account is known as the *IDEAL GAS EQUATION*:



$$\boxed{PV = nRT}$$

P	=	Pressure
V	=	Volume
n	=	Number of Moles
R	=	Universal Gas Constant
T	=	Temperature in Kelvin



►The value of "R" depends on the units chosen for P, V and T

* **R = 8.31 J.K^{-1} mol^{-1}** [V = m^3, T = K, P = Pa, n = moles]
L, kPa,

* It is best to stick to **one value** of "R" when doing all calculations even though there are, in reality, 3, different values depending on the units that you use for pressure and volume.

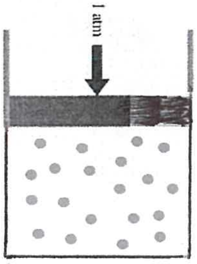
CONVERT ALL PRESSURES TO kPA AND USE VOLUME IN LITRES!

PV = nRT CALCULATIONS

THE IDEAL GAS EQUATION

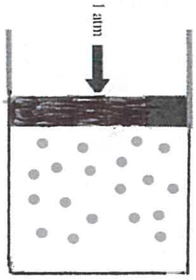
⇒ The pressure and volume of a gas are also affected by the number of moles that are present.

⇒ A new equation that takes this into account is known as the ideal gas equation and works for non STP conditions:



$$\boxed{PV = nRT}$$

P	=	Pressure
V	=	Volume
n	=	Number of Moles
R	=	Universal Gas Constant
T	=	Temperature in Kelvin



⇒ The value of "R" gas constant is on the data sheet.

* **R = 8.314 J K^{-1} mol^{-1}** [V = L, T = K, P = kPa, n = moles]

⇒ The equation applies to an IDEAL GAS, one in which the molecules have no volume. The equation is most accurate where the space between molecules is large (low pressure and high temperature). When the space is small the forces of attraction between molecules tend to cause non-ideal behaviour.

* As the gas constant is Kelvin, it is important to remember to convert degrees Celsius to Kelvin and this is simply done by adding 273.15 to the Degrees Celsius number. All pressures to kPascales and use volume in Litres.

CONVERSION:

For reference 1 Atm = 101.3 kPa

1 Litre = 1,000 cm^3 = 1,000 mLs = 1 dm^3

1 m^3 = 1,000,000 cm^3 = 1,000 L

TYPE example

What volume of hydrogen gas is generated when 6.5g of zinc metal is dissolved completely in dilute hydochloric acid at 298K and 100kPa pressure?

The reaction is: $Zn + 2H^+ \rightarrow Zn^{2+} + H_2$

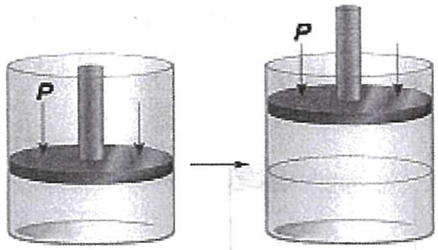
n = ?
m = 6.5g
M = 65 $gmol^{-1}$

$$n = \frac{m}{M} = \frac{6.5}{65}$$

$$\underline{n(Zn) = 0.1 \text{ mol}}$$

$$\mathbf{n(H_2) = n(Zn)}$$

$$\underline{n(H_2) = 0.1 \text{ mol}}$$



* Its volume under the stated conditions is given by:

P = 100 kPa
V = ?
n = 0.1 mole
R = 8.314 $J{\cdot}K^{-1}\ mol^{-1}$
T = 298 K

$$PV = nRT$$

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

$$\frac{0.1 \times 8.314 \times 298}{100}$$

$$\mathbf{V(H_2) = 2.48L}$$

What volume would 20 moles of ammonia occupy at 298 oC and 423 kPa?

P = 423kPa
V = ?L
n = 20 mole
R = 8.314 $J{\cdot}K^{-1}\ mol^{-1}$
T = 298+273.15

$$PV = nRT$$

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

$$= \frac{20 \times 8.314 \times 571.15}{423}$$

$$V(NH_3) = 224.52L$$

"ABSOLUTE ZERO" ► PV = nRT CALCULATIONS

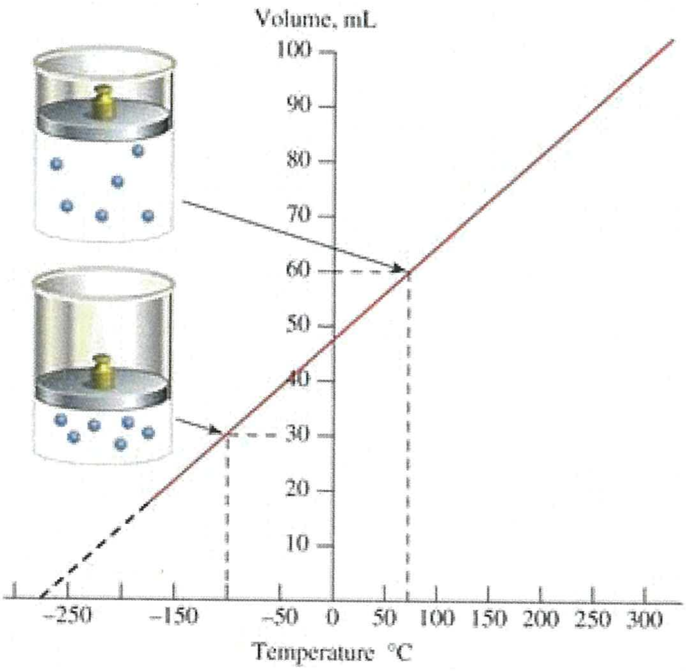
THE IDEAL GAS EQUATION

►An ideal gas is one whose particles exhibit NO cohesive force and move in random straight line motion.

• ***At HIGH temperatures and LOW pressures gases behave in an almost ideal fashion. When a gas cools the particles are moving slower and any cohesive intermolecular force will start to take effect. When the gas is under pressure the particles are close together and this will contribute to non-ideal behaviour as the cohesive forces again influence the motion of particles.***

• The theoretical point where all matter has cooled to the point that there is ***NO molecular motion*** is termed **ABSOLUTE ZERO**. This temperature is the starting point for the Kelvin temperature scale and is denoted as 0 K. Absolute zero has been determined to be equivalent to -273 ^{0} on the Celsius scale. To convert Celsius temperature to Kelvin you simply subtract 273 and the reverse when converting from Kelvin to Celsius.

► Absolute zero is determined experimentally by measuring the volume change of a fixed mole quantity or mass of gas in an elastic container with temperature. As the temperature of a gas decreases the molecular motion becomes slower, on average, which means that the gas particles collide less often with the walls of their container. The pressure will drop as will the volume that the elastic container can have given the external atmosphere pushing on it from the outside. There comes a point where theoretically the gas will have a "zero volume" as the particles have ceased molecular motion totally. The temperature at which this is the case is **absolute zero**. By the use of graphical "extrapolation" an estimate can be made of what this coldest of all temperatures will be.



- *If a MOLE of gas was used in this experiment the line would cut the "Y" axis at a value of 22.71 L at S.T.P.*