

GASES AND VAPOURS

Introduction

When a liquid evaporates, it becomes a vapour or a gas. Both of these are said to be in the “gaseous” state.

The **critical temperature** of a gas is the temperature above which the gas cannot be liquefied by pressure alone.

A gaseous substance is called a **vapour** below its critical temperature, and a **gas** above its critical temperature. For example, the critical temperature for CO₂ is 31.1°C. Below this temperature CO₂ is a “vapour” and can be liquefied by pressure. Above this temperature CO₂ is a gas and cannot be liquefied by pressure alone.

It is important that liquefied gases such as LPG, are not heated past their critical temperature (96.7°C for propane and 150°C for butane), since at this point all the liquid is converted to gas and the pressure will rise enormously.

Density of Vapours and Gases

The density of a gas or vapour compared with air is important to firefighters, since this determines whether gases will sink (into basements, wells, sewers etc). or rise (into attics and upper stories).

*Note: all gases, regardless of their density, will diffuse (mix) with air over a period of time, to give a **uniform** mixture of gases.*

The easiest way to compare the density with air is to calculate the molecular mass of the substance.

The molecular mass is obtained by adding the atomic masses of all the atoms that make up the molecule.

For example:

Methane CH₄ molecular mass = 12 + (4 x 1) = 16

(where atomic mass of C = 12. And atomic mass of H = 1).

Butane C₄H₁₀ molecular mass = (4 x 12) + (10 x 1) = 58

These molecular masses are compared with the average molecular mass of air, which is 30.

A gas with molecular mass greater than 30 is more dense than air, a gas with molecular mass less than 30 is less dense than air.

The “vapour densities” of gases are often listed in tables. These give the density of the gas compared to hydrogen gas. Again, to predict the behaviour of a gas in air, its vapour density should be compared to that of air.

Vapour Pressure

Liquids will vaporise to some degree at any temperature. The vapour pressure is a measure of the amount of vapour above a liquid. Vapour pressure increases with temperature. When the vapour pressure of a liquid equals atmospheric pressure, boiling occurs. The temperature at which this happens is called the “boiling point”. Thus the boiling point of a liquid can be raised or lowered by altering the external pressure surrounding the liquid.

Gases and Gas Laws

Gases consist of rapidly moving particles which move freely in the amount of space available to them. If this space is increased, the particles spread out to fill the available space – they have no fixed shape or volume. The particles of a gas are constantly colliding with the walls of its containing vessel. Gas pressure is a measure of the force per unit area of these impacts. The force per unit area (pressure) may be increased by:

- Adding more molecules to the container (more collisions).
- Increasing the temperature (particles collide with greater kinetic energy).

- Reducing the volume of the container (less surface area, but same number of collisions).

It can be seen that the behaviour of a gas is determined by four related factors:

- mass of gas (total number of particles)
- pressure,
- volume,
- temperature.

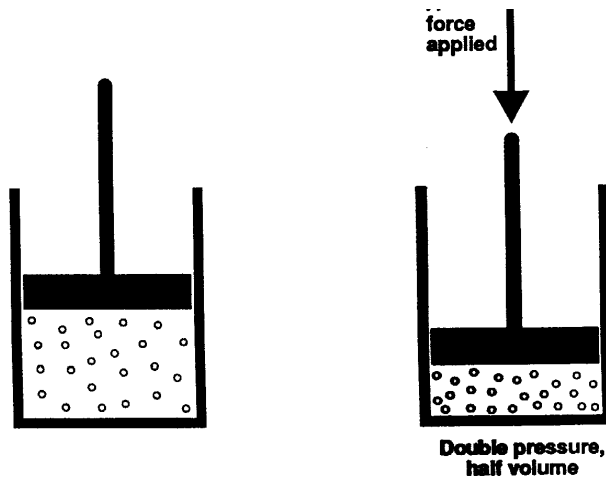
The gas laws look at the effect of changing two of these factors at a time.

Boyles Law

The volume of a gas is inversely proportional to its pressure (for a given mass at constant temperature).

For example:

A force is applied to a piston to reduce the volume of the cylinder by **half**. This results in **double** the pressure of gas in the cylinder.



Where V_1 and P_1 are the initial volume and pressure, and V_2 and P_2 are the final volume and pressure.

$$P_1 \cdot V_1 = P_2 \cdot V_2$$

Example

A gas cylinder contains five litres of air at 120 atmospheres pressure. What volume will it occupy if allowed to expand to one atmosphere pressure?

$$\begin{aligned}
 P_1 = 120 \text{ atmos, } V_1 = 5 \text{ litres, } P_2 = 1 \text{ atmos, } V_2 = ? \\
 P_1 V_1 &= P_2 V_2 \\
 120 \times 5 &= 1 \times V_2 \\
 V_2 &= 600 \text{ litres}
 \end{aligned}$$

Charles Law

The volume of a gas is directly proportional to its Kelvin temperature (for a given mass at constant pressure).

For example, a balloon will expand on heating, or the gases in an internal combustion engine expand on heating moving the piston in the cylinder.

Where V_1 and T_1 are the initial volume and Kelvin temperature, and V_2 and T_2 are the final volume and Kelvin temperature:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Example

What volume would 100 litres of gas at 20°C occupy if its temperature was raised to 300°C (at constant pressure)?

$$V_1 = 100 \text{ litres}$$

$$T_1 = 20 + 273 = 293\text{K}$$

$$V_2 = ?$$

$$T_2 = 300 + 273 = 573\text{K}$$

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

$$\frac{100}{293} = \frac{V_2}{573}$$

$$V_2 = \frac{100 \times 573}{293}$$

$$V_2 = 195.6 \text{ litres}$$

Gay-Lussacs Law

The pressure of a gas is directly proportional to Kelvin temperature (for a given mass at constant volume).

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

This law may be used to calculate the pressure of gas in a cylinder at a given temperature. Pressures will rise in a gas cylinder as the temperature is increased.

Example

A gas cylinder is charged to a pressure of 15180 kPa at 12°C. It is rupture tested to 28 000 kPa. At what temperature will it be liable to explode?

$$P_1 = 15180 \text{ kPa}$$

$$T_1 = 12 + 273 = 285\text{K}$$

$$P_2 = 28000 \text{ kPa}$$

$$T_2 = ?\text{K}$$

$$\frac{15180}{285} = \frac{28000}{T_2}$$

$$T_2 = \frac{285 \times 28000}{15180}$$

$$= 525.7\text{K}$$

$$= 525.7 - 273$$

$$T_2 = 252.7^\circ\text{C}$$

Note: Liquefied gases in cylinders do not obey the gas laws since any change in temperature, pressure or volume will result in either liquefaction of gas or evaporation of liquid, that is; the pressure in a cylinder of liquefied gas remains constant, since more liquid will evaporate if gas is drawn off.

A true gas (above its critical temperature) will obey the gas laws and the pressure will decrease as gas is drawn off.

Summary

- A gaseous substance is a gas above its critical temperature.
- A gaseous substance is a vapour below its critical temperature.
- The critical temperature for a gas is the temperature above which it cannot be liquefied by pressure alone.
- Gases or vapours with a molecular mass above 30 are more dense than air.
- Gases or vapours with a molecular mass below 30 are less dense than air.
- The “vapour density” of a gas or vapour, is the density compared with hydrogen gas.
- The “vapour pressure” is a measure of the amount of vapour above a liquid.
- **Vapour pressure increases with temperature.**

- At boiling point, the vapour pressure equals the external atmospheric pressure.
- Gas pressure is a measure of the force per unit area due to collisions of the gas particles with the walls of the container.
- The behaviour of a gas is determined by the mass of gas, the pressure, the volume and the temperature.
- Boyles Law – the volume of a gas is inversely proportional to its pressure (for constant mass, and temperature).

$$P_1 V_1 = P_2 V_2$$

- Charles Law – the volume of a gas is directly proportional to its Kelvin temperature (for constant mass and pressure).

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

- Gay-Lussac's Law – the pressure of a gas is directly proportional to its Kelvin temperature (for constant mass and volume).

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

- Combined gas law:

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

- Liquefied gases do not obey the gas laws.