Physics of gases

Gary Thomas
Stephen Stamatakis

Abstract

This article explores the physical principles of gases that are relevant to the specialities of anaesthesia and critical care medicine. Points covered include molecular theory, the gas laws, vaporization, pressure, solubility and gas flow. Definitions, examples and explanations are given in areas of particular importance.

Keywords diffusion; gases; gas flow; gas laws; phases; physics; pressure; solubility; states of matter

There are four fundamental states of matter: gases, liquids, solids and plasmas. The forces of attraction between the atoms and molecules of a compound will determine its state and physicochemical properties.

- **Solids** have a definite volume and shape. Particles are packed closely together and are incompressible. There is enough thermal energy to produce vibration of particles within the tight lattice.
- **Liquids** have volume but no definite shape. Particles are less tightly packed, and, although there is free movement within the volume, they are incompressible.
- **Gases** have no finite shape or volume. Particles are free to move rapidly in a state of random motion. They are compressible and shaped completely by the space in which they are held. **Vapours** exist as a gas phase in equilibrium with identical liquid or solid matter below its boiling point.
- **Plasmas** are the most prevalent state of matter in the universe, formed by heating atoms to very high temperatures to form ions.

Phases

A phase is a distinct, homogeneous state with no visible boundary separating it into parts. Conversion between states is called 'phase transition'. Phase diagrams or graphs are used to show an equilibrium that exists between thermodynamically distinct physical forms. Water can co-exist as three phases, solid, liquid and gas, at the triple point. The triple point of water is used to define the basic Système International (SI) unit of thermodynamic temperature, Kelvin or K, which is the fraction 1/273.15 K. The symbol T is used to express temperature $T_0 = 273.15$ K, the ice point.

Pressure

Pressure is exerted by a gas as a result of the continual collision of its molecules with the containing wall. It is the force (F) in newtons (N) exerted perpendicularly against an area (m^2); thus, 1 N acting over 1 m^2 produces a pressure of 1 pascal (Pa)

$$\text{Pressure} = \text{N/m}^2 = \text{kg/ms}^2 = \text{Pa}$$

Standard atmospheric pressure (absolute) is measured using a barometer and is defined at sea level and 273 K (0°C). This can be expressed as a number of different units: 1 atmosphere, 760 mm Hg, 101.3 kPa, 1.013 bar or 14.7 lb/in^2.

Pressure measured relative to atmospheric is known as gauge pressure. The absolute pressure is the total pressure exerted on a system, which is equal to the gauge.

Standard temperature and pressure

Standard temperature and pressure (STP) are the conditions used throughout science to enable comparisons between sets of data. These equate to 1 atmosphere pressure and 0° Celsius (273.15 K).

Partial pressure

In a mixture of ideal gases, each gas exerts a partial pressure. This is the pressure that it would have exerted had it occupied that volume alone. The total pressure of a mixture of gases is equal to the sum of the partial pressures of all of the constituent gases (Dalton's law). Mathematically, this can be represented as:

$$P_{\text{Total}} = P_1 + P_2 + \ldots + P_n$$

Air contains 78% N_2, 20.95% O_2, 0.93% argon, 0.038% CO_2 and between 1% and 5% water vapour. The partial pressure of oxygen in dry air is 0.209 multiplied by 101.3 kPa, or 21.17 kPa.

Saturated vapour pressure (SVP)

This is defined as the pressure exerted by a vapour in equilibrium with liquid of the same substance. A liquid boils at the temperature when its vapour pressure equals atmospheric pressure. The energy required to change a gram of liquid to a gas (phase transition) is called the latent heat of vaporization or enthalpy. This energy breaks down the intermolecular attractive forces.

The pressure gauge reading of a nitrous oxide (N_2O) cylinder reflects the SVP at that temperature. The relationship between pressure, volume and the temperature of a gas can be represented and displayed as a series of isotherms (Figure 1).

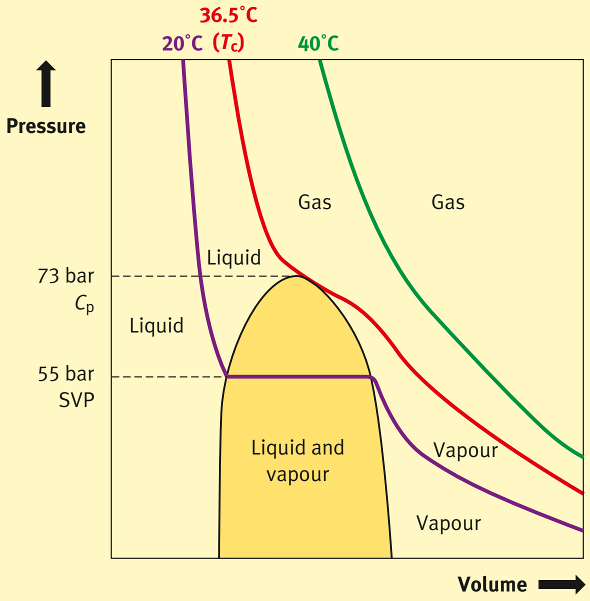
Critical temperature (T_c)

The critical temperature is the temperature at or above which a gas cannot be liquefied, no matter how much pressure is applied. For example, the critical temperature of nitrous oxide (N_2O) is 36.5°C, and oxygen (O_2) is −118°C.

***Gary Thomas**, MB, BCh (Wales), FRCA, is a Consultant Anaesthetist at Bro Morgannwg NHS Trust, Wales. He graduated from the Welsh National School of Medicine in 1981, and trained in anaesthesia in Wales, London (UK) and Melbourne (Australia). His main interests are anaesthesia for vascular surgery and teaching. He is currently a final FRCA examiner. Conflicts of interest: none declared.*

***Stephen Stamatakis**, MB, BCh, is a Specialist Trainee 3 in Anaesthesia currently on the Welsh rotation. He graduated from the University of Wales College of Medicine, UK. Conflicts of interest: none declared.*

Relationship between pressure and temperature



The relationship between pressure and temperature is shown at three different temperatures of nitrous oxide (isotherms). C_t represents the critical temperature isotherm (36.5°C) and C_p represents the critical pressure at that temperature. The saturated vapour pressure of nitrous oxide at room temperature is 55 bar. SVP, saturated vapour pressure

Figure 1

Critical pressure (P_c)

This is the pressure required to liquefy a substance at its critical temperature. The critical pressure of N_2O is 73 bar.

Pseudocritical temperature (overpressure effect)

The pseudocritical temperature is observed with Entonox, a 50:50 mixture of N_2O and O_2. Oxygen alters the critical temperature of N_2O (Poynting effect) to the pseudocritical temperature −6°C. Gas cylinders containing Entonox at a pressure of 137 bar should not be stored below this temperature.

Ideal gases

The ideal gas is one in which the gas molecules:

- are identical
- move in a straight line before colliding with each other or the sides of their container
- have collisions that are perfectly elastic with no loss of kinetic energy
- possess negligible volume
- move randomly
- have no attractive or repulsive forces between them.

The gas laws

These apply to ideal gases within closed systems.

Boyle's law

Boyle's law (Figure 2a) states that, for a fixed mass of gas at constant temperature, the pressure (P) and volume (V) are inversely proportional ($P \times V = k$, where k is a constant).

Pulmonary functional residual capacity (FRC) can be calculated using Boyle's law and data acquired from a body plethysmograph using the equation:

$$P_1 \times V_1 = P_2 \times V_2$$

Charles's law

Charles's law (Figure 2b) states that the volume occupied by a fixed mass of gas at constant pressure is directly proportional to its absolute temperature ($V/T = k$).

Third gas law

This states (Figure 2c) that the pressure of a fixed mass of gas at constant volume is directly proportional to its absolute temperature ($P/T = k$).

Universal gas equation

The state of a fixed mass of gas is determined by its pressure, volume and temperature according to the universal gas equation ($PV = nRT$, where n is the amount of substance (mol) and R is the universal gas constant).

Avogadro's hypothesis

This states that equal volumes of gases at the same temperature and pressure contain the same number of molecules (6.023×10^{23}, Avogadro's number). It is the number of molecules of 1 mol of any gas present in a volume of 22.4 litres at STP. For example, 1 mol of O_2 (molecular weight 32) at STP contains 6.023×10^{23} molecules, occupies 22.4 litres and weighs 32 g.

Adiabatic process

An adiabatic process is one in which there is no loss or gain of heat. When a compressed gas expands, external work occurs at the expense of internal energy from the gas molecule. The fall in temperature that occurs (Joule–Thompson effect) is the principle behind the working of a cryoprobe. Conversely, compressing a gas increases the pressure and internal energy of a system with heat production and the risk of fires and explosions.

Gas volumes

Gas volumes obtained in laboratory experiments can be expressed in a number of ways:

- ATPS (ambient temperature, pressure and saturated with water vapour)
- STPD (standard temperature, pressure and dry)
- BTPS (body temperature, pressure and saturated with water vapour).

Diffusion and solubility

Graham's law describes the relationship between molar mass and rate of diffusion and effusion of a gas:

- Diffusion is the rate at which two gases mix.
- Effusion is the process of gas molecules escaping through tiny holes in their container.