Physics of Gases

Alexander P L Goodwin

In whichever state a substance exists, it is made up of the same atoms or molecules. The difference between a solid and liquid, and a liquid and gas is the strength of the forces attracting the molecules and atoms to each other. These interparticular forces in a solid hold the molecules together in a lattice. When a solid is heated the kinetic energy of the individual molecules increases, leading to an increase in their vibrational energy, causing them to move apart and the substance to melt. When the molecules in a liquid acquire further kinetic energy, they break away from the interparticular forces and the substance becomes a gas. The kinetic theory accounts for all three states of matter by assuming that above absolute zero, molecules are in continual motion – they have kinetic energy. The molecules exert forces of attraction on each other and so possess potential energy. At small separations the forces must be repulsive, because if the attractive force were to exist down to zero separations, matter would collapse in on itself.

When a liquid and gas coexist, as occurs in a cylinder of *Entonox* (a 50:50 mixture of oxygen and nitrous oxide), molecules enter the liquid as well as leaving it. When the rate at which molecules are leaving and entering the liquid phase becomes equal, the vapour above the liquid is said to be saturated. When a liquid reaches its boiling point all the molecules are transferring into vapour. The terms gas and vapour are synonymous but vapour relates to the gaseous phase at a temperature and pressure close to that at which the gas would condense into a liquid.

In a gas, the atoms collide with each other and their surroundings, and thus a force is exerted. The force exerted over an area equals pressure.

Absolute and relative pressure

Atmospheric pressure at the surface of the earth is due to the gravitational force exerted on air molecules. The pressure depends on air density, which depends on altitude and weather conditions. (Absolute pressure = gauge pressure + atmospheric pressure.)

Zero gauge pressure is equal to atmospheric pressure. If this were not so, empty cylinders would collapse in on themselves. Anaesthetists tend to ignore absolute pressure and record gauge pressures such as ventilator and gas-cylinder pressures, arterial blood pressure and venous pressures.

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The gas laws

Boyle's law (Figure 1) – at a constant temperature, the volume of a mass of gas is inversely proportional to the pressure (PV = Constant).

Charles' law (Figure 2) – at a constant pressure the volume of a gas is directly proportional to its absolute temperature (V/T = Constant). Volume is proportional to temperature. Gases expand when they are heated and become less dense, thus hot air rises.

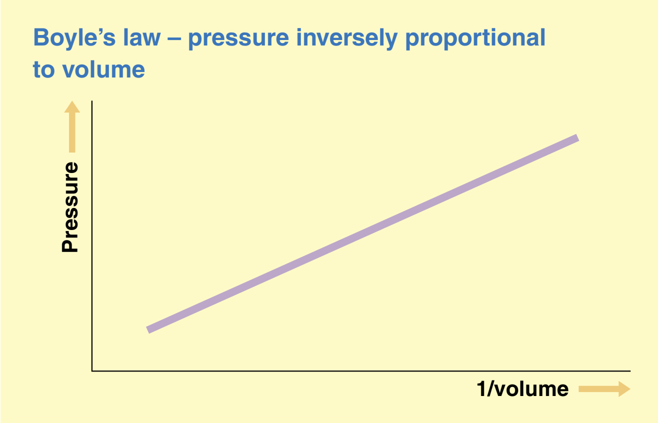
The third perfect gas law (Figure 3) – at constant volume the absolute pressure varies directly with absolute temperature (P/T = Constant). Pressure is proportional to temperature. An example is the hydrogen thermometer. A constant volume of hydrogen when heated produces a change in pressure.

Standard temperature and pressure (STP) – it is important to specify the temperature and pressure at which the measurement of a volume is made. Standard temperature and pressure is defined as 273.15°K (0°C) and 101.325 kPa (760 mm Hg). The practical effects of temperature change include:

- change in vaporization rates of volatile agents
- increased temperature reduces the density of fluids
- increased temperature reduces the viscosity of liquids
- increased temperature increases the viscosity of gases (increased molecular activity).

Adiabatic changes in a gas

Applying the three gas laws, for a change to occur in the state of a gas, heat energy is either added or taken away from the gas. If



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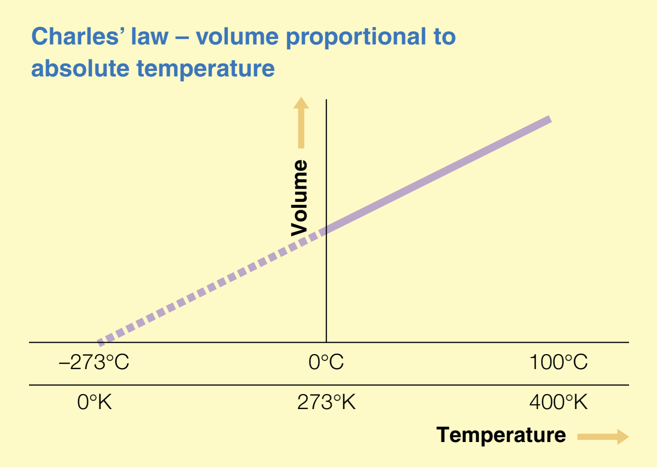

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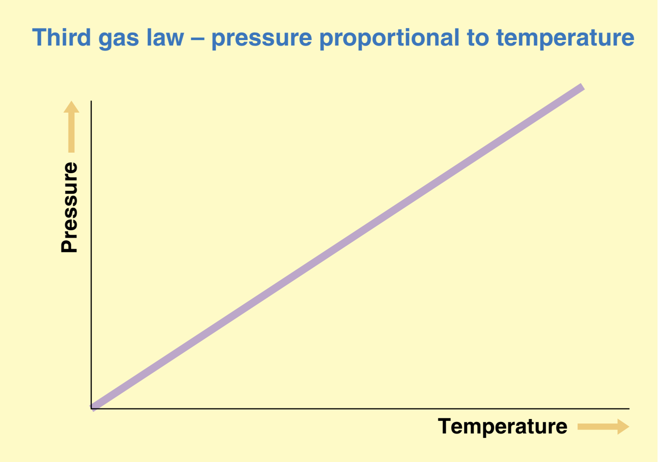

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the state of a gas is altered without a change in heat energy it is said to undergo adiabatic change. If a compressed gas expands adiabatically, cooling occurs as seen in the cryoprobe. Energy is required as the gas expands to overcome van der Waal's forces. No heat exchange occurs between the gas and its surroundings because the source of energy is from the molecule's own kinetic energy, thus the gas cools as it expands. Conversely, if a gas is rapidly compressed its temperature rises (the Joule–Kelvin principle). When a cylinder connected to an anaesthetic machine is turned on too quickly the temperature rises in gauges and pipelines and in the presence of oil or grease may lead to a fire or explosion.

Dalton's law of partial pressures

In a mixture of gases, the pressure each gas exerts is the same as that which it would exert if it alone occupied the container.

Avogadro's hypothesis

Equal volumes of gases at the same temperature and pressure contain equal numbers of molecules. As the mass of molecules present in a fixed volume varies depending on the individual gas, the number of molecules present is expressed as a mole. A mole is the quantity of a substance containing the same number of particles as there are atoms in 0.012 kg of carbon 12. The number of particles is 6.022×10^{23}. One mole of gas at standard temperature and pressure is contained in a volume of 22.4 litres.

A clinical application would be to calculate the volume of nitrous oxide in a cylinder. A nitrous oxide cylinder contains 2.2 kg of nitrous oxide. The molecular weight of nitrous oxide is 44. One mole is 44 g. At STP we know that 44 g occupies 22.4 litres, therefore 2200 g occupies $22.4 \times 2200/44 = 1120$ litres.

The universal gas equation (the ideal gas law)

If the perfect gas laws and Avogadro's hypothesis are combined $PV/T = \text{Constant}$. For one mole of gas, PV/T equals the universal gas constant R. The equation can be rearranged to $PV = nRT$ (the universal gas equation) where n equals the number of moles present. The practical application of this law is the use of pressure gauges to assess the contents of a cylinder. The volume, temperature and gas constant remain the same and pressure is therefore proportional to n, the number of moles.

Temperature scales – the triple point of water

Different thermometers use particular thermometric properties. For example, a mercury-in-glass thermometer uses the change in length of a column of mercury confined to a capillary tube of uniform bore; a platinum thermometer uses the increase in resistance with increasing temperature.

To establish a temperature scale it is necessary to make use of fixed points: a fixed point is the single temperature at which it can be confidently expected that a particular physical event always takes place.

The ice point is the temperature at which pure ice can exist in equilibrium with water at standard atmospheric pressure.

The steam point is the temperature at which pure water is in equilibrium with its vapour at standard atmospheric pressure.

The triple point of water is that unique temperature at which pure ice, pure water and pure water vapour can exist together at equilibrium. The triple point is particularly useful, because there is only one pressure at which all three phases (solid, liquid and gas) can be in equilibrium with each other.

Critical temperature

The critical temperature is the temperature above which a gas cannot be liquefied however much pressure is applied (for CO_2 Tc = 31.1°C).

Critical pressure is the minimum pressure that causes liquefaction of a gas at its critical temperature (for CO_2 pc = 73 atm).

Specific critical volume is the volume occupied by 1 kg of a gas at its critical temperature and pressure.

Therefore one can define a gas as a substance in the gaseous phase above its critical temperature. Vapour is the term applied to a substance in the gaseous phase below its critical temperature. Thus, simply increasing the pressure can liquefy a vapour, but not a gas. The relationship between pressure, volume and temperature is displayed as a family of isotherms (Figure 4).

Oxygen, nitrogen and hydrogen are traditionally called permanent gases, because it was thought they could not be liquefied. This is because each of these gases has a critical temperature below room temperature (oxygen –118°C, nitrogen –146°C, hydrogen – 240°C).

Poynting effect (overpressure effect) – the critical temperature and pressure of a gas may be affected when it is mixed with another gas. For example, in a cylinder of *Entonox*, the new critical temperature of nitrous oxide (known as the pseudo-critical temperature) changes to –6°C. Therefore, precautions regarding the cooling of cylinders should be taken into account.

Density and viscosity of gases – fluid flow

Liquids and gases are fluids. The density of a substance is the mass per unit volume ($kg/m^3 = \rho$) (silver, 10500; water, 1000; oxygen, 1.43; air, 1.29; helium, 0.18; hydrogen, 0.09).

If a fluid is viscous it offers resistance to the motion of any solid through it or to its own motion past a solid body. In both these circumstances (except where the fluid is a gas of very low density) the layer of fluid in immediate contact with the solid is stationary. The motion causes adjacent layers of fluid to move past each other. An internal friction offers resistance to the motion of one layer of fluid past another, and this is the origin of viscous force. In liquids, the internal friction is due to intermolecular forces of attraction. In gases, the friction is due to the interchange of molecules between different layers. This results in the average speed of molecules in adjacent layers changing.

If the flow of a fluid is steady (also known as streamline flow, orderly flow and uniform flow) all the fluid particles that pass any given point, follow the same path at the same speed – they have the same velocity. The path followed by a particle of the fluid is called the line of flow of the particle.

In steady flow, streamlines coincide with the lines of flow. A streamline is a curve whose tangent at any point is along the direction of the velocity of the fluid particle at that point. Streamlines never cross.

Laminar flow is a special case of steady flow in which the velocities of all the particles on any given streamline are the same, though the particles of different streamlines may move at different speeds (Figure 5).

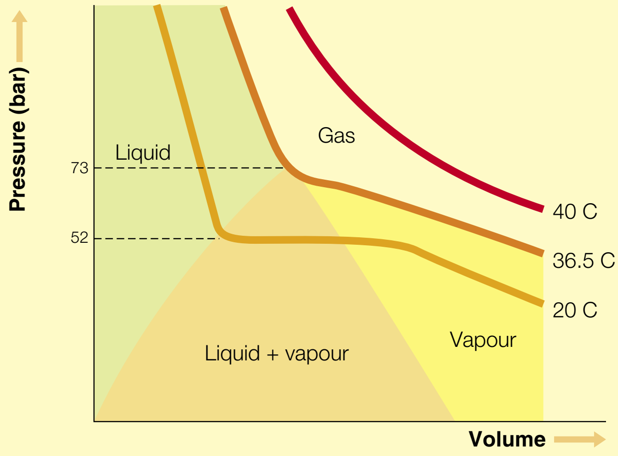
Poiseuille's formula – when considering a viscous liquid undergoing steady flow through a pipe of circular cross-section, the velocity varies from a maximum at the centre of the tube to zero at the walls. Poiseuille originally described the relationship between flow and the properties of the fluid as:

$$Q = \frac{kr^4p}{\eta l} \quad \text{mathematical analysis shows that } k = \frac{\pi}{8} \text{ therefore}$$

$$Q = \frac{\pi r^4 p}{8\eta l}$$

where: Q is flow; η is viscosity; p/l is the pressure gradient; r is the radius of the tube. The formula applies only to Newtonian fluids (in which viscosity is constant) undergoing steady flow.

Isotherms of nitrous oxide



The isotherm at 40 C is above the critical temperature of nitrous oxide (36.5 C) and threfore obeys Boyle's law. As the volume decreases the pressure rises. At the critical temperature 36.5 C there is a critical pressure at which nitrous oxide becomes a liquid. Liquids are relatively incompressible and therefore a decrease in volume leads to a dramatic rise in pressure. At 20 C as the nitrous oxide is compressed some of it liquefies at a pressure of 52 bar (saturated vapour pressure of nitrous oxide). Further reduction in volume causes more vapour to condense with no change in pressure. When all the vapour is condensed to liquid a rapid rise in pressure is seen with further decrease in volume.

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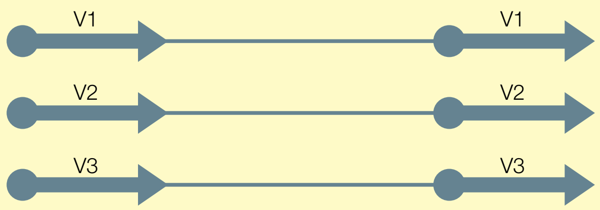
Streamlines of a liquid in laminar flow



Velocities V1, V2 and V3 are not necessarily equal

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This applies to all gases and some fluids. Water is a Newtonian fluid; blood is non-Newtonian.

The flow profile of a viscous fluid flowing in a pipe of circular diameter is conical (Figure 6). The fluid flows in a series of concentric cylinders. All the particles within an individual cylinder flow at the same speed. The speed of the cylinder adjacent to the wall of the pipe is zero, and the speeds increase towards the centre.

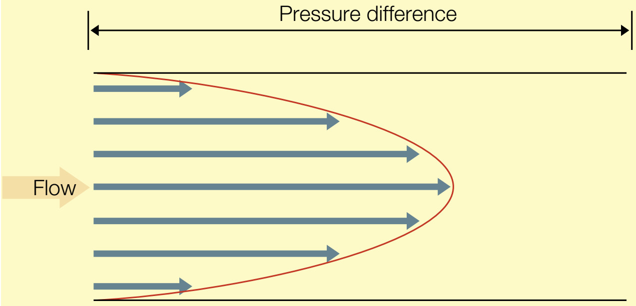
Turbulent flow is also known as disorderly flow. In this type of flow the speed and direction of the fluid particles passing any point varies with time. When laminar flow encounters a constriction, fluid velocity increases and turbulent flow occurs (Figure 7). At turbulent flows the resistance is higher than for a similar laminar flow. The variation in fluid velocity is different in turbulent flow and flow is no longer directly proportional to pressure. The property of a fluid that dictates the degree of turbulent flow is density.

The ability to predict the onset of turbulent flow is aided by calculating the Reynolds number (Re). If the Reynolds number exceeds 2000, then turbulent flow is likely to occur. When flow is turbulent there is a change in viscous forces and an increased pressure change along a tube:

$$Re = \frac{v \rho d}{\eta}$$

where: v is linear velocity of fluid; ρ is density; d is the diameter

Velocity profile at laminar flow



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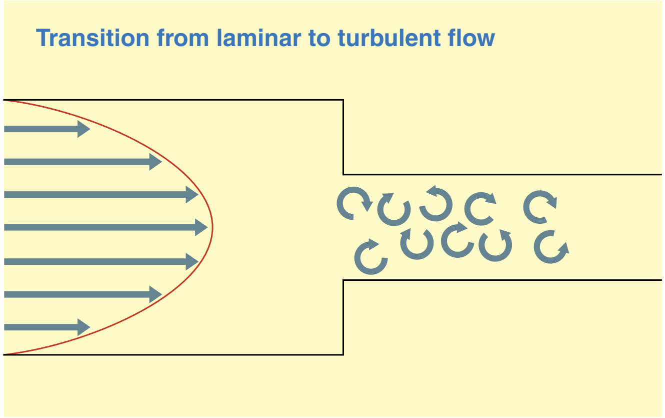
Transition from laminar to turbulent flow

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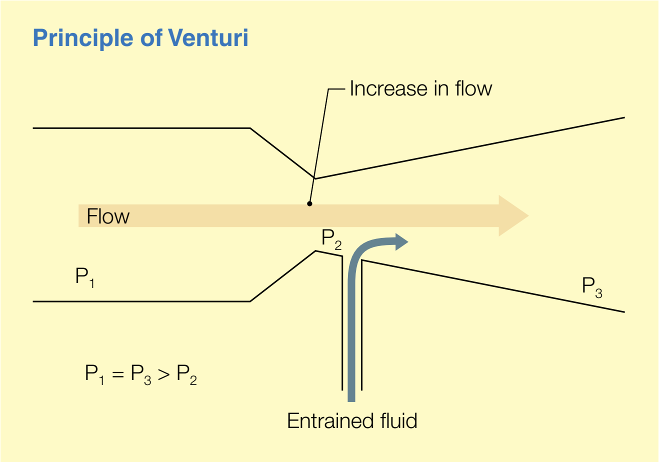
Principle of Venturi

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of the tube; η is viscosity. The effect of density (mass/volume) on flow is evident in the use of helium and oxygen to promote flow in patients with upper airway obstruction. The density of air is 1.29, of oxygen 1.43 and helium 0.18 at STP.

The Bernoulli equation states that for an incompressible, non-viscous fluid undergoing steady flow, the pressure plus the kinetic energy per unit volume plus the potential energy per unit volume is constant at all points on a streamline:

$$P + \tfrac{1}{2}v^2 + \rho g h = \text{Constant}$$

where: P is the pressure within the fluid; v is the velocity of the fluid; ρ is the density of the fluid; g is acceleration due to gravity; h is the height of the fluid above some arbitrary reference line. It follows from Bernoulli's equation that whenever a flowing fluid speeds up, there is a corresponding decrease in the pressure and/or the potential energy of the fluid and an increase in kinetic energy. If the flow is horizontal the whole of the velocity increase is accounted for by a decrease in pressure as the total energy must remain constant. A Venturi tube has a constriction in which the bore gradually decreases and then increases (Figure 8). At the narrowest point the pressure drops as the flow of a fluid through the constriction increases. In medicine, applications include oxygen masks and nebulizers. Everyday applications include an aerofoil, spinning ball, filter pumps, Bunsen burners and carburettors.

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