

Gases and Vapours

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BASIC CONCEPTS

All matter exists in one of three states or phases - solid, liquid or gas. When a gas co-exists in equilibrium with its corresponding liquid, the gas is termed a *vapour*. In this situation, molecules are moving from the liquid to the gas phase at the same rate as they are moving from the gas back to the liquid phase. Many liquids, including water, have vapour associated with them at room temperature. As the ambient temperature increases, the number of molecules that exist as a vapour rather than a liquid increases until a new equilibrium is reached. Eventually, at a certain temperature (the boiling point), the entirety of the liquid moves into the gas phase - at this point it is no longer termed a vapour. At temperatures above the boiling point it is still possible to partially convert a gas back to a liquid by increasing the pressure of the gas. But this becomes increasingly difficult, and eventually impossible, to achieve as the temperature of the gas increases. The *critical temperature* is defined as the temperature above which a substance cannot exist in a liquid state.

A related but slightly different concept is the critical pressure. The *critical pressure* is the pressure exerted by a gas at the critical temperature. It can also be thought of as the pressure required to liquefy a gas at the critical temperature. These values are equivalent.

Vapour pressure is the pressure exerted by a vapour when it is in equilibrium with its associated liquid. In anaesthesia the term *saturated vapour pressure* (SVP) is also frequently used, although the term 'saturation' incorrectly implies that vapour is 'dissolved' in the atmosphere. A vapour is a gas and, under normal circumstances, gases are infinitely soluble with respect to one another, i.e. there is no solute or solvent, gases simply mix with one another as if the other gas was not present. This may seem a minor point, but understanding that a vapour is a gas and therefore behaves like one is central to understanding what happens to vapours under different circumstances.

Vapour pressures increase non-linearly with increasing temperature and the *boiling point* of a liquid is defined as the temperature at which the vapour pressure is equal to atmospheric pressure (see Figure 1). Vapour pressures are not affected by atmospheric pressure,

for example the vapour pressure of water at any given temperature is the same at sea level as it would be at the top of Mount Everest. However, boiling points do decrease with increasing altitude and this is simply because the atmospheric pressure decreases, which means that the vapour pressure becomes equal to it at a lower temperature. The *standard boiling point* is the temperature at which the vapour pressure of a liquid equals 1bar (100kPa).

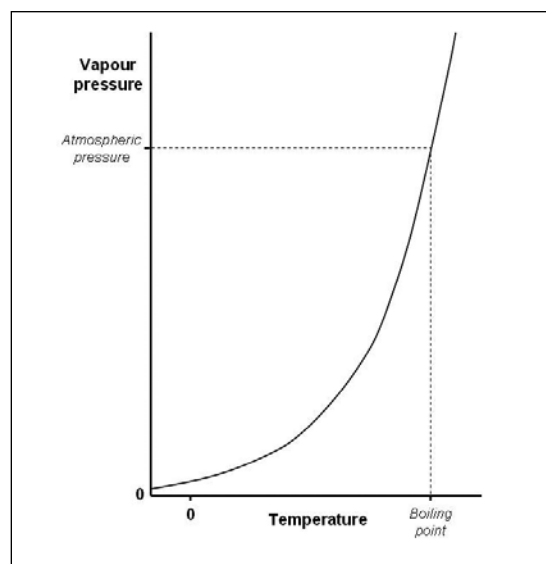


Figure 1. Graph of temperature versus vapour pressure for a typical anaesthetic agent

Similarly, vapour pressures are also strictly independent of the ambient air temperature. In practice however, the ambient air temperature will affect the temperature of the liquid and thus the vapour pressure. This makes sense if you remember that a vapour is just a gas in equilibrium with its associated liquid and therefore follows Dalton's Law (see below) - it behaves independently from the other gases with which it is mixing.

The fact that boiling point decreases with decreasing ambient pressure can be used to test the efficiency of clinical suction devices. The amount by which a suction device can lower the boiling point of a liquid in a sealed container will be related to the drop in pressure the device produces. Substances which have

Summary

The use of inhaled anaesthetic agents was pioneered during the 19th Century and had a huge impact on the development of medicine and surgery. Although a range of different inhaled anaesthetic agents are available in different settings around the world, the principles involved remain unchanged and a good understanding of the properties of commonly used gases and vapours is essential for the safe conduct of anaesthesia.

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low boiling points have high saturated vapour pressures and are often termed 'volatile liquids'.

The final basic concept is the *triple point*. The triple point of a substance is the temperature and pressure at which it exists simultaneously, in thermodynamic equilibrium, as a solid, liquid and gas. For water this occurs at 273.16 K (0.01°C) and 611.7Pa. This is notable only because the triple point of water is the set-point used to define the Kelvin temperature scale, the SI unit of temperature.

THE GAS LAWS

Pressure, volume and temperature

When describing the behaviour of gases the properties of temperature, pressure and volume are related in a consistent manner, which makes it possible to formulate three 'gas laws'. They can be concisely expressed as follows in Figure 2.

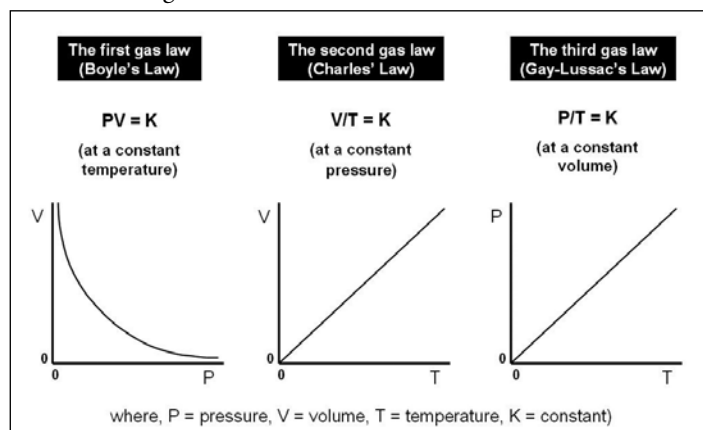


Figure 2. The Gas Laws

Note that a common pitfall is to state that pressure is proportional to volume - in fact it is *inversely* proportional and when plotted produces a hyperbola as can be seen in Figure 2. In the second and third gas laws the variables are proportional to one another and produce a straight line when plotted.

The combined gas law is derived from all three gas laws and is as follows:

$$\frac{PV}{T} = K$$

or alternatively expressed:

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

Providing two of the variables are known, and the third can be assumed to remain constant, the gas laws can be used to calculate changes in one of the known variables when the other alters. For example, if the initial pressure and volume of an oxygen cylinder is 137bar and 1.2litres respectively (and temperature is assumed to remain constant), then the volume of the oxygen at a pressure of 1bar can be calculated. Assuming room pressure is also roughly 1bar then this approximates to the volume of oxygen available to the patient, before the cylinder empties. Furthermore, if the rate of oxygen use is known, then the time remaining for use of that oxygen cylinder can be calculated.

When making these calculations it does not matter which units are used for pressure or volume providing consistency is maintained (see Table 1). Temperature, however, requires a scale that starts at absolute zero, therefore Kelvin must be used.

Unit	Equivalent value
Atmospheres (atm)	1
Bar (bar)	1
Kilopascals (kPa)	101.3
Millimetres of mercury (mmHg)	760
Torr (mmHg 0°C)	760
Centimetres of water (cmH ₂ O)	1033.2
Pounds per square inch (PSI)	14.7

Table 1. Units of pressure. The SI unit of pressure is the pascal (Pa) which is a force of 1Newton per metre squared (N.m²). In practice, however, many different units of pressure are used in anaesthesia. The table above shows equivalent values for all the units of pressure that you are likely to encounter. Gas cylinder pressures are commonly expressed in bar

Avagadro's law

Avagadro's law states that at a constant temperature and pressure a given volume of any gas will contain the same number of molecules. The converse of this is that at a given temperature and pressure, 1 mole of any gas will occupy the same volume (22.4litres at 1 atmosphere and 0°C). Both Avagadro's law and the combined gas law are used to derive the ideal gas law:

$$PV = nRT$$

where, n = number of moles of gas, R = universal gas constant (8.314)

The ideal gas law is of relevance when considering the behavior of nitrous oxide in cylinders (see below).

Henry's Law

Henry's law states that at a constant temperature, the amount of a given gas dissolved in a given liquid is directly proportional to the partial pressure of the gas in contact with the liquid. For any given combination of different gases, liquids and temperatures there is a unique solubility coefficient or constant. Temperature affects the solubility of gases such that at higher temperatures a gas will be less soluble in a liquid (given a constant pressure). Henry's law is of importance when considering the way inhaled anesthetic vapours and gases behave physiologically (see below).

Dalton's Law

Dalton's law states that the pressure of a gas in a mixture of gases is independent of the pressure of the other gases in the mixture. Alternatively, Dalton's law can be expressed as 'the total pressure of a mixture of gases is equal to the sum of the partial pressures of the constituent gases'. Dalton's law can be explained by the fact that in a mixture of gases the molecules are so far apart from one another, that each gas behaves as though the others were not present. As mentioned above, Dalton's Law explains why vapour pressure is not affected by ambient pressure.

Imperfections in the gas laws

In reality, the gas laws described above are not always true and they refer to a theoretical 'ideal' gas. However in reality, these concepts generally hold true and, as long as correction factors used, the gas laws have practical applications. Note that the gas laws are only accurate when applied to gases above their critical temperature.

APPLICATION TO ANAESTHETIC GASES AND VAPOURS

Anaesthetic gases are supplied in cylinders and via pipelines from the central gas supply in each hospital. Each cylinder is painted a colour according to the gas it contains. Conventions regarding cylinder colour coding vary from country to country and the colour of a cylinder should never be relied on as the sole guide to the contents of the cylinder - always read the label. In Europe, standard EN 1089-3¹ is currently being implemented, the aim being to increase conformity and hopefully safety between different countries. According to EN 1089-3 the colour of the *cylinder shoulder* is the only part used to identify the gas and the colour of the body may vary between manufacturers. Cylinder shoulder colours are given in Table 2. Carbon dioxide is currently rarely used in anaesthesia, but cylinders containing carbon dioxide may still be encountered in medical settings and in examinations. Cylinders should be tested by the manufacturers at regular intervals, with pressure testing on all cylinders and tensile, flattening, bend and impact testing on a sample of one cylinder in every hundred.

Gas	Cylinder colour
Oxygen	White shoulder
Nitrous Oxide	Blue shoulder
Carbon Dioxide	Grey shoulder
Helium	Brown shoulder
Medical Air	Black and white checked shoulder
Heliox	Brown and white checked shoulder
Entonox	Blue and white checked shoulder

Table 2. European cylinder colour coding

Individual medical gases are described in more detail below.

Oxygen

Oxygen has a boiling point of -183°C and a critical temperature of -119°C , which means that at room temperature it is above its critical temperature and always exists as a gas, obeying the gas laws. The importance of this is that Boyle's law can be applied to oxygen, which means that the reading on the pressure gauge of an oxygen cylinder gives a true indication of the volume remaining. However, inaccuracies may arise in this respect if large alterations in ambient temperature occur.

Oxygen manufacture and storage

Oxygen can be stored under pressure in cylinders made of molybdenum steel. Cylinders may be combined to form a bank attached to a manifold. The advantages of combining large cylinders into a bank include a reduction in cost, transportation and constant

change of exhausted cylinders. Oxygen cylinders come in various sizes, the most common used in operating theatres being sizes D and E. The filling pressures and volumes of various oxygen cylinders are given in Table 3.

O ₂ cylinder	Water capacity (l)	Filling pressure (bar)	O ₂ volume at 1bar (l)
C	1.20	137	170
D	2.32	137	340
E	4.68	137	680
F	9.43	137	1360

Table 3. Oxygen (O₂) cylinders. The values given are for full cylinders at 15°C as per BOC Medical data.² These may vary between manufacturers and with fluctuations in ambient temperature and pressure

As described above, oxygen has to be cooled to below -118°C to change to a liquid. When the gas changes form to a liquid, it occupies a much smaller volume. Therefore when a small volume of liquid oxygen is warmed it will make a very large volume of oxygen gas. As an alternative to cylinders, oxygen can be stored as a liquid in a specialised container. In the liquid form, a very large quantity of oxygen can be transported or stored in a low volume, although there are problems in keeping the liquid cold as explained below.

Vacuum insulated evaporator (VIE)

A VIE is a container designed to store liquid oxygen. It has to be designed to allow the liquid oxygen inside to remain very cold. It consists of two layers, where the outer carbon steel shell is separated by a vacuum from an inner stainless steel shell, which contains the oxygen (Figure 3). The oxygen temperature inside is about -170°C and the container is pressurised to 10.5bar. Gaseous oxygen above the liquid is passed through the superheater to raise the temperature to ambient (outside) levels. It then flows into the hospital pipeline system giving a continuous supply of piped oxygen to outlets on the wards and in theatre. Heat is always able to get into the container and provides the energy to evaporate the liquid oxygen, changing it into oxygen gas which is continuously drawn off into the pipeline system. This escape of gas into the pipeline system prevents the pressure inside the container from rising. If the pressure rises too high (above 17bar), oxygen is allowed to escape via a safety valve into the atmosphere.

In contrast, if the pressure inside the container falls because of heavy demand in the hospital for oxygen, liquid oxygen can be withdrawn, passed through the evaporator and returned to the VIE in the gaseous form to restore the pressure. The amount of oxygen available in the container is estimated by weighing the container with an in-built device. The VIE system is used in large hospitals which have a pipeline system, and where liquid oxygen can be supplied by road tanker.

Nitrous Oxide

The boiling point of nitrous oxide is -88.6°C and the critical temperature is $+36^{\circ}\text{C}$. Since in most countries nitrous oxide is below its critical temperature at room temperature, it exists as a vapour in equilibrium with its liquid phase and is dependent upon the pressure applied to it. Therefore, under normal circumstances, the gas laws do not apply to nitrous oxide.

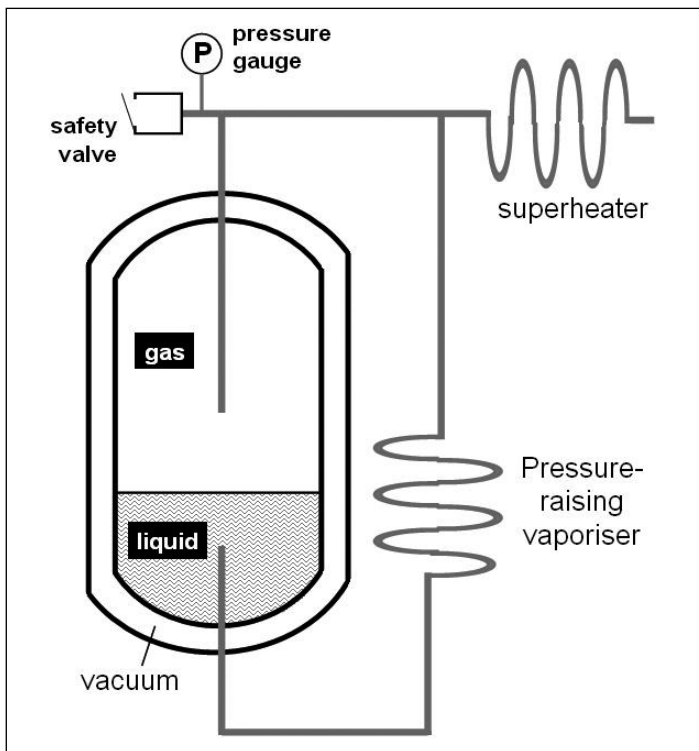


Figure 3. Vacuum insulated evaporator. Note the oxygen gas above the liquid oxygen. The gas enters the pipeline system at the top and if large quantities of oxygen are needed, liquid is drawn off at the bottom of the VIE and passes through the evaporator and the gas then enters the pipeline system

Unlike oxygen, the pressure gauge on a nitrous oxide cylinder tells you nothing about the amount of nitrous oxide remaining in the cylinder - it always reads around 52bar at room temperature. As shown in Figure 4, 52bar is the pressure at which nitrous oxide liquifies at 20°C and this is also the vapour pressure of nitrous oxide at 20°C. In a cylinder at room temperature, nitrous oxide exists as a liquid in equilibrium with its vapour. As vapour is drawn off, nitrous oxide moves from the liquid to the vapour phase, maintaining the equilibrium between the phases, and the vapour pressure within the cylinder. As nitrous is drawn off there is a small transient fall in vapour pressure, but once turned off, the contents will return to equilibrium and the vapour pressure is re-established at approximately 52bar.

To determine how much nitrous oxide is left in a cylinder it must be weighed, the weight of the empty cylinder subtracted, and then the number of moles of nitrous oxide in the cylinder calculated using Avagadro's number (see Box 1).

The ideal gas law can then be used to calculate the approximate volume of gas remaining. Given this, it is easy to understand why nitrous oxide cylinders are not filled to a given pressure. A value called the *filling ratio* is used instead. This is the ratio of the weight of the cylinder filled with nitrous oxide to the weight of the cylinder when filled with water. In the UK the filling ratio of nitrous oxide cylinders is 0.75, however this is reduced to 0.67 in hotter climates.

Entonox

Entonox is the trade-name from BOC Medical for 50% oxygen and 50% nitrous oxide. Entonox is supplied in cylinders at 137bar at

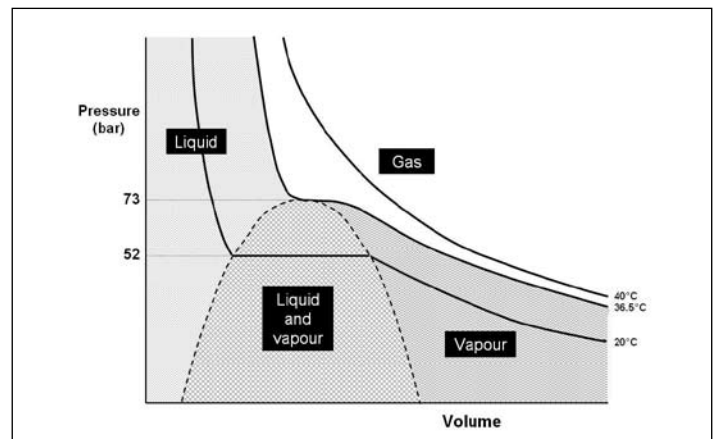


Figure 4. Nitrous oxide isotherms. Isotherms join points on the pressure volume graph that exist at the same temperature. Note that A - at 40°C nitrous oxide obeys Boyle's law; B - points 1 and 2 correspond to a nitrous oxide cylinder. A constant pressure is maintained despite alterations in volume

Avagadro's number (L):

The number of fundamental particles in 1mole of any substance is equal to the number of atoms in 12g of pure ¹²C.

The number is approximately $6 \times 10^{23} \text{ mol}^{-1}$.

In practice this can be used to calculate the number of moles of a substance if the total weight of the substance in question, and the molecular weight of the fundamental particle, is known:

$$\text{Number of moles} = \frac{\text{mass of substance (g)}}{\text{molecular or atomic mass}}$$

15°C or delivered via pipelines in the hospital at 4bar in the UK. For any mixture of gases, such as Entonox, the critical temperature is termed the *pseudocritical temperature*. In anaesthesia, however, the term *pseudocritical temperature* is almost always used to describe the temperature at which Entonox starts to separate (or 'laminar') into its constituent parts. Strictly speaking this temperature should be termed the 'laminating temperature', but *pseudocritical temperature* is a more widely used term.

As described above, at temperatures below the pseudocritical temperature it is possible for the individual gases in a mixture of Entonox to separate out into liquids. In practice this means that the nitrous oxide component of the entonox starts to move into the liquid phase. The pseudocritical temperature of entonox is approximately -6°C, allowing for slight variation due to small differences in cylinder pressure. At, or below, this temperature the concentration of the oxygen in the gaseous phase increases as nitrous oxide moves into the liquid phase. This has clinical importance. Although the inspired gas will initially contain a high concentration of oxygen, this gas is gradually exhausted, at which point the nitrous oxide will return to the gas phase, resulting in delivery of a hypoxic gas mixture of pure nitrous oxide. One design feature of Entonox cylinders to try and prevent this happening is that the tip of the pipe drawing the gas from the inside of the cylinder is generally placed near the bottom, close to the liquid surface. This means that if the nitrous oxide starts to liquefy, then an 'underwater seal' should form, preventing further gas

from being drawn. If there is a possibility of separation occurring, the manufacturers recommend that prior to use cylinders should be stored horizontally for 24hrs at a temperature above 10°C or alternatively, warmed to 10°C for two hours (or body temperature for 5 minutes) and then completely inverted 3 times.³

The gases in an Entonox mixture do not behave in a way that could be predicted from their individual properties and the pseudocritical temperature of Entonox alters with ambient pressure in a non-linear fashion. The pseudocritical temperature is highest at 117bar (-5.5°C) and decreases at pressures either side of this. In the UK, the pipeline supply pressure of 4bar gives a pseudocritical temperature around -30°C.

Heliox

Heliox is a mixture of oxygen and helium. The percentage of oxygen in the mixture can vary but may be as low as 21% and not higher than 50%. Heliox is useful in patients with upper airway obstruction but evidence of its clinical effectiveness is lacking.⁴ Theoretically patients with airway obstruction have a greater amount of turbulent compared to laminar air flow within their airways. Helium has a lower density than oxygen (and nitrogen) and this may increase airway gas flow when flow is turbulent. The density of a gas has no effect on flow when the flow is laminar - see Box 2.

The **Hagen-Poiseuille** equation for laminar flow through a tube:

$$\text{Flow, } Q = \frac{\pi \Delta P r^4}{8 \eta l}$$

Where ΔP = pressure differential, η = viscosity, l = length of tube, r = radius of tube

APPLICATION TO VOLATILE ANAESTHETIC AGENTS

The inhaled anaesthetic agents are also known as volatile anaesthetic agents because that they all have relatively high vapour pressures at room temperature. A distinction can be made between the volatile anaesthetic agents, such as isoflourane and halothane, which are usually a liquid at room temperature and gaseous anaesthetic agents, such as nitrous oxide and xenon, which are gases at room temperature. This section deals primarily with the former.

Volatile anaesthetic agents exert their effect according to the partial pressure of the agent in the blood - the greater the partial pressure, the greater the anaesthetic effect. According to Henry's law the partial pressure of anaesthetic agent dissolved in the blood is proportional to the partial pressure exerted by the anaesthetic vapour in the alveoli. Application of Dalton's law tells us that the partial pressure exerted by the anaesthetic vapour in the alveoli is independent of the other gases present in the mixture. So, the factors that alter the pressure exerted by the anaesthetic vapour are the vapour pressure itself and the amount of agent carried into the alveoli per unit volume (that is dictated by the concentration of anaesthetic vapour in the gas mixture).

Vaporisers

A vaporiser is a tool that accurately adjusts the amount of anaesthetic vapour added to the inhaled gas mixture and, in doing so, determines the concentration of vapour in the alveoli. A vaporiser does not generally alter the vapour pressure of an anaesthetic agent, and this remains relatively constant. The partial pressure of an anaesthetic agent in the alveoli increases when a vaporiser is turned up simply because it is at a higher concentration in the gas mix, and so its *partial pressure* increases. One variable that can alter the anaesthetic vapour pressure in a vaporiser is temperature.

When vapour is drawn off, evaporation of the liquid part of the anaesthetic agent takes place to maintain the equilibrium. This is an endothermic reaction that cools the liquid as the *latent heat of vaporization* comes from the liquid in the form of heat energy. The anaesthetic vapour pressure falls with the potential for delivery of a lower concentration of anaesthetic vapour and lightening of anaesthesia. Modern vaporisers incorporate various mechanisms to compensate for any drops in temperature to overcome this problem.

Altitude

A favorite examiner's question is 'What adjustment do you need to make to your vaporiser settings if you are anaesthetising a patient at altitude?' Two concepts answer this question. First, anaesthetic depth is controlled by altering the partial pressure of anaesthetic agent in the alveolus (Henry's law), and second, only two factors affect the partial pressure - the vapour pressure of the anaesthetic agent in the vaporiser and the concentration of this vapour in the inhaled gas mixture. Vapour pressure does not change with ambient pressure, so remains constant at altitude. The concentration of vapour in the inhaled gas mixture depends on the ratio of gas diverted through the vaporiser compared to the amount bypassing the vaporiser (*the splitting ratio*). Because this depends on a ratio it also does not change at altitude. So, the answer is that no change needs to be made to vaporiser settings at altitude. For completeness, however, you could point out that ambient temperatures are generally lower at altitude, and that this might affect the efficiency of the temperature compensation mechanisms of a vaporiser.

FURTHER READING

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