

# Theory, Measurements and Properties of Gases

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**Gases are one of the phases of matter where the particles are vastly separated unlike what takes place in solids and liquids where particles are closer together. Gases are hard to observe so they are classified according to temperature, a number of particles, pressure, and volume.**



## Gases: Basic Theory

Gases have **low density and viscosity** compared to other states of matter. Two laws explain their properties. **Boyle's law** states that at a constant temperature, the pressure of the gas varies inversely with its volume. **Charles's law** states that at a constant pressure, the volume of the gas is directly proportional to its temperature. These laws explain the movement of gases in different body compartments.

## Measurements of Volume, Temperature, and Numbers

p	pressure [Pa], [N/m <sup>2</sup> ]
F	force acting on a surface[N]

A	area of the surface, cross-section [m <sup>2</sup> ]
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**Liquids** have no definite shape due to the mutual relocatability of molecules, or atoms. They assume the shape of the available vessel. As a whole, the surface of liquids forms a horizontal plane. In **gases**, there are no binding forces between the individual molecules. The molecules are – except at absolute zero – constantly in motion. If they collide or bounce against surrounding walls, they are repelled elastically. Thus, they move on irregular zigzag paths.

A gas molecule undergoes about 10 quadrillion collisions per second.

In a fully sealed vessel, the force can be exerted on a fluid by means of a movable stamp. Unlike solids, where a force can be exerted on one point, the particles of fluid can avoid contact due to their movability. With a stamp, the force can act evenly through the entire surface of the stamp. The particles adjacent to the surface of the stamp experience an immediate pressure which they pass on in all directions due to their mobility. Therefore, the pressure is the same at any point within a fluid.

Pressure is defined as the ratio of a force applied perpendicular to a surface and the area of this surface:  $p = F / A$

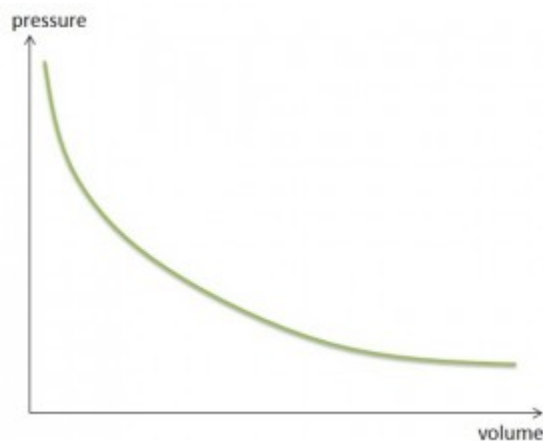
## Pressure and Volume of a Gas

At constant temperature, the pressure of a gas is proportional to the number of molecules present in the respective area. A measure for the number of molecules is the mass of the gas.

### **Boyle-Mariotte law:**

At constant temperature and in a closed container, the product of pressure and volume of a given amount of gas is constant.

Since a change in pressure affects the volume of a gas quantity, the density of gases must be pressure-dependent as well. At constant temperature, the density of a gas is proportional to the pressure. Densities behave the same as pressures.



## Real and Ideal Gases

In order to calculate gases easier, the following simplifications have been defined:

- Particles are elastic bodies of negligible small volumes.
- Elastic reflections at the vessel walls occur.
- Particles are evenly distributed (homogeneity).
- The velocities of the particles are evenly distributed (isotropy).

# Ideal Gas Law

V	Volume [l]
m	Mass [kg]
M	Molar mass
n	Amount of substance [mol]
R	Universal gas constant [J/(K*mol)]
T	Temperature [K], [°C]

For a description of ideal gases, a general equation of state (the ideal gas law) is used. It is defined as the simultaneous change of volume, pressure, and temperature.

$$p * V = m * R * T$$

In this equation, absolute pressure must be used. The ideal gas law does not apply in conditions of overpressure. Furthermore, it only applies to ideal gases and has only limited validity in regard to real gases and none in regard to vapors. From the ideal gas law, a body's standard volume can be calculated. Standard volume refers to the volume at **standard atmospheric pressure  $p_0 = 1013 \text{ mbar}$**  and at a **temperature of  $T = 0 \text{ °C}$** . At these standard conditions (STP), 1 mole of an ideal gas occupies a **volume of  $V_0 = 22.4 \text{ l}$** .

If the constant term  $p * V / T$  is proportional to the mass of the closed system, the associated proportionality factor is referred to as gas constant. The gas constant's numerical value depends on the type of gas.

The number of similar particles contained in a system is described as the amount of substance. A mole is the amount of a substance that contains as many particles as there are atoms in 12 grams of a carbon isotope C12. So in all substances, an amount of 1 mole contains  $6.0221367 * 10^{23}$  particles. At standard conditions, 1 mole of any gas has the same volume (see standard volume).

The product of universal gas constant with molar mass is called the molar gas constant. It is a universal constant and thus, non-specific to substances.

$$p * V = n * M * R * T$$

The equation of state in relation to the amount of substance:

$$p * V = n * R * T$$

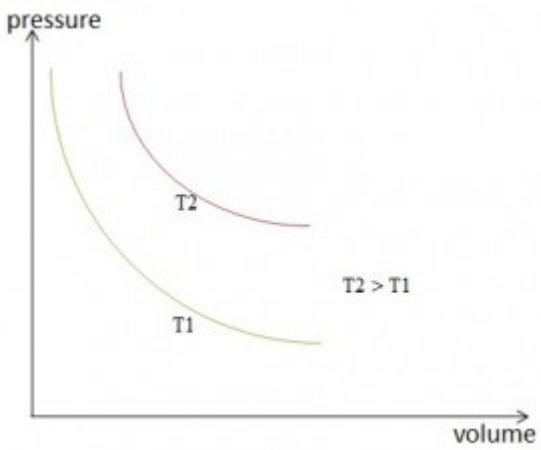
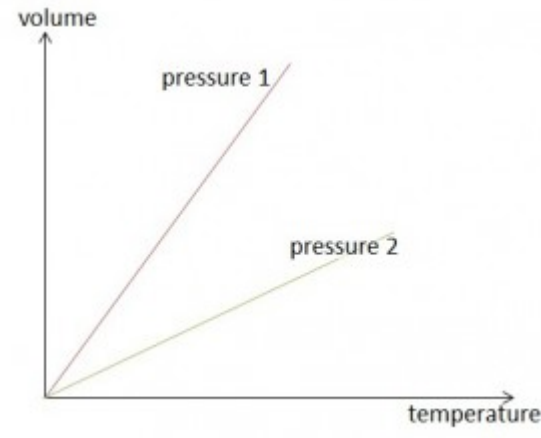
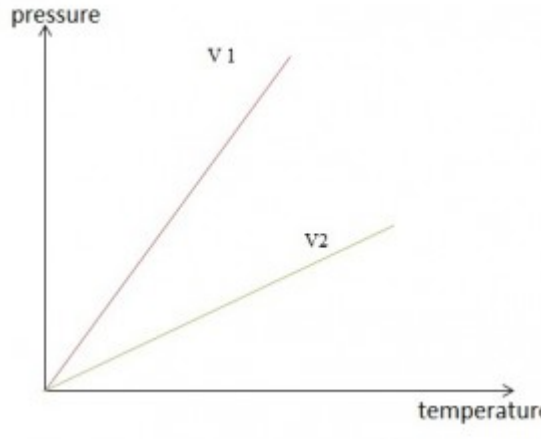
Thus, the state of a gas is determined by three state variables (pressure, volume, temperature). Changes of two or all state variables are referred to as a change of state.

There is a clearly defined value of internal energy for each state of a system. To understand these changes, we remember the first law of thermodynamics (see Thermodynamics I):

The supply of heat and mechanical work increases the internal energy of a closed system. The following applies:

$$\Delta U = Q + W$$

In ideal gases, mechanical work causes a volume change. The supplied thermal energy leads to an increase of the internal energy and an increase in volume.

<p><b>Isothermal change of state</b></p>	<p>Change of state of an ideal gas is isothermal when the temperature remains constant. <math>p \cdot V = \text{constant}</math></p>	
<p><b>Isobaric change of state</b></p>	<p>Change of state of an ideal gas is isobaric when pressure remains constant. <math>V / T = \text{constant}</math></p>	
<p><b>Isochoric change of state</b></p>	<p>Change of state of an ideal gas is isochoric when volume remains constant. <math>p / T = \text{constant}</math></p>	

## Adiabatic change

K	Adiabatic exponent
$\Delta S$	Change of entropy ( $S = 0$ in adiabatic change)
$C_p$	Isobaric heat capacity [J/(kg*K)]
$C_v$	Isochoric heat capacity [J/(kg*K)]

Adiabatic change of an ideal gas takes place without heat exchange with the environment. A complete heat insulation is required for this change of state. Adiabatic changes of state are also referred to as isentropic changes of state. The corresponding equation for an isentropic change of state is the following:

$$p * V^K = \text{const}; K = C_p / C_v$$

The work performed in an isentropic relaxation is when the amount of gas is given, only dependent on the change in temperature.

## Gases: Properties

### States of Aggregation

Substances can assume the following states of aggregation:

- Solid
- Liquid-gaseous

Each of these three states of matter implies specific properties for a substance. Solid substances have a fixed shape and volume. Their particles are held together by cohesive forces. Liquid substances have no fixed shape. However, they have a fixed volume and cohesive forces are acting between their particles. Gaseous substances neither possess a definite shape, nor a certain volume. Their particles exert only negligible cohesive forces.



To reach a higher state of aggregation (solid < liquid < gaseous), energy must be added. When a change into a lower state of aggregation takes place, energy is released.

## Heat Capacity

### Melting and Solidifying

The transition from a solid state into a liquid state is called melting. The reverse change is called solidification.

Melting of a body occurs at its melting temperature. Melting and solidification temperature are the same for one substance. During melting, the melting temperature remains constant despite the adding of heat. The added heat is used to transfer the substance from solid to liquid. The same applies to solidification: The temperature remains constant despite the release of heat. Only after the entire substance has solidified, further heat dissipation results in the cooling of the solid material.

### Vaporization and Condensation

Processes in which a substance changes from a liquid to a gaseous state are called vaporization. Reverse processes are called condensation.

There are two types of vaporization: Boiling implies the evaporation of a liquid where vapor bubbles form inside the liquid phase. The temperature of the liquid remains constant during boiling despite further heat supply. The boiling temperature is strongly dependent on the pressure of the liquid. Normal boiling temperature refers to the boiling temperature at atmospheric pressure of 1013 mbar. The other type of vaporization, where a liquid vaporizes below its boiling temperature, is called evaporation. It occurs only on the liquid surface and may occur at every temperature above zero. During evaporation, a liquid draws the required heat from its own energy content and from the environment.

**Example:** When a person is sweating, the sweat evaporates from the surface of the skin. Energy in the form of heat is released. The body gives off excess heat to prevent overheating.

Through evaporation and condensation of water, “pure” water can be produced. This type of liquid treatment is called distillation.

## Sublimation

Many substances change directly from the solid to the gaseous state and vice versa, without any formation of a liquid. This can be observed in the volatilization of naphthalene or the formation of ice crystals in the air. This phase transition from solid to gas and vice versa is called sublimation. The liquid state is skipped.

## Vapor Pressure

In the case of ideal gases, pressure and volume are inversely proportional to each other. In the case of real gases, this inverse proportionality is only accurate by approximation. When vapors change in volume, the pressure hardly changes at all. This difference between gases and vapors is based on the difference between the temperature and the pressure-dependent boiling point.

Vapor pressure (p) does not depend on the volume of the vapor. It only depends on the temperature.

The vapor is saturated when the saturation vapor pressure is reached, i.e. when it is in equilibrium with the liquid's pressure.

Gases are highly unsaturated vapors. Their temperature is far above the boiling point that corresponds to their pressure.

## Water Vapor in the Air

Since water constantly evaporates from the surface of all natural bodies of water, the air always contains water vapor, which is mostly unsaturated. To become saturated, it must be cooled to a specific temperature which is called dew point. In case of cooling below the dew point, so much water vapor is condensed that only the water vapor content corresponding to this temperature remains. The condensed water vapor appears in the form of fog, rain, snow or frost.

At each temperature, only a certain amount of water vapor can be contained in a certain volume of air. The water vapor content in the atmospheric air varies regarding time and location and is referred to as humidity. The maximum humidity is defined as the maximum amount of water vapor that can be contained in one cubic meter of air at a certain temperature.

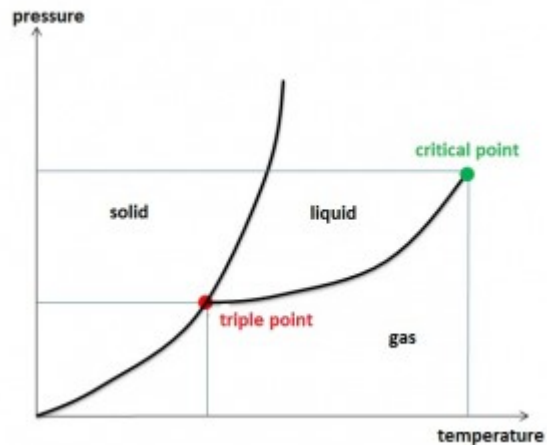
$F(\text{maximum}) = \text{Mass of water vapor in the air} / \text{Volume of humid air}$

## Critical Temperature

The critical temperature of a gas is the temperature at which liquefaction is no longer possible, regardless of how high the pressure is. The corresponding isothermal curve shows an inflection point with a horizontal tangent at the critical pressure. Only below the critical temperature, gases can be liquefied by applying pressure.

Real gases slightly cool down during a reduced relaxation.

## Triple point



Van der Waals' Equation

Partial Pressure

$p_A$	Partial pressure of a gas [bar]
A	Concentration of a gas in a solvent [mole/l]
K	Constant

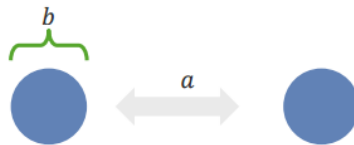
Mixtures of at least two different chemical elements that result in a gas are called gas mixtures. They have a homogeneous mixing ratio.

The solubility of a gas in a liquid is described by Henry's law. The gas concentration in the liquid is proportional to the partial pressure of the gas above the liquid.

$$A = K \cdot p_A$$

## Van der Waals Equation

Unlike ideal gas, allow...



...interactions between molecules:  $a$

$$P \rightarrow P + \left(\frac{n^2}{V^2}\right) a$$

...volume of molecules:  $b$

$$V \rightarrow V - n b$$

The van der Waals equation

$$\left(P + \frac{n^2}{V^2} a\right) (V - n b) = n R T$$

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