

Conductivity, conduction mechanisms in different materials

The relationship obtained from the molecular model for conductivity

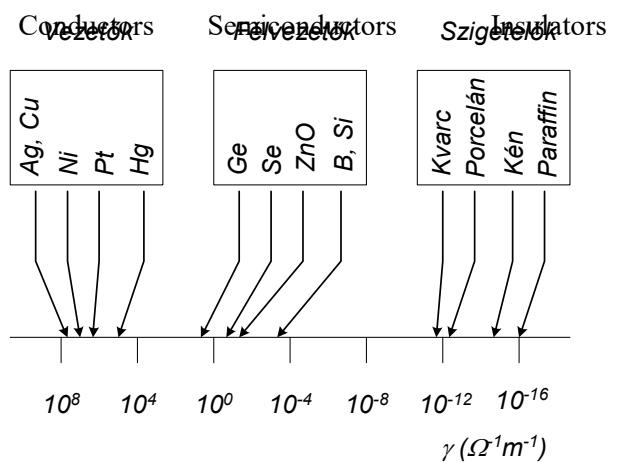
$$\gamma = qn\mu.$$

This means that the conductivity of a material is determined by the charge (q), the volume density (n) and the mobility (μ) of the charge-carriers.

There are different types of charge carriers in different materials, which move by different mechanisms, and the amount of charge carriers is also different, so the charge carrier properties described above can be very different. This is the reason why the conductivities of materials fall into a range of about 25 orders of magnitude (γ values are roughly in the range of 10^{-17} - 10^8 m/Ohm). Since the conductivity properties are closely related to the state of matter, it is useful to use the state of matter classification for conductivity testing.

Electrical conduction in solid materials

Conductive properties can also vary widely for solid materials. This is illustrated in the accompanying figure, where the materials are listed according to the usual grouping (conductors, semiconductors, insulators). Conductivities are given at room temperature.

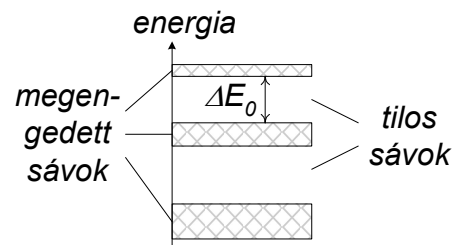


Conduction in crystalline solids

The conduction mechanism of solids is fundamentally affected by whether or not they have a crystalline structure. We first consider the case of crystalline materials, whose conductivity can also vary widely (e.g. Ag and quartz).

Such variations in conductivity have not been interpreted using classical physics, which requires the use of quantum theory to describe the specific behaviour of microparticles (in this case, electrons in atoms).

The part of quantum theory that deals with the behaviour of electrons in crystalline solids is called *band theory of solids*. The name 'band theory' comes from the fact that the theory states that electrons in such materials cannot have just any energy, but that their energy can only fall within a range of allowed energy, depending on the material. These ranges are called *allowed energy bands*. The electrons cannot take up energy in the energy range between the bands, the so-called *forbidden energy band or band-gap* (figure). The *width of the forbidden band* is important for conduction and is indicated by the symbol ΔE_0 (the width of a forbidden band is marked in the figure).



According to band theory, each band has a fixed number of energy sites, meaning that only a fixed number of electrons can have energy in an energy band. Electrons are first assigned to energy sites in the lowest energy band. If all the spaces in this band are already occupied (occupied band) and there are additional electrons in the atoms, they can only occupy spaces in the next higher energy band.

The band containing the highest energy, occupied energy slots can be fully occupied or partially occupied. How many of the allowed bands will be filled, and whether the highest

energy band will also be filled or only partially filled, depends on the number of electrons in the constituent atoms (i.e. the atomic number of the constituent atom), i.e. the band structure is different in different materials.

When matter is placed in an electric field, the electrons are subjected to a force in the opposite direction to the field, which tries to set the electrons in motion. This results in an increase in the energy of the electrons as they gain kinetic energy. If there is an allowed energy band in the matter where there are energy vacancies, the energy of the electron within the band can increase, so the force field actually causes it to move: an electric current is generated in the matter, caused by the movement of the electrons.

However, if the band structure is such that there are only filled energy bands, then the electron cannot increase its energy within the band (there is no higher unoccupied energy space), i.e. it cannot be set in motion by the electric field. In this case, the electrons in the matter cannot generate an electric current. In this case, the only way to accelerate the electrons is to give them energy from the electric field equal to the width of the forbidden band, which will allow them to move into the next (empty) allowed band. Under normal circumstances, however, the electric field cannot transfer such a large amount of energy to the electron.

In summary, it is essential for electron conduction that there is an allowed energy band that is only partially filled.

Let's then look at what energy bands can be created in different materials.

Figure a) shows the case where the topmost band containing electrons is only partially filled. In this case, as we have already discussed, electrons can move in an electric field, and electric conduction is created. Materials with this band structure are *conductors*. Most metals have such a band structure, which is why metals are generally good conductors.

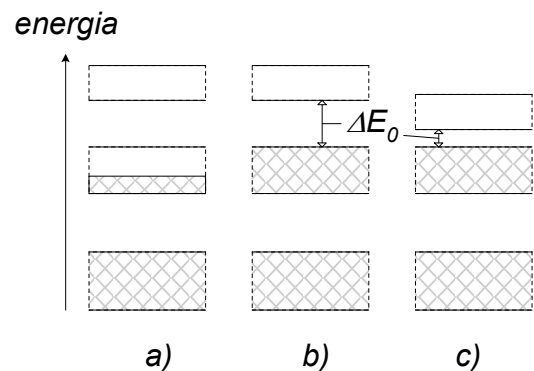
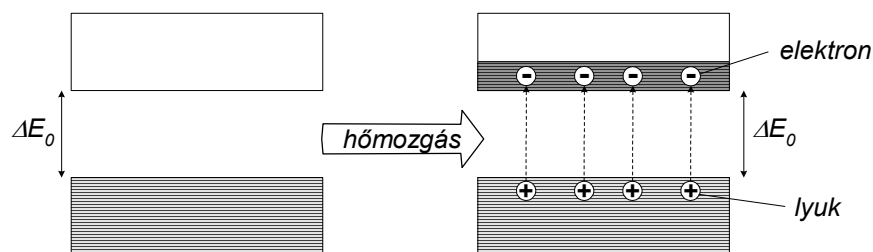


Figure b) shows the case where the topmost band containing electrons is completely filled, the width of the forbidden band is large, and therefore the electrons cannot normally generate a current. Materials with this band structure are *insulators*. Examples of crystalline solids are diamond, quartz, rock salt (*NaCl*).

Figure c) also shows the band structure of an insulator, but in this case the width of the band gap ΔE_0 is much smaller than in figure b). This fact can be of great significance: if the width of the forbidden band is so small that the thermal motion of the atoms can propel a



significant number of electrons from the filled band into the empty band (i.e. the average energy of the thermal motion is nearly as high as the energy ΔE_0 required for the transition of the electrons), then the originally empty energy band becomes partially filled (figure), and an electric current can be generated in the material. Such materials, which have an insulating band structure but are capable of conduction by thermal movement, are called

semiconductors. The best known semiconducting materials are *silicon (Si)* and *germanium (Ge)*.

In semiconductors, the charge carriers are electrons. However, not only the electrons in the initially empty band are involved in conduction, but also those in the initially filled band. The reason is that the energy states of the electrons that leave are released, so there is a possibility of energy change here too.

The current of electrons moving through vacancy states can also be understood as the current created by the movement of positive charges - the so-called *holes* - created by the absence of electrons. The holes move in the opposite direction to the electrons, but their charge is also opposite to that of the electrons, so the direction of the current is the same as the current caused by the movement of the electrons. This concept of charge movement makes it easier to understand the conduction of semiconductors. According to this view, the current in semiconductors is generated by electrons and holes.

In insulators, the width of the forbidden band is so large that, except at very high temperatures, thermal motion can only bring very few electrons into a mobile state. In materials with very low conductivity - called insulators - conduction is produced by the movement of this small number of mobile electrons (e.g. diamond) and any ions that may be present in the material (e.g. ion crystals).

Conductors

Solid conductors are virtually identical to metals. In these materials, a part of the atomic electrons - determined by the electron structure of the atom - can move virtually freely in the material. In conductors, the charge carriers are negatively charged electrons, the magnitude of their charge being the elementary charge, which is a natural constant (by definition, the charge of the electron).

The conductivity is given by the relation $\gamma = qn\mu$. Since the charge (q) of the charge carriers and the number density of free electrons (n) in a given metal are both given, the conductivity depends on the conditions practically only through the mobility (μ).

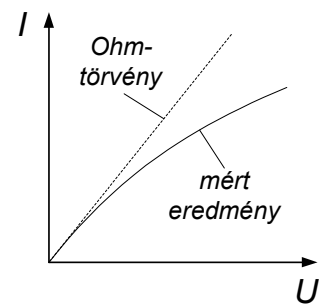
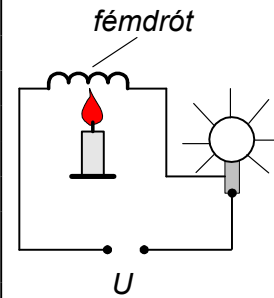
To determine the mobility, it is necessary to know how the electrons move, which in crystalline solids cannot be understood from classical physics models, and quantum theory must be used. All we need to know is that electrons in a perfect crystal lattice (where all atoms are in the right place in the perfect crystal lattice) could move without resistance: a perfectly ordered crystal - with electrons that can move - would have zero resistance. However, if there are disorder in the crystal lattice (e.g. an atom is missing somewhere or an atom is replaced by a foreign atom), the electron's motion becomes more difficult and its mobility is reduced. The same effect is caused by the fact that the ever-present thermal motion causes the atoms to oscillate around their equilibrium position, i.e. they are mostly not in the perfect lattice. In short, *any disorder in the crystal lattice reduces the mobility of the electrons* and thus increases the electrical resistance of the material under investigation.

From what has been said about mobility, we can understand the experience that the conductivity of a metal contaminated with a foreign substance is lower (its resistance is higher) than that of a pure metal: contamination = impurity $\Rightarrow \mu$ decreases $\Rightarrow \gamma$ decreases \Rightarrow resistance increases.

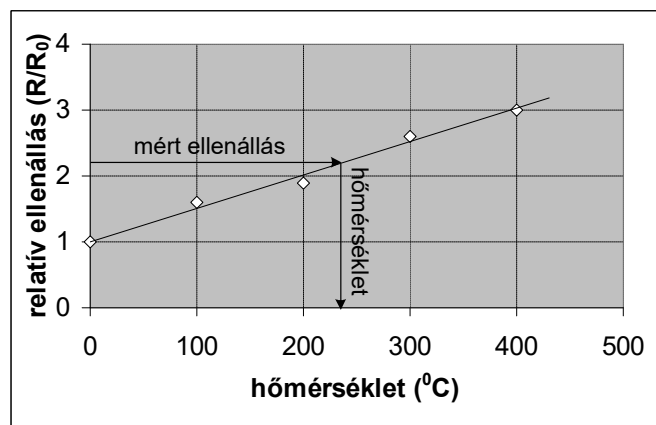
Another experimental finding is that the conductivity of metals decreases (resistance increases) as the temperature increases. The interpretation of this can also be given by the above theory. As the temperature rises, the thermal motion becomes more and more intense, the instantaneous position of the atoms in the crystal lattice becomes more and more distant from the ideal position, the disorder in the lattice increases: temperature increase = increasing disorder $\Rightarrow \mu$ decreases $\Rightarrow \gamma$ decreases \Rightarrow resistance increases.

Experiments:

- ◆ A voltage source is used to connect an incandescent lamp and a wire coil made of conductor in series. The voltage is adjusted so that the bulb glows, i.e. the current flowing through it is high enough to light it up. The wire filament is then heated with a gas flame. The light from the filament lamp gradually dims and then goes out completely. This shows that the current in the circuit has dropped, which can only be interpreted as the resistance of the conductor increasing as the temperature rises.
- ◆ Measure the relationship between current (I) and voltage (U) for an incandescent lamp. We find that Ohm's law is not satisfied because instead of a linear relationship, we get a curve with a decreasing slope as the voltage increases (the nature of the curve is shown in the figure below). The reason is that as the voltage increases, the filament heats up, its resistance increases, and therefore the current is less than the value expected from the initial (cold) resistance (dashed line).



The dependence of the resistance of metals on temperature can be used to measure temperature. A special, small metal resistance for this purpose is called a resistance thermometer or thermistor. If the temperature dependence of the resistance of a thermistor is measured once by measuring the resistance at known temperatures (validation), the unknown temperature of a location can be determined by measuring the resistance after the resistance thermometer has been placed there (Figure). The procedure is simplified by the fact that the temperature dependence of the resistance of metals is approximately linear over a wide temperature range. Such a temperature dependence is shown in the accompanying figure (R is the resistance measured at the current temperature R_0 is the resistance measured at 0°C).



Semiconductors

For semiconductors, the situation is a bit more complicated. Here, in addition to the mobility (μ), the concentration of charge carriers (n) is not predetermined.

In pure semiconductors, mobile charge carriers are created by transferring electrons from the fully populated valence band to the higher energy, initially empty conduction band by thermal motion. This process produces more mobile charge carriers the higher the temperature. This means that the concentration of mobile charge carriers (n) increases with increasing temperature. However, the mobility of charge carriers is the same as for conductors: as the temperature increases, the mobility (μ) decreases. Here, therefore, two opposite effects shape the conductivity:

temperature rise
(increasing disorder)

↓
 μ fall
↓
 $\gamma = qn\mu$ fall

temperature rise
(more electrons in conduction band)

↓
 n grow
↓
 $\gamma = qn\mu$ grow

Experience (and theoretical calculations) show that charge carrier concentration increases with temperature (n increases strongly) much faster than mobility decreases (μ decreases weakly), i.e. in pure semiconductors: temperature increase = increasing charge carrier concentration + increasing disorder) $\Rightarrow \gamma \Rightarrow$ resistance decreases.

Contamination of the semiconductor with a chemical impurity other than the chemical value of the base lattice atom can cause a very large increase in the concentration of charge carriers, while the decrease in mobility is not very significant. That is, at a given temperature, different chemical impurities increase the conductivity.

The resistance of semiconductors depends more strongly on temperature than metals, so semiconductors can be used to make more sensitive thermometers.

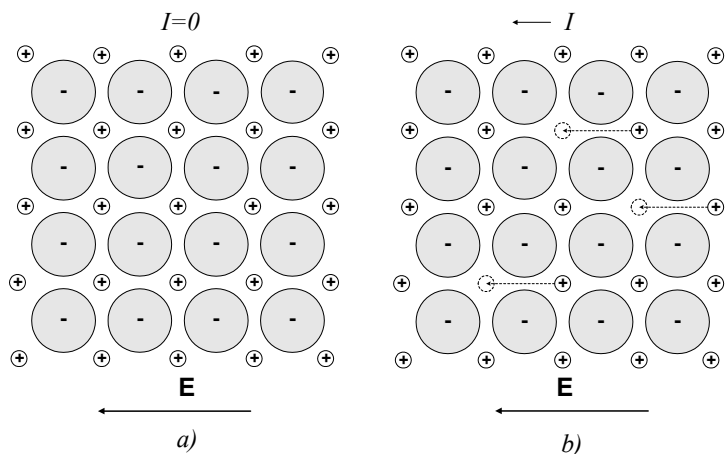
The temperature dependence of resistance is also used in circuits to reduce the effect of temperature change or to harness this effect by using temperature-dependent semiconductor resistors, known as thermistors.

Insulators

In crystalline insulators, the width of the forbidden band is so large that, except at very high temperatures, thermal motion can only bring very few electrons into a mobile state. Nevertheless, in some of these materials, where there is no other conduction mechanism, conduction is produced by the small number of electrons that are able to move (e.g. diamond).

In another part of the materials, where the crystal is made up of ions, another conduction mechanism may be involved:

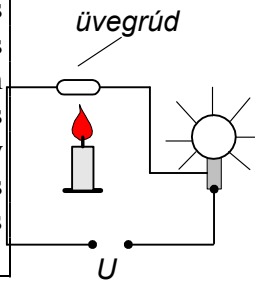
ions move in the crystal lattice. If the lattice of an ionic crystal were perfect, ions could not move in it (figure a). Ion motion is made possible by the fact that there are always empty lattice sites in crystals, and ions can move by jumping between these empty sites under the influence of the electric field (figure b).



The more such vacancies there are, the more ions can move, i.e. the higher the concentration of charge carriers that can move. Since vacancies in pure matter are created by thermal motion, the concentration of charge carriers increases as the temperature rises. However, ions are not completely free to move between lattice sites, because ions have to jump an "energy hill" to move from one lattice site to another. The energy needed to do this is provided by thermal motion, so the frequency of jumps increases as the temperature rises. This means that increasing the temperature also increases the mobility of the ions. Thus, in ionic conduction, the charge carriers are ions, and the temperature dependence of conductivity is: increasing temperature = more intense thermal motion $\Rightarrow n$ increases, μ increases $\Rightarrow \gamma$ increases \Rightarrow resistance decreases.

Experiment:

A voltage source is used to connect an incandescent lamp and a glass bulb in series. The voltage is adjusted so that the bulb does not light up, the bulb does not light up because the glass does not have enough current flowing through it due to the high resistance of the glass. The glass rod is then heated with a gas flame. The bulb starts to light up and its light gradually increases, i.e. the current flowing in the circuit increases. This is only possible because the resistance of the insulating glass decreases as the temperature rises.



Chemical impurities other than the ions in the base lattice usually also increase the concentration of charge carriers in these materials, resulting in an increase in conductivity. Typical ionic conductors are ionic crystals (e.g. *NaCl*).

Insulators also include a number of materials that are not crystalline in structure. In these materials, a band structure similar to that of crystalline materials is not formed, and the electrons do not play a significant role in conduction. The electric currents that can be generated in such materials - usually small - are a consequence of the low electron or ionic conductivity. Such materials include glass, many ceramics and most plastics.

The classic application for insulators is the elimination of electric current, i.e. electrical insulation. More recently, some ionic crystals have also been used to perform similar tasks to liquid electrolytes, such as making power sources (ionic crystals are actually solid electrolytes in which conduction is made possible by the movement of ions).

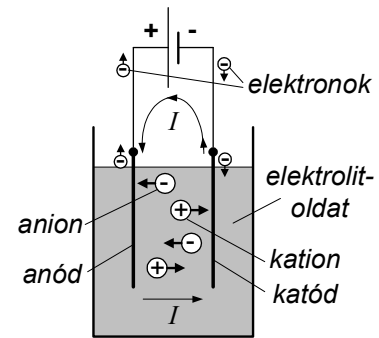
Electrical conduction in liquids

In liquids, electrical conduction occurs practically only when ions are present in the liquid (a well-known exception is the case of liquid metals, in which electron conduction is present). Such ionic liquids *are electrolytes*. The most common of these is the electrolyte solution, which can be prepared by dissolving an ionic substance in a non-ionic liquid. During the dissolution, the ionic substance breaks down (dissociates) into ions and the resulting ions are the mobile charge carriers. The role of the dissolved substance as a charge carrier is illustrated by the following experiment.

Experiment:

- ◆ Two metal plates - not in contact - are placed in clean (distilled) water. If you create a current through an incandescent bulb and the metal plates in the water with a current through a telephoto, the bulb will not light up. When salt is sprinkled into the water, the bulb lights up: the resistance of salt water is much lower than that of pure water.
- ◆ In the experiment, using tap water instead of distilled water, the bulb lights up even if nothing is added to the water. This shows that the tap water contains dissolved ionic substances.

In an electrolyte solution, the electric current is generated between conductive rods - called *electrodes* - immersed in the electrolyte, one of which - called *the anode* - is connected to the positive corner of a battery and the other - called *the cathode* - to the negative corner of the battery (figure). In solution, the negative ions migrate to the anode and the positive ions to the cathode, hence the negative ions are often called *anions* and the positive ions *cations*.



In the electrolyte solution, the electric current is therefore caused by the movement of positive and negative ions and electrons in the conducting parts of the circuit. The closed circuit is created by the negative ions arriving at the anode and donating electrons, which move in the conductor towards the positive corner of the battery. The electrons "transferred" by the battery move from the negative corner of the battery towards the solution, and are picked up by the positive ions at the cathode, closing the circuit.

An important aspect of the process is that the ions arriving at the electrodes lose their charge by electron donation or electron absorption *and leave the solution* as neutral particles. Depending on the composition of the specific electrolyte, the precipitated material may undergo further chemical reactions, resulting in different end products. These processes are not discussed in detail here, but only one important process is mentioned. The cations of the dissolved ionic material are usually metal ions, which are precipitated as neutral metal atoms on the cathode and form a coating on it. This phenomenon is the basis of one of the processes used to make metal coatings, known as electroplating.

The processes involved in the conduction of electrolytes (conduction, extraction, chemical reactions of the extracted substance) are collectively *known as electrolysis*.

In electrolyte solutions with a low concentration of solute (the so-called weak electrolytes), experiments carried out with due care¹ show that Ohm's law applies, so that the conductivity produced by a given ion can be obtained from the relationship $\gamma = qn\mu$ if the charge, volume fraction concentration and mobility of the ions are known. In electrolyte solutions, however, there are at least two types of ions, but in the case of several types of solute, there can be several positive and negative ions, which can have different charges (q_i), concentrations (n_i) and mobilities (μ_i). In this simple case, the conductivity is given by the sum of the conductivities ($\gamma_i = q_i n_i \mu_i$) of the individual ions:

$$\gamma = \sum \gamma_i = \sum_i q_i n_i \mu_i .$$

The conductivity of an electrolyte solution is essentially dependent on the concentration of the dissolved ionic material, which determines the concentration of mobile ions. As the concentration of the solution increases, the concentration of mobile charge carriers (and hence conductivity) usually increases at low concentrations, but due to the complex interactions of the ions in solution with each other and with the solvent, above a certain concentration, conductivity may decrease as the amount of solute increases.

The mobility of charge carriers depends on several factors. One such factor is the viscosity of the fluid. In an electrolyte, ions usually form a shell of ions or dipoles around themselves due to their electric charge and move with this shell under the influence of the electric field. This formation, usually much larger than the size of the ion, moves frictionally in the liquid, and this friction is significantly influenced by the viscosity of the liquid. As viscosity is generally lower at higher temperatures, the mobility increases with increasing temperature. This is why the conductivity of electrolytes generally increases with increasing temperature.

¹ In constant voltage measurements, the relationship between the junction voltage U and the current I is given by $U - U_p \sim I$ instead of $U \sim I$, where U_p is the constant voltage depending on the electrodes and the electrolyte, the so-called *polarization voltage*. This reverse voltage is a consequence of the processes taking place on the electrodes (this will be discussed in the discussion of contact phenomena). It can be eliminated by performing the measurement with a low frequency AC voltage. In this case, the material extraction causing the constant counter-voltage cannot occur on the electrodes.

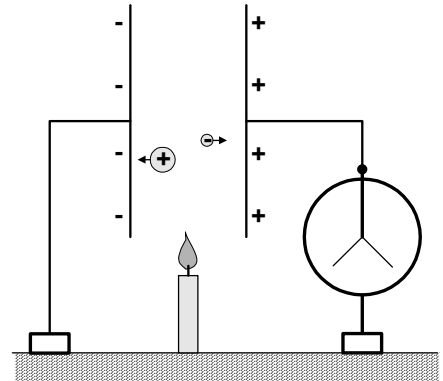
Electrical conduction in gases

Under normal conditions, gases are poor conductors. They can only be made conductive by the generation of charge carriers. There are two basic cases of charge carrier generation:

- ◆ The gas itself cannot "produce" the charge carriers, they are created by an external effect, this is *not self-conduction*.
- ◆ In gas, it is the electric current itself that creates the necessary charge carriers, that is, *self-conduction*.

Experiment:

The charge of a charged capacitor connected to an electrometer (Fig.) disappears if a flame (e.g. a burning candle) is held between its plates, because the electric charges generated by the flame neutralise the charge on the plates.

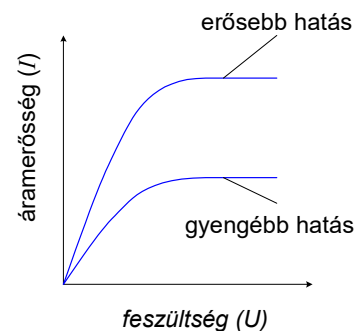


Non autonomous conduction

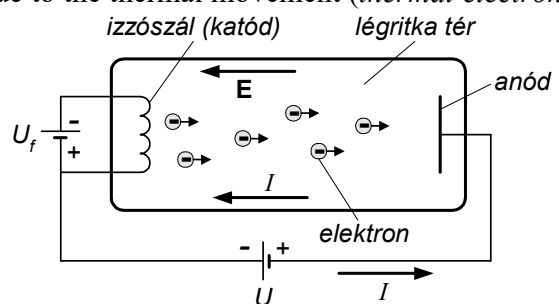
A charge carrier can be created by heat, radiation or any external energy source that can ionise gas molecules. This creates positively charged ions and negatively charged electrons, which move under the influence of an external force field: a current is generated.

At the same time as the charge carrier is created, the ions and electrons that come together at random are also reunited - so-called *recombination*. The concentration of charge carriers at any given time is determined by the intensity of the nucleation and recombination, and an equilibrium charge carrier concentration (n) is formed.

When a voltage (U) is applied between two electrodes in a gas, the electrons and ions created in the gas generate an electric current (I). At low voltages, the current is small, so the charge carriers that disappear at the electrodes do not significantly change the charge carrier concentration. In this case, $n \approx$ is constant, and Ohm's law is satisfied (the linear phase in the diagram). As the voltage is further increased, more and more charge carriers reach the electrodes without recombination, and the number of charge carriers - and hence the current - is determined by the rate of charge carrier generation: under a constant ionizing effect, the current cannot increase further, but takes a constant value, the *saturation current*. The saturation current depends on the strength of the ionizing effect (e.g. radioactive radiation) and can therefore be used to measure the strength of the ionizing effect (ionization chamber).



A special case of non-self-conduction is when charge carriers are produced by heating a metal filament. Electrons are emitted from the hot metal due to the thermal movement (*thermal electron emission*). If the filament is placed in a vacuum tube, the electrons are free to move (at higher pressures, their movement is limited by frequent collisions with gas molecules), so if an electric force field (\mathbf{E}) is created in the tube (figure), the electrons move against the field strength and generate an electric current. (Note that the electrons move against the field strength because of their



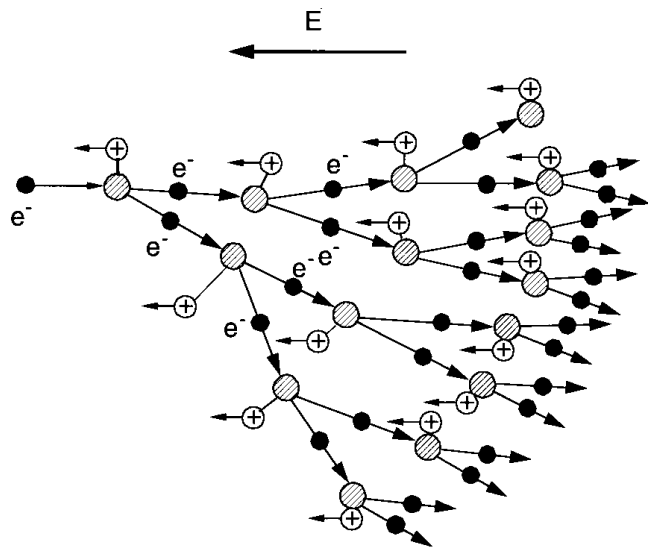
negative charge, but the direction of the current is the same as the direction of the field strength because of the definition discussed earlier.) This charge carrier generation mechanism is exploited in various electron tubes, in the cathode ray tube, which is the main component of oscilloscopes, and in the electron microscope.

Self-conduction

In a gas, a small number of charge carriers (electron-ion pairs) are always generated due to various external influences (e.g. cosmic radiation). Therefore, if a voltage is applied between electrodes in a gas and the voltage is increased, the electric field causes these charge carriers to accelerate to the point where they can ionise neutral gas molecules on collision with them. This process is called *collision ionisation*. Collision ionisation primarily involves electrons, because their mass is equal to the electron to be ejected in the ionisation process, and this is when the energy transfer is most efficient.

During the collision ionisation, new charge carriers (electron-ion pairs) are created, the electrons produced are accelerated and further atoms will be ionised (figure). The current starts to increase very rapidly (each electron generates two others, so the number of charge carriers increases in an avalanche-like manner, in powers of 2). At this point, the gas itself is already producing the charge carriers needed for conduction, such conduction is called *self-conduction*.

Collision ionisation is more effective at low pressures because the charged particles have a longer free path and can be accelerated to higher energies, which increases the ionisation capacity of the charges. During collisions, not only ionisation is possible, but also excitation of electrons, which can produce *light phenomena* when the electrons return to their ground state. This is where the electric current generated in gases gets the name *gas discharge*.



EXCERPT:

In a not very rare gas (between 5 kPa and 0.001 kPa), a nebula discharge occurs, in which charge carriers are created by collision ionisation and in which dark and luminous regions alternate due to rather complex processes (in figure 1 - cathode light, 2 - dark cathode field, 3 - negative nebula light, 4 - Faraday dark field, 5 - plasma, 6 - dark anode field, 7 - anode light). The length of each region may vary depending on the pressure or voltage applied to the tube, and some may disappear.

Generally speaking, in the dark regions, the charge carriers accelerate and accumulate energy (the absence of energy-absorbing collisions is indicated by the absence of light emission), while in the luminous regions they lose energy due to ionisation and excitation in the collisions (indicated by light emission).

Because of its practical importance, it is worth mentioning the negative fog lamp (3), the light of which is seen in fog lamps (also known as glow lamps). This region is created by ions colliding with the cathode, which eject electrons from the cathode material, and these electrons, accelerating towards the anode in the dark cathode space, reach the energy that allows them to ionise or excite the gas molecules (the excitation results in the emission of light).



An important range is plasma (5), which gives the light of the older advertising tubes and whose colour depends on the gas used. Electrons lose energy in the negative nebula and regain energy in the dark space in front of the plasma (4), ionising in the plasma region and causing light emission. The plasma is a special case: it contains equal amounts of positive and negative charge, a neutral mixture of electrons and ions, i.e. ionised, outwardly neutral gaseous matter. Its properties differ significantly from those of ordinary gases due to the presence of ions, and it is often referred to as a new (fourth) state of matter. Plasmonic states play an important role in the functioning of stars, in thermonuclear reactions and in many technological processes.

At higher air pressures (below 0.001 kPa), there are no light phenomena in the gas, but ions hitting the negative electrode (cathode) knock electrons out of the cathode, and these electrons move towards the positive electrode (anode) to create a strong electron current. This is the cathode radiation, which is what the electron was detected when it was discovered.

EXCERPT:

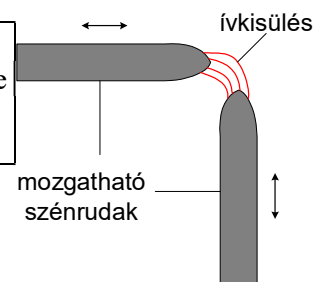
The properties of the cathode rays can be studied in a vacuum tube: they cause fluorescence, propagate in a straight line (shadow phenomenon), can be deflected by a magnetic field. The experiment is performed with an alternating field (spark inductor), which is possible with one of the electrodes in the tube having a large surface area and the other small. The large surface area has more electrons ejected, so it is always the negative electrode (i.e. there is rectification).

At higher (atmospheric) pressures, collision ionisation is only possible under very high field, but it is feasible. Such a high-voltage discharge is a spark discharge, where the multiplication of charge carriers in a narrow channel occurs and the excitation of the molecules causes light to be emitted along the channel ("spark"). Such a spark can be observed, for example, when switches are turned off, but also in the case of lightning in the atmosphere. Similar avalanche-like charge-carrier generation also occurs in solid insulators, where it is called *breakdown*. During breakdown, the insulator is destroyed along the breakdown channel and loses much of its insulating properties, so the strength of the insulating material without breakdown ('breakdown strength') is an important characteristic of insulating materials.

A special type of discharge is an arc discharge, which occurs when two carbon or metal rods are pulled apart from contact between them.

Experiment:

An arc is created by connecting a voltage between two movable carbon rods and producing light.



In arc discharge, the electrons leaving the glowing cathode (thermal electron emission) play a significant role in the generation of charge carriers, which ionise the gas between the rods. The significant current sustains the glow (Joule heat) and thus the discharge.

Arc discharge in a circuit behaves in a specific way: the higher the current, the lower the resistance of the arrangement (the higher the concentration of charge carriers), i.e. the lower the voltage across it. Ohm's law is therefore not valid here: increasing current is associated with decreasing voltage. Such a circuit element is called a negative resistance element. In order to maintain the discharge, the voltage must be prevented from decreasing (the current from increasing), which is achieved by connecting a constant resistor in series with the discharge (this is called a series resistor), which limits the current flowing through the discharge.

Arc discharges release considerable heat and light, which used to be used as a light source, but today arc discharges are used in various heat-intensive technological processes (e.g. cutting, welding of metals).

