Tutorial 3. Free electron gas

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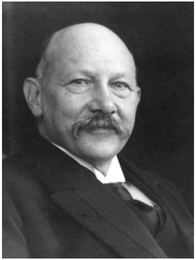
Mathematical models of the direct current
- History
- Drude's theory of conductivity
- Chemical sources of current
- $Y \to \Delta$ and $\Delta \to Y$ transforms
- Summary

Paul Drude

After discovering of electrons in the last of 1890-th years it was be clear that these particles can be considered as a carries of the charge and ordered moving of the electrons can be reason of the electric current.
At the same time the kinetic theory of ideal gas had successfully applied to describe numerous properties of real gases. An idea of usability that theory for the motion of electrons into the conductors was looked naturally.
One of initial step on this approach was be made by Paul Drude in 1900.

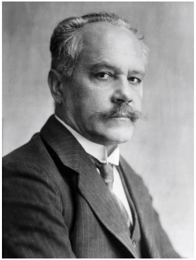
Kamerlingh Onnes



Physicists knew that the resistivity depends on a temperature. In spite of an observation of decreasing the resistivity for metals another materials show an opposite property. This reason for different opinion on the dependency of resistivity on the temperature. Kamerlingh Onnes was the first physicist who might study the metals on super low temperature. In 1911 he observed vanishing of the resistance of mercury.

Now this phenomenon is called superconductivity.

Arnold Sommerfeld



The Drude's
theory did not explain large distance of free motion of the electrons into the crystals and the low temperature effects. Therefore physicists were forced to develop new theory or partially new for low temperatures. The Drude's theory of free electron gas was based on Boltzmann-Maxwell statistics which define the distribution of large quantity of classical particles.
In 1926 year Pauli had formulated one of basic principle of quantum mechanics. The principle says the quantum particles cannot be in the same state.
After that year Enrico Fermi developed new statistics. That statistics applied the Pauli principle for the basic idea.
At least in 1928 Arnold Sommerfeld applied the Fermi-Dirac statistics to his approach to the problem of conductivity for the metals.

Free electron gas

Let us consider electrons in the metal as an ideal gas.
A motion in such gas if following

- Electrons moving as a free particles and the energy depends on the temperature:

$$E = \frac{3}{2}kT, \quad k \sim 1.38 \times 10^{-23}\frac{J}{K} \text{ is a Boltsmann constant.}$$

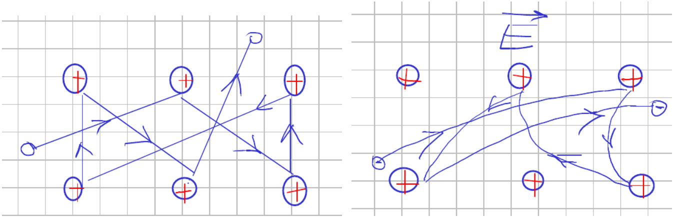
- The electrons collide with positive charged ions of the crystal chain and the velocity after the collision might be spontaneously changed. The mean value of speed after the collision can be defined using the formula:

$$m_e\frac{v_e^2}{2} = \frac{3}{2}kT.$$

- In the presence of difference of electrical field U every electron obtains the acceleration:

$$\frac{dv_e}{dt} = \frac{e}{m_e}U.$$

Free electron gas



- The mean time of the free motion of the electron between the collisions is equal to τ. The τ is a parameter of the theory which should be defined be defined experimentally.
- The equation for the drift of the electrons due to the electricity potential is following:

$$\frac{dv_e}{dt} = \frac{e}{m_e}U - \frac{v_e}{\tau}.$$

Free electron gas

So the mean speed of the drift is:

$$\tilde{v} \sim \frac{e}{m_e} U\tau.$$

The charge passes through a section of a conductor S is following:

$$dq = nedt.$$

Here n is a number of the free electrons which are going through a section of a conductor during dt.

$$n = \frac{m}{M} z N_A,$$

$m = S\rho\tilde{v}$ is a mass of the conductor which electrons passed through the section, M is molar mass, $N_A \sim 6 \times 10^{23}$ the Avogadro's number and z is a valency of the conductor.

Free electron gas

So the current equals to

$$\frac{dq}{dt} \equiv i = \frac{S\rho\tilde{v}}{M} z N_A e = \frac{S\rho}{M} z N_A \frac{e^2}{m_e} U\tau = z N_A \tau \frac{\rho}{M} \frac{e^2}{m_e} SU.$$

So the resistivity r which is equal to:

$$r^{-1} = z N_A \tau \frac{\rho}{M} \frac{e^2}{m_e}, \quad r = \frac{M m_e}{z N_A \tau \rho e^2}.$$

$$[r] = \left[\frac{kg \times kg \times m^3}{sec \times kg \times C^2}\right] = \left[\frac{kg \times m^3}{sec \times C^2}\right] = \left[\frac{kg \times m^3}{sec^3 \times A^2}\right].$$

The Ohm law looks like:

$$U = ir\frac{l}{S},$$

where l is the length and S is the cross section of the conductor.

Typical values of the electrical parameters in the conductor

Let us consider the electrical properties for the cooper as the conductor.

$$\rho \sim 8920 \frac{kg}{m^3}, \quad M \sim 0.064 kg, \quad r \sim 16.78 \times 10^{-9} \Omega \times m, \quad z = 2.$$

The mass and charge of the electron are:

$$m_e \sim 9.1 \times 10^{-31} kg, \quad e \sim -1.6 \times 10^{-19} C.$$

So the relaxing time for the cooper:

$$\tau = \frac{M m_e}{z N_a \rho e^2 r} \sim$$

$$\frac{0.064 \times 9.1 \times 10^{-31}}{2 \times 6 \times 10^{23} \times 8920 \times (1.6 \times 10^{-19})^2 \times 16.78 \times 10^{-9}} \sim 1.27 \times 10^{-14} sec$$

Typical values of the electrical parameters in the conductor

The thermal speed of the electron into the cooper at $T = 300K$:

$$m_e \frac{v_e^2}{2} = \frac{3}{2}kT, \quad v = \sqrt{\frac{3kT}{m_e}} \sim$$

$$\sqrt{\frac{3 \times 1.38 \times 10^{-23} \times 300}{9.1 \times 10^{-31}}} \sim 116826m/sec. \sim 117km/sec.$$

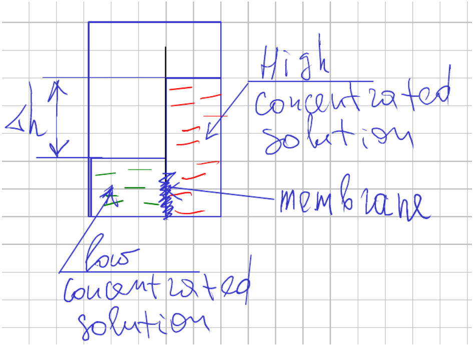
Let us consider the drift of the electron into the conductor of length $1m$, cross section $S = 1mm^2$ and current $1A$:

$$U = ir\frac{l}{S} \sim 16.78 \times 10^{-9} \frac{1}{10^{-6}} \sim 0.0168V.$$

In this case the electron drift due to the voltage is:

$$\tilde{v} = \frac{e}{m_e}\tau U \sim \frac{1.6 \times 10^{-19}}{9.1 \times 10^{-31}} \times 1.21 \times 10^{-14} \times 0.0168 \sim 37 \times 10^{-6} m/sec..$$

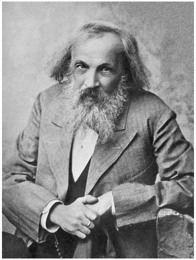
Abnormal osmotic pressure and conductivity



There were two different observations.

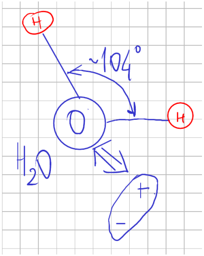
- The solutions of salts, acids and bases give an additional abnormal osmotic pressure.
- The solutions of salts, acids and bases are conductors of electrical current.

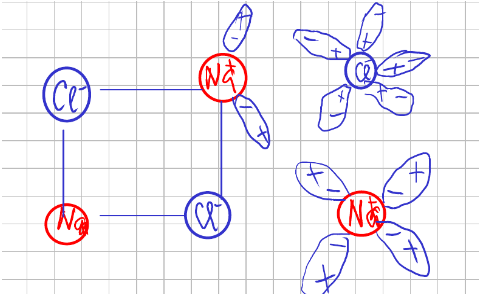
Svante Arrhenius, Dmitrii Mendeleev and electrolytes

S. Arrhenius was supposed in 1887 that such processes along sides by dissociation of the molecules dissociates on two ions with opposite charge which are positive charged **cations** and negative ones **anions**. These ions looks like two non-interacting ideal gases. This theory did not explained the reason of the dissociation and looks contradicted to the theory of **solvent-solute** interaction which was developed by D.I. Mendeleev.
Modern theory of electrolytes joints both approaches.

Current into the liquid solutions





The chemistry states hat the salts acids and bases are dissociating in a water. The molecule of water is a electrical dipole and dipole are the above listed substances. In these reason the Coulomb forces break the complex molecule of the salts ore the basis on two pieces with a positive and negative charge.

Now if one load into the solution two pin with different electric potentials then the electric current appears. The carrier of the current are ions.

Electric potentials of metals

Atoms of metals have different source to remains the electrons in their electronic surround. Therefore the electrical charge change the ions of one metal to another.

Let us consider the solution with ions of the Cooper like

$$CuSO_4 = Cu^{+2} + SO_4^{-2}.$$

If one include a zinc cylinder (Zn) into the solution then the cooper ions will take the electrons from the zinc and the ions of the zinc will migrate into the solution and the cooper will covered the surface of the zinc cylinder:

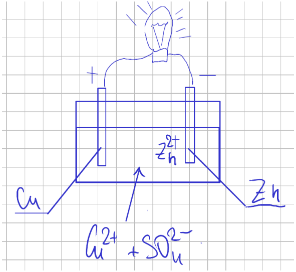
$$Zn + Cu^{+2} = Zn^{+2} + Cu.$$

This process is proceeded in as two different stage:

$$Zn = Zn^{+2} + 2e^{-}, \quad Cu^{+2} + 2e^{-} = Cu.$$

In this case of the chemical reaction proceeds at the place of contact of the ions and the electrons migrate directly on the contact surface of the cylinder.

The chemical source of the electrical current



Now one can divide two sources of the ions. Using two cylinders one of zinc and second one of cooper one obtain the simplest galvanic cell.

A part of these cylinders should be loaded into the solution of the acid. In this case the reaction will be working if one connect these cylinder by the conductor.

The electrons will migrated from zinc electrode to the cooper one over the conductor and the flow of ions appears in the liquid solution.

Lead accumulator

The lead accumulator is one of widespread chemical source of electrical current. It contains lead grids and lead oxide grids. These grids are placed into a water solution of H_2SO_4.
The acid H_2SO_4 is dissociated on the ions:

$$H_2SO_4 = 2H^+ + SO_4^{-2}.$$

The discharge process is defined by two the chemical reactions of oxidized of the lead:

$$Pb + SO_4^{-2} = PbSO_4 + 2e^-$$

and reduced of the lead dioxide:

$$PbO_2 + SO_4^{-2} + 4H^+ + 2e^- = PbSO_4 + 2H_2O.$$

Discharging leads to diminish the acid and metallic lead in the accumulator.

Charging of the lead accumulator

Charging the lead accumulator one should change the direction of the current. In this case following chemical reactions process:

$$PbSO_4 + 2e^- = Pb + SO_4^{-2}$$

and

$$2PbSO_4 + 2H_2O = Pb + PbO_2 + 4H^+ + SO_4^{-2} + 2e^-.$$

The reactions are opposite to the discharging reactions.
The voltage of one lead cell is about 2V.

Lithium-ion accumulators

A lithium-ion accumulators are based on the same electric-chemical processes. The cathode of the accumulator is a $LiCoO_2$ and the anode is the graphite C_6. The cathode and anode in the accumulators looks like a sheets divided by a separation layer which contains cell structure filled by electrolyte. The electrolyte might be the $LiPF_6$.
Charging supports the chemical reactions:

$$Li^+ + e^- + 6C = LiC_6, \quad LiCoO_2 = Li^+ + e^- + CoO_2.$$

In such accumulators lithium does not have a metallic form and the lithium ions change their location from cathode to anode and vice versa.
The voltage of lithium-ion cell should be between 2.5V and 4.1V.

Internal resistance of the chemical sources of electric current

It is clear that the motion of the ions into the accumulators is not ideal. The sources have internal resistance. The resistance depend on integrity of the stuff and the temperature.
So we should consider the source as the source with given voltage V internal resistance r.
This means the voltage under a load will decrease:

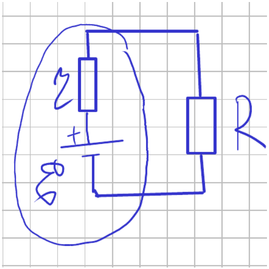
$$u = \mathcal{E} - ri,$$

where $\mathcal{E}$ is the electromotive force and i is the current passed through the battery.
So the short circuit current can be obtained by the formula:

$$i_c = \frac{\mathcal{E}}{r}.$$

Due to small value the internal resistance is neglected often.

Calculation of the circuits with non-ideal sources



Let us consider the circuit with with the non-ideal source of the voltage. The voltage on the source changes due to the external load. Let R is the resistance of an external load and r is an internal resistance of the source. In this case the Ohm's law give us a formula:

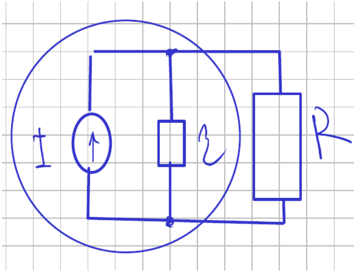
$$i = \frac{\mathcal{E}}{R + r},$$

and

$$U = \mathcal{E} - ir = \mathcal{E}\left(1 - \frac{r}{R + r}\right) = \mathcal{E}\frac{R}{R + r}.$$

The non-ideal source of the voltage can be changed into two serial connected elements of the circuit. One of them is an ideal source of the voltage and another one is a resistor with resistance equal to the internal resistance of modeled non-ideal source.

Non-deal source of current



The source of current with given value i also is non-ideal. So such source may be modeled as an ideal source of the current with given value which is parallel connected with an internal resistance r. For model of the source of current one obtain the fall of the voltage on such element as

$$U = ir.$$

Measurement of the electric properties

The ammeter is the device to measure the value of current. This device generally has extremely low resistance and connected in series with the circuit.

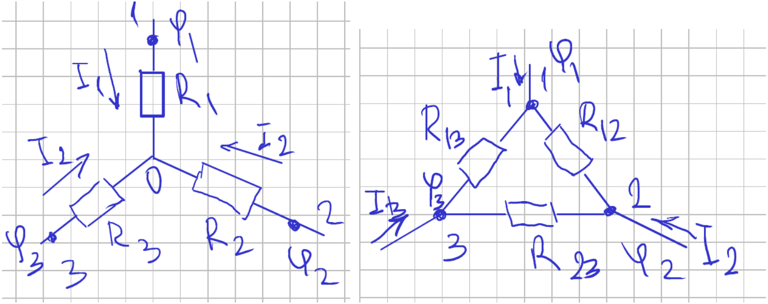
The voltmeter defines the voltage on one or on a group of elements. The voltmeter connected with parallel to the interval of the circuit to find the difference on the voltage on the given element of the circuit.

The ohmmeter is a device for measuring of the resistance. The ohmmeter must be used only for the single device which disconnected with other elements of the circuit.

Measurement of the electric properties

A wattmeter is a device which define the power of the element. To find the value of power one should know the current and full of the voltage on this element. So the connection for the wattmeter is shown here.

$Y \to \Delta$ transform



Let us consider two topologically non-equivalent graphs Y-like and Δ-like. The first Kirchhoff's law for the nod 1 can be written as follows:

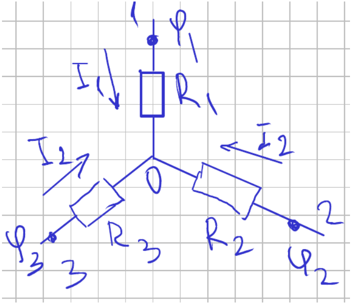
$$I_1 + I_2 + I_3 = 0.$$

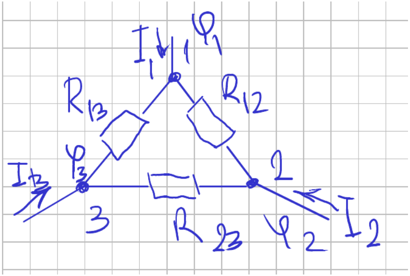
Define the potential of the point k as ϕ_k, then

$$I_k = (\phi_k - \phi_0) g_k.$$

Here $g_k = 1/R_k$ is conductivity.

$Y \to \Delta$ transform





Therefore

$$\sum_k (\phi_k - \phi_0) g_k = 0.$$

It yields:

$$\sum_k \phi_k g_k = \phi_0 \sum_k g_k.$$

As a result one can obtain the value of the potential

$$\phi_0 = \frac{\sum_k \phi_k g_k}{\sum_k g_k}.$$

$Y \to \Delta$ transform

The value I_1 if follows:

$$I_1 = \frac{\phi_1 g_1(g_1 + g_2 + g_3) - (g_1\phi_1 + g_2\phi_2 + g_3\phi_3)g_1}{g_1 + g_2 + g_3}.$$

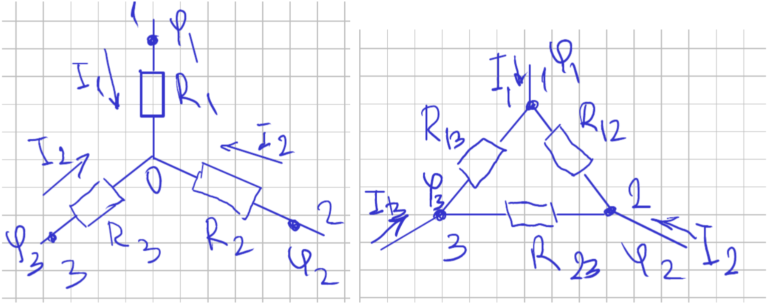
The same current for the triangle:

$$I_1 = g_{12}(\phi_1 - \phi_2) + g_{31}(\phi_3 - \phi_1)$$

The circuits equivalent for any values of ϕ_k. So all ϕ_k are independent parameters. For equivalency of the circuits we need the following equation:

$$g_{13} = \frac{g_3 g_1}{g_1 + g_2 + g_3}, \quad g_{12} = \frac{g_2 g_1}{g_1 + g_2 + g_3}$$

$Y \to \Delta$ transform



The current I_2 cab be written as follows:

$$I_2 = \frac{\phi_2 g_2(g_1 + g_2 + g_3) - (g_1\phi_1 + g_2\phi_2 + g_3\phi_3)g_2}{g_1 + g_2 + g_3}.$$

The same current for the triangle:

$$I_2 = g_{12}(\phi_1 - \phi_2) + g_{32}(\phi_3 - \phi_2)$$

Therefore for the value of g_{32}

$$g_{32} = \frac{g_2 g_3}{g_1 + g_2 + g_3}.$$

$Y \to \Delta$ transform

As a result we get:

$$g_{13} = \frac{g_3 g_1}{g_1 + g_2 + g_3}, \quad g_{12} = \frac{g_2 g_1}{g_1 + g_2 + g_3}, \quad g_{32} = \frac{g_2 g_3}{g_1 + g_2 + g_3}.$$

Let as try to rebuild this equations for the resistances:

$$\frac{1}{R_{13}} = \frac{\frac{1}{R_3}\frac{1}{R_1}}{\frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3}}. = \frac{R_2}{R_2 R_3 + R_1 R_3 + R_1 R_2}.$$

$$\frac{1}{R_{12}} = \frac{R_3}{R_2 R_3 + R_1 R_3 + R_1 R_2}, \quad \frac{1}{R_{23}} = \frac{R_1}{R_2 R_3 + R_1 R_3 + R_1 R_2}.$$

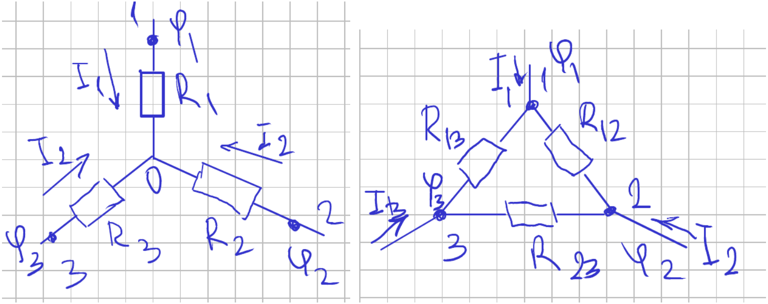
It is convenient to define $\rho = R_2 R_3 + R_1 R_3 + R_1 R_2$, then:

$$\frac{1}{R_{13}}\frac{1}{R_{12}} + \frac{1}{R_{13}}\frac{1}{R_{23}} + \frac{1}{R_{12}}\frac{1}{R_{23}} = \frac{1}{\rho}$$

and

$$\rho = \frac{R_{12} R_{23} R_{13}}{R_{12} + R_{23} + R_{13}}.$$

$\Delta \to Y$ transform



$$\frac{1}{R_{13}} = \frac{R_2}{\rho}, \quad \frac{1}{R_{12}} = \frac{R_3}{\rho}, \quad \frac{1}{R_{23}} = \frac{R_1}{\rho}.$$

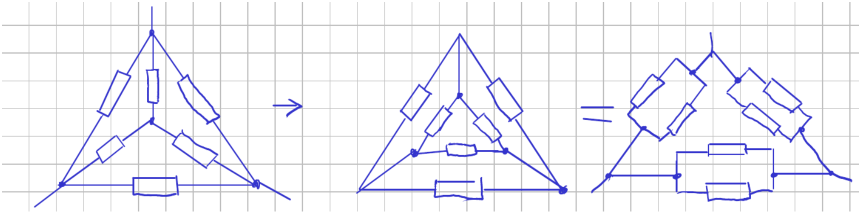
Therefore

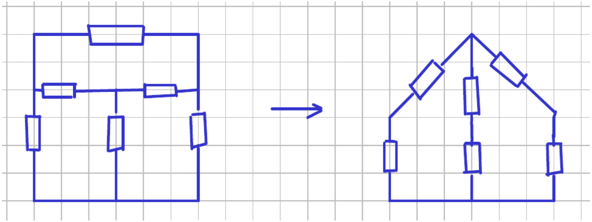
$$R_1 = \frac{R_{12}R_{13}}{R_{12}+R_{23}+R_{13}}, \; R_2 = \frac{R_{12}R_{23}}{R_{12}+R_{23}+R_{13}}, \; R_3 = \frac{R_{23}R_{13}}{R_{12}+R_{23}+R_{13}}$$

and

$$g_{13} = \frac{g_3 g_1}{g_1+g_2+g_3}, \quad g_{12} = \frac{g_2 g_1}{g_1+g_2+g_3}, \quad g_{32} = \frac{g_2 g_3}{g_1+g_2+g_3}.$$

Examples





Summary

- Drude's theory for free electronic gas.
- Chemical electrical sources.
- Star-triangle transformation.