On the Relationship between Electrical Conductivity and Electromigration in Liquid Metals

David K Belashchenko *

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Article

On the Relationship between Electrical Conductivity and Electromigration in Liquid Metals

D.K. Belashchenko

National Research Technological University "Moscow Institute of Steel and Alloys", Moscow 119049, Leninskij prospekt, 4, Russian Federation (retired from 2015); dkbel75@gmail.com.

Abstract: The phenomena of electrical conductivity and electromigration in metallic systems are related, since in both cases the basic physical process is the scattering of conduction electrons by metal ions. Numerous searches have been made for equations connecting the conductivity with elec-tromigration. In the case of a liquid metal, when using the Drude-Sommerfeld (DS) conductivity equation, it was not possible to obtain a quantitative relationship between these phenomena, which would be correct. Attempts to find such a relationship when taking into account the N. Mott correction (g - factor) in the DS equation were unsuccessful. This article proposes a different correction (b - factor) to the DS equation, which takes into account the possibility of varying the momentum transferred by the conduction electron to a metal ion during the scattering. This correction allows to establish a quantitative relationship between conductivity and electromigration, as well as between electromigration in various binary systems with common components, in agreement with experiment. The proposed theory describes well, in particular, two- and multi-component metal systems of any concentration (the consistency rule for triangles A-B, B-C, C-A). The value of b - factor smoothly changes depending on the heat of vaporization of the metal, per unit volume.

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1. Introduction

This article considers two phenomena that are close in physical nature: the electrical conductivity of a metal and the migration of metal components in an electric field. The closeness of these phenomena is beyond doubt, and therefore the search for relations linking them together began at the end of the first half of the last century. The objects of research were both solid and liquid solutions. The theory and practice of electromigration was discussed in monographs [1–9]. Reviews of experiment and theory of electromigration in liquid metals are published in [10–17]. A significant contributions to the mathematical theory of the electromigration were created by V.B. Fiks [3,18,19], H. Hungtington and A. Grone [11,20], R. Sorbello [21,22], B. Baranovski [23], D.K. Belashchenko [4,6], P.P. Kuzmenko and a number of others. To date, interest in electromigration in liquid metals has somewhat decreased. As for solid solutions, on the contrary, interest in them has recently grown greatly, since electromigration is the main cause of degradation of large integrated circuits in computer processors and various microcircuits.

Calculation of electrical resistance of metal.

When calculating the interaction of ions with conduction electrons and calculating the electrical resistance of a metal, the main characteristics are the ion charge ("true") and the scattering cross section of conduction electrons on metal ions. Liquid metals are an example of so-called monogenic systems, where the properties of all ions of a given component are the same (for example, there is no difference between the properties of particles in the ground and activated states). Let us consider the case when a one-component monogenic metal has a mean free path of conduction electrons.

The equation for the electrical resistance of a metal is well known. It was obtained by P. Drude in 1900 on the basis of classical physics:

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$$\rho = \frac{mv}{e^2 nL} \quad (1)$$

Here ϱ is the electrical resistance, m and v are the mass and average velocity of conduction electrons, e is the elementary charge, n is the number of conduction electrons per unit volume, L is the mean free path. It can be derived in various ways, for example, as P. Drude did, calculating the average charge transfer rate along the direction of the field E. In Drude's version, the velocity distribution of electrons was described by the Maxwell-Boltzmann formula. It was assumed that during each collision the electron velocity becomes equal to zero, and between collisions the electron moves uniformly accelerated in the field. The average time between collisions is $\tau = L/v$, the average ion velocity (in the direction of the field) at the moment of collision is $v = eE\tau/m$. The current density is $j = nev = ne^2E$, and taking into account that $\tau v = L$, Formula (1) is obtained.

In A. Sommerfeld's theory, instead of Maxwell-Boltzmann statistics, Fermi-Dirac statistics was used, and instead of direct electron-ion collisions, the concept of electron scattering by a potential field was introduced. Equation (1) has retained its form, but now only Fermi electrons, that are on the Fermi surface and have a velocity v_F, participate in the scattering events. Accordingly, their momentum is equal to $mv_F = \hbar k_F$, where the Fermi vector is:

$$k_F = \pi(3n/\pi)^{1/3} \quad (2)$$

and $n = n_a z$ is the number of conduction electrons per unit volume, where z is the ion charge. Obviously, $n_a = N/V$, where N is the Avogadro number and V is the molar volume. The equations for electrical resistance and conductivity take the form:

$$\rho = \frac{mv_F}{e^2 nL} \quad \text{и} \quad \varkappa = \frac{e^2 nL}{mv_F} \quad (3)$$

In modern theories of conductivity, for example, in the J. Ziman theory [24,25], the wave function of an electron is chosen in the form of a plane wave $\psi(\mathbf{r}) = a\exp(i\mathbf{kr})$, and find the scattering cross section σ of electrons on the atom/ion, which determines the magnitude of the momentum transferred from the electron to the ion during scattering. The calculation of conductivity is reduced to determining the probability of deflection of a conduction electron upon scattering by a system of force centers with a given ion-electron interaction potential. In the case of an isotropic liquid metal, the Fermi surface has the shape of a sphere in k-space with radius k_F. Substituting (2) into (3), we transform the conductivity (3) to the form:

$$\varkappa = \frac{e^2 SL}{12\pi^3 \hbar} \quad (4)$$

Here $S = 4\pi k_F^2$ is the area of the Fermi surface in k-space. The mean free path is related to the scattering cross section σ of electrons on an ion by the expression $n_a L\sigma = 1$, where n_a is the number of ions per unit volume. As a result, equations (1) and (4) can be written as:

$$\rho = \frac{mv_F}{e_0^2 z}\sigma \quad \text{or} \quad \varkappa = \frac{e^2 S}{12\pi^3 \hbar n_a \sigma} \quad (5)$$

where z is the true charge of the ion. Considering multicomponent systems, one should move from the values of z and σ to the average $\bar{z}$ and $\bar{\sigma}$.

2. Materials and Methods

Modification of the Drude - Sommerfeld Equation. Variant N. Mott

As will be shown below, the equations (3) and (4) for the conductivity of a liquid metal have a low accuracy. It can be found out by considering the results of the theory in combination with data for the electromigration of metallic melts. The calculated conductivities may differ by several times

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from the experimental data. However, there are only two players in this field: the free path length L and the magnitude of momentum transfer mv_F. How can the agreement of calculations with theory be improved?

N. Mott [26,27] used the Kubo-Greenwood formulas [28,29] to calculate the conductivity of liquid metals with a short mean free path. Estimates show that when deviating from the free electron model (FEM), the conductivity should depend on the relative density of states of electrons at the Fermi level:

$$g = \frac{N(\varepsilon_F)}{[N(\varepsilon_F)]\text{FEM}} \tag{6}$$

Here N(ε) is the density of states in the conduction band. Various options for the behavior of the density of states in liquid/amorphous conductors are shown in Figure 1:

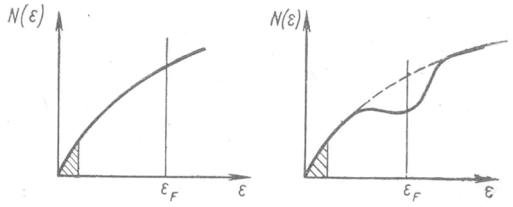

Figure 1. Density of states in melts according to N. Mott. The areas of localized states are shaded. ε_F is the Fermi energy.

According to N. Mott [26,27], in the case of poor conductors, the conductivity $\varkappa$ is expressed in terms of the factor g:

$$\boldsymbol{\varkappa} = \frac{e^2 S L g^2}{12\pi^3 \hbar} \tag{7}$$

According to the meaning of this expression, the factor g should be close to unity for good conductors and less than unity for conductors with a reduced mean free path, in which the character of electron motion approaches hopping. N. Mott's proposal is debatable. It was shown in [30] that taking into account the factor g, one obtains $L = L_z/g^2$, where L_z is the mean free path calculated according to J. Ziman. The result is an equation for conductivity in the form:

$$\boldsymbol{\varkappa} = \frac{e^2 S_z L_z}{12\pi^3 \hbar} \tag{8}$$

where S_z is the area of the Fermi surface in the Ziman approximation. Thus, according to Faber [30], the conductivity should not depend on the presence of the factor g.

Below it will be shown how the g factor of N. Mott can be calculated from the data of conductivity and electromigration.

Modification of the Drude-Sommerfeld Equation. Author's Variant

Let's return to the equations (3)-(5), which determine the resistance or conductivity. Taking into account the form of these expressions, we can consider the factor (mv_F) as the average value of the change in the electron momentum ΔP upon scattering by the ion: ΔP = 0 in the absence of deviation and $\Delta P = 2mv_F$ with a deviation angle of π. Therefore, a variation in the value of ΔP should be allowed. The value of ΔP may depend on the shape of the scattering potential; the more backscattering dominates, the larger the average value of ΔP will be. Let's take as an average momentum change during scattering in a given metal the value $\Delta P = bmv_F$ with a correction factor b. Then the Drude - Sommerfeld equation will be written with a correction in the form:

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$$\varkappa = \frac{e^2 nL}{bmv_F} = \frac{e^2 SL}{12\pi^3 \hbar \mathrm{b}} = \frac{e^2 S}{12\pi^3 \hbar n_a \sigma \mathrm{b}} \quad (9)$$

Comparing with (7), we see that the calculations of the alternative factor b can be carried out in exactly the same way as the calculations of the N. Mott factor g, but with subsequent replacement according to the formula $1/g^2 \rightarrow b$. Of course, the meaning of the factors b and g is completely different. The factor b is responsible for the spatial shape of the probability of electron scattering, and the greater is it, the stronger the backscattering predominates. By the meaning of expression (9), it is assumed that $b < 2$. As will be shown below, the joint consideration of the data on electrical resistance and electromigration makes it possible to calculate the coefficients g and b and choose the correct interpretation of equations (9) and (7).

3. Results

Electromigration Equations

When a current passes through a conductor, forces act on the particles of a metallic solution due to 1) the presence of an electric field and 2) the scattering of conduction electrons by ions. The F_{ifield} field forces depend on the true charges of the ions. Obviously, $F_{ifield} = eEz_i$, where e is the elementary charge, E is the field strength. By this relation we determine the "true" charge of the ion z_i. The concept of the “true” charge z in a metal is not simple and is determined by the type of experiment in which this charge is observed [13]. It was shown in [31] that the true charge z is equal to the number of electrons donated to the conduction band per atom (or the number of holes in the valence band with the opposite sign) if the contribution of Umklapp processes is small. There are no Umklapp processes in liquid and amorphous systems [25], so that z can be taken equal to the number of collectivized electrons per atom of the liquid metal, if no other specific effects inherent in the liquid appear.

The second type of forces acting on metal ions are the electron wind forces, which depend on the scattering of conduction electrons on ions. Let us denote by σ_i the cross section of the scattering of conduction electrons by the i -th ion. The connection of these forces with the scattering cross sections was first established quantum-mechanically by V.B. Fiks [3]:

$$F_{iwind} = - eEnL\sigma_i \quad (10)$$

It is important that this formula can be obtained without introducing into consideration the details of the interaction of ions with electrons, but only taking into account the proportionality between the electron wind force, the field strength, the electron scattering cross section, and the condition of mechanical equilibrium. Let us consider the monogenic multicomponent solutions, in which all particles of a given component behave in the same way [4,6]. Let's put:

$$F_{iwind} = - qeE\sigma_i \quad (11)$$

where i is the number of the component, and q is the coefficient unknown so far. The total force of the electron wind acting on all particles of the solution can be written:

$$F_{wind} = - qeE \sum_i n_i \sigma_i$$

where n_i is the number of particles of the i-th component, and the sum is taken over all components. Since the conductor as a whole is neutral, the total force acting on it from the electric current must be equal to zero. Therefore, the condition of mechanical equilibrium of all ions in an electric field looks like this:

$$\sum_i (F_{iField} + F_{iWind})\, n_i = 0$$

or

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$$eE\ (\sum_i n_i z_i\ -\ q\sum_i n_i \sigma_i) = 0$$

Let us divide this equality by the total number of atoms/ions n_a. The n_i/n_a ratios are the mole fractions X_i. From here we find q:

$$q = \frac{\sum_i n_i z_i}{\sum_i n_i \sigma_i} = \frac{\sum_i X_i z_i}{\sum_i X_i \sigma_i} = \frac{\bar{z}}{\bar{\sigma}}$$

Superscript symbols indicate average values. The mean cross section $\bar{\sigma}$ is related to the mean free path by the formula $n_a L\bar{\sigma} = 1$ (see above). Consequently, $q = \bar{z} n_a L = nL$, and substituting into (11) we obtain V.B. Fiks formula (10).

So, the total force acting on the i -th ion is equal to

$$F_i = eEz_i - qeE\sigma_i = eE\ (z_i - \sigma_i \frac{\bar{z}}{\bar{\sigma}})$$

Let's call the value in brackets the effective charge of the i -th ion z_i^* :

$$z_i^* = z_i - \sigma_i \frac{\bar{z}}{\bar{\sigma}} \qquad (12)$$

This expression is the **basic electromigration equation**. With respect to monogenic solutions, it is accurate and does not require any corrections. The total force acting on the i-th ion is:

$$F_i = eEz_i^*$$

The total force acting on the all particles of a binary solution is equal to zero:

$$X_1 z_1^* + X_2 z_2^* = 0, \text{ from which a useful relation follows: } {z_1^*}/{X_2} = -{z_2^*}/{X_1}. \qquad (13)$$

For the ratio of scattering cross sections, it follows from (12):

$$\frac{\sigma_i}{\bar{\sigma}} = \frac{z_i - z_i^*}{\bar{z}} \qquad (14)$$

Let us write expressions for the effective charges of the components of a binary monogenic solution of any concentration. In this case, $\bar{\sigma} = X_1\sigma_1 + X_2\sigma_2$ и $\bar{z} = X_1 z_1 + X_2 z_2$. Substituting these formulas into relation (12), we obtain

$$z_1^* = \frac{z_1\ \sigma_2 - z_2\ \sigma_1}{X_1\ \sigma_1 + X_2\sigma_2}\ X_2$$

or

$$z_1^* = \frac{\frac{z_1\ \sigma_2}{\sigma_1}\ -\ z_2}{1 -\ (1 -\ \sigma_2/\sigma_1)X_2} X_2 \qquad (15)$$

Similarly, for the second component we find: $z_2^* = \frac{\frac{z_2\ \sigma_1}{\sigma_2} - z_1}{1 - \left(1 - \frac{\sigma_1}{\sigma_2}\right)X_1} X_1$. We see that the effective charges are determined by the true charges of the ions and the ratio of the cross sections for the scattering of conduction electrons on the ions of the components.

As an example, Figure 2 shows the effective charges during electromigration in the Bi-Cd binary system at 300°C. The measurements were carried out in vertical glass capillaries with an inner diameter of about 1 mm and a length of 40 mm, with a direct current of 1 A. The steady state was achieved after annealing for several days [6,13], with Cd ions moving upwards. After rapid cooling, the metal wire-like samples were removed from the capillary, cut into pieces 4 mm long, and

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analyzed chemically or radiochemically. The effective charge was calculated according to the equation [4,13]:

$$\frac{dln\, a_i}{dx} = \frac{eEz_i^*}{kT}$$

where x is the sample length coordinate, a_i is the thermodynamic activity of the i -th component, E is the field strength, e is the elementary charge, k is the Boltzmann constant, T - temperature.

If in a given binary metallic system the ion charges z_i and the scattering cross section ratios σ_2/σ_1 do not depend on the concentration, then the expressions for the effective charges have the form:

$$z_1^* = \frac{a\, X_2}{1 - bX_2} \tag{16}$$

and accordingly for z_2^*. By measuring the concentration dependence of effective charges, one can calculate the ratios σ_2/σ_1 and estimate the ion charges z_i. In the case of the Cd-Bi system, the effective charges at 300°C are well described by the expression [4,13]:

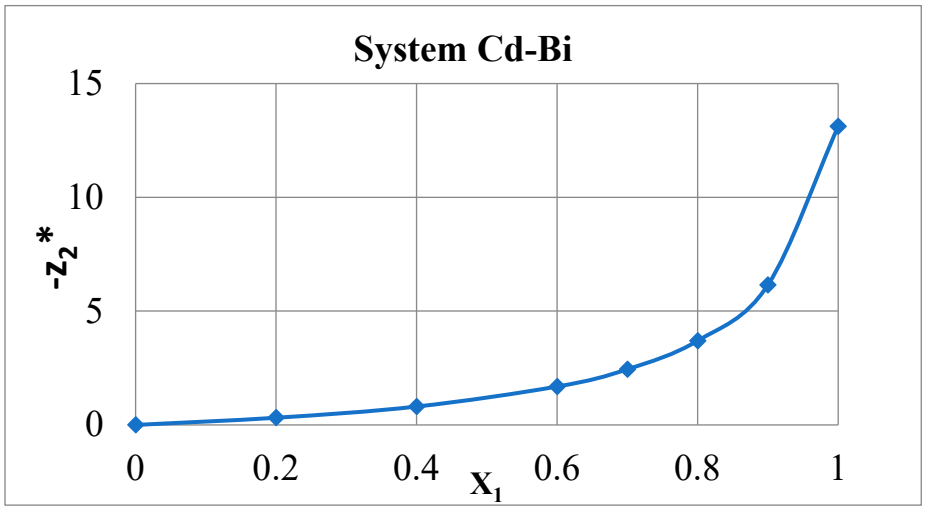

Figure 2. Effective charges in the Cd - Bi system at 300°C. X_1 - molar part of Cd.

z_{Bi}^* = -1.286 X_{Cd} / (1 - 0.902 X_{Cd}), in the system Bi-Pb $z_{Bi}^* = -\frac{1.50X_{Pb}}{(1+0.78X_{Pb})}$, in the system Cd-Pb $z_{Pb}^* = -1.111X_{Cd}/(1 - 0.813X_{Cd})$, in the system Bi-Sn $z_{Sn}^* = 2.56X_{Bi}/(1 + 0.337X_{Bi})$, in the system Pb-Sn $z_{Pb}^* = -\frac{0.546X_{Sn}}{(1-0.658X_{Sn})}$ etc.

The cross section ratios σ_B/σ_A can be calculated using formulas (15) and (16). These ratios may depend on the concentration. Figure 3 shows the concentration dependences of the ratios σ_B/σ_A for some binary systems. These data can be used to estimate the average values of σ_B/σ_A. For Sn-Cd, Bi-Cd, Bi-Sn, Pb-Cd, Pb-Sn, Bi-Pb systems, they are 0.30, 0.13, 0.46, 0.23, 0.81, 0.64, respectively [4]. If three binary systems formed by three components A, B, and C are studied at the same temperature, then the values σ_A/σ_B, σ_B/σ_C, and σ_C/σ_A can be determined for these systems. Their product must be equal to 1.00. For the Cd-Sn-Pb triangle we get 0.30*0.46/0.13 = 1.06, for the Cd-Pb-Bi triangle we find 0.23*0.64/0.13 = 1.13, for the Sn-Pb-Bi triangle we find 0.81*0.64/0.46 = 1.12. The deviations from unity are reasonable here.

Based on the estimated ratios of the cross sections σ_2/σ_1 given above, it is possible to calculate the ratios of the electrical resistances for pairs of pure liquid metals using the Sommerfeld equation (5). They are shown in Table 1.

It can be seen that in the above cases of the simplest eutectic systems, equation (5) gives an error of up to 20-30%, so its significant refinements are required.

So, the electrical resistance/conductivity of a metal is expressed in terms of the average electron scattering cross section on ions, and the effective charges are expressed in terms of the ratios σ_2/σ_1.

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Obviously, these phenomena are connected with each other, and it is required to find more exact correlations between them.

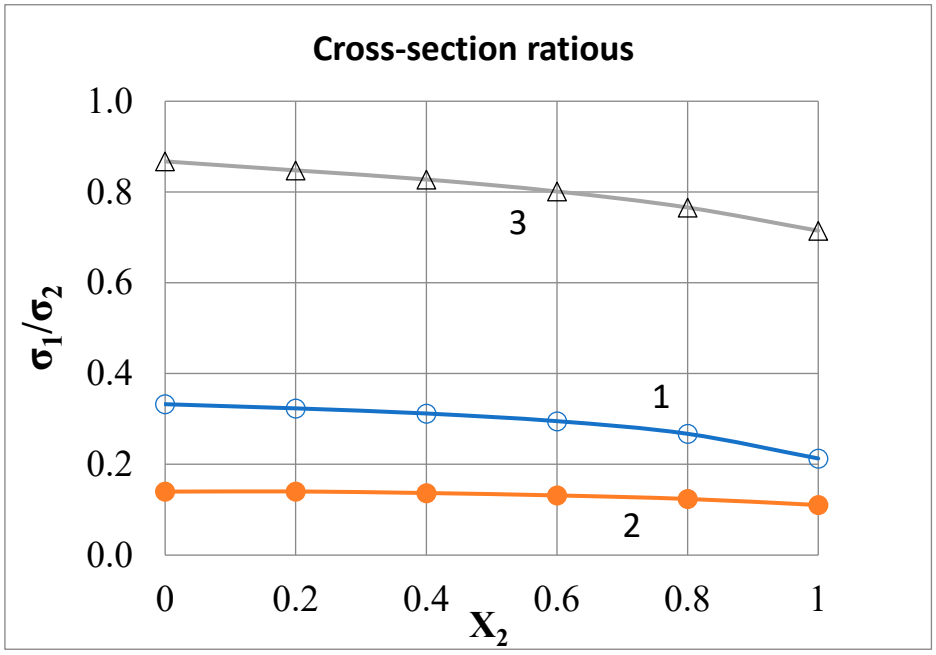

Figure 3. Scattering cross section ratios σ_1/σ_2 for systems: 1 - Cd-Sn at 300°C, 2 - Cd-Bi at 300°C, 3 - Sn-Pb at 350°C.

Table 1. Checking of Equation (5).

Pairs of metals	σ_2/σ_1	ϱ_1/ϱ_2 using (5)	ϱ_1/ϱ_2, exp
Sn-Cd	0.30	1.96	1.48
Bi-Cd	0.13	3.61	3.91
Pb-Cd	0.23	2.46	3.06
Bi-Pb	0.64	1.30	1.28
Pb-Sn	0.81	1.18	1.89
Bi-Sn	0.46	1.75	2.63

4. Discussing

Relationship between Effective Charge and Electrical Resistance. Drude-Sommerfeld Variant

Attempts to establish a relationship between electrical resistance and electrical transfer were made quite a long time ago [4]. They were based on the postulate that the scattering cross sections in the phenomena of conduction and electrotransport coincide. We will also proceed from this postulate.

The theory was tested by comparing data on the effect of impurities on the electrical resistance of solvents and electromigration data in highly dilute solutions. Usually, in calculations, equation (4) was used, written as:

$$\rho = \frac{(mv)_F}{e^2}\,\frac{\bar{\sigma}}{\bar{z}} \tag{17}$$

where ϱ is the electrical resistivity, $(mv)_F$ is the momentum of the Fermi electrons, and $\bar{z}$ and $\bar{\sigma}$ are the average values for the components of the metallic solution. Let us calculate the derivative $d\ln \varrho/dX_2$, assuming the true ion charges z_1 and z_2 to be constant. In addition, we take into account that

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the scattering cross sections σ_1 and σ_2 are related by the Gibbs-Duhem equation $X_1 d\sigma_1 + X_2 d\sigma_2 = 0$ [6]. Then for the averages $\bar{\sigma}$ and $\bar{z}$ it turns out:

$$d\bar{\sigma} = \sigma_1 dX_1 + \sigma_2 dX_2 = (\sigma_2 - \sigma_1)\, dX_2 = \sigma_1(\sigma_2/\sigma_1 - 1)\, dX_2$$

Taking into account equation (12), we obtain for a strongly diluted solution of the 2nd component in the 1st, when $z_1^* \to 0$ и $\bar{z} \to z_1$:

$$d\bar{\sigma} = (\sigma_1/z_1)(z_2 - z_1 - z_2^*)\, dX_2$$

Accordingly, for $\bar{z} = z_1X_1 + z_2X_2$ we find, assuming the charges z_i to be constants:

$$d\bar{z} = d(z_1X_1 + z_2X_2) = (z_2 - z_1)\, dX_2$$

Hence $d(\bar{\sigma}/\bar{z}) = -\frac{\sigma_1 z_2^*}{(\bar{z})^2}\, dX_2$. Taking into account (17) it turns out:

$$\frac{1}{\rho}\frac{d\rho}{dX_2} = -\frac{z_2^*}{\bar{z}}\frac{\sigma_1}{\bar{\sigma}}$$

For extremely dilute solutions based on the 1st component, we have:

$$\frac{1}{\rho}\frac{\Delta\rho}{X_2} = -\frac{z_2^*}{z_1} \qquad (18)$$

This equation was obtained earlier by E.I. Kharkov [32]. From this expression it follows that the positive effective charge should have impurities that lower the electrical resistance of the solvent.

An addition should be made. Since equation (17) includes the factor $(mv)_F = \hbar k_F = \pi\hbar(3N\bar{z}/\pi V)^{1/3}$ (according to Sommerfeld), then $\varrho = a(\bar{z}/V)^{1/3}$ and $\ln\varrho = \ln a + (1/3)\ln\bar{z} - (1/3)\ln V$ (a is some constant number). Thus, we get an additional term to the right side of equation (18):

$$\frac{1}{\rho}\frac{\Delta\rho}{X_2} = -\frac{z_2^*}{z_1} + \frac{1}{3}\left(\frac{z_2 - z_1}{z_1} - \frac{\Delta V}{V_1}\right) \qquad (19)$$

This additive usually has a value of the order of 0.01 - 0.1 and does not play a significant role.

Relation (19) can be verified on amalgams. The data are given in Table 2. The ΔV values were calculated according to the additivity rule taking into account the molar volume of mercury $V_1 = 14.81$ cm³/mol at 20°C. Figure 4 shows the dependence of the function $\Psi = -\frac{z_2^*}{z_1} + \frac{1}{3}\left(\frac{z_2 - z_1}{z_1} - \frac{\Delta V}{V_1}\right)$ on $\frac{1}{\rho}\frac{\Delta\rho}{X_2}$ for dilute solutions of impurities in mercury at 20°C according to [1]. If equation (19) is correct, the points in Figure 4 should be located on the diagonal passing through the origin and the 1st and 3rd quadrants. In fact, equation (19) does not hold well. In several cases, it is violated even in sign. However, the low accuracy of the experimental data should also be noted.

Table 2. Electromigration in amalgams and influence of impurities on the resistance of mercury at 20°C [1]. 1st component - Hg.

Impurity	$\Delta\varrho/c$, μΩ·cm/at.%	$\Delta\varrho/X_2\varrho_1$	V_2, cm³/mol	z_2^*/z_{Hg}
Li	-2.0	-1.67	13.48	0.16
Na	0.7	0.58	24.8	-0.22
K	2.9	2.42	47.9	-0.66
Cs	-	-	11.7	-2.43
Ag	-3.7	-3.08	29.08	0.72
Au	-	-	9.52	0.73
Mg	-	-	14	0.5
Ca	-3.51	2.92	14	<0.05
Zn	-4.4	-3.67	18.1	0.62
Cd	-3.7	-3.08	19.44	0.62
Cd	-	-	20.9	0.83 [33]
Tl	-2.1	-1.75	17.3	0.0

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Pb	-5.8	-4.83	11.8	0.0
Bi	-3.7	-3.08	13.48	-0.69
Sn	-6.5	-5.42	24.8	0.33

Another way to check Equation (17) is a direct comparison of the calculated resistances of liquid metals. In [34], the electrical resistance of a number of liquid metals was calculated using the expression following from Formula (17):

$$\frac{\rho_A}{\rho_B} = \frac{(mv)_{FA}}{(mv)_{FB}} \frac{\sigma_A}{\sigma_B} \frac{z_B}{z_A}$$

Here ϱ_A and ϱ_B are the electrical resistivity of pure metals A and B. The cross section ratios σ_A/σ_B can be taken from electromigration data when they depend little on concentration. Good agreement between calculation and experiment was obtained only for Pb, Bi, Sb; for Ag, Cu, Sn, the discrepancy reaches 50–100%, and for Hg and Al, it is even greater. In [7], especially noticeable discrepancies - by a factor of 2 - 3 - were obtained for Cd, Hg, Ga, In.

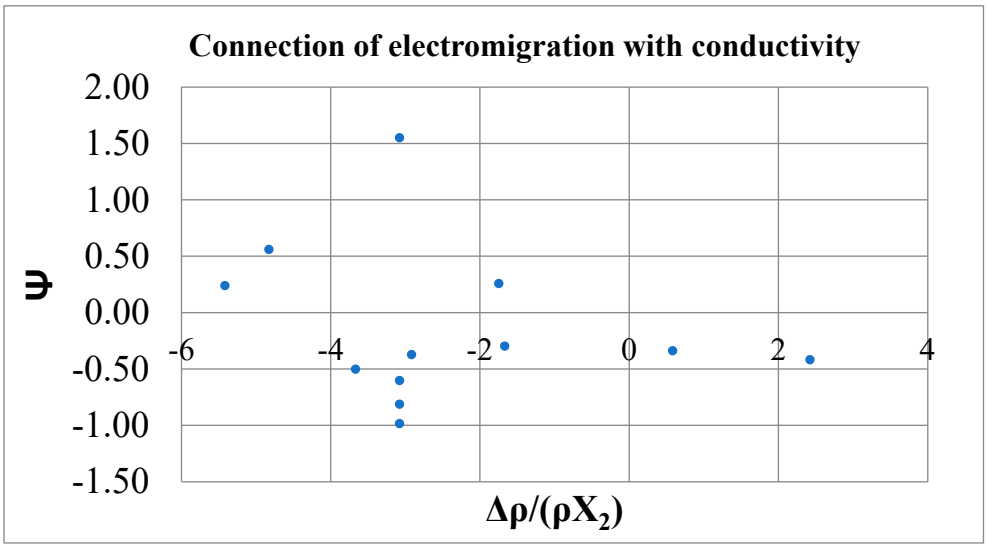

Figure 4. Relationship between effective charges and resistance increments. Dilute solutions of impurities in mercury at 20°C [1].

The main reason for the failure of the above calculations is the deviation of the properties of liquid metals from the Drude-Sommerfeld model (17) and from equation (1). Further development of the theory consists of taking into account deviations from this model.

N. Mott Variant. Integral Relations

Let us transform equation (9), taking into account the fact that $S = 4\pi k_F^2$ and $n_a = N/V$, where N is the Avogadro number and V is the molar volume of the liquid. In these notations, the conductivity is equal to:

$$\varkappa = \frac{e^2}{3\pi^2 \hbar N} \frac{k_F^2 g^2 V}{\bar{\sigma}} \quad (20)$$

Let us apply this formula to calculate the cross section $\bar{\sigma}$, assuming the factor g to be a given function of the concentration. In what follows, the results of [6,35,36] will be used. Let us express the cross section σ_i from Eq. (12):

$$\sigma_i = (z_i - z_i^*)\frac{\bar{\sigma}}{\bar{z}}$$

We multiply both sides of this equation by dX_i, sum over all components, and divide by $\bar{\sigma}$:

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$$\frac{1}{\bar{\sigma}} \sum \sigma_i dX_i = \frac{\sum z_i dX_i}{\bar{z}} - \frac{\sum z_i * dX_i}{\bar{z}} \quad (21)$$

On the left is just $d\bar{\sigma}/\bar{\sigma}$. Further, since $\bar{z} = \sum X_i z_i$, the same reasoning as for the connection between $\bar{\sigma}$ and σ_i applies to the charges z_i. Therefore, the equation $d\bar{z} = \sum z_i dX_i$ must also hold. Taking these formulas into account, expression (21) can be transformed: $\frac{d\sigma}{\sigma} = \frac{d\bar{z}}{\bar{z}} - \frac{\sum z_i^* dX_i}{\bar{z}}$.

Integrating from the 1st composition of the solution to the 2nd, we find:

$$\ln \frac{\sigma_{(2)}}{\sigma_{(1)}} = ln \frac{\bar{z}_2}{\bar{z}_1} - \int_{(1)}^{(2)} \frac{\sum z_i^* dX_i}{\bar{z}}$$

Let us now express the cross section $\bar{\sigma}$ from Eq. (20). Replacing the conductivity $\varkappa$ with ϱ^{-1}, we obtain [35,36]:

$$\ln \frac{\bar{z}_1 \rho_{(2)} V_{(2)} (k_F^2 g^2)_{(2)}}{\bar{z}_2 \rho_{(1)} V_{(1)} (k_F^2 g^2)_{(1)}} = - \int_{(1)}^{(2)} \frac{\sum z_i^* dX_i}{\bar{z}} \quad (22)$$

Here, the sum is taken over all components of the monogenic solution.

In the particular case of a two-component monogenic solution, equation (22) can be simplified. The mechanical equilibrium condition takes the form [13]: $X_1 z_1^* + X_2 z_2^* = 0$. Hence,

$$\sum z_i^* dX_i = z_1^* dX_1 + z_2^* dX_2 = z_1^* \frac{dX_1}{X_2} \quad (23)$$

From here

$$\ln \frac{\bar{z}_{(1)} \rho_{(2)} V_{(2)} (k_F^2 g^2)_{(2)}}{\bar{z}_2 \rho_{(1)} V_{(1)} (k_F^2 g^2)_{(1)}} = - \int_1^0 z_1^* \frac{dX_1}{\bar{z} X_2} = \int_0^1 z_1^* \frac{dX_1}{\bar{z} X_2} \quad (24)$$

The integral on the right has the meaning of the average value of the fraction $< z_1^*/\bar{z}X_2 >$ over the concentration interval. The simplest systems to analyze are those in which the fraction $\frac{z_1^*}{\bar{z}X_2}$ depends little on the concentration. The error of calculations increases for systems with inversion of electromigration, where the effective charge of the component changes sign over the integration interval.

Let us express the effective charges in terms of the other characteristics of the solutions. Differentiating equation (24) with respect to concentration of solution (2), we obtain [6]:

$$\frac{z_2^*}{X_1} = \bar{z} \left[\frac{d\ln \rho}{dX_1} + \frac{d\ln V}{dX_1} + \frac{d\ln (k_F^2 g^2)}{dX_1} - \frac{d\ln \bar{z}}{dX_1} \right]$$

Taking into account formula (23), this gives:

$$\frac{z_2^*}{X_1} = z_2 - z_1 + \bar{z} \left[\frac{d\ln \rho}{dX_1} + \frac{d\ln V}{dX_1} + \frac{d\ln (k_F^2 g^2)}{dX_1} \right]$$

Taking the usual expression $k_F = 2\pi \left(\frac{3N\bar{z}}{8\pi V} \right)^{1/3}$, then finally we find:

$$\frac{z_2^*}{X_1} = \frac{z_2 - z_1}{3} + \bar{z} \left[\frac{d\ln \rho}{dX_1} + \frac{1}{3} \frac{d\ln V}{dX_1} + 2 \frac{d\ln g}{dX_1} \right] \quad (25)$$

If in a given binary system the right side of equation (25) vanishes at some concentrations, then $z_1^* = z_2^* = 0$. This is the condition for inversion of the direction of electromigration. Such an inversion was observed in some systems (Na–K [29]; Na–Hg, K–Hg, Ba–Hg [38]; Cd–Zn [39]; Al–Zn [40], etc.). In the particular case when $z_1 = z_2$, V = const, and g = const, it follows from Eq. (25) that for $z_2^* = 0$ we have $d\ln\varrho/dX_1 = 0$. This condition for inversion was proposed by E.I. Kharkov [32].

Let us differentiate expression (25) with respect to temperature, assuming that the ion charges are independent of temperature. Then [6]:

$$\frac{1}{X_1} \frac{dz_2^*}{dT} = \bar{z} \left[\frac{d^2 \ln \rho}{dX_1 dT} + \frac{d^2 \ln V}{dX_1 dT} + 2 \frac{d^2 \ln g}{dX_1 dT} \right] \quad (26)$$

This equation describes the temperature dependence of effective charges in a binary monogenic solution.

Consistency Rule

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Let us take in binary system some solution of arbitrary composition X (state 1), and pure second component at $X_2 = 1$ as state (2). Then [6,35,36]:

$$\ln \frac{z_2^0 \rho V (k_F^2 g^2)}{\bar{z}_1 \rho_{(2)} V_{(2)} (k_F^2 g^2)_{(2)}} = \int_0^{X_1} z_2^* \frac{dX_1}{\bar{z} X_1} \quad (27)$$

and all factors with the index "2" on the left side refer to the pure 2nd component. Let us denote the ratio $k^2_F g^2/(k^2_F g^2)_{(2)} = \theta_2^X$. Then it turns out:

$$\theta_2^X = \frac{(k_F^2 g^2)_{(x)}}{(k_F^2 g^2)_{(2)}} = \frac{z_x \rho_2 V_2}{z_2 \rho_x V_x} exp\left[\int_0^X z_2^* \frac{dX_1}{\bar{z} X_1}\right]$$

If we take (X) = (1), then:

$$\theta_2^1 = \frac{(k_F^2 g^2)_{(1)}}{(k_F^2 g^2)_{(2)}} = \frac{z_1 \rho_2 V_2}{z_2 \rho_1 V_1} exp\left[\int_0^1 z_2^* \frac{dX_1}{\bar{z} X_1}\right] \quad (28)$$

Here, the values with indices 1 and 2 refer to the pure 1st and 2nd components. If we follow the theory of N. Mott, then as a result of calculations we can obtain the ratio $\theta_2^1 = \frac{(k_F^2 g^2)_{(1)}}{(k_F^2 g^2)_{(2)}}$ for components of the binary system.

Let us consider three binary systems formed by three components A, B, and C at the same temperature. Equation (28) can be used to determine the quantities θ_B^A, θ_C^B и θ_A^C for these systems. Their product, by definition of the function θ, must be equal to 1. From formula (28) it follows that [6]:

$$\int_0^1 z_B^* \frac{dX_A}{\bar{z} X_A} + \int_0^1 z_C^* \frac{dX_B}{\bar{z} X_B} + \int_0^1 z_A^* \frac{dX_C}{\bar{z} X_C} = 0$$

This is the so-called **consistency rule**. It must be satisfied if the above assumptions about the monogeneity of solutions and the existence of a mean free path are valid. This rule gives also a way to test the assumptions about the behavior of the "true" ion charges in binary systems A–B, B–C, and A–C.

In N. Mott's variant, one can also check the consistency of data for three binary systems of a triangle by multiplying the ratios g_A/g_B, g_B/g_C, and g_C/g_A calculated by (28). For the Ag-Cu-Sn triangle, three ratios of factors g are obtained [6]:

$$A = \frac{g_{Ag}}{g_{Sn}} \frac{g_{Sn}}{g_{Cu}} \frac{g_{Cu}}{g_{Ag}} = (1.11 \pm 0.02)(0.76 \pm 0.01)(1.165 \pm 0.01) = 0.98 \pm 0.03$$

Accordingly, for the triangle Hg-In-Tl [6]:

$$A = \frac{g_{Hg}}{g_{In}} \frac{g_{In}}{g_{Tl}} \frac{g_{Tl}}{g_{Hg}} = 0.342/(0.771*0.448) = 0.991 \pm 0.030$$

Therefore, for these triangles, the consistency rule holds well. According to [6], good reliability of the consistency rule was also obtained for many other triangles (see Table 3).

Table 3. Checking the consistency rule.

Triangle	A
Cd-Bi-Pb	1.057 ± 0.04
Sn-Bi-Pb	1.077 ± *0.04*
Cd-Sn-Bi	0.99 ± *0.04*
Ag-Cu-Sn	0.98 ± 0.03
Ag-Cu-Ge	1.03 ± 0.03
K-Na-Cs	0.97 ± 0.12
Cd-In-Tl, $z_{Tl} = 3$ everywhere	0.995
Cd-In-Tl, $z_{Tl} = 3$ in Tl, 5 in Cd and In, linearly depends on the concentration	1.043
Cd-In-Tl, $z_{Tl} = 5$ in Tl, 3 in Cd and In, linearly depends on the concentration	1.053
Cd-In-Tl, $z_{Tl} = 5$ everywhere	1.092

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Cd-In-Tl, $z_{Tl} = 3$ in Tl, 1 in Cd and In, linearly depends on the concentration	0.927
Cd-In-Tl, $z_{Tl} = 2$ everywhere	0.930
Hg-In-Tl, $z_{Tl} = 3$ everywhere	0.991 $\pm$ 0.03

For all triangles, except K-Na-Cs, the consistency is very good. In the case of alkali metals, the calculation accuracy is reduced due to the presence of electromigration inversion.

From Table 3 it can be seen that the values of the true ion charges can be chosen taking into account the values of consistency. It can be assumed that the correct choice of the ion charges provides the best consistency of the triangle. Table 3 shows that the best choice for Tl ions is $z_{Tl} = 3$ everywhere.

Calculation of the Factor g

Knowing the behavior of the function $\theta_2 = \theta_2^X$, we can calculate the ratio g/g_2, where g_2 is the value of the factor g of the pure 2nd component. From the formula for k_F it follows that $\left(\frac{k_F}{k_{F2}}\right)^2 = \left(\frac{\bar{z}}{z_2^0}\frac{V_2}{V}\right)^{\frac{2}{3}}$. Obviously, this ratio has the meaning of θ when the condition g = l is satisfied. This ratio can be denoted by θ_{FEM}. Then:

$\frac{g}{g_2} = \left(\frac{\theta_2}{\theta_{2FEM}}\right)^{1/2} = (\theta_2)^{1/2}\left(\frac{z_2^0 V}{\bar{z}\,V_2}\right)^{1/3}$. So one can calculate g/g_2 for various melts of binary system. For definiteness, we adopted the "cadmium" scale, at which $g_{Cd} = 1.00$. The Mott factors g calculated in this way are shown in Table 4.

Table 4. Factors g on the Cadmium scale ($g_{Cd} = 1.00$).

Metal	T, °C	g/g_{Cd} [6]	b/b_{Cd}	ΔH_{subl}, kcal/mol	V_{mol}, cm³/mol	$\Delta H_{subl}/V$
Cs	110	0.31	(10.41)	17.97	72.2	0.249
K	110	0.51	(3.84)	20.95	42.35	0.496
Te	500	0.58	(2.97)	11.9	22.15	0.538
Hg	300	0.77	1.69	14.54	14.67	0.981
Na	250	0.84	1.42	25.0	24.50	1.02
Cd	300-500	1.00	1.00	24.54	14.07	1.76
Bi	300-500	1.00	1.00	41.05	20.8	1.98
Pb	300-500	1.00	1.00	45.44	19.08	2.29
Tl	350	1.07	0.87	40.8	18.08	2.26
Zn	500	1.09	0.84	28.56	9.82	2.91
Sb	(500)	1.17	0.73	57.5	18.8	3.06
In	350	1.18	0.72	55.56	16.32	3.41
Sn	300-500	1.23	0.66	68.77	16.96	4.06
Ga	300	1.29	0.60	64.4	11.44	5.63
Al	580	1.33	0.57	67.8	10.96	6.18
Ag	1100	1.38	0.53	63.3	11.36	5.57
Ge	1100	1.58	0.40	78.2	13.2	5.92
Cu	1100	1.63	0.38	72.8	7.57	9.62
Li	-	1.20	0.69	32.2	13.72	2.35
Rb	-	0.42	5.67	18.11	57.9	0.313
Au	-	1.33	0.57	84.6	16.8	5.04
Be	-	2.21	0.20	74.1	5.3	14.0
Mg	-	0.99	1.02	31.5	15.33	2.05
Ca	-	0.88	1.29	38.6	27.4	1.41
Ba	-	0.76	1.73	35.7	38.7	0.92

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Si	-	1.45	0.48	71	11.2	6.44

Remark: 1 kcal/mol = 4.184 kJ/mol.

The factual material is shown above on electromigration in binary systems, from which it is clear that the factor g is indeed a function of state. Table 4 shows the calculated values of the factor g for the studied liquids. The most significant fact that is not consistent with the theory of N. Mott is that the value of g is not directly related to the mean free path and the dimensionless free path criterion Lk_F. Metals with a long mean free path - liquid Cs, Na, K - are characterized by a small (less than unity) factor g. Metals with low conductivity and low Lk_F (Pb, Sb, Bi) have higher g values. The factor g does not correlate with either the electron concentration in the conduction band or properties such as melting point and critical temperature. However, data analysis reveals a good correlation between the value of g and the heat of vaporization of a unit volume of the substance ΔH/V, i.e., the volumetric binding energy density of the liquid metal. The dependence of g on $(\Delta H/V)^{1/3}$ turns out to be close to linear at $(\Delta H/V)^{1/3} > 2$ $(kcal/cm^3)^{1/3}$ (Figure 5). At smaller values of ΔH/V, the points for Cs, K, and Te also lie on a smooth curve.

Hence it follows that the factor g, not having the properties of the supposed N. Mott factor, nevertheless plays an important role in the processes of scattering of conduction electrons and has the properties of function of the state. Apparently, some other reason for deviations from the equations of conductivity and electromigration is hidden behind the factor g. In this regard, another version of the description of these processes, proposed below, should be considered.

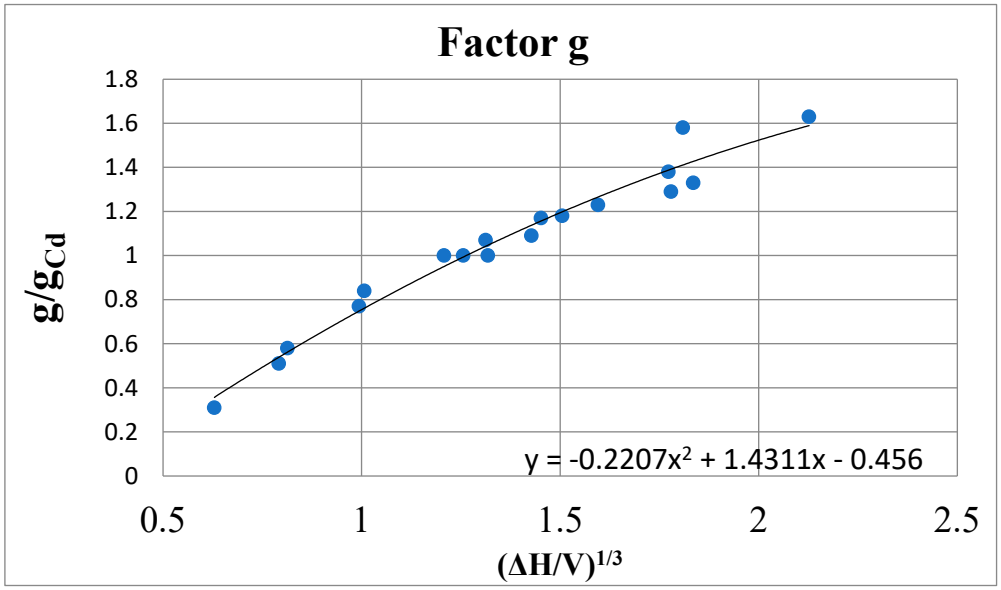

Figure 5. Dependence of the factor g/g_{Cd} on the heat of vaporization of the metal per unit volume $(\Delta H/V)^{1/3}$ $(kcal/cm^3)^{1/3}$. Data from Table 3.

Alternative Variant of the Author

In this option, it is required to calculate the factor b in the Drude-Sommerfeld equation (9) using data on conductivity and electromigration. It has already been noted above that the calculations of the alternative factor b can be carried out in exactly the same way as the calculations of the Mott factor g, but with its subsequent replacement according to the formula $1/g^2 \rightarrow b$. Of course, the meaning of the factors b and g is completely different. The factor b is responsible for the spatial shape of the probability of electron scattering, and the greater b is, the stronger the backscattering predominates. According to the meaning of the factor, it is assumed that $b < 2$. Formula (24) takes the form:

$$\ln \frac{\bar{z}_{(1)} b_{(1)} \rho_{(2)} V_{(2)} (k_F^2)_{(2)}}{\bar{z}_{(2)} b_{(2)} \rho_{(1)} V_{(1)} (k_F^2)_{(1)}} = \int_{(1)}^{(2)} z_2^* \frac{dX_1}{\bar{z} X_1} \qquad (29)$$

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Instead of the factor g^2 in the numerator, we get the factor b in the denominator. Therefore, the values of the factor b of the metals considered above can be determined by the formula $1/g^2 \rightarrow b$, using the g values from Table 4. They are shown in the same table and in Figure 6. The factor b monotonically decreases with increasing ΔH/V, and for $b < 2$ the graph is described by the exponent $y = 5.4612\exp(-1.327x)$. The minimum value $b = 0.38$ was obtained for copper, which has the maximum volumetric heat of evaporation.

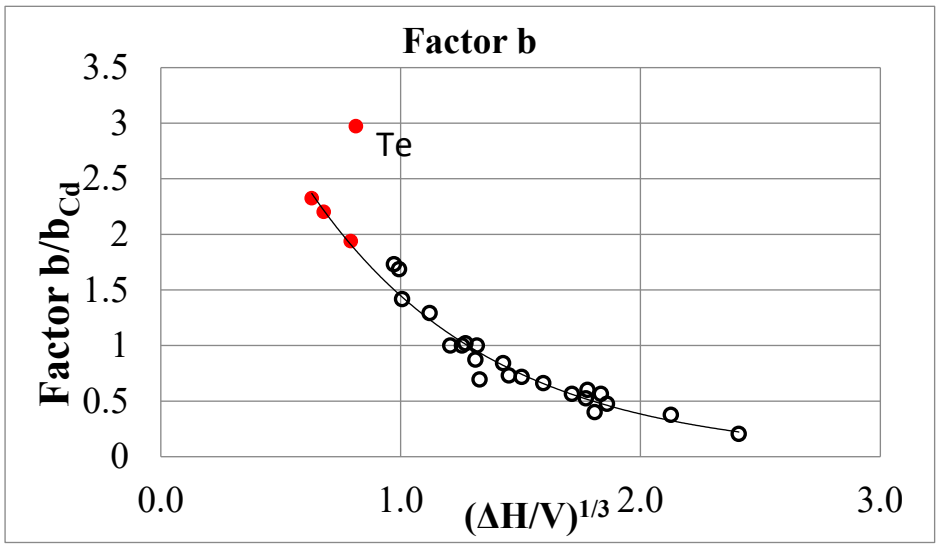

Figure 6. Dependence of factor b on the heat of vaporization per unit volume of metal. The points at $b > 1.75$ for Cs, Rb, and K were obtained by extrapolation. $|\Delta H/V|$ = kcal/cm^3.

These data are consistent with the meaning of the factor b, which is implied in the author's version. The magnitude of the momentum change upon scattering is in most cases less than $2(mv)_F$ and smoothly depends on the evaporation energy per unit volume. The abnormal value for Te is explained by the fact that this substance is a semimetal with high electrical resistance, and for it the above theory requires correction.

A special group is formed from alkali metals Na, K, Rb, Cs, which are the components of many systems with inversion of electromigration. An example of such a system - Na–K - is shown on Figure 7. The electrical resistance isotherm is bell-shaped with a high maximum at 59 at.% K [6].

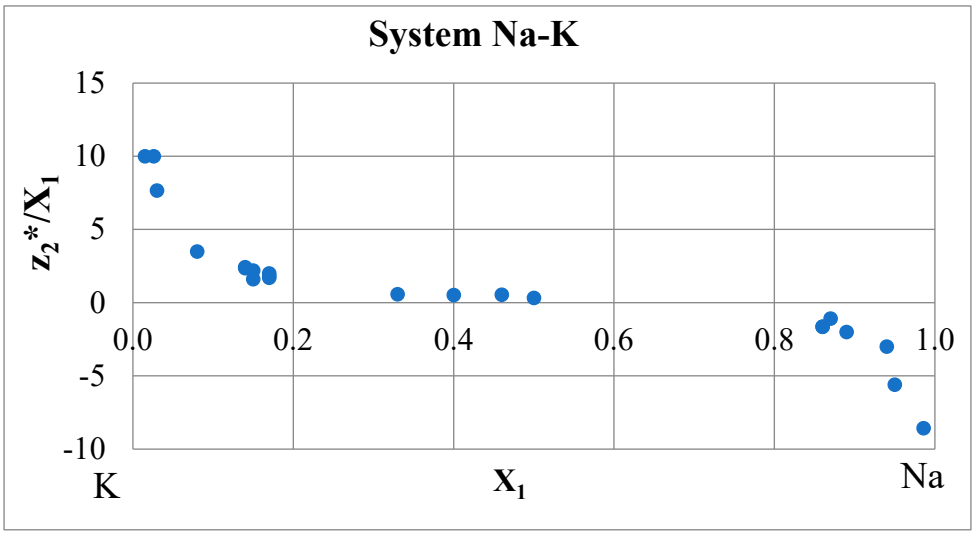

Figure 7. Effective charges in the Na-K system at 110°C [6,41].

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The effective charge isotherm on Figure 7 has an almost symmetric shape, and the integral in expression (28) is small due to the cancellation of the positive and negative contributions. Effective charges in dilute solutions strongly depend on concentration. In [42], the electromigration of traces of Na and K in liquid K and Na, respectively, was studied. The effective charges are approximately -20, that is noticeably more, than in Figure 7. Therefore, the error in calculating the area under the curve $z_2^*/X_1\bar{z}$ is rather large. This applies not only to the Na-K system, but also to similar Na-Cs and K-Cs systems [6,43].

The ratio of scattering cross sections σ_2/σ_1 in a binary system was calculated from electromigration data [formula (12)]. Figure 8 shows how the ratio σ_2/σ_1 changes where the electrical resistance isotherms are bell-shaped. In the Na-K system at 110°C and $X_1 \approx 0$ the ratio $\sigma_2/\sigma_1 = 0.077$, and at $X_1 \approx 1$ it is equal to $\sigma_2/\sigma_1 = 10.74$.

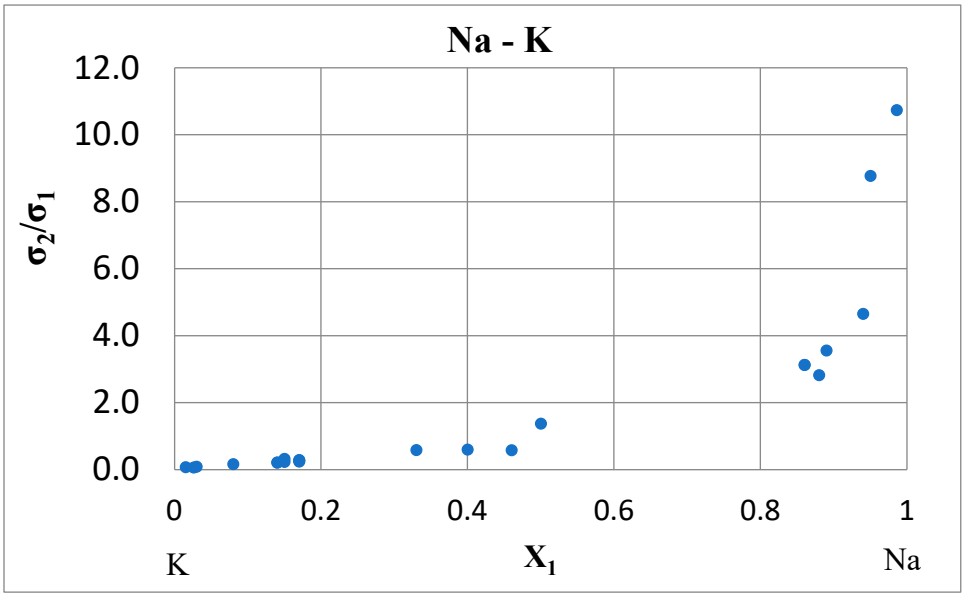

Figure 8. The ratio of scattering cross sections σ_2/σ_1 in the Na-K system at 110°C [41].

Let us estimate the role of the integral (29) in calculating the factor b. For the Na - K system at 110°C ϱ_1 = 10.13 μΩ·cm, ϱ_2 = 17.35 μΩ·cm, V_1 = 24.8 cm³/mol, V_2 = 47.9 cm³/mol, the left side of expression (29) is equal to $\ln \frac{b_{(1)}\rho_{(2)}V_{(2)}(k_F^2)_{(2)}}{b_{(2)}\rho_{(1)}V_{(1)}(k_F^2)_{(1)}} = \ln(b_{Na}/b_K) + 0.758$, and with the hypothetical value of the integral (29) 0.5 we would get $b_K \approx 1.84$ (see Table 4). The actual value of the integral is difficult to estimate due to ambiguities in highly dilute solutions. For the Na - Cs system at 110°C ϱ_1 = 10.13 μΩ·cm, ϱ_2 = 46.6 μΩ·cm, V_1 = 24.8 cm³/mol, V_2 = 74.0 cm³/mol, so that the left side of expression (29) is equal to $\ln\frac{b_{(1)}\rho_{(2)}V_{(2)}(k_F^2)_{(2)}}{b_{(2)}\rho_{(1)}V_{(1)}(k_F^2)_{(1)}} = \ln(b_{Na}/b_{Cs}) + 1.890$. Effective charges in the Na - Cs system at 110°C are shown in Figure 9 [6,43]. The integral in Equation (29) for the Na - Cs system is clearly greater than zero, but it is rather difficult to estimate it without accurate data in highly dilute solutions.

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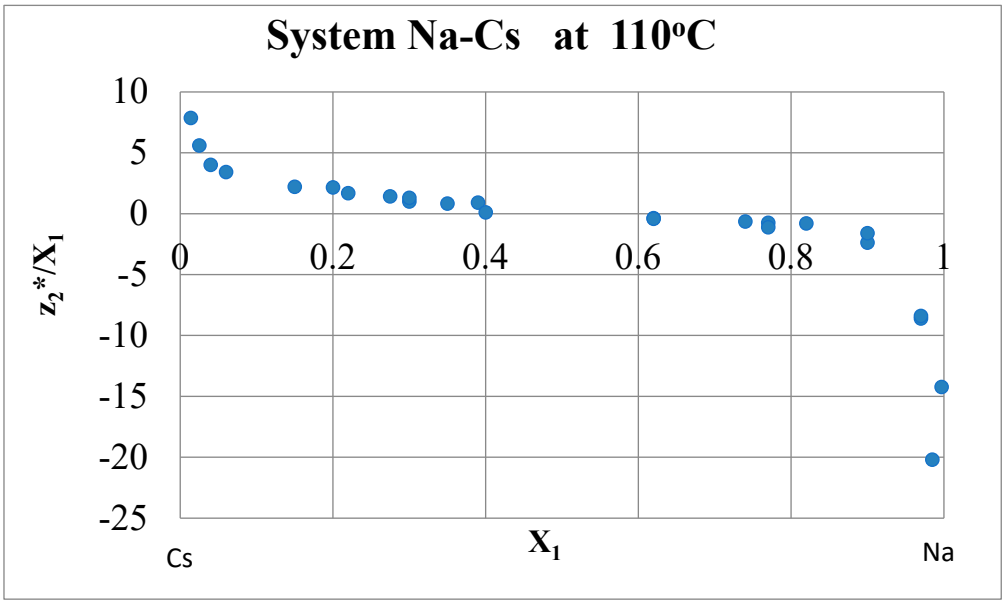

Figure 9. Effective charges in the Na-Cs system at 110°C [6,43].

The situation is similar in the K-Cs system [6,43]. Therefore, for the time being, we can accept the approximate values of the factors b/b(Cd) for K, Rb, Cs, obtained by extrapolation (see Figure 6).

5. Conclusions

A detailed evaluation of the Drude-Lorentz-Sommerfeld equation and electromigration equations shows that, taking into account the implied values of the momentum transfer of conduction electrons during scattering by metal ions/atoms, the original form of the conductivity equation (1) or (4) leads to irremovable discrepancies with experiment. These discrepancies can be eliminated by introducing an additional coefficient into the equation for conductivity/electrical resistance. The use of the correction factor g proposed by N. Mott makes it possible to eliminate these discrepancies, but the calculated corrections do not agree with the physical picture, proposed by N. Mott. The author of this article substantiated the introduction of a correction $b < 2$ into the Sommerfeld conductivity equation, which takes into account variations in the mean magnitude of momentum transfer during the scattering of conduction electrons by ions. The main point is an account of internal connection between conductivity and electromigration. The calculated values of factor b regularly change in accordance with the value of the volumetric heat of evaporation $\Delta H/V$. This means that the interaction potentials between ions and conduction electrons play a decisive role both in the phenomenon of scattering and in the energetics of the metal.

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