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ELECTROMIGRATION IN LIQUID METALS

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I. INTRODUCTION

The concept of electromigration (or electrodiffusion, electrolytic migration, etc.) covers a range of phenomena associated with the directed displacement of the components of a solution when an electric current is passed through the solution. Since a real substance, even when chemically pure, in general consists of a solution either of different isotopes or of defects of different types in a matrix (vacancies, displaced atoms, etc.) and, moreover, contains activated complexes in a transition state, the phenomenon of electromigration may be and is observed even in pure substances.

The magnitude of the electromigration effect depends on various factors: the nature of the solution, the magnitude of the electric field, concentration, temperature, and other parameters. Since the directed displacement (migration) during electromigration (e.m.) takes place due to and by means of the random diffusion movements of individual particles, the direct relation between the elementary acts of diffusion and e.m. is obvious. If the external electric field applied to the system is weak compared with the atomic field, the role of the external field is merely a certain ordering of the individual elementary acts of diffusion but does not lead to a change in the mechanism of the acts themselves. This feature is related to the fact that a weak external field may be regarded as a perturbation which alters the number of particles undergoing migration with the field and against the field but does not influence the frequency of these displacements. The frequency of the displacements may depend on the external field when the change in potential energy associated with the displacement of a charged particle and its environment in the external field becomes comparable with the activation energy of the diffusion process. For this it is necessary to use a field with an intensity of 10^7–10^8 V cm^{-1}, which is hardly possible.

The elementary act of diffusion is a fairly complex process, particularly in metals. A charge introduced into a metal should be screened by the conduction electrons. These screening electrons are usually not localised close to the central charge (impurity ion) and they cannot be regarded as moving behind the central charge like the rigid sheath of an ion. Thus the elementary act of diffusion in a metal involves not only the displacement of the charged impurity ion but also the redistribution of the conduction electrons in space, leading to more or less complete screening of the ion throughout the whole path of the displacement. In the case of electromigration, these processes take place together with the passage of current through the metal, so that the interaction of the ion itself and the screening charge with the stream of conduction electrons becomes significant. As a result of all these features, the electromigration effects characterise not only the charge of the ions of the components of the solution but also the state of the conduction electrons and the interaction of the former with the latter. Thus the study of electromigration makes it possible to investigate not only the electrical properties of the diffusing particles but also the mechanism and characteristic features of the elementary act of diffusion itself.

The phenomenon of e.m. has recently become one of the most widespread means of studying ionic crystals and semiconductors. In the case of ionic crystals this is due chiefly to the fact that in these crystals the e.m. (ionic conduction) is responsible for the electrical conductivity of the substance and is a property which is extremely sensitive to the formation of charged complexes, defects, etc., in the crystal. The study of e.m. in salts is facilitated by the possibility of producing intense electric fields (10^4–10^5 V cm^{-1}). The study of e.m. in semiconductors makes it possible to establish the sign and magnitude of the charge on the impurity, which determines its action as an alloying additive (donor or acceptor behaviour). In view of the importance of impurities in metallurgy and in semiconductor physics, the study of e.m. in these materials is being widely developed.

Unfortunately, insufficient attention is as yet being paid to the study of e.m. in metallic systems. This is due partly to the fact that the magnitude of e.m. in metals is relatively low (the transport numbers of ions in metallic solutions, in the most favourable case, amount to 10^{-4}–10^{-5} mole × × $faraday^{-1}$). In addition, the lack of a satisfactory theory of e.m. is hindering considerably the development of experimental work in this field. Only in recent years has interest in the study of e.m. increased, chiefly in connection with the discovery that it is possible to separate isotopes by means of e.m. in liquid metals. Work has also begun on the study of e.m in solid metallic solutions and pure metals, chiefly in the USSR. A characteristic feature is the effort to advance from qualitative on semi-quantitative studies to a precise quantitative characterisation of e.m. It should be noted, however, that until recently the interpretation of the results of e.m. measurements were oversimplified. Einstein's relationship between mobility and diffusion coefficient makes it possible to use the rate of movement of an impurity in an electric field to determine a certain characteristic with the dimensions of charge — "the effective charge" — whose magnitude is determined not only by the charge of the diffusing ion but also by all the interactions between this ion and the surrounding system of ions and electrons. In earlier work, however, this effective charge was identified with the "true charge" of the ion, and on this basis far-reaching conclusions were made regarding the nature of the interaction in solutions, etc. The position has recently changed somewhat. In the study of e.m., allowance is now being made for the so-called "electron wind", that is, the interaction of the stream of electrons (the electric current) with the impurity ions. These and other features complicate considerably the picture of diffusion migration in an electric field and make the interpretation of experimental data difficult. In particular, there is as yet no reliable method for calculating the "true charge" of an ion from the magnitude of the effective charge during electromigration in solid solutions.

In the study of e.m. in liquid metallic solutions, the position is even less satisfactory. Despite much work carried

out in this direction, there are very few trustworthy experimental data. This is due to the unreliability of the procedures used. The chief factor leading to incorrect results is apparently convection produced by the high current densities, heating of the alloy, and the influence of density gradients produced during electromigration.

Generally speaking, liquid solutions provide a simpler object for study than solid solutions. Since the activation energy of diffusion in liquid metals is smaller by about one order of magnitude than that in solid solutions and is close to the energy of the thermal movement of the atoms, the difference between the ground state and the transition state for a liquid is apparently of little significance. It is then possible, as a first approximation, to neglect the discontinuous nature of diffusion migrations and to take as a basis a model of electromigration according to which the impurity ion drifts at a constant velocity in a viscous liquid under the influence of an electric force. This treatment avoids the difficulties associated with a detailed examination of the immediate environment of the diffusing ion and facilitates the interpretation of experimental results.

Experimental work has revealed a fairly distinct boundary between e.m. in liquid and solid metals. This boundary apparently does not indicate any fundamental difference in their behaviour, but certain qualitative differences are evident. The main reasons for these differences may be assumed to be the absence of a rigid lattice in the crystals and, as already noted, the appreciable difference in the activation energies of diffusion. A position has thus arisen, in which studies in each of the two fields are carried out by different methods, and different results are obtained. The investigation of the reasons for the differences should lead to a better understanding of the mechanism of diffusion in both cases.

The present review deals with the results of the study of e.m. in liquid metallic solutions.

II. PHENOMENOLOGICAL DESCRIPTION OF ELECTROMIGRATION IN LIQUID METALS

The first attempts to give a quantitative description of e.m. for the particular case of extremely dilute binary metallic solutions were made by Wagner[1] and Schwarz[2]. Wagner introduced the mobilities of the solvent and impurity u_1 and u_2, the coefficients of self-diffusion of the solvent D_1 and diffusion of the impurity D_2, the charges of the ions of the solvent $z_1 e$ and impurity $z_2 e$, where e is the charge of the electron. The velocities of the ions in a field with intensity 1 V cm^{-1} are

$$v_1 = \frac{z_1 e u_1}{300}; \quad v_2 = \frac{z_2 e u_2}{300}. \tag{1}$$

Wagner introduced the transport number of the impurity t_2 as the increase in the mole fraction of impurity at the cathode, related to a constant number of moles of the mixture at the cathode and divided by the number of equivalents of charge passed. Using Einstein's relationship

$$u_i = \frac{D_i}{kT}, \tag{2}$$

Wagner obtained[1,3]

$$\frac{t_2}{N_2} = \frac{96\,500}{300}\,\frac{z_2 D_2 - z_1 D_1}{\varkappa}\,\frac{N e d_1}{RTA_1}, \tag{3}$$

where N_2 is the mole fraction of the impurity, $\varkappa$ the conductivity of the solution in Ω^{-1} cm^{-1}, N Avogadro's number, d_1 the density of the solvent, A_1 its atomic weight, R the gas constant, and T the absolute temperature. Wagner used formula (3) to calculate the values of t for a number of amalgams, taking z_1 and z_2 equal to the chemical valencies.

Wagner's treatment of e.m. in liquid solutions cannot be regarded as satisfactory, for the following reasons.

1. If diffusion processes take place in a liquid, in most cases it is rational to select a system of taking readings which is related not to the liquid but to the vessel containing it. The total volume flow (the flow of particles multiplied by their volume) due to the diffusion of each component should then be equal to zero. In this case the kinetics of the process would be determined not by the two diffusion coefficients D_1 and D_2 but merely by a single hetero-diffusion coefficient $D = D_1 N_2 + D_2 N_1$ (see, for example, Belashchenko[5] and Wagner[6]).

2. The ions in the solution are influenced not only by the force of the field $Ff = eEz$, where E is the field intensity, but also by other forces. In actual fact, in the presence of only field forces, all the ions of the solution or pure metal as a whole would be influenced by a force not equal to zero. Because of the electrical neutrality of the conductor, however, the passage of current through it should not lead to the production of a resultant force. It is therefore necessary to take account of other forces in addition to the field forces, and these should not be internal forces (of the type exemplified by Stokes' frictional forces), since the resultant of internal forces is equal to zero. These additional forces are produced by the interaction between the ion subsystems and the conductivity electrons. Moreover, it is necessary to take account of the interaction between different types of ion subsystem.

Schwarz[2] examined the problem of e.m. from a different viewpoint, making use of the analogy between the behaviour of charges in an electric field and that of particles of different mass in a gravitational field. A mass immersed in a liquid is acted upon by a displacing force. By analogy, when current is passed through a metallic solution, each impurity ion is acted upon by an "electrohydrostatic force" proportional to its volume and the solvent charge density. The charge densities of each component are

$$\alpha_1 = \frac{ez_1}{\bar{v}_1}; \quad \alpha_2 = \frac{ez_2}{\bar{v}_2}, \tag{4}$$

where $\bar{v}_1$ and $\bar{v}_2$ are the partial volumes of the solvent and impurity ions. Since the electrohydrostatic force opposes the field force (otherwise the components would not accumulate at the electrodes during e.m. but would be deposited on them), it should be directed towards the anode. Thus the impurity ion is acted upon by two forces: the field force $F_f = eEz_2$ and the electrohydrostatic force

$$F_{eh} = \bar{v}_2 \alpha_1 E, \tag{5}$$

which can be calculated from Archimides' law. The resultant force is

$$F_2 = F_f - F_{eh} = E\bar{v}_2(\alpha_2 - \alpha_1). \tag{6}$$

By using Einsten's relationship and taking the solvent as the fixed system of coordinates, Schwarz obtained

$$\frac{t_2}{N_2} = \frac{96\,500}{300}\,\frac{N D_2 d_1 e}{RTA_1 \varkappa}\left(\frac{z_2}{\bar{v}_2} - \frac{z_1}{\bar{v}_1}\right)\bar{v}_2. \tag{7}$$

The values of z in Schwarz' treatment are arbitrary and are not equal to the ordinary chemical valencies.

Schwarz' treatment is also unsatisfactory, although it is better than Wagner's method. Schwarz does in fact take account of the existence of a force acting in a direction opposite to that of the field force, but he arbitrarily assumes that it is proportional to the volume of the ion. With this assumption, the total force acting on all the ions of the solution is again not equal to zero, and the condition of mechanical equilibrium between the current and the conductor is broken down.

Wagner[6] showed that Schwarz' introduction of the "electrohydrostatic force" is equivalent to the statement that in the solution the quantities of equal magnitude are not the transport numbers of each of the two components, as in Wagner's work[1], but the volume streams of the ions of each type, and this provides a more satisfactory description of the properties of the liquid. Wagner[6] also pointed out that no method has yet been found for determining the charges of the ions z_1 and z_2 (that is, for taking account of the interaction between the ions and the stream of electrons) and that formulae (3) and (7) are only approximate.

Drakin[7] calculated the stationary state in a concentrated binary solution on the basis of classical thermodynamics. In the virtual transfer of one mole of the first component from the origin of coordinates to the point l, the work of transfer is

$$A_1 = RT \ln \frac{a_0'}{a_l'}, \tag{8}$$

where a_0' and a_l' are the activities of the first component at the origin of coordinates and at the point l. At equilibrium, this work should be equal to the electrical work, so that

$$RT \ln \frac{a_0'}{a_l'} = \Delta U z_1 F, \tag{9}$$

where ΔU is the potential drop on the given section, and F is the Faraday. Similarly, for the transfer of one mole of the second component in the opposite direction,

$$RT \ln \frac{a_l''}{a_0''} = -\Delta U z_2 F. \tag{10}$$

Combining (9) and (10), Drakin obtained the stationary-state equation

$$\ln \frac{a_0'}{a_0''} - \ln \frac{a_l'}{a_l''} = \frac{\Delta U F (z_1 - z_2)}{RT}. \tag{11}$$

The transport number t_i in dilute solution is given by

$$\frac{t_i}{N_i} = \frac{D (z_1 - z_2) F^2}{\varkappa RT}. \tag{12}$$

The method used by Drakin to calculate the stationary state in e.m. was criticised by Baranowski[8], who pointed out that since the solution–current system is not an equilibrium system but merely a stationary system, it is necessary to apply to it the methods of not classical thermodynamics but the thermodynamics of irreversible processes. This criticism also applies to the theories of Schwarz and Wagner.

Baranowski[9,10] examined e.m. using Onsager's method. Let us use the symbols I_k to denote the streams of the ions of the components, and I_e to denote the stream of electrons. We then have

$$I_k = \sum_1^n L_{ki} X_i + L_{ke} X_e,$$
$$I_e = \sum_1^n L_{ei} X_i + L_{ee} X_e, \tag{13}$$

where L_{ps} represents the kinetic coefficients ($L_{ps} = L_{sp}$), n the number of components, and X the thermodynamic forces

$$X_i = -\operatorname{grad} \mu_i - e_i \operatorname{grad} \varphi,$$
$$X_e = -\operatorname{grad} \mu_e + F \operatorname{grad} \varphi, \tag{14}$$

where μ_i is the molar chemical potential of the ith component, e_i its molar charge, μ_e the molar chemical potential of the electron, and φ the electric potential. Allowance is then made for the electrical-neutrality condition

$$\sum_1^n e_i c_i - F c_e = 0, \tag{15}$$

where c is the concentration, and for the relationship between the flows of the components

$$\sum_1^n I_i \bar{v}_i = 0, \tag{16}$$

where $\bar{v}_i$ represents the partial volumes of the components, and the quantities e_i' are introduced from the formulae

$$L_{ke} = \sum_{i=1}^{n-1} L_{ki} e_i'. \tag{17}$$

We then have[10]

$$I_k = \sum_{i=1}^{n-1} L_{ki} \left(X_i - \frac{\bar{v}_i}{\bar{v}_n} X_n + e_i' X_e \right),$$
$$I_e = \sum_{k=1}^{n-1} \sum_{i=1}^{n-1} L_{ki} e_i' \left(X_k - \frac{\bar{v}_k}{\bar{v}_n} X_n \right) + L_{ee} X_e. \tag{18}$$

The case of an extremely dilute binary solution is then taken. In this case

$$X_1 = -\operatorname{grad} \mu_1 - e_1 \operatorname{grad} \varphi,$$
$$X_2 = -e_2 \operatorname{grad} \varphi,$$
$$X_e = F \operatorname{grad} \varphi. \tag{19}$$

Introducing the symbol

$$e_1 - \frac{\bar{v}_1}{\bar{v}_2} e_2 - e_1' F = E^*, \tag{20}$$

Baranowski obtains for the stationary state ($I_1 = I_2 = 0$) the condition

$$\frac{\operatorname{grad} \mu_1}{\operatorname{grad} \varphi} = -E^*, \tag{21}$$

where the subscript "1" refers to the impurity.

In diffusion in a metallic solution, an electrodiffusion potential is produced

$$\frac{\operatorname{grad} \varphi}{\operatorname{grad} \mu_1} = \frac{t_1}{F}, \tag{22}$$

where t_1 is the transport number of the impurity, equal to I_1/I_e when $\operatorname{grad} \mu_1 = 0$.

The relationship between the diffusion coefficient, t_1, and E^* is given by

$$D = \frac{\varkappa t_1 RT [1 + \partial \ln f_1 / \partial \ln c_1]}{c_1 E^* F}, \tag{23}$$

where f_1 is the activity coefficient.

According to Baranowski[9,10], the quantity E^* is the characteristic transport charge and has the significance of the "effective charge" of the impurity ions, calculated for 1 g-ion.

When $e_1' = 0$ and $\bar{v}_1 = \bar{v}_2$, Eqn. (21) becomes Drakin's formula (11). In the case of solid alloys, where the condition for the relationship between the streams of ions can

be neglected, the quantity E^* becomes equal to $e_1 - e'_1F$ — see (20).

The quantities μ_i in (14) have the significance of the chemical potentials of the ions. The final result — Eqns. (21) and (22) — however, should contain the chemical potential of the "neutral" component, whose relation to the concentration of the solution is known from thermodynamic data. Let us denote the chemical potential of the first component (not the ion!) by the symbol μ_1^*. We then have

$$\mu_1^* = \mu_1 + \frac{e_1}{F}\mu_e, \tag{24}$$

since in solution we have the equilibrium

$$i\text{th atom} \rightleftarrows i\text{th ion} + \frac{e_i}{F}(\text{electron}).$$

Thus

$$\operatorname{grad}\mu_1^* = \operatorname{grad}\mu_1 + \frac{e_1}{F}\operatorname{grad}\mu_e. \tag{25}$$

For a very dilute solution, however, $\operatorname{grad}\mu_e = 0$, so that $\operatorname{grad}\mu_1^* = \operatorname{grad}\mu_1$ and in Eqns. (21) and (22) it is possible to replace μ_1 by μ_1^*.

An examination of e.m. in a two-component metallic solution with any concentration at constant temperature was made by Belashchenko and Zhukhovitskii [11] for the particular case where $\bar{v}_1 = \bar{v}_2$, i.e. $I_1 + I_2 = 0$. Onsager's equations were written in the form

$$I_i = L_{ik}X_k (i, k = 1, 2, 3), \tag{26}$$

where I_1 and I_2 are the streams of ions of the first and second components, and I_3 the stream of electrons (summation with respect to k). The forces X_i are

$$\begin{aligned} X_1 &= -\frac{\partial\mu_1}{\partial x} - e_1\frac{\partial\varphi}{\partial x}, \\ X_2 &= -\frac{\partial\mu_2}{\partial x} - e_2\frac{\partial\varphi}{\partial x}, \\ X_3 &= -\frac{\partial\mu_3}{\partial x} - e_3\frac{\partial\varphi}{\partial x}, \end{aligned} \tag{27}$$

where μ_1, μ_2, and μ_3 are the chemical potentials of the individual ions (not the atoms of the components!) of the first and second types and of the electrons, e_1, e_2, and e_3 their charges (in cgs units), x the coordinate of the length of the specimen, and φ the electric potential. The electrical-neutrality condition is of the form

$$\sum_{i=1}^{3} e_i I_i = I, \tag{28}$$

where I is the density of the external current passing through the system. From the condition $I_1 + I_2 = 0$, it follows [11] that

$$\begin{aligned} L_{11} &= -L_{12} = L_{22}, \\ L_{13} &= -L_{23}. \end{aligned} \tag{29}$$

The chemical potentials of the atoms μ^* (which can be measured in a thermodynamic experiment) were then introduced [11]:

$$\begin{aligned} \mu_1^* &= \mu_1 - \frac{e_1}{e_3}\mu_3, \\ \mu_2^* &= \mu_2 - \frac{e_2}{e_3}\mu_3. \end{aligned} \tag{30}$$

Eqns. (30) are equivalent to Eqns. (24). Solution of systems (26)–(27) with allowance for (28)–(30) and the Gibbs–Duhem equation gives the result [11]

$$I_1 = c_1u_1E - D\frac{\partial c_1}{\partial x}, \tag{31}$$

where μ_1 is the mobility of the first component, E the field intensity due to the external current, and $E = I/\varkappa$, where $\varkappa$ is the conductivity. In e.m. the gradients of the chemical potentials of the ion and electron are combined in such a way that the diffusion (or electrodiffusion) stream depends, in the final analysis, only on the gradient of the chemical potential of the neutral atoms. This feature confirms the familiar view that the measurement of the potential jump at a phase boundary, not only by equilibrium measurements but also by kinetic measurements, is impossible.

Belashchenko and Zhukhovitskii [11] defined the "effective charge of the ion" e_i^* by the relationship

$$u_i = \frac{D}{kT}e_i^*\frac{\partial\ln c_i}{\partial\ln a_i}, \tag{32}$$

where a_i is the thermodynamic activity of the ith component. This charge has a simple physical significance: if a total moving force F_i acts upon the ith ion in solution, we have

$$e_i^* = \frac{F_i}{E}, \tag{33}$$

where E is the field intensity due to the external current. Thus the effective charge of the ion e^* takes account of the ordinary field force, the interaction of the ion with the stream of electrons, the interaction of ion subsystems of different type, etc. The factor $d\ln c_i/d\ln a_i$ in (32) indicates, as usual, the deviations of the properties of the solution from ideal behaviour.

In the stationary state, $I_1 = 0$ and [11]

$$\frac{\partial\ln a_1}{\partial x} = \frac{e_1^*E}{kT}. \tag{34}$$

An analogous equation is applicable for the second component. The effective charges are related to one another by the condition that the total force acting on the whole of the solution is equal to zero (the condition of mechanical equilibrium)

$$c_1e_1^* + c_2e_2^* = 0. \tag{35}$$

It was shown [12] that Baranowski's formula (21) for the stationary state in the case of an infinitely dilute solution is equivalent to (34). In this case E^* from (20) is equal to Ne_1^*, where N is Avogadro's number.

In the case of diffusion in a non-uniform open specimen we should observe an effect which is the opposite of electromigration — the production of an electrodiffusion potential (e.d.p.). The suggestion that an e.d.p. exists in metals was first made by Lewis and coworkers [13]. For the value of the e.d.p. in the diffusion of an impurity from a very dilute solution into pure solvent, Schwarz [14] obtained the expression

$$t_1 = \frac{\Delta UF}{RT}, \tag{36}$$

where t_1 is the transport number of the impurity and ΔU the voltage between the solution and the solvent.

For the electric field in ordinary diffusion, the following expression was obtained [11]

$$\frac{\partial\varphi}{\partial x} = -\frac{1}{e_3}\frac{\partial\mu_3}{\partial x} - e_1^*\frac{D}{\varkappa}\frac{\partial c_1}{\partial x}\left(1 + \frac{c_1}{c_2}\right). \tag{37}$$

The first term on the right-hand side is the ordinary "internal" contact potential difference, that is, the contact potential difference when the jumps at the metal–vacuum interface are independent of composition; the second term

is the e.d.p. gradient. It can readily be shown that in the case considered by Schwarz, (36) and (37) are equivalent.

An interesting feature is that the e.d.p. gradient has a form which resembles Ohm's law. In actual fact, the factor $-D\frac{\partial c_1}{\partial x}$ in Eqn. (37) is equal to the flow of ions of the first component; the factor $-D\frac{\partial c_1}{\partial x}e_1^*\left(1+\frac{c_1}{c_2}\right)$ then describes a certain effective current density produced by the movement of the ions, and division of the current density by the conductivity $\varkappa$ gives the corresponding field intensity.

The heat of transport was also examined by Thompson's method [11]. It was shown that the heat of transport consists of two parts: a term related to the transport of the electronic charge $e_1 - e_2$ (compensating the transport of the ionic charges) from a point with one value for the chemical potential of the electron to a point with another value, and a term which describes the work of transport of ions with definite effective charges in the field of the external current E.

In this case the field and the electron stream perform work $(e_1^* - e_2^*)Edx$, where dx is the path.

The results of this work [11] were generalised [15] for the case of an arbitrary n-component alloy. The calculations showed that the stationary distribution of each component in any case is determined only by the effective charge of the corresponding ion:

$$\frac{\partial \ln a_i}{\partial x} = \frac{e_i^* E}{kT}. \qquad (38)$$

The effective charges of the ions of different components are related to one another by the expression [see (35)]:

$$\sum_{i=1}^{n} c_i e_i^* = 0. \qquad (39)$$

Another approach to the problem of e.m. for the particular case of the separation of isotopes in an electric field was given by Klemm [16,17]. If z_i is the valency, ζ_i the degree of ionisation, N_i the mole fractions, r_{ik} the "coefficients of friction" between particles of the ith and kth types and $v_{ik} = v_i - v_k$ the relative velocity of particles of the ith and kth types, the conditions for equality of the electric forces and the forces of friction for each type of particle can be written in the form:

$$\begin{aligned} -\zeta_1 z_1 F \operatorname{grad}\varphi &= r_{12}N_2 v_{12} + r_{1n}N_n v_{1n}, \\ -\zeta_2 z_2 F \operatorname{grad}\varphi &= r_{21}N_1 v_{21} + r_{2n}N_n v_{2n}, \\ \zeta_n z_n F \operatorname{grad}\varphi &= r_{n1}N_1 v_{n1} + r_{n2}N_2 v_{n2}, \end{aligned} \qquad (40)$$

where the subscript 1 refers to the light isotope, the subscript 2 to the heavy isotope, and the subscript n to the electrons. It is assumed that $r_{ik} = r_{ki}$ and $z_1 = z_2 = z$. We also have

$$N_1 + N_2 = N_p,\ N_p + N_n = 1,\ N_n = zN_p,$$

$$\zeta_p = (N_1\zeta_1 + N_2\zeta_2)/N_p. \qquad (41)$$

The solution of system (40) has the form

$$\frac{v_{12}}{v_{pn}} = \left(\frac{\zeta_1 - \zeta_2}{\zeta_p} - \frac{r_{1n} - r_{2n}}{r_{pn}}\right) \Big/ \left(1 + \frac{r_{12}}{zr_{pn}}\right). \qquad (42)$$

The subscript p is written where the difference between 1 and 2 is insignificant.

It was shown [16] that

$$z\zeta_p\left(1 + \frac{r_{12}}{zr_{pn}}\right) = \frac{RT\varkappa}{F^2 cD}, \qquad (43)$$

where c is the concentration of the substance in g-equiv. cm^{-3}.

Klemm considers that this model cannot explain the experimentally observed movement of the light isotope towards the anode during electromigration and suggests that the ions of each type may exist in two states — mobile (activated) and immobile. It is then necessary, instead of the three equations (40), to write four equations: for the mobile ions of the light isotope, the mobile ions of the heavy isotope, the immobile ions, and the electrons. Using the subscript b to denote the mobile ions and the subscript u to denote the immobile ions, Klemm [17] obtained

$$\frac{v_{12}}{v_{pn}} = \frac{N_b}{N_p}\frac{v_{bn}}{v_{pn}}\frac{r_{2bu} - r_{1bu}}{r_{bn}} \Big/ \left(1 + \frac{N_b}{N_n}\frac{r_{1bub}}{r_{bn}}\right). \qquad (44)$$

The available experimental data on e.m. and diffusion in liquid metallic solutions do not, however, give sufficient grounds for accepting the hypothesis that the properties of ions in the ground state and transition state differ significantly. On the contrary, it has been shown [18,19] that diffusion in liquid metals is described satisfactorily by a theory which differs from the Frenkel'–Eyring theory and does not introduce the activation energy. Thus the question of the extent to which it is necessary to allow for the differences in the properties of the same ion at different moments of time (that is, at different points in its path) remains open. Nevertheless, the fact that the Stokes–Einstein relationship

$$D = \frac{kT}{4\pi\eta r}, \qquad (45)$$

applies satisfactorily to metallic solutions (see, for example, Ma and Swalin [19] and Sobol' [20]) indicates that the drift model is quite satisfactory. If this is the case, the differences in the properties of the ions at different points in its path can as a first approximation be assumed to be insignificant. It is possible that this is not the case for the effect of isotope separation by the e.m. method in liquid metals. Unique features may also be produced in liquid systems with strong interaction between the components (with the formation of intermetallic compounds), particularly at points close to the corresponding maxima on the liquidus curves. This question requires further study.

In the transfer of ions in electrolyte solutions it is necessary to take account of the relaxation and cataphoretic effects. Effects analogous to these may be produced in molten metals. In particular, the "electron wind" may be regarded as essentially an electronic cataphoretic effect. The relaxation effect, proportional to the rate of drift of the ions, is apparently negligibly small in metals, since in this case the fields which can be produced are weak. We may also, however, have an ionic cataphoretic effect, that is, entrainment of an ion during e.m. by the surrounding ions. This effect was examined [22] by the Debye–Fal'kenhagen method, with the assumption that each ion entrains its first coordination sphere, which moves as a single unit.

In a completely disordered solution there is no ionic cataphoretic effect, since the force acting on the first coordination sphere is equal to zero. When a statistical correlation exists, the second approximation of the theory of solutions [22] gives

$$e_i^{**} = e_i^*\left(1 + \frac{\Delta H}{2\pi\eta r_c N D}\right), \qquad (46)$$

where e_i^{**} is the apparent effective charge, e_i^* the effective charge taking account of only the "true charge" and the interaction with the conductivity electrons, ΔH the enthalpy of mixing of the given solution, η its dynamic viscosity, r_c the radius of the first coordination sphere, N Avogadro's

number, and D the diffusion coefficient. Formula (46) is applicable for $|\Delta H| \ll RT$, when the quasichemical method of the theory of solutions is applicable. Substituting D from (45) and assuming that $r/r_c \simeq 1/3$, we obtain[22]

$$e_i^{**} \simeq e_i^{*}\left(1 + \frac{2}{3}\frac{\Delta H}{RT}\right). \quad (47)$$

Thus positive deviation from ideal behaviour should lead to the inequality $|e_i^{**}| > |e_i^{*}|$, and negative deviation should lead to the opposite inequality.

In the case where $|\Delta H| > RT$, it is fairly difficult to take account of the interaction of ions of different type during e.m. In this case, however, interesting effects are observed, particularly the inversion of the direction of e.m. at definite concentrations of the solution[23]. A solution of the problem of the influence of the strong interaction of ions in alloys on e.m. would be extremely useful.

III. METHODS OF STUDYING ELECTROMIGRATION IN LIQUID METALS

The most common method involves the study of the stationary distribution of the components of the solution in a capillary. The liquid alloy is poured into the capillary and direct current is passed through it until a stationary state is established. The alloy is then cooled and analysed, graphs giving the distribution of the components along the capillary are constructed, and the electromigration characteristics are calculated.

Studies have shown[24,25] that the position and shape of the capillary have a very marked influence on the results of the experiment. In particular, the straight horizontal capillary used by Kremann and coworkers is unsuitable for the study of e.m. During e.m., a density gradient is produced along the capillary, leading to longitudinal convection; the heavier layers of metal flow under the lighter layers. Increase in the capillary diameter facilitates this process. Thus the results obtained in horizontal capillaries of appreciable diameter (1.5–3 mm) may be regarded as only qualitative.

Zigzag and spiral capillaries have been used[24,26-29] to reduce convection. This precaution is inadequate, since in the bends in the capillary, where the heavier component should migrate upwards, an unfavourable density gradient is created and convection is produced.

It is possible to estimate the part played by convection from the time required for the stationary state to become established. The order of magnitude of this time interval is

$$\tau \sim l^2/D, \quad (48)$$

where l is half of the length of the capillary. For example, for a capillary with length 40–50 cm and $D \sim 10^{-5}$ cm^2 s^{-1}, the value of τ is ~ 300–400 d. The observed values, however, are $\tau_{obs} \simeq 20$ h,[23] $\tau_{obs} \simeq 300$–400 h,[27] and $\tau_{obs} \simeq 2000$ h,[24] that is, $\tau_{obs} \ll \tau$. Thus convection takes place in spiral and zigzag capillaries, so that the effective diffusion coefficient $D_{eff} \gg D$.

Straight vertical capillaries have also been used to study e.m.[25,30-34]. A vertical temperature gradient of ~ 0.5–1 deg cm^{-1} was produced with a heater, and the direction of the current in the specimen was chosen in such a way that the lighter component migrated upwards. These precautions ensured a decrease in density from below upwards, and this favours suppression of convection. Under these conditions $\tau_{obs} \simeq \tau$.[35,36] For example, for a 40 mm column of metal, $\tau_{obs} \simeq 2$ d.

The influence of free convection and surface phenomena on diffusion was verified[25] in studies which showed that with change in the capillary diameter from 0.64 mm to 2.09 mm the diffusion coefficient of $^{113-123}$Sn in Pb at 350° changes insignificantly. Thus under these conditions (small) vertical temperature gradient, concentration of light component decreasing from above downwards) free convection can be suppressed. The same result was obtained in a study of the effect of the e.m. of ^{110m}Ag in liquid Pb and Sn in capillaries with different diameters[25].

An extremely important factor in the capillary method is the current density. In work by Kremann and coworkers[23,37-47], a "saturation" effect was observed: at high current densities (10–20 A mm^{-2} and above), the e.m. became independent of current density; this was attributed to the turbulent nature of the movement of the melt in the capillaries. At low current densities (~ 1 A mm^{-2} and below) the e.m. effect is proportional to the current density[24,25].

It was established[48] that the scattering of electrons at the boundary between the molten metal and the walls of the capillary should produce electroconvection, in which the metal moves in the same direction as the electrons along the axis of the capillary, and in the opposite direction at the walls of the capillary. In this case the apparent effective charge will be less than the actual value. Let us introduce the symbol z^* to denote the effective charge, expressed in units of the charge of the electron e, that is, $z^* = e^*/e$. It was shown[25] that

$$\frac{z^*}{z^*_{app}} = 1 + \frac{10^{-4}}{0.48 D_0 D}(1-\varepsilon)^2\left(\frac{end\lambda^2}{\eta}\right)^2 E^2, \quad (49)$$

where D_0 is the coefficient of self-diffusion of the solvent, ϵ a coefficient defining the proportion of electrons undergoing mirror reflection from the boundary, d the diameter of the capillary, n the concentration of free electrons, λ the mean free path, η the viscosity, and E the field intensity.

It was found[22] that for the case of the e.m. of ^{60}Co in liquid Sn at 350° the dependence of z^*/z^*_{app} on E^2 is in fact linear up to a current density of 5.3 A mm^{-2}. The mean free path of the electrons, calculated from the slope of this straight line, is 2.2×10^{-7} cm (with the assumption that $\epsilon = 0$), which is of the same order of magnitude as the value of λ calculated from the electrical conductivity of tin (0.92×10^{-7} cm). The optimal current density in metals of the type Sn, Pb, and Bi, at which electroconvection can still be neglected, is 1–1.5 A mm^{-2}.

In this connection it should be noted that work on the separation of isotopes during e.m. in metals (the Haeffner effect)[49-52] is usually carried out at high current densities (10–20 A mm^{-2} and above). This should lead to the development of electroconvection, so that the results obtained in this work can hardly be regarded as quantitative. The marked influence of electroconvection is indicated by the fact that the values of the effective diffusion coefficient in liquid Rb, K, and In [52] varied from 2.5×10^{-4} cm^2 s^{-1} to 10^{-3} cm^2 s^{-1}, that is, they are greater by 1–2 orders of magnitude than the real values. To obtain accurate results, it is necessary to carry out e.m. experiments at low current densities.

Another possible mechanism of the influence of current density on the e.m. effect was considered[35]: excitation of laminar convection as a result of the heating of the metal in a vertical capillary by the direct current. Since the temperature at the axis is slightly higher than that at the walls

of the capillary, the metal begins to rise along the axis and to descend at the walls, leading to convective agitation. It was found[35] that

$$\frac{z^*}{z^*_{app}} = 1+2.26\times10^{-7}\frac{R^{10}}{D^3}\left(\frac{g\beta\rho j^2}{\nu\gamma}\right)^3, \quad (50)$$

where R is the capillary radius, g the acceleration due to gravity, β the coefficient of volume expansion, ρ the resistivity, j the current density, ν the kinematic viscosity, and γ the thermal conductivity.

The convection effect is extremely sensitive to the radius of the capillary. It follows from formulae (49) and (50) that for a radius of 1 mm and current densities less than 10 A mm^{-2}, the effect of electroconvection should be more marked than that of thermal convection. At a radius of 2 mm and j = 10 A mm^{-2}, however, the decisive role should be played by thermal convection (for common metals). In this case the ratio z^*/z^*_{app} should be proportional to j^4 and not j^2. It is necessary, however, to take account of the fact that the presence of rough areas on the walls of the capillary or the existence of an immobile surface layer of liquid should suppress electroconvection.

Other reasons for the convective agitation of melts in capillaries during the passage of direct current have been discussed[53]: these include electroosmosis[54] and magnetic movement resulting from conicity of the capillaries. It was shown that convection and hence increased effective diffusion coefficients may be produced by a magnetohydrodynamic effect at conicities of the order of 0.01 cm^{-1}; the effect is proportional to the current density to the fourth power and the capillary radius to the tenth power. Unlike thermal convection — formula (50) — which develops in vertical capillaries, magnetohydrodynamic convection should be observed for any position of the specimen.

When the stationary state has been reached and fixed by cooling, the specimens are divided into sections and analysed, and a curve is constructed giving the dependence of the logarithm of the thermodynamic activity of a given component on the length along the axis of the specimen. The effective charge $z^* = e^*/e$ can be found from Eqn. (38)[31,32]. The authors of the works cited restricted themselves to the determination of the difference between the concentrations at the ends of the specimens or the calculation of various e.m. characteristics (for example, a constant[27-29] for which the name "electrodiffusion coefficient" was proposed), whose relationship to the effective charge can be established.

An interesting feature is that the e.m. effect depends little on temperature. Experimental work[24,25,27,47] has shown that change in temperature over a range of 100 deg has no influence on z^* (there are grounds for expecting z^* to show this behaviour, see below). The study of e.m. over a wide temperature range would be extremely valuable, however. Unique features in the behaviour of z^* might possibly be observed at temperatures close to the melting point.

A direct determination of the rate of migration of an impurity in an electric field has been carried out[55,56]. Two identical capillaries, placed vertically and filled with mercury, were used. Contacts were sealed to the upper ends, and the lower ends were immersed in a dish containing mercury. If current is passed through the specimens in series, the two capillaries are heated to the same extent, and a differential thermocouple with junctions fixed at corresponding points in the capillaries will show no readings. If the mercury in one of the dishes is replaced by an amalgam, the impurity begins to migrate along the capillary and alters the resistance of the mercury. The temperature at different points in the capillary will then change as a result of the change in power. At the moment when the diffusion front reaches one of the thermocouple junctions, it will begin to give readings. From a knowledge of the time required for the diffusion front to move from the end of the capillary to the point where the junction was situated, Schwarz calculated the mobility of the impurities in mercury.

A feature of this method is that in the simultaneous e.m. of several impurities, the latter move at different rates and are separated in space, as in chromatography.

The mobilities of various impurities in mercury were studied[14] by measuring the electrodiffusion potential. To increase the effect, Schwarz connected ten cells in series, since the e.d.p. of a single cell amounted to 10^{-7}–10^{-8} V. The transport numbers of the impurities were determined from formula (36). The e.d.p. effect in liquid alloys of tin, lead, bismuth, tellurium, etc. has also been studied[57,58].

A method was recently proposed for studying e.m. in crossed electric and magnetic fields[59,60]. A gold amalgam was placed in a 10 cm × 1 cm × 0.025 mm vacuum-tight vessel. The electric current was passed in a direction parallel to the 1 cm edge and a magnetic field with induction 5500 G was applied in a direction perpendicular to the 10 cm × 1 cm face. After passage of a current of 15 A for 6 days, the amalgam at one end of the long edge showed threefold enrichment relative to that at the other end. The effect was assumed to be due to the fact that the velocities of the electrons directed at right angles to the electric and magnetic fields were not equal to zero (in a second approximation)[60]; the Hall field was assumed to be insignificant.

The force acting on the ion in crossed fields was calculated[61]. According to this calculation,

$$F_i = E_x e\bar{v}_i\left(\frac{z_i}{\bar{v}_i}-\frac{z_0}{\bar{v}_0}\right), \quad (51)$$

where z_i and z_0 are the true charges of the impurity and solvent ions, $\bar{v}_i$ and $\bar{v}_0$ their volumes, and E_x the intensity of the Hall field. Application of formula (51) to Knof's results[59] gives an absurd result for z for gold (of the order of 10^4 units of electronic charge[35]). Calculations made by Knof[60] also give a value for the effect which is smaller by two orders of magnitude than that observed in earlier work[59]. Further studies are required to find the reasons for this discrepancy. It is possible that in the earlier work[59] a characteristic multiplication effect operated, analogous to that in thermal-diffusion columns.

IV. DETERMINATION OF THE EFFECTIVE CHARGES OF IONS IN METALLIC SOLUTIONS

As pointed out above, in order to establish the significance of the effective charge it is necessary to examine all the forces acting on the ion of a given type. According to Mangelsdorf[62], it is necessary to take account of the following forces: (1) the ordinary field force; (2) a force due to polarisation of the non-localised electrons by the field; (3) a force due to polarisation of the electrons by the current (the conductivity electrons are scattered on the ions and should "push" the charge cloud screening the ion in the direction of their movement; (4) a force due to polarisation of the surrounding ions by the field; and (5) a force related to the polarisation of the surrounding ions by the current.

Finally, if chemical forces operate between the impurity ion and the surrounding solvent, an important factor, according to Mangelsdorf[62], is the ratio of the radius of influence of these forces to the mean free path of the electrons, that is, the number of collisions with ions undergone by an electron scattered by the impurity in the sphere of action of the chemical forces. Mangelsdorf[62] did not give an analysis of the relative part played by these factors.

If the interaction between the ions of the components is not significant (energy of mixing $\Delta\epsilon = \epsilon_{12} - \frac{\epsilon_{11} + \epsilon_{22}}{2} \ll kT$, where ϵ_{ik} is the energy of interaction of pairs of ions which are nearest neighbours), the chief forces acting on an ion in a metal during e.m. are the field force and the "force of the electron wind" (forces 1 and 3 according to Mangelsdorf[62]). The first of these is determined by the so-called "true charge" of the ion and the second by the intensity of the interaction of the ion with the current. To describe the interaction it is more convenient to use not the coefficients of friction r_{ik} introduced by Klemm[16,17] but the cross-section for the scattering of electrons on the ions[63].

Calculation of the interaction force of the electrons with the current, carried out by Fiks[64] for a free-electron model (degenerate gas), leads to the expression

$$F_e = -eEnl\sigma, \tag{52}$$

where e is the charge on the electron, E the field intensity, n the concentration of free electrons, l the mean free path on the Fermi level, and σ the cross-section of scattering of the electron on the impurity ion. In the case of a pure metal, $nl\sigma = z$, where z is the valency of the ion, so that the force F_e is equal to the field force zeE with the opposite sign; this satisfies the condition for mechanical equilibrium of the specimen.

Fiks[64], like Klemm[17], assumed that it is necessary to take account of the differences in the properties of the ions in the ground state and transition state for e.m. in liquid metals, at least for the case of the separation of isotopes. For the total force acting on the ith ion in the transition state ("activated ion"), Fiks[64] obtained

$$F_i = eE\left(z_{ti} - \bar{z}\frac{\sigma_i^*}{\bar{\sigma}}\right), \tag{53}$$

where z_{ti} is the "true charge" of the ith ion in the transition state, σ_i^* the corresponding cross-section of scattering, $\bar{z}$ and $\bar{\sigma}$ the mean values of z and σ for all the components of the solution. Thus for the effective charge the following expression is applicable

$$e_i^* = ez_i^* = \frac{F_i}{E} = e\left(z_{ti} - \bar{z}\frac{\sigma_i^*}{\bar{\sigma}}\right), \tag{54}$$

that is,

$$z_i^* = z_{ti} - \bar{z}\frac{\sigma_i^*}{\bar{\sigma}}. \tag{55}$$

It was shown[31] that relationship (55) can be obtained directly from the condition for mechanical equilibrium of the specimen (39). Here it was assumed that the difference in the electrical properties (z and σ) of different ions of the same component is insignificant for e.m. in liquid metallic solutions. Thus for a two-component solution the following expressions are applicable[31]:

$$z_1^* = \frac{N_2(\sigma_2 z_1 - \sigma_1 z_2)}{\sigma_1 N_1 + \sigma_2 N_2},$$

$$z_2^* = \frac{N_1(\sigma_1 z_2 - \sigma_2 z_1)}{\sigma N_1 + \sigma_2 N_2}, \tag{56}$$

where z_i, σ_i, and N_i are the "true charge" of the ith ion, the cross-section of scattering of the conductivity electrons on the ith ion, and the mole fraction of the ith component respectively. For a very dilute solution ($N_2 \to 0$):

$$z_1^* \simeq 0, z_2^* = z_2 - z_1\frac{\sigma_2}{\sigma_1}. \tag{57}$$

Determination of the values of the true charges on the ions of the components in different solutions would give information on the type of bond and the distribution of electrons close to the impurity atom, and would undoubtedly be extremely valuable for the theory of the metallic state. On the other hand, a knowledge of the cross-section of scattering is of interest for the theory of electrical conductivity, the thermal conductivity of metals, etc. It can be seen from (57)–(59) that it is impossible to calculate unambiguously all the values of z and σ for the ions of the components of the solution merely from e.m. data. It has been shown[30,31,33,34], however, that fairly reliable data on z and σ can be obtained by studying e.m. in a series of suitably selected solutions, for example, with a common solvent or a common impurity.

To estimate the cross-section for scattering of the electrons on the impurity ion σ it is possible to use the relationship between σ and the influence of the impurity on the electrical resistance of the solvent[65,66]

$$\Delta\rho_i = \frac{mv_0}{e^2} N_i\sigma_i, \tag{58}$$

where mv_0 is the impulse of the electron on the Fermi level, e its charge, N_i the atomic fraction of the impurity, and $\Delta\rho_i$ the residual resistance due to the impurity. In the case of liquid alloys, however, Eqn. (58) appears to be unsuitable. According to (58), $\Delta\rho_i$ should always be positive. For solid solutions this is almost always the case. In the case of liquid alloys, however, positive values of $\Delta\rho$ are encountered no more frequently than negative values. This is due to the fact that in systems with low affinity of the components (for example, in simple eutectic systems) a tendency towards additivity of the resistivity of the alloys is observed. The applicability of Eqn. (58) to liquid alloys is thus doubtful.

Mott[65,66] examined a solution of a multivalent impurity in a univalent metal and used, to calculate σ, the ordinary theory of scattering of electrons by a force centre with spherically symmetrical field[63]. The form of the force field was obtained by the Thomas–Fermi method as a screened coulombic potential

$$\varphi = \frac{\Delta ze}{r}e^{-\beta r}, \tag{59}$$

where Δz is the difference in the valencies of the impurity and solvent, β a screening constant, and r the distance from the ion. Thus for the value of σ we have[65]

$$\sigma = \frac{\pi}{2}\frac{e^4(\Delta z)^2}{\epsilon_0^2}\left\{\ln\left(1+\frac{1}{y}\right) - \frac{1}{1+y}\right\}, \tag{60}$$

and

$$\frac{1}{y} = \frac{(2mv_0)^2}{\beta^2\hbar^2}. \tag{61}$$

where ϵ_0 is the Fermi energy and $\hbar$ Planck's constant divided by 2π. Substitution of the value of β gives for $1/y$ the expression

$$1/y = 5.1 \times 10^{-8} n^{1/3} z^{1/3}, \tag{61a}$$

where n is the concentration of free electrons and z the charge of the ion.

It was also pointed out[65], however, that in metals the electron density is insufficiently high for the Thomas–Fermi method to be completely applicable. Kun[67] calculated the residual resistance for a solution of gold in silver; the electron density was found by the Thomas–Fermi method. and also by exact solution of the Schrödinger equation. The two methods gave similar values for $\Delta\rho$ (0.16 $\mu\Omega^{-1}$ per 1 at.% Au), which showed poor agreement with the experimental value (0.38 $\mu\Omega$ cm^{-1} per 1 at.% Au). According to Kun[67], the discrepancy is due to the fact that the free-electron model is not completely applicable to the phenomenon of electrical conductivity. The results given by formula (60) are therefore only of the correct order of magnitude.

The cross-sections of scattering for impurities in multivalent-metal solvents have apparently not been calculated.

V. RESULTS OF STUDIES OF ELECTROMIGRATION IN LIQUID METALLIC SOLUTIONS

1. Electromigration in Amalgams

A number of studies have been made of the phenomenon of e.m. in amalgams[13,14,23,24,43,46,55,56,68-72]. Some of these studies[13,14,24,55,56,72] produced more accurate results than the others, in which inadequate procedures made it impossible to obtain reliable results.

Lewis and coworkers[13] found that traces of sodium and potassium in dilute amalgams move towards the anode during e.m., that is, exhibit a negative effective charge. They therefore suggested[13] that the alkali metal atoms undergo chemical reaction with mercury, forming more or less stable complexes which are the actual diffusion units. These investigators noted[13] a relationship between the magnitude of the e.m. effect and the influence of the impurity on the electrical resistance of mercury. This correlation led them to the conclusion[13] that e.m. in amalgams is due to "friction" between the complexes and the stream of conductivity electrons.

The existence of "friction" between complexes and the stream of conductivity electrons was suggested even earlier by Skaupy[73,74], in whose opinion these complexes should also influence the viscosity, the conductivity being smaller, the greater the increase in viscosity of mercury when the impurity is added. If the impurity decreases the resistance of mercury, it should move to the cathode during e.m.

Results obtained[24] for amalgams of Na, Ba, Li, and Ca confirmed this viewpoint (see Table 1). The movement of complexes towards the cathode can be understood, however, only if account is taken of the action of the ordinary field force on the positive charge.

The results obtained by Schwarz by different methods are summarised in his monograph[14] and are given in Table 2. The second column gives the values of the transport numbers at 25°, divided by the atomic fraction of the impurity. The third column gives the values of the velocity of migration V (cm h^{-1}) for a field intensity of 1 V cm^{-1}. The positive sign denotes that the impurity migrates towards the cathode. An interesting feature is that the values of the mobilities of the impurities in mercury, obtained by three different methods (establishment of the stationary state in a capillary, direct measurement of the velocity of migration, and measurement of the e.d.p.) show satisfactory agreement with one another[14], apparently indicating that in Schwarz's measurements convection played little part.

The fourth column of Table 2 gives the values of the diffusion coefficients D for impurities in mercury at 25°, measured by Schwarz[76]. We used this data and the relationship

$$V(\text{cm h}^{-1}) = \frac{3600ez^*D}{300\,kT}, \qquad (62)$$

to calculate the effective charges z^* of the impurities in mercury (fifth column in Table 2). The sixth column gives the values of the increments in the resistivity per 1 at.% of impurity[75].

It can be seen that for most impurities a relationship is observed between the signs of z^* and $\Delta\rho$: a positive value of z^* corresponds to a negative $\Delta\rho$, and vice versa. This correlation is not observed for Tl, Pb, and Bi; the first two undergo almost no migration in the field, and bismuth moves on the "wrong" direction. The suggestion that there exists friction between complexes and the stream of electrons evidently does not make it possible to explain all the phenomena of e.m. in amalgams.

The dependence of z^* on $\Delta\rho/c$ (Fig. 1) constructed from the data in Table 2, shows that most impurities can be divided into groups, within which the relationship between z^* and $\Delta\rho/c$ is approximately linear. However, if we construct the dependence of $\Delta\rho/c$ on the relative change in volume on the dissolution of impurities in mercury, we find that Zn, Cd, Tl, Sn. Pb, and Bi lie satisfactorily on the

TABLE 1. Electromigration of impurities in mercury[13] and their influence on the resistivity of mercury[75].

Impurity	Composition, at.%	Current density j, A mm^{-2}	Specific e.m. effect, Δ/j	Increment in resistance $\Delta\rho/c$, $\mu\Omega$ cm (at.%)$^{-1}$	Direction of movement
Na	2.89	0.43	1.24	0.7	towards the anode
Ba	0.509	0.36	0.10	1.6*	towards the anode
Li	1.267	0.35	−0.11	−2.0	towards the cathode
Ca	1.245	0.40	−0.14	−3.51	towards the cathode

* Taken from Lewis and coworkers[13].

TABLE 2. Electromigration in amalgams[14] and the influence of impurities on the resistivity of mercury[75] at 20°.

Impurity	$\frac{10^8 t}{c}$, g-atom (at. fraction)$^{-1}$ × × faraday^{-1}	V, $cm^2 V^{-1} h^{-1}$	$10^5 D$, $cm^2 s^{-1}$	z^*	$\Delta\rho/c$, $\mu\Omega$ cm (at.%)$^{-1}$
Li	7.5	0.41	0.92	0.31	−2.0
Na	— 7.8	−0.43	0.86	−0.43	0.7
K	−23	−1.3	0.71	−1.31	2.9
Cs	−79	−4.3	0.63	−4.87	—
Ag	40	2.2	1.11	1.43	−3.7
Au	27	1.5	0.73	1.47	—
Mg	63	3.5	—	~1	—
Ca	—	<0.2	—	<0.1	−3.51
Zn	77	4.2	2.4	1.25	−4.4
Cd	64	3.5	2.0	1.25	−3.7
Tl	1	0.0	1.18	0.0	−2.1
Pb	1	0.0	2.08	0.0	−5.8
Bi	−52	−2.9	1.5	−1.38	−3.7
Sn	35	1.9	2.09	0.65	−6.5
Ga	52	2.9	—	~1	—

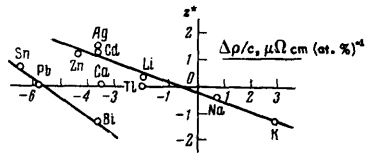


Fig. 1. Dependence of the effective charges of impurities in mercury on the increments in the electrical resistance.

same straight line[62]. The point corresponding to the changes in volume and resistivity during the crystallisation of mercury lies on the same straight line. This gave grounds for the suggestion[62] that the influence on the resistivity of mercury shown by those impurities which lower the resistance is that which would be expected if a certain volume of mercury "crystallised" around the impurity atom. This process leads to a decrease in resistance.

A noteworthy feature is that traces of Sn, Pb, and Bi in mercury form a separate group in Fig. 1. The displacement of the effective charges for these impurities towards more negative values compared with the other impurities may be due to the fact that, in addition to the above-mentioned complexes formed close to the impurity atoms, other factors also have an influence in this case, for example, the true charge z. It is significant that Sn, Pb, and Bi are multivalent, whereas the other metals given in Fig. 1 are univalent or bivalent (the properties of thallium resemble those of a univalent metal). The large excess of charge on the Sn, Pb, and Bi ions should lead to increased scattering of electrons on the impurity ions and should therefore displace z^* towards more negative values.

The interesting phenomenon of inversion of e.m. was observed in amalgams of Na, K, and Ba.[23,43] The experiments were carried out in 20–80 cm capillaries with internal diameter 0.4–1.6 mm, at 240° and current density 3–7 A mm^{-2}. The duration of the experiment was 70 h. It was found that at impurity concentrations less than 15 at.% Na, 11 at.% K, and 3.9 at.% Ba, the impurities move towards the anode, whereas at higher concentrations they move towards the cathode.

In these systems the interionic interaction apparently has a significant influence on e.m. In the solid state a whole series of intermetallic compounds is formed ($BaHg_{11}$, KHg_3, KHg_2, KHg, $NaHg_4$, $NaHg_2$, etc.)[77], so that the short-range order in liquid amalgams should show corresponding characteristic features. There may be a change (even in the sign) of the "true charge" of each ion. Moreover, in systems with appreciable interionic interaction, the ionic cataphoretic effect discussed above may play an important part.

2. Electromigration of Impurities in Alkali Metals

From the viewpoint of the theory of the e.m. of impurities in alkali metals, an extremely interesting feature is that these metals are the simplest materials for study, and it is possible to carry out quantitative calculations for them; a number of studies have been made of e.m. in alkali metals[27–29,35,78–80]. Drakin and Mal'tsev[27] studied e.m. in the sodium–potassium system at 100° in bent capillaries and found that in this case inversion of the e.m. takes place; at concentrations less than 48 wt.%, sodium migrates towards the anode, and at higher concentrations it migrates towards the cathode. Study of the e.m. of traces of mercury (0.4 at.%) and lead (0.6 at.%) in liquid potassium at 100° [28] showed that in both cases the impurity migrates towards the anode, the e.m. effect being much greater than that in the liquid systems previously studied.

The e.m. of traces of thallium in potassium (0.19 at.%), mercury in sodium (0.6 at.% and 1.1 at.%), lead in sodium (0.45 at.%), and cadmium in sodium (0.21 at.%) was studied at 110° in a 15 cm capillary with internal diameter 2 mm.[29] The capillary was bent to form a spiral, and ten platinum leads were sealed into the walls of the capillary at equal intervals to measure the electrical resistance. It was possible to measure the e.m. effect with sufficient accuracy only for solutions of mercury in sodium and of thallium in potassium. More precise data for Pb and Cd in Na, and for Hg in K, were obtained later[78].

The effective charges z^* of impurities in sodium and potassium, calculated from electrodiffusion coefficients[28,29,78] had the following values:

Solvent	Na	Na	Na	K	K	K
Impurity	Hg	Pb	Cd	Tl	Hg	Pb
z^*	−18	−27.2	−7.3	−20	−12.6	−22

It was suggested[29] that the reason for such high negative values of z^* for impurities in sodium and potassium is the entrainment of the particles of impurity by the stream of electrons ("electron wind").

The e.m. of ^{115m}Cd and ^{204}Tl in liquid sodium at 120° (impurity concentration 0.5 wt.%) was studied[35] in straight vertical capillaries with a 50 mm column of metal and internal diameter 1 mm. Electrodiffusion annealing was continued for 20 days with the passage of a current with strength 1.5 A through the specimens. The values found for the effective charges of Cd and Tl in sodium at 120° were -70 units and -55 units (accuracy ±15%). These charges were calculated for specimens with favourable direction of migration of the impurity (from above downwards).

The e.m. in a ternary K–Na–Hg system containing 46 wt.% Na, 50 wt.% K, and the rest Hg for different annealing times at 30° was studied[79] in a 77 mm vertical capillary with internal diameter 1.67 mm. Ten sealed-in platinum leads were used to follow the change in the concentration of the solution during e.m. It was assumed that in a melt with the above composition, potassium and sodium do not take part in e.m. (without allowance for the mercury, the composition coincides with that for which inversion of e.m. was observed[27]). The kinetic e.m. curves gave for the diffusion coefficient of mercury the value 1.16×10^{-5} cm^2 s^{-1} and for the "electrodiffusion constant" the value 1.82×10^5 deg V^{-1}. This value corresponds to an effective charge $z^* = -15$. This value is approximately equal to the mean of the values of z^* for mercury in sodium and potassium.

The results of the measurement of the e.m. of impurities in alkali metals can be compared with their influence on the resistance of the solvent. Since the absolute value of z^* for the impurities is high in all cases, it may be assumed that $|z| \ll |z^*|$. It then follows from (52) that

$$z_i^* \simeq -nl\sigma_i. \qquad (63)$$

From (63) and (58) we obtain

$$z_i^* \simeq -\frac{\Delta\rho_i}{N_i\rho_0}, \qquad (64)$$

where $\Delta\rho_i$ is the change in the electrical resistance of the solvent when the impurity is introduced, N_i its mole fraction, and $\rho_0 = mv_0/(e^2nl)$ the electrical resistivity of the pure solvent.

Values were obtained for $\Delta\rho$ for a number of impurities in liquid sodium[81]. These can be used to calculate z_i^*(calc.). These values of z^* are given in Table 3, together with published values[28,29,35].

The values of z^* obtained experimentally in spiral capillaries[28,29] (Table 3) are much lower than the values obtained in vertical capillaries[35] and the values calculated from formula (64). On the other hand, the results obtained in vertical capillaries[35] show satisfactory agreement with the values of z^* calculated from Eqn. (64). It may thus be assumed that Eqn. (58) is applicable to dilute solutions based on liquid sodium.

It is possible to verify the applicability of the Thomas–Fermi model for the case of solutions of impurities in sodium. The cross-section of scattering σ for impurities with different ion charges in Na and K at 100° was calculated from Eqn. (60)[35] and the effective charges z^* were calculated from the formula[61]:

$$z^* = z - nl\sigma \qquad (65)$$

(see Table 4). It can be seen from Table 4 that the calculated values of z^* for impurities with an ion charge $z \leqslant 2$ have a reasonable order of magnitude, but that for $z = 3$ the calculation gives values of z^* which are not observed experimentally.

The use of the Thomas–Fermi method in this case is hardly valid, since there is a fairly strong interaction between the atoms of the impurities Cd, Pb, Hg, etc. and the solvent. In the solid state, the alkali metals react with heavy metals to form intermetallic compounds of the type $NaCd_2$, K_2Pb, KTl, etc.[77] This interaction leads to ordering of the solvent close to the impurity atom: the bond becomes covalent or even partly heteropolar. The valency electrons of the impurity will therefore not become non-localised in the usual sense.

TABLE 3. Effective charges of impurities in liquid sodium.

Impurity	$\Delta\rho_i/N_i$ (Ref. 81), $\mu\Omega$ cm (at. %)$^{-1}$	z^* calc. from Eqn. (64)	z^* (Refs. 28, 29, and 78)	z^* (Ref. 35)
Cd	4.45	—44	—7.3	—70±10
Tl	7.5*	—75	—	—56± 8
Hg	6.0	—60	—18	—
Sn	9.5	—95	—	—
Pb	10.8	—108	—27	—

* By interpolation.

TABLE 4. Effective charges of impurities in alkali metals at 100°, found by Thomas–Fermi method.

z for impurity	$\Delta z = z - 1$	In potassium		In sodium	
		$10^{16}\sigma_i$, cm^2	z^*	$10^{16}\sigma_i$, cm^2	z^*
1	0	0	1	0	1
2	1	2.27	—42	1.34	—49
3	2	10.7	—207	6.16	—235
4	3	25.8	—	15.3	—

TABLE 5. Effective charge of the spherical nonconducting complexes (radius = r) in potassium and sodium at 100°.[35]

$10^8 r$, cm	Effective charge	
	in potassium	in sodium
1	—24	—48
2	—97	—192
3	—219	—435

It was shown[22] that when the bonding is strong, it is possible to use a model according to which the impurity atom forms a stable complex with the solvent which behaves during e.m. as a non-conducting sphere of radius r. In this case[63]

$$\sigma = 4\pi r^2, \qquad (65a)$$

from which, in accordance with (63),

$$z^* = -4\pi nlr^2. \qquad (66)$$

The calculated values of z^* for impurities in K and Na (Table 5) show that the non-conducting sphere model gives reasonable values of z^* when the radii of the complexes have the values 1–2 Å. The real radius should be about twice this value. Thus the non-conducting sphere model gives values of z^* which are too high by a factor of ~ 2–4. A possible reason is that the region inside the complex is not completely inaccessible to the conduction electrons, so that the non-conducting sphere model is not applicable in these cases.

The e.m. of oxygen in liquid sodium at 300° was studied[80] in U-shaped Pyrex capillaries with broadened sections at the ends. Extensive migration of oxygen towards the anode was observed, amounting to several tenths of a milligramme of oxygen for every 3600 C of electricity passed, at an average oxygen concentration of $\sim 5 \times 10^{-2}$ wt.%. Calculation using formula (62) shows that the value of z^* for oxygen in liquid sodium has an order of magnitude of -10^4. If these results are reliable, they may be explained by means of the non-conducting sphere model. According to (66), the value of z^* is -10^4 for $r \simeq 15$ Å, that is, the complex should contain 100–150 atoms of oxygen and sodium.

3. Electromigration in Various Solvents (Semiquantitative Data)

Here we shall deal chiefly with the results of Kremann and coworkers, but also some data obtained by others[26,82,83]. Kremann characterised the e.m. effect by the difference (Δ) in the weight percentages of each component at the ends of the specimens. The results which he obtained can be regarded as only qualitative, because of the unsatisfactory features of the procedure used.

Drakin[26] made a special study of e.m. in eutectic tin–bismuth and cadmium–bismuth alloys close to the eutectic

point. If the initial state of the alloy is given by a point close to the eutectic on the equilibrium diagram, the portions of the alloy at the ends of the specimen during e.m. may fall in two-phase regions of the diagram, as a result of enrichment in one of the components. The corresponding solid solutions or pure metals begin to separate from the melt. It was shown[26] that the e.m. method makes possible the fairly satisfactory separation of the original eutectic alloy into almost pure components, particularly if the solid components have a higher resistivity than the liquid.

The results obtained by Kremann and coworkers and by other workers[26,82,83] are given in Table 6. The sixth column gives the components migrating towards the cathode, the fifth column gives the current density j, and the seventh column gives the e.m. effect Δ.

Kremann[84] tried to explain his results on the basis of Skaupy's ideas[73] regarding dissociation in metallic solutions. According to Kremann, the more positive component in the solution should be the one with the lower ionisation energy; this component will also migrate to the cathode during e.m. Kremann[84] arranged the substances which he studied in the following order:

$$\text{Br Sb Hg Pb Sn Zn Cd Cu Ag Al Na K}. \qquad (67)$$

A solution component lying to the right in series (67) should migrate to the cathode during e.m.

Let us write in the same order the first ionisation potentials of the atoms of series (67) (in eV):

$$7.25\ \ 8.35\ \ 10.41\ \ 7.37\ \ 7.54\ \ 9.37\ \ 8.94\ \ 7.67\ \ 7.58\ \ 5.94\ \ 5.09\ \ 4.32. \qquad (68)$$

TABLE 6. Electromigration in liquid metallic alloys[26,82,83,14].

System	Temperature, °C	Concentration, wt. %	Duration of annealing, h	Current density, A mm^{-2}	Component moving to cathode	Effect Δ, wt. %	Refs.
Ag—Al	900	50—80 Al			Al	15	*
Ag—Bi		30 Ag			Ag	3	*
Ag—Cu—Sn	1000	30 Cu, 1—11 Sn	4	2.8	Ag, Cu	2.6 Cu	45
Ag—Pb	1000	50 at. %	4	13.2	Ag	4.2	38, 42
Ag—Sb		10 Ag			Ag	5	*
Al—Sn		16 Ag			Ag	2.5	*
Al—Cu	1050	50	4	13.2	Cu	4.5	37
Al—Sn	800—1600	58 at. % Sn	4	4.3	Al	5.4	40
Al—Au	700	9 Au			Al	0.4	*
Al—Fe—Sn	660				Fe		*
Au—Bi	680	50			Au	2	*
Au—Pb	450	50			Au	3	*
Au—Sb	400	50			Au	14	*
Be—Cu—Fe	1050	10 Be			Be (Fe)		*
Bi—Cd		25—75			Cd	65	*
Bi—Pb	240—400	60 Bi		10	Pb	42	47
Bi—Sb	300	25—88		8	Sn	40	47
Bi—Cu—Sn	1000	30 Cu, 2—20 Bi	4		Cu		46
Cd—Pb	300	40			Cd	30	*
Cd—Sn	300	25—75			Cd	6	*
Cu—Sn	1000	50 at. %		6	Cu	6	47
Cu—Pb—Sn	1000	1 Pb			Cu	10	44
Cu—Pb—Zn	1000				Cu		*
Hg—Na—Sn	240	1—5 Sn, 40 Na	20	6	Sn, Na		46
Pb—Sn	350	37 Pb		16	Sn	11	47
Sb—Zn	620	53—61 Sb		7.6	Zn	75	47
Sn—Zn	400	50 at. %	4	12.3	Zn	12	39
Fe—C	1300	2.6 C	0.25	0.1	C	0.11	83
Pb—Sb	470	13.5 Sb		1.1	Pb		82
Sn—Sb					Sn		82
Cd—Pb	360	3 Pb	6.5	1.2—2.1	Cd	0.6—1.1	82
Cd—Sn	330	20—30 Cd	5—6	1	Cd	1.3—2.6	82
Bi—Pb	225—300	eutectic alloy	4.5	0.5—0.8	Pb	3.9—6.6	82
Bi—Sn					Sn		82
Bi—Cd					Cd		82
Ag—Pb	360—390	2 Ag	5—6.5	1	Ag	0.84—1.06	82
Al—Cu					Cu	2	82
Cu—Sn	370—420	3 Cu	3—6.5	1—1.5	Cu	1—3.3	82

* Summarised results[14].

No appreciable tendency towards a monotonic change in ionisation potential is observed in series (68), so that the sequence (67) proposed by Kremann is purely empirical. Series (67) cannot explain all the observed e.m. data. For example, Na and K in amalgams migrate to the cathode only in sufficiently concentrated solutions. Sometimes series (67) predicts incorrectly the direction of migration, so that it may be assumed that the description of the direction of e.m. in different systems by a simple analogy with the potential series is hardly possible.

4. Electromigration in Dilute Solutions Based on Cd, In, Sn, Pb, Bi, Ag, Fe, Ni, etc.

The e.m. of traces of the radioactive isotopes ^{65}Zn, $^{113-123}$Zn, ^{115m}Cd, ^{72}Ga, ^{210}Bi, ^{75}Se, ^{45}Ca, and ^{110m}Ag was studied in liquid lead, cadmium, bismuth, and tin[30,85], in 40 mm capillaries with internal diameter ~ 1 mm, at a current strength of 1.5 A, with duration of electrodiffusion annealing equal to 15 days. An interesting feature is that in most cases the value obtained for the effective charge was slightly higher when the light component migrated upwards. This means that the slight changes in density during e.m. in dilute solutions are still able to produce weak convection currents in the capillary. It can be seen from Table 7 that the direction of e.m. in the systems studied agrees with that found earlier by Kremann — see the "potential" series (67).

A semi-empirical relationship which makes it possible to explain the values of z^* for the solutions studied was obtained[30]. An attempt was made to calculate the effective charges of the impurities in various solvents making the following assumptions: (1) the cross-section of scattering is proportional to the square of the "true charge" of the ion (of both impurity and solvent); and (2) the "true charge" of the ion is equal to the number of its group $\bar{z}$ in Mendeleev's Periodic System. Thus from (57) we have

$$z_2^* = \bar{z}_2 - \bar{z}_1\left(\frac{\bar{z}_2}{\bar{z}_1}\right)^2 = \bar{z}_2 - \frac{\bar{z}_2^2}{\bar{z}_1}. \qquad (69)$$

The values of z_2^* calculated from formula (69) are given in the sixth and last columns of Table 7. The good agreement between experiment and formula (69) is noteworthy. Deviations from the calculated values are observed only for silver and calcium. These results indicate that Belashchenko's suggestions[30] regarding z and σ for metallic solutions are apparently correct.

From this it follows, in particular, that the model assuming incoherent scattering of the conductivity electrons on the force centres is applicable to the case of liquid alloys

TABLE 7. Effective charges of impurities in various solvents[30,85].

Solvent	Impurity: element	Impurity: wt. %	Temperature, °C	z_2^* (mean)	$\bar{z}_2 - \frac{\bar{z}_2^2}{\bar{z}_1}$	Solvent	Impurity: element	Impurity: wt. %	Temperature, °C	z_2^* (mean)	$\bar{z}_2 - \frac{\bar{z}_2^2}{\bar{z}_1}$
Pb	Zn	0.04	360	0.9	1.0	Pb	Se	0.05	360	—2.9	—3.0
Cd	Sn	0.41	360	—5.4	—4.0	Bi	Ag	0.001	300	0.14	0.8
Bi	Cd	2.53	300	1.36	1.2	Pb	Ag	0.001	360	0.4	0.75
Cd	Bi	4.75	350	—16.4	—7.5	Sn	Ga	0.1	300	0.7	0.75
Sn	Bi	4.8	350	—0.8	—1.25	Bi	Ca*	?	300	0.4	1.2
Bi	Se	0.085	300	—0.9	—1.2	Cd	Ca*	?	360	—3.0	0

* Taken from Belashchenko[35].

not only for the impurities but also for the solvent. Thus the resistance of a pure liquid metal can be described not by the approximation assuming scattering of the electrons on phonons but by the approximation assuming incoherent scattering on individual atoms. This conclusion agrees with the almost linear behaviour of the electrical-resistance isotherms in a number of simple binary eutectic systems. When the electrical-resistance isotherm has a clearly--defined parabolic form, similar to that for solid solutions, this may mean either that the coherence of the scattering is largely preserved, or that the cross-section of scattering for the components depends on the composition, or that the scattering of the electrons by the ions is related not only to the charge on the ion but also to other properties of the ion. In the last case the cross-section may depend, for example, on the difference in the volumes of the atoms of solvent and impurity. In this case we would hardly expect that the cross-section of scattering would be related in simple fashion to the position of the components in Mendeleev's Periodic System.

The behaviour of the noble metals silver and gold in various solvents is of considerable interest, in view of their increased electron affinity. The results of a preliminary study of the e.m. of silver (Table 7) showed that z^* for silver differs significantly from that calculated from formula (69). The effective charges of the isotopes ^{110m}Ag and ^{198}Au in liquid Cd, In, Tl, Sn, Pb, and Bi at 350° were determined[25] in vertical capillaries with diameter 1 mm and length of metal column 40 mm, at a current strength of 1.5 A. The results are given in Table 8 and Fig. 2 (the values of z^* for gold and silver in mercury at 25° are taken from Table 2).

TABLE 8. Effective and "true" charges of noble metals in various solvents[25].

Solvent	Period V			Period VI			
	Cd	In	Sn	Hg*	Tl	Pb	Bi
z^* for silver	—1.25	—0.74	—1.07	1.43	0.64	0.48**	0.14
z^* for gold	—2.2	—	—2.0	1.47	—0.28	—0.10	—0.18
z for silver	—0.87	—0.6	—0.9	?	0.9	0.56	0.14
z for gold	—1.3	—	—1.5	?	—0.26	—0.10	—0.18

* Data from Table 2.

** More accurate value than that given in Table 7.

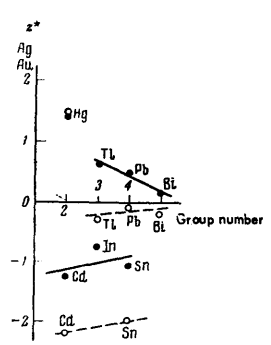


Fig. 2. Effective charges of traces of gold and silver in various solvents. ● — z^* for silver, ○ — z^* for gold.

To find the "true charge" of the Ag and Au ions in the solution[25], it was assumed, as in other work[30], that the cross-section of scattering is proportional to the square of the true charge. Eqn. (57) is then written in the form

$$z_2^* = z_2 - \frac{z_2^2}{\bar{z}_1}, \qquad (70)$$

where $\bar{z}_1$ is the Group number of the solvent.

It can be seen from Fig. 2 that the charges z^* and z for silver and gold change fairly regularly with change in the Group number of the solvent within a given period of Mendeleev's Periodic System. On going from solvents of the Fifth Period (Cd, In, and Sn) to solvents of the Sixth Period (Hg, Tl, Pb, and Bi), the charges of silver and gold change significantly, becoming more positive in the solvents of the Sixth Period. This change in z^* is approximately the same for silver and gold and amounts to 1.5–2 electronic charges.

The simple zone model, which assumes that the valency electrons are free, does not explain this result. According to Friedel[86], a local bound-electron level may be produced in metals close to an impurity atom if the ionisation energy of the impurity atom is greater than the depth of the potential well for an electron in the solvent. The production of local levels should lead to the formation of neutral impurity atoms or even negative ions. Since Pb has a greater atomic volume, that is, a lower concentration of valency electrons, than Sn, the Fermi energy in Pb is smaller. If we assume that the work functions for Pb and Sn are about equal, we find that the bottom of the potential well in Pb is higher than that in Sn. Thus according to Friedel[86], the formation of local states is more probable in Pb than in Sn, that is, an impurity should be more negative in Pb than in Sn.

The data in Table 8 do not agree with this conclusion. Since the above discussion is applicable not only to Sn and Pb, the reasons for the deviation from Friedel's theory[86] should be general for all the solutions studied. Either this theory is inapplicable to multivalent solvents, or the interaction of the impurity ion with the surrounding ions of the solvent produces a significant displacement of local levels, not taken into account by this theory.

The marked influence of the nature of the interaction between the impurity and solvent is revealed by examining the equilibrium diagrams for the systems formed by silver and gold with the metals of Periods V and VI.[77] With metals of Period V (Cd, In, and Sn), silver and gold form exclusively diagrams with electron compounds and intermetallic compounds, but with metals of Period VI (Tl, Pb, and Bi) they form chiefly eutectic systems. Eutectic character in a system A–B is usually associated with a positive value for the energy of mixing

$$\varepsilon = \varepsilon_{AB} - \frac{1}{2}(\varepsilon_{AA} + \varepsilon_{BB}), \qquad (71)$$

where ϵ_{ik} is the potential energy of the pairing interaction. In systems with appreciable affinity of the components, the energy of mixing is usually negative. Thus the increase in the negative character of the charges of silver and gold on going from solvents of Period VI to solvents of Period V should be associated with a decrease in the energy of mixing (on going from positive values of ϵ to negative values) or should even be responsible for this decrease. The extremely incomplete data on heats of dissolution[87] suggest that these heats decrease on going from silver to gold and from solvents of Period VI to solvents of Period V; in the last case the sign of the heat of dissolution changes from negative to positive.

It can be seen from Table 8 that for the Ag–Sn, Au–Bi, and Au–Pb systems the direction of e.m. is opposite to those given in Table 4. This is apparently due to the inadequacy of Kremann's procedures.

The e.m. of traces of ^{204}Tl in liquid Cd, In, Sn, Pb, and Bi was studied at 350°.[32] The values of z^* for thallium are given in Table 9. The dependence of z^* for thallium on the position of the solvent in Mendeleev's Periodic System is the same as that for the noble metals silver and gold. Change in the Group number of the solvent again leads to a small change in z^* for thallium, and change from solvents of Period VI to solvents of Period V is accompanied by a decrease in z^* by 1.5–2 units. In the case of thallium, however, there is no sharp boundary between the types of equilibrium diagram which it forms with the metals of Periods V and VI.

The fact that for e.m. in dilute solutions thallium behaves like silver and gold is apparently related to the similarity between the structures of the electron clouds of the Ag, Au, and Tl atoms. The inner levels of these atoms have identical structures. The differences lie in the number of valency electrons ($5s^1$ for silver, $6s^1$ for gold, and $6s^26p^1$ for thallium). The similarity between Ag, Au, and Tl apparently indicates that the dissolution of thallium in a metal is accompanied by an appreciable displacement of the $6s^2$ level, so that the corresponding electrons remain bound.

The influence of incomplete filling of the 3*d* level on e.m. was studied[32,34] for the case of solutions of ^{60}Co and ^{63}Ni in Cd, In, Sn, Pb, and Bi at 350° in straight vertical capillaries with diameter ~ 1 mm at a current strength of ~ 2 A. The length of the metal columns was 40 mm. The results[32,34] (Table 10) show that z^* for the transition-metal impurity depends to a marked extent on the Group number of the solvent. It was suggested[32] that the "true charge" of the transition metal is the same in all solvents and that, as before, the "true charge" of the solvent z_1 is equal to its Group number $\bar{z}_1$ in Mendeleev's Periodic Table, and $\sigma_1 \simeq k\bar{z}_1^2$. Eqn. (57) then acquires the form

$$z_2^* = z_2 - \frac{a}{z_1}, \qquad (72)$$

where z_2 and a are constants which depend on the nature of the impurity but not on the nature of the solvent. The plot of z^* for the impurity against $1/\bar{z}_1$ should be given by straight lines. Fig. 3 shows that this relationship is satisfied fairly well. The equations for the graphs in Fig. 3 are

$$z^*(\mathrm{Co}) = 10 - \frac{64}{\bar{z}_1}, \qquad (73)$$

$$z^*(\mathrm{Ni}) = 3 - \frac{22.8}{\bar{z}_1}. \qquad (74)$$

In all the solutions the predominant part in e.m. is played by the "electron wind".

Two explanations for the unique features of the e.m. of transition-metal impurities were put forward[32,34]. The first is based on Friedel's concept[88,89], according to which the 3*d* states of the impurity electrons are raised into the conductivity zone of the solvent and take part in resonance with the valency states, so that the 3*d* cloud of the transition-metal impurity is "smeared out". To explain the high value of the "true charge" of traces of Co and Ni — 10 and 3 according to formulae (73) and (74) — it was suggested[32] that the 3*d* electrons taking part in the resonance behave during e.m. in the same way as the valency electrons of non-transition elements. This is also responsible for the high values of the cross-sections of the scattering of electrons on transition-metal impurities.

Another reason for the high negative values of z^* may be the scattering of the conductivity electrons on unfilled states of the 3*d* level[34]. In this case the e.m. effect should increase with increase in the number of unfilled 3*d* states[90]. It is suggested that an analogous mechanism is responsible, in particular, for the increased electrical resistance of pure transition metals[90].

It can be seen from Table 10 that the cross-section of scattering is approximately proportional to the square of the number of unfilled states in the free Co and Ni atoms. If we assume that the "true charges" of Co and Ni are small and positive, we find from Table 10 that $z^*_{Co}/z^*_{Ni} \simeq \sigma_{Co}/\sigma_{Ni} = 2.5$ (for solutions in Cd and In). The ratio of the numbers of unfilled 3*d* states in Co and Ni is 3 : 2, however. It is possible that the two mechanisms described are of equal importance in the e.m. of transition-metal impurities.

The electromigration of impurities in liquid transition metals (Fe and Ni) was studied[91] at 1500–1600° with wire specimens in quartz capillaries. A liquid zone of length 12–15 mm was produced by heating a section of the capillary with the wire in a molybdenum spiral. The results (Table 11) show that z^* for impurities lying to the left of

TABLE 9. Electromigration of thallium in various solvents at 350°.[32]

Solvent	Period V			Period VI	
	Cd	In	Sn	Pb	Bi
z^* for thallium	−2.1	−1.5	−1.3	0.4	0.2

TABLE 10. Electromigration of traces of ^{60}Co and ^{63}Ni in various solvents at 350°.[32,34]

Solvent	Cd	In	Sn	Pb	Bi
z^* for cobalt	−22	−12	−6	−11	−1.2
z^* for nickel	−8.4	−4.7	−2.8	−	−0.7

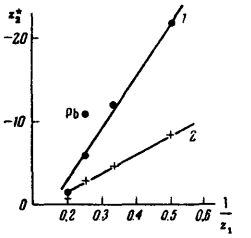


Fig. 3. Dependence of z^* for traces of Co and Ni on the reciprocal of the Group number of the solvent.
1) z^* for cobalt; 2) z^* for nickel.

TABLE 11. Electromigration of impurities in liquid iron (~1600°) and nickel (~1500°).[91]

Solvent	Impurity	At. fraction of impurity	z^*
Fe	Mn	0.005	5
Fe	Ni	0.08	—4
Ni	Mn	0.10	56—76
Ni	Fe	0.02	15
Fe	C	0.016	11

the solvent in the Periodic System are positive, the values being greater, the further the impurity from the solvent. The high positive values of z^* for the impurities were attributed[91] to the influence of the "hole wind", that is, to the scattering of holes in the 3*d* zone of the alloy on unfilled states of the 3*d* level of the impurity or on the ions of non-transition impurities (C in Fe).

The e.m. of traces of Cu, Ni, Mg, Zr, Pd, and U in liquid bismuth was studied[92] at 500°. The method involved the measurement of the quantity of impurity passing under the influence of current from a large volume of solution into a capillary with one end immersed in the solution (or in the opposite direction). The concentration of impurity amounted to 0.05–0.5 wt.%. The mobilities of the impurities (in the order given above) had the following values ($cm^2\ s^{-1}\ V^{-1}$): -1.95×10^{-4}, 5.0×10^{-4}, -5.97×10^{-4}, 2.61×10^{-4}, 3.05×10^{-4}, and 2.57×10^{-4} (the results for nickel contradict those in Table 10). It was assumed[92] that the e.m. method can be used to separate the components of the solution.

Studies were made[93,94] of the e.m. of traces of sulphur in molten cast iron (1340°, duration of heating 11–29 h), length of specimens 35–40 mm, average composition 0.07–0.11 wt.% sulphur, cast iron saturated with carbon) and silver (1080°, duration of heating 12 h, length of specimens 35 mm, average composition 0.1% sulphur). The values found for the effective charges z^* were 1.5–2.4 for sulphur in cast iron and -5.5–10.8 for sulphur in silver. These results indicate that the electron wind plays a significant part in e.m. in liquid silver, whereas in the case of cast iron the forces of the field, the electron wind, and the hole wind almost balance. The determination of the "true charge" of sulphur in cast iron and silver on the basis of the data obtained is difficult.

5. Electromigration in Binary Liquid Alloys

It was shown[30] that e.m. in the simplest cases is described satisfactorily by formula (69), that is, it agrees with the suggestion that the "true charge" z is equal to the Group number of the element $\bar{z}$ and with the proportionality $\sigma \simeq k\bar{z}^2$. The applicability of these assumptions for concentrated solutions was verified[31,33] for the Cd–Sn, Cd–Bi, Cd–Pb, and Bi–Sn systems. Formula (56) can be written in the form

$$z_1^* = \frac{N_2\left(\frac{\sigma_2}{\sigma_1}Z_1 - Z_2\right)}{1-\left(1-\frac{\sigma_2}{\sigma_1}\right)N_2}. \qquad (75)$$

If z_1, z_2, and σ_2/σ_1 are constant within a given binary system, we have

$$z_1^* = \frac{aN_2}{1-bN_2}. \qquad (76)$$

It was found[31,33] that e.m. in the systems studied is described satisfactorily by equations of type (76):

in the cadmium–tin system

$$z_{Sn}^* = -\frac{1.01N_{Cd}}{1-0.813N_{Cd}}, \qquad (77)$$

in the bismuth–cadmium system

$$z_{Bi}^* = -\frac{1.87N_{Cd}}{1-0.886N_{Cd}}, \qquad (78)$$

in the bismuth–tin system

$$z_{Sn}^* = \frac{2.5N_{Bi}}{1+0.552N_{Bi}}, \qquad (79)$$

in the cadmium–lead system

$$z_{Pb}^* = -\frac{1.06N_{Cd}}{1-0.78N_{Cd}}. \qquad (80)$$

These equations were used to find the ratios σ_i/σ_{Bi}:

$$\frac{\sigma_{Cd}}{\sigma_{Bi}} = 0.114;\quad \frac{\sigma_{Sn}}{\sigma_{Bi}} = 0.644;\quad \frac{\sigma_{Pb}}{\sigma_{Bi}} = 0.519. \qquad (81)$$

It was shown[31] that

$$\sigma_i \sim (\bar{z}_i)^{2.36}, \qquad (82)$$

that is, the proportionality $\sigma \simeq k\bar{z}^2$ is satisfied approximately, but not rigorously.

The experimental values of z^* for lead and tin in the cadmium–lead and cadmium–tin systems at 300°[31,33] are given in Fig. 4, together with a curve calculated from Eqn. (75) on the assumption that $z_1 = 4$, $z_2 = 2$, and $\sigma_2/\sigma_1 = \left(\frac{2}{4}\right)^{2.36}$ [in accordance with (82)]:

$$z_{Pb,Sn}^* = -\frac{1.222N_{Cd}}{1-0.805N_{Cd}}. \qquad (83)$$

It can be seen from Fig. 4 that as a first approximation, the agreement between calculation and experiment is satisfactory. The discrepancy amounts to ~10%. The discrepancy is slightly greater (40%) in the Cd–Bi and Bi–Sn systems[31]. Thus the assumptions that the true charge is

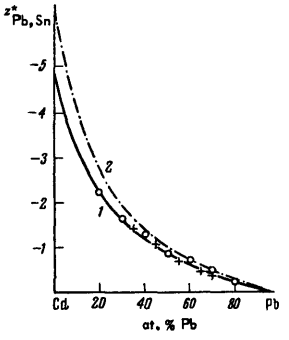


Fig. 4. Effective charges of tin and lead in the cadmium–tin and cadmium–lead systems. + — z^* for tin, ○ — z^* for lead. 1) Plot of $z^*_{Pb} = -\frac{1.06N_{Cd}}{1-0.78N_{Cd}}$, 2) plot of $z^*_{Pb,Sn} = -\frac{1.222N_{Cd}}{1-0.805N_{Cd}}$.

equal to the Group number and that σ is approximately proportional to the square of the charge apply fairly satisfactorily to simple eutectic systems.

On going to more complex systems, however, the hyperbolic relationship (76) no longer applies. For example, in the Au–Sn system at 450°,[33] z^* for gold shows a maximum in the range 20–30 at.% Au, but with further increase in the gold concentration, z^* decreases. In the Cd–Tl system[35] the value of σ for thallium is anomalously high (3 times the calculated value). It is as yet difficult to discuss the results of e.m. in these systems, because of the lack of experimental material.

6. Relationship Between Electrical Conductivity and Electromigration in Liquid Metals

The relationship between the scattering cross-sections responsible for e.m. and electrical resistance has been examined[33]. If it is assumed that these cross-sections are equal, it is possible to use the e.m. data and a knowledge of σ_2/σ_1 to calculate the ratio of the electrical resistivities of the corresponding pure liquid metals. The results[33] are given in Table 12. In the absence of e.m. data, the σ_2/σ_1 values were calculated from formula (82). Table 12 shows that the discrepancy between ρ_{exp} and ρ_{calc} is small for Pb, Bi, Sb, Ag, Cu, and Na. An appreciable difference is observed for Sn, Hg, and Al. The last two metals also show anomalous behaviour in the jump in the values of ρ on fusion[95].

The results obtained indicate that the ratios of the cross-sections of scattering σ_2/σ_1 for the phenomena of e.m. and electrical conductivity are fairly close. The electrical resistivity of a liquid metal can evidently be regarded, as a first approximation, as due to incoherent scattering on ions.

It was shown[33], however, that constant values of σ_2/σ_1 within a given binary system should not be observed if the ρ isotherms show a maximum. An example of this is the potassium–sodium system. It was observed[29] that the concentration dependence of the e.m. effect (with inversion) is similar to the function $\frac{\partial}{\partial N_2}(V_{mean}/\rho)$, where N_2 is the atom fraction of potassium, V_{mean} the mean atomic volume of the alloy, and ρ its electrical resistivity. The relationship between e.m. and ρ for K–Na alloys was also examined by Belashchenko[33]. It was found that in systems with a maximum value of ρ it is more convenient, as in the case of solid solutions, to consider the individual components of the electrical resistance: the additive component and the residual resistance, and also the corresponding components of the cross-section of scattering σ. Simultaneous examination of the data for e.m. and ρ made it possible to determine the fraction f of the residual resistance corresponding to all the sodium atoms in the solution[33]:

$$f \simeq 0.1 + 0.9 N_{Na}. \qquad (84)$$

TABLE 12. Calculation of the electrical resistivity ρ of liquid metals from e.m. data[33].

Metal	z	Temp., °C	ρ_{exp}/ρ_{calc}	Metal	z	Temp., °C	ρ_{exp}/ρ_{calc}
Cd	2	321	1.00	Hg	2	0	2.81
Sn	4	232	0.45	Al	3	658	0.35
Pb	4	327	1.09	Ag	1	1000	1.52
Bi	5	269	0.77	Cu	1	1100	1.56
Sb	5	631	0.79	Na	1	100	1.11

The inversion of e.m. in the K–Na system is attributed[33] quantitatively to the fact that the potassium ion (diameter 4.76 Å) dissolved in sodium (diameter 3.82 Å) distorts the arrangement of the ions in several coordination spheres, whereas the sodium ion dissolved in potassium influences only its first coordination sphere.

7. Study of the Electrodiffusion Potential in Liquid Metallic Solutions

The first studies of electrodiffusion potential (e.d.p.) in amalgams were made by Schwarz[14]. The mobilities of the impurities, calculated from the results of e.d.p. measurements, showed good agreement with the e.m. data and are given in Table 2.

The e.d.p. effect was studied[35,57,58] in liquid alloys of the Pb–Sn, Bi–Sn, Bi–Cd, Bi–Te, and Na–Tl systems. In the last two systems, marked deviations from ideal behaviour were observed. In the solid state the components form intermetallic compounds Na_2Tl, NaTl, and Bi_2Te_3.

Since the magnitude of the e.d.p. is of the order of 10^{-6}–10^{-5} V, special precautions were necessary to eliminate the Seebeck effect. The experiments were carried out in glass capillaries of internal diameter 1 mm. The denser component was poured into the capillary first, followed by the second metal. The total length of the specimen was 20–40 mm. The heating was carried out in an oil thermostat at temperatures up to 350°, or in a vacuum furnace; the specimens were kept in a copper thermostat block. In the measurement of the e.d.p., molybdenum leads sealed to the ends of the capillary were connected to a galvanometer.

The initial values of the e.d.p. (after rapid heating to the required temperature) were 1.5×10^{-6} V in the Bi–Sn system at 280°, 5×10^{-6} V in the Pb–Sn system at 375°, 5×10^{-5} V in the Bi–Cd system at 330°, 8×10^{-5} V in the Na–Tl system at 310°, and 5×10^{-5} V in the Bi–Te system at 590°. During the heating of the specimens, a sudden decrease in e.d.p. was observed at the melting points of the intermetallic compounds NaTl and Bi_2Te_3. During isothermal treatment the value of the e.d.p. decreased smoothly to zero as a result of the equalisation of the composition.

The results of e.d.p. measurements[57,58] were used to calculate the effective charges of the components. By integrating Eqn. (37) with allowance for (76), we obtain[35,58]

$$\epsilon \simeq -\frac{\bar{D}}{\bar{\varkappa}} e \left(\frac{\bar{N}}{\bar{V}}\right) z_{10}^{*} \frac{(1-b)\ln(1-b)}{b}, \qquad (85)$$

where the bar above the symbols denotes that the quantity is averaged with respect to composition within the binary system, V is the volume of 1 g-atom of the alloy, and z_{10}^{*} is the value of z_1^* as $\bar{N}_1 \to 0$. If we assume that $\sigma_2/\sigma_1 = (\bar{z}_2/\bar{z}_1)^2$, where $\bar{z}$ is the Group number of the component, we can use the value of the e.d.p. ϵ to calculate z_{10}^* and compare these results with the e.d.p. results. Since the averaging process is not sufficiently rigorous, the calculated values of z_{10}^* are only approximate. Nevertheless, these values of z^* show satisfactory agreement with those found from e.m., with respect to both sign and magnitude[96]. The calculation of z^* for systems with intermetallic compounds was not carried out, since in these cases the values of D, V, and $\varkappa$ should depend to a marked extent on composition. The sign of the e.d.p. in these cases is given by the rule according to which z^* for the component with the smaller Group number is positive — see Eqn. (69). The high values of the e.d.p. in these systems indicate, however,

that when there is a specific interaction between the ions of the components, formula (69) may give marked deviations from reality.

It was shown[57] that the temperature dependence of the e.d.p. is due chiefly to the change in the diffusion coefficient; this makes it possible to determine the activation energy of diffusion Q in liquid alloys. For the Pb–Sn system, the mean value of Q was found[57] to be 7 kcal mole^{-1} with an accuracy of ~ 20%.

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The results of the study of e.m. in liquid alloys of metals of the type Cd, Sn, Pb, Bi, etc. make it possible to assume that the "true charge" z is approximately equal to the Group number of the given element in the Periodic System. In other words, despite the small screening radii in metals (less than 10^{-8} cm), the valency electrons of these elements are almost completely delocalised for e.m. (and electrical conductivity). This is evidently related directly to the familiar Hume–Rothery rule. In the case of transition-metal impurities, the concept of "true charge" is more complicated. Data on the migration of traces of Co and Ni do not agree with the assumption that their 3d levels are filled by the conductivity electrons of the solvent (so-called donor–acceptor interaction).

In the simplest cases, σ depends on the Group number of the element and is approximately proportional to the square of the Group number. For systems with linear electrical-resistivity isotherms, the scattering on the ions of the components is found to be for the most part not a collective act but a separate act. The presence of unfilled d levels leads to an increased scattering of electrons. From this it follows that the e.m. method is convenient for the study of interaction in systems containing transition metals. Filling of the sublevels should lead to a decrease in the contribution made to z^* by the scattering of the charge carriers. Moreover, z^* is extremely sensitive to specific interionic interaction. The limiting case of a strong bond is apparently exemplified by solutions of cadmium, etc. in alkali metals, where it is possible to use the spherical-complex model. In these systems inversion of e.m. may be expected.

In view of the similarity in the energetic properties of liquid and solid metallic alloys, it may be assumed that the "true charges" of the ions are similar in the two cases. However, the mechanisms of the scattering of conductivity electrons on the ions of the impurity and solvent are not the same. Moreover, the values of σ for ions in the ground state and transition state also differ[16,17,64]. Thus other relationships are to be expected for e.m. in solid solutions.

NOTE ADDED IN PROOF

It has been shown[97] that traces of Tl, In, and Ba in liquid Na move during e.m. to the positive electrode; however, traces of Sr and Ag, which do not form compounds with Na, take almost no part in e.m. These results provide evidence in support of the model according to which the complex is entrained by the electron wind. It has been proposed[98] that the characteristic features of interatomic bonding in solutions be studied by a "probe" method, in which the e.m. of an impurity with a known true charge in the solution being studied is determined. The method was applied to the Cd–Bi system; a trace of $^{113-123}$Sn was used as probe.

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PYRAZOLONE DERIVATIVES AS ANALYTICAL REAGENTS

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