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Coupled Chemical Diffusion of Ions and Electrons in Non-stoichiometric Crystals

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The theory of the coupled chemical diffusion of ions and electrons in solids under the influence of the gradient of the degree of deviation from the stoichiometric composition is described consistently on the basis of the phenomenological and statistical-thermodynamic approaches. Within the framework of the model of non-interacting defects, the behaviour of crystals with the following types of disorder is examined: Frenkel', structural, Schottky, Wagner, impurity, and electronic disorder. Account has been taken of the influence of the degeneracy of the electrons. The main principles of the experimental methods for the determination of the coupled chemical diffusion coefficient are described and the experimental data are compared with the theory.
The bibliography includes 85 references.

CONTENTS

I. Introduction 495
II. Phenomenological equations 496
III. The chemical diffusion coefficient of electrons under conditions where ionic disorder is dominant 498
IV. Coupled chemical diffusion coefficient of ions and electrons in crystals with different defect structures 501
V. Experimental determination of chemical diffusion coefficients 504

I. INTRODUCTION

Studies of diffusion processes in solids have already had a history extending over a century. Nevertheless, the theory of these processes is still far from being perfect. Perhaps the only exception is that of the simplest type of diffusion, namely self-diffusion, characterising the rate of migration of species in chemically homogeneous substances. Considerable advances in this field have been achieved as a result of the employment of radioactive tracers which are chemically indistinguishable from the principal atoms of the material investigated.

However, when a more complex phenomenon is tackled, namely the diffusion of impurity atoms in a chemically homogeneous substance (heterodiffusion), considerable difficulties arise owing to the need to take into account the correlation factors as a consequence of the different mobilities of the main and impurity atoms, the formation of different kinds of associated species, etc. Finally, the picture becomes very greatly complicated when one considers diffusion in variable-composition chemical compounds (chemical diffusion), otherwise referred to as non-stoichiometric compounds. In non-stoichiometric ionic compounds of the type $M_{1+\delta}X_r$, where r is an integer and δ the degree of deviation from stoichiometry, the excess content of cations and ions leads to the appearance of excess quasi-free electrons in the conductivity band or of electron holes in the valence band. When a gradient of the deviation from stoichiometry exists in a compound of this kind, the chemical potential gradients of both the metallic and non-metallic components, M and X, under the influence of which the cations and anions diffuse towards one another, are also present under these conditions. The local electroneutrality of the specimen is maintained by the equivalent flux of electrons. Such a process is usually referred to as chemical diffusion but this term requires revision. Strictly speaking, the term "chemical" refers to any diffusion in the field of chemical potentials, including the mutual diffusion of the components of non-ideal solutions. In a narrower sense the phenomena considered in this review will therefore be referred to as the coupled chemical diffusion (CCD) of ions and electrons in a chemical field, due to the deviations of the composition from stoichiometry (DCS), and in the electric field arising owing to the difference between the mobilities of species of different kinds.

The most important characteristic of CCD is the coupled chemical diffusion coefficient D, which is determined by the combination of the coefficients of the random diffusion of the cations and anions, the mobilities of the electron carriers, and the non-stoichiometry parameters. All these quantities are related to the defect structure of the crystal in different ways. For this reason, comparison of the CCD coefficient in the DCS field with other transport characteristics makes it possible to construct models of the disorder in crystalline bodies at the atomic level, which is one of the most important tasks of the modern solid state chemistry.

Chemical diffusion plays an important and in many cases also a decisive role in real processes accompanied by solid-phase chemical reactions: processes involving the formation of complex compounds from simpler compounds (the oxidation of metals and the solid-phase synthesis of materials) and the decomposition of complex compounds into simpler ones (the isolation of metals from ores, the purification of materials, etc.) and processes in which matter and electricity are transported in the elements of control systems (solid electrolytes and electrodes in microionics and electrochromic materials in optics) and in power plants (electrolysers and galvanic cells, thermoelectric converters, the electrodes of MHD generators, etc.).

A distinctive feature of the CCD in the DCS field relative to, for example, the self-diffusion of labelled atoms is the extremely high effective diffusion coefficients. Thus, whereas at 1000 K the self-diffusion coefficients are in the range 10^{-15}–10^{-8} $cm^2\ s^{-1}$ for the majority of crystalline bodies, reaching 10^{-5} $cm^2\ s^{-1}$ only in structurally disordered crystals (superionic conductors), the coupled chemical diffusion coefficient (CCDC) of ions, for example, in silver chalcogenides, is 10^{-1} $cm^2\ s^{-1}$. Such high values of the CCDC ensure an intense transport of matter for an insignificant driving force, i.e. for a small gradient of the degree of DCS.

The present review is devoted mainly to a consistent description of the theory of the CCD in the DCS field on the basis of ideas described in a monograph.[2] The methods for the measurement of the calculated quantities are also examined and the measured transport parameters of a series

of non-stoichiometric compounds are briefly discussed. The author did not attempt to give a detailed survey of the experimental studies and confined himself to the most reliable data. A more complete bibliography can be found, for example, in a number of other reviews.[3-6]

II. PHENOMENOLOGICAL EQUATIONS

1. General Expressions

For the non-correlated diffusion in solids, where the movement of carriers of different kinds is independent, the flux of charged species of type k in the chemical (concentration) and electrical field is defined by the Wagner equation[7]

$$J_k = -\frac{\varkappa_k}{q_k^2}(\nabla\mu_k + q_k\nabla\varphi) \ . \qquad (1)$$

Here the flux is measured as the number of species passing per unit time through a unit surface in a coordinate system rigidly linked to crystal lattice sites. The symbol $\varkappa_k$ denotes the partial specific electrical conductance of such species, q_k is their charge, and $\nabla\mu_k$ and $\nabla\phi$ are respectively the chemical potential and electrostatic potential gradients. The following expression is equivalent to the above equation:

$$J_k = -\frac{N_k D_k}{kT}(\nabla\mu_k + q_k\nabla\varphi) \ , \qquad (2)$$

where N_k is the concentration (number of k species per unit volume) and D_k the "random" diffusion coefficient of the k species linked to their electrical conductivity $\varkappa_k$ by the Nernst–Einstein relation:[2]

$$kT\varkappa_k = q_k^2 N_k D_k \ . \qquad (3)$$

In contrast to Eqn.(1), Eqn.(2) contains no charge in the denominator and is applicable not only to charged but also to neutral species (atoms, molecules, and defects) with $q_k = 0$.

By virtue of their phenomenological character, Eqns.(1) to (3) are equally valid for two different methods of describing the structure of defective crystals and the set of current carriers present in them.[2,13] In the first case the systems of structural elements, where the mobile carriers are assumed to be atoms or ions, may be adopted as a basis. The corresponding random diffusion coefficients of ions and electrons are referred to as macroscopic.[13] Eqn.(2) is applicable both in the absence of correlation (for example, for the direct intersite transport mechanism and probably in structurally disordered phases), where the values of D_k for atoms and ions are identical with their self-diffusion coefficients D^* measured with the aid of radioactive isotopes, and in the presence of a correlation effect. In the latter case, the quantity D_k in Eqn.(2) is linked to the self-diffusion coefficient by the Heyven relation[8] $D_k = f_k D_k$, where f_k is the correlation factor. In the second case, which is preferable in the statistical description of transport, the mobile carriers are assumed to be the atomic and ionic or electronic defects in the crystal lattice differing in their nature and also in their charge and energy state. The corresponding diffusion coefficients are referred to as microscopic.[2,13]

2. Neutral Species

Neutral species diffuse only under the influence of their chemical potential gradient $\nabla\mu_k$ and their diffusion is independent of the electric field. Assuming that, for the known composition of the specimen, the chemical potential of the species μ_k is a single-valued function of the concentration N_k, we can express $\nabla\mu_k$ in the form

$$\nabla\mu_k = \frac{d\mu_k}{dN_k}\nabla N_k = kT\frac{d\ln a_k}{dN_k}\nabla N_k \ ,$$

where a_k is the thermodynamic activity of the k component. Then Eqn.(2) assumes the form of Fick's first equation $J_k = -D_k\nabla N_k$ with an individual chemical diffusion coefficient (ICDC) of species of type k:[2]

$$\tilde{D}_k = F_k D_k \ , \qquad (4)$$

where the multiplier

$$F_k = \frac{N_k}{kT}\frac{d\mu_k}{dN_k} = \frac{d\ln a_k}{d\ln N_k} \qquad (5)$$

represents the so-called thermodynamic chemical diffusion factor. In the case of substitutional solid solutions, where $\Sigma N_k = \text{const}$. and $d\ln N_k$ can be replaced by $d\ln c_k$, where

$$c_k = N_k / \sum_k N_k$$

is the atomic fraction of atoms of type k in the corresponding sublattice, Eqn.(5) becomes identical with Darken's equation.[9]

Eqns.(4) and (5) belong to the set of principal equations of the modern theory of chemical diffusion and the calculation of thermodynamic factors is the central task in the latter.

3. Ions and Electrons. The General Case

The coupled diffusion of ions and electrons takes place as a rule in an electric field, which is determined both by an external source and by the charge of the moving species. The field accelerates the movement of the less mobile charge carriers and retards that of the more mobile ones. Accordingly, in the general case the role of the electric field in transport processes is just as important as the role of chemical fields. Nevertheless, for further consideration, it is convenient to introduce the concept of the individual chemical diffusion coefficient of charged species of type k, defined by the same equations (4) and (5) as for neutral species. The definition of the diffusion coefficient $\tilde{D}_k$, as the ratio of the flux of species of type k to the chemical potential gradient multiplied by N_k/kT subject to the condition that the electric field gradient is zero, follows from Eqn.(2).

In the general case of the coupled diffusion of electrons and several ions of the k type, their fluxes are linked by the condition

$$-eJ_e + \sum_k q_k J_k = I,$$

where I is the electric current density in the specimen. This makes it possible to eliminate the electric field strength from Eqn.(1) for the electron flux:

$$J_e = \frac{-\sigma}{e(\varkappa+\sigma)}\left[I + \sum_k \varkappa_k\left(\frac{\nabla\mu_k}{q_k} + \frac{\nabla\mu_e}{e}\right)\right] \ , \qquad (6)$$

where $\sigma = \varkappa_e$ is the electronic conductivity and $\varkappa = \sum_k \varkappa_k$ the overall ionic conductivity.

Eqn.(6) is phenomenological in character and is therefore applicable to systems containing mobile ions with any effective charges q_k, including arbitrarily selected charges. This factor is extremely important because the true ionic charges in solids are frequently unknown. In the calculation of the transport characteristics of the system within the framework of the phenomenological approach, it is more

convenient to choose classical ions as the moving species with the nominal charges $q_k = \pm z_k e$ determined by the valences of the corresponding elements z_k. In this case, it follows from the electro-neutrality condition for the crystals $eN_e = \sum_k q_k N_k$ that the valence electrons at a concentration N_e, in excess relative to the stoichiometric composition $\left(\sum_k q_k N_k = 0\right)$, participate in the transport regardless of whether these electrons exist in a quasi-free state or are localised at some donor or acceptor centres.

It is convenient to select the concentration of the excess (of deficient) electrons as a measure of the DCS. For example, in the case of a binary crystal MX_r the quantity

$$N_e = z_1 N_1 - z_2 N_2$$

(z_1 and z_2 are the valences of the metal M and the non-metal X) determines the difference between the concentrations of the cations and anions measured in terms of the number of elementary charges per unit volume (equivalent concentration multiplied by the Avogadro number). For the specified overall composition of the specimen, the chemical potential of both its components can be unambiguously related to N_e. In the absence of an electric current in the specimen, the expression for the electron flux [Eqn.(6)] can therefore be represented in the form of Fick's first equation $J_e = -\tilde{D}\nabla N_e$ with an effective CCDC:

$$\tilde{D} = t_i \tilde{D}_e + t_e \tilde{D}_i \ , \qquad (7)$$

where

$$t_i = \sum_k t_k = \varkappa/(\varkappa+\sigma)$$

is the overall transport number of the ions, $t_e = \sigma/(\varkappa+\sigma)$ the transport number of the electrons, and $\tilde{D}_e$ and $\tilde{D}_i$ are defined by the expressions

$$\tilde{D}_e = \frac{\sigma}{e^2}\frac{d\mu_e}{dN_e}; \qquad \tilde{D}_i = \sum_k \frac{\varkappa_k}{q_k e}\frac{d\mu_k}{dN_e} \ ,$$

where μ_e is the chemical potential of the electrons.

The physical significance of these quantities becomes apparent on further transformation. We shall represent the electronic conductivity by the sum of the conductivity due to the movement of n- and p-type carriers (conductivity electrons and holes): $\sigma = \sigma_n + \sigma_p$. With the aid of the Nernst–Einstein equation, we express the partial conductivities σ_n and σ_p in terms of the diffusion coefficients of the conductivity electrons and holes:

$$kT\sigma = e^2(nD_n + pD_p),$$

where n and p are their volume concentrations. The partial conductivities $\varkappa_k$ of ions of the kth type can also be expressed in terms of their diffusion coefficients:

$$kT\varkappa_k = q_k^2 N_k D_k.$$

Taking into account the evident relation $\mu_e = \mu_n = -\mu_p$, where μ_n and μ_p are the chemical potentials of the conductivity electrons and holes, and also the definitions specified by Eqns.(4) and (5), we obtain the equations

$$\tilde{D}_e = \frac{dn}{dN_e}\tilde{D}_n - \frac{dp}{dN_e}\tilde{D}_p; \quad \tilde{D}_i = \sum_k \frac{q_k}{e}\frac{dN_k}{dN_e}\tilde{D}_k \ . \qquad (8)$$

Hence it is seen that $\tilde{D}_e$ is the effective CDC of the electrons averaged with respect to n- and p-type carriers. The weighting factors dn/dN_e and $-dp/dN_e$ of the ICDC of the electron carriers $\tilde{D}_n$ and $\tilde{D}_p$ in Eqn.(8) determine the contributions of the conductivity electrons and holes to the overall DCS gradient. The coefficients $(q_k/e)dN_k/dN_e$ of the ICDC of the ions $\tilde{D}_k$ have an analogous significance, so that $\tilde{D}_i$ is the effective CDC of the ions averaged with respect to all the ionic species.

An equation similar to Eqn.(7) was first derived[10] for the coupled diffusion of cations and anionic vacancies in a structurally disordered solid electrolyte. Since Grafov and Ukshe[10] used the relations of the thermodynamics of ideal solutions, their equation contained the usual diffusion coefficients of the corresponding species D_k instead of the individual chemical diffusion coefficients $\tilde{D}_k$. A more rigorous derivation of Eqn.(7) taking into account thermodynamic factors was achieved by the author of the present review for the coupled diffusion of two arbitrary kinds of charged species.[1]

A remarkable feature of Eqn.(7) is the close relation between the electrical (t) and diffusional ($\tilde{D}$) characteristics of the ions and electrons due to the self-consistent character of the electrochemical fields in the diffusion zone. In the general case, this relation precludes the separation in Eqn.(7) of the individual terms due to the electrical and chemical fields. Such a separation becomes possible only in the limiting cases at $t \to 0$ or $t_e \to 0$, which are considered below.

Eqn.(7) can be conveniently used in the statistical calculation of the CCDC when the thermodynamic factors of the ions and electrons are determined by specific microscopic models of the disorder in the crystal. On the other hand, in the phenomenological approach, these factors remain undefined, because the chemical potentials of the ions and electrons are not susceptible to direct measurement separately. For this reason, within the framework of the phenomenological theory, it is useful to resort to the chemical potentials of the neutral components A_k corresponding to the k ions with the aid of the evident relation

$$\mu_{A_k} = \mu_k + \frac{q_k}{e}\mu_e \ .$$

Under these conditions, a simple and at the same time general formula for the effective CCDC follows from Eqn.(6):

$$\tilde{D} = \sum_k \frac{q_k dN_k}{e\, dN_e}\tilde{D}_{ke} \ . \qquad (9)$$

As in Eqn.(8), the summation for $\tilde{D}_i$ is carried out in this case over all types of ions. The partial quantities $\tilde{D}_{ke}$ have the significance of the CCDC for ions of the k type and electrons and are expressed either in terms of the partial conductivities of the k ions and electrons:

$$\tilde{D}_{ke} = \frac{\varkappa_k \sigma}{q_k^2(\varkappa_k+\sigma)}\frac{d\mu_{A_k}}{dN_k} \ , \qquad (10)$$

or in terms of the transport number of electrons and the macroscopic diffusion coefficients of the k ions:

$$\tilde{D}_{ke} = t_e D_k \frac{d\ln a_{A_k}}{d\ln N_k} \ . \qquad (11)$$

4. Ions of One Kind

In the simplest case where mobile ions of only one kind are present and the concentrations of all the remaining ions are constant, the electroneutrality condition is $eN_e = q_k \Delta N_k$, where ΔN_k is the excess content of the mobile ions relative to the stoichiometric composition. In this case Eqn.(9) assumes the simple form $\tilde{D} = D_{ke}$, which has two important corollaries.

Firstly, for mobile ions of one kind the CCDC is expressed, according to Eqn.(10), in terms of quantities susceptible to direct determination from independent experiments, which leads to the possibility of a rigorous comparison of the phenomenological theory with experiment. The derivation of Eqn.(10) for the case under consideration is due to Yokota,[11] who used it to calculate the transfer of charge in non-stoichiometric compounds of the type of silver sulphide in which the charge carriers are electrons and cations.

Secondly, when mobile ions of only one kind are present, Eqn.(11) for the CCDC of ions and electrons differs from Eqns.(4) and (5) for the ICDC of neutral atoms A_K only by the multiplier t_e and becomes identical with the latter for $t_e \cong 1$, i.e. when the electronic conductivity predominates ($\sigma \gg \varkappa$). In this case the coupled diffusion of ions of the same sign and of electrons is formally equivalent to the diffusion of the corresponding atoms. This conclusion is entirely understandable. Indeed, when $\sigma \gg \varkappa$, electrons exist under virtually equilibrium conditions and can compensate for the charge transfer by ions having low mobilities without much difficulty. The diffusional jumps of ions therefore lead to the same migration of substance as the jumps of neutral atoms and the diffusion in electronic conductors can be described with equal success in terms of the movement of both atoms and ions in the mobile electron medium. This factor is very important for the phenomenological theory of diffusion in solids with an intermediate ionic-covalent character of the bond, for example, in semiconducting compounds of the type $A^{III}B^{V}$, where the exact atomic mechanism of diffusion is usually unknown.

5. Ions of Two Kinds in a Binary Compound

We shall now consider a more complex case—the crystal of a binary ionic compound MX_r in which ions of both kinds are mobile. By designating the parameters of the cations and anions by the subscripts 1 and 2 respectively, we obtain $q_1 = z_1 e$ and $q_2 = -z_2 e$. For not unduly large DCS, $r = N_2/N_1 \cong z_1/z_2$ and one can therefore formulate the Gibbs–Duhem relation for the chemical potentials of the components in the form $z_2 d\mu_M + z_1 d\mu_X = 0$. Then, on substituting Eqn.(10) in Eqn.(9), we obtain the following expression:

$$\tilde{D} = \frac{\varkappa\sigma}{z_1 e^2 (\varkappa + \sigma)} \frac{d\mu_M}{dN_e} = -\frac{\varkappa\sigma}{z_2 e^2 (\varkappa + \sigma)} \frac{d\mu_X}{dN_e} \cdot \qquad (12)$$

Substitution of Eqn.(11) in Eqn.(9) leads to equivalent relations:

$$\tilde{D} = t_e N_1 (z_1 D_1 + z_2 D_2) \frac{d\ln a_M}{dN_e} = -t_e N_2 (z_1 D_1 + z_2 D_2) \frac{d\ln a_X}{dN_e} \cdot \qquad (13)$$

Eqns.(12) and (13) are analogous to the familiar Wagner formulae[7] which Wagner derived in connection with the development of the theory of the oxidation of metals.† Like Eqns.(9)–(11), they contain the absolute concentrations of the mobile components, namely the numbers of species per unit volume, as the variables.

Together with the relations quoted, an expression for $\tilde{D}$, incorporating the relative concentrations (atomic fractions) of the components, i.e. $c_1 = N_1/(N_1 + N_2)$ and $c_2 = N_2/(N_1 + N_2)$, is sometimes used in the literature. In terms of these variables, Eqns.(13) assume the simple form

$$\tilde{D} = c_2 \tilde{D}'_{1e} + c_1 \tilde{D}'_{2e} \; ; \qquad (14)$$

$$\tilde{D}'_{1e} = t_e D_1 \frac{d\ln a_M}{d\ln c_1} \; ; \quad \tilde{D}'_{2e} = t_e D_2 \frac{d\ln a_X}{d\ln c_2} \cdot \qquad (15)$$

Eqn.(14) is formally identical with Darken's equation[9] for binary metallic alloys (more precisely for atomic substitutional solid solutions—see also Chebotin,[2] p.248). However, the partial coefficients $\tilde{D}'_{1e}$ and $\tilde{D}'_{2e}$, corresponding to the coupled diffusion of cations and electrons or of anions and electrons, differ from the ICDC for neutral atoms [Eqns.(4) and (5)] and from the CCDC [Eqn.(11)] for the diffusion of ions of the same size and electrons even under conditions where $t_e \cong 1$, since in the case considered the cations and anions are distributed in different sublattices and $N_1 + N_2 = \text{const.}$, so that $d\ln c_k \neq d\ln N_k$.

All the equations quoted above were obtained by resorting to some kind of model ideas concerning the microscopic structure and the mechanisms of transport in solids. Their character is therefore phenomenological and they can be applied, in principle, to crystals with any types of disorder and with any types of chemical bonding. The diffusion coefficients of the components D_k and the thermodynamic factors F_k then play the role of phenomenological parameters susceptible either to experimental determination or to calculation on the basis of the microscopic theory. The subsequent exposition will concern the solution of the latter problem within the framework of the statistical-thermodynamic theory of disorder in crystalline bodies.[2]

III. THE CHEMICAL DIFFUSION COEFFICIENT OF ELECTRONS UNDER CONDITIONS WHERE IONIC DISORDER IS DOMINANT

We shall consider below crystals with dominant ionic disorder—either with structural disorder, where the classical ions are distributed among a large number of sites, or with ionic point defects whose effective charges correspond to the state of total ionisation. In all cases we shall neglect the possibility of the capture of electrons or holes by any electron-donating or electron-accepting centres. All the excess valence electrons are then present in the conductivity band and the missing electrons (holes) are in the valence band, DCS being defined as the difference between the volume concentrations of the conductivity electrons and holes:

$$N_e = n - p \; . \qquad (16)$$

The activities of conductivity electrons and holes, a_n and a_p, are linked by the following equation according to the Law of Mass Action:

$$\ln a_n + \ln a_p = 2 \ln K_i \; , \qquad (17)$$

which corresponds to the intrinsic ionisation reaction of the crystal, K_i being the reaction equilibrium constant. On differentiating Eqns.(16) and (17) with respect to N_e and on substituting the derivatives dn/dN_e and dp/dN_e in Eqn.(8) taking into account the definition of the thermodynamic factors for conductivity electrons $F_n = d\ln a_n/d\ln n$ and the analogous expression for holes, we find

$$\tilde{D}_e = \frac{nD_n + pD_p}{n/F_n + p/F_p} \cdot \qquad (18)$$

Hence it is seen that, when one type of electron carrier predominates, the CDC for electrons ($\tilde{D}_e$) is identical with the ICDC for these carriers, i.e. with $\tilde{D}_n$ for $n/F_n \gg p/F_p$ and with D_p for $p/F_p \gg n/F_n$.

The dependence of $\tilde{D}_e$ on the degree of DCS in the region of comparable concentrations of electrons and holes can be readily determined by assuming that in this region the

†In the second of Wagner's communications[7] where the concentrations were expressed in equivalents per unit volume, the coefficient z_1 was omitted in the denominator of Eqn.(23c).

electrons are non-degenerate as a consequence of the smallness of n and p. Eqn.(17) then assumes the simple form

$$np = K_i^2 \tag{19}$$

corresponding to the Boltzmann statistics and the solution of Eqns.(16) and (19) with subsequent substitution in Eqn.(8) yields the following results:

$$D_e = {}^1/_2 [\tilde{D}_n + \tilde{D}_p + (\tilde{D}_n - \tilde{D}_p) N_e (N_e^2 + 4K_i^2)^{-1/2}] \cdot \tag{20}$$

The parameters, D_n, D_p, F_n, and F_p for electrons and holes are determined from the electrophysical properties of the crystal. Thus the random diffusion coefficient of conductivity electrons is linked to their mobilities u_n by the Einstein relation $eD_n = kTu_n$, while the thermodynamic factor is equal to the ratio of the Fermi–Dirac integrals whose orders are 1/2 and −1/2:[12]

$$F_n = \frac{\Phi_{1/2}(\eta)}{\Phi_{-1/2}(\eta)}; \quad \Phi_j(\eta) = \frac{1}{j!}\int_0^\infty \frac{x^j\,dx}{\exp(x-\eta)+1}, \tag{21}$$

where

$$\eta = (\mu_n - E_c)/kT$$

is the reduced Fermi energy and E_C the energy of the bottom of the conductivity band. Analogous relations hold also for holes.

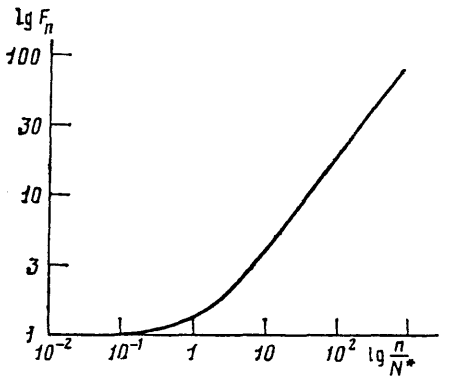


Figure 1. Dependence of the thermodynamic factor for conductivity electrons on their concentration.

Since $\Phi_{1/2}(\eta)$ is equal to the ratio of the concentrations of the electronic defects (n or p) to the effective density of states in the corresponding band $N^* = 2(2\pi m^* kT)^{3/2}h^{-3}$ (where m^* is the effective mass of the electron in the conductivity band and h the Planck constant), Eqn.(21) makes it possible to calculate directly the thermodynamic factor F_n (or F_p) as a function of the relative concentration of carriers n/N^* or p/N^*. The result of this calculation, carried out with the aid of tables of Fermi–Dirac integrals,[13] is presented in Fig.1 for conductivity electrons; the result is analogous for holes. As can be seen from this plot, the electron gas can be regarded as virtually non-degenerate for $n < 0.1\,N^*$, where $F_n \cong 1$. When the degeneracy is marked, i.e. $n > 10\,N^*$, the thermodynamic factor can be defined to a satisfactory approximation by the formula

$$F_n = (\pi/6)^{1/3}(n/N^*)^{2/3}.$$

We shall establish several further useful relations between the electronic conductivity, the thermodynamic factors, and the CCD of electrons. We introduce an auxiliary quantity—the average macroscopic diffusion coefficient of electron carriers:

$$D_e = \frac{nD_n + pD_p}{n+p} = \frac{kT\sigma}{e^2(n+p)} \tag{22}$$

and define an effective thermodynamic factor for electrons with the aid of the relation $\tilde{D}_e = F_e D_e$. Comparison of the last equation with Eqn.(18) yields the expression

$$F_e = \frac{n+p}{n/F_n + p/F_p} \cdot \tag{23}$$

Hence it is seen that the quantity F_e is unity in the absence of degeneracy and is equal to F_n or F_p when degeneracy obtains (for $n/F_n \gg p/F_p$ and $p/F_p \gg n/F_n$ respectively). Expressing D_e in terms of $\tilde{D}_e$ in Eqn.(22), we obtain

$$\sigma = \frac{e^2(n+p)\tilde{D}_e}{kTF_e} \cdot \tag{24}$$

1. Structural Disorder

More than 300 solid-phase compounds belonging to a comparatively new class of crystal structures with properties which until recently appeared to be unique have now been synthesised. Their distinctive feature is the structural disorder of one of the components (silver, copper, or alkali metal cations and in certain alkaline earth metal or lanthanide halides at high temperatures, also the halide anions), statistically distributed among a large number of sites, several times greater than the number of ions.[1,14–18] As a result, the disordered component resembles an ionic liquid, i.e. its transport properties are similar to those of solutions or fused electrolytes. The electrical conductivity of these compounds is 10^{-2} – 10^{-1} Ω^{-1} cm^{-1} even at room temperature, and, as a consequence of the high degree of disorder of the sublattice of only one of the components, the electrical conductivity of the crystal is unipolar. In the best solid electrolytes with structural disorder, also referred to as superionic conductors, the electronic component of the conductivity is negligible.[19,20] At the same time there exist a number of structurally disordered compounds which possess, together with the ionic component, also a considerable electronic component of the conductivity due to the deviations of their composition from stoichiometry.[21,22]

As a consequence of the unipolar ionic conductivity of structurally disordered phases, the effective CDC of the ions in them is identical with the ICDC of the disordered k component. On the other hand, the latter is independent of the concentration of any species according to the theory of diffusion in solids[2] (p.243) and is defined by the expression

$$\tilde{D}_i = \tilde{D}_k = \frac{D_k}{[V_k]} = \nu r_0^2 \exp\left(-\frac{U_k}{kT}\right), \tag{25}$$

where $[V_k]$ is the fraction of vacant sites in the k sublattice, ν the vibration frequency of the ions, r_0 the length of the elementary jump, and U_k the height of the potential barrier separating neighbouring sites.#

#It is easy to demonstrate that Eqn.(25) remains valid also when, as a consequence of the closeness of the allowed sites, each ion blocks $s > 1$ sites, so that the fraction of vacant sites is $1 - sN_k/N_L$, where N_L is the total number of allowed sites.

Eqn.(25) reflects the following significant factor: if the k sublattice contains ions of one kind only and vacancies, then the ICDC of these ions is the same as in systems with an unlimited free volume, i.e. with $[V_k] \to 1$, which are described by Einstein's diffusion theory. This result is important; it shows that an increase in the chemical diffusion coefficient owing to the increase in the thermodynamic factor occurs only for the upper limit of the quantities defined by Eqn.(25), specified by Einstein's theory.

We shall now proceed to the discussion of the CCDC of ions and electrons defined by the phenomenological Eqn.(7). Using Eqns.(3) and (25), we shall express the ionic conductivity in terms of the CDC of the ions: $kT\varkappa = q^2{}_k N_k \cdot [V_k]\tilde{D}_i$. Taking into account also Eqn.(24), we find from Eqn.(7) for $[V_k] \cong 1$

$$\tilde{D} = \frac{z_k^2 N_k F_e + (n+p)}{z_k^2 N_k F_e \tilde{D}_i + (n+p)\tilde{D}_e} \tilde{D}_i \tilde{D}_e \quad . \tag{26}$$

For not unduly large DCS, where $n + p \ll N_k$, the second term in the numerator in Eqn.(26) may be neglected. This is equivalent to the neglect of the second term of the phenomenological Eqn.(7), which is now formulated in a simplified form:

$$\tilde{D} = t_i \tilde{D}_e \quad . \tag{27}$$

We obtained Eqns.(26) and (27) for a crystal containing in the structurally disordered sublattice ions of only one kind k. It is easy to demonstrate that the above estimate of the second term in Eqn.(7) is at least qualitatively valid also for solid solutions containing ions of two or more kinds in the disordered sublattice.[23] In this case t_i in Eqn.(27) should be understood as the total transport number of the ions.

The smallness of the second term in Eqn.(7) compared with the first has a definite physical basis associated with the high concentration of vacant sites N_V in structurally disordered crystals. Since $N_V \cong N_k \gg |N_e|$, in most cases the relative changes in the concentrations of both ions and vacant sites actually attained remain negligibly small compared with the relative changes in the concentrations of electrons. By virtue of this relation, the intrinsic diffusional flux of ions in structurally disordered compounds is negligible and ions move virtually only under the influence of the internal electric field, which is directed in such a way that it diminishes the electron flux to a fraction t_i of their intrinsic diffusional flux.

Since the mobilities and hence also the diffusion coefficients of the conductivity electrons and holes in solids are usually of the same order of magnitude, the dependence of $\tilde{D}_e$ on the degree of non-stoichiometry (Fig.1) is comparatively weak. For this reason, according to Eqn.(27), the character of the dependence of $\tilde{D}$ on N_e is determined mainly by the change in the transport number of the ions. The corresponding curves have a maximum near the stoichiometric composition (for $D_n = D_p$ when the composition is exactly stoichiometric) and descend monotonically on either side of the maximum.

2. Fully Ionised Point Defects

We shall now consider a binary ionic crystal in which pair combinations of ionic point defects predominate for the stoichiometric composition: the Frenkel and Schottky defects or impurity atoms with effective charges corresponding to their complete ionisation. In this case the effective charges for the defects are determined by the valences of the corresponding components and amount to[1,2,24] $+z_1 e$ and $-z_2 e$ for the interstitial cations and anions, $-z_1 e$ and $+z_2 e$ for the cationic and ionic vacancies, and $\Delta q_f = q_f - q_k$ for the impurity centres formed by the substitution of the k ion by an impurity ion f. Classical examples of crystals with impurity disorder are provided by the solid solutions AgCl + $CdCl_2$ ($\Delta q_f = +e$, compensating defects—cationic vacancies), ZrO_2 + CaO ($\Delta q_f = -2e$), and ZrO_2 + Y_2O_3 ($\Delta q_f = -e$, compensating defects—anionic vacancies).

In the general case the ionic conductivity of a binary compound, both pure and in the presence of impurities, can be determined by the interstitial cations and anions and also by the cationic and anionic vacancies. For this reason, the ionic conductivity of the k component is expressed, according to the Nernst–Einstein relation, in terms of the diffusion coefficients of these defects:

$$kT\varkappa_k = q_k^2 (N_{ki} D_{ki} + N_{Vk} D_{Vk}) , \tag{28}$$

where the subscripts ki and Vk refer to the interstitial ions k and the vacancies in the k sublattice. According to the microscopic model of the transport of defects, their diffusion coefficients are determined by expressions of the type of Eqn.(25): $D = \nu r_0^2 \exp(-U/kT)$ and, in terms of the approximation of non-interacting defects, are independent of their concentrations and hence also of the DCS. On the other hand, within the framework of the phenomenological description of diffusion, the ionic conductivity of a binary compound is expressed in terms of the macroscopic diffusion coefficients of ions

$$D_k, \quad kT\varkappa_k = q_k^2 N_k D_k .$$

Comparison of this relation with Eqn.(28) leads to the familiar expression for D_k in terms of the microscopic characteristics of the system:

$$N_k D_k = N_{ki} D_{ki} + N_{Vk} D_{Vk} , \tag{29}$$

Furthermore, if there is a local equilibrium between ionic point defects in the crystal, then their concentrations are related by the expressions for the chemical potentials of the ions (at no unduly high concentrations):

$$\mu_k = \mu_{ki}^0 + kT \ln N_{ki} = -\mu_{Vk}^0 - kT \ln N_{Vk} , \tag{30}$$

where μ^0_{ki} and μ^0_{Vk} are the standard chemical potentials of the ions and vacancies in the k sublattice. By virtue of the Gibbs–Duhem relation, the following equation is then valid:

$$z_2 \mu_1 + z_1 \mu_2 = 0 . \tag{31}$$

In addition, the concentrations of the defects are linked by the electroneutrality condition for the crystal:

$$N_e = z_1 (N_{MI} - N_{VM}) + z_2 (N_{VX} - N_{XI}) + (\Delta q_f / e) N_f , \tag{32}$$

where N_f is the constant volume concentration of the impurity ions.

On differentiating Eqns.(30) and (32) with respect to N_e and on substituting the derivatives in Eqn.(8), taking into account Eqn.(29), we obtain the expression for the average CDC for the ions:

$$\tilde{D}_i = \frac{z_1^2 (N_{MI} D_{MI} + N_{VM} D_{VM}) + z_2^2 (N_{XI} D_{XI} + N_{VX} D_{VX})}{z_1^2 (N_{MI} + N_{VM}) + z_2^2 (N_{XI} + N_{VX})} \quad . \tag{33}$$

Here the summation has been carried out over the principal cations and anions and the contribution of the impurity ions to the transport was assumed to be negligible.

The exact dependence of $\tilde{D}_i$ on the DCS can be obtained by solving simultaneously for the concentration of the defects one of the equations of the Law of Mass Action [Eqns.(30) and (31)], which corresponds to a dominant disorder, and the simplified equation for the electroneutrality condition [Eqn.(32)]. It is readily seen that in the case of intrinsic

ionic defects (Frenkel or Schottky) the solutions are analogous to Eqn.(20) for the CDC for electrons in the absence of degeneracy and the corresponding plots of $\tilde{D}_i$ against N_e are similar to those in Fig.1. In particular, for high DCS, where one kind of ionic defect predominates, the $\tilde{D}_i$ curves approach asymptotically the diffusion coefficient of the given defect: D^i_{Mi} or D_{VX} in the presence of an excess of the metal and D_{Xi} or D_{VX} in the presence of an excess of the non-metal.

In the case of the impurity disorder, the excess charge of the impurity is compensated by one specific kind of intrinsic ionic defect. For this reason, according to Eqn.(8), $\tilde{D}_i$ is identical with the ICDC of the corresponding ions $\tilde{D}_k$ and, according to Eqn.(33), has a constant value equal to the diffusion coefficient of the compensating defect (D_{ki} or D_{Vk}) over a wide range of N_e.

Comparison of the results with Eqn.(29) shows that, in transport by point defects, the CDC for the ions exceed appreciably, usually by several orders of magnitude, the corresponding values of their macroscopic diffusion (self-diffusion) coefficients. The accelerating effect of thermodynamic factors, which increase $\tilde{D}$ up to the Einstein values D_{ki} or D_{Vk}, is in this case manifested even more distinctly than in the case of structural disorder.

On comparing Eqns.(28) and (33), we also obtain a relation between the ionic conductivity of the binary crystal and the CDC for the ions:

$$kT\varkappa = e^2\left[z_1^2(N_{\mathrm{Mi}}+N_{\mathrm{VM}})+z_2^2(N_{\mathrm{Xi}}+N_{\mathrm{VX}})\right]\tilde{D}_i \quad . \qquad (34)$$

Together with Eqn.(24), this relation makes it possible to express the transport numbers of the ions and electrons in terms of the corresponding CDC and to determine the CCDC for the ions and electrons in accordance with Eqn.(7):

$$\tilde{D}=\frac{\left[z_1^2(N_{\mathrm{Mi}}+N_{\mathrm{VM}})+z_2^2(N_{\mathrm{Xi}}+N_{\mathrm{VX}})\right]F_e+(n+p)}{\left[z_1^2(N_{\mathrm{Mi}}+N_{\mathrm{VM}})+z_2^2(N_{\mathrm{Xi}}+N_{\mathrm{VX}})\right]F_e\tilde{D}_i+(n+p)\tilde{D}_e}\,\tilde{D}_i\tilde{D}_e \quad . \qquad (35)$$

The instances of not unduly high DCS, where the term $n + p$ in the numerator in Eqn.(35) can be neglected compared with the concentrations of the ionic defects, are of special interest. The solutions thus obtained will be analysed in detail in the next Section; here it is sufficient to note that the above simplification is equivalent to the formulation of the phenomenological Eqn.(7) in the abbreviated form (27). The physical significance of this simplification is the same as in the case of structural disorder: the gradients of the chemical potentials of the ions are negligible compared with those for electrons and ions move virtually only under the influence of the electric fields.

IV. COUPLED CHEMICAL DIFFUSION COEFFICIENTS OF IONS AND ELECTRONS IN CRYSTALS WITH DIFFERENT DEFECT STRUCTURES

1. The Wagner Disorder. Neutral Defects

We shall refer to the Wagner disorder by the term combined ionic-electronic disorder in which the electroneutrality condition assumes one of the following simplified forms:

$$n=\zeta N^{\zeta+}_{\mathrm{Mi}};\quad n=\zeta N^{\zeta+}_{\mathrm{VX}};\quad p=\zeta N^{\zeta-}_{\mathrm{Xi}};\quad p=\zeta N^{\zeta-}_{\mathrm{VM}} \quad . \qquad (36)$$

Here the effective charge on the dominant ionic defect ζ can assume any integral value ranging from unity to one equal to the valence of the corresponding component z_k. The special case of the Wagner disorder, corresponding to the total ionisation of the defects ($\zeta = z_k$) satisfies the formal treatment developed in the previous Section and can be described with the aid of Eqn.(35). We shall discuss below the cases of an arbitrary degree of ionisation of defects ($\zeta \leq z_k$), including the case of dominant neutral defects.§

We shall now re-examine the binary compound MX_r; we shall assume that in the most general case it contains interstitial cations and anions as well as cationic and anionic vacancies with arbitrary integral effective charges ζ ranging from zero (neutral defects) to z_k (fully ionised defects). Assuming that the concentration of the impurity is negligibly small, we can formulate the electroneutrality condition in the following form:

$$N_e = z_1\sum_{\zeta=0}^{z_1}(N^{\zeta+}_{\mathrm{Mi}}-N^{\zeta-}_{\mathrm{VM}})+z_2\sum_{\zeta=0}^{z_2}(N^{\zeta+}_{\mathrm{VX}}-N^{\zeta-}_{\mathrm{Xi}}) \quad . \qquad (37)$$

In conformity with the last equation, the overall flux of electrons in excess of the stoichiometric composition is described by the expression

$$J_e = z_1\sum_{\zeta=0}^{z_1}(J^{\zeta+}_{\mathrm{Mi}}-J^{\zeta-}_{\mathrm{VM}})-z_2\sum_{\zeta=0}^{z_2}(J^{\zeta-}_{\mathrm{Xi}}-J^{\zeta+}_{\mathrm{VX}}) \quad . \qquad (38)$$

According to the Wagner equation [Eqn.(2)], the fluxes of defects are proportional to the gradients of their electrochemical potentials, the electrochemical potentials of the defects being linked to the chemical potentials of the atoms and electrons by the obvious relations

$$\begin{aligned}&\mu^{\zeta+}_{\mathrm{Mi}}=\mu_{\mathrm{M}}-\zeta\mu_e;\quad \mu^{\zeta-}_{\mathrm{VM}}=-\mu_{\mathrm{M}}+\zeta\mu_e;\\ &\mu^{\zeta-}_{\mathrm{Xi}}=\mu_{\mathrm{X}}+\zeta\mu_e;\quad \mu^{\zeta+}_{\mathrm{VX}}=-\mu_{\mathrm{X}}-\zeta\mu_e\,.\end{aligned} \qquad (39)$$

Furthermore, in the case of the Wagner disorder, the concentrations of the electron and ion carriers in the crystals are comparable according to Eqn.(36). On the other hand, since the mobility of the conductivity electrons and holes as a rule exceeds by several orders of magnitude the mobility of the interstitial ions and vacancies, such crystals always have a predominantly electronic conductivity. On this basis, we put $\sigma \gg \varkappa$. The electric field gradient $\nabla\phi$ is then determined from the condition that the electrochemical potential of the electron is constant ($\nabla\phi = \Delta\mu_e/e$) and we obtain from Eqn.(38)

$$\begin{aligned}kTJ_e=-\Bigg[&z_1\sum_{\zeta=0}^{z_1}(N^{\zeta+}_{\mathrm{Mi}}D^{\zeta+}_{\mathrm{Mi}}+N^{\zeta-}_{\mathrm{VM}}D^{\zeta-}_{\mathrm{VM}})\frac{\mathrm{d}\mu_{\mathrm{M}}}{\mathrm{d}N_e}-\\ &-z_2\sum_{\zeta=0}^{z_2}(N^{\zeta-}_{\mathrm{Xi}}D^{\zeta-}_{\mathrm{Xi}}+N^{\zeta+}_{\mathrm{VX}}D^{\zeta+}_{\mathrm{VX}})\frac{\mathrm{d}\mu_{\mathrm{X}}}{\mathrm{d}N_e}\Bigg]\Delta N_e \quad .\end{aligned} \qquad (40)$$

The coefficient of ∇N_e is the CCDC for the ions and electrons $\tilde{D}$ multiplied by kT. Taking into account the Gibbs–Duhem relation in the form

$$\mathrm{d}\mu_{\mathrm{M}}=-\frac{z_1}{z_2}\mathrm{d}\mu_{\mathrm{X}}=-\frac{z_1kT}{2z_2}\mathrm{d}\ln p_{\mathrm{X}_2} \quad , \qquad (41)$$

where p_{X_2} is the partial pressure of the non-metal in the surrounding medium, we obtain the following expression for $\tilde{D}$:

$$\begin{aligned}\tilde{D}=-\Bigg[&z_1^2\sum_{\zeta=0}^{z_1}(N^{\zeta+}_{\mathrm{Mi}}D^{\zeta+}_{\mathrm{Mi}}+N^{\zeta-}_{\mathrm{VM}}D^{\zeta-}_{\mathrm{VM}})+\\ &+z_2^2\sum_{\zeta=0}^{z_2}(N^{\zeta-}_{\mathrm{Xi}}D^{\zeta-}_{\mathrm{Xi}}+N^{\zeta+}_{\mathrm{VX}}D^{\zeta+}_{\mathrm{VX}})\Bigg]\frac{1}{2z_2}\frac{\mathrm{d}\ln p_{\mathrm{X}_2}}{\mathrm{d}N_e} \quad .\end{aligned} \qquad (42)$$

§ Although the diffusion of neutral defects is not associated with the separate movement of electrons, the formal treatment employed here remains valid also for such diffusion, provided that we put $q_k = 0$ in the Wagner equation [Eqn.(2)].

Eqn.(42) is a generalisation of the formula obtained[26] for bivalent metal oxides with the Wagner disorder involving interstitial cations or cationic vacancies with arbitrary degrees of ionisation.

The reciprocal of the derivative in Eqn.(42) will be expressed in the following form taking into account Eqn.(37):

$$\frac{d\,N_e}{d\ln p_{X_2}} = z_1 \sum_{\zeta=0}^{z_1} \left(N_{Mi}^{\zeta+} \frac{d\ln N_{Mi}^{\zeta+}}{d\ln p_{X_2}} - N_{VM}^{\zeta-} \frac{d\ln N_{VM}^{\zeta-}}{d\ln p_{X_2}} \right) + + z_2 \sum_{\zeta=0}^{z_2} \left(N_{VX}^{\zeta+} \frac{d\ln N_{VX}^{\zeta+}}{d\ln p_{X_2}} - N_{Xi}^{\zeta-} \frac{d\ln N_{Xi}^{\zeta-}}{d\ln p_{X_2}} \right) .$$

Under the conditions of the Wagner disorder, the concentrations of all the defects are power functions of the partial pressure of the non-metallic component X_2: the quantities N_{VM} and N_{Xi} are proportional to $p_{X_2}^{1/m}$, while N_{Mi} and N_{VX} are proportional to $p_{X_2}^{-1/m}$. The values of the parameter m can be readily calculated by the Kroger–Wink method[27] for a specified simplified form of the electroneutrality condition and those for the dominant defects can be obtained by direct experimental determination.[28] Taking into account this relation, we obtain finally

$$\tilde{D} = \frac{z_1^2 \sum_{\zeta=0}^{z_1} (N_{Mi}^{\zeta+} D_{Mi}^{\zeta+} + N_{VM}^{\zeta-} D_{VM}^{\zeta-}) + z_2^2 \sum_{\zeta=0}^{z_2} (N_{Xi}^{\zeta-} D_{Xi}^{\zeta-} + N_{VX}^{\zeta+} D_{VX}^{\zeta+})}{2z_1 z_2 \sum_{\zeta=0}^{z_1} (N_{Mi}^{\zeta+}/m_{Mi}^{\zeta+} + N_{VM}^{\zeta-}/m_{VM}^{\zeta-}) + 2z_2^2 \sum_{\zeta=0}^{z_2} (N_{Xi}^{\zeta-}/m_{Xi}^{\zeta-} + N_{VX}^{\zeta+}/m_{VX}^{\zeta+})} . \quad (43)$$

A special case of this formula was obtained in our earlier study in connection with the description of the coupled diffusion of oxygen ions and electrons in vanadium oxide compounds.[29]

2. Electronic Disorder

When electronic disorder of the intrinsic type is dominant, the concentrations of electrons and holes are equal and identical with the ionisation constant K_i – $n \cong p \cong k_i$. When disorder of the impurity type predominates, the concentration of electrons is equal to the concentration of donors $N_d - n \cong N_d^+$ or the concentration of holes is equal to the concentration of acceptors $N_A - p = N_A$. The concentrations of defects in these formulae can be calculated for each specific type of disorder predominating under the conditions of the stoichiometric composition. The corresponding expressions for the CCDC, which are valid over a wide range of concentrations of defects, include only the deviation from the stoichiometric composition N_e and also some of the equilibrium constants (the intrinsic ionisation constant K_i and the defect formation constants K_F for the Frenkel defects, K_{AF} for the anti-Frenkel defects, and K_S for the Schottky defects) or the impurity concentration N_f. As an example one may point to a study[30] in which the CCDC for ions and electrons in a uni-univalent ionic crystal with Schottky defects and dominant electronic conductivity, corresponding to a non-degenerate state, was calculated.

We shall not formulate here the exact expressions for $\tilde{D} = \tilde{D}(N_e)$ in view of their cumbersome nature and we shall confine ourselves to the analysis of simplified solutions to which the above expressions reduce in certain limiting cases of interest for practical application. All these expressions can be divided into two groups depending on the dominant type of conductivity in the crystal.

(a) *Case where the ionic conductivity is dominant* ($\varkappa \gg \sigma$, $t_i \cong 1$). This case obtains in solid electrolytes within the electrolytic region[1] where the DCS are comparatively small and the concentrations of the electronic carriers ($n + p$) can be neglected in Eqns.(26) and (35) compared with the concentrations of the ionic carriers. For both structurally disordered compounds and for crystals with point defects, intrinsic or impurity, the relation $\tilde{D} \cong \tilde{D}_e$ follows from Eqn.(27) under these conditions. From the standpoint of physics, this implies that the electrons move solely under the influence of the gradient of the chemical potential; on the other hand, ions have virtually constant chemical potentials and move solely under the influence of the electric field.

This result is analogous to that well known in the electrochemistry of solutions for the diffusion of charged species present at low concentration in the supporting electrolyte.[7,31] In the present case, such species are conductivity electrons or holes and the disordered ions form a conducting background, which fully screens off the influence of the electric field. This factor is widely used in the study of electron transport in solid electrolytes, in particular in the experimental determination of the mobilities of electrons and holes.[20,32,33]

(b) *Case where the electronic conductivity is dominant* ($\sigma \gg \varkappa$; $t_e \cong 1$). We shall consider initially crystals with structural disorder and with fully ionised point defects for not unduly high DCS where one can neglect the term $n + p$ in the numerators of Eqns.(26) and (35) and the first terms incorporating $\tilde{D}_i$ in their denominators by virtue of the condition $\sigma \gg \varkappa$. Further simplifications are possible in the following limiting cases.

I. Small DCS. For compositions close to the stoichiometric, where $|N_e| \ll K_i$, the concentrations of conductivity electrons and holes are approximately the same and equal to the intrinsic ionisation constant K_i; the electron–hole gas is non-degenerate. The concentrations of the ionic carriers in this region are also approximately constant and are determined either by the crystallography of the compound (structural disorder), or by the formation constants of the dominant ionic defects K_F, K_{AF}, and K_S (intrinsic ionic disorder), or by the content of the heterovalent impurity N_f (impurity ionic disorder).

In the case of structural disorder, Eqn.(26) for the CCDC is simplified to the expression

$$\tilde{D}_k = \frac{z_k^2 N_k}{2K_i} D_k . \quad (44)$$

Simplified expressions can be obtained from Eqn.(35) for various types of dominant point defects. Having used Eqn.(29) to replace the microscopic diffusion coefficients D_{ki} and D_{Vk} in these expressions by the macroscopic coefficients D_k for all types of dominant ionic disorder, both structural and point disorder, we obtain a single formula for small DCS:

$$\tilde{D} = \frac{z_1^2 N_1 D_1 + z_2^2 N_2 D_2}{2K_i} . \quad (45)$$

II. Intermediate DCS. This includes very high degrees of DCS where $|N_e|$ is large compared with the intrinsic ionisation constant K_i but small compared with the characteristic concentration of the disordered ions (N_k for structural disorder and the largest of the quantities K_F, K_{AF}, K_S, or N_f in the case of fully ionised point defects). In this region the electronic carriers consist virtually of conductivity electrons only or holes only, so that their total concentration is specified by the DCS: $n + p \cong |N_e|$. On the other hand, the concentrations of the ionic defects are the same as in the previous case. Simplified solutions for the CCDC taking into account Eqn.(29) can be represented

in a single form expressing $\tilde{D}$ in terms of the macroscopic diffusion coefficients of the ions:

$$\tilde{D} = \frac{F_e}{|\delta|}(z_1 D_1 + z_2 D_2) \ . \qquad (46)$$

The relative DCS is in this case designated by δ: $\delta = N_e/z_1 N_1 = N_e/z_2 N_2$. In the absence of degeneracy of electrons, $F_e = 1$ and Eqn.(46) becomes identical with the familiar Wagner formula.[7]

Together with the two approximations considered, Eqn.(35) permits yet another approximation corresponding to the Wagner disorder under the conditions of the total ionisation of the defects. The solution for this situation constitutes a special case of the solutions examined below.

III. Large DCS. In this range of DCS the relation $|N_e| \cong n + p$ is retained and in addition the quantity $|N_e|$ exceeds the concentration of the ionic point defects characteristic of the stoichiometric composition, i.e. the largest of the constants K_F, K_{AF}, K_S, or N_f. This case corresponds to either the Wagner disorder, characterised by one of the electroneutrality conditions [Eqn.(36)], or the neutral defects $K_i^{\times}$ of $V_k^{\times}$ (an effective zero charge has come to be designated by the oblique cross $\times$). In both cases the DCS is determined by Eqn.(37). Simplified expressions for the CCDC follow directly from Eqn.(43), provided that one term, corresponding to the dominant defect, is left in its numerator and denominator.

The parameter m for the dominant defects can be readily calculated, taking into account the possible degeneracy of electrons, by differentiating Eqn.(39) with respect to $\ln p_{X_2}$, having first transformed $d\mu_e$ with the aid of the relation $d \ln a_e = F_n d \ln n = -F_p d \ln p$ and taking into account Eqns.(36) and (41). Then one obtains the values of $m_1 = 2z_2(\zeta F_e + 1)/z_1$ for the dominant cationic defects $M_i^{\zeta+}$ or $V_M^{\zeta-}$ and $m_2 = 2(\zeta F_e + 1)$ for the anionic defects $X_i^{\zeta-}$ or $V_X^{\zeta+}$— both charged and neutral. In both cases Eqn.(43) reduces to simple expressions, namely under the conditions of the Schottky disorder to

$$\tilde{D}_k = (\zeta F_e + 1) D_{ki}$$

and in the case of the impurity vacancy disorder to

$$\tilde{D}_k = (\zeta F_e + 1) D_{Vk} \ .$$

When Eqn.(29) is taken into account, the above solutions reduce to the general formula

$$\tilde{D} = \frac{\zeta F_e + 1}{|\delta|} D_k \qquad (47)$$

For $F_e = 1$, this formula was obtained by Childs and Wagner.[34] The unity added to the numerator (47) compared with Eqn.(46) is due to the fact that in this case the ions move not only under the influence of the electric field but also as a result of the gradient of their chemical potential, which is related to the variable concentration of defects.

Despite the formal similarity of Eqns.(46) and (47), they determine significantly different dependences of $\tilde{D}$ on the degree of DCS δ. Thus, when $F_e = 1$, the coefficient D_k in region II is constant and, according to Eqn.(46), $\tilde{D}$ is inversely proportional to $|\delta|$; in region III the quantity D_k is directly proportional to $|\delta|$ and, according to Eqn.(47), $\tilde{D}$ is constant.

The qualitative form of the dependence of $\lg \tilde{D}$ on δ is represented in Fig.2 for a crystal with fully ionised Schottky defects, which are converted into Wagner defects for high values of $|\delta|$ when $K_S \gg K_i$ and $D_{VM} > D_{VX}$. The maximum value of $\lg \tilde{D}$ is attained for the stoichiometric composition. The characteristic values of $\delta = \pm K_S/N_k$, for which solution II [Eqn.(46)] is converted into solution III [Eqn.(47)], are shown on the abscissa axis. For crystals with Frenkel defects, analogous relations are obtained; for the structural disorder, the difference consists in the fact that the simplified solution III is not obtained and the horizontal sections on the plots of $\lg \tilde{D}$ against δ are not attained even for the maximum value of $|\delta|$.

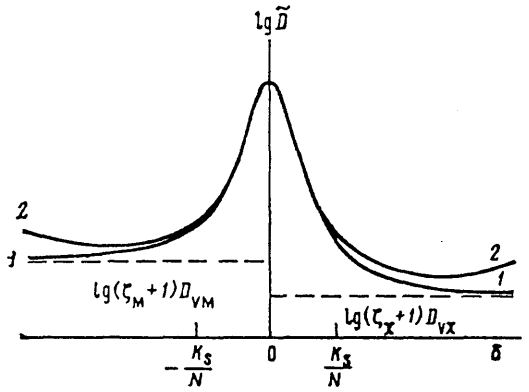


Figure 2. Dependence of the coupled diffusion coefficient $\tilde{D}$ on the degree of non-stoichiometry of a crystal with Schottky defects in the absence (curve *1*) and presence (curve *2*) of degeneracy of the electrons.

When electronic disorder is dominant, Eqn.(44) also simplifies markedly, but only one term corresponding to atomic defects with the maximum concentration is left in its numerator and denominator. One then obtains $\tilde{D} \cong D_{def}$— a result which is formally identical with solution II for the case where neutral defects with $\zeta = 0$ predominate. Such agreement is entirely understandable, because under conditions where the electronic disorder predominates the gradient of the chemical potential of the electrons is negligible. Under the conditions of electronic equilibrium, this also leads to a low electric field strength, since the ionic defects move only under the influence of the intrinsic chemical potential gradient.

An especially important feature of the results obtained is very high values of CCDC compared with the self-diffusion coefficients of the ions. Indeed, even for high degrees of DCS, the coefficients $\tilde{D}$ are of the same order of magnitude as the diffusion coefficient of the dominant ionic defects and, as the stoichiometric composition is approached, they increase still further in inverse proportion to $|\delta|$ in the region of moderate DCS (region II).

The large number of limiting solutions for the CCDC greatly hinders the interpretation of the experimental data even as regards fundamental characteristics such as the effective activation energy. For crystals with ionic point defects, this quantity has the simple significance of the height of the potential barrier U to ion jumps only in region III. Since the values of $\tilde{D}$ in region I can vary as a function of the transport numbers of the ions from $\tilde{D}_e$ for $t_i \cong 1$ to $z_k^2 N_k D_k / 2K_i$ for $t_i \ll 1$, in this region the effective activation energy has indefinite values or totally loses its significance.

Thus, according to Weppner,[36] $\tilde{D}$ in the β-modification of silver sulphide increases with temperature in accordance with the usual exponential law only in the region of fairly high values of δ; for the stoichiometric composition, this relation is reversed partly owing to the decrease of the mobility of the electron carriers with temperature.

V. EXPERIMENTAL DETERMINATION OF CHEMICAL DIFFUSION COEFFICIENTS

1. Theoretical Principles

The majority of the methods for the experimental determination of chemical diffusion coefficients in solids used nowadays are based on the study of the relaxation of the concentration profile in the diffusion medium under the influence of some kind of external perturbation—an abrupt change in potential, current, or composition of the ambient atmosphere.[6,34] The problem is as a rule reduced to the solution, subject to appropriate initial and boundary conditions, of the phenomenological equation of Fick's Second Law:

$$\frac{\partial N}{\partial t} = \tilde{D}\,\mathrm{div}\,\nabla N \equiv \tilde{D}\nabla^2 N\,, \qquad (48)$$

where the effective CDC is assumed to be independent of the concentration in the experimental range. On the basis of the observed dependence of the concentration N on the coordinate x and the time t, the response of the system to the perturbation, i.e. the time variation of the measured quantity (current, potential, weight, or electrical conductivity of the specimen) is calculated. The effective CDC is found by comparing the theoretical and experimental results.

In the case of the coupled chemical diffusion considered in this review, the flux of electrons in a non-stoichiometric crystal is described by the expression

$$J_e = -\frac{t_e}{e} I - \tilde{D}\nabla N_e\,, \qquad (49)$$

where the first term corresponds to the contribution of these electrons to the electric current I which has passed through the specimen. The material balance condition $\partial N_e/\partial t = -\mathrm{div}\,J_e$ converts Eqn.(49) into a differential equation, which is converted into Fick's Second Law [Eqn.(48)] for constant t_e and $\tilde{D}$. Thus the principal approximation in the problem reduces to the assumption of a low degree of inhomogeneity of the diffusion medium, for which the relative change in N_e or δ is small compared with unity (so that the kinetic parameters $\varkappa$, σ, t_i, t_e, and $\tilde{D}$ can be assumed constant). This requires in its turn the use in experiments of weak perturbations to stimulate the diffusion process.

Investigations during the last decade have shown that electrochemical methods using galvanic cells with solid electrolytes are most convenient and reliable.[6,37–41] We shall therefore concentrate attention on them in the present review.

In the electrochemical method the principal element of the measuring circuit is a cell of the following type:

auxiliary electrode	solid electrolyte	test specimen	inert electrode.	(50)

The solid electrolyte must exhibit unipolar ionic conductivity with respect to one of the ions forming part of the composition of the test compound, so that the electric current passing through the cell can serve as an exact measure of the change in the composition of the test specimen. The majority of the investigations have been carried out with ZrO_2, β-Al_2O_3, AgI, and CuBr specimens satisfying the above requirement over a fairly wide range of temperatures and compositions of the gaseous medium.[38–42] The auxiliary electrode, which is reversible with respect to the electrolyte, serves as a source of ions, which are supplied to the test specimen via the electrolyte, and also ensures the measurement of the chemical potential of the electrochemically active element at the electrolyte/specimen boundary.

2. Potentiostatic Method

In this method[6,38,40–46] the test specimen is first maintained under equilibrium conditions so that its composition becomes homogeneous throughout its thickness. Then, at a time $t = 0$, a potential $\Delta\phi$, different from the e.m.f. E of the cell at equilibrium, is applied to this cell. The potential difference at the boundaries of the test specimen with a length L, given by $\phi|_{x=0} - \phi|_{x=L}$, where $\phi|_{x=0}$ is the potential at the electrolyte–specimen boundary and $\phi|_{x=L}$ the potential at the specimen–inert electrode boundary, amounts to $\Delta\phi - E$. This quantity must be sufficiently small so that it is possible to neglect the concentration dependence of the transport number t_e and the diffusion coefficient $\tilde{D}$ and also the overpotential (the additional potential jump due to the slow charge transfer through the electrolyte/specimen interface and the ohmic losses in the electrolyte and the specimen). Furthermore, the cell must be constructed in such a way that there is no transport of ions through the lateral surfaces of the specimen and through its end surface opposite to the electrode. This is usually achieved by constructing the current lead at the right-hand end of cell (50) from an inert material (platinum, graphite) while the right-hand side of cell (50) is placed in an inert atmosphere. In subsequent calculations it is also assumed that the current, which during the short time interval after the application of the potential $\Delta\phi$ to the cell transports a certain amount of electricity consumed in altering the charge of the double layer at the interfaces, is likewise small.

Under these conditions at time $t = 0$, a concentration of excess electrons N_∞, different from the initial concentration N_0 and corresponding to equilibrium in relation to the new potential, is established in the layer of specimen adjoining the electrolyte ($x = 0$). The subsequent relaxation process is effected by the coupled diffusion of ions and electrons through the specimen, as a result of which the concentration of electrons throughout the bulk of the specimen tends to the finite value N_∞. Since this process involves a continuous supply of the corresponding amount of ions from the auxiliary electrode through the electrolyte, the electric current flowing through the cell is a measure of its rate. In its experimental aspect, the potentiostatic method therefore reduces to the measurement of the current as a function of time.

The current density in the cell is determined from the condition that there is no electron flux at the boundary between the specimen and the electrolyte. According to Eqn.(49), this gives rise to the boundary condition

$$t_e I = e\tilde{D}\nabla N_e \text{ when } x=0\,. \qquad (51)$$

At the specimen–inert electron boundary, the flux of ions is zero and the current passed through the system is wholly due to electrons ($I = -eJ_e$ and, in conformity with Eqn.(49), the second boundary condition is obtained in the form

$$t_i I = e\tilde{D}\nabla N_e \text{ when } x=L\,. \qquad (52a)$$

The authors of the above studies used the simpler boundary condition at $x = L$ in the form

$$\nabla N_e(L) = 0\,, \qquad (52b)$$

which is valid, as can be seen from Eqn.(52a), for small ionic transport numbers t_1.

In the subsequent exposition, we shall also confine ourselves to the boundary condition (52b), which is applicable to materials in which electronic conductivity predominates.

Thus, in the case of the one-dimensional diffusional problem, i.e. for plane-parallel boundaries of the specimen located at $x = 0$ and $x = L$, it is necessary to solve Fick's Second Law $\partial N/\partial t = \tilde{D}\partial^2 N/\partial x^2$ subject to the initial condition $N(x, 0) = N_0$ and the boundary conditions $N|_{x=0} = N_\infty$ and $(\partial N/\partial x)_{x=L} = 0$ (here and henceforth the subscript e is omitted in the symbol N denoting concentration).

The solution has the form[47,48]

$$N(x,t) = N_\infty + (N_0 - N_\infty)\,\psi(x,t)\,. \qquad (53)$$

The function

$$\psi(x,t) = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{1}{2n+1}\sin\frac{(2n+1)\pi x}{2L}\exp\left[-\frac{(2n+1)^2\pi^2\tilde{D}t}{4L^2}\right] \qquad (54)$$

assumes the following limiting values: $\psi(0, 0) = 0$, $\psi(L, 0) = 1$, and $\psi(x, \infty) = 0$. Depending on t, this function can be synthesised in two limiting cases.

1. Short times ($t \gg L^2/\tilde{D}$). At the beginning of the process the effective length of the diffusion zone $2(Dt)^{1/2}$ is small compared with the length of the specimen L and the diffusion can be described by the solution for a semi-infinite medium: $\psi(x, t) \cong \mathrm{erf}\,[x/2(Dt)^{1/2}]$. Hence, according to Eqn.(51), we obtain the following expression for $t_e \cong 1$:

$$I \cong e(N_\infty - N_0)(\tilde{D}/\pi t)^{1/2}\,. \qquad (55)$$

Consequently the CCDC can be determined from the slope of the experimental I–$t^{-1/2}$ line, provided that the difference between the final and initial concentrations $N_\infty - N_0$ is known. This difference can be expressed in terms of the total amount of electricity passed through the specimen before the attainment of equilibrium: $Q = V_e(N_\infty - N_0)$, where V is the volume of the specimen. However, this method is associated with the integration of the current with respect to time and can lead to a major error as a consequence of the slow decay of the current in the range of its values close to the limit of the sensitivity of the measuring apparatus.

The coulometric titration method developed by Wagner[49–51] and used widely nowadays in research practice is much more convenient for the determination of the difference between the final and initial concentrations of electrons in the specimen $N_\infty - N_0$. In this method a cell of type (50), for example

$$\mathrm{M}\,\left|\begin{matrix}\text{electrolyte}\\ \mathrm{M}^{z+}\end{matrix}\right|\,\mathrm{M}_{1+\delta}\mathrm{X}_r\,\left|\,\mathrm{Pt}\right.\,. \qquad (56)$$

is also used. A definite amount of electricity is passed through the cell, after which it is allowed to stand for a time until the attainment of a homogeneous value of δ over the entire length of the specimen; for each fixed value of δ, the cell e.m.f. E is measured. The $E = E(\delta)$ curve plotted in this way is a calibration curve and is used to determine the unknown value of δ from the measured e.m.f. Furthermore, the e.m.f. of cell (56) is equal to $(\mu_M^0 - \mu_M)/ze$, where μ_M^0 and μ_M are the chemical potentials of the atoms M in the metallic electrode and in the compound $\mathrm{M}_{1+\delta}\mathrm{X}_r$. Graphical differentiation of the $E(\delta)$ curve therefore makes it possible to determine directly the thermodynamic factor F_M:

$$F_M = \frac{\mathrm{d}\ln a_M}{\mathrm{d}\ln N_M} = -\frac{ze}{kT}\cdot\frac{\mathrm{d}E}{\mathrm{d}\delta}\,, \qquad (57)$$

which can be used to calculate $\tilde{D}$ from self-diffusion data in accordance with Eqn.(4).

2. Long times ($t > L^2/4\tilde{D}$). In this case Eqn.(54) for $\psi(x, t)$ is fitted by the first member of the series and we obtain the following expression for the current (to within <1%):

$$I \cong \frac{2e(N_\infty - N_0)}{L}\exp\left(-\frac{\pi^2\tilde{D}t}{4L^2}\right)\,. \qquad (58)$$

Eqn.(58) describes the $\ln|I| - t$ straight line. $\tilde{D}$ can be determined from its slope.

Using the potentiostatic method, Rickert and Weppner,[45] determined the CCDC in non-stoichiometric wustite $\mathrm{Fe}_{1-\delta}$ = 0 in the range $0.06 \leqslant \delta \leqslant 0.13$ using all the three methods described. The discrepancy between the data obtained by different procedures does not exceed 30%, indicating their adequate reliability.

Relations similar to those described above are also obtained for the cylindrical geometry of cell (48) in which the test substance is first fused within a solid electrolyte tube.[41] In this case the overall solution of Fick's second equation is expressed in terms of Bessel functions, but for short times it is identical with Eqn.(55).

3. The Galvanostatic Method

This method, which is fairly simple as regards apparatus, has been widely used by many investigators.[6,11,38–46,52,53] Its theory has been developed by Yokota[11] for compounds of the type of silver sulphide exhibiting cationic and electronic conductivities. However, his equations proved valid for any binary ionic compound and we shall therefore quote the general relations.

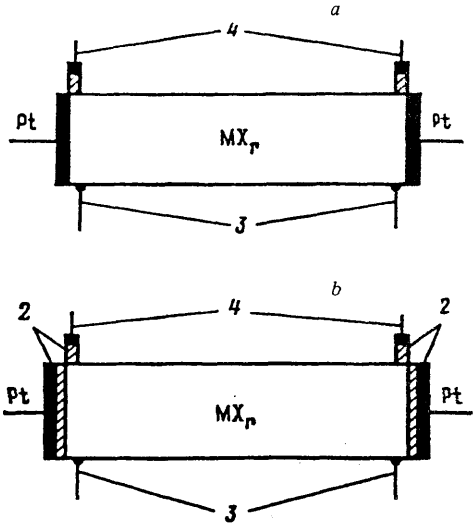


Figure 3. Cell with electronic (*a*) and ionic (*b*) electrodes for the determination of the CCDC by the galvanostatic method: 1) inert electrodes; 2) electrolyte; 3) electronic probes; 4) ionic probes.

We shall consider cells of two types, illustrated schematically in Fig.3. Cell *a* has electrodes made of platinum, graphite, or another inert material which is permeable to electrons only. Cell *b* is fitted with more complex electrodes, containing a layer of solid electrolyte impermeable to electrons and reversible with respect to the ions M^{z+} or X^{z-} forming

the given binary compound MX_ν. Such electrodes can consist, for example, of the combinations $M|M^{z+}$ with a cation-conducting electrolyte or X_2, $Pt|X^{z-}$ with an anion-conducting electrolyte. (O_2, S_2, etc. can be used as the substance X_2 generating the anions.) Furthermore, each cell can be provided with a pair of electronic or ionic measuring probes playing the role of the corresponding electrodes.

If a direct electronic or ionic current is passed through the cell, concentration polarisation, associated with the presence of a DCS gradient, arises in it. The potential difference between like probes serves as a measure of this polarisation; the method consists of the measurement of the potential difference between the probes as a function of time when the direct current is switched on or switched off. The corresponding theoretical relations have been obtained from the solution of Fick's second equation for a specimen $2L$ long and are compiled in the Table. $\Psi(t)$ denotes the function

$$\Psi(t) = \frac{1}{L}\int_0^L \psi(x,t)\,dx = \frac{1}{L}\int_L^{2L} \psi(x,t)\,dx = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left[-\frac{(2n+1)^2\pi^2\tilde{D}t}{4L^2}\right], \quad (59)$$

which varies in the range from $\Psi(0) = 1$ to $\Psi(\infty) = 0$.

Time variation of the potential difference between the probes $\phi(0) - \phi(L) = \phi(L) - \phi(2L)$ in Yokota's method when the direct current is switched on and off.

Electrodes	Probes	$\varphi:0)-\varphi(L)=\varphi(L)-\varphi(2L)$	
		establishment of polarisation	decrease of polarisation
Electronic	ionic	$\frac{IL}{\sigma}[1-t_i\Psi(t)]$	$\frac{IL}{\sigma}t_i\Psi(t)$
Electronic	electronic	$\frac{IL}{\varkappa+\sigma}\Psi(t)$	$-\frac{IL}{\varkappa+\sigma}\Psi(t)$
Ionic	electronic	$\frac{IL}{\varkappa+\sigma}\Psi(t)$	$-\frac{IL}{\varkappa+\sigma}\Psi(t)$
Ionic	ionic	$\frac{IL}{\varkappa}[1-t_e\Psi(t)]$	$\frac{IL}{\varkappa}t_e\Psi(t)$

Different workers have used cells which constituted various simplified versions of Yokota's cell and have made measurements under conditions where the current was either switched on or switched off. Experimental curves are usually analysed by comparing them with the corresponding approximate expressions for the function $\Psi(t)$.

1. For short times $t \ll L^2/\tilde{D}$, one can use the solution for a semi-infinite medium:

$$\Psi(t) \cong 1 - 2\left(\frac{\tilde{D}t}{\pi}\right)^{1/2}/L \quad . \quad (60)$$

When the partial electrical conductivity is unknown, the CCDC can be determined from the slopes of the $\phi - t^{1/2}$ linear plots in accordance with the formulae in the Table.

2. For long times, only the first term of the infinite series (59) is retained:

$$\Psi(t) \cong \frac{8}{\pi^2}\exp\left(-\frac{\pi^2\tilde{D}t}{4L^2}\right) \quad (61)$$

and the CCDC are found from linear plots in terms of the corresponding semilogarithmic coordinates in the same way as in the potentiostatic method.

A pulse method which is a version of the galvanostatic method, has been used.[6,54,55] This method involves the measurement of the potential difference between the probes when short d.c. pulses, whose duration is small compared with $L^2/2\tilde{D}$, are passed through the specimen.

4. The Gravimetric Method

In this method, proposed by Bruce Wagner,[34,56,57] the test specimen is maintained in an atmosphere with a fixed pressure of the non-metallic component p_{X_2} until the attainment of equilibrium. At time $t = 0$, the pressure p_X changes abruptly to a new value. Under these conditions, the concentration of electrons at the end-faces of the specimen for $x = 0$ and $x = 2L$ changes from N_0 to a new equilibrium value N_∞, which is established throughout the entire specimen after a time. The change in electron concentration, which is unambiguously related to the change in the stoichiometry of the specimen, corresponds to the dissolution or removal of the non-metallic component from the test specimen and hence to a change in its mass.

Evidently the distribution of concentrations in a plate with a thickness $2L$, which is permeable to the non-metallic component on either side at $x = 0$ and $x = 2L$, is identical with the distribution defined by Eqn.(53), which is calculated under conditions where plates with a thickness L are permeable on one side. Integration of Eqn.(53) with respect to the thickness of the plate permits the calculation of the change in the mass of the specimen as a function of time:

$$\frac{M - M_0}{M_\infty - M_0} = 1 - \Psi(t) \quad . \quad (62)$$

The values of $\tilde{D}$ are determined from the slopes of the experimental $M - t^{1/2}$ curves for short times ($t < 0.32L^2/\tilde{D}$) and $\lg|M_\infty - M| - t$ curves for long times ($t > 0.14L^2/\tilde{D}$) in conformity with the asymptotic formulae (67) and (68), the error of the solutions not exceeding 1%.[58] Furthermore, there exists a region $0.14 < \tilde{D}t/L^2 < 0.32$ in which the two solutions overlap. The error, associated with the representation of the specimen as an infinite plate does not exceed 1%, provided that the thickness of the plate is much smaller than its length and width.

For specimens in the form of a $2a \times 2b \times 2c$ rectangular parallel-piped, the approximate solution corresponding to long times ($|M - M_0| \geq 0.5|M_\infty - M_0|$) is described by the formula[56]

$$\frac{M_\infty - M}{M_\infty - M_0} \approx \frac{512}{\pi^6}\exp\left[-\frac{\pi^2\tilde{D}t}{4}\left(\frac{1}{a^2}+\frac{1}{b^2}+\frac{1}{c^2}\right)\right], \quad (63)$$

while for spherical specimens with a radius R the solution is given by the formula[59]

$$\frac{M_\infty - M}{M_\infty - M_0} \cong \frac{6}{\pi^2}\exp\left(-\frac{\pi^2\tilde{D}t}{R^2}\right) \quad . \quad (64)$$

For specimens in the form of an infinite cylinder, the solution is expressed in terms of Bessel functions and in the general case requires numerical analysis.[60]

The solutions quoted above have been obtained on the assumption of the instantaneous attainment of the equivalent concentration of charge carriers on the surface of the specimen. When the reactions on the surface are slow, the solutions include the corresponding rate constants.[34,61,62]

An important disadvantage of the gravimetric method is its relatively low sensitivity and the associated necessity for the use of comparatively large changes in the composition of the

specimens, which leads to the breakdown of the condition that $\tilde{D}$ is independent of the degree of DCS and ultimately to a considerable uncertainty in the measured values of $\tilde{D}$.

5. The Conductimetric Method

This method presupposes the same experimental conditions as the gravimetric method, but differs from the latter by a higher sensitivity (for a suitable disposition of the electrodes and measuring probes).[34,56,63,64] In this method the average electrical conductivity of the specimens serves as a measure of the changes in concentration. It is assumed that the mobility of the current carriers and the effective charge of the diffusing defects remains constant. Under these conditions, the electrical conductivity varies linearly with the concentration of the excess component N, i.e. $\sigma = AN +$ const.,[58,60] so that the solutions are obtained from Eqns.(62)–(64) by the simple replacement of M by σ and the experimental σ–t relations are analysed in the same way as in the gravimetric method. If ionic defects with different effective charges are involved in the diffusion, the proportionality between the electrical conductivity and the mass of the specimen breaks down and measurements of these quantities lead to different values of $\tilde{D}$.[26]

6. Other Methods

Apart from the relaxation methods described above, mention should be made of the method based on the kinetics of solid-phase reactions[4–6,34,65,66] involving the measurement of the rate of growth of the solid phases in processes involving the oxidation of metals, for example, Fe → FeO, or of lower oxides (chalcogenides) to higher oxides (chalcogenides), for example, FeO → Fe_3O_4 → Fe_2O_3. It is then assumed that the reaction product (scale) forms a compact non-porous layer in good contact with the metal or lower oxide and the oxidation reaction proceeds under diffusional conditions. According to Wagner's theory,[7] in this case the change in the thickness L of the layer of scale is described by parabolic time law $L^2 = 2K_p t$ with the constant $K_p = \int \tilde{D} d\delta \cong \tilde{D} \Delta\delta$, where $\Delta\delta$ is the total change in the degree of non-stoichiometry along the thickness of the scale, which is independent of time. Wagner[66] also proposed equations for the calculation of the effective CCDC for the formation of multiphase reaction products under diffusional conditions.

Together with the direct measurements of the thickness or mass of the layer of scale as a function of time, in the study of oxidation kinetics one uses also electrochemical cells in which one of the reactants is supplied to the reaction zone by passing a current through a suitable solid electrolyte. For example, in the cell[40,41]

$$(-)\,\mathrm{Pt}\,|\,\mathrm{Ag}\,|\,\mathrm{AgI}\,|\,\underset{\mathrm{Pt}(+)}{\underline{\mathrm{Ag_2S}}}\,|\,\mathrm{NiS}\,|\,\mathrm{Ni} \qquad (65)$$

the electrolyte AgI is used to transfer silver ions from Ag_2S to metallic silver; the layer of the NiS scale grows as a result of the diffusion through it of nickel ions and electrons as well as the sulphur liberated in the electrolysis of the auxiliary layer of Ag_2S. The cell e.m.f. then serves as a measure of the chemical potential of sulphur in Ag_2S and hence of the Gibbs free energy of the sulphidisation of nickel. Since the current density is a direct measure of the rate of growth to the layer of scale dL/dt in the parabolic increase of the thickness of the layer, the following time relation should be observed:

$$I = \frac{F}{v} \cdot \frac{dL}{dt} = \frac{F}{v} (K_p/l)^{1/2}, \qquad (66)$$

where F is the Faraday and v the equivalent volume of the scale.

The main disadvantage of the method of solid-phase reactions is the fact that the values of $\tilde{D}$ determined from the measured K_p for known $\Delta\delta$ are averaged over the entire range $\Delta\delta$. In principle, the dependence of $\tilde{D}$ on δ can be found by differentiating the values of K_p obtained for different cell e.m.f.'s with respect to the corresponding values of δ at the NiS|Ag_2S boundary. However, since this involves considerable experimental difficulties, the method of solid-phase kinetics is used mainly for the rough estimation of the CCDC.

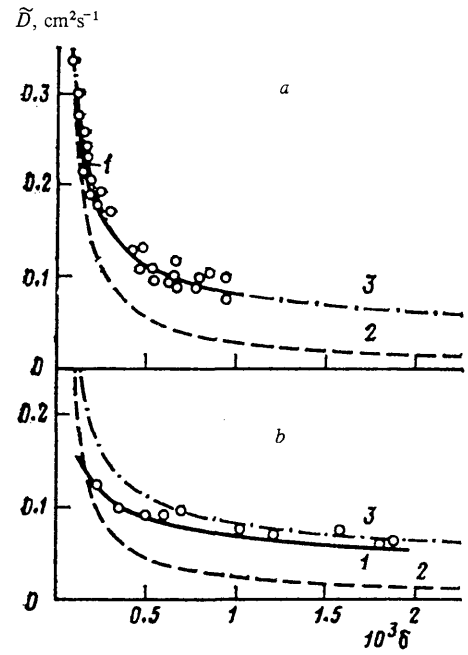


Figure 4. Dependence of the CCDC in the $Ag_{2(1+\delta)}S$ (*a*) and $Ag_{2(1+\delta)}Se$ (*b*) cubic phases on the excess content of silver δ at 200 °C. Circles—experimental values;[53] curves—calculation: 1) according to Eqn.(4); 2) and 3) according to Eqn.(46) for $F_e = 1$ (curve 2) and F_e calculated from the data in Fig.2 (curve 3).

Finally, we may mention the method involving the study of the permeability of solids to gases.[67,68] In this method, the difference between the partial pressures of the non-metallic components p_{X_2} is established on the two sides of a membrane of the test substance and the time variation of the pressure in a calibrated volume as a result of the diffusion of X_2 through the membrane is recorded. If the concentration of the gas within the membrane at the inlet is higher than at the outlet and the concentration at the outlet is equal to the initial value, then the pressure at the outlet begins to increase when a time $\tau = L^2/6D$ has elapsed since the establishment of the pressure difference (L is the thickness of the membrane) and subsequently varies linearly with time. The determination of $\tilde{D}$ therefore reduces to the measurement of the intercept τ made by the experimental linear p_{X_2}–t plot.

7. Experimental Data

(a) *Silver and copper chalcogenides.* The most reliable CCDC data as a function of the degree of non-stoichiometry have been obtained for silver[36,53] and copper[69,70] sulphides and selenides. The high-temperature cubic phases of these two compounds have a structurally disordered cationic sublattice and exhibit a mixed cationic-electronic conductivity of *n*- and *p*-types respectively. In terms of their electronic properties, they belong to the class of degenerate semi-conductors.

Fig.4 illustrates the results of the direct measurement of $\tilde{D}$ for the $Ag_{2(1+\delta)}S$ and $Ag_{2(1+\delta)}Se$ cubic phases for different excess ($\delta > 0$) contents of silver.[53] The continuous curves *1* were calculated[53] from the phenomenological formula (4) using the experimental random diffusion coefficients of silver and the thermodynamic factor found from measurements of the e.m.f.'s of a galvanic cell. We calculated curves *2* and *3* on the basis of a statistical theory, in accordance with Eqn.(46), which for the compounds considered has the simple form $\tilde{D} = F_e D_{Ag}/\delta$, derived for the first time by Fomenkov.[71] Curve *2* corresponds to the non-degenerate state of the electrons ($F_e = 1$). Curve *3* takes into account the degeneracy; the values of $F_e = F_n$ have been found from the data in Fig.2, using the ratios of the effective mass of the electron to its real mass, $m^*/m_0 = 0.21$ and 0.17, obtained by averaging the literature data[72-76] for the sulphide and selenide respectively.

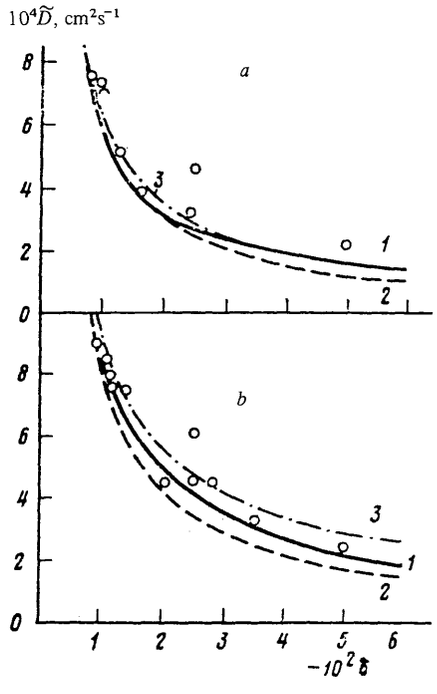


Figure 5. Dependence of the CCDC in the $Cu_{2(1+\delta)}S$ (*a*) and $Cu_{2(1+\delta)}Se$ (*b*) phases on the copper deficit at 400 °C. Circles—experimental values;[69,70] curves *1–3* were calculated in the same way as the corresponding curves in Fig.4.

Fig.5 presents analogous data for the $Cu_{2(1+\delta)}S$ and $Cu_{2(1+\delta)}Se$ cubic phases characterised by deficiency of copper in relation to stoichiometry ($\delta < 0$). The circles represent experimental values of $\tilde{D}$.[69,70] In the calculation of curves *1–3* for the stoichiometric sulphide and selenide, the values $D_{Cu} = 6 \times 10^{-6}$ and 8.5×10^{-6} $cm^2\ s^{-1}$, which agree within the limits of experimental error with the corresponding D^*_{Cu} for radioactive isotopes,[77,78] were adopted. The effective masses of holes $m^*/m_0 = 7.6$ and 4.6 were taken from Konev et al.[79]

Figs.4 and 5 indicate a satisfactory agreement of the experimental data with the values and relations derived from both the phenomenological and statistical theories, allowance for the degeneracy of the electronic states when $|\delta| > 10^{-3}$ and 10^{-2} for silver and copper chalcogenides respectively being important in the latter case. A satisfactory agreement with both theories has also been obtained for the $(Cu_{1-x}Ag_{x+\delta})_2S$ and $(Cu_{1-x}Ag_{x+\delta})_2Se$ cubic solid solutions containing both an excess and a deficiency of the metal and showing maxima on the $\tilde{D}(\delta)$ curves in the vicinity of the stoichiometric composition.[23]

The results of the study of the impedance of the $Pt|\beta\text{-}Ag_{2(1+\delta)}S$ boundary as a function of the excess content of silver in $\beta\text{-}Ag_{2(1+\delta)}S$, which is a non-degenerate *n*-type semiconductor, merit attention.[80]

A readily measurable Warburg impedance, comparable to the resistances of the traditional elements of the equivalent circuit of the cell, was observed. The temperature dependence of the logarithm of the Warburg constant, obtained from the experimental impedance hodographs for a fixed $\delta = 5 \times 10^{-5}$ and the same relation calculated subject to an assumption concerning the CDC of the ions and electrons[1] are almost parallel. The experimental and theoretical values are linked by a constant multiplier of ~0.08, which may be due to the effective area of contact of the solid phases; one can therefore speak of a satisfactory agreement between the theory and experiment in this case also.

(b) *Oxides.* The majority of the experimental data for oxides have been obtained for a large and frequently not measureable difference between the δ values. The dependences of $\tilde{D}$ on δ or p_{O_2}, which is of greatest theoretical interest, have been investigated for an extremely limited range of compounds.

Reliable data are available for nickel monoxide with a deficiency of the metal, which exhibits Wagner disorder.[81] These data demonstate the constancy of the values of $\tilde{D}$ at 900–1200 °C over a fairly wide range of oxygen partial pressures (from 1 to 10^{-5} atm). Analogous results have been obtained for a cobalt single crystal,[56,82] where $\tilde{D}$ is independent of p_{O_2} at 900–1300 °C in the same pressure range.

These results are in good agreement with the expression obtained for $\tilde{D}$ in the case of the vacancy mechanism of the diffusion of cations in the absence of degeneracy of the holes:[34]

$$\tilde{D} = (\zeta_M + 1) D_{VM} . \qquad (67)$$

The validity of Eqn.(67) for $Co_{1-\delta}O$ has also been confirmed by Fryt et al.[35] At the same time Morin's results for $Co_{1-\delta}O$ at 1000 °C [83] demonstrate some (approximately by a factor of 2) increase of the chemical diffusion coefficient $\tilde{D}$ in proportion to $p_{O_2}^{1/4}$ when p_{O_2} $(atm)^{1/4}$ changes from 0.2 to 1. The values of ζ_{Co}, calculated by Eqn.(67), are then close to 2, while the effective charge of the dominant cationic vacancies, determined from the dependence of the electrical conductivity on p_{O_2} is unity at the same oxygen pressures. According to the author,[83] this discrepancy is associated with the anomalies in the mobility of the vacancies, in particular with the dependence of their mobility on p_{O_2} in the region where the $Co_{1-\delta}O$ phase exists.

The available information about the dependence of CCDC on δ or p_{O_2} for other oxides is not only scarce but frequently contradictory. As an example, one may refer to the results of experiments by different investigators on wüstite $Fe_{1-\delta}O$,[34,45,57] which differ by factors amounting to hundreds for the same temperatures and values of δ and the dependences of $\tilde{D}$ on δ obtained by different methods exhibit even qualitative differences. Apparently the main cause of such discrepancy is the complexity of the defect structure of wüstite, in particular its tendency to form extended multiclusters which are not reproducible between different experiments.[2,5] The significant deviations of the defects in wüstite from ideal behaviour are indicated by the observed linearity of the dependence of the logarithm of the activity of oxygen on δ instead of the expected logarithmic relation.[45]

A considerable variety of the dependences of $\lg \tilde{D}$ on $\lg p_{O_2}$ has been observed for vanadium oxide compounds.[29] The results for the diffusion of oxygen in VO_2 and of sodium in $Na_{1/3}V_2O_5$, demonstrating the constancy of the coefficient $\tilde{D}$ within certain ranges of values of p_{O_2}, are consistent with the solutions (see Table) for the dominant electronic disorder. On the other hand, for the diffusion of oxygen in V_2O_5, $Na_{1/3}V_2O_5$, and $Ca_3Fe_{3.5}V_{1.5}O_{12}$, the horizontal sections on the $\lg \tilde{D}$–$\lg p_{O_2}$ plots are altogether absent and the slopes of their different sections vary from 1/6 to 1, while the theory described can explain only slopes equal to 0 and ±1. The cause of this discrepancy is probably to be sought in the formation of extended defects of the type of shear planes.[2,84] This hypothesis is supported by the observed linear dependence of the partial free energy of oxygen on δ [85] and also by the low mechanical strength of vanadium oxide compounds and by their tendency to split into separate layers.

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Summarising the above discussion, one may conclude that the joint employment of the phenomenological theory and the statistical-thermodynamic theory based on the model of non-interacting ionic defects can yield much information about the dependence of the CCDC on the degree of CDS or the pressure of the non-metal in the gas phase. The degeneracy of the electrons exerts a significant influence on the CCDC. However, despite the major advances made with the aid of the model of non-interacting defects, its possibilities are apparently close to being exhausted.

The discrepancy between the conclusions derived from the theory and experiment for some of the systems investigated necessitates an increase in the complexity of the existing models, in the first place the allowance for the interaction of ions or point defects and also for the involvement of models of extended defects. It is quite evident that appreciable progress on these lines can be achieved by combined theoretical and experimental studies of both static and kinetic characteristics of solids at the atomic level using microscopic working models of the defect structure and of the mechanisms of the elementary transport steps.

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