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KINETICS AND THERMODYNAMICS OF POINT DEFECTS IN NON-STOICHIOMETRIC METAL OXIDES AND SULPHIDES
Microthermogravimetric study

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Kinetic methods for studying the transport properties of non-stoichiometric transition metal oxides and sulphides have been described. It has been shown that modern microthermogravimetric techniques enable, in rather simple way, the determination of the concentration and the mobility of point defects in these materials as a function of temperature and oxidant activity, with an accuracy difficult to attain with other, much more complicated and time consuming methods. The advantages of the kinetic methods described in this paper have been illustrated by the results obtained on Mn–MnS–S_2 system which has been extensively studied in detail by different authors using various conventional techniques.

Keywords: *diffusion, metal evaporation, reequilibration, two-stage kinetic method*

Introduction

A number of important properties of transition metal oxides and sulphides is inherently related to atomic disorder. Point defects are responsible for lattice diffusion which determines or strongly influences such important processes as mass transport, solid state reactions, high temperature creep, phase transformations, etc. Electronic defects, in turn, which are strongly related to and often determined by ionic disorder, are responsible for semiconductive, thermoelectric, electro-optical and many other important properties of these compounds. This is the reason why the defect structure and transport properties of metal oxides and sulphides are being extensively studied, for years.

Due to the variable valence of cations transition metal oxides and sulphides show deviations from stoichiometry resulting from disorder prevailing in one sublattice, only. In contrast to thermally generated intrinsic ionic and electronic disorder, always present in any crystalline solid, the concentration of predominant extrinsic defects resulting from non-stoichiometry depends not only on temperature but also on oxidant activity, because these defects are formed on the crystal surface in gas–solid interaction. Thus, transport properties of the discussed compounds may be explained in studying the kinetics of non-stoichiometry changes as a function of temperature and oxidant activity using modern microthermogravimetric techniques. The present paper is an attempt to demonstrate that due to a very high accuracy of modern microthermogravimetry important information on the concentration and the mobility of point defects in the discussed non-stoichiometric metal oxides and sulphides may be obtained in rather simple experimental procedure.

Theory

In contrast with gases and liquids, the transport properties of solids cannot be described by one diffusion coefficient because ions (or atoms) in the crystal lattice of inorganic solids are not ‘self-driver’ and can jump from one lattice site to another only via point defects. In the case of metal deficient binary metal monoxide and sulphides ($M_{1-y}X$), discussed here as an example, cation sublattice is predominantly defected and the mass transport proceeds by simple vacancy mechanism of diffusion, consisting in jumping of cations from the lattice sites to neighbouring vacancies. Under thermodynamic equilibrium the random walk of defects describes defect diffusion coefficient, D_d, (vacancy diffusion coefficient, D_V, in the discussed case) being the direct measure of defect mobility, and the random walk of ions, self-diffusion coefficient, D_i, which is the product of defect concentration, expressed in mole fraction, C_d, and defect diffusion coefficient. All these three important transport parameters are interrelated by the following general relationship [1–3]:

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$$C_iD_i = C_dD_d \tag{1}$$

where C_i denotes the mole fraction of ions in the sublattice predominantly defected. In the case under discussion the concentration of cation vacancies in $M_{1-y}X$ compound is simply equal to non-stoichiometry, y, and the above equation assumes the form:

$$(1-y)D_M = yD_V \tag{2}$$

where D_M is the self-diffusion coefficient of cations.

If the non-stoichiometry and thereby defect concentration is very low ($y<<1$), as in the case of majority of metal oxides and in a number of sulphides, Eq. (2) assumes the following simplified form:

$$D_M = yD_V = [V_M^\alpha]D_V \tag{3}$$

where $[V_M^\alpha]$ denotes the concentration of cation vacancies expressed in mole fraction and α the degree of their ionisation.

From these short remarks it follows clearly that in addition to non-stoichiometry at least two diffusion coefficients are necessary to describe the transport properties of a given oxide or sulphide. However, none of these two diffusion coefficients can directly be determined experimentally, because they describe the random walk of ions and defects under thermodynamic equilibrium. Self-diffusion coefficient of ions can be calculated from tracer diffusion coefficient, D_t, if the diffusion mechanism and the corresponding correlation factor for a given crystal structure are known [3]:

$$D_i = D_t/f \tag{4}$$

Defect diffusion coefficient, on the other hand, can be obtained from chemical diffusion data if only the dependence of defect concentration on oxidant activity, is known [3, 4]:

$$D_d = 2\tilde{D}\frac{\mathrm{d}\ln C_d}{\mathrm{d}\ln p_{X_2}} \tag{5}$$

where $\tilde{D}$ is the chemical diffusion coefficient. If the concentration of defects is low enough, so that they do not interact, the thermodynamic factor($\mathrm{d}\ln C_d/\mathrm{d}\ln p_{X_2}$) remains constant and general Eq. (5) assumes the following simplified form:

$$D_d = \frac{\tilde{D}}{1+\alpha} \tag{6}$$

This simple relationship between D_d and $\tilde{D}$ results from the fact that chemical diffusion is an ambipolar process of defect migration under their concentration gradient and consequently, the chemical diffusion coefficient is a direct measure of the rate of defect diffusion in a given oxide or sulphide under non-equilibrium conditions. Thus, the only difference between the rate of random walk of point defects and their migration under a concentration gradient results from accelerating effect of much more mobile electronic defects, the enhancement factor (1+α) being the more effective, the higher is the degree of defect ionisation.

From the above discussion it follows, that the self-diffusion coefficient of defects, D_d, and that of ions, D_i – two fundamental transport parameters – can easily be obtained from chemical diffusion data, if only the concentration of predominant defects (non-stoichiometry) in a given oxide or sulphide is known. In fact, self-diffusion coefficient of ions, D_i, can also be obtained from tracer diffusion data, however, these experiments are rather difficult and very time-consuming, and in addition the results are not always very accurate. On the other hand, non-stoichiometry and chemical diffusion coefficients can be determined at present with rather high accuracy in fairly simple experimental procedure using modern microthermogravimetric techniques. Thus, the present paper is an attempt to show the value of kinetic methods in studying the transport properties of transition metal oxides and sulphides, the methods which in authors' opinion deserve more attention in this area of research.

Reequilibration kinetic method

As the chemical diffusion is the process of defect migration under their concentration gradient, the chemical diffusion coefficient in non-stoichiometric compounds can be determined from mass changes of a given sample as a function of time when going from one thermodynamic state to another [4, 5]. If, for instance, a metal-deficient $M_{1-y}X$ type compound, discussed here as an example, is equilibrated at a given temperature and oxidant pressure, the non-stoichiometry, y, reaches a constant value and the mass of the sample remains constant. When, subsequently the oxidant pressure is suddenly changed to a lower value, reduction process starts to operate and the sample begins to lose gradually its mass as a result of evolution of gaseous oxidant to the environment, and liberated electrons and cations fill electron holes and cation vacancies, respectively. As a consequence, between the surface and the interior of the sample a concentration gradient of ionic and electronic defects is established, resulting in their ambipolar outward diffusion. The concentration of defects and thereby the non-stoichiometry in the compound gradually decreases until a new equilibrium is reached. When, on the other hand, the oxidant pressure is suddenly raised to a higher value, the oxidant is bonded on the sample surface with electrons and cations diffusing there from the lattice, leaving behind electron holes and cation vacancies, respectively. Thus, as a result of such an oxidation process the mass of the sample, and thereby the concentration of defects and non-stoichiometry of the $M_{1-y}X$ compound, increases.

Figure 1 shows schematically defect distribution as a function of reequilibration time, *t*, in the cross-section of a flat $M_{1-y}X$ specimen of the thickness '2a'. Predominant defects in this case have been assumed to be doubly ionised cation vacancies and electron holes, the formation of which is described by the reaction (i) on this diagram (Kröger–Vink notation of defects is used throughout of this paper [6]). Dotted lines mark point defect concentrations at a constant temperature and two different equilibrium states, corresponding to different oxidant pressures, p'_{X_2} and p''_{X_2}. In the oxidation experiments (Fig. 1a) the $M_{1-y}X$ sample is first equilibrated, for instant, at low oxidant pressure, p'_{X_2}, until the defect concentration and thereby non-stoichiometry throughout the cross-section of the sample reach a corresponding low value, $y'=C'_{V_M}$. When the oxidant pressure is then suddenly raised to a higher value, p''_{X_2}, the system will gradually approach a new equilibrium state with higher defect concentration, C''_{V_M}. In the reduction process, on the other hand (Fig. 1b) the system approaches gradually a new equilibrium with lower defect concentration ($C'_{V_M}<C''_{V_M}$). The kinetics of both these reequilibration processes can continuously be followed thermogravimetrically because of very high sensitivity of the modern micro-thermogravimetric equipments [7–9]. In our experiments we have been able to determine the mass changes of a given sample as a function of time with the accuracy of the order of 10^{-6} g [9].

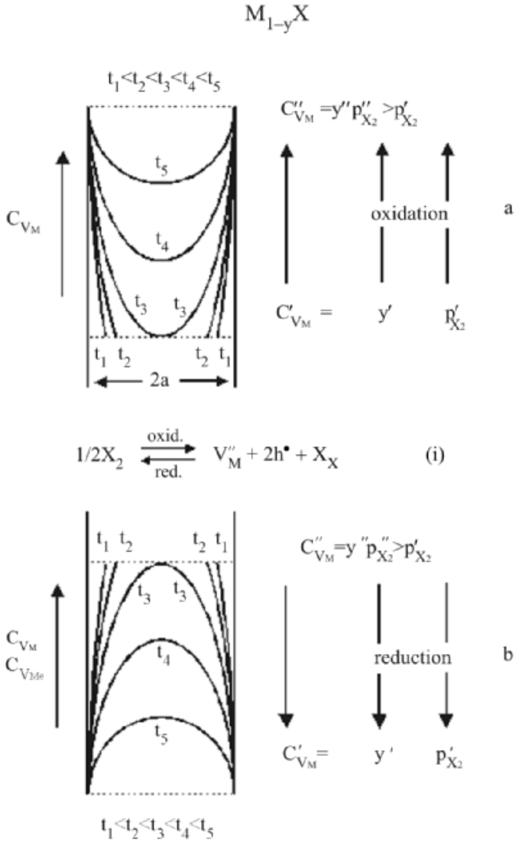

Fig. 1 Defect distribution in the cross-section of a $M_{1-y}X$ type specimen

At high temperatures chemical reactions at solid–gas interface proceed usually much faster than the solid state diffusion and consequently the overall reduction and oxidation rates of a given non-stoichiometric compound should be diffusion controlled. Thus, from the kinetics of mass changes of a given sample, i.e., from reequilibration kinetics, the chemical diffusion coefficient can be calculated. The most important problem in this experimental procedure is to verify the fundamental assumption concerning the rate determining step of the overall reequilibration process. This can be done by making oxidation and reduction runs under the same experimental conditions. If no hysteresis is observed and the same value of chemical diffusion coefficient is obtained from both reequilibration runs, it may be considered as an experimental proof that the slowest step of the overall reaction rate is the ambipolar diffusion of defects.

In order to calculate the chemical diffusion coefficient from such reequilibration rate measurements, an appropriate solution of Fick's second law must be applied. For flat, rectangular samples, commonly utilized in these experiments, such a solution leads to the following exponential equation [4, 5]:

$$1-\frac{\Delta m_{\mathrm{t}}}{\Delta m_{\mathrm{k}}}=\frac{8}{\pi^2}\exp\left(-\frac{\widetilde{D}\pi^2 t}{4a^2}\right) \qquad (7)$$

where Δm_{t} denotes the mass change of the sample after any time *t*, and Δm_{k} is the total mass change when new equilibrium state is established.

It should be noted that Eq. (7) is equally valid for the oxidation and reduction runs, since the boundary conditions in the solution of Fick's second law are identical for both cases and consequently, the same value of $\widetilde{D}$ should be obtained in both such experiments carried out under the same experimental conditions. It is convenient to express the exponential Eq. (7) in logarithmic form, so that the chemical diffusion coefficient can easily be calculated from the slope of the straight line obtained by plotting the results of reequilibration kinetics in semi-logarithmic system of coordinates:

$$\ln\left(1-\frac{\Delta m_{\mathrm{t}}}{\Delta m_{\mathrm{k}}}\right)=\ln\frac{8}{\pi^2}-\frac{\widetilde{D}\pi^2 t}{4a^2} \qquad (8)$$

The application of this method, as well as of two other kinetic methods discussed later, will be illustrated by the results obtained on non-stoichiometric manganous sulphide, $Mn_{1\pm y}S$, the defect structure and transport properties of which have been extensively studied by different authors using various experimental techniques [10–18]. In contrast with the majority of transition metal sulphides, manganous sulphide shows very low deviations from stoichiometry, and thereby defect concentration, of the order of that in nickel oxide. It has been shown that over the major part of the phase field, corresponding to higher sulphur activities, α-MnS, showing rock-salt structure, is a metal deficit, *p*-type semiconductor with predominant defects being doubly ionised cation vacancies and electron holes ($Mn_{1-y}S$).

At very low sulphur activities only, near and at the Mn/MnS phase boundary, this sulphide has been found to be a metal excess *n*-type semiconductor with doubly ionised interstitial cations and quasi-free electrons as predominant defects ($Mn_{1+y}S$) [12, 13, 15, 17].

As the non-stoichiometry and thereby defect concentration in the discussed sulphide, even at very high temperatures is very low, the interaction between defects has been assumed to be negligible and defect equilibria have been considered in terms of point defect thermodynamics [2, 3]. Thus, the formation of predominant defects in metal deficient $Mn_{1-y}S$ can be described by the following quasi-chemical defect reaction:

$$\frac{1}{2}S_2 \Leftrightarrow V''_{\mathrm{M}} + 2h^{\bullet} + S_{\mathrm{S}} \qquad (9)$$

Applying to this defect equilibrium the mass action law and the appropriate electroneutrality condition ($2[V''_{\mathrm{M}}]=[h^{\bullet}]$), one obtains the following theoretical equation describing the temperature and sulphur pressure dependence of the concentration of prevailing defects in $Mn_{1-y}S$:

$$y=[V''_{\mathrm{M}}]=\frac{1}{2}[h^{\bullet}]= \\ =0.63\,p_{\mathrm{S}_2}^{1/6}\exp\left(\frac{\Delta S_{\mathrm{f}}}{3R}\right)\exp\left(-\frac{\Delta H_{\mathrm{f}}}{3RT}\right) \qquad (10)$$

where ΔS_{f} and ΔH_{f} denote entropy and enthalpy of defect formation, respectively.

In agreement with these theoretical relationship it has been found that the non-stoichiometry, y, in $Mn_{1-y}S$, determined thermogravimetrically, is described by the following empirical equation [18]:

$$y=4.43\cdot10^{-2}\,p_{\mathrm{S}_2}^{1/6}\exp\left(-\frac{41.0\ \mathrm{kJ\ mol^{-1}}}{RT}\right) \qquad (11)$$

On the other hand, self-diffusion coefficient of cations in $Mn_{1-y}S$ has been determined as a function of temperature and sulphur activity in rather difficult and time consuming tracer experiments and these results, considering the correlation factor f=0.7815, can be described by the following relationship [15, 17]:

$$D_{\mathrm{Mn}}=6\cdot10^{-4}\,p_{\mathrm{S}_2}^{1/6}\exp\left(-\frac{142\ \mathrm{kJ\ mol^{-1}}}{RT}\right) \qquad (12)$$

Analogous pressure dependence of D_{Mn} and y strongly suggests that the mobility of point defects (cation vacancies) in $Mn_{1-y}S$ does not depend on their concentration and consequently, defect diffusion coefficient, D_{V}, being the direct measure of their mobility, may be estimated by introducing Eqs (11) and (12) into Eq. (3):

$$D_{\mathrm{V}}=1.35\cdot10^{-2}\exp\left(-\frac{101\ \mathrm{kJ\ mol^{-1}}}{RT}\right) \qquad (13)$$

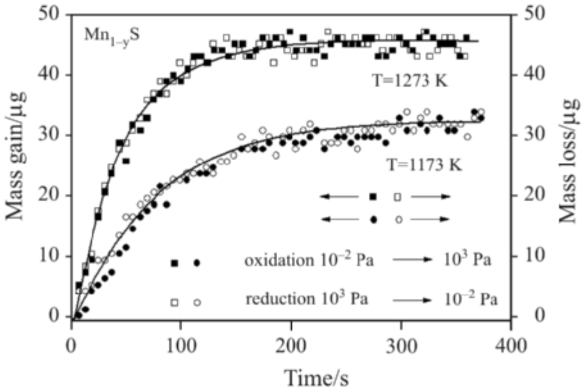

Fig. 2 Reequilibration kinetics of $Mn_{1-y}S$ [5]

However, this important transport parameter can directly be obtained, with very high accuracy, from chemical diffusion data using the discussed reequilibration method. For illustration, Fig. 2 shows selected reequilibration (relaxation) curves obtained at two different temperatures. As can be seen, no hysteresis was observed between the oxidation and reduction runs, clearly indicating that the reequilibration kinetics of $Mn_{1-y}S$ were diffusion controlled. In order to determine the possible dependence of chemical diffusion coefficient on defect concentration, the relaxation curves were obtained for small steps in $p(S_2)$ traversing the phase field of $Mn_{1-y}S$. Several oxidation and reduction runs obtained in such steps are shown in Fig. 3. Some of all these results are presented once again in Figs 4 and 5 in semi-logarithmic plot and in agreement with Eq. (8) straight lines have been obtained, enabling $\widetilde{D}$ to be calculated as a function of temperature and sulphur activity. The results of these calculations are shown in Figs 6 and 7 in double logarithmic and Arrhenius plots, respectively. As can be seen, chemical diffusion coefficient in $Mn_{1-y}S$ does not depend on sulphur activity and its temperature dependence can be expressed by the following empirical equation [5]:

$$\widetilde{D} = 5.9 \cdot 10^{-2} \exp\left(-\frac{83.4 \text{ kJ mol}^{-1}}{RT}\right) \qquad (14)$$

As the concentration of cation vacancies in the discussed sulphide is the simple power function of equilibrium sulphur pressure (Eq. (11)) chemical diffusion coefficient can easily be recalculated into defect (vacancy) diffusion coefficient, D_V, using Eq. (6) with α=2:

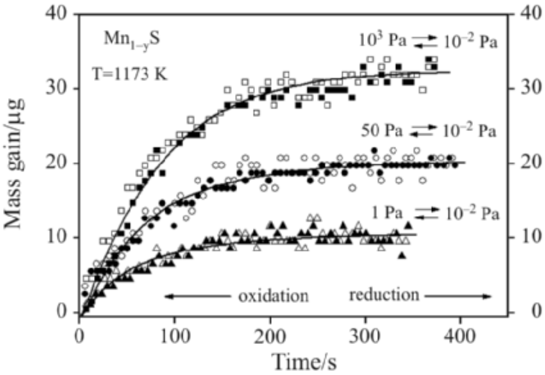

Fig. 3 Reequilibration kinetics of manganese sulphide at 1173 K for different sulphur pressures intervals [5]

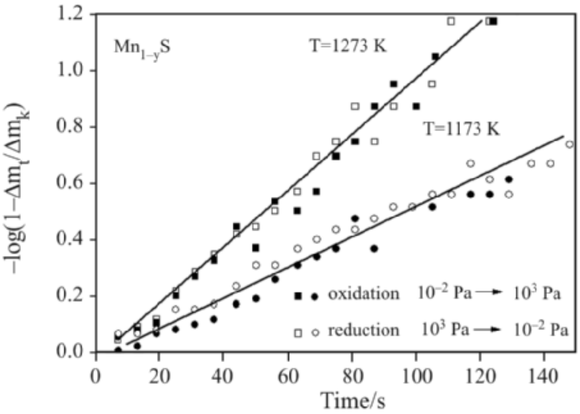

Fig. 4 The results of reequilibration measurements of Mn$_{1-y}$S obtained at different temperatures presented in semilogarithmic plot [5]

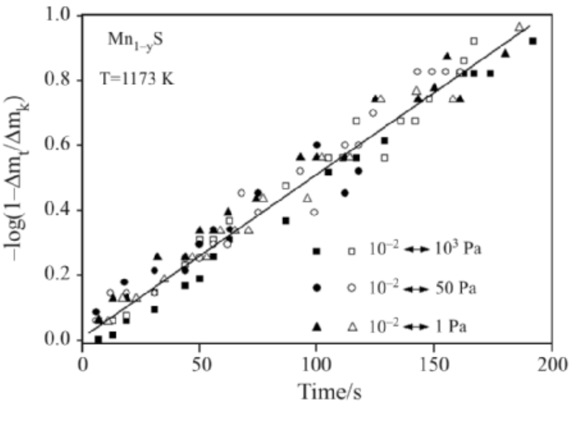

Fig. 5 The results of reequilibration measurements of Mn$_{1-y}$S obtained at 1173 K for different sulphur pressure intervals, presented in semilogarithmic plot [5]

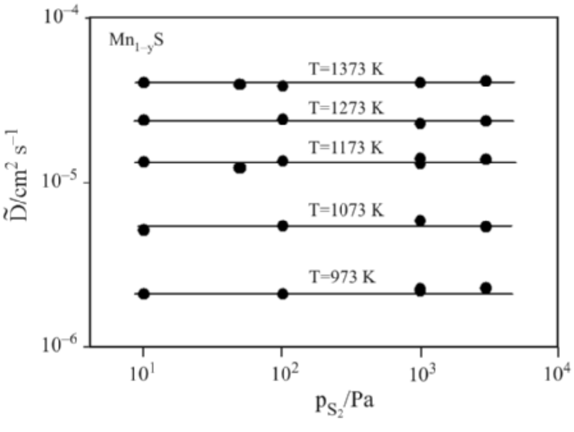

Fig. 6 Pressure dependence of chemical diffusion coefficient in Mn$_{1-y}$S for several temperatures [5]

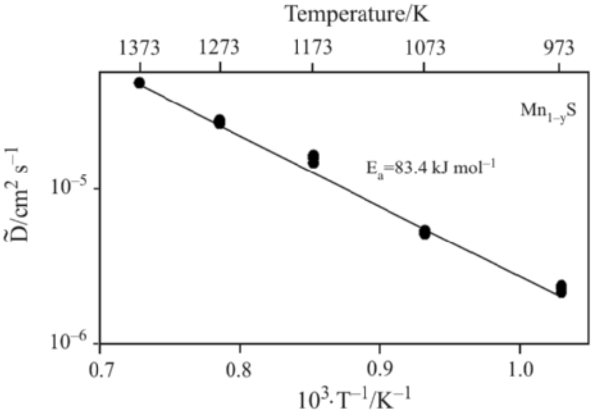

Fig. 7 Temperature dependence of chemical diffusion coefficient in Mn$_{1-y}$S [5]

$$D_V = 1.97 \cdot 10^{-2} \exp\left(-\frac{83.4 \text{ kJ mol}^{-1}}{RT}\right) \qquad (15)$$

As predicted, the diffusivity and thereby the mobility of cation vacancies in Mn$_{1-y}$S does not depend on their concentration, which is not surprising because the concentration of defects – even in very high temperatures (>1473 K) and sulphur pressures (≈10^4 Pa) – is very low ($y<10^{-3}$) and consequently, they do not interact and are randomly distributed in the crystal lattice. However, from the comparison of Eqs (13) and (15) it follows that the value of experimentally determined activation energy of vacancy diffusion in Mn$_{1-y}$S is lower from that estimated from y and D_{Mn} (Eqs (11) and (12)).

From Eq. (3) it follows that the self-diffusion coefficient of cations in Mn$_{1-y}$S is the product of nonstoichiometry, y, and the defect diffusion coefficient, D_V, in this sulphide. Thus, D_{Mn} can be calculated as a function of temperature and sulphur activity by introducing empirical Eqs (11) and (15) into Eq. (3):

$$D_{\mathrm{Mn}} = 8.73 \cdot 10^{-4} p_{\mathrm{S}_2}^{1/6} \exp\left(-\frac{124.4 \text{ kJ mol}^{-1}}{RT}\right) \quad (16)$$

From the comparison of Eqs (12) and (16) it follows clearly that the results obtained in very difficult and time consuming tracer experiments are in good agreement with those calculated from fairly simple reequilibration rate measurements and non-stoichiometry data.

Two-stage oxidation method

There is the second kinetic method enabling not only the determination of the diffusivity but also the concentration of predominant point defects in non-stoichiometric metal oxides and sulphides, in one series of relatively simple thermogravimetric experiments. This method is based on Wagner's theory of metal oxidation [19] and consequently, the main assumptions of this theory have to be fulfilled, i.e., the layer of the reaction product (scale) must be compact and well adherent to the substrate, and its growth rate has to be governed by volume diffusion of cations (or anions) through point defects in the growing scale (parabolic kinetics). If the mobility of defects is concentration independent, i.e., when the defect concentration is low, the parabolic rate constant of metal oxidation (or sulphidation) is the product of the concentration of defects in the scale at the interface where they are created and the chemical diffusion coefficient [19–21]:

$$k_{\mathrm{p}} = C_{\mathrm{d}} \tilde{D} \quad (17)$$

where k_{p} is the parabolic rate constant, expressed in $\mathrm{cm}^2\ \mathrm{s}^{-1}$ in agreement with the familiar Tammann's parabolic rate law:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{k_{\mathrm{p}}}{x} \quad (18)$$

where x denotes the scale thickness at time t. Considering Eq. (6), Eq. (17) may be extended to the following form:

$$k_{\mathrm{p}} = C_{\mathrm{d}}(1+\alpha)D_{\mathrm{d}} = (1+\alpha)D_{\mathrm{i}} \quad (19)$$

As can be seen, Wagner's approach enables the calculation of the product of C_{d} and D_{d} when the degree of defect ionisation is known, and thereby the self-diffusion coefficient of ions, but not the separation of C_{d} and D_{d} which have the fundamental significance.

Some fourty years ago Rosenburg [22] proposed a method for separating these two important quantities by alternative, yet simple thermogravimetric procedure. However, in those times this fascinating method remained purely theoretical because of insufficient sensitivity of thermogravimetric equipments. Nowadays, modern microthermogravimetry offers excellent possibility for the application of this method in studying the kinetics and thermodynamics of point defects in non-stoichiometric metal oxides and sulphides, and in fact it has already been used successfully in several cases [23–25]. It consists in the interruption of the metal oxidation process at a given stage by removing of the oxidant from the reaction chamber and, after equilibrating the metallic phase with the reaction product (scale), continuing the oxidation by readmission of the oxidizing gas to the reaction space. At the beginning of the experiment the oxidation follows familiar parabolic kinetics with the linear concentration gradient of diffusing defects in the growing scale, as shown schematically in Fig. 8 by the dotted line. When the thickness of the scale reaches a required value, the oxidation process is interrupted and the M–MX–X_2 system goes gradually to equilibrium. In the discussed case of metal deficient oxide or sulphide scales ($M_{1-y}X$) equilibrium means that at a given temperature the non-stoichiometry and thereby the concentration of cation vacancies over the whole thickness of the reaction product (Fig. 8) reaches the minimum value. If now the oxidant pressure is suddenly raised to its value prior interruption, the ambipolar diffusion of defects is resumed and their original concentration gradient is gradually reestablished (Fig. 9). Two stages of this process may be distinguished. Immediately after readmission of the oxidant the reaction proceeds much faster than before the interruption, as a result of rapid changes of defect concentration in deeper and deeper parts of the scale, and this stage last the longer the thicker is the scale layer formed before the interruption. It should be noted that in this stage ($t<t_5$, Fig. 9) the scale is only 'oxidized' (non-stoichiometry is changing) and consequently, in terms of diffusion theory this process proceeds in semi-infinitive system. The reaction rate in this stage gradually decreases and

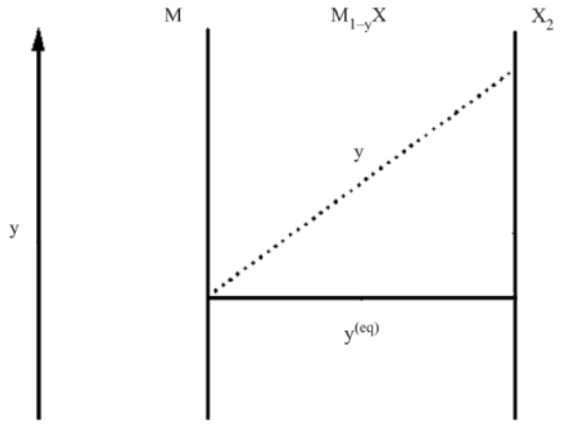

Fig. 8 Defect distribution (schematic) in the growing $M_{1-y}X$ scale under steady-state condition (dotted line) and at the thermodynamic equilibrium in the M–MX–X_2 system (solid lines) [25]

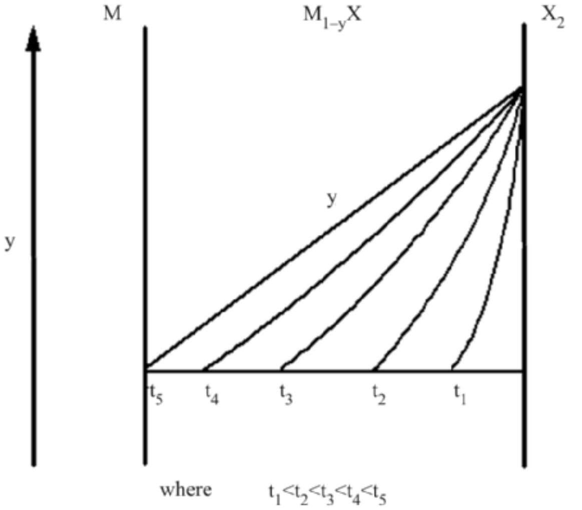

Fig. 9 Defect concentration changes (schematic) in the growing $M_{1-y}X$ scales after readmission of the oxidant to the reaction chamber [25]

after restoration of the linear concentration gradient of defects in the scale ($t>t_5$, Fig. 9) the oxidation process proceeds again with parabolic kinetics observed before the interruption. However, if the increase in the scale thickness after interruption may be neglected, in the first stage a 'new' parabolic kinetics should be observed (diffusion in semi-infinitive system) and in the second stage the course of oxidation may be approximated by the linear rate law (steady state diffusion problem). Thus, the course of the reaction in these two stages constitutes the paralinear kinetic curve, as shown schematically in Fig. 10.

Considering appropriate boundary conditions for the solution of this problem in terms of Fick's second law, Rosenburg [22] derived a rather complicated differential equation which he solved numerically obtaining two simple limiting solutions, describing the discussed paralinear kinetic curve with the accuracy of 1%:

$$\left(\frac{\Delta m}{A}\right)_1 = 1.128 C_0 \sqrt{\tilde{D}}\sqrt{t} \text{ for } t \ll X_0^2/\tilde{D} \qquad (20)$$

and

$$\left(\frac{\Delta m}{A}\right)_2 = \frac{\tilde{D} C_0}{X_0} t + \frac{X_0 C_0}{3} \text{ for } t > X_0^2/2\tilde{D} \qquad (21)$$

where $(\Delta m/A)_1$ and $(\Delta m/A)_2$ denote mass gains of the oxidized sample per unit surface area in two successive stages of the reaction after readmission of the oxidant to the reaction chamber; C_0 is the concentration of defects in the scale (expressed in g cm^{-3}) at the interface where they are created, and X_0 – the scale thickness obtained before the break of the reaction ($X_0 \gg \Delta X$, where ΔX is the increase in the scale thickness during the determination of the whole paralinear kinetic curve). Equation (20) describes the initial, parabolic section of the paralinear kinetic curve under discussion (Fig. 10) when the condition $t \ll X_0^2/\tilde{D}$ is fulfilled and Eq. (21) the linear part of this curve for times longer than $t > X_0^2/2\tilde{D}$.

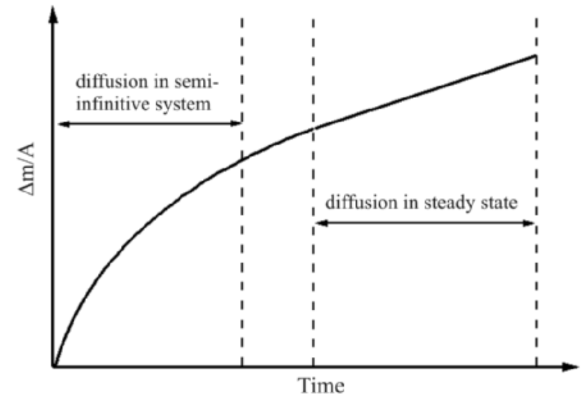

Fig. 10 Rosenburg's paralinear kinetic curve (schematic) [25]

These two equations can be expressed in a slightly different form, more suitable for graphical interpretation:

$$\left(\frac{\Delta m}{A}\right)_1 = k_\mathrm{p}\sqrt{t} + C_\mathrm{p} \qquad (22)$$

and

$$\left(\frac{\Delta m}{A}\right)_2 = k_\mathrm{l} t + C_\mathrm{l} \qquad (23)$$

where k_p and k_l are parabolic and linear rate constants in successive two stages of the reaction, expressed in g cm^{-2} s$^{-0.5}$ and g cm^{-2} s^{-1}, respectively. C_p characterizes deviations from parabolic course of the reaction at its very beginning, resulting from not yet constant oxidant pressure after its readmission to the reaction space, and C_l is directly given by extrapolation of the linear section of paralinear curve to the *y*-axis.

Since k_p and k_l, as well as C_p and C_l can be determined in one oxidation experiment, two unknown quantities, $\tilde{D}$ and C_0 may be calculated separately using the following relationships:

$$\tilde{D} = \left(\frac{1.128 k_\mathrm{l} X_0}{k_\mathrm{p}}\right)^2 \qquad (24)$$

and

$$C_\mathrm{d} = \frac{\left(\frac{k_\mathrm{p}}{1.128}\right)^2}{k_\mathrm{l} X_0} \qquad (25)$$

The concentration of defects can also be obtained from the following equation:

$$C_{\mathrm{d}} = \frac{3(C_{\mathrm{l}} - C_{\mathrm{p}})}{X_0} \qquad (26)$$

It is important to note that two-stage oxidation experiments can be repeated several times at different temperatures and oxidant pressures without removing the sample from the reaction chamber. Thus, in one series of such experiments – carried out on one and the same specimen – the mobility and the concentration of defects in a given oxide or sulphide can be determined as a function of temperature and oxidant activity with very high precision, difficult or even impossible to achieve with conventional experimental techniques.

The following conditions must be fulfilled in order to obtain the correct results:

- The scale layer formed on the metal surface in preliminary and subsequent stages of the reaction must be compact and well adherent to the substrate.
- The overall growth rate of the scale in every stages of the reaction must be diffusion controlled.
- The homogenisation time after preliminary stage of oxidation must exceed $X_0^2/\tilde{D}$.
- The parabolic rate constant, k_{p}, must be determined at a time much shorter than $X_0^2/\tilde{D}$, and the linear constant, k_{l}, at a time longer than $X_0^2/2\tilde{D}$.
- During the determination of the whole paralinear kinetic curve the increase of the scale thickness, ΔX, must be much smaller than the initial thickness X_0 ($\Delta X \ll X_0$).

In order to illustrate the advantages of this method some of the results obtained on Mn–$Mn_{1-y}S$–S_2 system [25] will be shown and compared with those obtained with other experimental techniques. For illustration, several kinetic curves obtained at different temperatures for sulphur pressure 10^3 Pa are shown in Fig. 11. In spite of very low deviation from stoichiometry of $Mn_{1-y}S$ two stages of the reaction are clearly visible, manifesting themselves by initial parabolic and subsequent linear kinetics. k_{l} and C_{l} values were obtained from linear parts of these paralinear curves, and k_{p} and C_{p} – from initial, parabolic parts, shown ones again in Fig. 12 in parabolic plot. Analogous results have been obtained at different temperatures and sulphur pressures. Using all these data the concentration of cation vacancies and chemical diffusion coefficient have been calculated as a function of temperature and sulphur activity (Figs 13–15). From Fig. 13 it follows that in agreement with directly deter-

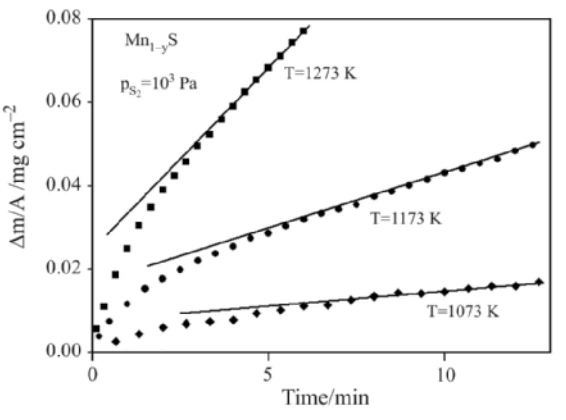

Fig. 11 Paralinear kinetic curves of manganese sulphidation for several temperatures (linear plot) [25]

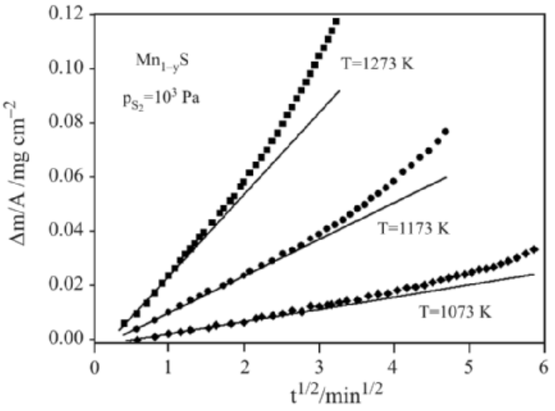

Fig. 12 Paralinear kinetic curves of manganese sulphidation for several temperatures (parabolic plot) [25]

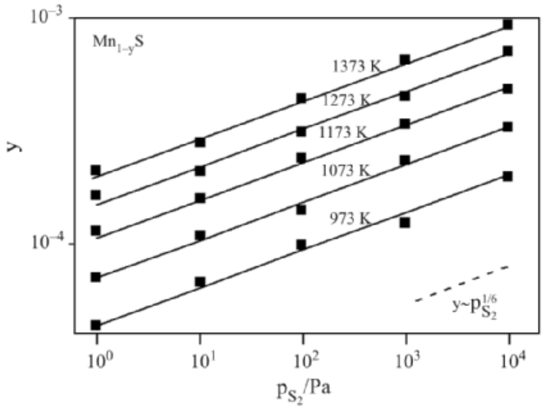

Fig. 13 Dependence of non-stoichiometry in $Mn_{1-y}S$ on sulphur vapour pressure for several temperatures [25]

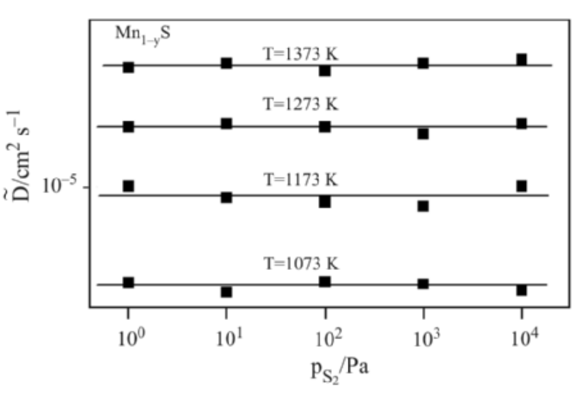

Fig. 14 Pressure dependence of chemical diffusion coefficient in $Mn_{1-y}S$ for several temperatures [25]

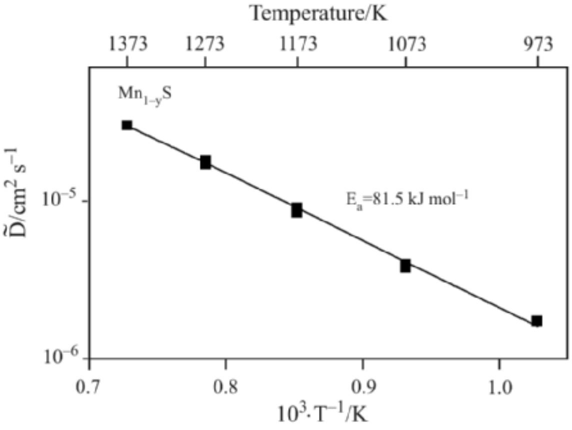

Fig. 15 Dependence of chemical diffusion coefficient in $Mn_{1-y}S$ on temperature, in Arrhenius plot [25]

mined non-stoichiometry data (Eq. (11)) the concentration of predominant defects in $Mn_{1-y}S$ is a simple power function of sulphur pressure with the slope 1/6 and this dependence does not change with temperature. Thus, the discussed results may be presented in the following analytical form [25]:

$$y = 5.41 \cdot 10^{-2} p_{S_2}^{1/6} \exp\left(-\frac{42.0 \text{ kJ mol}^{-1}}{RT}\right) \quad (27)$$

From Figs 14 and 15, in turn, it follows that in agreement with reequilibration rate measurements (Fig. 6) chemical diffusion coefficient in $Mn_{1-y}S$ does not depend on sulphur activity and is the following function of temperature:

$$\tilde{D} = 3.88 \cdot 10^{-2} \exp\left(-\frac{81.5 \text{ kJ mol}^{-1}}{RT}\right) \quad (28)$$

Introducing this equation into theoretical Eq. (6) with α=2, yields:

$$D_V = 1.29 \cdot 10^{-2} \exp\left(-\frac{81.5 \text{ kJ mol}^{-1}}{RT}\right) \quad (29)$$

It is possible, finally, to calculate the self-diffusion coefficient of cations in $Mn_{1-y}S$ as a function of temperature and sulphur pressure by introducing empirical Eqs (27) and (29) into Eq. (3):

$$D_{Mn} = 6.98 \cdot 10^{-4} p_{S_2}^{1/6} \exp\left(-\frac{123.5 \text{ kJ mol}^{-1}}{RT}\right) \quad (30)$$

It seems reasonable to compare the results obtained with the use of two-stage kinetic method with other literature data. From the comparison of Eqs (11) and (27), as well as (14) and (28) it follows clearly that the concentration of cation vacancies and their mobility in metal deficient $Mn_{1-y}S$ determined in one series of two-stage sulphidation procedure, on one and the same sample, are in excellent agreement with the corresponding data obtained in much more difficult and time consuming experiments. Analogous agreement is observed between self-diffusion coefficients of cations in $Mn_{1-y}S$ determined experimentally using tracer technique (Eq. (12)) and those calculated from reequilibration and

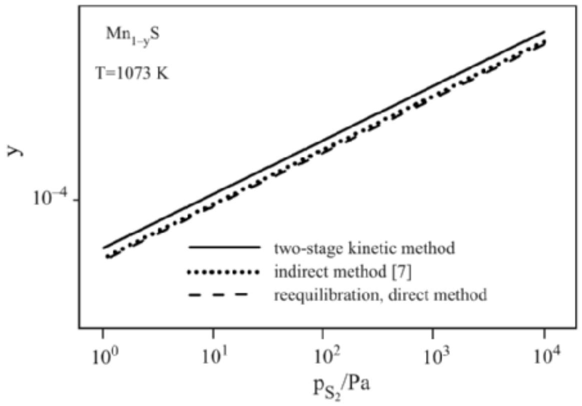

Fig. 16 Dependence of non-stoichiometry in $Mn_{1-y}S$ on sulphur vapour pressure (collective plot) [25]

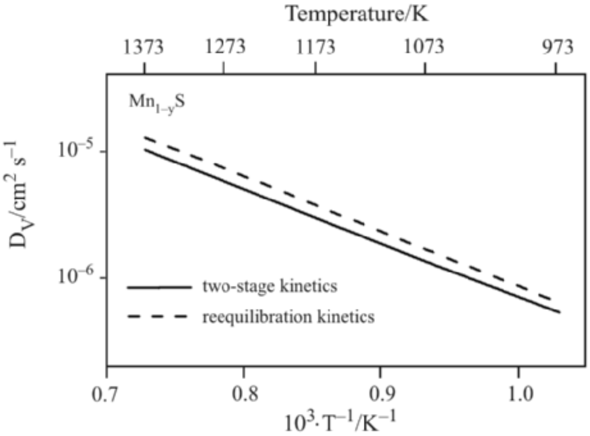

Fig. 17 Temperature dependence of defect (vacancy) diffusion coefficient in $Mn_{1-y}S$ (collective plot) [25]

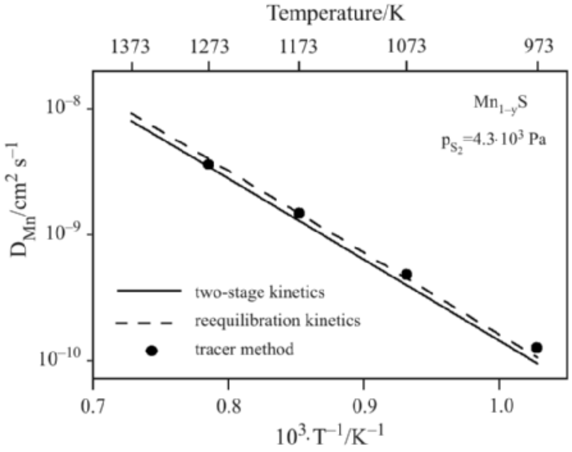

Fig. 18 Temperature dependence of self-diffusion coefficient of cations in $Mn_{1-y}S$ (collective plot) [25]

two-stage sulphidation rate measurements (Eq. (30)). These agreements are better visualized in Figs 16–18.

Diffusion–evaporation method

A distinct and very important problem constitutes the determination of self-diffusion coefficients of cations (or anions) in the discussed non-stoichiometric metal oxides and sulphides at extremely low oxidant activities, i.e., near to – and in equilibrium with the metallic phase. Such low oxygen or sulphur pressures may only (if any) be obtained in CO–CO_2 or H_2–H_2O (H_2S–H_2) gas mixtures and consequently, the influence of doping by carbon and/or hydrogen on defect concentration and thereby on diffusion kinetics, cannot be excluded. About twenty years ago Kofstad [26] developed a thermogravimetric method enabling the determination of self-diffusion coefficients of cations in oxides and sulphides in equilibrium with the metallic phase under carbon – (and hydrogen) free conditions and applied this method to Mn–MnO [27] and Cr–Cr_2O_3 [28] systems. However, it was impossible to verify the obtained results because of a lack of appropriate experimental data which were impossible to be obtained in conventional experimental procedures. As a consequence, this very simple, outstanding method did not find due response in the literature. Several years ago only, in very careful and difficult tracer experiments Gilewicz–Wolter *et al.* [15–17], have been able to determine self-diffusion coefficient of cations in metal–excess manganous sulphide, $Mn_{1+y}S$, being close to and in the equilibrium with the metallic phase. The possibility has been then created to compare these results with those obtained by Danielewski and Mrowec [13] using Kofstad's method. Excellent agreement between these results clearly indicates that this original, outstanding method may successfully be applied to determination of accurate diffusion data, which otherwise can only be obtained in few cases in very difficult conventional experimental procedure and in the majority of cases can not be obtained at all.

This method involves oxidation (or sulphidation) of a given metal in microthermogravimetric apparatus to form a dense single-layer scale of the lowest valent oxide (or sulphide), i.e., the compound which is in equilibrium with the metallic phase. The specimen is then treated in high vacuum. As no oxidation (or sulphidation) takes place, metal ions and electrons diffuse outward through the scale and metal atoms continuously evaporate from the specimen surface, as depicted in Fig. 19. If the evaporation rate of the metal is governed by its diffusional transport through the scale, the self-diffusion coefficient of cations in the compound forming the scale can be calculated from evaporation rate measurements. This rate can easily be determined thermogravimetrically by measuring the mass loss of the sample as a function of time.

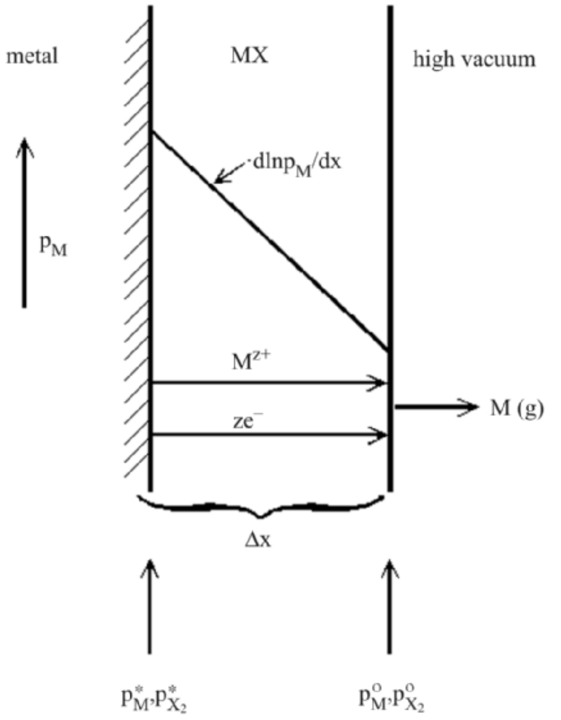

Fig. 19 Schematic representation of the diffusion–evaporation method [26]

Several requirements must be met in order that this method can be used: (a) the vapour pressure of the compound forming the scale at the experimental conditions must be sufficiently low that no oxide (or sulphide) is lost by evaporation from the specimen surface during high-vacuum treatment; (b) the oxidant activity in the compound forming the scale at its outer surface must be sufficiently low that essentially no oxidant is lost from the scale by its decomposition during high-vacuum annealing; (c) the vapour pressure of the metal at the outer scale surface must be several orders of magnitude higher than that of the oxidant, so that only metal atoms evaporate; (d) the predominant defects in the compound forming the scale should occur in the cation sublattice and the rate determining step of the overall diffusion–evaporation process must be diffusional transport of cations through the scale (volume diffusion).

These requirements limit to some extent the applicability of the method to selected systems involving oxides (or sulphides) with rather high thermodynamic stability and metals showing relatively high vapour pressures at elevated temperatures. Kofstad [26] has shown, however, that a number of important systems meets satisfactorily all these requirements. In particular, Mn–MnO [27] and Cr–Cr_2O_3 [28], as well as Mn–MnS [13] systems have successfully been studied with this diffusion–evaporation method.

If then, the above mentioned requirements are fulfilled, during thermal annealing in high vacuum of a metal specimen, covered with a dense oxide (or sulphide) scale, the metal ions and electrons diffuse outwardly through this scale of constant thickness and metal atoms evaporate from the scale surface at a constant rate. Thus, the flux of cations, j_M, (i.e., the measured rate of mass loss) through a scale with thickness ΔX is given by the following relationship:

$$j_M = -\left(C_M \int_{p^*_{X_2}}^{p^0_{X_2}} D_M \mathrm{d}\ln p_M \right) \frac{1}{\Delta X} \qquad (31)$$

where C_M is the concentration of metal atoms in the compound forming the scale; D_M is the self-diffusion coefficient of metal in the scale, and $p^*_{X_2}$ and $p^0_{X_2}$ denote the partial pressures of metal vapour at the inner and outer scale surface, respectively. To integrate Eq. (31) it is necessary to express D_M as a function of p_M. In the case of volume diffusion this relationship depends on the defect structure of the compound forming the scale. Kofstad has shown that if cation vacancies predominate ($M_{1-y}X$ type compounds) j_M is the following function of the scale thickness:

$$j_M = (\alpha + 1) C_M D^0_M / \Delta X \qquad (32)$$

where α denotes degree of defect ionisation, and D^0_M is the self-diffusion coefficient of cations in the scale at its outer surface. In this case, the self-diffusion coefficient of cations depends upon the scale thickness and the expression for the flux of Mn atoms in the scale is given by:

$$j_M = \mathrm{const}(\Delta X)^{-\frac{\alpha+1}{\alpha+2}} \qquad (33)$$

On the other hand, if interstitial cations are the prevailing defects ($M_{1+y}X$ type compounds) the discussed dependence assumes the following form:

$$j_M = \frac{(\alpha + 1) C_M D^*_M}{\Delta X} \qquad (34)$$

where D^*_M denotes the self-diffusion coefficient of cations at the metal-scale interface in equilibrium with the metallic phase. In this case then D^*_{Mn} is independent of the scale thickness and the flux of cations is the following function of this parameter:

$$j_M = \mathrm{const}(\Delta X)^{-1} \qquad (35)$$

From the comparison of Eqs (33) and (35) it follows clearly that in studying the diffusional evaporation rate of the metal as a function of the scale thickness, not only the diffusion coefficient but also important information concerning the type of predominant disorder in the scale in equilibrium with the metallic phase, can be obtained.

The discussed diffusion–evaporation method has been tested on Mn–MnS system because it meets all the requirements mentioned above. For instance, at 1373 K $p^*_M / p^*_{S_2} = 6\cdot 10^{10}$, and the evaporation and decomposition rates of MnS are many orders of magnitude lower than the evaporation rate of manganese metal. In addition, the anion sublattice of this sulphide is virtually perfect in comparison with the cation sublattice disorder.

As already mentioned in the introduction, predominant defects in α-MnS at very low sulphur activities, near and at the Mn/MnS phase boundary, is a metal excess *n*-type semiconductor with doubly ionised interstitial cations and quasi-free electrons as predominant defects ($Mn_{1+y}S$). Consequently, the concentration of these defects is the following function of temperature and equilibrium sulphur pressure [13]:

$$[\mathrm{Mn}_i^{\bullet\bullet}] = \frac{1}{2}[e] = 2.27 p_{S_2}^{-1/6} \exp\left(-\frac{151 \text{ kJ mol}^{-1}}{RT} \right) \qquad (36)$$

As the defect concentration is very low it could have been assumed that their mobility is only temperature dependent and consequently, self-diffusion coefficient of cations must depend on sulphur pressure in the same way as the concentration of defects:

$$D_{Mn} = D_i [\mathrm{Mn}_i^{\bullet\bullet}] = D_i^0 p_{S_2}^{-1/6} \exp\left(-\frac{E_D}{RT} \right) \qquad (37)$$

where D_i is the defect diffusion coefficient, and E_D – activation energy of Mn self-diffusion. In agreement with this relationship it has been found in very careful experiments, using ^{54}Mn radioactive isotope as the tracer, that the self-diffusion coefficient of cations in metal excess manganous sulphide is the following function of temperature and sulphur activity [16, 17]:

$$D_{Mn} = 0.56 p_{S_2}^{-1/6} \exp\left(-\frac{261 \text{ kJ mol}^{-1}}{RT} \right) \qquad (38)$$

Thus, for the first time the basis has been created to verify the discussed diffusion–evaporation method. Figure 20 shows for illustration several evaporation runs for different MnS scale thickness [13]. As can be seen, in agreement with the method, the evaporation of manganese into vacuum from the surface of MnS scale in equilibrium with the metallic phase follows linear kinetics, the rate of this process being the lower the higher is the scale thickness. Figure 21, in turn, shows the dependence of diffusion flux on the scale thickness for several temperatures. It is clearly seen that this dependence is described by Eq. (35) and consequently, D_{Mn} in $Mn_{1+y}S$ can be calculated as a function of temperature with the use of Eq. (34):

$$D_{\mathrm{Mn}} = 1.89\cdot 10^{-3}\exp\left(-\frac{158\ \mathrm{kJ\ mol^{-1}}}{RT}\right) \qquad (39)$$

However, this relationship and, in particular, the value of activation energy of diffusion, cannot be used for verification of the discussed diffusion–evaporation method because it does not describe the temperature dependence of D_{Mn} at constant sulphur pressure. Self-diffusion coefficients calculated from evaporation rate measurements, carried out at different temperatures are related, namely, to different sulphur pressures which are equal to the dissociation pressures of the sulphide in equilibrium with the metallic phase. Nevertheless, these results can be utilized for the calculation of the temperature dependence of D_{Mn} at constant sulphur activity because the pressure dependence of the defect concentration in $\mathrm{Mn}_{1+y}\mathrm{S}$ is known (Eq. (36)). It is then possible to construct the D_{Mn}–$p(\mathrm{S}_2)$ diagram, as shown on Fig. 22,

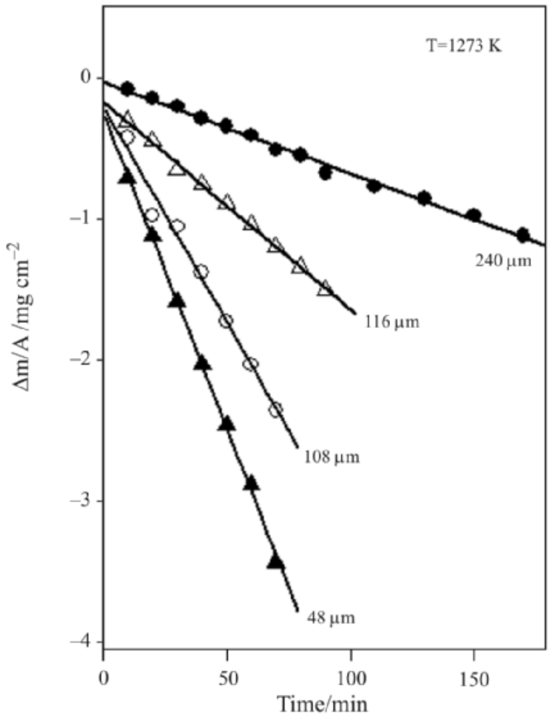

Fig. 20 Diffusional evaporation runs at 1273 K for $\mathrm{Mn}_{1+y}\mathrm{S}$ scales with different thicknesses [13]

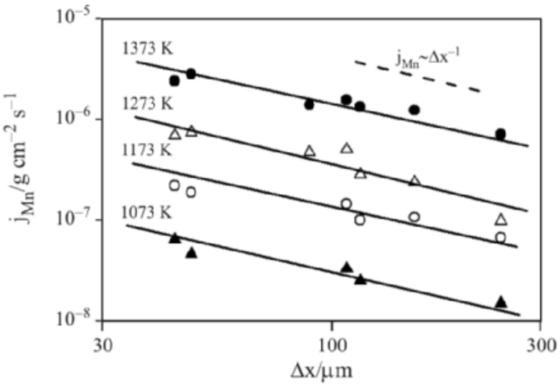

Fig. 21 Dependence of Mn flux through the $\mathrm{Mn}_{1+y}\mathrm{S}$ scale on its thickness [13]

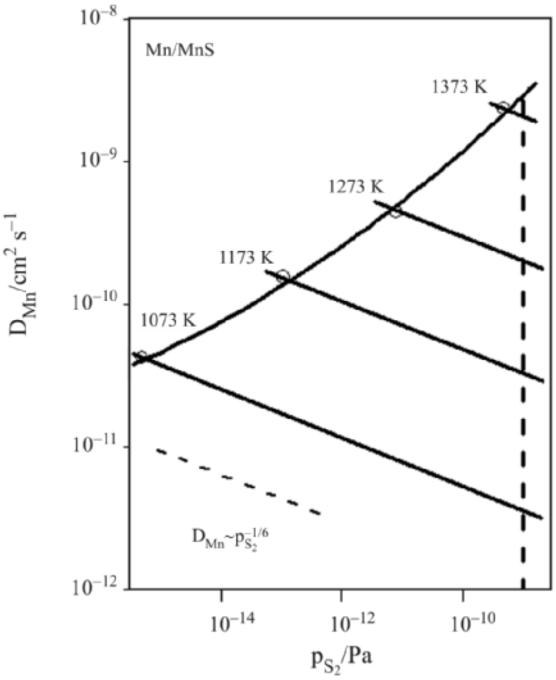

Fig. 22 Pressure dependence of the self-diffusion coefficient of cations in $\mathrm{Mn}_{1+y}\mathrm{S}$ [13]

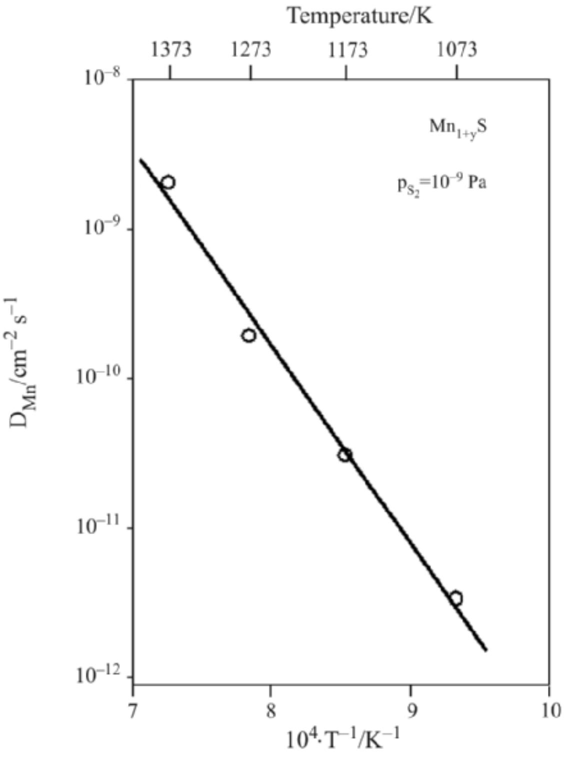

Fig. 23 Temperature dependence of the self-diffusion coefficient of cations in $\mathrm{Mn}_{1+y}\mathrm{S}$, for constant sulphur pressure [13]

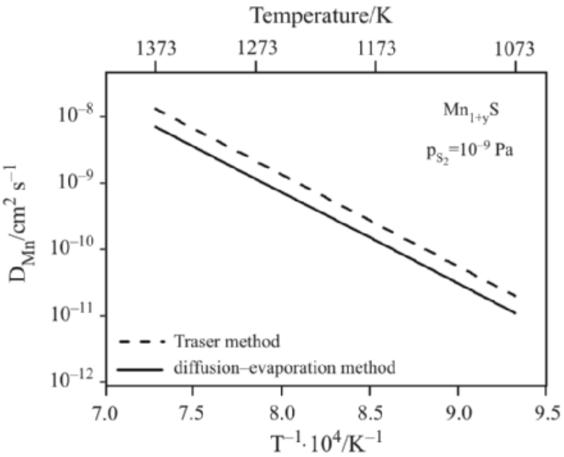

Fig. 24 Temperature dependence of the self-diffusion coefficient of cations in $Mn_{1+y}S$, calculated from evaporation rate measurements and determined in direct tracer experiments [13]

and select from this plot appropriate D_{Mn} values, corresponding at different temperatures to constant sulphur pressure. These data form a straight line in Arrhenius plot (Fig. 23) which makes it possible to express the discussed dependence in the following empirical equation:

$$D_{\mathrm{Mn}} = 0.252\, p_{S_2}^{-1/6} \exp\left(-\frac{259\ \mathrm{kJ\ mol^{-1}}}{RT} \right) \qquad (40)$$

From the comparison of Eqs (38) and (40) it follows clearly that there is an excellent agreement between the activation energy of Mn self-diffusion in $Mn_{1+y}S$ determined in direct tracer experiments and that calculated from evaporation rate measurements. In addition, the absolute values of D_{Mn} coefficients determined by both methods are also self-consistent, as shown in Fig. 24.

Conclusions

From description of kinetic methods presented in this paper the following conclusions may be formulated.

- Chemical diffusion and thereby the defect mobility in non-stoichiometric metal oxides and sulphides can be successfully studied using reequilibration and two-stage kinetic methods, provided that mass changes of a given sample can be followed with sufficient accuracy as a function of time and rapid changes of the oxidant activity in the reaction chamber of microthermogravimetric apparatus, are possible.
- One of the most important advantages of two-stage kinetic method consists in the possibility of determining not only the chemical diffusion coefficient but also the concentration of point defects in a given non-stoichiometric compound in one series of two-stage oxidation or sulphidation rate measurements, without necessity of removing the oxidizing metal sample from the reaction chamber. As the modern microthermogravimetric equipments offer now very high accuracy in following the kinetics of mass changes under strictly determined thermodynamic conditions, reequilibration and two-stage kinetic methods create very interesting possibilities in studying the transport properties of non-stoichiometric metal oxides and sulphides, however, at oxidant pressures much higher from the dissociation pressure of these materials.
- The third kinetic method, developed by Kofstad [26], eliminates this limitation by creating the possibility to calculate the self-diffusion coefficient of cations in a given oxide or sulphide from the evaporation rate of metal atoms into vacuum from the surface of the scale being in equilibrium with the metallic phase, i.e., at lowest oxidant activity. One of the notable features of this method consists in the fact that diffusional transport of cations is studied under carbon or hydrogen free conditions, while in conventional tracer experiments $CO–CO_2$ or $H_2–H_2O$ ($H_2–H_2S$) gas mixtures must be utilized in order to obtain very low oxidant activities. Consequently, the influence of doping by carbon and/or hydrogen on defect concentration and thereby on diffusion kinetics, cannot be excluded. The only limitation of this method results from the requirement that the studied oxides or sulphides must show rather high thermodynamic stability and the vapour pressure of the corresponding metals should be relatively high at elevated temperatures.

Acknowledgements

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