

Thermal diffusion and Soret effect in $(U,Me)O_{2+\delta}$: the heat of transport of oxygen

J. Janek^{*}, H. Timm

Institut für Physikalische Chemie und Elektrochemie der Universität Hannover, Callinstr. 3-3A, 30167 Hannover, Germany

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Abstract

Experimental results for thermal diffusion of oxygen in both hypo- and hyperstoichiometric uranium based oxides are reviewed, and the influence of a metallic encapsulation on thermal diffusion in nuclear fuel pellets is analysed. The collected data for the heat of transport Q_O^* of the mobile oxygen component show a minimum in the vicinity of the stoichiometric composition which is interpreted on the basis of a straightforward analysis of thermal diffusion in mixed conductors with a variable composition. It is further shown that the experimental data for the heat of transport Q_O^* in $(U,Me)O_{2+\delta}$ can be used to extract information on the defect structure. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Uranium dioxide, $UO_{2+\delta}$, is one of the few mixed conducting binary compounds which shows an appreciable phase width and can be produced with either oxygen deficiency ($\delta < 0$) or excess ($\delta > 0$) [1]. In general, it is assumed that by crossing the stoichiometric composition, the majority defects change from oxygen vacancies $V_O^{\bullet\bullet}$ and electrons e' to oxygen interstitials O_i' and electron holes h^\bullet . The composition of the binary oxide, described by the deviation δ from stoichiometry, can be controlled at a given temperature by the oxygen activity a_{O_2} in the gas phase. Thus, the partial diffusivities (or electric conductivities) which depend on the defect concentrations can also be controlled by a_{O_2} .

Chemical potential gradients ($\nabla\mu_{O_2}$) or temperature gradients (∇T), applied to $UO_{2+\delta}$, lead to coupled fluxes of ionic and electronic defects which can be described quantitatively by the single chemical diffusion coefficient \tilde{D}_O . An originally homogeneous oxide specimen which is exposed to a temperature gradient will be subject to thermal segregation of the oxygen component (if $Q_O^* \neq 0$, see

below) in the stationary state. If the surface of the specimen is closed for the exchange of its components with the surrounding atmosphere, this thermal segregation is called Soret effect.

In case of $UO_{2+\delta}$ and its solid solutions with CeO_2 and PuO_2 , thermal diffusion data have been collected mainly in the 60s due to their technological relevance, i.e., due to the importance of a quantitative understanding of transport processes in nuclear fuel pellets [2]. A review of corresponding experimental results for the heat of transport of oxygen can be found in Ref. [3]. It reports a pronounced dependence of the heat of transport of oxygen on the composition of the oxide which has not been understood to date.

Most thermal diffusion experiments have been performed on oxide pellets encapsulated in a metal cover. Thus, the evaluation leads only to a 'practical' heat of transport Q_O^{exp} , its magnitude depending both on the heat of transport Q_O^* and the electronic thermopower of the oxide specimen. A formal analysis is given in Section 2.4 (cf. Ref. [4]).

In the following, we summarize briefly the general prerequisites which are necessary for the formal description of thermal diffusion in mixed conducting compounds and propose an interpretation of the composition dependence of Q_O^* in $(U,Me)O_{2+\delta}$. The experimental results on thermal diffusion of oxygen in uranium-based oxides are

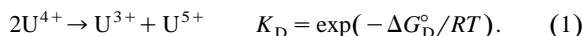
^{*} Corresponding author. Tel.: +49-511 762 5298; fax: +49-511 762 4009; e-mail: janek@mbox.pci.uni-hannover.de.

reviewed and discussed with respect to our formal analysis. The influence of an electronic short-circuit by the metal cover of fuel pellets is analysed, and a brief comparison with results for thermal diffusion in other binary compounds completes the discussion.

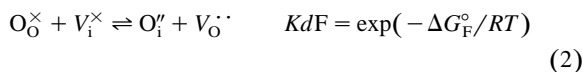
2. Formal treatment

2.1. Defect structure of $UO_{2+\delta}$

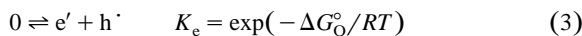
The defect structure and transport properties of $UO_{2+\delta}$ (fluorite-type lattice) have been investigated by several groups (e.g., see Fryxell and Aitken [5], Evans et al. [6], Adamson [7], Adamson and Carney [8] and Sari and Schumacher [9], cf. Matzke for reviews [10,11]). The range of homogeneity of $UO_{2+\delta}$ is large (between $O/U = 1.65$ and $O/U = 2.25$), but hypostoichiometric compositions are thermodynamically stable only at very high temperatures. It is generally accepted that the dominating ionic defects are oxygen Frenkel defects (i.e., vacancies for $\delta < 0$ and oxygen interstitials for $\delta > 0$). Experimental evidence for these defects is provided by neutron diffraction studies [12]. In addition, the electronic defects are attributed mainly to the thermally induced disproportionation [13]



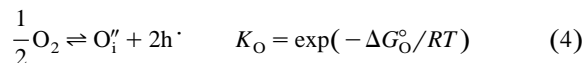
In conclusion, the concentrations of Frenkel defects and electronic defects which are governed by the local equilibria



and



can be controlled by the heterogeneous equilibrium



with molecular oxygen in the gas phase. Eqs. (2)–(4) are formulated by using the Kröger–Vink notation, with O_i' denoting the oxygen interstitial and V_O^\cdot denoting an oxygen vacancy in the anion sublattice. O_O^\times and V_i^\times represent an oxygen ion on a regular lattice site and a vacant interstitial position, respectively.

ΔG_D° in Eq. (1) is of the order of 160 kJ/mol at $T = 2000$ K [14], leading to molar fractions $x_n = x_p \approx 8 \times 10^{-3}$ of electrons and holes at the stoichiometric composition. ΔG_F° is in the order of 190 kJ/mol at $T = 2000$ K [15], leading to molar fractions $x_i = x_v \approx 3.2 \times 10^{-3}$ of oxygen interstitials and vacancies at the stoichiometric composition. Thus, ionic point defects dominate the defect structure in the vicinity of the stoichiometric composition. Eq. (3) represents the electron hole equilibrium in general and can be identified with the specific process in Eq. (1).

The deviation δ from the stoichiometric composition is defined as $\delta \equiv x_i - x_v = (x_p - x_n)/2$, with $x_i = c_i/v_m$, $x_v = c_v/v_m$, $x_p = c_p/v_m$ and $x_n = c_n/v_m$ (v_m : molar volume; c : molar concentration). Combining this definition with Eqs. (1) and (2), one obtains the following relations between the defect concentrations and the composition of non-stoichiometric $UO_{2+\delta}$ (ideal solution of point defects is assumed):

$$x_v = -\frac{1}{2}\delta + \sqrt{\frac{1}{4}\delta^2 + K_F} \quad x_i = \frac{1}{2}\delta + \sqrt{\frac{1}{4}\delta^2 + K_F} \quad (5)$$

$$x_n = -\delta + \sqrt{\delta^2 + K_D} \quad x_p = \delta + \sqrt{\delta^2 + K_D}. \quad (6)$$

2.2. Thermal diffusion and Soret effect

For a binary mixed conductor with an immobile cation sublattice, which is nearly correct for $UO_{2+\delta}$, the fluxes

$$j_{O^{2-}} = -L_{O^{2-}} \left[\nabla \tilde{\mu}_{O^{2-}} + \left(\bar{S}_{O^{2-}} + \frac{Q_{O^{2-}}^*}{T} \right) \nabla T \right] \quad (7)$$

$$j_{e^-} = -L_{e^-} \left[\nabla \tilde{\mu}_{e^-} + \left(\bar{S}_{e^-} + \frac{Q_{e^-}^*}{T} \right) \nabla T \right] \quad (8)$$

of anions O^{2-} and excess electrons e^- are sufficient for the formal description of all matter-transport processes, with $L_{O^{2-}}$ and L_{e^-} denoting the phenomenological transport coefficients of oxygen ions and electrons, with $\bar{S}_{O^{2-}}$ and \bar{S}_{e^-} representing their partial entropies, and with $\tilde{\mu}_{O^{2-}}$ and $\tilde{\mu}_{e^-}$ denoting the electrochemical potential of ions and electrons, respectively [16]. For experiments in temperature gradients, the flux j_Q of heat has to be taken into account. In the case of chemical or thermal diffusion, the fluxes of anions and electrons are coupled by the electroneutrality condition ($j_{e^-} = -2j_{O^{2-}}$), and a single flux equation

$$j_O = -L_O \left[\nabla \mu_O + \left(\bar{S}_O + \frac{Q_O^*}{T} \right) \nabla T \right] \quad (9)$$

describes the transport of the oxygen component (with $\nabla \mu_O = \nabla \tilde{\mu}_{O^{2-}} - 2\nabla \tilde{\mu}_{e^-}$, $\bar{S}_O = \bar{S}_{O^{2-}} - 2\bar{S}_{e^-}$ and $Q_O^* = Q_{O^{2-}}^* - 2Q_{e^-}^*$). The chemical potential gradient $\nabla \mu_O$ itself is a function of the composition gradient $\nabla \delta$ and the temperature gradient ∇T ,

$$\nabla \mu_O = -\bar{S}_O \nabla T + \left(\frac{\partial \mu_O}{\partial \delta} \right)_T \nabla \delta, \quad (10)$$

and thus, Eq. (9) can be rewritten alternatively as

$$j_O = -L_O \left[\left(\frac{\partial \mu_O}{\partial \delta} \right)_T \nabla \delta + \frac{Q_O^*}{T} \nabla T \right] \quad (11)$$

relating the molar flux of oxygen with the gradient $\nabla \delta$ of the oxygen excess and the temperature gradient ∇T . The

thermodynamic factor $(\partial\mu_{\text{O}}/\partial\delta)_T$ is an indirect measure of the phase width and relates the change in composition with a change in the oxygen activity. The phenomenological transport coefficient L_{O} is directly related to the chemical diffusion coefficient of oxygen via the relation $\tilde{D}_{\text{O}} = L_{\text{O}}(\partial\mu_{\text{O}}/\partial c_{\text{O}})_T$ and is a combination of the ionic and the electronic transport coefficients, i.e., $L_{\text{O}} \equiv L_{\text{O}^{2-}} \cdot L_{\text{e}^-}/(L_{\text{O}^{2-}} + L_{\text{e}^-})$.

If a temperature gradient is applied to a chemically homogeneous specimen ($\nabla\delta = 0$), an oxygen flux $j_{\text{O}} \equiv -L_{\text{O}}(Q_{\text{O}}^*/T)\nabla T$ is caused which finally leads to the establishment of a stationary composition gradient $\nabla\delta$ (and a chemical potential gradient $\nabla\mu_{\text{O}}$). This stationary thermal segregation (Soret effect, ‘demixing’ of the components) results as

$$\left(\frac{d\mu_{\text{O}}}{dT}\right) = -\left(\bar{S}_{\text{O}} + \frac{Q_{\text{O}}^*}{T}\right) \quad (j_{\text{O}} = 0) \quad (12)$$

in terms of the chemical potential μ_{O} and as

$$\begin{aligned} \left(\frac{d\delta}{dT}\right) &= -\frac{1}{T} \frac{Q_{\text{O}}^*}{\left(\frac{\partial\mu_{\text{O}}}{\partial\delta}\right)_T} \\ &= -\frac{\delta}{RT^2} \frac{Q_{\text{O}}^*}{\left(\frac{\partial\ln a_{\text{O}}}{\partial\ln \delta}\right)_T} \quad (j_{\text{O}} = 0) \end{aligned} \quad (13)$$

in terms of the deviation δ from stoichiometry, if the oxygen flux vanishes in the stationary state ($j_{\text{O}} = 0$). Besides the always positive values of the absolute temperature T and the thermodynamic factor, the heat of transport Q_{O}^* of oxygen determines the direction and the degree of the segregation. If Q_{O}^* is positive, oxygen diffuses downwards the temperature gradient to build up a counter-directed composition gradient. If Q_{O}^* is negative, oxygen diffuses upwards the temperature gradient to build up an equally directed composition gradient. Despite several attempts, no theory for the heat of transport, which would allow the prediction of either sign or magnitude of Q_{O}^* , is available to date. Thus, only experiments provide the necessary information on the degree of thermal diffusion.

2.3. Heat of transport of a mobile component

The heat of transport Q_{O}^* of the mobile oxygen component equals the sum of the ionic and electronic heats of transport,

$$Q_{\text{O}}^* = Q_{\text{O}^{2-}}^* - 2Q_{\text{e}^-}^* \quad (14)$$

as implied by the flux coupling. For $\text{UO}_{2+\delta}$ as a material which contains different types of ionic or electronic defects at different compositions, it is obvious that the ionic and electronic heats of transport itself depend on the actual defect structure. Thus, $Q_{\text{O}^{2-}}^*$ is a quantity which combines the properties of both interstitials and vacancies, depending

on their relative concentration, and $Q_{\text{e}^-}^*$ combines the properties of both electrons and holes. As shown in a previous paper (Ref. [17]; see also Ref. [16]), the ionic and electronic heats of transport themselves can be expressed as

$$Q_{\text{O}^{2-}}^* = t_{\text{i}}Q_{\text{i}}^* - t_{\text{v}}Q_{\text{v}}^* + (y_{\text{v}}t_{\text{i}} - y_{\text{i}}t_{\text{v}})\Delta H_{\text{F}}^{\circ} \quad (15)$$

$$Q_{\text{e}^-}^* = t_{\text{n}}Q_{\text{n}}^* - t_{\text{p}}Q_{\text{p}}^* + (y_{\text{p}}t_{\text{n}} - y_{\text{n}}t_{\text{p}})\Delta H_{\text{e}}^{\circ} \quad (16)$$

with t_{i} defined as partial electrical transference numbers according to $t_{\text{i}} \equiv L_{\text{i}}/(L_{\text{i}} + L_{\text{v}})$ and $t_{\text{n}} \equiv L_{\text{n}}/(L_{\text{n}} + L_{\text{p}})$, with $y_{\text{i}} \equiv c_{\text{i}}/(c_{\text{i}} + c_{\text{v}})$ and $y_{\text{n}} \equiv c_{\text{n}}/(c_{\text{n}} + c_{\text{p}})$. Q_{n}^* , Q_{p}^* , Q_{i}^* and Q_{v}^* denote the heats of transport of electrons, electron holes, interstitials and vacancies; $\Delta H_{\text{e}}^{\circ}$ and $\Delta H_{\text{F}}^{\circ}$ represent the enthalpies of reaction for the electron hole and the cation Frenkel equilibrium. The transference numbers t_{i} are functions of the concentrations and mobilities of different defects. Rewriting Eqs. (15) and (16) we obtain

$$\begin{aligned} Q_{\text{O}^{2-}}^* &= \frac{\alpha_{\text{i}}^2\psi_{\text{i}}}{1 + \alpha_{\text{i}}^2\psi_{\text{i}}}Q_{\text{i}}^* - \frac{1}{1 + \alpha_{\text{i}}^2\psi_{\text{i}}}Q_{\text{v}}^* \\ &\quad + \frac{\alpha_{\text{i}}(\psi_{\text{i}} - 1)}{(\alpha_{\text{i}} + \alpha_{\text{i}}^{-1})(1 + \alpha_{\text{i}}^2\psi_{\text{i}})}\Delta H_{\text{F}}^{\circ} \end{aligned} \quad (17)$$

$$\begin{aligned} Q_{\text{e}^-}^* &= \frac{\alpha_{\text{e}}^2\psi_{\text{e}}}{1 + \alpha_{\text{e}}^2\psi_{\text{e}}}Q_{\text{n}}^* - \frac{1}{1 + \alpha_{\text{e}}^2\psi_{\text{e}}}Q_{\text{p}}^* \\ &\quad + \frac{\alpha_{\text{e}}(\psi_{\text{e}} - 1)}{(\alpha_{\text{e}} + \alpha_{\text{e}}^{-1})(1 + \alpha_{\text{e}}^2\psi_{\text{e}})}\Delta H_{\text{e}}^{\circ} \end{aligned} \quad (18)$$

in terms of α_{i} , α_{n} , ψ_{i} and ψ_{n} , with $\psi_{\text{e}} = u_{\text{n}}/u_{\text{p}}$ as the mobility ratio of electrons and holes and $\psi_{\text{i}} = u_{\text{i}}/u_{\text{v}}$ as the mobility ratio of interstitials and vacancies. The concentration variables $\alpha_{\text{i}} \equiv c_{\text{i}}/c_{\text{i}}^{\#}$ and $\alpha_{\text{e}} \equiv c_{\text{n}}/c_{\text{n}}^{\#}$ denote the actual concentrations of interstitials or electrons, respectively, relative to their intrinsic concentration $c_{\text{i}}^{\#}$ or $c_{\text{n}}^{\#}$ at the stoichiometric composition (cf. Wagner [16]).

Depending on the defect concentrations and mobilities, the heats of transport $Q_{\text{O}^{2-}}^*$ and $Q_{\text{e}^-}^*$ take different values. If the mobile defects are completely extrinsic, i.e., if one type of defect dominates the defect structure, Eqs. (17) and (18) simplify considerably. Thus, under oxidizing conditions the deviation δ from stoichiometry is positive, and the defect structure is dominated by oxygen interstitials O_{i}' and electron holes h^{\cdot} . Correspondingly, α_{i} takes a large value while α_{e} takes a small value, and the heat of transport of the oxygen component can be equated from Eqs. (17), (18) and (14) as

$$Q_{\text{O}}^* \approx Q_{\text{i}}^* + 2Q_{\text{p}}^* \quad (\alpha_{\text{i}} \gg 1, \alpha_{\text{e}} \ll 1). \quad (19)$$

Thus, at high oxygen activities the heat of transport is determined mainly by the interstitial heat of transport Q_{i}^* and the electron hole heat of transport Q_{p}^* . If these quantities are independent of δ , Q_{O}^* should take a constant value at sufficiently high oxygen activities. Under reducing conditions the deviation δ from stoichiometry is negative, and

the defect structure is dominated by oxygen vacancies $V_{\text{O}}^{\bullet\bullet}$ and electrons e^- . Correspondingly, α_i takes a small value while α_e takes a large value, and the heat of transport of the oxygen component can be equated from Eqs. (17), (18) and (14) as

$$Q_{\text{O}}^* \approx -Q_v^* - 2Q_n^*. \quad (\alpha_i \ll 1, \alpha_e \gg 1) \quad (20)$$

Thus, at sufficiently low oxygen activities the heat of transport of oxygen is determined mainly by the vacancy heat of transport Q_v^* and the electron heat of transport Q_n^* . Again, if these are concentration independent, Q_{O}^* should take a constant value at low oxygen activities. If one assumes small values for the heats of transport Q_n^* and Q_p^* of electrons and holes, which is correct at least for delocalized charge carriers [18], the heat of transport of oxygen can be approximated by the corresponding heats of transport of ionic defects in the extrinsic region.

The picture complicates if the defect concentrations differ not too much from their intrinsic values, i.e., if both types of defects are present in comparable concentrations. In this case the third terms of the right hand sides of Eqs. (17) and (18) do not vanish, rather they may take appreciable values. Thus, even with vanishing heats of transport of the mobile defects, the heats of transport of ions and electrons need not be zero in the nearly intrinsic region.

The general concentration dependence of the heat of transport Q_{O}^* of atomic oxygen (according to Eqs. (14),

(17) and (18)) is depicted in Fig. 1 to provide a basis for the discussion of the measured heat of transport of the oxygen component in uranium based oxides. Only the reaction enthalpy terms are taken into account, since the values of Q_i^* , Q_v^* , Q_n^* and Q_p^* are unknown at this point. If the mobility ratio of interstitials and vacancies is different from unity, the enthalpy term leads always to an extremum of the heat of transport in the vicinity of the stoichiometric composition. The exact shape of this extremum depends on the defect structure and mobilities. Thus, a maximum of Q_{O}^{*2-} occurs always for $\psi_i > 1$ ($\psi_e > 1$), i.e., if the interstitials (electrons) are more mobile than the vacancies (electron holes) (see Fig. 1a and b). Correspondingly, a minimum occurs if $\psi_i < 1$ ($\psi_e < 1$), i.e., if the vacancies (holes) are more mobile (see Fig. 1c and d). A simple explanation for the nonvanishing heat of transport of ions in a pure crystal with Frenkel disorder (with zero heats of transport of interstitials and vacancies) and its dependence on the defect mobilities is provided by the following relations: The concentration gradient of Frenkel defects in a temperature gradient results from Eq. (2) as

$$\frac{\nabla c_i}{c_i} = \frac{\nabla c_v}{c_v} = \frac{\Delta H_{\text{F}}^{\circ}}{2RT^2} \nabla T. \quad (21)$$

Since the net flux j_{ion} of ions in the temperature gradient is given as the difference ($j_{\text{ion}} = j_i - j_v$) of

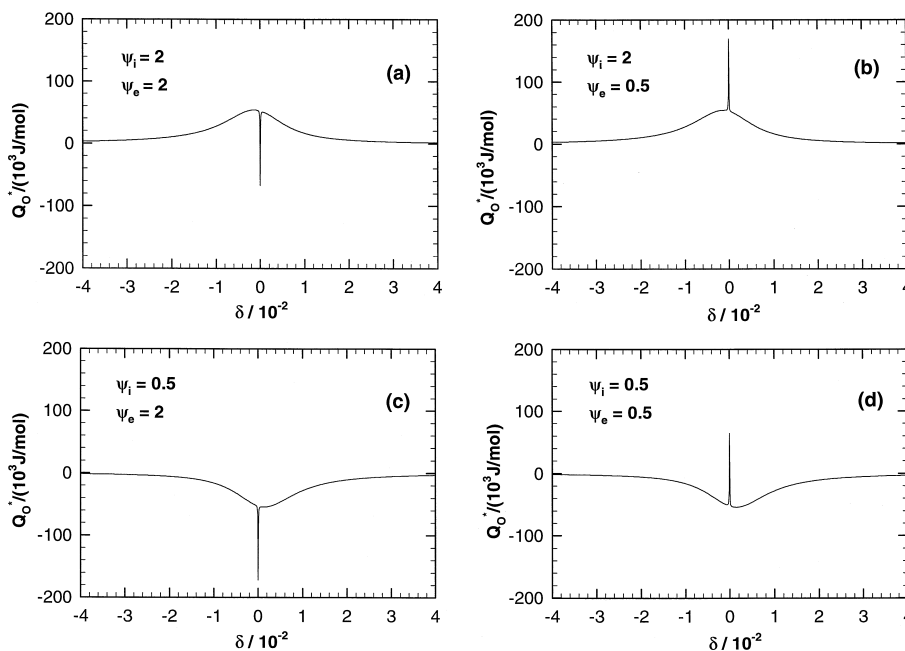


Fig. 1. (a)–(d) Schematic graphs of the heat of transport Q_{O}^* of atomic oxygen in $\text{UO}_{2+\delta}$ as a function of the deviation δ from stoichiometry for different mobility ratios of the mobile defects (cf. Eqs. (14), (17) and (18), $\Delta H_{\text{F}} = 315.7$ kJ/mol, $\Delta S_{\text{F}} = 66$ J/mol K, $\Delta H_{\text{e}} = 355$ kJ/mol, $\Delta S_{\text{e}} = 9$ J/mol K).

the interstitial ($j_i = -D_i \nabla c_i$) and vacancy flux ($j_v = -D_v \nabla c_v$), one obtains

$$j_{\text{ion}} = -(D_i - D_v) \frac{c}{RT} \frac{\Delta H_F^0}{2T} \nabla T \quad (22)$$

with $c = c_i = c_v$. The direction of the net flux of ions depends simply on the difference of the defect diffusion coefficients, if the heats of transport Q_i^* and Q_v^* are both zero. If the interstitials are more mobile, a net flux, which is directed downwards the temperature gradient is observed. In the opposite case, the ion flux is counter-directed towards the temperature gradient.

To visualize the superposition of the ionic and electronic extrema, we assume that $K_F \gg K_D$ in Fig. 1. Thus, in addition to a broad extremum of the ionic heat of transport, the electronic heat of transport shows a narrow extremum, which is also included in Fig. 1. The different shapes of the two extrema are caused by the different intrinsic defect concentrations, as discussed more extensively below. Similar to the ionic heat of transport, the mobility ratio of the electronic defects causes the extremum of the electronic peak. A maximum occurs always for $\psi_e > 1$, i.e., the electrons are more mobile than the holes. A minimum occurs always for $\psi_e < 1$, i.e., the holes are more mobile than the electrons. As a consequence of Eq. (14), a maximum of $Q_{e^-}^*$ always results in a minimum of $Q_{O^{2-}}^*$ and vice versa (compare Figs. 1 and 3). As the experimental results will show, the two extrema are not too different in their shape, indicating the K_F and K_D are of the same order and clearly showing that $\psi_i < 1$ and $\psi_e > 1$.

As treated explicitly in Section 2.4, the analysis of experimental data from metal-covered oxide specimens is complicated by the electronic short-circuit. Thus, the flux coupling is not maintained and the measured ‘practical’ heat of transport is not identical to the heat of transport as it is defined by Eq. (12).

2.4. Thermal diffusion in electronically short-circuited specimens

The influence of the metal encapsulation on thermal diffusion in a uranium dioxide fuel pellet has already been considered by Millot and Gerdanian [4]. However, their formal treatment is based on a very specific formal assumption (perfect short-circuit, i.e., zero resistance in the metal cover), and thus, we summarize briefly in the following our more general treatment of thermal diffusion in electronically short-circuited fuel pellets. As indicated in Fig. 4, the metal capsule acts as an ion-blocking electrode, i.e., we can still assume $j_{O^{2-}} = 0$ in the stationary state. Thus, if we further neglect kinetic interactions between the ionic and electronic flux ($L_{O^{2-}-e} = 0$), the gradient of the electrochemical potential of the oxygen ions remains unchanged:

$$\nabla \tilde{\mu}_{O^{2-}} = - \left(\bar{S}_{O^{2-}} + \frac{Q_{O^{2-}}^*}{T} \right) \nabla T. \quad (23)$$

The corresponding gradient $\nabla \tilde{\mu}_{e^-}$ of the electrochemical potential of electrons cannot be derived in a similar

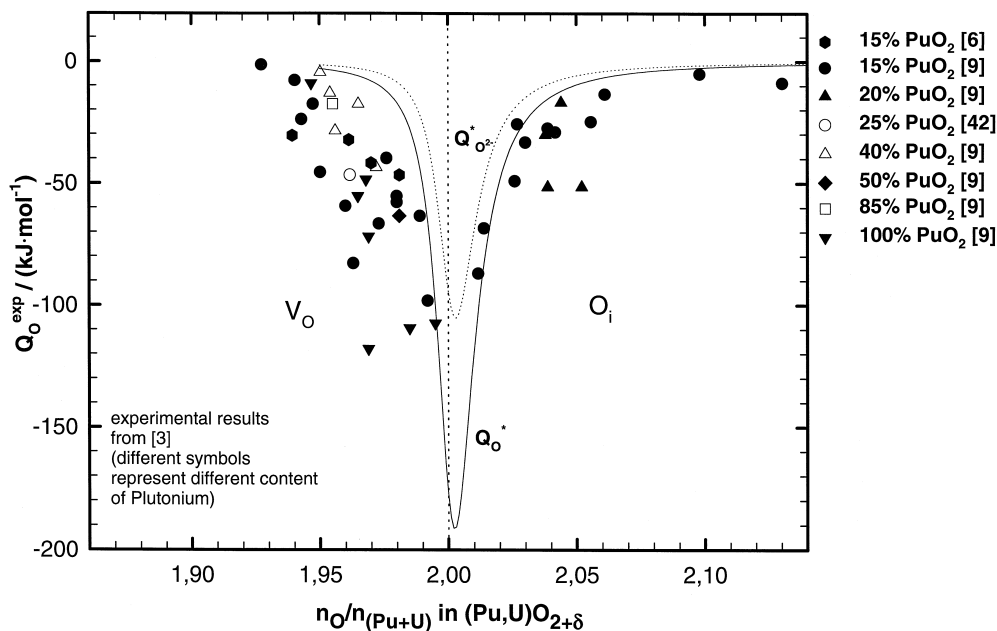


Fig. 2. Experimental data for the heat of transport in Ref. [3]. The curve is calculated from Eqs. (17), (18) and (14) using the thermodynamic data in Table 1.

way, due to the non-zero electron flux in the short-circuited specimen. Rather the evaluation of $\nabla\tilde{\mu}_{e^-}$ grounds on the equality of the electronic current $I_e^{UO_2}$ in the oxide and the electronic current I_e^{Me} in the short-circuiting metal:

$$j_e^{UO_2} = -I_e^{Me}. \quad (24)$$

Inserting the flux equations

$$j_e^{UO_2} = -L_e^{UO_2} \left[\nabla\tilde{\mu}_{e^-}^{UO_2} + \left(\bar{S}_e^{UO_2} + \frac{Q_e^{*UO_2}}{T} \right) \nabla T \right] \quad (25)$$

$$j_e^{Me} = -L_e^{Me} \left[\nabla\tilde{\mu}_{e^-}^{Me} + \left(\bar{S}_e^{Me} + \frac{Q_e^{*Me}}{T} \right) \nabla T \right] \quad (26)$$

and using the relation $I_i = (z_i F) j_i A$ with A denoting the cross area of the oxide specimen or the metal short-circuit, respectively, we obtain

$$\begin{aligned} & \left[\nabla\tilde{\mu}_{e^-}^{UO_2} + S_e^{*UO_2} \nabla T \right] \\ &= - \frac{L_e^{Me} A^{Me}}{L_e^{UO_2} A^{UO_2}} \left[\nabla\tilde{\mu}_{e^-}^{Me} + S_e^{*Me} \nabla T \right]. \end{aligned} \quad (27)$$

For the sake of a simplified formalism, we use the definition of the so-called entropy of transport, $S_i^* \equiv \bar{S}_i + Q_i^*/T$. This quantity is directly related to the corresponding partial thermopower in the stationary (Soret) state as $\varepsilon_{e^-} = F^{-1} S_{e^-}^*$. Furthermore, with the general relations $\sigma_i = (z_i F)^2 L_i$ and $R_i = l/(\sigma_i A)$ we can rewrite the pre-factor in Eq. (27) as the ratio of the actual electronic resistances R of the oxide specimen and the metal short-circuit, i.e., $R^{UO_2}/R^{Me} = (L_e^{Me} A^{Me})/(L_e^{UO_2} A^{UO_2})$:

$$\left[\nabla\tilde{\mu}_{e^-}^{UO_2} + S_e^{*UO_2} \nabla T \right] = - \frac{R^{UO_2}}{R^{Me}} \left[\nabla\tilde{\mu}_{e^-}^{Me} + S_e^{*Me} \nabla T \right]. \quad (28)$$

If local equilibrium prevails at the contact between the oxide and the metal cover, we can assume that

$$\nabla\tilde{\mu}_{e^-}^{UO_2} = \nabla\tilde{\mu}_{e^-}^{Me}. \quad (29)$$

This equality leads finally to the following expression for the electrochemical potential gradient of electrons in a short-circuited thermocell:

$$\nabla\tilde{\mu}_{e^-} = - \left(\frac{R^{Me}}{R^{UO_2} + R^{Me}} S_e^{*UO_2} + \frac{R^{UO_2}}{R^{UO_2} + R^{Me}} S_e^{*Me} \right) \nabla T \quad (30)$$

$$= -F \left(r^{Me} \varepsilon_{e^-}^{UO_2} + r^{UO_2} \varepsilon_{e^-}^{Me} \right) \nabla T \quad (31)$$

with r^{Me} and r^{UO_2} defined by the resistance ratios in Eq. (30) and with $\varepsilon_{e^-} \equiv S_{e^-}^*/F$ denoting the absolute electronic thermopower of a material. Regarding Eq. (30), two limiting cases can be obtained: (a) If $R^{Me} \ll R^{UO_2}$, the electrochemical potential gradient of the short-circuited cell is determined exclusively by the electronic thermopower of the metal. (b) If $R^{Me} \gg R^{UO_2}$, the electronic

flux is not short-circuited, and the electrochemical potential gradient of electrons is determined by the partial electronic thermopower of the oxide.

The chemical potential gradient of the oxygen component,

$$\nabla\mu_O = \nabla\tilde{\mu}_{O^{2-}} - 2\nabla\tilde{\mu}_{e^-}, \quad (32)$$

is also affected by the electronic short-circuit. Inserting Eqs. (30) and (23) into Eq. (32), we obtain the expression

$$\nabla\mu_O = - \left(\bar{S}_O + \frac{Q_O^*}{T} \right) \nabla T - 2r^{UO_2} (\varepsilon_{e^-}^{UO_2} - \varepsilon_{e^-}^{Me}) F \cdot \nabla T. \quad (33)$$

Again, as for $\nabla\tilde{\mu}_{e^-}$, one can distinguish two limiting cases: (a) If $R^{Me} \ll R^{UO_2}$, i.e., if the metal short-circuits the electronic flux efficiently, the chemical potential gradient in the stationary state differs seriously from that given in Eq. (13). (b) If $R^{Me} \gg R^{UO_2}$, the electronic flux is not short-circuited, and Eq. (13) follows from Eq. (33).

Finally, the composition gradient within a short-circuited oxide specimen has to be equated. Combining the total differential in Eq. (10), which is valid also under short-circuit conditions, with Eq. (33), we obtain

$$\nabla\delta = - \left(\frac{\partial\mu_O}{\partial\delta} \right)_T^{-1} \left[\frac{Q_O^*}{T} + 2r^{UO_2} F (\varepsilon_{e^-}^{UO_2} - \varepsilon_{e^-}^{Me}) \right] \nabla T \quad (34)$$

Comparing this expression with the Soret effect under zero-flux conditions (Eq. (12)), it is reasonable to define a ‘practical’ heat of transport,

$$Q_O^{exp} = Q_O^* + 2F \cdot r^{UO_2} (\varepsilon_{e^-}^{UO_2} - \varepsilon_{e^-}^{Me}) T, \quad (35)$$

which takes the contribution from the electronic short-circuit into account. If we assume that the electric resistance of the metal cover is much smaller than the electric resistance of the oxide specimen ($R^{UO_2} \approx 1$), and if we further assume that the thermopower of the metal is negligibly small compared to the electronic thermopower of the semiconducting oxide (i.e., $\varepsilon_{e^-}^{Me} \ll \varepsilon_{e^-}^{UO_2}$), we obtain

$$Q_O^{exp} \approx Q_O^* + 2F \varepsilon_{e^-}^{UO_2} T. \quad (36)$$

Thus, the practical heat of transport Q_O^{exp} which is determined experimentally from nuclear fuel pellets (short-circuited thermocells) differs from the original heat of transport Q_O^* by a term which includes the electronic thermopower of the oxide. As long as the electronic short-circuit leads to a negligible flux of electrons through the oxide at all ($R^{Me} \ll R^{UO_2}$) and the metal thermopower is small, the stationary composition gradient $\nabla\delta$ is nevertheless determined exclusively by the transport properties of the oxide itself. Eq. (35) is also obtained by Millot and Gerdanian [4]. However, their derivation starts with the assumption of a complete short-circuit which is not always true, rather depends on the geometry of the encapsulation.

3. Experimental evidence

UO₂ is probably the best studied solid compound with respect to thermal diffusion. Several experimental studies of thermal diffusion in UO_{2+δ} and its solid solutions with PuO₂ and CeO₂ can be found in the literature (e.g., see Fryxell and Aitken [5], Evans et al. [6], Adamson [7], Adamson and Carney [8] and Sari and Schumacher [9]). However, the reliability of the experimental studies is different and not all provide relevant data.

Two problems of thermal diffusion studies in general have not always been recognized with the necessary care: (a) The formal relations which describe the Soret effect, cf. Eqs. (12) and (13), correspond to the zero flux condition $j_O = 0$. Strictly speaking, the non-isothermal specimen has to be enclosed in an inert material which suppresses any exchange of crystal components with the surrounding. In case of a permeable cover, metal or non-metal may diffuse out, thus leading to a non-zero flux j_O . The realisation of an impermeable encapsulation is the main problem in any thermal diffusion experiment, particularly at high temperatures. In case of an encapsulation including pores, some authors proposed an additional oxygen transport via the gas phase [19,20]. (b) The flux coupling $2j_{O^{2-}} = -j_e^-$, which leads to the derivation of Eqs. (12) and (13), provides an additional and important experimental constraint. To maintain this coupling, i.e., to avoid an electronic short-circuit, an electrically insulating encapsulation is required in thermal diffusion studies on mixed conductors. For practical reasons, most thermal diffusion experiments on (U,Me)O_{2+δ} have been performed with metal encapsulated pellets, and thus, Eqs. (12) and (13) cannot be applied. Rather, modified equations which take an electronic short-circuit into account have to be applied (Eqs. (33) and (36)).

One of the first studies of thermal diffusion in UO_{2+δ} was performed by Beisswenger et al. [21]. The demixing of CeO₂/UO₂ – mixtures in temperature gradients of approximately 700 K/cm was studied, and an enrichment of CeO₂ at the hot end was found. The nonstoichiometry of UO_{2+δ} was not taken into account, and thermal segregation of the oxygen component was not investigated.

The first studies of thermal diffusion of the oxygen component in pure UO_{2+δ} have been reported by Fryxell and Aitken [5]. Similar experiments on (U,Pu)O_{2+δ} have been performed by Evans et al. [6]. Both groups investigated oxide specimens with hyper- ($\delta > 0$) and hypostoichiometric ($\delta < 0$) compositions. The specimens were encapsulated in rhenium and tantalum [5] or molybdenum and tungsten [6] capsules. Temperature gradients of approximately 50 K/cm have been applied, and data for the heat of transport were determined via the relation

$$\ln \delta = \frac{Q_O^{\text{exp}}}{RT} + C \quad (37)$$

with C representing a constant number. Eq. (37) represents

a simplified version of Eq. (13), assuming an ideal solution of point defects, i.e., neglecting the thermodynamic factor. As discussed above, experiments on specimens with a metal cover lead only to the evaluation of a ‘practical’ heat of transport Q_O^{exp} (cf. Eq. (36)) which is not identical with the heat of transport Q_O^* . Both Fryxell and Evans neglect the influence of the electronic short-circuit, and therefore, their data cannot be identified simply with Q_O^* .

Adamson [7] and Adamson and Carney [8] investigated thermal diffusion of oxygen in hyperstoichiometric UO_{2+δ} and (U,Pu)O_{2+δ} in temperature gradients similar to those of Beisswenger. Since Aitken [19] suggested that carbon impurities undergo partial oxidation to produce a CO/CO₂ mixture inside pores of the fuel pins, he spent considerable effort in the removal of these carbon impurities. A CO/CO₂ mixture provides a well-defined oxygen activity and might lead to oxygen transport via the gas phase in pores of the metal cover. The cylindrical pellets of Adamson were enclosed in Pt/20% Rh capsules, thus, the electronic short-circuit was an experimental problem, too. Also Adamson, as Fryxell and Evans, neglected the influence of the short-circuit and used Eq. (37) for the evaluation of the heat of transport. Discussing his results, he assumed that the transport of oxygen in temperature gradients might be dominated by gas phase diffusion in general. In addition to the possible gas-phase transport by a CO/CO₂ mixture he assumed transport of oxygen in the gas phase via UO₃ at temperatures above $T = 1600^\circ\text{C}$ both for hyperstoichiometric UO_{2+δ} and (U,Pu)O_{2+δ}.

Sari and Schumacher [9] studied thermal diffusion of oxygen in (U,Pu)O_{2+δ} in metal capsules, too. Transport of oxygen via the gas phase was prevented by the use of high-density fuel pellets which were coated with molybdenum. From the agreement of their experimental data with the data of previous studies, Sari and Schumacher conclude that oxygen transport via the gas phase does not contribute seriously to the transport of oxygen.

After these major experimental works, frequent formal studies were published in order to improve the theoretical understanding of thermal diffusion in uranium-based oxides (e.g., Refs. [22,23]), but a conclusive interpretation of the magnitude and composition dependence of Q_O^* is not available to date.

Millot and Gerdanian [4] were the first to take the influence of a metal encapsulation into account in their formal considerations. They derive an equation for the Soret effect in a perfectly short-circuited thermocell. In reviewing experimental data, they conclude that electrotransport provides an important contribution to the experimental results and estimated this contribution from literature data.

In a recent paper, Kamata and Esaka [24] concluded after formal considerations that the heat of transport might decrease to minus infinity as the composition of the sample becomes stoichiometric. This conclusion has no acceptable formal basis and is necessarily incorrect, as our

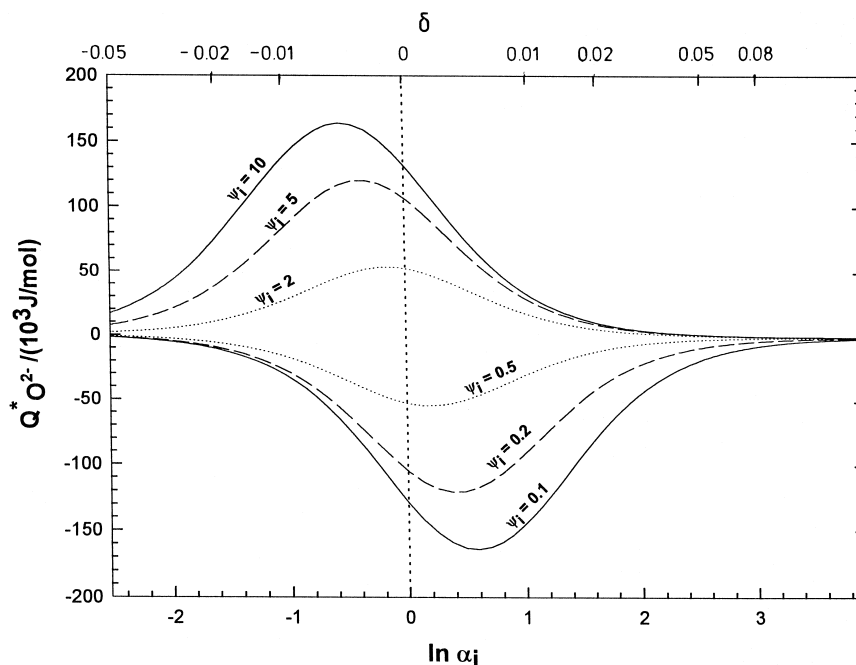


Fig. 3. Ionic heat of transport $Q_{O^{2-}}^*$ calculated from Eq. (17) for different mobility ratios of interstitials and vacancies by using the data in Table 1.

formal analysis shows. Rather the heat of transport exhibits a more or less pronounced extremum, see Fig. 1 and cf. Ref. [25].

In Fig. 2 [42], the collected experimental data so far (taken from Ref. [3]) are depicted, together with a theoretical curve which is calculated from our model by using existing defect data. A problem in their analysis is the restricted availability of thermodynamic data. While most measurements of thermal diffusion were carried out on $(U,Pu)O_{2+\delta}$, thermodynamic data are only published for $UO_{2+\delta}$. Thus, in the following we estimate the heat of the transport Q_O^* on the basis of our formalism using available thermodynamic and defect data for pure $UO_{2+\delta}$ from the literature and compare the results with experimental data for Q_O^* in $(Pu,U)O_{2+\delta}$. In addition, we estimate the contribution of the electronic short-circuit (see Eq. (36)) from thermopower measurements to the practical heat of transport.

4. Calculation of the heat of transport and the Soret effect

Regarding Eqs. (17) and (18), several independent data are required for the calculation of the heats of transport $Q_{O^{2-}}^*$ and Q_e^* : (a) The individual heats of transport of the mobile defects: in principle, at least the heats of transport of the ionic defects could be extracted from the plateaus of the heat of transport in the far extrinsic regions if one

neglects the electronic heats of transport. As can be seen in Fig. 4, the accessible composition range is too narrow as to run into these plateau regions, and thus, it is impossible to extract the heats of transport Q_i^* , and Q_v^* of the ionic defects itself from the existing experimental data. Data for the heats of transport of vacancies and interstitials have been determined for $SrCl_2$ as another fluorite-type system [26]. One might use these data as well for the $(Pu,U)O_{2+\delta}$ system. However, at present there is no formal argument which supports the equivalence of the heat of transport for identical defects in different materials. Furthermore, no theoretical model at all is currently available that predicts heats of transport of individual point defects. Most theoretical models result in more or less close relations between the enthalpy of migration ΔH_m and the heat of transport of a mobile point defect. In an early and influential work Wirtz [27,28] concluded very generally from a detailed analysis of the thermally activated defect motion that $|Q_i^*| \leq \Delta H_m$. In contrast to this, very recent theoretical work by Jones et al. [29,30] results in heats of transport of point defects in solid argon which are considerably larger than the corresponding migration enthalpy. Thus, no conclusive idea for the magnitude of heats of transport for individual point defects is yet existing, and therefore, we will only take the enthalpy terms in Eqs. (17) and (18) into account, to interpret at least the observed composition dependence of Q_O^* .

(b) Enthalpy terms: Six independent data have to be provided for the calculation of the enthalpy terms. (i) The

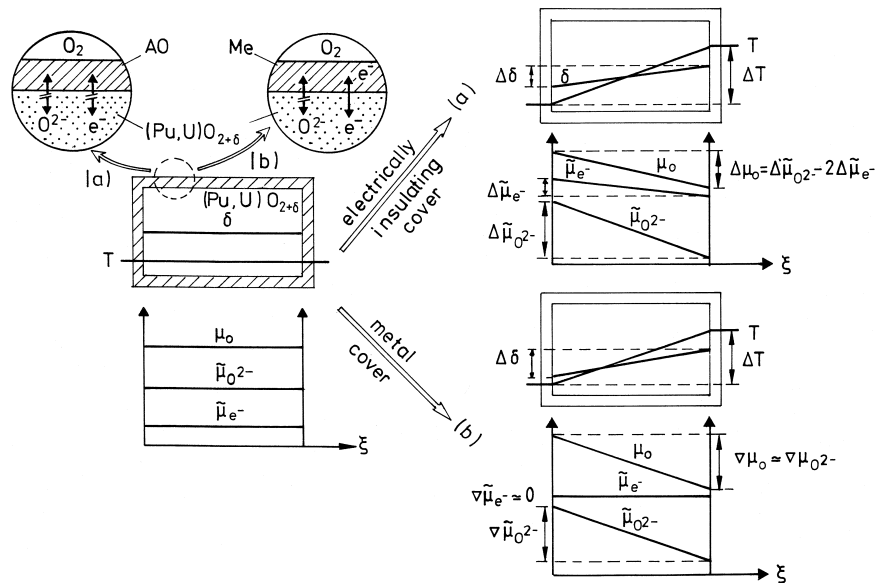


Fig. 4. Schematic representation of a Soret experiment under different boundary conditions: (a) 'Ideal' Soret experiment with closed surfaces (electrically insulating cover) for matter exchange. The stationary composition gradient corresponds to Eq. (13). (b) Complete electronic short circuit. The stationary composition gradient differs from that in (a) and has to be calculated by Eq. (34).

Gibbs energies of reaction ΔG_F° and G_e° for the Frenkel equilibrium and the electron hole equilibrium are required for the calculation of the defect concentrations (α_i and α_e) at various compositions. (ii) The defect formation enthalpies ΔH_F° and ΔH_e° itself are required for the application of Eqs. (17) and (18) and finally, (iii) the mobility ratios of the ionic and electronic defects are necessary ingredients.

Breitung [15] analysed experimental data from Kerrisk and Clifton [31] using a procedure proposed by Szwarz [32] and obtained values for $\Delta H_F^\circ = (315.7 \pm 20) \times 10^3$ J/mol and $\Delta S_F^\circ = (66.0 \pm 1.1)$ J/mol K. The value for ΔH_F° agrees favorably with the result of Auskern and Belle [33].¹

For the electronic equilibrium (Eq. (1)), Winter [14] calculated $\Delta H_D^\circ = 193 \times 10^3$ J/mol and $\Delta S_D^\circ = 16.6$ J/K mol). Using these data we calculated K_F and K_D and were thus able to compute the mole fractions of the different defects and the related concentration variables α_i and α_e as a function of δ (see Eqs. (5) and (6), summary in Table 1).

The mobility ratio ψ_e for the electronic defects in stoichiometric UO₂ has been determined by Killeen [34] at

various temperatures, e.g., he found $\psi_e = 2.5 \pm 0.2$ at $T = 1700^\circ\text{C}$. The mobilities of the ionic defects were investigated both experimentally and theoretically. Catlow [35] calculated the migration enthalpies ΔH_v^m and ΔH_i^m for oxygen vacancies and interstitials and thereupon concluded that vacancies are more mobile than interstitials. Although Catlow revised his results in a later study [13,40] other experimental and theoretical studies (e.g., Ref. [10]) support the idea that the migration enthalpy of an oxygen vacancy ($\Delta H_v^m \approx 0.5\text{--}0.7$ eV) is lower than the migration enthalpy of an oxygen interstitial ($\Delta H_i^m \approx 0.6\text{--}1.0$ eV) and that $\psi_i = u_i/u_v < 1$.

The curve in Fig. 2 is calculated from Eqs. (14), (17) and (18) by using the data which are summarized in Table 1. It is composed from a minimum of the ionic heat of transport $Q_{O^{2-}}^*$ and a maximum of the electronic heat of transport Q_e^* . For the calculation of the heat of transport of oxygen, $2Q_e^*$ has to be subtracted from $Q_{O^{2-}}^*$, and thus, the two extrema superpose additively. This combined extremum describes the composition dependence of the measured data quite satisfactorily. To obtain qualitative agreement between the experimental and the calculated data for Q_O^* , we assume that $\psi_i < 1$ and $\psi_e > 1$. More precisely, only if we take the vacancies as the more mobile defects, we calculate a minimum for $Q_{O^{2-}}^*$. In order to obtain an acceptable fit of the depth of the minimum, we used a value of $\psi_i \approx 0.25$ in Fig. 2. The width of the calculated minimum is too small compared with the experimental data. Since the width depends on the intrinsic

¹ The enthalpy ΔH_F° is derived from the temperature dependence of diffusion data. Thus, it cannot be identified with ΔG_F° , as done by Matzke [11].

Table 1

Thermodynamic and kinetic data used for the calculation of the heat of transport of oxygen in $\text{UO}_{2+\delta}$

	Frenkel disorder	Electronic disorder
Enthalpy of formation ΔH (kJ/mol)	315.7	193
Entropy of formation ΔS (J/K mol)	66	16.6
Mobility ratio ψ	0.25	2.5
Heats of transport Q_i^* and Q_v^* of interstitials and vacancies	0	–
Heats of transport Q_n^* and Q_p^* of electrons and holes	–	0

References are given in the text.

disorder (and its ratio to extrinsically produced defects), this is caused by the unprecise thermodynamic data which we had to use for the computation of the defect concentrations.

An complicating feature of the curve in Fig. 2 is the electronic maximum which is subtracted from the minimum of the ionic heat of transport. Due to the comparable concentrations of intrinsic electronic and ionic defects, the values for α_e and α_i do not differ too much. As a consequence, it is difficult to separate the ionic and electronic contribution unequivocally. However, the width of the extremum clearly suggests relatively high intrinsic defect concentrations, i.e., correspondingly low free enthalpies of formation. A quantitative comparison with the literature data for $\text{UO}_{2+\delta}$ appears questionable, since the thermal diffusion experiments have been mostly performed on plutonia–urania mixtures.

As the treatment of short-circuited thermocells in Section 2.4 shows, the experimental data in Fig. 2 correspond

rather to ‘practical’ heats of transport Q_O^{exp} than to the well-defined heats of transport Q_O^* in Eqs. (17) and (18). In this respect, the foregoing analysis is necessarily restricted to qualitative arguments. In the extreme case of a perfectly short-circuited specimen, the measured data are related to the heat of transport by Eq. (36). Thus, data for the partial electronic thermopower are additionally required, to estimate the ‘real’ heat of transport Q_O^* from Fig. 2. Experimental data for $\varepsilon_e^{\text{UO}_2}$ are reported, e.g., by Aronson et al. [36] and D’Annuncci et al. [37]. Theoretical calculations have been performed by Winter [14]. The experimental results are summarized in Fig. 5. The data are not in good agreement because Aronson investigated pure $\text{UO}_{2+\delta}$ and D’Annuncci studied $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_{2+\delta}$. Summarizing their results, one finds that the term $2F\varepsilon_e^{\text{UO}_2}T$ shows a strong composition dependence for both pure and doped $\text{UO}_{2+\delta}$. Whereas the data for pure $\text{UO}_{2+\delta}$ show virtually no temperature dependence, the absolute data for the doped oxide decrease with increasing temperature, and

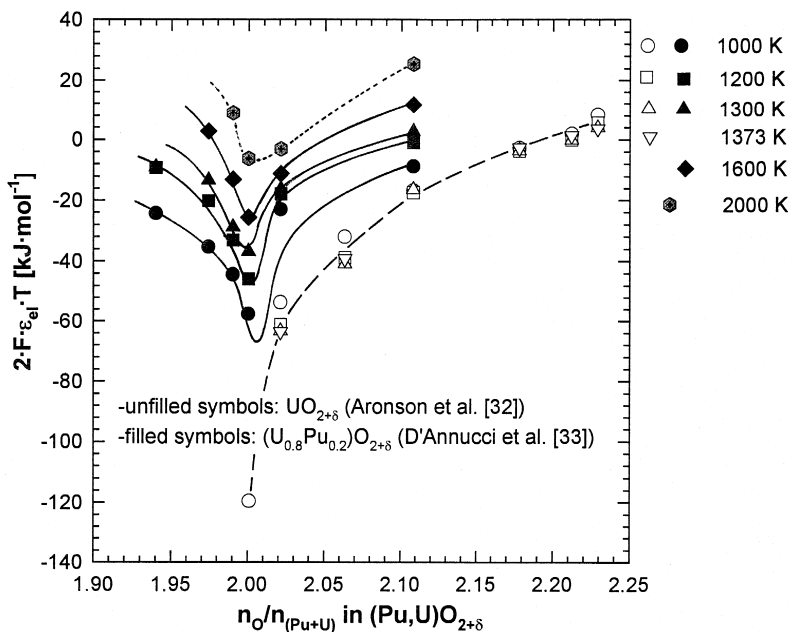


Fig. 5. Experimental data for the electronic thermopower of $\text{UO}_{2+\delta}$ and $(\text{U}_{0.8}\text{Pu}_{0.2})\text{O}_{2+\delta}$, respectively. The values for $T = 2000$ K are extrapolated from D’Annuncci et al. [37].

become relatively small at high temperatures. To our knowledge, no experimental information on the electronic thermopower is available for $T > 1600$ K, which is the temperature range of the collected data in Fig. 3. Thus, we extrapolate the data of D'Annunzi [37] to 2000 K (see Fig. 5) and estimate values in the range $-20 \text{ kJ/mol} < 2F_e^{UO_2} T < +20 \text{ kJ/mol}$ for $-2\% < \delta < +10\%$. The data also suggest a minimum of the thermopower term at the stoichiometric composition, being definitely smaller than the measured practical heat of transport Q_O^{exp} . Thus the electronic thermopower term leads to a non-negligible contribution, however, being still small enough not to change the composition dependence of Q_O^* completely. We therefore conclude that the measured data for Q_O^{exp} are still dominated by Q_O^* .

Finally, some comments have to be given in respect to thermal diffusion in other mixed conducting compounds. The influence of a local defect equilibrium on the heat of transport of a mobile component is well known for diffusion in reacting gases (p. 166 of Ref. [38]) and has been proven experimentally for the solid state so far only for the cation conductors $\alpha\text{-Ag}_{2+\delta}\text{S}$ [18] and $\alpha\text{-Ag}_{2+\delta}\text{Se}$ [39] (cf. $\beta\text{-Ag}_{2+\delta}\text{S}$ [41]). However, in these systems the composition changes are restricted to very small values, and the extrema of the heat of transport cannot be determined completely. In this respect, the oxide $(\text{U,Me})\text{O}_{2+\delta}$ provides a model system for the study of thermal diffusion in solid compounds.

5. Conclusions

From our formal analysis, we conclude that the strong composition dependence of the heat of transport Q_O^* of atomic oxygen in uranium-based oxides of the type $(\text{U,Me})\text{O}_{2+\delta}$ can be described by a minimum in the vicinity of the stoichiometric composition ($\delta = 0$). This minimum is caused by both the contribution Q_O^{*2-} of the oxygen ions and of Q_e^* of electrons and resembles the influence of the corresponding local defect equilibria on transport of oxygen in a temperature gradient. Using existing data for the defect properties of $\text{UO}_{2+\delta}$, we can understand the experimental data on the basis of a simple model of the defect structure (Frenkel and electron hole equilibrium). The minimum of the heat of transport is composed of two extrema, namely the ionic and electronic contribution. The shape suggests that oxygen vacancies are more mobile than oxygen interstitials (i.e., $\psi_i < 1$) and electrons are more mobile than holes (i.e., $\psi_e > 1$). The width of the minimum is caused by both the high degree of intrinsic Frenkel and electronic disorder.

Since the thermal diffusion experiments have been performed with metal-covered oxide pellets, a non-negligible contribution of the electronic short-circuit to the measured heat of transport has to be taken into account. We estimate this contribution and find that it also shows a

minimum at the stoichiometric composition, being less pronounced than the measured minimum of Q_O^* . Thus, we conclude that Q_O^* , which is obtained by subtracting the thermopower term from Q_O^{exp} , still shows a minimum near the stoichiometric composition.

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