Matter transport in temperature gradients — the heat of transport of silver in β-Ag$_{2+\delta}$S

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Abstract

By the use of nonisothermal galvanic cells, the (reduced) heat of transport of silver metal in β-Ag$_{2+\delta}$S as a function of both temperature and composition has been determined. We compare results from two independent experiments and comment on the interpretation of the heat of transport. An interesting aspect of thermal diffusion in β-Ag$_{2+\delta}$S is the occurrence of a sign reversal of the heat of transport with increasing temperature.

Keywords: Thermal diffusion; Soret effect; Heat of transport; β-Ag$_{2+\delta}$S

1. Introduction

The local microscopic and the macroscopic transport of charge and mass by diffusional or reactive processes is always coupled to the transport of heat. Experimentally, this coupling of heat and matter transport leads to different effects, e.g. stationary mass transport in a temperature gradient, the Soret effect (thermal demixing), thermoelectricity, and the Peltier effect, which are all based on the transference of heat by mobile structural elements of a crystal.

With respect to ionic conductors, our interest in the coupling of heat and matter fluxes is two-fold. Mainly, we are interested in the microscopic interpretation of the heat of transport. According to its definition (see Eq. (1)), Q_i^* contains information on the basic matter transport processes, i.e. on the dynamics of the defect jumps. Additionally, the

coupling is of interest for several applications. The Peltier effect, e.g., leads to a temperature effect at the electrodes of solid state fuel cells, if an ionic current is drawn through the cells [1]. Also, segregation of impurities or compound components by thermal diffusion may lead to the degradation of ceramic materials which are exposed to temperature gradients at high temperatures.

The phenomenological description of the nonisothermal transport processes in the framework of irreversible thermodynamics is straightforward [2–4]. The essential quantity within the phenomenological approach is the so-called "heat of transport", which is defined by the amount of heat being transferred under isothermal conditions by a unit flux of matter,

$$j_Q = Q_i^* \cdot j_i; \quad \nabla T = 0 \tag{1}$$

and which, by the validity of Onsager's reciprocity relation, also determines the magnitude of matter

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fluxes in nonisothermal systems (see Eq. (6)). Unfortunately, the use of the expression "*heat of transport*" in the literature is not very rigorous. Frequently, the energy of transport U_i^* which denotes the amount of transferred internal energy [2], is also called heat of transport. But both quantities, Q_i^* and U_i^*, are by no means equal. Rather they are related by the equation

$$Q_i^* = U_i^* - h_i \tag{2}$$

in which h_i represents the partial molar enthalpy of the transferred species.

By their definition, Q_i^* and U_i^* are kinetic quantities and cannot be interpreted by means of thermodynamic arguments. It may be, however, that in special and unforeseeable cases the energy of transport is a small quantity compared to h_i. In these cases, the heat of transport would essentially be dominated by a pure thermodynamic quantity, namely the partial enthalpy of the mobile component, h_i. Regrettably, to date no generally accepted model exists for the heat of transport of defects in the crystalline state. Several approaches may be found in the literature [5–8], but no reliable predictions, even in respect to the sign of Q_i^*, can be made. Hence, it seems to us quite important to determine experimentally the heat of transport for model systems.

2. Thermal diffusion and thermal demixing in β-Ag$_{2+\delta}$S

The cubic β-phase of silver sulfide, which is the stable phase above 178°C, exhibits structural disorder in the cation sublattice [12]. Besides this intrinsic disorder, β-Ag$_{2+\delta}$S exhibits a rather narrow range of homogeneity which is described by the deviation from stoichiometry, δ (with $c_{Ag}=(2+\delta)/V_m$ denoting the molar concentration of silver, and V_m representing the molar volume of the sulfide). In equilibrium with liquid sulphur, the deviation from stoichiometry within the high temperature phase equals almost zero. In equilibrium with silver metal, a temperature-dependent silver excess of $\delta \approx 2.5 \cdot 10^{-3}$ can be found. For more detailed information on the phase diagram of Ag$_{2+\delta}$S, we refer the reader to [13].

In the case of chemical or thermal diffusion in β-Ag$_{2+\delta}$S, the fluxes of mobile cations and electrons are coupled by the zero electric current condition ($j_{Ag^+}=j_{e'}\equiv j_{Ag}$), and the flux of silver metal results as:

$$j_{Ag} = -L_{Ag}\left[\nabla\mu_{Ag} + \left(\frac{Q_{Ag}^*}{T} + s_{Ag}\right)\nabla T\right]. \tag{3}$$

Here Q_{Ag}^*, L_{Ag}, s_{Ag} and μ_{Ag} denote the heat of transport, the phenomenological transport coefficient, partial entropy and the chemical potential of silver metal in the sulfide, respectively. Due to the negligible mobility of sulfur, the anion sublattice is taken as a natural frame of reference for the transport processes. Inserting the differential

$$\nabla\mu_{Ag} = \left(\frac{\partial\mu_{Ag}}{\partial c_{Ag}}\right)_T \nabla c_{Ag} + \left(\frac{\partial\mu_{Ag}}{\partial T}\right)_{c_{Ag}} \nabla T$$

$$= \left(\frac{\partial\mu_{Ag}}{\partial c_{Ag}}\right)_T \nabla c_{Ag} - s_{Ag}\nabla T \tag{4}$$

into Eq. (3), the silver flux can also be written as a function of the metal concentration gradient and the temperature gradient,

$$j_{Ag} = -L_{Ag}\left(\frac{\partial\mu_{Ag}}{\partial c_{Ag}}\right)_T \nabla c_{Ag} - L_{Ag}\frac{Q_{Ag}^*}{T}\nabla T$$

$$= -\tilde{D}_{Ag}\nabla c_{Ag} - L_{Ag}\frac{Q_{Ag}^*}{T}\nabla t \tag{5}$$

where $\tilde{D}_{Ag}$ represents the chemical diffusion coefficient of silver in the sulfide. The term $(\partial\mu_{Ag}/\partial c_{Ag})_T$ is a thermodynamic factor and takes appreciably large and always positive values for the case of β-Ag$_{2+\delta}$S [14].

According to Eq. (5), diffusion of silver metal may either be driven by a gradient in composition (concentration of silver) or by a temperature gradient. In principle, both forces can be chosen independently, but generally the application of a temperature gradient causes the simultaneous creation of a concentration gradient, depending on the boundary conditions. Thus, for the experimental determination of the heat of transport, it is *not* sufficient to apply a temperature gradient without simultaneous control of the composition gradient.

For the evaluation of thermal diffusion experiments, Eq. (5) has to be integrated with respect to

the geometric variables. As has been discussed explicitly in [15] for a one-dimensional geometry, the flux j_{Ag} in Eq. (5) can generally be written in an integral form as a function of both $\Delta c_{Ag}/\Delta x$ and $\Delta T/\Delta x$, if the applied temperature gradient is small. Thus, if the boundary conditions can be chosen to give a vanishing concentration difference, $\Delta c_{Ag} = 0$ (i.e., a vanishing difference in the deviation from stoichiometry, $\Delta \delta = 0$), one obtains

$$j_{Ag}\big|_{\Delta\delta=0} = -L_{Ag}\frac{Q^*_{Ag}}{T}\frac{\Delta T}{\Delta x}, \quad \text{if } \Delta T << T. \qquad (6)$$

According to Eq. (6), it is possible to evaluate the heat of transport directly from a measurement of the flux $j_{Ag}\big|_{\Delta\delta=0}$, if data for the transport coefficient L_{Ag} are available. Eq. (6) can be used even in those cases where the coefficients L_{Ag}, $(\partial\mu_{Ag}/\partial\delta)_T$ and Q^*_{Ag} are itself functions of temperature and composition, as long as the applied temperature difference is small compared to the absolute temperature. For the general cases where a temperature or composition dependence cannot be neglected, explicit integral expressions for the flux of metal j_A are given in [15].

A different thermal diffusion experiment can be realized by applying boundary conditions, such that the metal flux vanishes in the steady state, i.e. $j_{Ag} = 0$ (Soret effect, thermal demixing). From Eq. (3) it follows then that

$$\left(\frac{d\mu_{Ag}}{dT}\right)_{j_{Ag}=0} = -\left(s_{Ag} + \frac{Q^*_{Ag}}{T}\right) \qquad (7)$$

and from Eq. (5) one obtains:

$$\left(\frac{dc_{Ag}}{dT}\right)_{j_{Ag}=0} = -\frac{Q^*_{Ag}}{T}\cdot\left(\frac{\partial\mu_{Ag}}{\partial c_{Ag}}\right)_T^{-1}. \qquad (8)$$

Eq. (8) demonstrates the importance of Q^*_{Ag}. Any concentration demixing in the steady state can only be observed if Q^*_{Ag} is non-zero. If Q^*_{Ag} takes positive values, a transient flux of silver metal will be directed down a temperature gradient, tending to produce a counterdirected concentration gradient.

Based on the preceding relationships, experiments have been performed on both thermal diffusion under the particular condition $\Delta c_{Ag} = \Delta\delta = 0$ [9,10] and on thermal demixing under the particular condition $j_{Ag} = 0$ [11].

3. Experimental

β-Ag$_{2+\delta}$S is a mixed conductor with exceptional conductivity properties. Both the ionic partial conductivity, which is nearly independent of the composition ($\sigma_{Ag^+} \approx 380$ S m^{-1} at 200°C), and the partial electronic conductivity (e.g., $\sigma_{e^-} \approx 4.1\cdot10^4$ S m^{-1} at 200°C and $\delta = 1.0\cdot10^{-3}$), which is dependent on the deviation from stoichiometry, have appreciable values. In combination with a large thermodynamic factor, $(\partial \ln a_{Ag}/\partial \ln c_{Ag})_T$, this leads to an unusually large chemical diffusion coefficient of silver, $\tilde{D}_{Ag}$, in β-Ag$_{2+\delta}$S. For example, at 200°C and $\delta = 1.0\cdot10^{-3}$, the thermodynamic factor takes a value of approximately $4.1\cdot10^{-3}$, leading to a chemical diffusion coefficient of $\tilde{D}_{Ag} = 1.14\cdot10^{-5}$ m^{2}s^{-1} [14]. Thus, in the course of chemical or thermal diffusion, steady states are generally attained rapidly.

3.1. The experimental arrangement

As depicted in Fig. 1, four galvanic cells of the type

$$Pt(1)|Ag|AgI|\beta - Ag_{2+\delta}S|Pt(2) \qquad (9)$$

were used for the measurement of the chemical potential of silver in β-Ag$_{2+\delta}$S, via the EMF:

$$U = \varphi_2 - \varphi_1 = -\frac{1}{F}(\mu_{Ag} - \mu^0_{Ag})$$

$$= -\frac{RT}{F}\ln a_{Ag} \qquad (10)$$

and for the purpose of coulometric titration. In Eq. (1), φ_1 and φ_2 denote the electric potentials in the platinum contacts, respectively, and μ^0_{Ag} represents the chemical potential of the pure silver electrode. The electric charge, which is transported through such a cell by an electric current $I(t)$, is a precise measure of the amount of silver, Δn_{Ag}, which is supplied to, or removed from, the silver sulfide crystal:

$$\Delta n_{Ag} = \frac{1}{F}\int_{t_1}^{t_2} I(t)\,dt, \quad j_{Ag} = \frac{I(t)}{FA}. \qquad (11)$$

Under open cell conditions, the composition and temperature dependence of the EMF is given by:
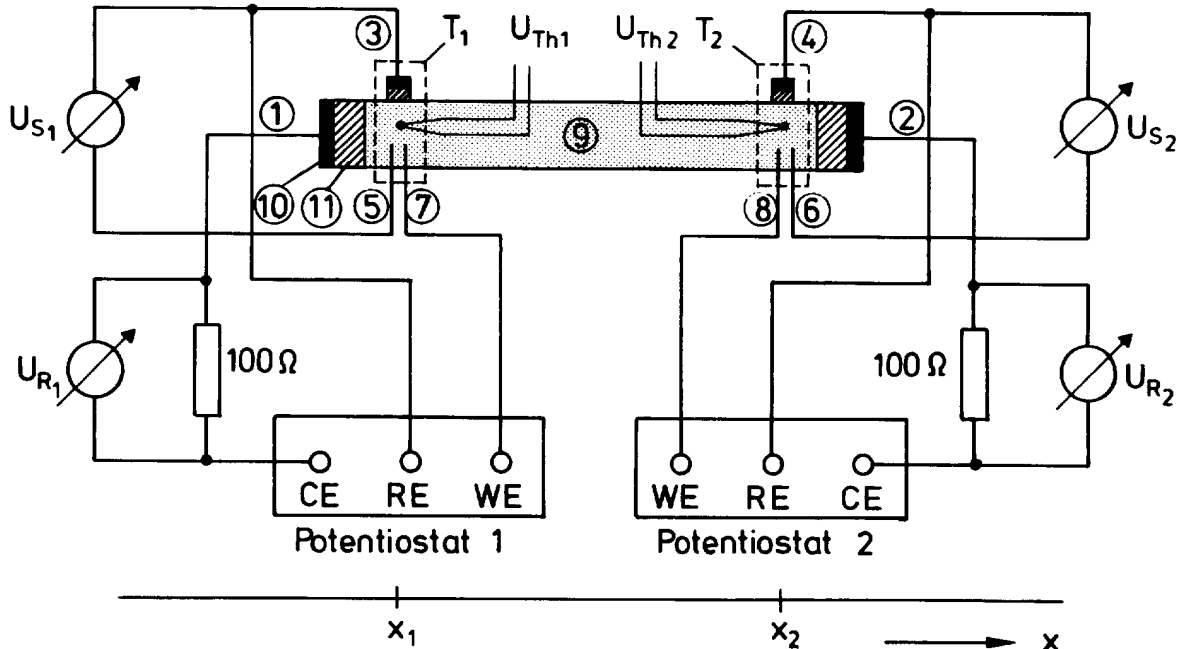
Fig. 1. Experimental arrangement of the nonisothermal galvanic cell. 1–4, ionic electrodes; 5–8, electronic electrodes; 9, silver sulfide crystal; 10, silver metal; 11, silver iodide.

$$-F\,dU = \left(\frac{\partial(\mu_{Ag} - \mu_{Ag}^0)}{\partial c_{Ag}}\right)_T dc_{Ag}$$

$$+ \left(\frac{\partial(\mu_{Ag} - \mu_{Ag}^0)}{\partial T}\right)_{c_{Ag}} dT \qquad (12)$$

with

$$\left(\frac{\partial(\mu_{Ag} - \mu_{Ag}^0)}{\partial T}\right)_{c_{Ag}} = -(s_{Ag} - s_{Ag}^0). \qquad (13)$$

Thus, if an isothermal silver sulfide crystal is closed completely for the exchange of silver, from a measurement of the temperature dependence of the EMF, U, the relative partial entropy, $(s_{Ag} - s_{Ag}^0)$, can be determined.

3.2. Thermal diffusion

For the measurement of Q_{Ag}^* via thermal diffusion, a temperature gradient has to be applied, and the composition at both ends of the nonisothermal crystal has to be controlled by galvanic cells, to meet

the condition $\Delta\delta = 0$. In the stationary state, definite and constant titration currents have to be supplied at both ends of the β-$Ag_{2+\delta}S$ crystal which can be used for the evaluation of Q_{Ag}^* by Eqs. (6) and (11). Details of the procedure can be found in [10]. Data obtained for Q_{Ag}^* are presented in Fig. 2.
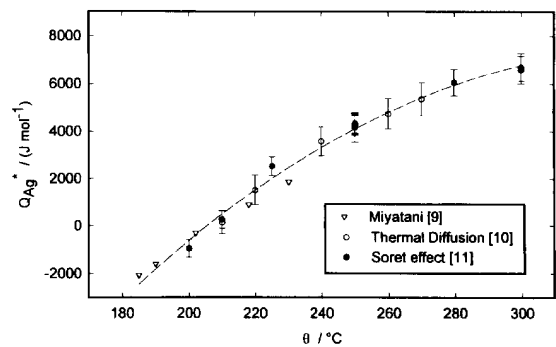

Fig. 2. Heat of transport of silver in β-$Ag_{2+\delta}S$ as a function of temperature for $\delta = 9.6 \cdot 10^{-4}$.

3.3. Thermal demixing

For the measurement of Q_{Ag}^* via the Soret effect, a temperature gradient has to be applied to the sulfide crystal, and the compositions at both ends of the crystal in the stationary state ($j_{Ag}=0$) have to be determined by the use of the galvanic cells, without drawing an electric current. Essentially, the so-called entropy of transfer, ($s_{Ag}-s_{Ag}^0+Q_{Ag}^*/T$), results from the measurements, see Eq. (11). By subtraction of the relative partial entropy of silver, ($s_{Ag}-s_{Ag}^0$), which has to be determined from independent measurements (see Eq. (13)), values for Q_{Ag}^* can be obtained (see Figs. 2 and 3). More details of the experimental procedure may be found in [11].

A comment has to be given with respect to the investigated composition and temperature range. Both thermal diffusion and thermal demixing experiments (and measurements of the partial entropy) can be performed with high precision at high silver activities. At low silver activities, the equilibrium partial pressure of sulfur increases and thus generally leads to continuous changes of the composition by evaporation, if the cell is not completely encapsulated. To avoid this problem, we restricted our experiments to the range of medium-to-high silver activities.

The experimental temperature range has been fixed by the phase transformation of the sulfide at 178°C and by the fact that the electronic conductivity of the solid electrolyte AgI increases appreciably at
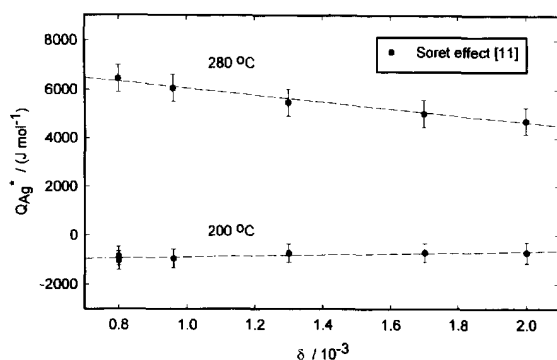

Fig. 3. Heat of transport of silver in β-Ag$_{2+\delta}$S as a function of the deviation from stoichiometry at two different temperatures.

temperatures over 300°C, which also leads to a drift in the composition.

4. Results

Representative results for the heat of transport as a function of temperature and composition are depicted in Figs. 2 and 3.

According to the measurements, the reduced heat of transport, Q_{Ag}^*, of silver metal in β-Ag$_{2+\delta}$S is only slightly dependent on the composition, but strongly dependent on the temperature. It increases from approximately -1 kJ mol^{-1} at 200°C to 7 kJ mol^{-1} at 300°C. A sign reversal of Q_{Ag}^* is observed with increasing temperature, at a temperature of approximately 205°C. The results of both thermal diffusion and thermal demixing experiments [10,11] coincide, thus giving us confidence in the reliability of our data. Additionally, data from a study of Miyatani [9] are included in Fig. 2 which are also in excellent agreement with our data.

5. Discussion

As can be seen from Fig. 2, the heat of transport of silver exhibits a strong temperature dependence. Despite this dependence, the absolute values remain relatively small within the investigated temperature range, i.e. the heat of transport takes values in the order of RT. To illustrate this result, two numerical examples shall be given. (a) *Thermal demixing*: A relative change in composition at both ends of a β-Ag$_{2+\delta}$S crystal of $\Delta\delta/\delta\approx1.3\%$ results at a mean temperature of 250°C, if the crystal is exposed to a temperature difference of 20 K. Thus, the effect of Q_{Ag}^* is small, mainly due to the large thermodynamic factor (see Eq. (8)), but also showing the precision and performance of the electrochemical technique. (b) *Thermal diffusion*: A flux of silver metal of $j_{Ag}\approx1.4\cdot10^{-4}$ mol m^{-2} s^{-1} results at a mean temperature of 250°C under the boundary condition $\Delta\delta=0$, if a temperature gradient of 4 K cm^{-1} is applied (typical gradient in our experiments). This flux density is equivalent to a silver ion current density of $1.33\cdot10^{-3}$ A cm^{-2}, again a rather small value.

The interpretation of our results in terms of microscopic transport processes is difficult, since Q^*_{Ag} combines the contributions of the mobile cations and the electronic charge carriers:

$$Q^*_{Ag} = Q^*_{Ag^+} + Q^*_{e^-} .$$ (14)

Nevertheless, some interesting phenomenological conclusions can be drawn. From thermodynamic measurements [11], the relative partial molar enthalpy of silver in β-Ag$_{2+\delta}$S, $(h_{Ag} - h^0_{Ag})$, was determined (see Fig. 4). By the addition of h^0_{Ag}, which represents the molar enthalpy of pure silver metal, the partial molar enthalpy, h_{Ag}, was calculated (see also Fig. 4), whereby the reference state[1] for h^0_{Ag} is chosen arbitrarily as $h^0_{Ag}(T = 298.15 \text{ K}) = 0$.

As can be seen from Fig. 4, the resulting partial enthalpy, h_{Ag}, and the heat of transport, Q^*_{Ag}, show opposite behaviour with increasing temperature, whereby the temperature dependence of Q^*_{Ag} is more pronounced. As a consequence, the energy of transport, U^*_{Ag}, (see Eq. (2)) also increases with temperature, the slope being approximately $6R$ (since the absolute values of U^*_{Ag} depend on the choice of a reference state for the enthalpy, only the slope of U^*_{Ag} versus temperature will be regarded here). The finding of such strong temperature dependence for both Q^*_{Ag} and U^*_{Ag} is definitely not in agreement with various models for the heat of transport [6]
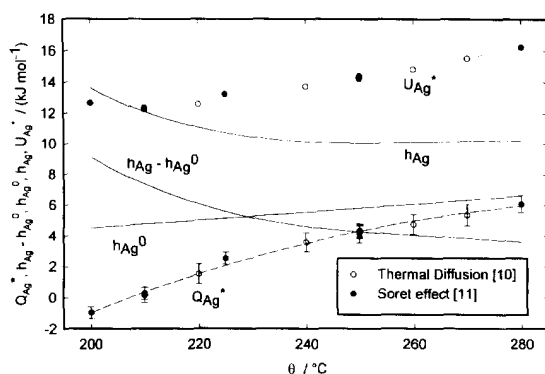
which claim an equivalence of this quantity with the migration enthalpy, i.e. the activation energy of the thermally activated ion jumps. Particularly, our result makes the simple analysis of thermopower measurements of superionic conductors doubtful, which assumes a temperature-independent heat of transport of ionic charge carriers [16].

6. Conclusions

In this paper, experimental results from our own studies and from the literature are reported and discussed, in order to contribute to a more coherent picture for the heat of transport of silver metal in β-Ag$_{2+\delta}$S. To our knowledge, β-Ag$_{2+\delta}$S is the first compound for which reliable data for the heat of transport of the mobile component exist as a function of both temperature and composition [9–11]. A surprising aspect of the heat of transport of β-Ag$_{2+\delta}$S is a sign reversal at approximately 205°C, from minus to plus with increasing temperature, and its strong temperature dependence. Both the heat of transport, Q^*_{Ag}, and the energy of transport, Q^*_{Ag}, possess a pronounced temperature dependence which is almost linear, with an approximate slope of $9R$ and $6R$, respectively. Absolute values for the energy of transport depend on the choice of a reference energy.

Fig. 4. Comparison of the measured heat of transport, Q^*_{Ag}, and the energy of transport, U^*_{Ag}. The relative partial enthalpy $(h_{Ag} - h^0_{Ag})$ has also been determined experimentally.

[1]For a discussion of the reference state, see [11].

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