

Zusammenfassung

Es wird gezeigt, daß sich Nb₃Sn mit Jod über den Gasraum transportieren läßt. Die Versuche deuten darauf hin, daß die β -W-Phase des Systems Nb–Sn eine energetisch bevorzugte Phase ist; anders ließe sich der Transport des Nb₃Sn nur schwer erklären. Es wird außerdem gezeigt, daß die β -W-Phase des Systems

Nb–Sn bei erhöhter Temperatur einen ausgedehnten Existenzbereich von ca. 5 Atom-Proz. besitzt. Letztlich wird die Abhängigkeit der Gitterkonstante von der Zusammensetzung des Nb₃Sn gedeutet.

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On the Concept of Activation Energy for Transport Processes in Molten and Solid Salts

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Experimental results on transport properties (electrical conductivity, self-diffusion and viscosity) are frequently expressed by equations of the form

$$A = A_0 \exp(-B/T), \quad (1)$$

and, provided that a linear relation is obtained between $\ln A$ and $1/T$ over the investigated temperature range, cf. ref.¹, the constant B , is assumed to be proportional to the activation energy of the transport process. This energy is then kB or RB (k is BOLZMANN's and R is the gas constant). The base of reference is unambiguous for mono-mono valent salts, but when salts are considered where e. g. one ion is divalent, it is not always evident which quantity of salt an "activation energy" RB corresponds to. Thus for solid α -Li₂SO₄ it is generally agreed that the sole mobile units are Li⁺ ions, and the activation energies for self-diffusion, RB_{D^+} , and conductivity RB_A ^{2,3} as well as the heat of transport for thermal diffusion, Q^* , correspond to one gram-equivalent of Li₂SO₄, but the situation is different for e. g. molten divalent halides MX₂, where it can be questioned, see below, whether the mobile ions are M²⁺ and 2 X⁻, MX⁺ and X⁻ or larger "clusters". To avoid difficulties of this kind, it is preferable that experimental results are expressed merely by means of eqn. (1), and that the concept "activation energy" is not introduced without stating which model it refers to.

By assuming e. g. that the STOKES-EINSTEIN and the NERNST-EINSTEIN relations hold, at least as a first approximation, it is easy to show that the activation energies should be related for the three transport processes

considered⁴. Conversely, if B_η , B_A , B_{D^+} and B_{D^-} are found to be interrelated, this can be taken as evidence that the mechanisms of viscosity, conductivity and self-diffusion are similar. Regarding self-diffusion in pure solids, it is generally considered that one of the ions is much more mobile than the other, which means that the activation energies should differ. The available experimental data on self-diffusion in pure solid salts are fairly meager, and the results are often diverging, which is not unexpected, if the experimental difficulties and the marked influence of impurities are considered. However, it seems to be clear that $B_{D^-} > B_{D^+}$ for NaCl⁵, while the evidence is not so conclusive for AgCl⁶. An extreme case is α -AgI where $B_{D^-} = 6.5 \times B_{D^+}$ ⁷. In contrast, for all molten salts investigated so far, there is a strong tendency that B_{D^+} and B_{D^-} coincide within experimental error⁸⁻¹¹. Furthermore B_D , B_η and B_A seem to be interrelated^{4,12}. The self-diffusion data thus support the view that the elementary transport processes in molten salts are of a collective nature involving several atoms rather than distinct "jumps" of single ions from one position to another. Regarding divalent halides, MX₂, it has been claimed that conductivity data support a hole model for most of the investigated salts, where the migrating entities are MX⁺ and X⁻ ions¹². Most typical in this case were the group II A halides. The conductivities of zinc halides deviated from the main behavior, and the lead halides were not included in the investigation in question, but since ZnBr₂ and PbCl₂ are the only divalent salts for which self-diffusion has been studied, it should be mentioned that in both these salts B_{D^+} was close to B_{D^-} , while for a hole model with MX⁺ as dominating cation it seems likely from space considerations that B_{D^+} should be significantly higher than B_{D^-} . Additional self-diffusion measurements, preferably on divalent salts, are thus urgently needed to test various models proposed for molten salts.

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