3 / 1 Elektrolyte und Leitfähigkeit

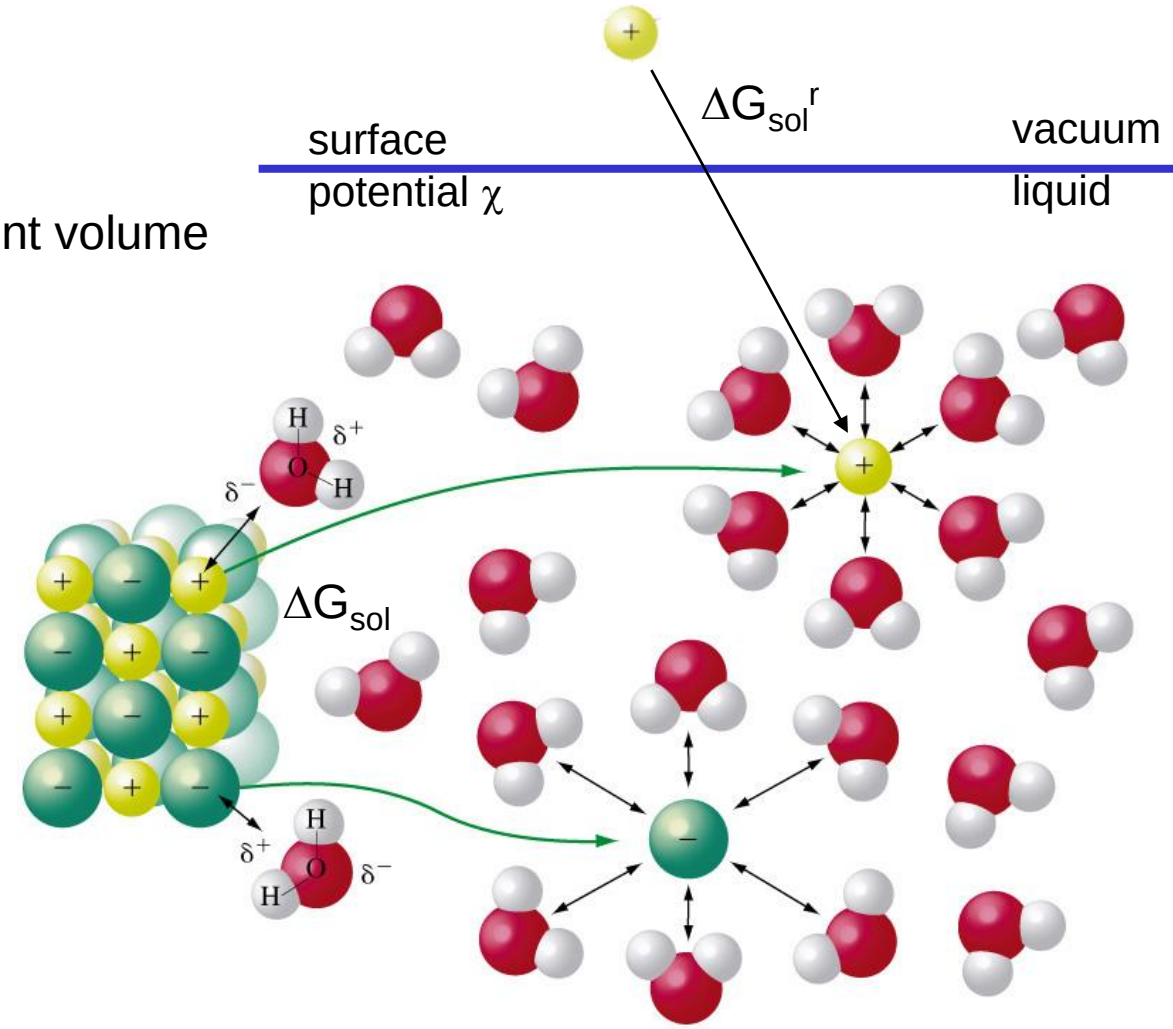
Themen:

- Elektrolyte
- Mechanismus der Ionenleitung
- Leitfähigkeit von Lösungen
- ionische Leitfähigkeit von Festkörpern

Löslichkeit

Interaction of ions with dipole moments of solvent:

- real free energy of solvation ΔG_{sol}^{r} :
  - interaction energy with solvent volume
  - work due to surface dipole
- tabulated values ΔG_{sol} :
  - interaction energy with solvent volume measured vs. reference (H^+)
  - increases with z_{ion}, ε_{solv}
  - decreases with r_{ion}

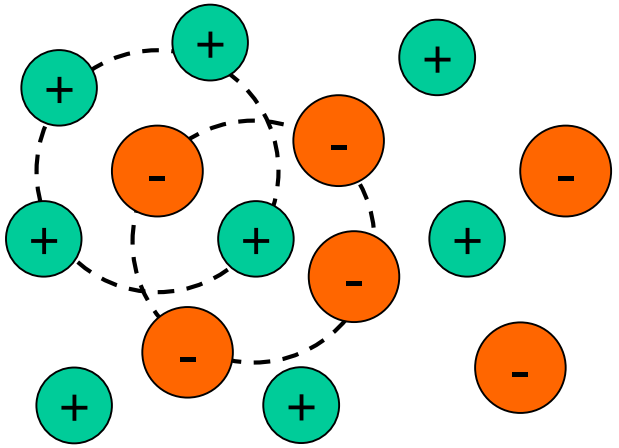


Struktur von Elektrolytlösungen

Positions of (solvated) ions in equilibrium determined by:

- electrostatic interactions ($\rightarrow$ ordering)
- thermal motion ($\rightarrow$ random arrangement)

$\rightarrow$ spherical distribution of counter ions



Screening of ionic electrostatic potential $\phi(r)$ by excess charge $\rho(r)$ of counter ions quantitatively described by Debye-Hückel model:

$$\phi(r) = \frac{ze_0}{4\pi\varepsilon_0\varepsilon r}\cdot e^{-r/L_D} \quad ; \quad \rho(r) = \frac{ze_0}{4\pi r L_D^2}\cdot e^{-r/L_D}$$

$$L_D \equiv \text{Debye screening length} = \left(ze_0\sqrt{2n_0/\varepsilon\varepsilon_0 k_B T}\right)^{-1}$$

$$n_0 \equiv \text{ion number density in electrolyte volume}$$

1-1 electrolyte (NaCl), 300 K

c [mol/dm^3]	10^{-4}	10^{-3}	10^{-2}	(10^{-1})
L_D [nm]	30.4	9.6	3.04	(0.96)

Ionische Leitfähigkeit

Ion migration in electric field:

Acceleration in electric field compensated by Stokes friction term:

$$\vec{F} = \vec{F}_E + \vec{F}_R = ze_0\vec{\varepsilon} - 6\pi\eta r_{ion}\vec{v} = 0$$

$$\vec{v} = u \cdot \vec{\varepsilon}; \quad \text{ion mobility } u \equiv \frac{ze_0}{6\pi\eta r_{ion}}$$

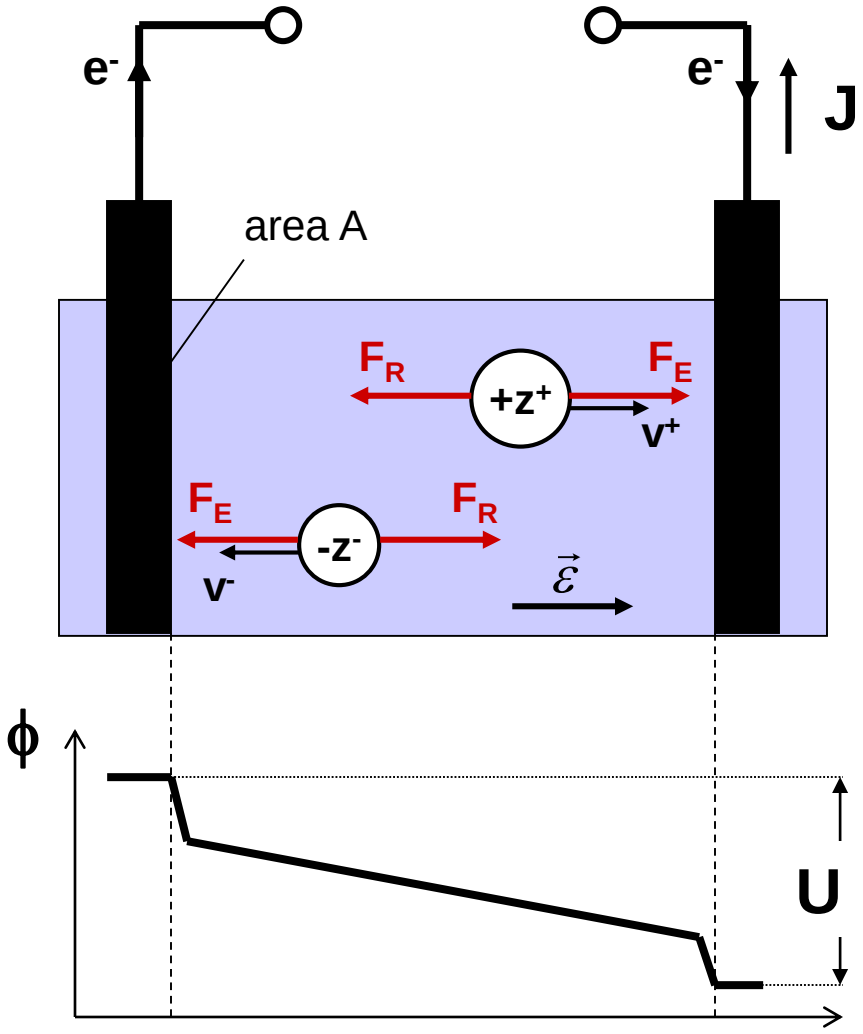
Total current carried by anions and cations:

$$I = Q/t = F \cdot A \cdot (z^- v^- c^- + z^+ v^+ c^+)$$

$$= A \cdot \underbrace{F \cdot (z^- u^- c^- + z^+ u^+ c^+)}_{\text{specific conductivity}} \cdot \vec{\varepsilon}$$

$\rightarrow$ I $\propto$ U: ohmic behavior

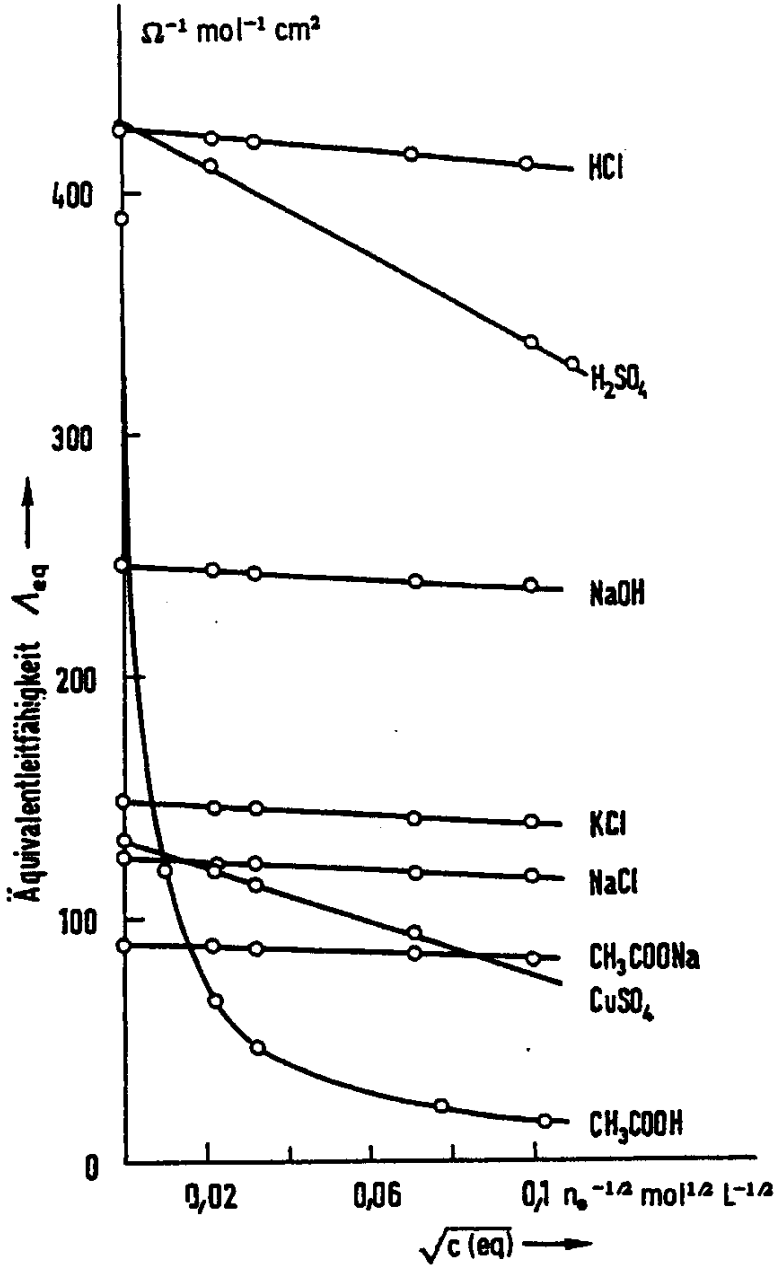
Experimental conductivities confirm assumption of independent migration of ions (Kohlrausch's law)



Ionische Leitfähigkeit

Conductivity at room temperature

	conductivity [$\Omega^{-1}cm^{-1}$]	ions
pure benzene	$5 \cdot 10^{-14}$	H^+, OH^- (H_2O traces)
pure water	$6 \cdot 10^{-8}$	H_3O^+, OH^- (dissoziation)
1 M NaCl	0.07	Na^+, Cl^-
1 M KOH	0.18	K^+, OH^-
1 M H_2SO_4	0.37	H_3O^+, SO_4^{2-}
copper	$6 \cdot 10^5$	free electrons



Haman/Vielstich

Ionische Leitfähigkeit

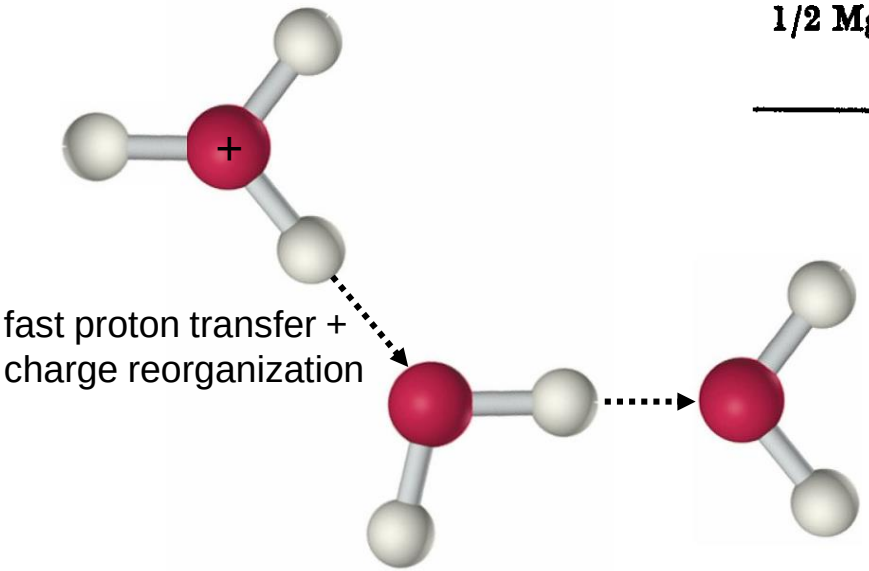
Conductivity per ion at infinite dilution:

- Experimental trends explained by:

$$u \equiv \frac{z e_0}{6\pi\eta\, r_{ion}}$$

radius of hydrated ion

- Anomalous high conductivity of H_3O^+ and OH^-:



Ionen-Äquivalent	λ_0^+, λ_0^- $\Omega^{-1}\,mol^{-1}\,cm^2$	Ionen-Äquivalent	λ_0^+, λ_0^- $\Omega^{-1}\,mol^{-1}\,cm^2$
		Ag^+	62,2
H^+	349,8	Na^+	50,11
OH^-	197	Li^+	38,68
K^+	73,5	$1/4\ Fe(CN)_6^{4-}$	110
NH_4^+	73,7	$1/3\ Fe(CN)_6^{3-}$	101
Rb^+	77,5	$1/2\ CrO_4^{2-}$	83
Cs^+	77	$1/2\ SO_4^{2-}$	80,8
		J^-	76,5
$1/2\ Ba^{2+}$	63,2	Cl^-	76,4
$1/2\ Ca^{2+}$	59,8	NO_3^-	71,5
$1/2\ Mg^{2+}$	53	CH_3COO^-	40,9
		$C_7H_5O_2^-$	32,4

Haman/Vielstich

Ionische Leitfähigkeit

Quantitative microscopic theory (Debye-Hückel-Onsager theory)

Spherical distribution of counter ions in electric field →

- Relaxation effect:

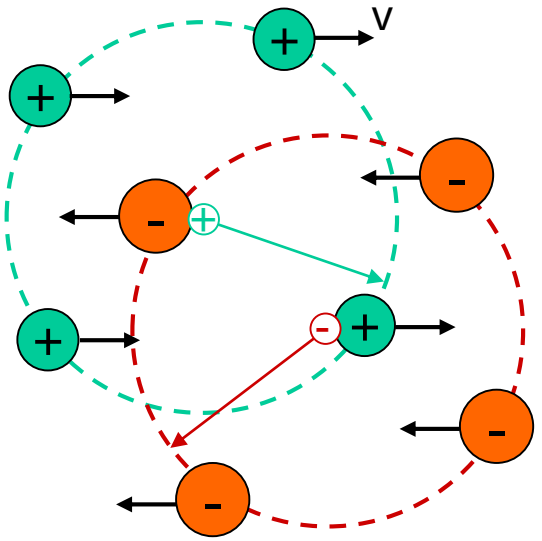
  ion shifted vs. center of counterion distribution

  → retarding electrostatic force

- Electrophoretic effect:

  microscopic collisions with (solvated) counter ions

  → friction force

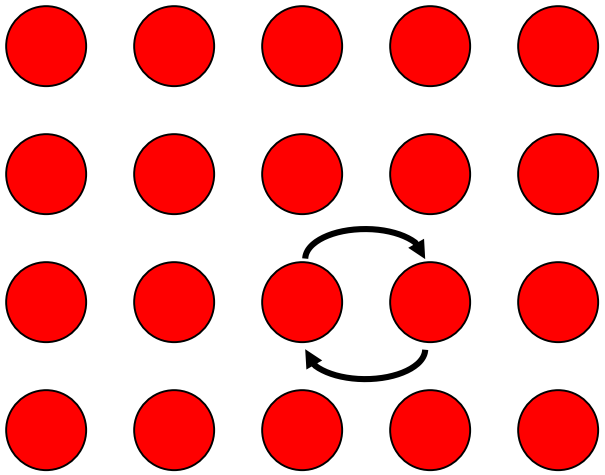


Results confirm Kohlrausch's law

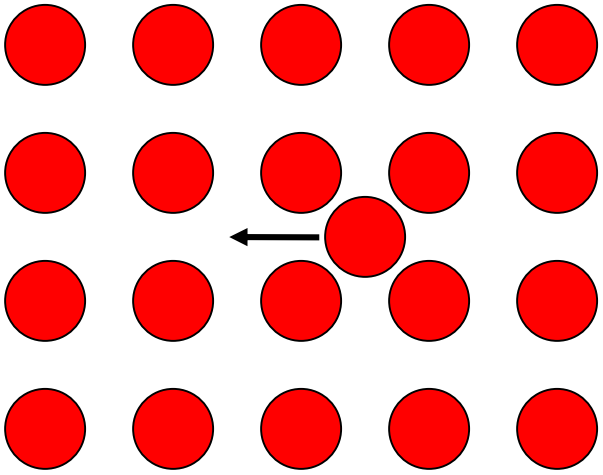
Ionenleitende Festkörper

Transportmechanismen in Festkörpern

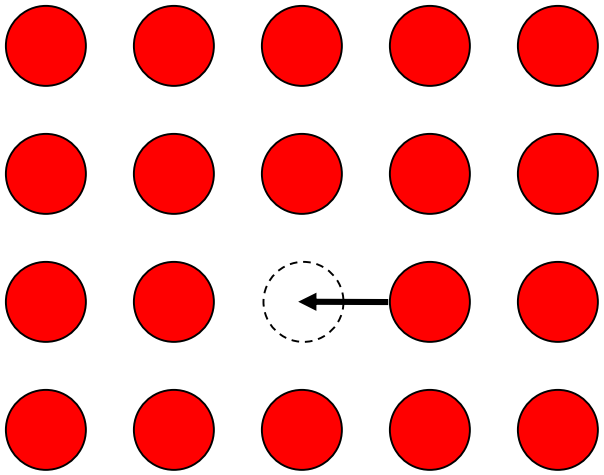
Direkter Austausch

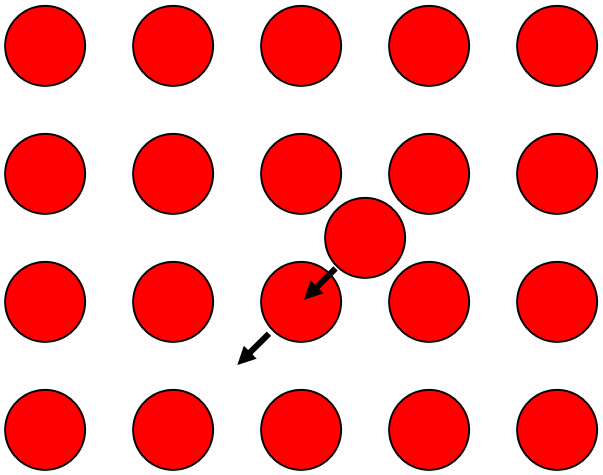


Transport über Zwischengitterplätze

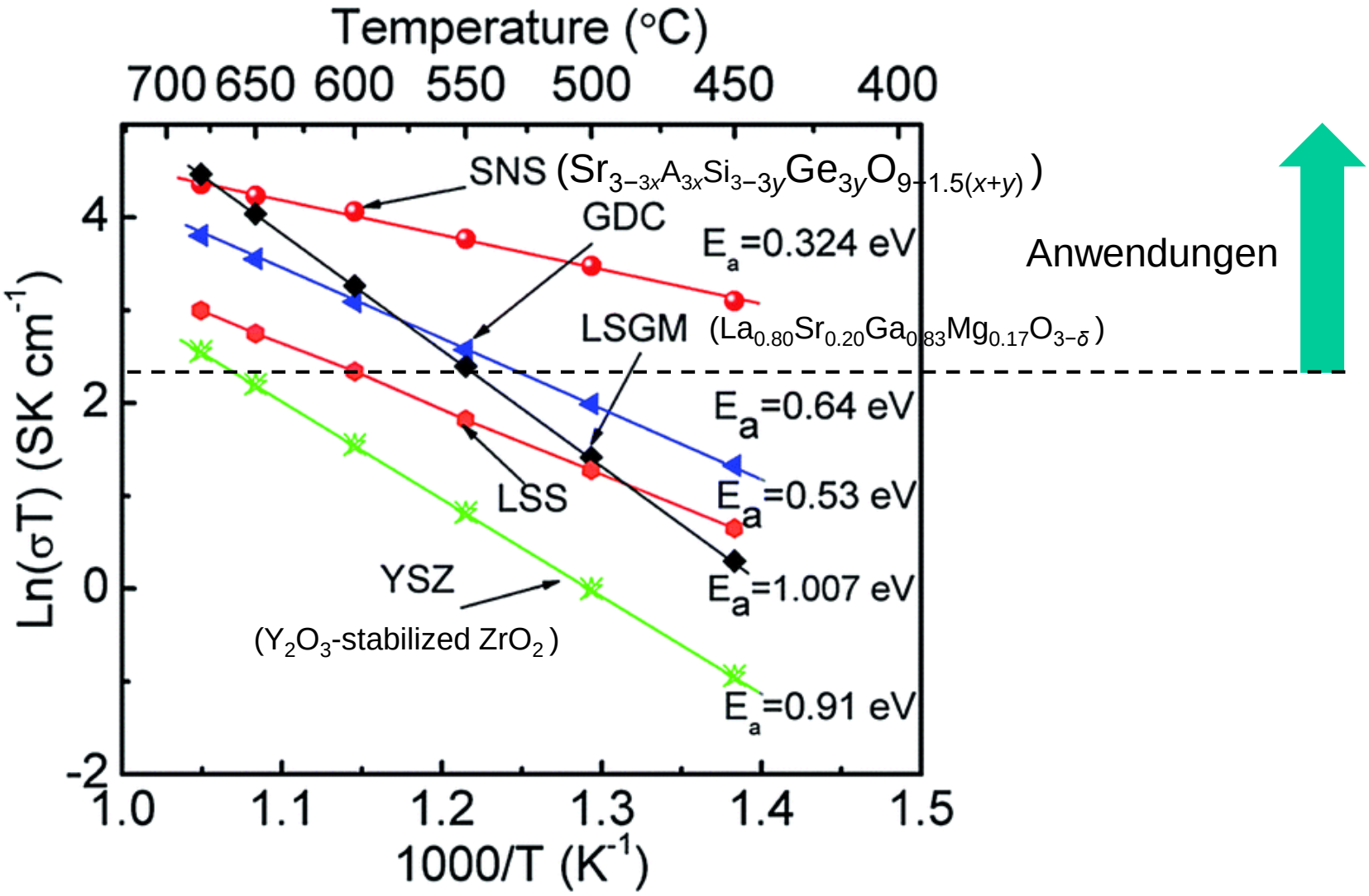


Transport über Fehlstellen





Ionenleitende Festkörper



T. Wei et al., Energy Environ. Sci., 2014,7, 1680-1684