

Elektrochemie, HS2019

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3rd Exercise: Stofftransport im Elektrolyten

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Cave: a) present the result in the desired units, b) sign and staple all written pages.

1 General Considerations on Mass Transport in Electrolytes

(a) Typically three types of mass transport exist in electrolyte. Describe their mechanisms:

Diffusion**Migration****Convection**

- (b) Draw a schematic view of the concentration (c) variation as a function of the distance (x) to the electrode during an electrochemical reaction when only the diffusion occurs as mass transport mechanism. Mark the thickness of the Nernst diffusion layer (δ).
- (c) Explain why the Nernst diffusion layer is both time and diffusion coefficient dependent, i.e. $\delta = \delta(D, t)$.
- (d) The reaction $\text{H}^+ + \text{e}^- \rightarrow \frac{1}{2} \text{H}_2$ may occur at a Pt catalyst. Consider a Pt electrode with a surface area of $1.1 \text{ cm} \times 1.1 \text{ cm}$ in a 1 M^1 solution of HCl. A steady state current of 1.5 mA is observed. Calculate the current density (j , [A/cm^2]) and the flux (J , [$\text{mol}/(\text{cm}^2 \text{ s})$]).

2 Diffusion and Migration

- (a) Calculate the diffusion coefficient (D , [m^2/s]) for a Na^+ cation in H_2O at room temperature (ionic mobility $\mu_{\text{Na}^+} = 5.2 \times 10^{-4} \text{ cm}^2/(\text{s V})$, viscosity $\eta_{\text{H}_2\text{O}} = 1 \times 10^{-3} \text{ kg}/(\text{m s})$). Then use the Stokes-Einstein equation to calculate the effective hydrodynamic radius (r , [pm], [Å]).

$$D = \frac{RT}{6N_A\pi\eta r} \quad \text{Stokes-Einstein equation}$$

- (b) In Table 1 below the ionic mobilities for several ions are listed². Why is there a large difference between H^+ , OH^- and the other ions?
- (c) Assume an ideal diluted aqueous electrolyte solution in a very long electrochemical cell. Will a charged particle experience a constant acceleration in the electrolyte due to the electric potential gradient induced by the charged electrodes? And why?

¹[M=mol/L]

²Bard, Allen J.; Faulkner, Larry R. (2000): Electrochemical methods and applications. 2nd ed. New York, London: Wiley-Interscience.

Table 1: Ionic mobilities at infinite dilution in aqueous solutions at 25°C.

Cation	$\mu[\text{cm}^2/(\text{s V})]$	Anion	$\mu[\text{cm}^2/(\text{s V})]$
H ⁺	3.625×10^{-3}	OH ⁻	2.05×10^{-3}
Li ⁺	7.619×10^{-4}	Cl ⁻	7.912×10^{-4}
Na ⁺	5.193×10^{-4}	3/2 SO ₄ ²⁻	8.27×10^{-4}
K ⁺	4.010×10^{-4}	HCO ₃ ⁻	4.61×10^{-4}

3 Convection

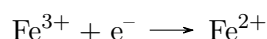
- (a) A rotating disk electrode (RDE) rotates with the angular frequency $\omega = 2\pi \cdot f^3$ in 1 M HCl. With this setup, the Nernst diffusion layer thickness can be expressed as:

$$\delta_N = 1.61 \cdot D^{1/3} \nu^{1/6} \omega^{-1/2}$$

The diffusion limited current density is defined as:

$$j = 0.62 \cdot nFD^{2/3} \nu^{-1/6} \omega^{1/2} c_0$$

where n is the number of electrons involved in the electrode reaction. Consider the reduction of Fe³⁺ to Fe²⁺:



and calculate the Nernst diffusion layer (δ , [μm]) and the diffusion limited current density (j , [A/cm^2]) for the disk electrode rotating at 250 Hz.

(Use the following electrolyte properties for HCl: $D_{\text{Fe}^{3+}} = 4.96 \times 10^{-6} \text{ cm}^2/\text{s}$, $c_{\text{Fe}^{3+}} = 1.5 \text{ mmol/L}$, kinematic viscosity $\nu_{\text{H}_2\text{O}} = 1 \times 10^{-6} \text{ m}^2/\text{s}$.)

- (b) Explain the interest of the rotating disks for electro-analytical application.

4 Multiple Choice Summary

1. Which condition(s) has/have to be fulfilled for diffusion limited current?⁴

- (a) $c_{\text{bulk}} = 0$
 (b) $c_{\text{bulk}} = c_{x=0}$
 (c) $c_{x=0} = 0$

2. Consider a 0.1 M aqueous solution of HCl. Which transport mode in the electrolyte (migration (M), diffusion (D) or convection (C)) is affected by the following changes:

(Multiple answers as well as none of the above are possible.)

- (a) Increasing the potential gradient M D C
 (b) Increasing the concentration gradient of the reactant M D C
 (c) Increasing the concentration of the electrolyte from 0.1 M to 1 M HCl M D C
 (d) Increasing the temperature M D C
 (e) Changing the transference number⁵ of the ion M D C
 (f) Increasing the radius of the solvated ion M D C
 (g) Changing the density gradient of the solvent M D C
 (h) Changing the solvent of the electrolyte M D C
 (i) Changing the external wires from copper to gold M D C

³[rad/s=2 π Hz]

⁴ $c_{x=0}$: concentration at the electrode surface; c_{bulk} : bulk concentration

⁵Überführungszahl