3.5

DEFINITION OF POLARIZATION AND OVERVOLTAGE

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IN order to define the significance of 'polarization', 'overvoltage' and other related terms as exactly as possible and so as to be generally valid, a synopsis is given of the polarization phenomena occurring for single or double electrodes, first of all for the stationary condition.

Single electrodes

Polarization = overvoltage of the potential-determining electrodic reaction.
Example: Me^+ electrode with solvent bonding of the Me^+ ions.

Polarization as part of the measurable change ΔU in the reference potential U.

Distribution of the overvoltage into different portions corresponding to different kinds of limited partial processes: overvoltage of resistance, concentration and activation. Different kinds of currents: diffusion current, limiting current, exchange current. Introduction (formal) of resistances: polarization resistance and overvoltage resistance, or the corresponding conductivity constants as a simple quantitative indication of the polarization phenomena.

Double electrodes

(*a*) *with double equilibrium in the currentless state*—Polarization = overvoltage of the electrode reaction α = overvoltage of the electrode reaction β.

Example: 1; double Me^+ electrode with solution and complex bonding of the Me^+-ions. Counterpart: 1, double electronic-electrodes. Assistance of a chemical reaction inside the diffusion layer. Occurrence of 'reaction overvoltage' with conclusive checking of this reaction.

(*b*) *Double electrodes with mixed-galvanic potential*—No electrochemical equilibrium in the currentless state, prolonged irreversible transformations. Polarization and overvoltages of both electrodic reactions α and β are different.

Examples: corrosion electrodes, solution of silver halides at corresponding electrodes. Relationships between polarization, overvoltages, total current and partial currents with application of appropriate secondary ideas such as polarization resistance, overvoltage resistance or the corresponding conductivity constant (total conductivity constant of the electrodes, partial conductivity constants of the electrodic reactions).

Exact definition of the conception 'electrodic reaction' and the limits between single, double and multiple electrodes.

Definition of the 'difference effect' concerning the reaction partial currents I_α and I_β.