

## Electrochemical kinetics (heterogeneous dynamic electrochemistry)

- P79. A typical exchange current density, that for  $\text{H}^+$  discharge at platinum, is  $0.79 \text{ mA cm}^{-2}$  at  $25.0 \text{ }^\circ\text{C}$ . Calculate the current density at an electrode when its overpotential is  $10 \text{ mV}$  (a),  $100 \text{ mV}$  (b), and  $-0.5 \text{ V}$  (c). Take  $\alpha = 0.50$ . ((a)  $0.309 \text{ mA cm}^{-2}$ , (b)  $5.42 \text{ mA cm}^{-2}$ , (c)  $-13.3 \text{ A cm}^{-2}$ )
- P80. The exchange current density for  $\text{H}^+$  discharge at zinc is about  $5 \cdot 10^{-11} \text{ A cm}^{-2}$ . Can zinc be deposited from a unit activity aqueous solution of a zinc salt? Take  $\alpha = 0.50$  and  $T = 25 \text{ }^\circ\text{C}$ . The minimal exchange current density for hydrogen evolution is  $j(\text{min}) = 1 \text{ mA cm}^{-2}$ . ( $j(\text{H}^+) = 1.33 \cdot 10^{-4} \text{ A cm}^{-2}$ . Since this value is lower than  $1 \text{ mA cm}^{-2}$ ,  $\text{H}_2$  cannot be formed, so, Zn is deposited on the electrode instead.)
- P81. Estimate the limiting current density at an electrode in which the concentration of  $\text{Ag}^+$  is  $2.5 \text{ mmol dm}^{-3}$  at  $25.0 \text{ }^\circ\text{C}$ . The thickness of the Nernst diffusion layer is  $0.40 \text{ mm}$ . The ionic conductivity of  $\text{Ag}^+$  ion at infinite dilution and  $25.0 \text{ }^\circ\text{C}$  is  $61.9 \text{ S cm}^2 \text{ mol}^{-1}$ . ( $0.994 \text{ A/m}^2$ )
- P82. Calculate the minimum (zero-current) potential difference of a Ni-Cd cell, and the maximum possible power output when  $100 \text{ mA}$  is drawn at  $25.0 \text{ }^\circ\text{C}$ . Standard redox potential values are listed below. ( $E = 1.30 \text{ V}$  and  $P = 0.130 \text{ W}$ )
- P83. The corrosion current density  $j_{\text{corr}}$  at an iron anode is  $1.0 \text{ A m}^{-2}$ . What is the corrosion rate in  $\text{mm/year}$ ? Assume uniform corrosion. Iron has a density of  $7.874 \text{ g cm}^{-3}$  and a molar mass of  $55.845 \text{ g/mol}$ . ( $0.773 \text{ mm/year}$ )
- P84. Which of the following metals has a thermodynamic tendency to corrode in moist air at  $\text{pH} = 7.0$ : Fe, Cu, Pb, Al, Ag, Cr, Co? Take as a criterion of corrosion a metal ion concentration of at least  $10^{-6} \text{ mol dm}^{-3}$ . Use the standard redox potential values from the list below. (In the absence of  $\text{O}_2$ : Fe, Al, Co, Cr; in the presence of  $\text{O}_2$ : all.)

Standard redox potential values:

Half-reaction	$E^\ominus$ (V)
$\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$	-1.66
$\text{Cd}(\text{OH})_2 + 2\text{e}^- \rightarrow \text{Cd} + 2\text{OH}^-$	-0.81
$\text{Zn}^{2+} + 2\text{e}^- \rightarrow \text{Zn}$	-0.76
$\text{Cr}^{3+} + 3\text{e}^- \rightarrow \text{Cr}$	-0.74
$\text{Fe}^{2+} + 2\text{e}^- \rightarrow \text{Fe}$	-0.44
$\text{Co}^{2+} + 2\text{e}^- \rightarrow \text{Co}$	-0.28
$\text{Pb}^{2+} + 2\text{e}^- \rightarrow \text{Pb}$	-0.13
$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$	-0.04
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	0.00
$\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$	0.40
$\text{NiO}(\text{OH}) + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{Ni}(\text{OH})_2 + \text{OH}^-$	0.49
$\text{Cu}^+ + \text{e}^- \rightarrow \text{Cu}$	0.52
$\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$	0.80
$\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 4 \text{H}_2\text{O}$	1.23