

Dinâmica em sistemas eletroquímicos

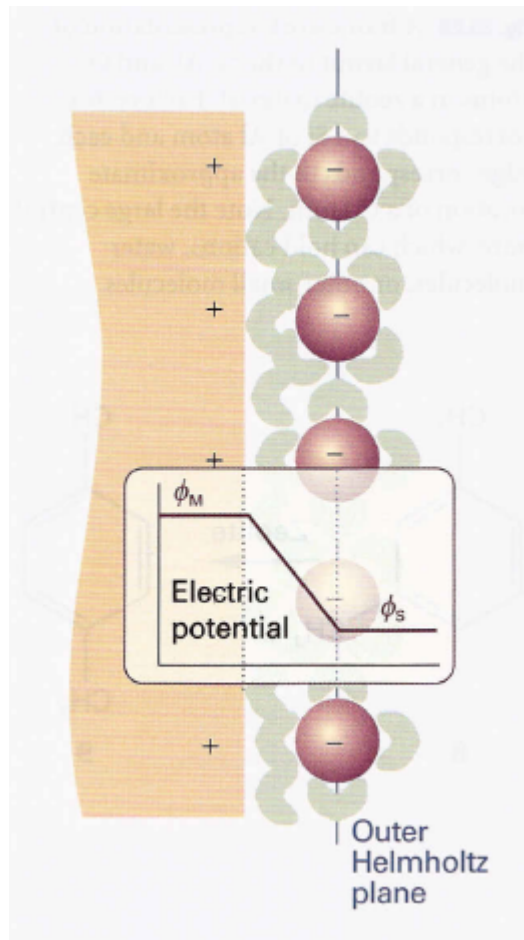


Fig. 25.30 A simple model of the electrode–solution interface treats it as two rigid planes of charge. One plane, the outer Helmholtz plane (OHP), is due to the ions with their solvating molecules and the other plane is that of the electrode itself. The plot shows the dependence of the electric potential with distance from the electrode surface according to this model. Between the electrode surface and the OHP, the potential varies linearly from ϕ_M , the value in the metal, to ϕ_S , the value in the bulk of the solution.

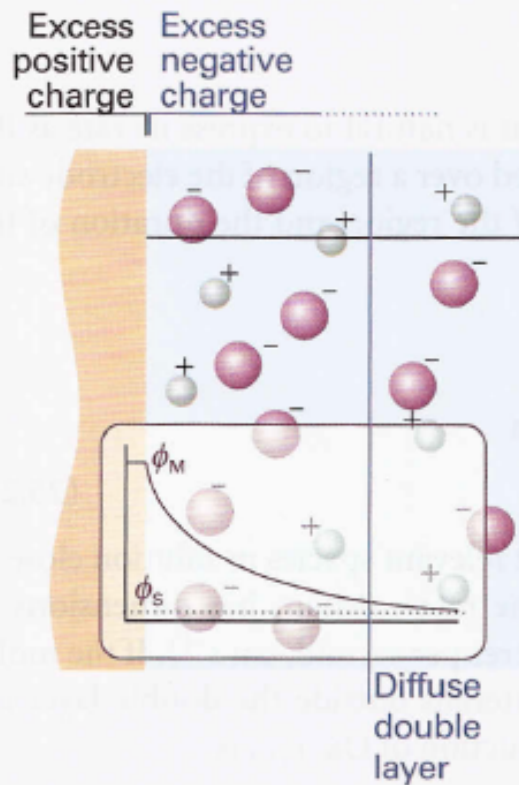


Fig. 25.31 The Gouy–Chapman model of the electrical double layer treats the outer region as an atmosphere of counter-charge, similar to the Debye–Hückel theory of ion atmospheres. The plot of electrical potential against distance from the electrode surface shows the meaning of the diffuse double layer (see text for details).

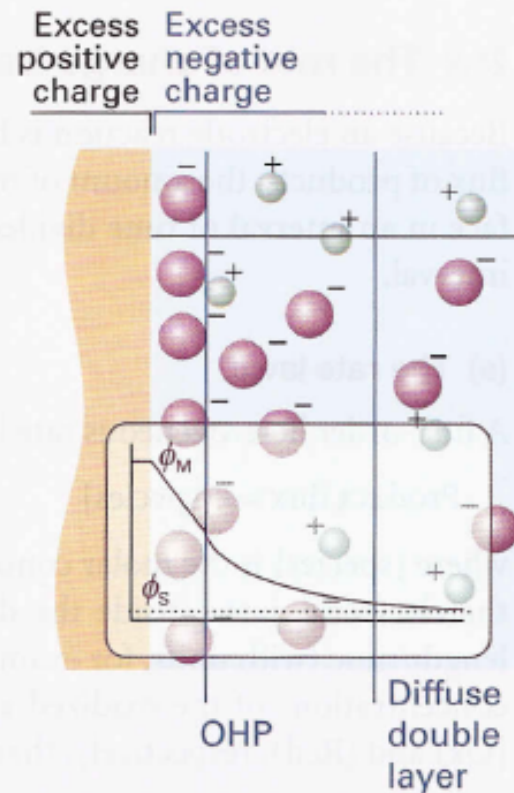


Fig. 25.32 A representation of the Stern model of the electrode–solution interface. The model incorporates the idea of an outer Helmholtz plane near the electrode surface and of a diffuse double layer further away from the surface.

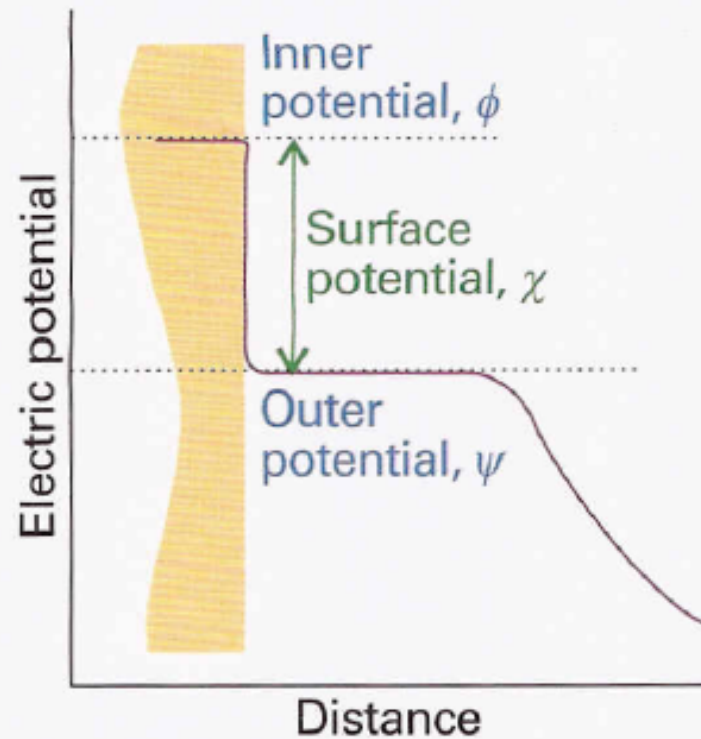


Fig. 25.33 The variation of potential with distance from an electrode that has been separated from the electrolyte solution without there being an adjustment of charge. A similar diagram applies to the separated solution.

$$v_{\text{Ox}} = k_c[\text{Ox}]$$

$$j_c = Fk_c[\text{Ox}] \quad \text{for} \quad \text{Ox} + e^- \rightarrow \text{Red}$$

$$v_{\text{Red}} = k_a[\text{Red}]$$

$$j_a = Fk_a[\text{Red}] \quad \text{for} \quad \text{Red} \rightarrow \text{Ox} + e^-$$

$$j = j_a - j_c = Fk_a[\text{Red}] - Fk_c[\text{Ox}]$$

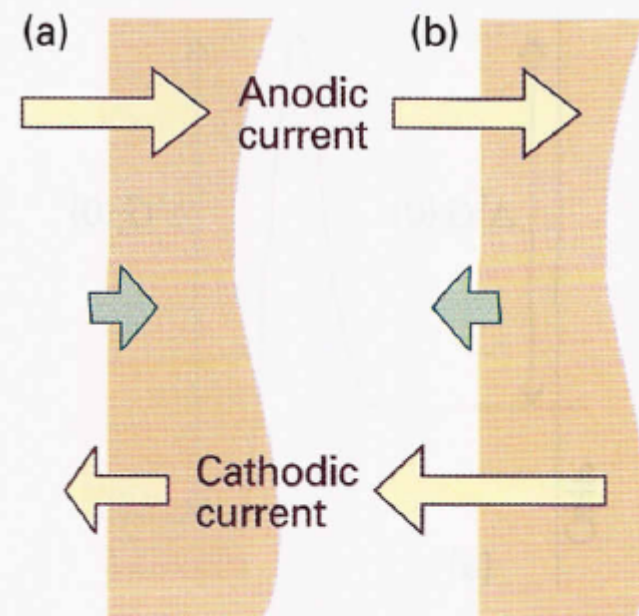


Fig. 25.35 The net current density is defined as the difference between the cathodic and anodic contributions. (a) When $j_a > j_c$, the net current is anodic, and there is a net oxidation of the species in solution. (b) When $j_c > j_a$, the net current is cathodic, and the net process is reduction.

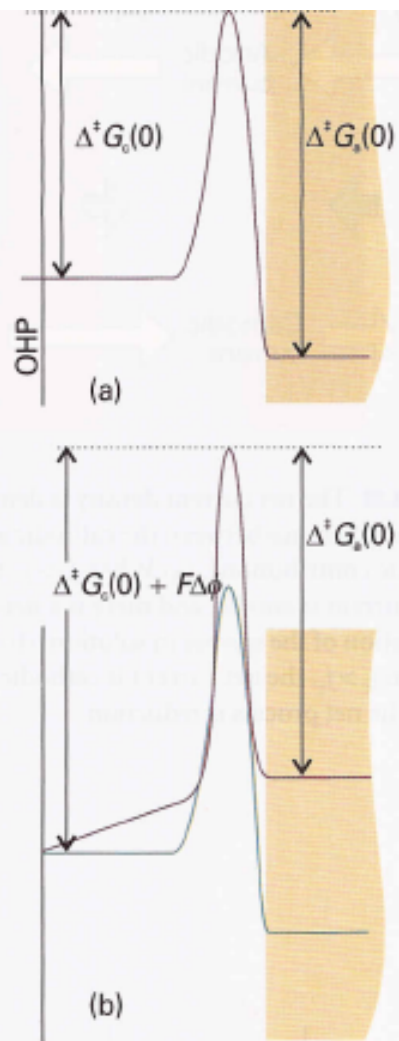


Fig. 25.37 When the transition state resembles a species that has undergone reduction, the activation Gibbs energy for the anodic current is almost unchanged, but the full effect applies to the cathodic current. (a) Zero potential difference; (b) nonzero potential difference.

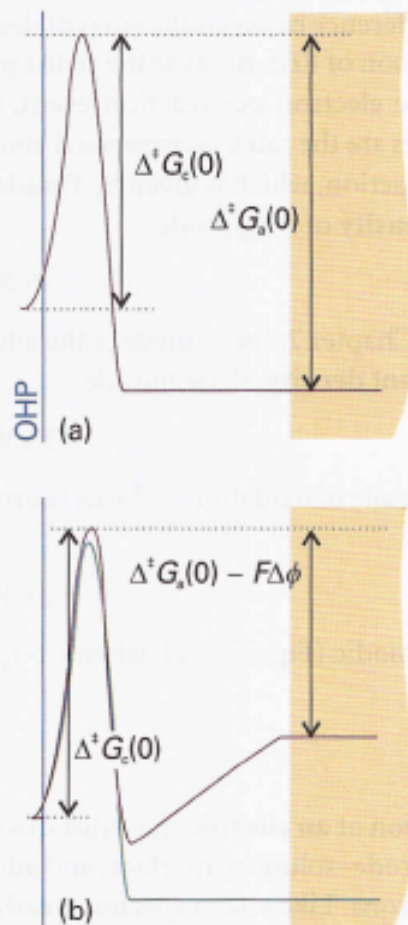


Fig. 25.38 When the transition state resembles a species that has undergone oxidation, the activation Gibbs energy for the cathodic current is almost unchanged but the activation Gibbs energy for the anodic current is strongly affected. (a) Zero potential difference; (b) nonzero potential difference.

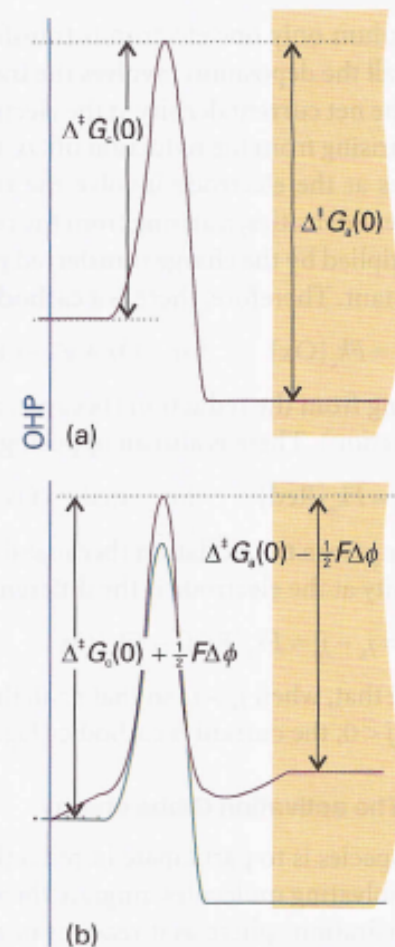


Fig. 25.39 When the transition state is intermediate in its resemblance to reduced and oxidized species, as represented here by a peak located at an intermediate position as measured by α (with $0 < \alpha < 1$), both activation Gibbs energies are affected; here, $\alpha \approx 0.5$. (a) Zero potential difference; (b) nonzero potential difference.

$$j = j_a - j_c = Fk_a[\text{Red}] - Fk_c[\text{Ox}]$$

$$k = B e^{-\Delta^\ddagger G/RT}$$

$$j = FB_a[\text{Red}]e^{-\Delta^\ddagger G_a/RT} - FB_c[\text{Ox}]e^{-\Delta^\ddagger G_c/RT}$$

$$\Delta^\ddagger G_c = \Delta^\ddagger G_c(0) + \alpha F \Delta \phi$$

$$\Delta^\ddagger G_a = \Delta^\ddagger G_a(0) - (1 - \alpha) F \Delta \phi$$

$$j = FB_a[\text{Red}]e^{-\Delta^\ddagger G_a(0)/RT} e^{(1-\alpha)F\Delta\phi/RT} - FB_c[\text{Ox}]e^{-\Delta^\ddagger G_c(0)/RT} e^{-\alpha F\Delta\phi/RT}$$

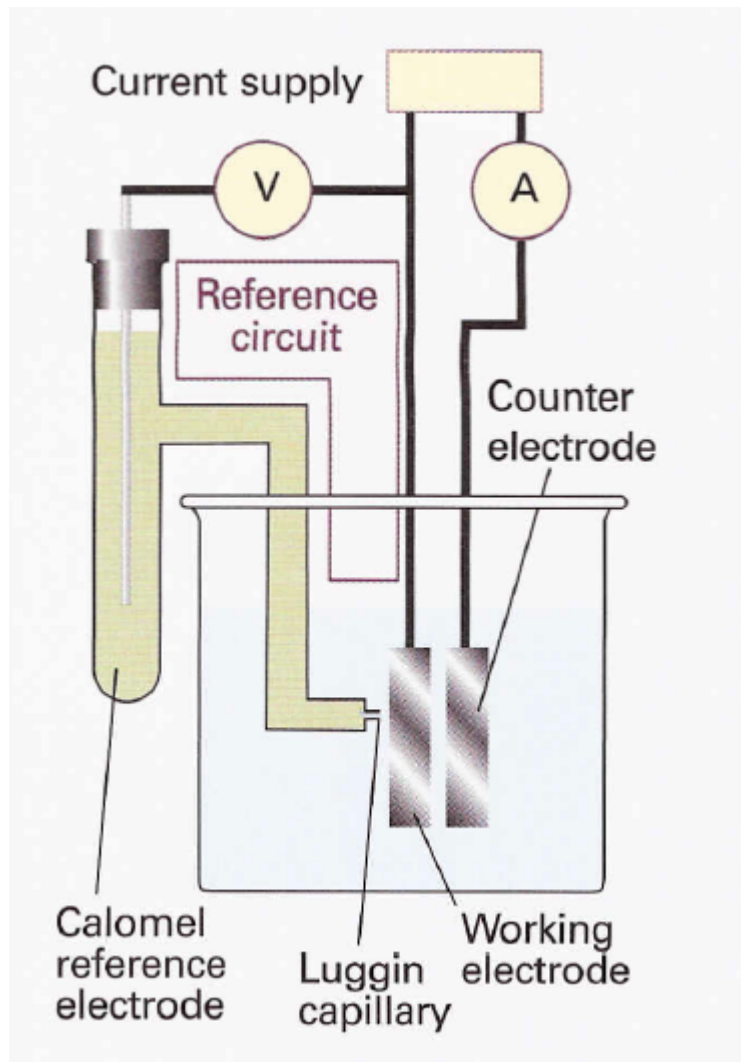
$$\left. \begin{aligned} j_a &= FB_a[\text{Red}]e^{-\Delta^\ddagger G_a(0)/RT} e^{(1-\alpha)f\Delta\phi} \\ j_c &= FB_c[\text{Ox}]e^{-\Delta^\ddagger G_c(0)/RT} e^{-\alpha f\Delta\phi} \end{aligned} \right\} j = j_a - j_c$$

$$f = \frac{F}{RT}$$

Equação de Butler-Volmer

$$j = j_0 \{ e^{(1-\alpha)f\eta} - e^{-\alpha f\eta} \}$$

$$\eta = E - E^0$$



Gráficos de Tafel

The data below refer to the anodic current through 2.0 cm^2 in contact with an $\text{Fe}^{3+}, \text{Fe}^{2+}$ aqueous solution. The exchange current density and the transfer coefficient are unknown.

η/mV	50	100	150	200	250
I/mA	8.8	25.0	58.0	131	290

η/mV	50	100	1
$j/(\text{mA cm}^{-2})$	4.4	12.5	2
$\ln(j/(\text{mA cm}^{-2}))$	1.48	2.53	3

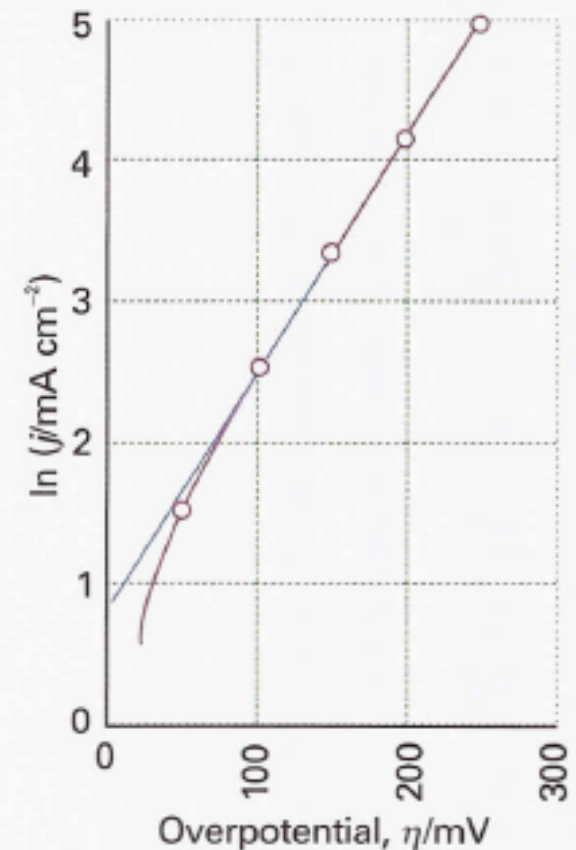


Fig. 25.41 A Tafel plot is used to measure the exchange current density (given by the extrapolated intercept at $\eta = 0$) and the transfer coefficient (from the slope). The data are from Example 25.4.

Corrosão



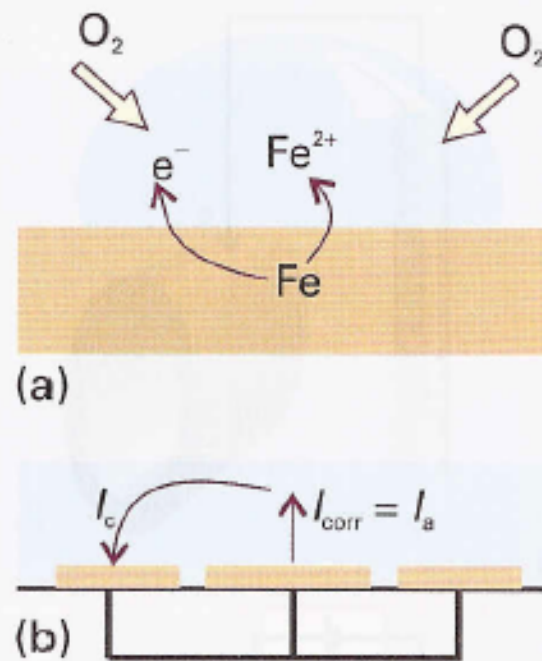


Fig. 25.50 (a) A simple version of the corrosion process is that of a droplet of water, which is oxygen rich near its boundary with air. The oxidation of the iron takes place in the region away from the oxygen because the electrons are transported through the metal. (b) The process may be modelled as a short-circuited electrochemical cell.

