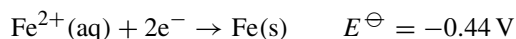


29 Dynamics of electron transfer

Solutions to exercises

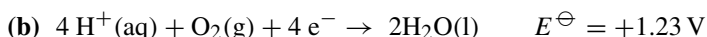
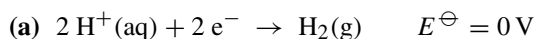
Discussion questions

- E29.1(b)** No solution.
- E29.2(b)** The net current density at an electrode is j ; j_0 is the exchange current density; α is the transfer coefficient; f is the ratio F/RT ; and η is the overpotential.
- (a) $j = j_0 f \eta$ is the current density in the low overpotential limit.
- (b) $j = j_0 e^{(1-\alpha)f\eta}$ applies when the overpotential is large and positive.
- (c) $j = -j_0 e^{-\alpha f\eta}$ applies when the overpotential is large and negative.
- E29.3(b)** In cyclic voltammetry, the current at a working electrode is monitored as the applied potential difference is changed back and forth at a constant rate between pre-set limits (Figs 29.20 and 29.21). As the potential difference approaches E^\ominus (Ox, Red) for a solution that contains the reduced component (Red), current begins to flow as Red is oxidized. When the potential difference is swept beyond E^\ominus (Ox, Red), the current passes through a maximum and then falls as all the Red near the electrode is consumed and converted to Ox, the oxidized form. When the direction of the sweep is reversed and the potential difference passes through E^\ominus (Ox, Red), current flows in the reverse direction. This current is caused by the reduction of the Ox formed near the electrode on the forward sweep. It passes through the maximum as Ox near the electrode is consumed. The forward and reverse current maxima bracket E^\ominus (Ox, Red), so the species present can be identified. Furthermore, the forward and reverse peak currents are proportional to the concentration of the couple in the solution, and vary with the sweep rate. If the electron transfer at the electrode is rapid, so that the ratio of the concentrations of Ox and Red at the electrode surface have their equilibrium values for the applied potential (that is, their relative concentrations are given by the Nernst equation), the voltammetry is said to be *reversible*. In this case, the peak separation is independent of the sweep rate and equal to $(59 \text{ mV})/n$ at room temperature, where n is the number of electrons transferred. If the rate of electron transfer is low, the voltammetry is said to be *irreversible*. Now, the peak separation is greater than $(59 \text{ mV})/n$ and increases with increasing sweep rate. If homogeneous chemical reactions accompany the oxidation or reduction of the couple at the electrode, the shape of the voltammogram changes, and the observed changes give valuable information about the kinetics of the reactions as well as the identities of the species present.
- E29.4(b)** Corrosion is an electrochemical process. We will illustrate it with the example of the rusting of iron, but the same principles apply to other corrosive processes. The electrochemical basis of corrosion in the presence of water and oxygen is revealed by comparing the standard potentials of the metal reduction, such as

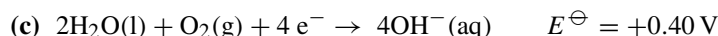


with the values for one of the following half-reactions

In acidic solution



In basic solution:



Because all three redox couples have standard potentials more positive than $E^\ominus(\text{Fe}^{2+}/\text{Fe})$, all three can drive the oxidation of iron to iron(II). The electrode potentials we have quoted are standard values, and they change with the pH of the medium. For the first two

$$E(\text{a}) = E^\ominus(\text{a}) + (RT/F) \ln a(\text{H}^+) = -(0.059 \text{ V})\text{pH}$$

$$E(\text{b}) = E^\ominus(\text{b}) + (RT/F) \ln a(\text{H}^+) = 1.23 \text{ V} - (0.059 \text{ V})\text{pH}$$

These expressions let us judge at what pH the iron will have a tendency to oxidize (see Chapter 10). A thermodynamic discussion of corrosion, however, only indicates whether a tendency to corrode exists. If there is a thermodynamic tendency, we must examine the kinetics of the processes involved to see whether the process occurs at a significant rate. The effect of the exchange current density on the corrosion rate can be seen by considering the specific case of iron in contact with acidified water. Thermodynamically, either the hydrogen or oxygen reduction reaction (a) or (b) is effective. However, the exchange current density of reaction (b) on iron is only about $10^{-14} \text{ A cm}^{-2}$, whereas for (a) it is $10^{-6} \text{ A cm}^{-2}$. The latter therefore dominates kinetically, and iron corrodes by hydrogen evolution in acidic solution. For corrosion reactions with similar exchange current densities, eqn 29.62 predicts that the rate of corrosion is high when E is large. That is, rapid corrosion can be expected when the oxidizing and reducing couples have widely differing electrode potentials.

Several techniques for inhibiting corrosion are available. First, from eqn 62 we see that the rate of corrosion depends on the surfaces exposed: if either A or A' is zero, then the corrosion current is zero. This interpretation points to a trivial, yet often effective, method of slowing corrosion: cover the surface with some impermeable layer, such as paint, which prevents access of damp air. Paint also increases the effective solution resistance between the cathode and anode patches on the surface.

Another form of surface coating is provided by galvanizing, the coating of an iron object with zinc. Because the latter's standard potential is -0.76 V , which is more negative than that of the iron couple, the corrosion of zinc is thermodynamically favoured and the iron survives (the zinc survives because it is protected by a hydrated oxide layer).

Another method of protection is to change the electric potential of the object by pumping in electrons that can be used to satisfy the demands of the oxygen reduction without involving the oxidation of the metal. In cathodic protection, the object is connected to a metal with a more negative standard potential (such as magnesium, -2.36 V). The magnesium acts as a sacrificial anode, supplying its own electrons to the iron and becoming oxidized to Mg^{2+} in the process.

Numerical exercises

E29.5(b) Equation 29.14 holds for a donor–acceptor pair separated by a constant distance, assuming that the reorganization energy is constant:

$$\ln k_{\text{et}} = -\frac{(\Delta_{\text{r}}G^\ominus)^2}{4\lambda RT} - \frac{\Delta_{\text{r}}G^\ominus}{2RT} + \text{constant},$$

or equivalently

$$\ln k_{\text{et}} = -\frac{(\Delta_{\text{r}}G^\ominus)^2}{4\lambda kT} - \frac{\Delta_{\text{r}}G^\ominus}{2kT} + \text{constant},$$

if energies are expressed as molecular rather than molar quantities. Two sets of rate constants and reaction Gibbs energies can be used to generate two equation (eqn 29.14 applied to the two sets) in

two unknowns: λ and the constant.

$$\ln k_{\text{et},1} + \frac{(\Delta_r G_1^\ominus)^2}{4\lambda kT} + \frac{\Delta_r G_1^\ominus}{2kT} = \text{constant} = \ln k_{\text{et},2} + \frac{(\Delta_r G_2^\ominus)^2}{4\lambda kT} + \frac{\Delta_r G_2^\ominus}{2kT},$$

$$\text{so } \frac{(\Delta_r G_1^\ominus)^2 - (\Delta_r G_2^\ominus)^2}{4\lambda kT} = \ln \frac{k_{\text{et},2}}{k_{\text{et},1}} + \frac{\Delta_r G_2^\ominus - \Delta_r G_1^\ominus}{2kT}$$

$$\text{and } \lambda = \frac{(\Delta_r G_1^\ominus)^2 - (\Delta_r G_2^\ominus)^2}{4 \left(kT \ln \frac{k_{\text{et},2}}{k_{\text{et},1}} + \frac{\Delta_r G_2^\ominus - \Delta_r G_1^\ominus}{2} \right)},$$

$$\lambda = \frac{(-0.665 \text{ eV})^2 - (-0.975 \text{ eV})^2}{\frac{4(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{1.602 \times 10^{-19} \text{ J eV}^{-1}} \ln \frac{3.33 \times 10^6}{2.02 \times 10^5} - 2(0.975 - 0.665) \text{ eV}} = \boxed{1.531 \text{ eV}}$$

If we knew the activation Gibbs energy, we could use eqn 29.12 to compute $\langle H_{\text{DA}} \rangle$ from either rate constant, and we *can* compute the activation Gibbs energy from eqn 29.4:

$$\Delta^\ddagger G = \frac{(\Delta_r G^\ominus + \lambda)^2}{4\lambda} = \frac{[(-0.665 + 1.531) \text{ eV}]^2}{4(1.531 \text{ eV})} = 0.122 \text{ eV}.$$

$$\text{Now } k_{\text{et}} = \frac{2 \langle H_{\text{DA}} \rangle^2}{h} \left(\frac{\pi^3}{4\lambda kT} \right)^{1/2} \exp \left(\frac{-\Delta^\ddagger G}{kT} \right),$$

$$\text{so } \langle H_{\text{DA}} \rangle = \left(\frac{hk_{\text{et}}}{2} \right)^{1/2} \left(\frac{4\lambda kT}{\pi^3} \right)^{1/4} \exp \left(\frac{\Delta^\ddagger G}{2kT} \right),$$

$$\begin{aligned} \langle H_{\text{DA}} \rangle &= \left(\frac{(6.626 \times 10^{-34} \text{ J s})(2.02 \times 10^5 \text{ s}^{-1})}{2} \right)^{1/2} \\ &\times \left(\frac{4(1.531 \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})}{\pi^3} \right)^{1/4} \\ &\times \exp \left(\frac{(0.122 \text{ eV})(1.602 \times 10^{-19} \text{ J eV}^{-1})}{2(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} \right) = \boxed{9.39 \times 10^{-24} \text{ J}} \end{aligned}$$

E29.6(b) Equation 29.13 applies. In E29.6(a), we found the parameter β to equal 12 nm^{-1} , so:

$$\ln k_{\text{et}}/\text{s}^{-1} = -\beta r + \text{constant} \quad \text{so} \quad \text{constant} = \ln k_{\text{et}}/\text{s}^{-1} + \beta r,$$

$$\text{and constant} = \ln 2.02 \times 10^5 + (12 \text{ nm}^{-1})(1.11 \text{ nm}) = 25.$$

Taking the exponential of eqn 29.13 yields:

$$k_{\text{et}} = e^{-\beta r + \text{constant}} \text{s}^{-1} = e^{-(12/\text{nm})(1.48 \text{ nm}) + 25} \text{s}^{-1} = \boxed{1.4 \times 10^3 \text{ s}^{-1}}.$$

E29.7(b) Disregarding signs, the electric field is the gradient of the electrical potential

$$\mathcal{E} = \frac{d\Delta\phi}{dx} \approx \frac{\Delta\phi}{d} = \frac{\sigma}{\varepsilon} = \frac{\sigma}{\varepsilon_r \varepsilon_0} = \frac{0.12 \text{ C m}^{-2}}{(48) \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1})} = \boxed{2.8 \times 10^8 \text{ V m}^{-1}}$$

E29.8(b) In the high overpotential limit

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \frac{j_1}{j_2} = e^{(1-\alpha)f(\eta_1 - \eta_2)} \quad \text{where} \quad f = \frac{F}{RT} = \frac{1}{25.69 \text{ mV}}$$

The overpotential η_2 is

$$\begin{aligned} \eta_2 &= \eta_1 + \frac{1}{f(1-\alpha)} \ln \frac{j_2}{j_1} = 105 \text{ mV} + \left(\frac{25.69 \text{ mV}}{1-0.42} \right) \times \ln \left(\frac{7255 \text{ mA cm}^{-2}}{17.0 \text{ mA cm}^{-2}} \right) \\ &= \boxed{373 \text{ mV}} \end{aligned}$$

E29.9(b) In the high overpotential limit

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

$$j_0 = (17.0 \text{ mA cm}^{-2}) \times e^{\{(0.42-1) \times (105 \text{ mV}) / (25.69 \text{ mV})\}} = \boxed{1.6 \text{ mA cm}^{-2}}$$

E29.10(b) In the high overpotential limit

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \frac{j_1}{j_2} = e^{(1-\alpha)f(\eta_1 - \eta_2)} \quad \text{and} \quad j_2 = j_1 e^{(1-\alpha)f(\eta_2 - \eta_1)}$$

So the current density at 0.60 V is

$$j_2 = (1.22 \text{ mA cm}^{-2}) \times e^{\{(1-0.50) \times (0.60 \text{ V} - 0.50 \text{ V}) / (0.02569 \text{ V})\}} = \boxed{8.5 \text{ mA cm}^{-2}}$$

Note. The exercise says the data refer to the same material and at the same temperature as the previous exercise (29.10(a)), yet the results for the current density at the same overpotential differ by a factor of over 5!

E29.11(b) (a) The Butler–Volmer equation gives

$$\begin{aligned} j &= j_0 (e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}) \\ &= (2.5 \times 10^{-3} \text{ A cm}^{-2}) \times (e^{\{(1-0.58) \times (0.30 \text{ V}) / (0.02569 \text{ V})\}} - e^{-\{(0.58) \times (0.30 \text{ V}) / (0.02569 \text{ V})\}}) \\ &= \boxed{0.34 \text{ A cm}^{-2}} \end{aligned}$$

(b) According to the Tafel equation

$$\begin{aligned} j &= j_0 e^{(1-\alpha)f\eta} \\ &= (2.5 \times 10^{-3} \text{ A cm}^{-2}) e^{\{(1-0.58) \times (0.30 \text{ V}) / (0.02569 \text{ V})\}} = \boxed{0.34 \text{ A cm}^{-2}} \end{aligned}$$

The validity of the Tafel equation improves as the overpotential increases.

E29.12(b) The limiting current density is

$$j_{\text{lim}} = \frac{zFDc}{\delta}$$

but the diffusivity is related to the ionic conductivity (Chapter 24)

$$D = \frac{\lambda RT}{z^2 F^2} \quad \text{so} \quad j_{\text{lim}} = \frac{c\lambda}{\delta z f}$$

$$\begin{aligned} j_{\text{lim}} &= \frac{(1.5 \text{ mol m}^{-3}) \times (10.60 \times 10^{-3} \text{ S m}^2 \text{ mol}^{-1}) \times (0.02569 \text{ V})}{(0.32 \times 10^{-3} \text{ m}) \times (+1)} \\ &= \boxed{1.3 \text{ A m}^{-2}} \end{aligned}$$

E29.13(b) For the iron electrode $E^\ominus = -0.44 \text{ V}$ (Table 10.7) and the Nernst equation for this electrode (Section 10.5) is

$$E = E^\ominus - \frac{RT}{\nu F} \ln\left(\frac{1}{[\text{Fe}^{2+}]}\right) \quad \nu = 2$$

Since the hydrogen overpotential is 0.60 V evolution of H_2 will begin when the potential of the Fe electrode reaches -0.60 V . Thus

$$-0.60 \text{ V} = -0.44 \text{ V} + \frac{0.02569 \text{ V}}{2} \ln[\text{Fe}^{2+}]$$

$$\ln[\text{Fe}^{2+}] = \frac{-0.16 \text{ V}}{0.0128 \text{ V}} = -12.5$$

$$[\text{Fe}^{2+}] = \boxed{4 \times 10^{-6} \text{ mol L}^{-1}}$$

Comment. Essentially all Fe^{2+} has been removed by deposition before evolution of H_2 begins.

E29.14(b) The zero-current potential of the electrode is given by the Nernst equation

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q = E^\ominus - \frac{1}{f} \ln \frac{a(\text{Fe}^{2+})}{a(\text{Fe}^{3+})} = 0.77 \text{ V} - \frac{1}{f} \ln \frac{a(\text{Fe}^{2+})}{a(\text{Fe}^{3+})}$$

The Butler–Volmer equation gives

$$j = j_0(e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}) = j_0(e^{(0.42)f\eta} - e^{-0.58f\eta})$$

where η is the overpotential, defined as the working potential E' minus the zero-current potential E .

$$\eta = E' - 0.77 \text{ V} + \frac{1}{f} \ln \frac{a(\text{Fe}^{2+})}{a(\text{Fe}^{3+})} = E' - 0.77 \text{ V} + \frac{1}{f} \ln r,$$

where r is the ratio of activities; so

$$j = j_0(e^{(0.42)E'/f} e^{\{(0.42) \times (-0.77 \text{ V}) / (0.02569 \text{ V})\}} r^{0.42} - e^{(-0.58)E'/f} e^{\{(-0.58) \times (-0.77 \text{ V}) / (0.02569 \text{ V})\}} r^{-0.58})$$

Specializing to the condition that the ions have equal activities yields

$$j = \boxed{(2.5 \text{ mA cm}^{-2}) \times [e^{(0.42)E'/f} \times (3.41 \times 10^{-6}) - e^{(-0.58)E'/f} \times (3.55 \times 10^7)]}$$

E29.15(b) *Note.* The exercise did not supply values for j_0 or α . Assuming $\alpha = 0.5$, only j/j_0 is calculated. From Exercise 29.14(b)

$$j = j_0(e^{(0.50)E'/f} e^{-(0.50)E^\ominus/f} r^{0.50} - e^{(-0.50)E'/f} e^{(0.50)E^\ominus/f} r^{-0.50}) \\ = 2j_0 \sinh\left[\frac{1}{2}fE' - \frac{1}{2}fE^\ominus + \frac{1}{2} \ln r\right],$$

so, if the working potential is set at 0.50 V, then

$$j = 2j_0 \sinh\left[\frac{1}{2}(0.91 \text{ V}) / (0.02569 \text{ V}) + \frac{1}{2} \ln r\right] \\ j/j_0 = 2 \sinh(8.48 + \frac{1}{2} \ln r)$$

$$\text{At } r = 0.1: \quad j/j_0 = 2 \sinh(8.48 + \frac{1}{2} \ln 0.10) = 1.5 \times 10^3 \text{ mA cm}^{-2} = \boxed{1.5 \text{ A cm}^{-2}}$$

$$\text{At } r = 1: j/j_0 = 2 \sinh(8.4\bar{8} + 0.0) = 4.8 \times 10^3 \text{ mA cm}^{-2} = \boxed{4.8 \text{ A cm}^{-2}}$$

$$\text{At } r = 10: j/j_0 = 2 \sinh(8.4\bar{8} + \frac{1}{2} \ln 10) = 1.5 \times 10^4 \text{ mA cm}^{-2} = \boxed{15 \text{ A cm}^{-2}}$$

E29.16(b) The potential needed to sustain a given current depends on the activities of the reactants, but the overpotential does not. The Butler–Volmer equation says

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

This cannot be solved analytically for η , but in the high-overpotential limit, it reduces to the Tafel equation

$$j = j_0 e^{(1-\alpha)f\eta} \quad \text{so} \quad \eta = \frac{1}{(1-\alpha)f} \ln \frac{j}{j_0} = \frac{0.02569 \text{ V}}{1-0.75} \ln \frac{15 \text{ mA cm}^{-2}}{4.0 \times 10^{-2} \text{ mA cm}^{-2}}$$

$$\eta = \boxed{0.61 \text{ V}}$$

This is a sufficiently large overpotential to justify use of the Tafel equation.

E29.17(b) The number of singly charged particles transported per unit time per unit area at equilibrium is the exchange current density divided by the charge

$$N = \frac{j_0}{e}$$

The frequency f of participation per atom on an electrode is

$$f = Na$$

where a is the effective area of an atom on the electrode surface.

For the Cu, $\text{H}_2|\text{H}^+$ electrode

$$N = \frac{j_0}{e} = \frac{1.0 \times 10^{-6} \text{ A cm}^{-2}}{1.602 \times 10^{-19} \text{ C}} = \boxed{6.2 \times 10^{12} \text{ s}^{-1} \text{ cm}^{-2}}$$

$$f = Na = (6.2 \times 10^{12} \text{ s}^{-1} \text{ cm}^{-2}) \times (260 \times 10^{-10} \text{ cm})^2 \\ = \boxed{4.2 \times 10^{-3} \text{ s}^{-1}}$$

For the Pt| Ce^{4+} , Ce^{3+} electrode

$$N = \frac{j_0}{e} = \frac{4.0 \times 10^{-5} \text{ A cm}^{-2}}{1.602 \times 10^{-19} \text{ C}} = \boxed{2.5 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}}$$

The frequency f of participation per atom on an electrode is

$$f = Na = (2.5 \times 10^{14} \text{ s}^{-1} \text{ cm}^{-2}) \times (260 \times 10^{-10} \text{ cm})^2 = \boxed{0.17 \text{ s}^{-1}}$$

E29.18(b) The resistance R of an ohmic resistor is

$$R = \frac{\text{potential}}{\text{current}} = \frac{\eta}{jA}$$

where A is the surface area of the electrode. The overpotential in the low overpotential limit is

$$\eta = \frac{j}{fj_0} \quad \text{so} \quad R = \frac{1}{fj_0A}$$

$$(a) \quad R = \frac{0.02569 \text{ V}}{(5.0 \times 10^{-12} \text{ A cm}^{-2}) \times (1.0 \text{ cm}^2)} = 5.1 \times 10^9 \Omega = \boxed{5.1 \text{ G}\Omega}$$

$$(b) \quad R = \frac{0.02569 \text{ V}}{(2.5 \times 10^{-3} \text{ A cm}^{-2}) \times (1.0 \text{ cm}^2)} = \boxed{10 \Omega}$$

E29.19(b) No reduction of cations to metal will occur until the cathode potential is dropped below the zero-current potential for the reduction of Ni^{2+} (-0.23 V at unit activity). Deposition of Ni will occur at an appreciable rate after the potential drops significantly below this value; however, the deposition of Fe will begin (albeit slowly) after the potential is brought below -0.44 V . If the goal is to deposit pure Ni, then the Ni will be deposited rather slowly at just above -0.44 V ; then the Fe can be deposited rapidly by dropping the potential well below -0.44 V .

E29.20(b) As was noted in Exercise 29.10(a), an overpotential of 0.6 V or so is necessary to obtain significant deposition or evolution, so H_2 is evolved from acid solution at a potential of about -0.6 V . The reduction potential of Cd^{2+} is more positive than this (-0.40 V), so Cd will deposit (albeit slowly) from Cd^{2+} before H_2 evolution.

E29.21(b) Zn can be deposited if the H^+ discharge current is less than about 1 mA cm^{-2} . The exchange current, according to the high negative overpotential limit, is

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

At the standard potential for reduction of Zn^{2+} (-0.76 V)

$$j = (0.79 \text{ mA cm}^{-2}) \times e^{-\{(0.5) \times (-0.76 \text{ V}) / (0.02569 \text{ V})\}} = 2.1 \times 10^9 \text{ mA cm}^{-2}$$

$\boxed{\text{much too large to allow deposition}}$. (That is, H_2 would begin being evolved, and fast, long before Zn began to deposit.)

E29.22(b) Fe can be deposited if the H^+ discharge current is less than about 1 mA cm^{-2} . The exchange current, according to the high negative overpotential limit, is

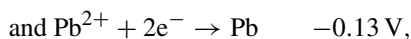
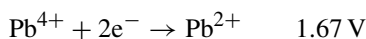
$$j = j_0 e^{-\alpha f \eta}$$

At the standard potential for reduction of Fe^{2+} (-0.44 V)

$$j = (1 \times 10^{-6} \text{ A cm}^{-2}) \times e^{-\{(0.5) \times (-0.44 \text{ V}) / (0.02569 \text{ V})\}} = 5.2 \times 10^{-3} \text{ A cm}^{-2}$$

$\boxed{\text{a bit too large to allow deposition}}$. (That is, H_2 would begin being evolved at a moderate rate before Fe began to deposit.)

E29.23(b) The lead acid battery half-cells are



for a total of $E^\ominus = \boxed{1.80 \text{ V}}$. Power is

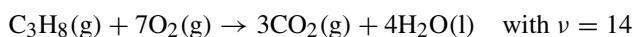
$$P = IV = (100 \times 10^{-3} \text{ A}) \times (1.80 \text{ V}) = \boxed{0.180 \text{ W}}$$

if the cell were operating at its zero-current potential yet producing 100 mA .

E29.24(b) The thermodynamic limit to the zero-current potential under standard conditions is the standard potential E^\ominus , which is related to the standard Gibbs energy by

$$\Delta_r G^\ominus = -\nu F E^\ominus \quad \text{so} \quad E^\ominus = \frac{-\Delta_r G^\ominus}{\nu F}$$

The reaction is



$$\begin{aligned} \Delta_r G^\ominus &= 3\Delta_f G^\ominus(\text{CO}_2) + 4\Delta_f G^\ominus(\text{H}_2\text{O}) - \Delta_f G^\ominus(\text{C}_3\text{H}_8) - 7\Delta_f G^\ominus(\text{O}_2) \\ &= (3 \times (-394.36)) + 4 \times (-237.13) - (-23.49) - 0 \text{ kJ mol}^{-1} = -1319.4 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{so } E^\ominus = \frac{1319.39 \times 10^3 \text{ J mol}^{-1}}{14 \times (96485 \text{ C mol}^{-1})} = \boxed{0.97675 \text{ V}}$$

E29.25(b) Two electrons are lost in the corrosion of each zinc atom, so the number of zinc atoms lost is half the number of electrons which flow per unit time, i.e. half the current divided by the electron charge. The volume taken up by those zinc atoms is their number divided by their number density; their number density is their mass density divided by molar mass times Avogadro's number. Dividing the volume of the corroded zinc over the surface from which they are corroded gives the linear corrosion rate; this affects the calculation by changing the current to the current density. So the rate of corrosion is

$$\begin{aligned} \text{rate} &= \frac{jM}{2e\rho N_A} = \frac{(1.0 \text{ A m}^{-2}) \times (65.39 \times 10^{-3} \text{ kg mol}^{-1})}{2(1.602 \times 10^{-19} \text{ C}) \times (7133 \text{ kg m}^{-3}) \times (6.022 \times 10^{23} \text{ mol}^{-1})} \\ &= 4.8 \times 10^{-11} \text{ m s}^{-1} \\ &= (4.8 \times 10^{-11} \text{ m s}^{-1}) \times (10^3 \text{ mm m}^{-1}) \times (3600 \times 24 \times 365 \text{ s y}^{-1}) \\ &= \boxed{1.5 \text{ mm y}^{-1}} \end{aligned}$$

Solutions to problems

Solutions to numerical problems

P29.3
$$E = E^\ominus + \frac{RT}{zF} \ln a(\text{M}^+)$$

Deposition may occur when the potential falls to below E and so simultaneous deposition will occur if the two potentials are the same; hence the relative activities are given by

$$E^\ominus(\text{Sn}, \text{Sn}^{2+}) + \frac{RT}{2F} \ln a(\text{Sn}^{2+}) = E^\ominus(\text{Pb}, \text{Pb}^{2+}) + \frac{RT}{2F} \ln a(\text{Pb}^{2+})$$

$$\text{or } \ln \frac{a(\text{Sn}^{2+})}{a(\text{Pb}^{2+})} = \left(\frac{2F}{RT} \right) \{E^\ominus(\text{Pb}, \text{Pb}^{2+}) - E^\ominus(\text{Sn}, \text{Sn}^{2+})\} = \frac{(2) \times (-0.126 + 0.136) \text{ V}}{0.0257 \text{ V}} = 0.78$$

That is, we require $a(\text{Sn}^{2+}) \approx 2.2a(\text{Pb}^{2+})$

P29.8
$$r_D = \left(\frac{\varepsilon RT}{2\rho F^2 I b^\ominus} \right)^{1/2} \quad [22.50]$$

where $I = \frac{1}{2} \sum_i z_i^2 (b_i/b^\ominus)$, $b^\ominus = 1 \text{ mol kg}^{-1}$ [10.18]

For NaCl: $Ib^\ominus = b_{\text{NaCl}} \approx [\text{NaCl}]$ assuming 100 per cent dissociation.

For Na_2SO_4 : $Ib^\ominus = \frac{1}{2} ((1)^2(2b_{\text{Na}_2\text{SO}_4}) + (2)^2b_{\text{Na}_2\text{SO}_4})$
 $= 3b_{\text{Na}_2\text{SO}_4} \approx 3[\text{Na}_2\text{SO}_4]$ assuming 100 per cent dissociation.

$$r_D \approx \left(\frac{78.54 \times (8.854 \times 10^{-12} \text{ J}^{-1} \text{ C}^2 \text{ m}^{-1}) \times (8.315 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298.15 \text{ K})}{2 \times (1.00 \text{ g cm}^{-3}) \times \left(\frac{10^{-3} \text{ kg}}{\text{g}}\right) \times \left(\frac{10^6 \text{ cm}^3}{\text{m}^3}\right) \times (96485 \text{ C mol}^{-1})^2} \right)^{1/2} \times \left(\frac{1}{Ib^\ominus}\right)^{1/2}$$

$$\approx \frac{3.043 \times 10^{-10} \text{ m mol}^{1/2} \text{ kg}^{-1/2}}{(Ib^\ominus)^{1/2}}$$

$$\approx \frac{304.3 \text{ pm mol}^{1/2} \text{ kg}^{-1/2}}{(Ib^\ominus)^{1/2}}$$

These equations can be used to produce the graph of r_D against b_{salt} shown in Fig. 29.1. Note the contraction of the double layer with increasing ionic strength.

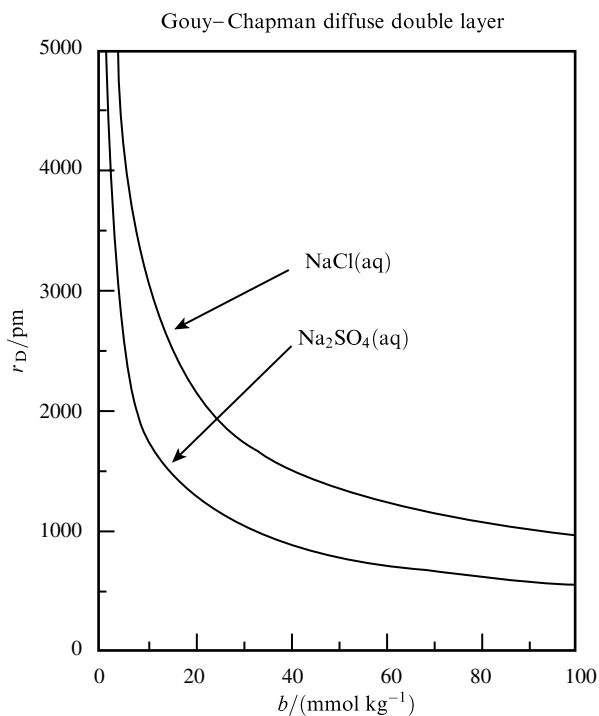
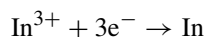


Figure 29.1

P29.9 This problem differs somewhat from the simpler one-electron transfers considered in the text. In place of $\text{Ox} + e^- \rightarrow \text{Red}$ we have here



namely, a three-electron transfer. Therefore eqns 29.25, 29.26, and all subsequent equations including the Butler–Volmer equation [29.35] and the Tafel equations [29.38–29.41] need to be modified by

including the factor z (in this case 3) in the equation. Thus, in place of eqn 29.26, we have

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

and in place of eqns 29.39 and 29.41

$$\ln j = \ln j_0 + z(1 - \alpha)f\eta \quad \text{anode}$$

$$\ln(-j) = \ln j_0 - z\alpha f\eta \quad \text{cathode}$$

We draw up the following table

$j/(\text{A m}^{-2})$	$-E/\text{V}$	η/V	$\ln(j/(\text{A m}^{-2}))$
0	0.388	0	
0.590	0.365	0.023	-0.5276
1.438	0.350	0.038	0.3633
3.507	0.335	0.053	1.255

We now do a linear regression of $\ln j$ against η with the following results (see Fig. 29.2)

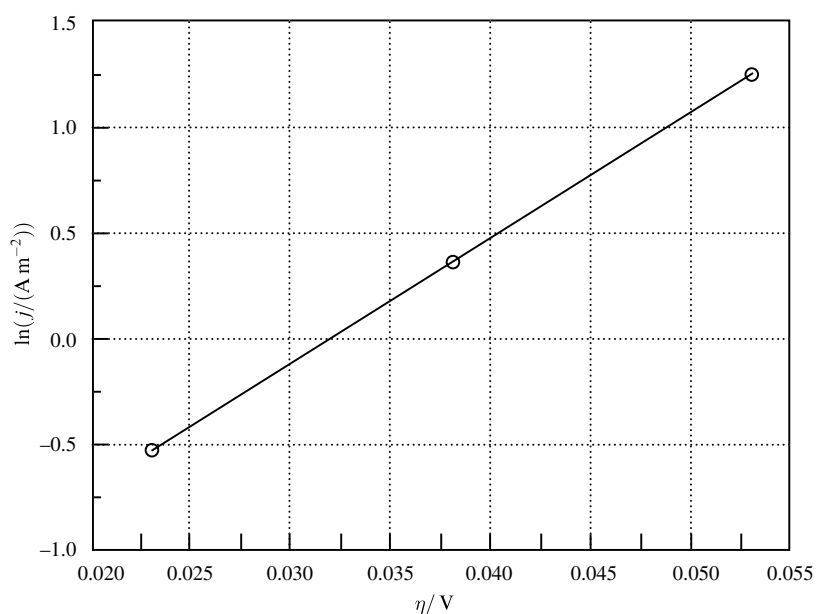


Figure 29.2

$$z(1 - \alpha)f = 59.42 \text{ V}^{-1}, \quad \text{standard deviation} = 0.0154$$

$$\ln j_0 = -1.894, \quad \text{standard deviation} = 0.0006$$

$$R = 1 \text{ (almost exact)}$$

Thus, although there are only three data points, the fit to the Tafel equation is almost exact. Solving for α from $z(1 - \alpha)f = 59.42 \text{ V}^{-1}$, we obtain

$$\begin{aligned} \alpha &= 1 - \frac{59.42 \text{ V}^{-1}}{3f} = 1 - \left(\frac{59.42 \text{ V}^{-1}}{3} \right) \times (0.025262 \text{ V}) \\ &= 0.4996 = \boxed{0.50} \end{aligned}$$

which matches the usual value of α exactly.

$$j_0 = e^{-1.894} = \boxed{0.150 \text{ A m}^{-2}}$$

The cathodic current density is obtained from

$$\begin{aligned} \ln(-j_c) &= \ln j_0 - z\alpha f\eta \quad \eta = 0.023 \text{ V at } -E/V = 0.365 \\ &= -1.894 - (3 \times 0.4996 \times 0.023)/(0.025262) \\ &= -3.259 \end{aligned}$$

$$-j_c = e^{-3.259} = 0.0384 \text{ A m}^{-2}$$

$$j_c = \boxed{-0.038 \text{ A m}^{-2}}$$

P29.12 At large positive values of the overpotential the current density is anodic.

$$j = j_0 \left[e^{(1-\alpha)f\eta} - e^{-\alpha f\eta} \right] \quad [29.35]$$

$$\approx j_0 e^{(1-\alpha)f\eta} = j_a \quad [29.34]$$

$$\ln j = \ln j_0 + (1-\alpha)f\eta$$

Performing a linear regression analysis of $\ln j$ against η , we find

$$\ln(j_0/(\text{mA m}^{-2})) = -10.826, \quad \text{standard deviation} = 0.287$$

$$(1-\alpha)f = 19.550 \text{ V}^{-1}, \quad \text{standard deviation} = 0.355$$

$$\boxed{R = 0.99901}$$

$$j_0 = e^{-10.826} \text{ mA m}^{-2} = \boxed{2.00 \times 10^{-5} \text{ mA m}^{-2}}$$

$$\alpha = 1 - \frac{19.550 \text{ V}^{-1}}{f} = 1 - \frac{19.550 \text{ V}^{-1}}{(0.025693 \text{ V})^{-1}}$$

$$\boxed{\alpha = 0.498}$$

The linear regression explains 99.90 per cent of the variation in a $\ln j$ against η plot and standard deviations are low. There are deviations from the Tafel equation/plot.

Solutions to theoretical problems

P29.14 (a) First, assume that eqn 4 applies to the bimolecular processes under consideration in this problem. (Cf. P29.1.) Thus,

$$\Delta^\ddagger G_{11} = \frac{(\Delta_r G_{11}^\ominus + \lambda_{11})^2}{4\lambda_{11}}, \quad \Delta^\ddagger G_{22} = \frac{(\Delta_r G_{22}^\ominus + \lambda_{22})^2}{4\lambda_{22}}, \quad \Delta^\ddagger G_{12} = \frac{(\Delta_r G_{12}^\ominus + \lambda_{12})^2}{4\lambda_{12}}$$

Because the standard free energy for electron self-exchange is zero, these simplify to:

$$\Delta^\ddagger G_{11} = \frac{\lambda_{11}^2}{4\lambda_{11}} = \lambda_{11}/4 \quad \text{and} \quad \Delta^\ddagger G_{22} = \lambda_{22}/4.$$

$$\Delta^\ddagger G_{12} = \frac{(\Delta_r G_{12}^\ominus)^2 + \lambda_{12}^2 + 2\lambda_{12}\Delta_r G_{12}^\ominus}{4\lambda_{12}}$$

(b) If $\Delta_r G_{12}^\ominus \ll \lambda_{12}$, then we may drop the quadratic term in the numerator, leaving:

$$\Delta^\ddagger G_{12} \approx \lambda_{12}/4 + \Delta_r G_{12}^\ominus/2.$$

Assume that $\lambda_{12} = (\lambda_{11} + \lambda_{22})/2$, so

$$\lambda_{12}/4 = (\lambda_{11}/4 + \lambda_{22}/4)/2 = (\Delta^\ddagger G_{11} + \Delta^\ddagger G_{22})/2.$$

Thus, we have:

$$\Delta^\ddagger G_{12} \approx (\Delta^\ddagger G_{11} + \Delta^\ddagger G_{22} + \Delta_r G_{12}^\ominus)/2.$$

(c) According to activated complex theory, we can write for the self-exchange reactions:

$$k_{11} = \kappa_{11} \nu_{11} \exp\left(\frac{-\Delta^\ddagger G_{11}}{RT}\right) \quad \text{and} \quad k_{22} = \kappa_{22} \nu_{22} \exp\left(\frac{-\Delta^\ddagger G_{22}}{RT}\right).$$

(d) According to activated complex theory, we can write:

$$k_{12} = \kappa_{12} \nu_{12} \exp\left(\frac{-\Delta^\ddagger G_{12}}{RT}\right) \approx \kappa_{12} \nu_{12} \exp\left(\frac{-\Delta^\ddagger G_{11} - \Delta^\ddagger G_{22} - \Delta_r G_{12}^\ominus}{2RT}\right).$$

(e) Finally, we simplify by assuming that all $\kappa \nu$ terms are identical, so:

$$k_{12} \approx \left[\kappa \nu \exp\left(\frac{-\Delta^\ddagger G_{11}}{RT}\right) \kappa \nu \exp\left(\frac{-\Delta^\ddagger G_{22}}{RT}\right) \exp\left(\frac{-\Delta_r G_{12}^\ominus}{RT}\right) \right]^1 / 2.$$

The final exponential is the equilibrium constant; the first two exponentials with their factors of $\kappa \nu$ are electron self-exchange rate constants, so:

$$k_{12} \approx (k_{11} k_{22} K)^{1/2}.$$

P29.16 Let η oscillate between η_+ and η_- around a mean value η_0 . Then η_- is large and positive (and $\eta_+ > \eta_-$),

$$j \approx j_0 e^{(1-\alpha)\eta f} = j_0 e^{(1/2)\eta f} \quad [\alpha = 0.5]$$

and η varies as depicted in Fig. 29.3(a).

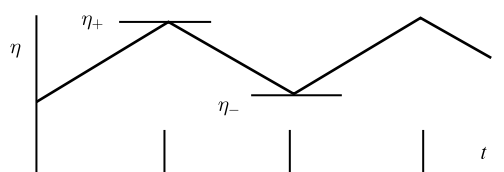


Figure 29.3(a)

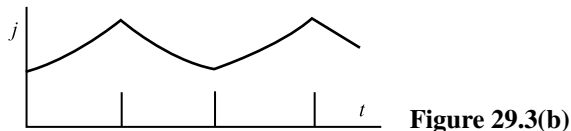
Therefore, j is a chain of increasing and decreasing exponential functions,

$$j = j_0 e^{(\eta_+ + \gamma t) f / 2} \propto e^{-t/\tau}$$

during the increasing phase of η , where $\tau = \frac{2RT}{\gamma F}$, γ a constant, and

$$j = j_0 e^{(\eta_+ - \gamma t) f / 2} \propto e^{-t/\tau}$$

during the decreasing phase. This is depicted in Fig. 29.3(b).



P29.17

$$j = \left(\frac{cFD}{\delta} \right) \times (1 - e^{f\eta^c}) [29.51; z = 1] = j_L (1 - e^{F\eta^c/RT})$$

The form of this expression is illustrated in Fig. 29.4.

For the anion current, the sign of η^c is changed, and the current of anions approaches its limiting value as η^c becomes more positive (Fig. 29.4).

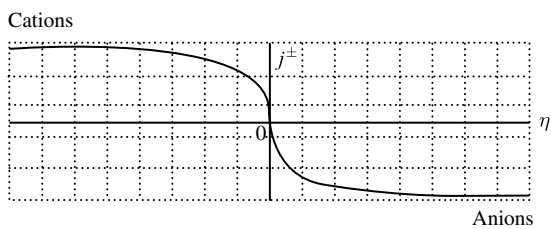


Figure 29.4

P29.19 Does eqn 29.13

$$\ln k_{\text{et}} = -\beta r + \text{constant}$$

apply to these data? Draw the following table:

r/nm	$k_{\text{et}}/\text{s}^{-1}$	$\ln k_{\text{et}}/\text{s}^{-1}$
0.48	1.58×10^{12}	28.1
0.95	3.98×10^9	22.1
0.96	1.00×10^9	20.7
1.23	1.58×10^8	18.9
1.35	3.98×10^7	17.5
2.24	6.31×10^1	4.14

and plot $\ln k_{\text{et}}$ vs. r

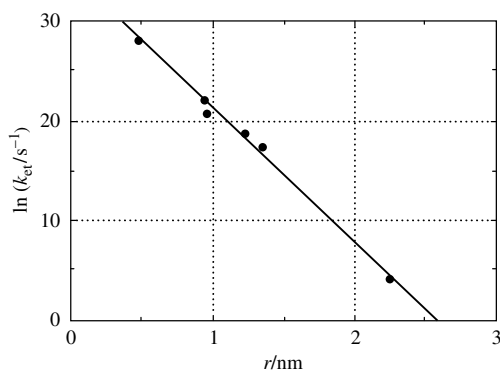


Figure 29.5

The data fall on a good straight line, so the equation appears to apply. The least squares linear fit equation is:

$$\ln k_{\text{et}}/s = 34.7 - 13.4r/\text{nm} \quad r^2(\text{correlation coefficient}) = 0.991$$

so we identify $\beta = 13.4 \text{ nm}^{-1}$.

P29.20 The theoretical treatment of section 29.1 applies only at relatively high temperatures. At temperatures above 130 K, the reaction in question is observed to follow a temperature dependence consistent with eqn 29.12, namely increasing rate with increasing temperature. Below 130 K, the temperature-dependent terms in eqn 29.12 are replaced by Frank–Condon factors; that is, temperature-dependent terms are replaced by temperature-independent wavefunction overlap integrals.

P29.21 (a) The electrode potentials of half-reactions (a), (b), and (c) are (Section 29.8)

$$\text{(a)} \quad E(\text{H}_2, \text{H}^+) = -0.059 \text{ V pH} = (-7) \times (0.059 \text{ V}) = -0.14 \text{ V}$$

$$\text{(b)} \quad E(\text{O}_2, \text{H}^+) = (1.23 \text{ V}) - (0.059 \text{ V})\text{pH} = +0.82 \text{ V}$$

$$\text{(c)} \quad E(\text{O}_2, \text{OH}^-) = (0.40 \text{ V}) + (0.059 \text{ V})\text{pOH} = 0.81 \text{ V}$$

$$E(\text{M}, \text{M}^+) = E^\ominus(\text{M}, \text{M}^+) + \left(\frac{0.059 \text{ V}}{z_+} \right) \log 10^{-6} = E^\ominus(\text{M}, \text{M}^+) - \frac{0.35 \text{ V}}{z_+}$$

Corrosion will occur if $E(\text{a})$, $E(\text{b})$, or $E(\text{c}) > E(\text{M}, \text{M}^+)$

$$\text{(i)} \quad E^\ominus(\text{Fe}, \text{Fe}^{2+}) = -0.44 \text{ V}, \quad z_+ = 2$$

$$E(\text{Fe}, \text{Fe}^{2+}) = (-0.44 - 0.18) \text{ V} = -0.62 \text{ V} < E(\text{a}, \text{b}, \text{ and c})$$

$$\text{(ii)} \quad E(\text{Cu}, \text{Cu}^+) = (0.52 - 0.35) \text{ V} = 0.17 \text{ V} \begin{cases} > E(\text{a}) \\ < E(\text{b and c}) \end{cases}$$

$$E(\text{Cu}, \text{Cu}^{2+}) = (0.34 - 0.18) \text{ V} = 0.16 \text{ V} \begin{cases} > E(\text{a}) \\ < E(\text{b and c}) \end{cases}$$

$$\text{(iii)} \quad E(\text{Pb}, \text{Pb}^{2+}) = (-0.13 - 0.18) \text{ V} = -0.31 \text{ V} \begin{cases} > E(\text{a}) \\ < E(\text{b and c}) \end{cases}$$

$$\text{(iv)} \quad E(\text{Al}, \text{Al}^{3+}) = (-1.66 - 0.12) \text{ V} = -1.78 \text{ V} < E(\text{a}, \text{b}, \text{ and c})$$

$$\text{(v)} \quad E(\text{Ag}, \text{Ag}^+) = (0.80 - 0.35) \text{ V} = 0.45 \text{ V} \begin{cases} > E(\text{a}) \\ < E(\text{b and c}) \end{cases}$$

$$\text{(vi)} \quad E(\text{Cr}, \text{Cr}^{3+}) = (-0.74 - 0.12) \text{ V} = -0.86 \text{ V} < E(\text{a}, \text{b}, \text{ and c})$$

$$\text{(vii)} \quad E(\text{Co}, \text{Co}^{2+}) = (-0.28 - 0.15) \text{ V} = -0.43 \text{ V} < E(\text{a}, \text{b}, \text{ and c})$$

Therefore, the metals with a thermodynamic tendency to corrode in moist conditions at pH = 7 are Fe, Al, Co, Cr if oxygen is absent, but, if oxygen is present, all seven elements have a tendency to corrode.

(b) A metal has a thermodynamic tendency to corrosion in moist air if the zero-current potential for the reduction of the metal ion is more negative than the reduction potential of the half-reaction



The zero-current cell potential is given by the Nernst equation

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q = E^\ominus - \frac{RT}{\nu F} \ln \frac{[\text{M}^{z+}]^{\nu/z}}{[\text{H}^+]^\nu p(\text{O}_2)^{\nu/4}}$$

We are asked if a tendency to corrode exists at pH 7 ($[\text{H}^+] = 10^{-7}$) in moist air ($p(\text{O}_2) \approx 0.2 \text{ bar}$), and are to answer yes if $E \geq 0$ for a metal ion concentration of 10^{-6} , so for $\nu = 4$

and 2+ cations

$$E = 1.23 \text{ V} - E_{\text{M}}^{\ominus} - \frac{0.02569 \text{ V}}{\nu} \ln \frac{(10^{-6})^2}{(1 \times 10^{-7})^4 \times (0.2)} = 0.983 \text{ V} - E_{\text{M}}^{\ominus}$$

In the following, $z = 2$

For Ni: $E^{\ominus} = 0.983 \text{ V} - (-0.23 \text{ V}) > 0$ corrodes

For Cd: $E^{\ominus} = 0.983 \text{ V} - (-0.40 \text{ V}) > 0$ corrodes

For Mg: $E^{\ominus} = 0.983 \text{ V} - (-2.36 \text{ V}) > 0$ corrodes

For Ti: $E^{\ominus} = 0.983 \text{ V} - (-1.63 \text{ V}) > 0$ corrodes

For Mn: $E^{\ominus} = 0.983 \text{ V} - (-1.18 \text{ V}) > 0$ corrodes

P29.22

$$I_{\text{corr}} = \bar{A} j_0 e^{fE/4} \quad [29.62]$$

with $E = -0.62 - (-0.94) \text{ V} = 0.32 \text{ V}$ [as in Problem 29.21]

$$I_{\text{corr}} \approx (0.25 \times 10^{-6} \text{ A}) \times (e^{0.32/4 \times 0.0257}) \approx \boxed{6 \mu\text{A}}$$