Class Activity 02-06

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Chem 524
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For a one-electron couple $O + e^- \rightleftharpoons R$, the Nernst equation relates the electrode potential to the ratio of the surface concentrations at $x = 0$. In these three cases we use the Nernst relation and the surface mass balance $C_O(x=0) + C_R(x=0) = C^*$ with $C^* = 1\mathrm{mM}$.

Part A $E = E^\circ$

Surface Equilibrium at E°

What are the surface concentrations $C_O(x=0)$ and $C_R(x=0)$ when the electrode potential equals the formal potential, given the Nernst relation and total concentration $C_O(x=0) + C_R(x=0) = C^* = 1\mathrm{mM}$?

At $E = E^\circ$, we evaluate the Nernst equation at the surface and use the result to determine the ratio C_R/C_O.

$$E = E^\circ - \frac{0.059}{n}\log_{10}\left(\frac{C_R(x=0)}{C_O(x=0)}\right)$$

Substitute the condition $E = E^\circ$ and $n = 1$:

$$E^\circ = E^\circ - 0.059\log_{10}\left(\frac{C_R(x=0)}{C_O(x=0)}\right)$$

$$\begin{aligned}
E^\circ = E^\circ - 0.059\log_{10}\left(\frac{C_R}{C_O}\right) &\Rightarrow E^\circ - E^\circ = \left(E^\circ - 0.059\log_{10}\left(\frac{C_R}{C_O}\right)\right) - E^\circ \\
&\Rightarrow 0 = -0.059\log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow \frac{0}{-0.059} = \log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow 0 = \log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow 10^0 = \frac{C_R}{C_O} \\
&\Rightarrow 1 = \frac{C_R}{C_O} \\
&\Rightarrow C_R = C_O
\end{aligned}$$

Use the surface mass balance $C_O(x=0) + C_R(x=0) = C^*$

$$\begin{aligned} C_O + C_R = C^* &\Rightarrow C_O + C_O = C^* \\ &\Rightarrow 2C_O = C^* \\ &\Rightarrow C_O = \frac{C^*}{2} \end{aligned}$$

Plug in $C^* = 1\mathrm{mM}$:

$$C_O = \frac{1\mathrm{mM}}{2} \Rightarrow C_O = 0.5\mathrm{mM}$$

Finally, since $C_R = C_O$:

$$C_R = 0.5\mathrm{mM}$$

So when $E = E^\circ$, the Nernst relation gives $C_R/C_O = 1$, so the surface concentrations split evenly:

$$C_O(x=0) = C_R(x=0) = 0.5\mathrm{mM}$$

Part B $E = E^\circ - 0.12\ \mathrm{V}$

Cathodic Polarization

What are the surface concentrations $C_O(x=0)$ and $C_R(x=0)$ when the electrode potential is 0.12 V below the formal potential, given the Nernst relation and total concentration $C_O(x=0) + C_R(x=0) = C^* = 1\mathrm{mM}$?

A cathodic shift ($E < E^\circ$) makes the logarithm term positive, so the surface ratio C_R/C_O becomes greater than 1. We compute that ratio and apply the mass balance.

$$E = E^\circ - 0.059 \log_{10}\left(\frac{C_R(x=0)}{C_O(x=0)}\right)$$

Substitute $E = E^\circ - 0.12\ \mathrm{V}$ (and $n = 1$):

$$E^\circ - 0.12 = E^\circ - 0.059\log_{10}\left(\frac{C_R(x=0)}{C_O(x=0)}\right)$$

$$\begin{aligned}
E^\circ - 0.12 = E^\circ - 0.059\log_{10}\left(\frac{C_R}{C_O}\right) &\Rightarrow (E^\circ - 0.12) - E^\circ = \left(E^\circ - 0.059\log_{10}\left(\frac{C_R}{C_O}\right)\right) - E^\circ \\
&\Rightarrow -0.12 = -0.059\log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow \frac{-0.12}{-0.059} = \log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow \frac{0.12\times 1000}{0.059\times 1000} = \log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow \frac{120}{59} = \log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow 10^{120/59} = \frac{C_R}{C_O} \\
&\Rightarrow C_R = 10^{120/59} C_O
\end{aligned}$$

$$\begin{aligned}
10^{120/59} &\approx 10^{2.03} \approx 1.08\times 10^2 \approx 108 \\
&\Rightarrow \frac{C_R(x=0)}{C_O(x=0)} \approx 108 \\
&\Rightarrow C_R(x=0) \approx 108 C_O(x=0)
\end{aligned}$$

Now use the surface mass balance $C_O(x=0) + C_R(x=0) = C^*$:

$$\begin{aligned}
C_O + C_R = C^* &\Rightarrow C_O + 108C_O = C^* \\
&\Rightarrow 109C_O = C^* \\
&\Rightarrow C_O = \frac{C^*}{109} \\
&\Rightarrow C_R = 108C_O = \frac{108C^*}{109}
\end{aligned}$$

With $C^* = 1\mathrm{mM}$, we have:

$$\begin{aligned}
C_O &= \frac{1\mathrm{mM}}{109} \approx 9.17\times 10^{-3}\mathrm{mM} \\
C_R &= 1\mathrm{mM} - C_O \approx 1\mathrm{mM} - 0.00917\mathrm{mM} \approx 0.991\mathrm{mM}
\end{aligned}$$

$$9.17\times 10^{-3}\mathrm{mM} = 9.17\mu\mathrm{M}$$

Under cathodic polarization, $C_R/C_O \approx 108$, so the reduced form dominates at the surface:

$$C_O(x=0) \approx 9.17\mu\mathrm{M}, \quad C_R(x=0) \approx 0.991\mathrm{mM}.$$

Part C $E = E^\circ + 0.12\ \mathrm{V}$

Anodic Polarization

What are the surface concentrations $C_O(x=0)$ and $C_R(x=0)$ when the electrode potential is 0.12 V above the formal potential, given the Nernst relation and total concentration $C_O(x=0)+C_R(x=0)=C^*=1\text{mM}$?

An anodic shift $(E > E^\circ)$ reverses the ratio from Part B. The surface ratio C_R/C_O becomes less than 1 by the same factor, and the mass balance then gives the individual concentrations.

$$E = E^\circ - 0.059\log_{10}\left(\frac{C_R(x=0)}{C_O(x=0)}\right)$$

Substitute the Part C condition $E = E^\circ + 0.12\ \text{V}$:

$$E^\circ + 0.12 = E^\circ - 0.059\log_{10}\left(\frac{C_R(x=0)}{C_O(x=0)}\right)$$

$$\begin{aligned}
E^\circ + 0.12 = E^\circ - 0.059\log_{10}\left(\frac{C_R}{C_O}\right) &\Rightarrow (E^\circ + 0.12) - E^\circ = \left(E^\circ - 0.059\log_{10}\left(\frac{C_R}{C_O}\right)\right) - E^\circ \\
&\Rightarrow 0.12 = -0.059\log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow \frac{0.12}{-0.059} = \log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow -\frac{120}{59} = \log_{10}\left(\frac{C_R}{C_O}\right) \\
&\Rightarrow 10^{-120/59} = \frac{C_R}{C_O} \\
&\Rightarrow \frac{C_R}{C_O} = \frac{1}{10^{120/59}}
\end{aligned}$$

$$\begin{aligned}
&10^{120/59} \approx 108 \\
&\Rightarrow \quad \frac{C_R}{C_O} = \frac{1}{10^{120/59}} \approx \frac{1}{108} \\
&\Rightarrow \quad C_R \approx \frac{1}{108}C_O
\end{aligned}$$

Use the surface mass balance $C_O(x=0)+C_R(x=0)=C^*$:

$$\begin{aligned}
C_O + C_R = C^* &\Rightarrow C_O + \frac{1}{108}C_O = C^* \\
&\Rightarrow \left(1 + \frac{1}{108}\right)C_O = C^* \\
&\Rightarrow \frac{109}{108}C_O = C^* \\
&\Rightarrow C_O = \frac{108}{109}C^* \\
&\Rightarrow C_R = C^* - C_O
\end{aligned}$$

Now plug in $C^* = 1\text{mM}$:

$$C_O(x=0) = \frac{108}{109}(1\text{mM}) \approx 0.991\text{mM}$$
$$C_R(x=0) = 1\text{mM} - 0.991\text{mM} \approx 9.17 \times 10^{-3}\text{mM}$$

Under anodic polarization, the oxidized form dominates at the surface:

$$C_O(x=0) \approx 0.991\text{mM}, \quad C_R(x=0) \approx 9.17 \times 10^{-3}\text{mM} \approx 9.17\mu\text{M}$$