ELECTROCHEMISTRY

THE NERNST EQUATION: NONSTANDARD CONDITIONS

CHEMISTRY 165 // SPRING 2020

DR. MIOY T. HUYNH | 2020

PRACTICE PROBLEM 1

$Co\ (s)\ |\ Co^{2+}\ (0.15\ M)\ ||\ Fe^{2+}\ (1.94\ M)\ |\ Fe\ (s)$ $\qquad E^{o}_{\text{cell}} = -0.170\ \text{V}$

Based on the cell diagram above and standard cell potential, is the constructed cell spontaneous at 298.15 K?

— answer —

PRACTICE PROBLEM 1

Co (s) | Co^{2+} (0.15 M) || Fe^{2+} (1.94 M) | Fe (s) $E^{o}_{cell} = -0.170\ \mathrm{V}$

Based on the cell diagram above and standard cell potential, is the constructed cell spontaneous at 298.15 K?

— answer —

First, write out the balanced net ionic equation for the cell reaction.

Cathode (Reduction):	Fe^{2+} (aq)	+	2 e^-	→	Fe (s)		
Anode (Oxidation):			Co (s)	→	Co^{2+} (aq)	+	2 e–
Cell	Co (s)	+	Fe^{2+} (aq)	→	Co^{2+} (aq)	+	Fe (s)

We can use the Nernst equation to determine the nonstandard cell potential:

$$E_{\text{cell}} = E^{o}_{\text{cell}} - \frac{RT}{nF}\ln\frac{[\text{Co}^{2+}]}{[\text{Fe}^{2+}]}$$

$$= -0.170\ \text{V} - \frac{\left(8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15\ \text{K})}{(2\ \text{mol}\ e^{-})\left(96485\,\frac{\text{C}}{\text{mol}}\right)}\ln\frac{0.15}{1.94}$$

$$E_{\text{cell}} = -0.137\ \text{V}$$

Because the $E_{\text{cell}} < 0$, this reaction/cell is still nonspontaneous.

PRACTICE PROBLEM 2

$$Cu\ (s) + 2\ Ag^{+}\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s) \qquad E^{o}_{cell} = +0.458\ \mathrm{V}$$

If the value of $E_{cell} = +0.396\ \mathrm{V}$ when $[Ag^{+}] = 2.56 \times 10^{-3}$ M at 298 K, what is $[Cu^{2+}]$?

— answer —

PRACTICE PROBLEM 2

$$Cu\ (s) + 2\ Ag^{+}\ (aq) \rightarrow Cu^{2+}\ (aq) + 2\ Ag\ (s) \qquad E^{o}_{\text{cell}} = +0.458\ \text{V}$$

If the value of $E_{\text{cell}} = +0.396\ \text{V}$ when $[Ag^{+}] = 2.56 \times 10^{-3}$ M at 298 K, what is $[Cu^{2+}]$?

– answer –

We can apply the Nernst equation find $[Cu^{2+}]$.

Be careful about the form of Q!

$$E_{\text{cell}} = E^{o}_{\text{cell}} - \frac{RT}{nF} \ln \frac{[\text{Cu}^{2+}]}{[\text{Ag}^{+}]^{2}}$$

$$+0.396\ \text{V} = +0.458\ \text{V} - \frac{\left(8.314 \frac{\text{J}}{\text{mol} \cdot \text{K}}\right)(298\ \text{K})}{(2\ \text{mol}\ e^{-})\left(96485 \frac{\text{C}}{\text{mol}}\right)} \ln \frac{[\text{Cu}^{2+}]}{(2.56 \times 10^{-3})^{2}}$$

$$[\text{Cu}^{2+}] = 8.25 \times 10^{-4}\ \text{M}$$

PRACTICE PROBLEM 3

What is the equilibrium constant (K) for the following cell reaction when the reaction reaches equilibrium at 25 °C?

$$2\ Ag^{+}\ (aq) + Fe\ (s) \rightleftharpoons 2\ Ag\ (s) + Fe^{2+}\ (aq) \qquad E^{o}_{\text{cell}} = +1.247\ \text{V}$$

— answer —

PRACTICE PROBLEM 3

What is the equilibrium constant (K) for the following cell reaction when the reaction reaches equilibrium at 25 °C?

$$2\ Ag^{+}\ (aq) + Fe\ (s) \rightleftharpoons 2\ Ag\ (s) + Fe^{2+}\ (aq) \qquad E^{o}_{\text{cell}} = +1.247\ \text{V}$$

— answer —

Recall that when a reaction reaches equilibrium $\Delta G = 0$ and $E_{\text{cell}} = 0\ \text{V}$ because $\Delta G = -nFE_{\text{cell}}$.

We can apply this in the Nernst equation to find the equilibrium constant (recall 1 V = 1 J/C):

$$E_{\text{cell}} = E^{o}_{\text{cell}} - \frac{RT}{nF}\ln K$$

$$0 = E^{o}_{\text{cell}} - \frac{RT}{nF}\ln K$$

$$\ln K = \frac{nFE^{o}_{\text{cell}}}{RT}$$

$$\ln K = \frac{(2)\left(96485\,\frac{\text{C}}{\text{mol}}\right)\left(1.247\,\frac{\text{J}}{\text{C}}\right)}{\left(8.314\,\frac{\text{J}}{\text{mol}\cdot\text{K}}\right)(298.15\ \text{K})}$$

$$K = 1._{4} \times 10^{42}$$

This should make sense since the E^{o}_{cell} value is very positive, so we expect a large K, which is a spontaneous reaction $\Delta G^{o} < 0$.