Example 1

What is the value of Ecell for the voltaic cell below:

$$Pt(s)|Fe^{2+}(0.1M),Fe^{3+}(0.2M)||Ag^{+}(0.1M)|Ag(s)$$

E_{cell}= ?

SOLUTION

To use the Nersnt equation, we need to establish $E°_{cell}$and the reaction to which the cell diagram corresponds so that the form of the reaction quotient (Q) can be revealed. Once we have determined the form of the Nernst equation, we can insert the concentration of the species.

Solve:

E°cell = E°*cathode*- E° *anode*

$= E°_{Ag/Ag} - E°_{Fe^{3+}/Fe^{2+}}$

= 0.800V-0.771V = 0.029V

Now to determine Ecell for the reaction

$$Fe^{2+}(0.1M) + Ag^{+}(1.0M) \rightarrow Fe^{3+}(0.20M) + Ag(s)$$

Use the Nernst equation

E_{cell}= 0.029V -(0.0592V/1)log $[Fe^{3+}]/[Fe^{2+}][Ag]$

=0.029V - 0.0592V*log [0.2]/[0.1]*[1.0]

=0.011V

Example 2

Question Find the E° cell for the following coupled half-reactions

SOLUTION

1. Determine the cathode and anode in the reaction

$Zn_{(s)} \leftrightarrow Zn^{2+}_{(aq)} + 2e^-$	Anode, Oxidation (since $Zn_{(s)}$ increase oxidation state from 0 to +2)
$Cu^{2+}_{(aq)} + 2e^- \leftrightarrow Cu_{(s)}$	Cathode, Reduction (since $Cu^{2+}_{(aq)}$ decreases oxidation state from +2 to 0)

2. Determine the E° cell values using the standard reduction potential table

$Zn_{(s)} \leftrightarrow Zn^{2+}_{(aq)} + 2e^-$	-0.763
$Cu^{2+}_{(aq)} + 2e^- \leftrightarrow Cu_{(s)}$	+0.340

3. Use **E° cell = E°cathode - E°anode**

= 0.340 - (-0.763)

= 1.103 V

Example: Using ΔG=-RTlnK

Given K = 2.81×10^{-16} for a following reaction $Cu^{2+}_{(aq)} + Ag_{(s)} \rightharpoonup Cu_{(s)} + 2Ag^{+}$ find ΔG.

Solution:

Use the following formula: **ΔG=-RTlnK**

$= 8.314 \times 298 \times \ln(2.81 \times 10^{-16}) = -8.87 \times 10^{5}$

= 8.871 kJ

Example: Using $\Delta G=-nFE^{\circ}_{cell}$

Find ΔG for the following reaction:

$$2Al_{(s)} + 3Br_{2(l)} \rightharpoonup 2Al^{3+}_{(aq,\ 1M)} + 6Br^{-}_{(aq,\ 1M)}$$

Solution:

Step 1: Separate the reaction into its two half reactions

$$2Al_{(s)} \rightharpoonup 2Al^{3+(aq)}$$

$$3Br^{2}_{(l)} \rightharpoonup 6Br^{-}_{(aq,\ 1M)}$$

Step 2: Balance the half equations using O, H, and charge using e-

$$2Al_{(s)} \rightharpoonup 2Al^{3+(aq)} + 6e^{-}$$

$$6e^{-} + 3Br^{2}_{(l)} \rightharpoonup 6Br^{-}_{(aq)}$$

Step 3: From the balanced half reactions, we can conclude the number of moles of e^{-} for use later in the calculation of ΔG. Determine the E° values using the standard reduction potentials, using the E° cell table.

$2Al_{2(s)} \rightharpoonup Al^{3+}_{(aq)} + 6e-$ -1.676V

$3Br_{2(l)} + 6e^{-} \rightharpoonup 6Br^{-}_{(aq)}$ +1.065V

Step 4: Determine $E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$.

$= 1.065 - (-1.676)$

= 2.741 V

Step 5: Once E° cell has be calculated and the number of moles of electrons have been determined, we can use $\Delta G = -nFE^{\circ}_{cell}$

$= (-6 \text{ mol } e^{-})(96458 \text{ C/mol } e^{-})(2.741 \text{ V})$

$= -1586 kJ$

This equation can be used to calculate E° cell given K or K given E°_{cell}. If T=298 K, the RT is a constant then the following equation can be used: $E^{\circ}_{cell} = (0.025693V/n) \ln K$

Example: Using E° cell=(RT/nF) lnK

Given the E° cell for the reaction $Cu_{(s)} + 2H^{+}_{(aq)} \rightharpoonup Cu^{2+}_{(aq)} + H_{2(g)}$ is -0.34V, find the equilibrium constant (K) for the reaction.

SOLUTION

Step 1: Split into two half reaction

$$Cu_{(s)} \rightharpoonup Cu^{2+}_{(aq)}$$

$$2H^{+}_{(aq)} \rightharpoonup H_{2(g)}$$

Step 2: Balance the half reactions with charges to determine n

$$Cu_{(s)} \rightharpoonup Cu^{2+}_{(aq)} + 2e^{-}$$

$$2H^{+}_{(aq)} + 2e^{-} \rightharpoonup H_{2(g)}$$

Therefore n=2

Step 3: From the example above, E° cell = -0.34V

$$-0.34 = (0.025693/2) \ln K$$

$$K = e^{(-0.34 \times 2/0.025693)}$$

$$K = 3.19 \times 10^{-12}$$

Example 1: I see you

Given the following reaction determine ΔG, K, and E°_{cell} for the following reaction at standard conditions? Is this reaction spontaneous?

$$Mn^{2+}_{(aq)} + K_{(s)} \hookrightarrow MnO_{2(s)} + K_{(aq)}$$

SOLUTION

Step 1: Separate and balance the half reactions. Label which one is reduction and which one is oxidation. Find the corresponding E° values for the half reactions.

$MnO_{2(s)} + 4H^{+}_{(aq)} + 2e \hookrightarrow Mn^{2+}_{(aq)} + 2H_2O_{(l)}$ Reduction +1.23V

$K^{+}_{(aq)} + e^{-} \hookrightarrow K_{(s)}$ Oxidation -2.92V

Step 2: Write net balanced reaction in acidic solution, and determine the E° cell.

E° cell = $E^{\circ}_{cathode} - E^{\circ}_{anode}$ = +1.23 - (-2.92) = 4.15

$Mn^{2+}_{(aq)} + 2K^{+}_{(aq)} + 2H_2O_{(l)} \hookrightarrow MnO_{2(s)} + 4H^{+}_{(aq)} + K_{(s)}$ E° cell = 4.15V

Step 3: Find ΔG for the reaction.

Use $\Delta G = -nFE^{\circ}_{cell}$

= -2 mol e^{-} x 96458 C x 4.15 = -800.60kJ

Therefore, since E°cell is positive and ΔG is negative, this reaction is spontaneous.

Source:http://chemwiki.ucdavis.edu/Analytical_Chemistry/Electrochemistry/Electrochemistry_and_Thermodynmics