Electrochemistry II

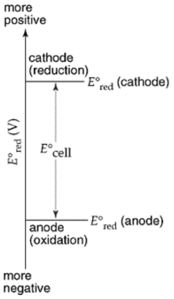
Electrochemistry

Cell Potential: Output of a Voltaic Cell

Free Energy and Electrical Work

Cell EMF

Standard Reduction Potentials



- The larger the difference between $E°_{red}$ values, the larger $E°_{cell}$.
- In a voltaic (galvanic) cell (spontaneous) $E°_{red}$(cathode) is more positive than $E°_{red}$(anode).

$$E°_{cell} = E°_{red}(\text{cathode}) - E°_{red}(\text{anode})$$

Note Cell Diagram:

Anode || Cathode

Standard Electrode (Half-Cell) Potentials E^o

A standard electrode potential always refers to the half-reaction written as a ***reduction:***

Oxidized form + n e^- $\longrightarrow$ reduced form $E^o_{half\text{-}cell}$

Reversing a reaction changes the sign of the potential:

Reduced form $\longrightarrow$ oxidized form + n e^- $-E^o_{half\text{-}cell}$

For the zinc-copper reaction:

$Zn^{2+}_{(aq)} + 2\ e^- \longrightarrow Zn_{(s)}$ E^o_{zinc} (E^o_{anode}) [reduction]

$Cu^{2+}_{(aq)} + 2\ e^- \longrightarrow Cu_{(s)}$ E^o_{copper}($E^o_{cathode}$) [reduction]

Standard Electrode (Half-Cell) Potentials E^o

Since the overall cell reaction involves the oxidation of zinc, we reverse the Zn reaction, and change the sign to get the cell potential:

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\ e^-$ $-E^o_{zinc}$($-E^o_{anode}$) [oxidation]

$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$ E^o_{copper}($-E^o_{cathode}$) [reduction]

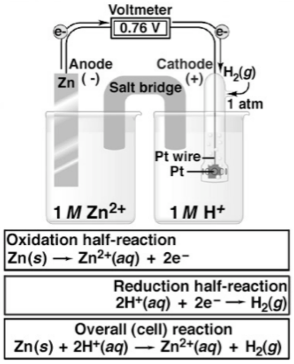
The overall redox reaction is the sum of these two:

$$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$$

$$E^o_{cell} = = E^o_{copper} - E^o_{zinc}$$

$$\mathbf{E^0_{cell} = E^o_{cathode\ (reduction\ potential)} - E^o_{anode\ (reduction\ potential)}}$$

Determining an Unknown $E°_{half\text{-}cell}$ with the Standard Reference (hydrogen) Electrode



Oxidation half-reaction
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Reduction half-reaction
$2H^+(aq) + 2e^- \longrightarrow H_2(g)$

Overall (cell) reaction
$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$

Standard Electrode Potentials - Part 1

Standard Electrode (Half-Cell) Potentials (298 K)*

Half-Reaction	E^0 (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-(aq)$	+2.87
$O_3(g) + 2H^+(aq) + 2e^- \rightleftharpoons O_2(g) + H_2O(l)$	+2.07
$Co^{3+}(aq) + e^- \rightleftharpoons Co^{2+}(aq)$	+1.82
$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightleftharpoons 2H_2O(l)$	+1.77
$PbO_2(s) + 4H^+(aq) + SO_4^{2-}(aq) + 2e^- \rightleftharpoons PbSO_4(s) + 2H_2O(l)$	+1.70
$Ce^{4+}(aq) + e^- \rightleftharpoons Ce^{3+}(aq)$	+1.61
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.51
$Au^{3+}(aq) + 3e^- \rightleftharpoons Au(s)$	+1.50
$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e^- \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$MnO_2(s) + 4H^+(aq) + 2e^- \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.07
$NO_3^-(aq) + 4H^+(aq) + 3e^- \rightleftharpoons NO(g) + 2H_2O(l)$	+0.96
$2Hg^{2+}(aq) + 2e^- \rightleftharpoons Hg_2^{2+}(aq)$	+0.92
$Hg_2^{2+}(aq) + 2e^- \rightleftharpoons 2Hg(l)$	+0.85
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$MnO_4^-(aq) + 2H_2O(l) + 3e^- \rightleftharpoons MnO_2(s) + 4OH^-(aq)$	+0.59
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.53
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$AgCl(s) + e^- \rightleftharpoons Ag(s) + Cl^-(aq)$	+0.22

*Written as reductions; E^0 value refers to all components in their standard states: 1 *M* for dissolved species; 1 atm pressure for gases; the pure substance for solids and liquids.

Using Standard Potentials: Cell EMF

Oxidizing and Reducing Agents

- The more positive $E°_{red}$ the stronger the oxidizing agent on the left. Cathode
- The more negative $E°_{red}$ the stronger the reducing agent on the right. Anode
- A species on the higher to the left of the table of standard reduction potentials will spontaneously oxidize a species that is lower to the right in the table.
- That is, F_2 will oxidize H_2 or Li; Ni^{2+} will oxidize Al(*s*).
- Any species on the right will spontaneously reduce anything that is higher to the left in the series.

QUESTION

Using the Standard Reduction Potentials taken from the Table, determine the voltage for a galvanic cell made from Ca(*s*)|Ca^{2+}(*aq*)||Al^{3+}(*aq*)|Al(*s*) at 25.0°C.

$Al^{3+} + 3e^- \rightarrow Al$ $E° = -1.66$ V
$Ca^{2+} + 2e^- \rightarrow Ca$ $E° = -2.76$ V

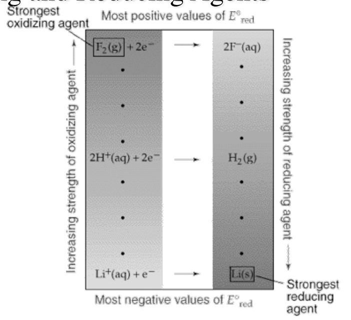
A. 4.42 V
B. –4.22 V
C. 1.10 V
D. –1.10 V

Cell Reduction Potentials

http://chemconnections.org/general/movies/emf Potentials.MOV

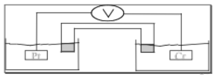
Using Standard Potentials: Cell EMF

Oxidizing and Reducing Agents



QUESTION

Consider the galvanic cell shown below (the contents of each half-cell are written beneath each compartment):



0.50 M Br_2
0.10 M Br^-

0.20 M Cr^{3+}

The standard reduction potentials are as follow

$Cr^{3+} + 3e^- \rightarrow Cr(s)$ $E° = -0.73$ V
$Br_2(aq) + 2e^- \rightarrow 2Br^-$ $E° = +1.09$ V

What is *E*° for this cell?

A. 1.82 V
B. 0.36 V
C. 4.75 V
D. 1.79 V
E. 4.40 V

Relative Reactivities of Metals

- ***Which metals can displace H_2 from acid?***

The standard hydrogen half-reaction represents the reduction of H^+ from acids to form molecular hydrogen, H_2:

$$2\,H^+_{(aq)} + 2\,e^- \longrightarrow H_{2\,(g)} \qquad E^o = 0.00\ V$$

The metals Li through Pb lie below hydrogen in the electromotive series Table. These will give a positive E^o_{cell} when reducing H^+.

For example iron:

$$\begin{array}{lll} Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2\,e^- & -E^o = 0.44\ V & [oxidation] \\ 2\,H^+_{(aq)} + 2\,e^- \longrightarrow H_{2\,(g)} & E^o = 0.00\ V & [reduction] \\ \hline Fe_{(s)} + 2\,H^+_{(aq)} \quad H_{2\,(g)} + Fe^{2+}_{(aq)} & E^o_{cell} = 0.44\ V & \end{array}$$

If E^o_{cell} of metal A for the reduction of H^+ is more positive than E^o_{cell} of metal B, metal A is a stronger reducing agent than metal B. A is more reactive than B and is a more "active" metal.

QUESTION

A galvanic cell constructed by using the standard hydrogen electrode and a solid piece of cadmium in a solution of $CdCl_2$ produces a voltage of 0.40V. Hydrogen gas is produced in the reaction. Without consulting any tables, what would you predict for the voltage of the cadmium half reaction? What would be the reducing agent in the cell?

A. –0.40 V; the reducing agent would be H^+
B. –0.40 V; the reducing agent would be Cd
C. 0.40 V; the reducing agent would be H^+
D. 0.40 V; the reducing agent would be Cd

Relative Reactivities of Metals

- ***Metals that cannot displace H_2 from acid.***

The coinage metals [Group 1B(11)]–Cu, Ag, and Au–are not strong enough reducing agents to reduce H^+ from acids:

$$\begin{array}{ll} Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^- & -E^o = -\ 0.80\ V \\ 2\,H^+_{(aq)} + 2\,e^- \longrightarrow H_{2\,(g)} & E^o = \ 0.00\ V \\ \hline 2\,Ag_{(s)} + 2\,H^+_{(aq)} \longrightarrow 2\,Ag^+_{(aq)} + H_{2\,(g)} & E^o_{cell} = -\ 0.80\ V \end{array}$$

If the E^o_{cell} is negative, the reaction is not spontaneous.

The higher the metal in the table, the more negative is its E^o_{cell}, The lower its reducing strength, and the less active it is. Thus, gold is less active than silver, which is less active than copper.

Relative Reactivities of Metals

- ***Metals that displace H_2 from water. MREs and a hot meal?.***

Metals active enough to displace H_2 from water lie below the half-reaction for the reduction of water:

$$2\,H_2O_{(l)} + 2\,e^- \longrightarrow H_{2\,(g)} + 2\,OH^-_{(aq)} \qquad E^o = -\ 0.42\ V$$

Consider the reaction of sodium with water:

$$\begin{array}{lll} 2\,Na_{(s)} \longrightarrow 2\,Na^+_{(aq)} + 2\,e^- & -E^o = 2.71\ V & [oxidation] \\ 2\,H_2O_{(l)} + 2\,e^- \longrightarrow H_{2\,(g)} + 2\,OH^-_{(aq)} & E^o = -\ 0.42\ V & [reduction] \\ \hline 2\,Na_{(s)} + 2\,H_2O_{(l)} \longrightarrow 2\,Na^+_{(aq)} + H_{2(g)} + 2\,OH^-_{(aq)} & E^o_{cell} = 2.29\ V & \end{array}$$

- ***Metals that can displace other metals from solution.***

Metals below others in the Table, can replace them from solution:

$$\begin{array}{lll} Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\,e^- & -E^o = \ 0.76\ V & [oxidation] \\ Fe^{2+}_{(aq)} + 2\,e^- \longrightarrow Fe_{(s)} & E^o = -\ 0.44\ V & [reduction] \\ \hline Zn_{(s)} + Fe^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Fe_{(s)} & E^o_{cell} = 0.32\ V & \end{array}$$

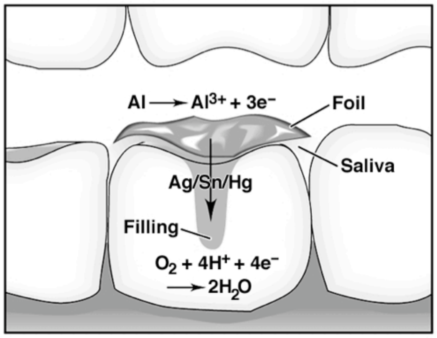
The Reaction of Calcium in Water

Oxidation half-reaction
$Ca(s) \longrightarrow Ca^{2+}(aq) + 2e^-$

Reduction half-reaction
$2H_2O(l) + 2e^- \longrightarrow 2OH^-(aq) + H_2(g)$

Overall (cell) reaction
$Ca(s) + 2H_2O(l) \longrightarrow Ca(OH)_2(aq) + H_2(g)$

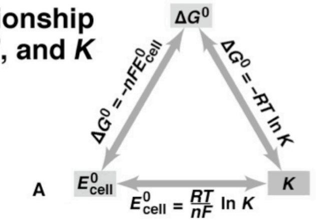
The Pain of a Dental Voltaic Cell



Interrelationship of ΔG^0, E^0, and K

A. Any one of these thermodynamic parameters
can be used to find
the other two.

B. The signs of G^o and E^o_{cell} determine the reaction direction at standard-state conditions.



B

ΔG^0	K	E^0_{cell}	Reaction at standard-state conditions
< 0	> 1	> 0	Spontaneous
0	1	0	At equilibrium
> 0	< 1	< 0	Nonspontaneous

Comparison of Voltaic and Electrolytic Cells

Cell Type	ΔG	E_{cell}	Electrode Name	Electrode Process	Electrode Sign
Voltaic	< 0	> 0	Anode	Oxidation	-
Voltaic	< 0	> 0	Cathode	Reduction	+
Electrolytic	> 0	< 0	Anode	Oxidation	+
Electrolytic	> 0	< 0	Cathode	Reduction	-

Spontaneity of Redox Reactions

EMF and Free-Energy Change

- We can show that

$$\Delta G = -nFE$$

- ΔG is the change in free-energy, n is the number of moles of electrons transferred, F is Faraday's constant, and E is the emf of the cell.
- We define

$$1F = 96{,}500 \text{ C/mol} = 96{,}500 \text{ J/Vmol}$$

- C = Coulomb, the charge of 6.242×10^{18} electrons
- V = Volt (the electric potential)
- Since n and F are positive, if $\Delta G > 0$ then $E < 0$.

Effect of Concentration on Cell EMF

- A voltaic cell is functional until $E = 0$ at which point equilibrium has been reached.
- The point at which $E = 0$ is determined by the concentrations of the species involved in the redox reaction.

The Nernst Equation

- The Nernst equation relates emf to concentration using

$$\Delta G = \Delta G^\circ + RT \ln Q$$

and noting that

$$-nFE = -nFE^\circ + RT \ln Q$$

Effect of Concentration on Cell EMF

The Nernst Equation

- This rearranges to give the Nernst equation:

$$E = E^\circ - \frac{RT}{nF} \ln Q$$

- The Nernst equation can be simplified by collecting all the constants together using a temperature of 298 K:

$$E = E^\circ - \frac{0.0592}{n} \log Q$$

- (Note that change from natural logarithm to base-10 log.)
- Remember that n is number of moles of electrons.

Calculating K and ΔG^o from E^o_{cell}

Problem: Lead can displace silver from solution:

$$Pb_{(s)} + 2\,Ag^+_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + 2\,Ag_{(s)}$$

Silver is a valuable by-product in the industrial extraction of lead from its ore. Calculate K and ΔG^o at 25°C for this reaction.

First calculate E^o_{cell} and then substitute the value to find K and ΔG^o.

Calculating K and ΔG° from E^o_{cell}

$$\mathrm{Pb_{(s)} + 2\,Ag^+_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + 2\,Ag_{(s)}}$$

Solution: Writing the half-reactions and their E^o values:

(1) $\mathrm{Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}}$ $E^o = 0.80$ V

(2) $\mathrm{Pb^{2+}_{(aq)} + 2\,e^- \longrightarrow Pb_{(s)}}$ $E^o = -0.13$ V

Calculating E^o_{cell}: We double (1), reverse (2), and add the half-reactions:

$\mathrm{2\,Ag^+_{(aq)} + 2\,e^- \longrightarrow 2\,Ag_{(s)}}$ $E^o = 0.80$ V

$\mathrm{Pb_{(s)} \longrightarrow Pb^{2+}_{(aq)} + 2\,e^-}$ $-E^o = 0.13$ V

$\mathrm{Pb_{(s)} + 2\,Ag^+_{(aq)} \longrightarrow Pb^{2+}_{(aq)} + 2\,Ag_{(s)}}$ $E^o_{cell} = 0.93$ V

Calculating K and ΔG° from E^o_{cell}

Calculating K: the adjusted half reactions show that 2 mol e^- are transferred per mole of reactant as written, so $n = 2$:

$$E^o_{cell} = \frac{0.0592\text{ V}}{n}\log K = \frac{0.0592\text{ V}}{2}\log K = 0.93\text{ V}$$

so, $$\log K = \frac{(0.93\text{ V})(2)}{0.0592\text{ V}} = 31.42 \quad\text{and}\quad K = 2.6 \times 10^{31}$$

Calculating ΔG^o:

$$\Delta G^o = -nFE^o_{cell} = \frac{2\text{ mol }e^-}{\text{mol rxn}} \times \frac{96.5\text{ kJ}}{\text{V}\cdot\text{mol }e^-} \times 0.93\text{ V}$$

$$\Delta G^o = -1.8 \times 10^2\text{ kJ/mol rxn}$$

QUESTION

The following questions refer to the following system:

$\mathrm{3Ag(s) + NO_3^-(aq) + 4H^+(aq) \rightarrow 3Ag^+(aq) + NO(g) + 2H_2O(l)}$

Anode reaction:

$\mathrm{Ag \rightarrow Ag^+_{(aq)} + le^-}$ $E^o = -0.799$ V

Cathode reaction:

$\mathrm{NO_3^-(aq) + 4H^+(aq) + 3e^- \rightarrow NO(g) + 2H_2O(l)}$
$E^o = 0.964$ V

Determine the equilibrium constant at 25°C.

A. 3.21×10^5
B. 6.41×10^2
C. 9.97×10^{12}
D. 2.41×10^8
E. 4.43×10^{15}

Summary:
The Effect of Concentration on Cell Potential

$$E_{cell} = E^o_{cell} - \frac{RT}{nF}\ln Q$$

$$E_{cell} = E^o_{cell} - \frac{0.0592\text{ V}}{n}\log Q \qquad (\text{at } 25^oC)$$

When $Q < 1$; [reactant] > [product], $\ln Q < 0$, so $E_{cell} > E^o_{cell}$
When $Q = 1$; [reactant] = [product], $\ln Q = 0$, so $E_{cell} = E^o_{cell}$
When $Q > 1$; [reactant] < [product], $\ln Q > 0$, so $E_{cell} < E^o_{cell}$

Using the Nernst Equation to Calculate E_{cell}

Problem: In a test of a new reference electrode, a chemist constructs a voltaic cell consisting of a $\mathrm{Zn/Zn^{2+}}$ electrode and the $\mathrm{H_2/H^+}$ electrode under the following conditions:

$[\mathrm{Zn^{2+}}] = 0.010\,M$ $[\mathrm{H^+}] = 2.5\,M$ $P_{\mathrm{H_2}} = 0.30$ atm

Calculate E_{cell} at 25°C.

Plan: Find E^o_{cell} and Q: 1) write the spontaneous reaction,
2) calculate E^o_{cell} from standard electrode potentials (Table 21.2),
3) use the given pressure and concentrations to find Q.

Solution: Determining the cell reaction and E^o_{cell}:

$\mathrm{2\,H^+_{(aq)} + 2\,e^- \longrightarrow H_{2\,(g)}}$ $E^o = 0.00$ V

$\mathrm{Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\,e^-}$ $-E^o = 0.76$ V

$\mathrm{2\,H^+_{(aq)} + Zn_{(s)} \longrightarrow H_{2\,(g)} + Zn^{2+}_{(aq)}}$ $E_{cell} = 0.76$ V

Using the Nernst Equation to Calculate E_{cell}

Calculating Q:

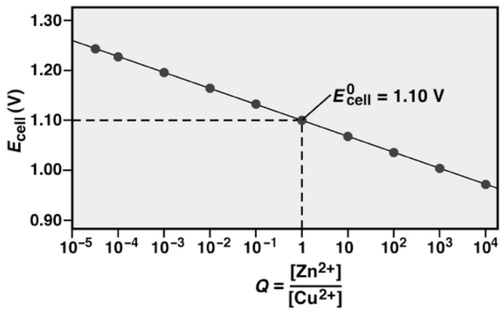
$$Q = \frac{(P_{\mathrm{H2}})[\mathrm{Zn^{2+}}]}{[\mathrm{H^+}]^2} = \frac{(0.30)(0.010)}{(2.5)^2} = 4.8 \times 10^{-4}$$

Solving for E_{cell} at 25°C (298 K), with $n = 2$:

$$E_{cell} = E^o_{cell} - \frac{0.0592\text{ V}}{n}\log Q = 0.76\text{ V} - \left[\frac{0.0592\text{ V}}{2}\log(4.8 \times 10^{-4}\right]$$

$E_{cell} = 0.76$ V $- (-0.098$ V$) =$ **0.86 V**

The Relation Between E_{cell} and Log Q for the Zinc-Copper Cell



How a Concentration Cell Works

In a concentration cell, the half-reactions are the same but the concentrations are different. Because of this, the nonstandard cell potential, E_{cell}, is nonzero because it depends upon the ratio of ion concentrations. In Fig 21.11A we see a system with 0.10 *M* Cu^{2+} in the anode half-cell and 1.0 *M* Cu^{2+}, a 10-fold higher concentration, in the cathode half-cell.

$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq, 0.10\,M)} + 2\,e^-$ [anode; oxidation]

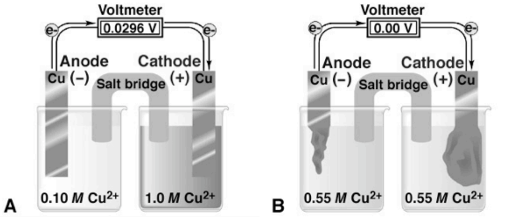
$Cu^{2+}_{(aq,\,1.0\,M)} + 2\,e^- \longrightarrow Cu_{(s)}$ [cathode; reduction]

$Cu^{2+}_{(aq,\,1.0\,M)} \longrightarrow Cu^{2+}_{(aq, 0.10\,M)}$ $E_{\text{cell}} = ?$

Using the Nernst equation, and $n = 2$, we get:

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{0.0592\ \text{V}}{2} \log \frac{[Cu^{2+}]_{\text{dil}}}{[Cu^{2+}]_{\text{conc}}} = 0\ \text{V} - \left(\frac{0.0592\ \text{V}}{2} \log \frac{0.10\ M}{1.0\ M}\right)$$

$$E_{\text{cell}} = 0\ \text{V} - \left[\frac{0.0592\ \text{V}}{2}(-1.00)\right] = +\,0.0296\ \text{V}$$



Oxidation half-reaction
$Cu\,(s) \longrightarrow Cu^{2+}(aq,\ 0.10\ M) + 2e^-$

Reduction half-reaction
$Cu^{2+}(aq,\ 0.10\ M) + 2e^- \longrightarrow Cu\,(s)$

Overall (cell) reaction
$Cu^{2+}(aq,\ 1.0\ M) \longrightarrow Cu^{2+}(aq,\ 0.10\ M)$

A Concentration Cell Based on the Cu/Cu^{2+} Half-Reaction

QUESTION

A concentration cell is constructed using two Ni electrodes with Ni^{2+} concentrations of 1.0 M and 1.00×10^{-4} M in the two half-cells. The reduction potential of Ni^{2+} is –0.23 V. Calculate the potential of the cell at 25°C.

A. –0.368 V
B. +0.132 V
C. –0.132 V
D. +0.118 V
E. +0.0592 V

The Laboratory Measurement of pH