BIG IDEA 3: ELECTROCHEMISTRY

Big Idea 3

Changes in matter involve the rearrangement and/or reorganization of atoms and/or the transfer of electrons.

Electrochemistry is the study of the interchange of electrical and chemical energy through transfer of electrons. There are two types of electrochemical cells, galvanic and electrolytic. In galvanic cells, spontaneous oxidation–reduction (redox) reactions generate electric current. In electrolytic cells, a nonspontaneous chemical reaction occurs with the application of an electric current.

You should be able to

- ◼ Identify and compare the two types of electrochemical cells: galvanic and electrolytic.
- ◼ Draw and label a galvanic cell, including labeling the electrodes, the flow of electrons, and the flow of ions.
- ◼ Write half-reactions and determine which reaction occurs at the anode and which reaction occurs at the cathode.
- ◼ Give the line notation for a galvanic cell or write a balanced redox reaction from the given line notation.
- ◼ Calculate the cell potential for a galvanic cell and an electrolytic cell.
- ◼ Determine if a reaction is spontaneous from its cell potential.
- ◼ Use the table of reduction potentials to determine which substances are more likely to be reduced or oxidized.

- Draw and label an electrolytic cell.
- Determine the reactions occurring at the anode and the cathode during electrolysis.
- Perform stoichiometric calculations involving electrolysis.

GALVANIC CELLS

COMPONENTS OF THE GALVANIC CELL

(*Chemistry* 8th ed. pages 823–825/9th ed. pages 839–842)

In a galvanic cell, a spontaneous chemical reaction is used to produce electrical energy. The current produced by the cell is measured in volts by a voltmeter. One compartment of the galvanic cell contains the anode, where oxidation, a loss of electrons, occurs. The other compartment contains the cathode where reduction, a gain of electrons, occurs. The electrodes (the anode and the cathode) are immersed in solutions containing metal cations. The two compartments of a galvanic cell are connected by a salt bridge or a porous disk that allows ion flow between the compartments to maintain a net zero charge in each. This is shown in the figure to the right. The anode may be a strip of zinc metal immersed in a $ZnSO_4$ solution, and the cathode may be a strip of copper metal immersed in a $CuSO_4$ solution. Zn is oxidized to Zn^{2+}, and the electrons travel to the Cu cathode, where Cu^{2+} in solution is reduced. Zn^{+2} ions travel across the salt bridge to the cathode to replace the reduced Cu^{2+}. SO_4^{2-} ions travel to the anode to balance the additional positive charge as Zn^{2+} is formed.
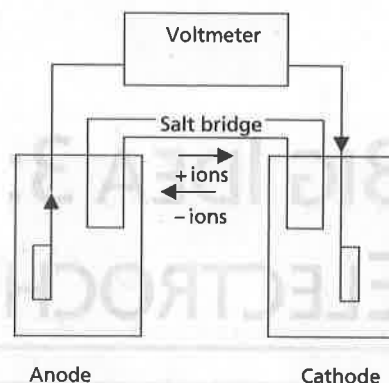
The oxidizing agent is the substance being reduced at the cathode. The reducing agent is the substance being oxidized at the anode.
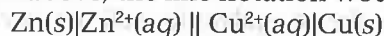

LINE NOTATION

(*Chemistry* 8th ed. pages 831–832/9th ed. pages 847–848)

A galvanic cell can be abbreviated with line notation.

reactant | product || reactant | product
anode reaction   cathode reaction

The salt bridge is indicated by the symbol ||.
For the cell described above, the line notation would be:

$Zn(s)|Zn^{2+}(aq) \parallel Cu^{2+}(aq)|Cu(s)$

Sometimes an inert (nonreactive) electrode is used. The example below has a platinum cathode which transports electrons to the cations, in this case H^+.

> **EXAMPLE:** Give the correct line notation for the galvanic cell pictured on the following page.

SOLUTION: $Zn(s)|Zn^{2+}(aq) \parallel H^+(aq)|H_2(g)|Pt(s)$
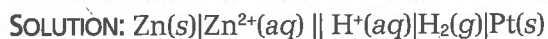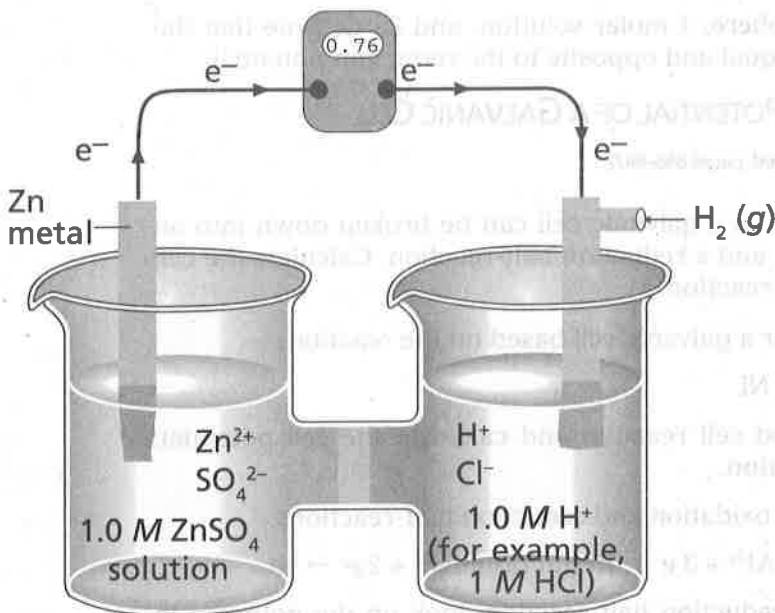
AP Tips

Here are some mnemonic devices to help you remember some facts about electrochemistry and redox reactions.

- "LEO" goes "GER" means Loss of Electrons is Oxidation and Gain of Electrons is Reduction.

- To recall what happens at the anode and the cathode: RedCat and AnOx means reduction occurs at the cathode and oxidation occurs at the anode.

- To know the migration of ions toward the electrodes for both types of cells, "CAT" ions move to the "CAT" hode and "AN" ions move to the "AN" ode.

You will be provided any standard reduction potentials necessary to solve a problem on the AP test.

You should be able to sketch a galvanic cell and label the electrodes, the flow of electrons, and the flow of ions.

STANDARD REDUCTION POTENTIALS

(*Chemistry* 8th ed. pages 826–830/9th ed. pages 842–846)

The cell potential, E_{cell}, is the potential of the cell to do work on its surroundings by driving an electric current through a wire. By definition, a potential of 1 volt is produced when 1 joule of energy moves 1 coulomb of electric charge across a potential. The magnitude of the cell potential is a measure of the driving force behind an electrochemical reaction. Sometimes it is referred to as the electromotive force or emf. Tables of reduction potentials give E°_{cell}, standard voltages for reduction half-reactions measured at standard

conditions of 1 atmosphere, 1 molar solution, and 25°C. Note that the oxidation potential is equal and opposite to the reduction potential.

CALCULATING THE CELL POTENTIAL OF A GALVANIC CELL

(*Chemistry* 8th ed. pages 830–831/9th ed. pages 846–847)

The reaction occurring in a galvanic cell can be broken down into an oxidation half-reaction and a reduction half-reaction. Calculate the cell potential of the overall reaction.

> **EXAMPLE:** Consider a galvanic cell based on the reaction:
>
> $Al + Ni^{2+} \rightarrow Al^{3+} + Ni$
>
> Give the balanced cell reaction and calculate the cell potential, $E°_{cell}$, for the reaction.
>
> Step 1: Write the oxidation and reduction half-reactions.
>
> **Oxidation:** $Al \rightarrow Al^{3+} + 3\ e^-$ **Reduction:** $Ni^{2+} + 2\ e^- \rightarrow Ni$
>
> Step 2: For the reduction half-reaction, look up the potential in the table.
>
> $Ni^{2+} + 2\ e^- \rightarrow Ni$ $E°_{red} = -0.23\ V$
>
> Step 3: For the oxidation half-reaction, $E°_{ox} = -E°_{red}$.
>
> Oxidation: $Al \rightarrow Al^{3+} + 3\ e^-$
>
> $E°_{ox} = -E°_{red} = -(-1.66\ V) = +1.66\ V.$
>
> Step 4: The cell potential for the overall reaction is equal to the sum of the reduction potential, $E°_{red}$, and the oxidation potential, $E°_{ox}$.
>
> $E°_{cell} = E°_{ox} + E°_{red}$
>
> $E°_{cell} = -0.23\ V + 1.66\ V = 1.43\ V$
>
> To obtain the balanced cell reaction, you must make sure that the electrons lost equal the electrons gained. When multiplying the half-reactions through by a coefficient, do not change the value of $E°$, because potential is an intensive property: it does not depend on how many times a reaction occurs.
>
> | | |
> |---|---|
> | 3 $(Ni^{2+} + 2\ e^- \rightarrow Ni)$ | $E°_{red} = -0.23\ V$ |
> | 2 $(Al \rightarrow Al^{3+} + 3\ e^-)$ | $E°_{ox} = +1.66\ V$ |
> | 3 $Ni^{2+} + 2\ Al \rightarrow 3\ Ni + 2\ Al^{3+}$ | $E°_{cell} = 1.43\ V$ |

SPONTANEOUS REACTIONS

(*Chemistry* 8th ed. pages 833–836/9th ed. pages 849–852)

Gibbs free energy, $\Delta G°$, is discussed in Chapter 11. It can be calculated from the cell potential, $E°_{cell}$.

$$\Delta G° = -nFE°_{cell}$$

Faraday's constant, F, has a value of 96,500 C/mol e⁻.

The number of moles of electrons transferred in a redox reaction is represented by n.

A spontaneous reaction is one that has a negative value for $\Delta G°$ or a positive value for $E°_{cell}$.

> **EXAMPLE:** Will 1 M HCl dissolve silver metal and form Ag^+ solution?
>
> **SOLUTION:** Write the half-reactions and calculate $E°_{cell}$.
>
> | | |
> |---|---|
> | $2\,H^+ + 2\,e^- \rightarrow 2\,H_2$ | $E°_{red} = 0.00\ V$ |
> | $2\,Ag \rightarrow 2\,Ag^+ + 2\,e^-$ | $E°_{ox} = -0.80\ V$ |
> | $2\,H^+ + 2\,Ag \rightarrow H_2 + 2\,Ag^+$ | $E°_{cell} = -0.80\ V$ |
>
> The negative value for $E°_{cell}$ indicates that the reaction will not occur.

DETERMINING WHICH SUBSTANCES ARE MORE LIKELY TO BE OXIDIZED OR REDUCED

(*Chemistry* 8th ed. pages 851–852/9th ed. pages 867–868)

You may be asked if an element or ionic species is capable of reducing another element or ion. To determine if the reaction will occur, write the half-reactions and calculate the cell potential as in the previous example.
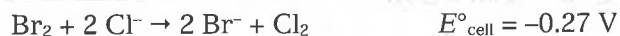
> **EXAMPLE:** Bromine, Br_2, can oxidize iodide, I^-, to iodine, I_2. However, Br_2 cannot oxidize chloride, Cl^-, to chlorine, Cl_2. Explain why the first reaction occurs yet, the second one does not.
>
> **SOLUTION:** Begin by writing the appropriate half-reactions. Then calculate the cell potential for the overall reaction.
>
> First the reaction in which Br_2 oxidizes I^-:
>
> | | |
> |---|---|
> | $Br_2 + 2\,e^- \rightarrow 2\,Br^-$ | $E°_{red} = 1.09\ V$ |
> | $2\,I^- \rightarrow I_2 + 2\,e^-$ | $E°_{ox} = -0.54\ V$ |
> | $Br_2 + 2\,I^- \rightarrow 2\,Br^- + I_2$ | $E°_{cell} = 0.55\ V$ |
>
> This reaction occurs; $E°_{cell}$ is positive.
>
> | | |
> |---|---|
> | $Br_2 + 2\,e^- \rightarrow 2\,Br^-$ | $E°_{red} = 1.09\ V$ |
> | $2\,Cl^- \rightarrow Cl_2 + 2\,e^-$ | $E°_{ox} = -1.36\ V$ |
> | $Br_2 + 2\,Cl^- \rightarrow 2\,Br^- + Cl_2$ | $E°_{cell} = -0.27\ V$ |
>
> This reaction does not occur; $E°_{cell}$ is negative

For a substance to be oxidized, it must lose electrons and another substance must gain electrons because oxidation and reduction always occur together.

In any pair, the substance with the larger (more positive) $E°_{red}$ is more likely to gain electrons. It will be the reactant in the reduction

half-reaction. The substance with the smaller (more negative) $E°_{red}$ is more likely to lose electrons. It will be the reactant in the oxidation half-reaction.

EXAMPLE: Classify each of the following as more likely to be oxidized, more likely to be reduced, or both. Within each list, arrange in order of increasing likelihood of being oxidized or reduced.

Br_2, Mg, Fe^{2+}, I_2, Cl^-, Cu^{2+}

SOLUTION:

Reduced: $Fe^{2+} < Cu^{2+} < I_2 < Br_2$

Oxidized: $Cl^- < Fe^{2+} < Mg$

The reduction potentials for these substances are:

$Br_2 + 2\ e^- \rightarrow 2\ Br^-$	$E°_{red} = 1.09$ V
$Mg^{2+} + 2\ e^- \rightarrow Mg$	$E°_{red} = -2.37$ V
$Fe^{2+} + 2\ e^- \rightarrow Fe$	$E°_{red} = -0.44$ V
$I_2 + 2\ e^- \rightarrow 2\ I^-$	$E°_{red} = 0.54$ V
$Cl_2 + 2\ e^- \rightarrow 2\ Cl^-$	$E°_{red} = 1.36$ V
$Cu^{2+} + 2\ e^- \rightarrow Cu$	$E°_{red} = 0.34$ V

To be reduced, a substance must be capable of gaining electrons. Of the species listed, Mg and Cl^- cannot gain any more electrons. The others are listed in order of reduction potentials, with the largest positive number first.

To be oxidized, a substance must be able to lose electrons. Br_2 and I_2 are unlikely to lose electrons, and Cu^{2+} is already in its highest oxidation state. On the other hand, Cl^- and Mg can go to Cl and Mg^{2+}. Fe^{2+} can exist as Fe^{3+} or Fe so it can be oxidized or reduced. These are listed in *reverse* order of reduction potentials, with the most negative number (smallest) first.

ELECTROLYTIC CELLS

(*Chemistry* 8th ed. pages 847–850/9th ed. pages 864–867)

In an electrolytic cell, a nonspontaneous reaction is made to occur by forcing an electric current through the cell. In an earlier example, it was shown that the following reaction is spontaneous:
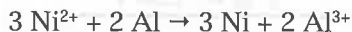
$$3\ Ni^{2+} + 2\ Al \rightarrow 3\ Ni + 2\ Al^{3+}$$

The reverse of this reaction: $3\ Ni + 2\ Al^{3+} \rightarrow 3\ Ni^{2+} + 2\ Al$ is nonspontaneous and can be made to occur by the addition of an external power source. This electrolytic cell can be set up with two compartments just like the galvanic cell, with the replacement of a power supply for the voltmeter.

In the process of electroplating, the electrolytic cell can also be set up using only one compartment, as shown in the figure below.
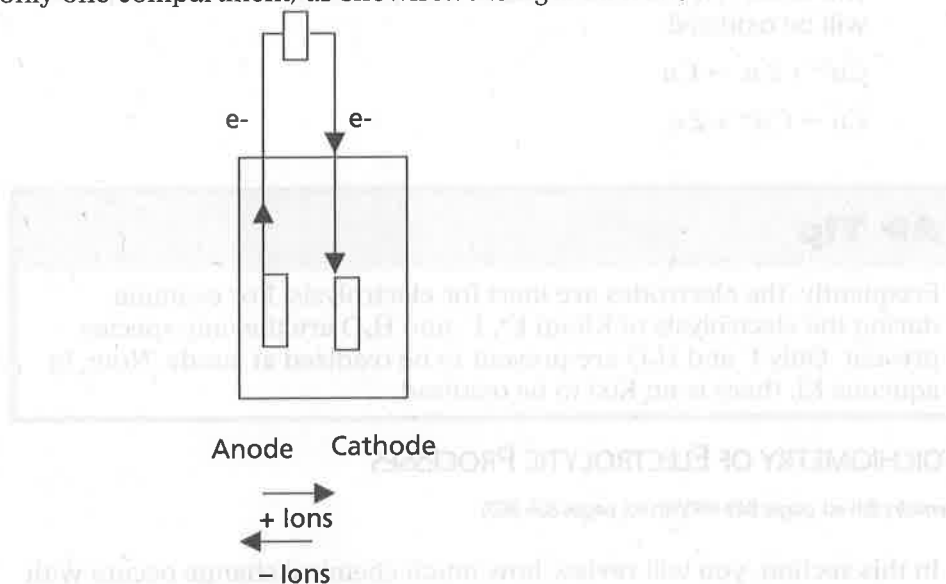
For example, an object to be plated with copper is the cathode and is immersed in a copper(II) sulfate solution. The reduction reaction $Cu^{2+} + 2 e^- \rightarrow Cu$ will deposit copper onto the object. The anode can also be made of copper, and the oxidation of the copper anode will replace the Cu^{2+} ions.

REACTIONS THAT OCCUR IN AN ELECTROLYTIC CELL

To determine which reactions occur at the anode and the cathode during electrolysis, you must consider all possible reactions and their reduction and oxidation potentials. If the reaction takes place in an aqueous solution, the oxidation and reduction of water must be considered.

EXAMPLE: A solution of copper(II) sulfate is electrolyzed. Calculate the cell potential of the reaction, $E°_{cell}$.

SOLUTION:

	Possible reactions[1]		Cell potential, $E°$(V)
Cathode	$Cu^{2+} + 2 e^-$	$\rightarrow Cu$	0.34
	$SO_4^{2-} + 4 H^+ + 2 e^-$	$\rightarrow H_2SO_3 + H_2O$	0.20
	$2 H_2O + 2 e^-$	$\rightarrow H_2 + 2 OH^-$	−0.83
Anode	Cu	$\rightarrow Cu^{2+} + 2 e^-$	−0.34
	$2 H_2O$	$\rightarrow O_2 + 4 H^+ + 4 e^-$	−1.23

[1]Note: There is no half-reaction for the oxidation of SO_4^{2-}. S in SO_4^{2-} is in its highest oxidation state, +6, and cannot be oxidized further.

For each electrode, the reaction with the more positive potential will occur. At the cathode, Cu^{2+} will be reduced. At the anode, Cu will be oxidized.

$$Cu^{2+} + 2\ e^- \rightarrow Cu$$

$$Cu \rightarrow Cu^{2+} + 2\ e^-$$
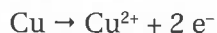
AP Tip

Frequently, the electrodes are inert for electrolysis. For example, during the electrolysis of KI(aq) K^+, I^-, and H_2O are the only species present. Only I^- and H_2O are present to be oxidized at anode. Note: In aqueous KI, there is no K(s) to be oxidized.

STOICHIOMETRY OF ELECTROLYTIC PROCESSES

(Chemistry 8th ed. pages 849–850/9th ed. pages 866–867)

In this section, you will review how much chemical change occurs with the flow of a given current for a specified time. You might be asked how much metal was plated (formed) or how long an electroplating process will take or how much current is required to produce a specified amount of metal over a period of time.

Some units to know how to use include A, amperes; 1 A = 1 C/s; coulombs, C; Faraday's constant is 96,500 C = 1 mol e^-.

EXAMPLE: A current of 10.0 A is passed through a solution containing M^{2+} for 30.0 min. It produces 5.94 g of metal, M. Determine the identity of metal, M.

SOLUTION: Since the metal forms a cation with a 2+ charge, 2 moles of electrons are required to reduce 1 mole of the metal.

$$10.0\ A = \frac{10.0\ C}{sec} \times \frac{60\ s}{min} \times 30.0\ min = 1.80 \times 10^4\ C$$

$$1.80 \times 10^4\ C \times \frac{1\ mole\ e^-}{96500\ C} \times \frac{1\ mol\ M}{2\ mol\ e^-} = 9.33 \times 10^{-2}\ mol\ M$$

$$5.94\ g\ M \times \frac{1}{9.33 \times 10^{-2}\ mol\ M} = 63.7\ g/mol$$

The metal is copper.

This can also be shown in one step:

$$5.94\ g\ M \times \frac{2\ mole\ e^-}{1\ mol\ M} \times \frac{96500\ C}{mole\ e^-} \times \frac{1\ s}{10.0\ C} \times \frac{1\ min}{60\ s} \times \frac{1}{30.0\ min} = 63.7\ g/mol$$

COMPARISON OF GALVANIC AND ELECTROLYTIC CELLS

Galvanic and electrolytic cells have a few features in common. For both types of cells, reduction always occurs at the cathode and oxidation at the anode. In an electrolytic cell, electrons travel from the

battery to the cathode. In both cases, electrons travel in the wire, but you wouldn't say the electrons travel from the anode to the cathode in an electrolytic cell. Positive ions are always attracted to the cathode whether the cell is electrolytic or galvanic. The table below compares the galvanic cell to the electrolytic cell.

	Galvanic	**Electrolytic**
Ions attracted to the cathode	Cations (+)	Cations (+)
Ions attracted to the anode	Anions (–)	Anions (–)
Sign of $E°_{cell}$	+	–
Spontaneity	Spontaneous	Nonspontaneous

In both types of cells, the + ions or cations move toward the cathode because there is an excess of negative ions at the cathode caused by the reduction of + ions in solution. Likewise, oxidation at the anode produces + ions, so negative ions or anions in the salt bridge must move to the anode to maintain electrical neutrality.

MULTIPLE-CHOICE QUESTIONS

No calculators are to be used on this part of the exam.

1. In the reaction, $MnO_4^- + 5\ Fe^{2+} + 8\ H^+ \rightarrow Mn^{2+} + 5\ Fe^{3+} + 4\ H_2O$,
   (A) Fe^{3+} is oxidized and Mn^{2+} is reduced
   (B) H^+ is oxidized and MnO_4^- is reduced
   (C) Fe^{2+} is oxidized and MnO_4^- is reduced
   (D) electrons are transferred from Mn^{2+} to Fe^{2+}

AP Tip

Remember that you may be asked to write a balanced equation such as the one used in Question 1, and then answer a related question about the chemical species being oxidized or reduced or about the change in oxidation of one of the elements.

2. The $E°$ for $Mg \rightarrow Mg^{2+} + 2\ e^-$ is +2.37 volts.
   The $E°$ for $2\ Mg^{2+} + 4\ e^- \rightarrow 2\ Mg$ is
   (A) 2.37 volts
   (B) –2.37 volts
   (C) 4.74 volts
   (D) –4.74 volts

3. The function of a salt bridge (or porous barrier) in an electrochemical cell (galvanic cell) is to allow ions to flow
   (A) through the wire from reducing agent to oxidizing agent
   (B) to encourage charge building up on both sides of the cell
   (C) to keep the net charge on each side at zero
   (D) from the oxidizing side of the cell to the reducing side

4. What is the value of $\Delta G°$ for the reaction written below?

   $2 \, MnO_4^-(aq) + 16 \, H_3O^+(aq) + 5 \, Zn(s) \rightarrow 2 \, Mn^{2+}(aq) + 24 \, H_2O(l) + 5 \, Zn^{2+}(aq)$
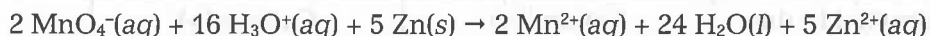
   You are given the following standard reduction potentials for the two half-reactions:

   $E°\,(MnO_4^- \mid Mn^{2+}) = +1.49 \, V$

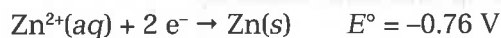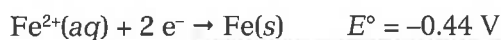 $E°\,(Zn^{2+} \mid Zn) = -0.76 \, V$

   (A) -7.04×10^6 J
   (B) -1.34×10^6 J
   (C) -1.92×10^6 J
   (D) -2.17×10^6 J

5. Given: $Mg^{2+} + 2 \, e^- \rightarrow Mg$ -2.37 V
              $Fe^{3+} + 1 \, e^- \rightarrow Fe^{2+}$ $+0.77$ V

   When the reaction $2 \, Mg + Fe^{3+} \rightarrow 2 \, Mg^{2+} + Fe^{2+}$ comes to equilibrium, the $E°_{cell}$ value (cell potential) becomes
   (A) 3.14 V
   (B) 1.60 V
   (C) 0.83 V
   (D) 0.00 V

6. For the reaction $Cu^{2+}(aq) + Zn(s) \rightarrow Zn^{2+}(aq) + Cu(s)$, $E° = +1.10$ V. When 1.00 mole of zinc is consumed, how many faradays are transferred?
   (A) $96,500 \times 2.00 \times 6.023 \times 10^{23}$
   (B) 96,500
   (C) $96,500 \times 2$
   (D) 2.00

7. The galvanic cell based on the reactions $Ag^+ + 1 \, e^- \rightarrow Ag$ ($E° = +0.80$ V) and $Fe^{3+} + 1 \, e^- \rightarrow Fe^{2+}$ ($E° = +0.77$ V)
   (A) has electrons lost by Ag^+ and gained by Fe^{2+}
   (B) has the mass of the silver electrode decreasing as this reaction proceeds
   (C) has an overall cell potential difference (voltage) of +1.57 V
   (D) has electrons flowing from Fe^{2+} to Ag^+

8. Iron can be protected from oxidation by putting it into electrical contact with a substance that is more likely to be oxidized than iron. Given the reduction potentials below, which metals could be used to protect iron?

$Fe^{2+}(aq) + 2 e^- \rightarrow Fe(s)$ $E° = -0.44$ V

$Zn^{2+}(aq) + 2 e^- \rightarrow Zn(s)$ $E° = -0.76$ V

$Cu^{2+}(aq) + 2 e^- \rightarrow Cu(s)$ $E° = 0.34$ V

$Sn^{2+}(aq) + 2 e^- \rightarrow Sn(s)$ $E° = -0.14$ V

$Mg^{2+}(aq) + 2 e^- \rightarrow Mg(s)$ $E° = -2.37$ V
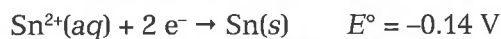
(A) Zn or Mg
(B) Sn or Cu
(C) Zn or Ag
(D) Cu or Mg

9. Copper may be used for electroplating, with a half-reaction of $Cu^{2+} + 2 e^- \rightarrow Cu$. If a current of 10.0 A is applied to a Cu^{2+} solution for 60.0 minutes, the mass of copper plated out can be calculated as
(A) $10.0 \times 3600. \times (1/96,500) \times (2.00/1) \times 63.5$
(B) $10.00 \times 3600. \times (6.02 \times 10^{23}) \times (1/2.00) \times 63.5$
(C) $96,500 \times (1/10.0) \times (1/2.00) \times (1/3600.) \times 63.5$
(D) $96,500 \times (1/10.0) \times (1/2.00) \times (1/3600.) \times (1/63.5)$
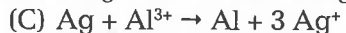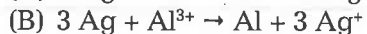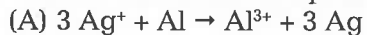
10. Given the following data:

$Ca^{2+}(aq) + 2 e^- \rightarrow Ca(s)$ $E° = -2.87$ V

$Zn^{2+}(aq) + 2 e^- \rightarrow Zn(s)$ $E° = -0.76$ V

$Co^{2+}(aq) + 2 e^- \rightarrow Co(s)$ $E° = -0.28$ V

$Sn^{2+}(aq) + 2 e^- \rightarrow Sn(s)$ $E° = -0.14$ V

$Pb^{2+}(aq) + 2 e^- \rightarrow Pb(s)$ $E° = -0.13$ V

Which of the following correctly describes the ease of oxidation of the substances listed under standard state conditions?
(A) $Ca^{2+} > Zn^{2+} > Co^{2+} > Sn^{2+} > Pb^{2+}$
(B) $Pb^{2+} > Sn^{2+} > Co^{2+} > Zn^{2+} > Ca^{2+}$
(C) Ca > Zn > Co > Sn > Pb
(D) Pb > Sn > Co > Zn > Ca

Use the following data to answer questions 11, 12, and 13.

$Ag^+ + e^- \rightarrow Ag \quad E° = 0.80 \text{ V}$

$Al^{3+} + 3e^- \rightarrow Al \quad E° = -1.66 \text{V}$
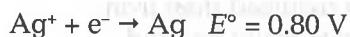
11. What is the balanced equation for the spontaneous reaction?
    (A) $3 Ag^+ + Al \rightarrow Al^{3+} + 3 Ag$
    (B) $3 Ag + Al^{3+} \rightarrow Al + 3 Ag^+$
    (C) $Ag + Al^{3+} \rightarrow Al + 3 Ag^+$
    (D) $Ag^+ + Al^{3+} \rightarrow Al + Ag^+$

12. What is $E°_{cell}$ for a voltaic cell using the two half-reactions at 25°C?
    (A) –2.46 V
    (B) –0.74 V
    (C) +0.74 V
    (D) +2.46 V

13. What would happen to the cell emf if NH_3 were added to the silver cell and $Ag(NH_3)_2^+$ forms?
    (A) no change
    (B) increased
    (C) reduced
    (D) cannot be determined without additional information

14. Which of the following statements concerning galvanic cells is/are true?
    (A) The two half-cells are connected by a salt bridge.
    (B) Electrons flow from the anode to the cathode.
    (C) Reduction occurs at the cathode.
    (D) All of the above are true.

15. Metal A is more easily oxidized than metal B. What is true of A^+ and B^+?
    (A) A^+ is more easily reduced than B^+.
    (B) B^+ is more easily reduced than A^+.
    (C) If a strip of metal B is plated with metal A, the metal A plating will corrode first.
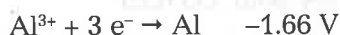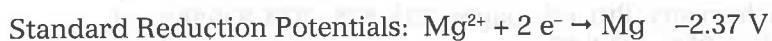   (D) Both (B) and (C) are true.

FREE-RESPONSE QUESTIONS

Calculators, Tables, and Equations may be used on this part of the exam.

1. (a) Which occurs more often in nature, oxidation or reduction? Discuss your answer.
    (b) The half-reaction for the hydrogen electrode, $2 H^+ + 2 e^- \rightarrow H_2$, has been given the $E°$ value of zero. Explain why such a standard is necessary.
    (c) The system $Mg(s) + Cu^{2+}(aq) \rightarrow Mg^{2+}(aq) + Cu(s)$ has a value of $E°_{cell}$ of +2.71 V. What is the value of $\Delta G°$ for this system?

2. Consider the following galvanic cell: $Mg(s)|Mg^{2+}(aq) \parallel Al^{3+}(aq)|Al(s)$

   Standard Reduction Potentials: $Mg^{2+} + 2\,e^- \rightarrow Mg$ -2.37 V

   $$Al^{3+} + 3\,e^- \rightarrow Al \quad -1.66\text{ V}$$

   (a) Give the equation for the spontaneous cell reaction which produces charge flow.
   (b) Indicate which substance is oxidized and which is reduced in this reaction. Label the anode and the cathode electrodes for this cell.
   (c) Calculate the $E°_{cell}$.
   (d) How will the potential difference (voltage) of the galvanic cell $Cu(s) + 2\,Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2\,Ag(s)$ be affected by the addition of $NaCl(aq)$? Explain.
   (e) How does increasing the mass of the anode affect the voltage? Justify your response.
   (f) The electrolysis of aqueous $NaCl$ does not produce metallic sodium. Explain.

Answers

MULTIPLE-CHOICE QUESTIONS

1. **C** In changing from Fe^{2+} to Fe^{3+}, each iron(II) ion loses an electron, which is oxidation; MnO_4^- changing to Mn^{2+} is a gain of electrons, which is reduction (*Chemistry* 8th ed. page 823/9th ed. page 839). LO 3.8

2. **B** When the half-reaction is reversed, the sign of the potential is also reversed. However, the $E°$ does not change. The potential is an intensive property, which means that it is not dependent upon how many times the reaction takes place (*Chemistry* 8th ed. pages 829–830/9th ed. pages 845–846). LO 3.12

3. **C** While electrons flow through the wire from reducing agent to oxidizing agent, ions flow from one side of the cell through the salt bridge to the other side to keep the net charge at zero. If this were not done, a large amount of energy would be required to 'force' electrons to move from a positive environment into a negative environment; with such charge differences due to the charge buildup on the two sides the cell would not function; the current would be zero (*Chemistry* 8th ed. pages 823–825/9th ed. pages 839–842). LO 3.13

4. **D** In examination of the balanced oxidation–reduction reaction equation written above, you can quickly determine that the number of electrons transferred is 10 ($5\,Zn \rightarrow 5\,Zn^{2+}$) and that the cell potential is determined by $E°_{cell} = E°(ox) + E°(red) = +0.76 + 1.49 = 2.25$ V. Using $\Delta G° = -nFE°$ where $n = 10$ and F is 96,500 coulombs, $= -(10)(96500)(2.52) = -2.17 \times 10^6$ J (*Chemistry* 8th ed. pages 835–836/9th ed. pages 851–852). LO 5.13

5. **D** When the cell reaction reaches equilibrium, no electrons flow and $E°_{cell} = 0$ (*Chemistry* 8th ed. pages 831–835, 838–839/9th ed. pages 847–851, 854–855). LO 6.25

6. **D** The charge on one mole of electrons is called the faraday (*F*, named for the Englishman Michael Faraday). In this case, two moles of electrons are transferred, hence 2.00 faradays of charge are transferred. (One faraday is 96,500 coulombs of charge, the charge on one mole of electrons.) (*Chemistry* 8th ed. pages 833–835/9th ed. pages 849–852). LO 3.13

7. **D** The overall equation for this cell reaction is $Fe^{2+}(aq) + Ag^+(aq) \rightarrow Fe^{3+}(aq) + Ag(s)$ in which Fe^{2+} is oxidized (loses electrons) and is therefore the anode. Because Fe^{2+} loses electrons, they flow from Fe^{2+} to Ag^+, which is reduced to $Ag(s)$, and the mass of the silver electrode increases (*Chemistry* 8th ed. pages 831–833/9th ed. pages 847–849). LO 3.13

8. **A** Metals with an $E°$ more negative than iron are more likely to be oxidized (*Chemistry* 8th ed. pages 846–847/9th ed. pages 861–864). LO 3.12

9. **A** Adding units to the style of responses where a setup is given is often very helpful. In this case it might better look like: (10.0 C/s)(3600/s)(1 mole e⁻/96,500 C)(2.00 mole e⁻/1 mole Cu)(63.5g/mol Cu) (*Chemistry* 8th ed. pages 847–850/9th ed. pages 864–868). LO 3.12

10. **C** Oxidation is the loss of electrons, and oxidation half-reactions would be the reverse of each of the above equations. This means the potential for each of the oxidation half-reactions would have a positive value; thus calcium would be most easily oxidized and lead is the least easily oxidized (*Chemistry* 8th ed. pages 828–830/9th ed. pages 844–846). LO 3.12

11. **A** Ag^+ has the more positive reduction potential, so it will be reduced and Al will be oxidized (*Chemistry* 8th ed. pages 828–830/9th ed. pages 844–846). LO 3.12

12. **D** Reverse the $Al^{3+} \rightarrow Al$ to give +1.66 V, and add to the potential for $Ag^+ \rightarrow Ag$ of +0.80 V to give +2.46 V (*Chemistry* 8th ed. pages 830–831/9th ed. pages 846–847). LO 3.13

13. **C** If you reduce the $[Ag^+]$ by formation of $Ag(NH_3)_2^+$ then the reaction $3 Ag^+ + Al \rightarrow 3 Ag + Al^{3+}$ will be driven to the left and the cell emf will be reduced (*Chemistry* 8th ed. page 836/9th ed. page 852). LO 6.8

14. **D** In a galvanic cell, the half-cells are connected with a salt bridge. Electrons flow from the anode, where oxidation takes place, to the cathode, where reduction takes place. All are correct (*Chemistry* 8th ed. pages 831–833/9th ed. pages 847–849). LO 3.13

15. **D** If metal A is more easily oxidized, its cation is less easily reduced, and a plating of metal A will act as a sacrificial anode,

oxidizing instead of the metal B. Both (B) and (C) are true (*Chemistry* 8th ed. pages 826–831/9th ed. pages 842–847). LO 3.12

FREE-RESPONSE QUESTIONS

1 (a) They occur equally; for every electron lost by one substance an electron must be gained by another substance (*Chemistry* 8th ed. page 829/9th ed. page 845). LO 3.12

   (b) Because the potential of any half-reaction cannot be measured directly, some standard is required to rank the potentials of all half-reactions. Using the hydrogen half-reaction as an arbitrary standard allows such calculations. When we say, for example, that $Zn^{2+} + 2\ e^- \rightarrow Zn$ has a potential of –0.76 V, we really mean with respect to the potential for the hydrogen half-reaction. A good comparison might be assigning sea level as the zero measure for altitude and then comparing mountain heights and ocean depths to this standard marker (*Chemistry* 8th ed. page 826/9th ed. page 842). LO 3.13

   (c) Find $\Delta G°$ using the relationship $\Delta G° = -nFE°_{cell}$:
   –(2)(96,500 C)(2.71 V) = –5.23 × 10^5 V-C (1 J = 1 V-C). (*Chemistry* 8th ed. pages 833–836/9th ed. pages 849–852). LO 5.13

2. (a) $3\ Mg(s) + 2\ Al^{3+}(aq) \rightarrow 3\ Mg^{2+}(aq) + 2\ Al(s)$ (*Chemistry* 8th ed. pages 829–838/9th ed. pages 845–854). LO 3.2

   (b) Mg loses e^-, therefore is oxidized and is the site of oxidation called the anode. In like manner, Al^{3+}, which is gaining these same electrons, is reduced, and the Al electrode is the site of reduction, called the cathode (*Chemistry* 8th ed. pages 829–838/9th ed. pages 845–854). LO 3.13

   (c) +2.37 V

   <u>–1.66 V</u>
   +0.71 V

   (*Chemistry* 8th ed. pages 829–838/9th ed. pages 845–854). LO 3.13

   (d) The added $Cl^-(aq)$ will react with the $Ag^+(aq)$, precipitating as $AgCl(s)$. This lowers the silver ion concentration, which shifts the equilibrium to the left, making the silver ions less available to react with the solid copper, and <u>lowers</u> the voltage (*Chemistry* 8th ed. page 836/9th ed. page 852). LO 6.8

   (e) If the mass of the anode (site of oxidation) is changed there will be no effect on the voltage. The oxidation and reduction potentials are determined by the nature of the metal and not the amount of the metal. You might be able to "run" the cell longer by changing the size of certain electrodes, but would not produce more voltage (*Chemistry* 8th ed. pages 829–838/9th ed. pages 845–854). LO 3.12

(f) When the standard reduction potentials for the two possible reactions are compared,

$$Na^+ + 1 e^- \rightarrow Na \quad E° = -2.71 \text{ V}$$

$$2 H_2O + 2 e^- \rightarrow H_2 + 2 OH^- \qquad\qquad E° = -0.83 \text{ V}$$

It is evident that water is the better competitor for electrons of these two ($E°$ for water is the more positive value) (*Chemistry* 8th ed. pages 829–838/9th ed. pages 845–854). LO 3.12