Electrochemistry I

Electrochemistry

Half-Reactions and Electrochemical Cells

Voltaic Cells: Using Spontaneous Reactions to Generate ElectricalEnergy

Cell Potential: Output of a Voltaic Cell

Free Energy and Electrical Work

Electrochemical Processes in Batteries

Corrosion: A Case of Environmental Electrochemistry

Electrolytic Cells: Nonspontaneous Reaction

Oxidation Numbers

Periodic Trends:
Common Oxidation States

http://chemconnections.org/general/movies/OXIDSTAT.MOV

QUESTION

What is the oxidation state of Hg in Hg_2Cl_2?

A. +2
B. –1
C. –2
D. +1
E. 0

A Review of Oxidation-Reduction (Redox) Terminology

Terminology	Example: $Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$	
OXIDATION • Electrons are lost • Reducing agent is oxidized • Oxidation number increases	Zinc **loses** electrons. Zinc is the reducing agent and becomes **oxidized**. The oxidation number of Zn **increases** from 0 to +2.	
REDUCTION • Electrons are gained • Oxidizing agent is reduced • Oxidation number decreases	Hydrogen ion **gains** electrons. Hydrogen ion is the oxidizing agent and becomes **reduced**. The oxidation number of H^+ **decreases** from +1 to 0.	

QUESTION

Which of the following species cannot function as an oxidizing agent?

A. S(s)
B. $NO_3^-(ag)$
C. $Cr_2O_7^{-2}(aq)$
D. I^- (aq)
E. $MnO_4^-(aq)$

Balancing Redox Equations
The Half-Reaction Method
See: Chem 120 Slides & (Handout) Sophie's PLTL Method

Step 1: Divide the skeleton reaction into two half-reactions, each of which contains the oxidized and reduced forms of one of the species.

Step 2: Balance the atoms and charges in each half-reaction.

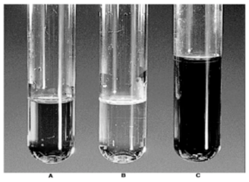
- ❖ Atoms are balanced in the following order: Atoms other than O and H, then O, and then H.
- ❖ Charge is balanced by *adding electrons* (e^-). To the *left* for the *reduction eqn*., and to the *right* for the *oxidation eqn*.

Step 3: Multiply each half-reaction by an integer to make the number of e^- gained in the reduction equal the number of e^- lost in the oxidation. (Least Common Denominator)

Step 4: Add the balanced half-reactions. Include states of matter.

Step 5: Check that the atoms and charges are balanced.

The Reaction of Dichromate Ion and Iodide Ion



Balance the redox equation for the reaction in acidic solution.

$$Cr_2O_7^{2-}{}_{(aq)} + I^-{}_{(aq)} \longrightarrow Cr^{3+}{}_{(aq)} + I_{2\,(s)} \qquad \text{(in acid)}$$

Balancing Redox Equations in Acid

$$Cr_2O_7^{2-}{}_{(aq)} + I^-{}_{(aq)} \longrightarrow Cr^{3+}{}_{(aq)} + I_{2\,(s)}$$

Step #1: *Break into oxidation and reduction equations:*

$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$ [reduction]

$I^- \longrightarrow I_2$ [oxidation]

Step #2: *Balance atoms and charges in each half-reaction:*

For the $Cr_2O_7^{2-}/Cr^{3+}$ half-reaction:

a) *Balance atoms other than O and H:* Balance the Chromium

$$Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+}$$

Balancing Redox Equations in Acid

b) *Balance O atoms by adding H_2O molecules*.

$$Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

c) *Balance H atoms by adding H^+ ions*.

$$14\,H^+ + Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

d) *Balance charge by adding electrons*.

$$6\,e^- + 14\,H^+ + Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$

For the I^-/I_2 reaction:

a) *Balance atoms other than O and H*.

$$2\,I^- \longrightarrow I_2$$

Balancing Redox Equations in Acid

b) *Balance O atoms with water*. Not needed.

c) *Balance H atoms with H^+*. Not needed

d) *Balance charge with electrons*.

$$2\,I^- \longrightarrow I_2 + 2\,e^-$$

Step #3 *Multiply each half-reaction by some integer to balance the # e^- !*

$$3(2I^- \longrightarrow I_2 + 2\,e^-)$$
$$6\,I^- \longrightarrow 3\,I_2 + 6\,e^-$$

Step #4 *Add the half-reactions together, canceling things that are on both sides of the equation:*

$$6\,e^- + 14\,H^+ + Cr_2O_7^{2-} \longrightarrow 2\,Cr^{3+} + 7\,H_2O$$
$$6\,I^- \longrightarrow 3\,I_2 + 6\,e^-$$

$$6\,I^-{}_{(aq)} + 14\,H^+{}_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} \longrightarrow 3\,I_{2\,(s)} + 7\,H_2O_{(L)} + 2\,Cr^{3+}{}_{(aq)}$$

Step #5 Check:√

Balancing Redox Equations in Base

Balance the reaction between permanganate ion and oxalate ion to form carbonate ion and solid manganese dioxide in basic solution.

$$MnO_4^-{}_{(aq)} + C_2O_4^{2-}{}_{(aq)} \longrightarrow MnO_{2\,(s)} + CO_3^{2-}{}_{(aq)}$$

1) *Divide into half-reactions:* (reduction)

$$MnO_4^- \longrightarrow MnO_2$$

2) *Balance*

a) *Atoms other than O and H* Not needed

b) *O atoms with water* $MnO_4^- \longrightarrow MnO_2 + 2\,H_2O$

c) *H atoms with H^+* $4\,H^+ + MnO_4^- \longrightarrow MnO_2 + 2\,H_2O$

d) *Charge with e^-* $3\,e^- + 4\,H^+ + MnO_4^- \longrightarrow MnO_2 + 2\,H_2O$

Balancing Redox Equations in Base

1) *Divide into two half-reactions:* (oxidation)

$$C_2O_4^{2-} \longrightarrow CO_3^{2-}$$

2) *Balance*

a) *Atoms other than O and H* $C_2O_4^{2-} \longrightarrow 2\ CO_3^{2-}$

b) *O atoms with water* $2\ H_2O + C_2O_4^{2-} \longrightarrow 2\ CO_3^{2-}$

c) *H atoms with* H^+ $2\ H_2O + C_2O_4^{2-} \longrightarrow 2\ CO_3^{2-} + 4\ H^+$

d) *Charge with* e^-

$$2\ H_2O + C_2O_4^{2-} \longrightarrow 2\ CO_3^{2-} + 4\ H^+ + 2\ e^-$$

3) *Multiply each half-reaction to equalize the electrons.*
oxidation = $2e^-$, reduction = $3e^-$, therefore (LCD = $6e^-$)

ox = $6\ H_2O + 3\ C_2O_4^{2-} \longrightarrow 6\ CO_3^{2-} + 12\ H^+ + 6\ e^-$
red = $6\ e^- + 8\ H^+ + 2\ MnO_4^- \longrightarrow 2\ MnO_2 + 4\ H_2O$

Balancing Redox Equations in Base

4) *Add half-reactions and cancel substances appearing on both sides.*

oxidation = $6\ H_2O + 3\ C_2O_4^{2-} \longrightarrow 6\ CO_3^{2-} + 12\ H^+ + 6\ e^-$
reduction = $6\ e^- + 8\ H^+ + 2\ MnO_4^- \longrightarrow 2\ MnO_2 + 4\ H_2O$

$$2\ MnO_4^- + 2\ H_2O + 3\ C_2O_4^{2-} \longrightarrow 2\ MnO_2 + 6\ CO_3^{2-} + 4\ H^+$$

4a) *Base: Add* OH^- *to both sides of the equation to neutralize* H^+ *.*

$$\mathbf{4\ OH^- + 2\ MnO_4^- + 2\ H_2O + 3\ C_2O_4^{2-} \rightarrow 2\ MnO_2 + 6CO_3^{2-} + \underbrace{4H^+ + 4\ OH^-}_{4\ H_2O}}$$

Subtract out the water that is on both sides:

$$4\ OH^- + 2\ MnO_4^- + 3\ C_2O_4^{2-} \longrightarrow 2\ MnO_2 + 6\ CO_3^{2-} + 2\ H_2O$$

$$2\ MnO_{4\ (aq)}^- + 3\ C_2O_{4\ (aq)}^{2-} + 4\ OH^-_{(aq)} \rightarrow 2\ MnO_{2(s)} + 6CO_{3\ (aq)}^{2-} + 2\ H_2O_{(l)}$$

5) Check: √

Electrochemical Cells

- There are two types of electrochemical cells.
- They are based on the general thermodynamic nature of the reaction, i.e., the Gibbs Free Energy, ΔG.

1) A **voltaic cell** (or **galvanic cell**) uses a spontaneous reaction to generate electrical energy, ($\Delta G < 0$). The reaction is the system. It does work on the surroundings. All batteries contain one or more voltaic cells.

2) An **electrolytic cell** uses electrical energy to drive a nonspontaneous reaction ($\Delta G > 0$), the surroundings do work on the reacting system.

Electrochemical Cells

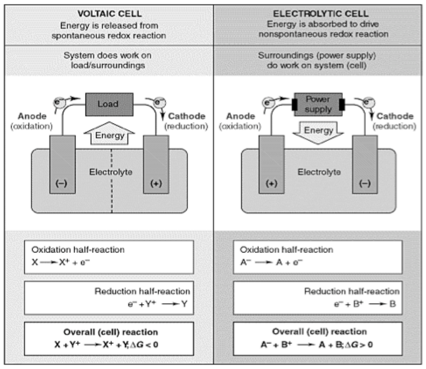
All electrochemical cells have several common features:

1) They have two electrodes:
Anode (-) *–The oxidation half-reaction takes place at the anode.*

Cathode (+) –*The reduction half-reaction takes place at the cathode.*

2) The electrodes are immersed in an ***electrolyte****, an ionic solution containing a mixture of ions that conduct electricity.*

General Characteristics of Voltaic and Electrolytic Cells

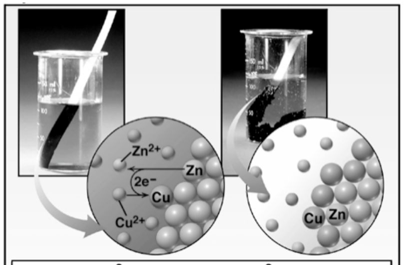


QUESTION

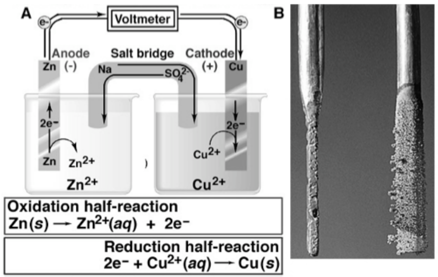
The diagram depicts a functioning galvanic cell. Which statement correctly explains the role of the small gray connecting area between the two beakers?

A. The connecting area works like a “salt bridge” where electrons can travel from the reducing agent to the oxidizing agent.
B. Although mixing of the solutions is prevented, this area allows ions to pass from one solution to another.
C. This porous area works like a “salt bridge” and allows a way for electrons to flow through it, which can provide useful work.
D. This porous area permits the circuit to be complete by allowing the reducing agent to gain electrons.

The Spontaneous Reaction Between Zinc and Copper(II) Ion



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



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

Reduction half-reaction
$2e^- + Cu^{2+}(aq) \rightarrow Cu(s)$

Overall (cell) reaction
$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$

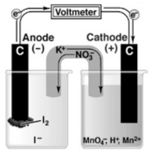
A Voltaic Cell Based on the Zinc-Copper Reaction

Voltaic Cells

Voltaic Cells I:
The Copper-Zinc Cell

http://chemconnections.org/general/movies/Cu-Zn Cell.MOV

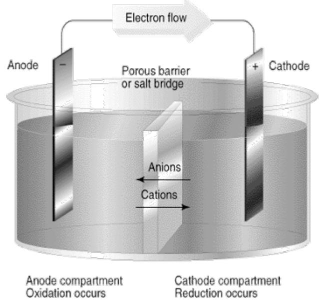
Voltaic Cells: Redox Reactions



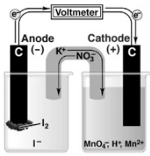
The cell is constructed by placing components of each half-reaction into a separate compartment, or half-cell, which are connected by a salt bridge.

The oxidation half-cell (anode compartment) is written on the left. The reduction half-cell (cathode compartment) is on the right.

Voltaic Cells

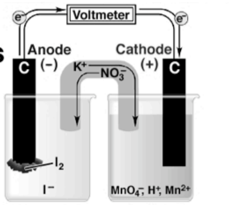


Voltaic Cells: Redox Reactions



1) *The oxidation half-cell*–The electrode conducts electrons out of its half-cell.
2) *The reduction half-cell*–The electrode conducts electrons into its half-cell.
3) *Relative charges on the electrodes*–In any **voltaic** cell, the anode is negative and the cathode is positive
4) *Purpose of the salt bridge*–As electrons move left to right through the wire, anions and cations move in the salt bridge.

Voltaic Cell using Inactive Electrodes



Oxidation half-reaction
$2I^-(aq) \longrightarrow I_2(s) + 2e^-$

Reduction half-reaction
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$

Overall (cell) reaction
$2MnO_4^-(aq) + 16H^+(aq) + 10I^-(aq) \longrightarrow 2Mn^{2+}(aq) + 5I_2(s) + 8H_2O(l)$

Cell Diagram / Notation for a Voltaic Cell

There is a shorthand notation for describing the components of a voltaic cell. For example, the notation for the Zn/Cu^{2+} cell is:

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

The key parts of this notation are:

1) The components of the anode compartment (oxidation half-cell) are written to the left of the components of the cathode compartment (reduction half-cell).
2) A vertical line represents a phase boundary. For example, in the anode $Zn_{(s)}$ $Zn^{2+}_{(aq)}$ represents zinc metal in the solid phase and zinc ions in solution. If they are in the same phase, they are separated by a comma (e.g. $H^+_{(aq)}$, MnO_4^-).
3) Half-cell components usually appear in the same order as in the cell.
4) A double vertical line represents the separation of the cells, or the phase boundary set up by the salt bridge.

Diagramming Voltaic Cells

Problem: 1) Diagram the following cell, 2) show balanced equations, and 3) write the notation for the voltaic cell that consists of one half-cell with a Cr bar in a $Cr(NO_3)_3$ solution, another half-cell with an Ag bar in an $AgNO_3$ solution, and a KNO_3 salt bridge.

Measurements show that the Cr electrode is negative relative to the Ag electrode.

Diagramming Voltaic Cells

Plan: Determine which is the anode compartment (oxidation) and which is the cathode (reduction). To do so, we must find the direction of the spontaneous redox reaction, which is given by the relative electrode charges. Since electrons are released into the anode during oxidation, it has a negative charge. We are told that Cr is negative, so it must be the anode and, therefore, Ag is the cathode.

Solution: Write the balanced half-reactions. Since the Ag electrode is positive, the half-reaction consumes electrons:

$$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)} \qquad \text{[reduction; cathode]}$$

Diagramming Voltaic Cells

Since the Cr electrode is negative, the half-reaction releases electrons:

$$Cr_{(s)} \longrightarrow Cr^{3+}_{(aq)} + 3\,e^- \qquad \text{[oxidation; anode]}$$

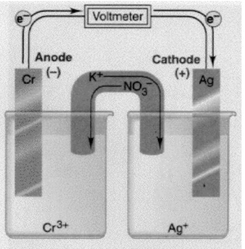
Writing the balanced overall cell reaction. We triple the reduction half-reaction to balance electrons, and combine the half-reactions to obtain the overall spontaneous reaction:

$$Cr_{(s)} + 3\,Ag^+_{(aq)} \longrightarrow Cr^{3+}_{(aq)} + 3\,Ag_{(s)}$$

Determining direction of electron and ion flow. The released e$^-$ in the Cr electrode (negative) flow through the external circuit to the Ag electrode (positive). As Cr^{3+} ions enter the anode electrolyte, NO_3^- ions enter from the salt bridge to maintain neutrality. As Ag$^+$ ions leave the cathode electrolyte and plate out on the Ag electrode, K$^+$ ions enter from the salt bridge to maintain neutrality.

$$\mathbf{Cr_{(s)} \mid Cr^{3+}_{(aq)} \parallel Ag^+_{(aq)} \mid Ag_{(s)}}$$

The Cr-Ag Cell



Oxidation half-reaction
$Cr(s) \longrightarrow Cr^{3+}(aq) + 3e^-$

Reduction half-reaction
$Ag^+(aq) + e^- \longrightarrow Ag(s)$

Overall (cell) reaction
$Cr(s) + 3Ag^+(aq) \longrightarrow Cr^{3+}(aq) + 3Ag(s)$

Cell EMF

- Electromotive force (emf) is the force required to push electrons through an external circuit.
- Cell potential: E_{cell} is the emf of a cell. A spontaneous cell has a positive value.
- Potential difference: difference in electrical potential. Measured in volts.

$$E^\circ_{\text{cell}} = E^\circ_{\text{red}}(\text{cathode}) - E^\circ_{\text{red}}(\text{anode})$$

- One volt is the potential difference required to impart one joule of energy to a charge of one coulomb: $1\,\text{V} = \dfrac{1\,\text{J}}{1\,\text{C}}$

Voltages of Some Voltaic Cells

Voltaic Cell	**Voltage (V)**
Common alkaline battery	1.5
Lead-acid car battery (6 cells = 12 V)	2.0
Calculator battery (mercury)	1.3
Electric eel (~ 5000 cells in 6-ft eel = 750 V)	0.15
Nerve of giant squid (across cell membrane)	0.070

Voltages of Some Voltaic Cells

Voltaic Cells/Voltage (V)	
Electric eel (~ 5000 cells in 6-ft eel = 600750 V)	0.15V/ cell

Habitat: Amazon & Orinoco Rivers

Nerve of giant squid
(across cell membrane) 0.070V
Active human axon ~ 0.100V

QUESTION

Which metal, Al or Ni could reduce Zn^{2+} to Zn(s) if placed in a Zn^{2+} (aq) solution?

$Zn^{2+} + 2e^- \rightarrow Zn \quad E^\circ = -0.76\text{ V}$

$Al^{3+} + 3e^- \rightarrow Al \quad E^\circ = -1.66\text{ V}$

$Ni^{2+} + 2e^- \rightarrow Ni \quad E^\circ = -0.23\text{ V}$

A. Al
B. Ni
C. Both Al and Ni would work.
D. Neither Al nor Ni would work.
E. Cannot be determined.