

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



QUESTION

What is the oxidation state of Hg in Hg₂Cl₂? 1) +2 2) -1 3) -2 4) +1 5) 0

A Review of Oxidation-Reduction (Redox) Terminology Terminology Example: Zn(s) + 2H⁴(aq) → Zn²⁺(aq) + H₂(g) OxIDATION Zinc Ioses electrons. • Reducing agent is oxidized Zinc Ioses electrons. • Oxidation number increases Zinc Ioses electrons. • Oxidation number increases Zinc Ioses electrons. • Oxidation number increases Tin of the oxidized. • Oxidation number increases Hydrogen ion gains electrons. • Dictors are gained Hydrogen ion gains electrons. • Oxidation number Hydrogen ion gains electrons. • Oxidation number Hydrogen ion gains electrons. • Oxidation number Hydrogen ion sithe oxidizing agent and becomes reduced. • Oxidation number The oxidation number of 2H⁺ • Oxidation number Hydrogen ion sithe oxidizing agent and becomes reduced. • Oxidation number The oxidation number of 2H⁺ • decreases From Y = 0.



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

- 1) S(s)
- 2) $NO_3(ag)$
- 3) $Cr_2O_7^{-2}(aq)$
- 4) l⁻ (aq)
- 5) MnO₄⁻(aq)

Balancing Redox Equations The Half-Reaction 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.

 $\operatorname{Cr}_{2}O_{7}^{2}_{(aq)} + I_{(aq)} \longrightarrow \operatorname{Cr}^{3+}_{(aq)} + I_{2(s)}$ (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 $\operatorname{Cr}_2O_7^{2-}/\operatorname{Cr}^{3+}$ half-reaction: a) *Balance atoms other than O and H:* Balance the Chromium $\operatorname{Cr}_2O_7^{2-}\longrightarrow 2 \operatorname{Cr}^{3+}$



For the I^{-}/I_{2} reaction: a) Balance atoms other than O and H. $2 I^{-} \longrightarrow I_{2}$





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) <i>H</i> atoms with H^+ 2 H ₂ O + C ₂ O ₄ ²⁻ \longrightarrow 2 CO ₃ ²⁻ + 4 H ⁺	
d) Charge with e^{-} 2 H ₂ O + C ₂ O ₄ ² \longrightarrow 2 CO ₃ ²⁻ + 4 H ⁺ + 2 e ⁻	
 Multiply each half-reaction to equalize the electrons. oxidation = 2e⁻, reduction = 3e⁻, therefore (LCD = 6e⁻) 	
$ox = 6 H_2O + 3 C_2O_4^{2-} \longrightarrow 6 CO_3^{2-} + 12 H^+ + 6 e^-$	
$red = 6 e^{-} + 8 H^{+} + 2 MnO_{4}^{-} \longrightarrow 2 MnO_{2} + 4 H_{2}O$	



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:

 They have two electrodes: <u>Anode</u> (-) –*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.





QUESTION

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

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















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 AgNO₃ solution, and a KNO₃ 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: $Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$ [reduction; cathode]

Diagramming Voltaic Cells

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

 $Cr_{(s)} \longrightarrow Cr^{3+}_{(aq)} + 3 e^{-}$

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:

[oxidation; anode]

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

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.

 $\operatorname{Cr}_{(s)} \mid \operatorname{Cr}^{3+}_{(aq)} \mid\mid \operatorname{Ag}^{+}_{(aq)} \mid \operatorname{Ag}_{(s)}$



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: $1V = \frac{1J}{1C}$

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 = 75	50 V) 0.15
Nerve of giant squid (across cell membr	rane) 0.070

QUESTION

Which metal, Al or Ni could reduce Zn²⁺ to Zn(s) if placed in a Zn²⁺ (aq) solution? $Zn^{2+} + 2e^{-} \neq Zn \qquad E^{\circ} = -0.76 \text{ V}$ $Al^{3+} + 3e^{-} \neq Al \qquad E^{\circ} = -1.66 \text{ V}$ $Ni^{2+} + 2e^{-} \Rightarrow Ni \qquad E^{\circ} = -0.23 \text{ V}$ 1) Al 2) Ni

- 3) Both Al and Ni would work.
- 4) Neither Al nor Ni would work.
- 5) Cannot be determined.