

## Electrochemistry

Applied Oxidation-Reduction  
Reactions

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## Redox Review

- oxidation numbers
- balancing redox reactions

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## Oxidation Numbers

- Ox. No. of free elements is zero.
- Ox. No. of monatomic ions is equal to the charge.
- Ox. No. of F in compounds is always -1.
- Ox. No. of O in compounds is usually -2 except in peroxides (-1).
- Ox. No. of H is usually +1 except in hydrides (-1).
- Sum of all Ox. Nos. in compounds must add to the overall charge.

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## Balancing redox reactions in acid

- Write the skeleton equation and assign ox. nos. to all elements.
- Split the reaction into two half-reactions:
  - One that contains all species being reduced
  - One that contains all species being oxidized
- Balance all atoms in each half-reaction except for H and O
- Balance O by adding water to side needing O.
- Balance H by adding  $H^+$  to side needing H.

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## Balancing redox reactions in acid

- Balance charge by adding  $e^-$  to side with more positive charge.
- Balance  $e^-$  by multiplying each half-reaction by the number of electrons in the other half-reaction.
- Add the half-reactions together and cancel similar terms.
- Check to make sure atoms and charges are balanced.

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## Balancing redox reactions in base

- Write the skeleton equation and assign ox. nos. to all elements.
- Split the reaction into two half-reactions:
  - One that contains all species being reduced
  - One that contains all species being oxidized
- Balance all atoms in each half-reaction except for H and O
- Balance O by adding water to side needing O.
- Balance H by adding  $H_2O$  to side needing H and  $OH^-$  to the other side at the same time.

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## Balancing redox reactions in acid

- Balance charge by adding  $e^-$  to side with more positive charge.
- Balance  $e^-$  by multiplying each half-reaction by the number of electrons in the other half-reaction.
- Add the half-reactions together and cancel similar terms.
- Check to make sure atoms and charges are balanced.

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## Electrochemistry

- Electrochemistry is the process of using oxidation-reduction reactions to obtain useful work
- Half-reactions must be separated to do this

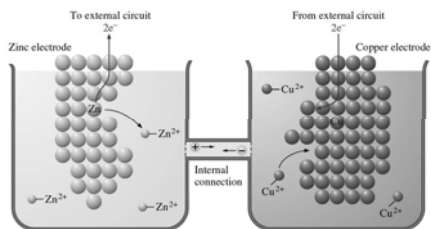
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## Electrochemical cells

- Electrochemical cell
  - electrodes dipped into solutions of electrolyte – half-cell
  - salt bridge
  - external circuit
- Types of cells
  - voltaic or galvanic – spontaneous reactions
  - electrolytic – uses energy to drive a non-spontaneous reaction

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## Electrochemical cell



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## Electrodes

- Two processes
  - oxidation – anode
  - reduction – cathode
- Definitions are the same regardless of type of cell

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## Cell notation

- A short-hand way of representing an electrochemical cell
  - “|” is used to separate one phase from another in a half-cell
  - “,” is used to separate substances in the same phase in a half-cell
  - “||” is used to represent the salt-bridge, separates half-cells

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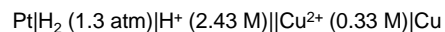
## Cell Notation

- For a reaction in which Iron is oxidized to Iron(II) ion and Chromate ion is reduced to Chromium(III) ion the cell notation would be
  - $\text{Fe}|\text{Fe}^{2+}||\text{CrO}_4^{2-},\text{Cr}^{3+}|\text{Pt}$ 
    - The platinum is needed as an inert electrode to carry the current

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## Cell notation

- We can fully specify a cell by including concentrations and pressures.



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## Electromotive Force – what causes electrons to move?

- Moving electron is like moving water
- A difference in pressure is needed.
- This difference in pressure is called the potential of the cell
- half-cell potentials are tabulated in the book for reductions only
  - Standard reduction potentials

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## Standard Reduction potentials

- Intensive properties – don't depend on amount of material
- Sign changes for oxidations
- Valid only at 25 C
  - Value does change at other temperatures
  - We won't explore that change (see website)
- Measured in volts (1 V = 1J/C)

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## Standard Reduction potentials

- All are defined in terms of the **Standard Hydrogen Electrode (SHE)**
  - $\text{Pt}|\text{H}^+|\text{H}_2|$
  - $2 \text{H}^+ + 2 \text{e}^- \rightarrow \text{H}_2$
  - 0.00 V
  - Every other reduction potential is defined relative to SHE.

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## Standard Cell Potentials, $E_{\text{cell}}$

- The standard cell potential can be found from the reduction and oxidation potentials
$$E_{\text{cell}}^{\circ} = E_{\text{reduction}}^{\circ} + E_{\text{oxidation}}^{\circ}$$
- The oxidation potential is the negative of the reduction potential for the electrode

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## Standard Cell Potentials, $E_{\text{cell}}$

- We can take that into account and calculate cell potentials only from the standard reduction potentials

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

- $E_{\text{cathode}}$  and  $E_{\text{anode}}$  are both standard **reduction** potentials. The negative sign takes into account the fact that the anode is oxidation.

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## Example

- What is the standard cell potential of a cell with the overall reaction  $\text{Cd} + 2 \text{Ag}^+ \rightarrow 2 \text{Ag} + \text{Cd}^{2+}$ .
- Look up standard reduction potentials
  - $\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$   $E = 0.80\text{V}$
  - $\text{Cd}^{2+} + 2 \text{e}^- \rightarrow \text{Cd}$   $E = -0.40\text{V}$
- Calculate:  $E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ} = E_{\text{Ag}}^{\circ} - E_{\text{Cd}}^{\circ}$   
 $= 0.80 \text{ V} - (-0.40 \text{ V}) = 1.20 \text{ V}$

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## Work done

- The work done by a cell can be shown to be  $w = -nFE_{\text{cell}}^{\circ}$
- F is Faraday's constant and is equal to the charge on 1 mol of electrons, 96485 C.
- n is the number of electrons transferred in the balanced chemical equation.

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## Free energy and electrochemical cells

- We saw in the last chapter the free energy change,  $\Delta G$ , is the maximum work done by a chemical system.
- The work done by an electrochemical cell is  $-nFE_{\text{cell}}^{\circ}$ .
- Therefore

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

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## Electrochemical cells and equilibrium constants

- Because of the previous result we also get

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ} = -RT \ln K$$

$$nFE_{\text{cell}}^{\circ} = RT \ln K$$

$$E_{\text{cell}}^{\circ} = \frac{RT}{nF} \ln K \quad \text{or} \quad K = e^{nFE_{\text{cell}}^{\circ}/RT}$$

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## Cell potential under non-standard conditions

- We can also derive the cell potential under non-standard conditions
- $$\Delta G = \Delta G^{\circ} + RT \ln Q$$
- $$-nFE = -nFE^{\circ} + RT \ln Q$$
- $$E = E^{\circ} - \frac{RT}{nF} \ln Q$$
- This is called the Nernst equation
  - Q is the thermodynamic reaction quotient

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## Electrolysis

- Electrolysis uses electrical energy to drive a non-spontaneous reaction
- We will look at two kinds of electrolysis
  - molten salts
  - aqueous solutions

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## Electrolysis of molten salts

- When we melt ionic compounds (salts) the liquid can carry a current.
- With enough voltage we can cause the compound to decompose.
- NaCl
  - Anode – oxidation –  $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-$
  - Cathode – reduction –  $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$

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## Electrolysis of molten salts

- For a salt there is generally only one thing that can happen at each electrode.

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## Electrolysis of aqueous solutions

- When we have an ionic substance dissolved in water, there are now two possibilities at each electrode.

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## NaCl

- Anode
  - $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-$
  - $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$
- Cathode
  - $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
  - $2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$
- How do we decide which happens?
  - Electrode potentials

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## Anode -- Oxidation

- Two possibilities are
  - $2 \text{Cl}^- \rightarrow \text{Cl}_2 + 2 \text{e}^-$   $E = -1.36 \text{ V}$
  - $2 \text{H}_2\text{O} \rightarrow \text{O}_2 + 4 \text{H}^+ + 4 \text{e}^-$   $E = -1.23 \text{ V}$
- The oxidation of water to oxygen gas is more likely to happen
  - the oxidation potential is more positive

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## [ Cathode – Reduction ]

- Two possibilities are
  - $\text{Na}^+ \rightarrow \text{Na} + \text{e}^-$   $E = -1.36 \text{ V}$
  - $2 \text{H}_2\text{O} + 4 \text{e}^- \rightarrow \text{H}_2 + 2 \text{OH}^-$   $E = +0.83 \text{ V}$
- The reduction of water to hydrogen gas is more likely to happen
  - the reduction potential is more positive

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## [ Stoichiometry of electrolysis ]

- The main purpose of electrolysis is to produce solid metal from either a solution or a molten salt.
- The moles of metal produced is proportional to the number of electrons needed to make the metal from its ion.
- The number of electrons can be found from the current and time.
- Current is charge per unit time. ( $1 \text{ C s}^{-1} = 1 \text{ amp}$ )

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## [ Example ]

- How many grams of sodium metal can be produced from molten sodium chloride when 15.0 amp flows for 12.0 hours?

$$\begin{aligned} ? \text{ g Na} &= 12.0 \text{ h} \times \frac{3600 \text{ s}}{1 \text{ h}} \times \frac{15.0 \text{ C}}{\text{s}} \times \frac{1 \text{ mol e}^-}{96485 \text{ C}} \times \frac{1 \text{ mol Na}}{1 \text{ mol e}^-} \\ &\quad \times \frac{22.9898 \text{ g Na}}{1 \text{ mol Na}} = 154 \text{ g Na} \end{aligned}$$

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