Redox Chemistry: Electron Transfer

THE UNIVERSITY OF TEXAS AT EL PASO

CHEM 3151

APRIL 23RD, 2014
The Layout

Introduction to Electron Transfer

Mixed-valent Compounds

Electrochemistry
Redox

What happens in a reduction reaction?

A) Electrons are removed
B) Electrons are added
C) Protons are added
D) Protons are removed
What happens in a reduction reaction?

A) Electrons are removed

B) Electrons are added  ✔

C) Protons are added

D) Protons are removed

Redox

\[ X + e^- \rightarrow X^- \]
Electron Transfer

In an electron transfer reaction, there is an electron exchange between a donor ($D$) and an acceptor ($A$).

$$D + A \leftrightarrow D^+ + A^-$$

The exchange results in an oxidized donor ($D^+$) and a reduced acceptor ($A^-$). The donor has lost an electron and the acceptor has gained an electron.
Introduction to Electron Transfer

ET reactions are commonplace in biological systems such as:

- Photosystem II
- Nitrogen fixation
- Cellular respiration
Water Splitting

According to the diagram on the right, the reaction above is:

A) exothermic, spontaneous
B) endothermic, spontaneous
C) exothermic, non-spontaneous
D) endothermic, non-spontaneous

\[ 2H_2O \rightarrow O_2 + 2H_2 \]
Water Splitting

According to the diagram on the right, the reaction above is:

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- C) exothermic, non-spontaneous
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![Diagram showing the reaction 2H₂O → O₂ + 2H₂ with energy level curves and reaction coordinate graph.](image)
Introduction to Electron Transfer: Photosystem II

Photosystem II utilizes ET to split water:

\[ 2H_2O \rightarrow O_2 + 2H_2 \]

- \( H_2O \rightarrow O_2 + 4e^- + 4 H^+ \) (H\(_2\)O oxidation half-reaction)
- \( 4H^+ + 4e^- \rightarrow 2H_2 \) (H\(^+\) reduction half-reaction)
Inner versus Outer

Inner-sphere electron transfer:

Outer-sphere electron transfer:
Marcus Theory

In 1992 Rudolph Marcus received the Nobel Prize in Chemistry for his contribution to the understanding of the thermodynamics and the kinetics of electron transfer.
Mixed-valent compounds

Mixed-valent (MV) molecules are capable of inner-sphere electron transfer.

\[ \text{D} - \text{A} \]

The electron donor and electron acceptor are the same element, a metal (not always the case)...

\[ \text{M} \rightarrow \text{M} \]

...but they have different oxidation states.

\[ \text{M}^{+2} \rightarrow \text{M}^{+3} \]
Mixed-valent Compounds

One of the first and most thoroughly studied MV compounds was the Creutz-Taube Ion:

In a MV compound, two metal centers are connected by a linker.

\[ \text{M-L-M} \]
My Research

[Chemical structures and formulas]

Dr. Villagrán
Equilibrium Equation

\[ [M^{3+} L M^{3+}] + [M^{2+} L M^{2+}] \rightleftharpoons 2 [M^{3+} L M^{2+}] \]

Assuming the reaction above is at equilibrium, what should the equilibrium constant equation be?

A) \[ K_c = \frac{[M^{3+} L M^{2+}]^2}{[M^{3+} L M^{3+}][M^{2+} L M^{2+}]} \]

B) \[ K_c = \frac{[M^{3+} L M^{3+}][M^{2+} L M^{2+}]}{[M^{3+} L M^{2+}]^2} \]

C) \[ K_c = \frac{[M^{3+} L M^{3+}][M^{2+} L M^{2+}]}{2[M^{3+} L M^{2+}]} \]

D) \[ K_c = \frac{2 [M^{3+} L M^{2+}]}{[M^{3+} L M^{3+}][M^{2+} L M^{2+}]} \]
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D) \( K_c = \frac{2[M^3+ L M^2+]}{[M^3+ L M^3+][M^2+ L M^2+]} \)
Equilibrium Equation

\[ aA + bB \iff cC \]

\[ K = \frac{[C]^c}{[A]^a[B]^b} \]
Equilibrium Constant and MV

We can use the equilibrium constant to determine if electron transfer will proceed thermodynamically.

\[ K_c = \frac{[M^{3+} L M^{3+}]^2}{[M^{3+} L M^{3+}][M^{2+} L M^{2+}]} \]
Electrochemistry

What should the axis labels be for the graph below?

A) X = current, Y = potential
B) X = potential, Y = current
C) X = time, Y = potential
D) X = time, Y = current
Electrochemistry

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B) X = potential, Y = current
Cyclic voltammetry

In the graph above, A refers to what event?

A) Oxidation  B) Reduction
C) Both A and B  D) None of the above
Cyclic voltammetry

In the graph above, A refers to what event?

A) Oxidation  B) Reduction  C) Both A and B  D) None of the above

Correct answer: B) Reduction
Electrochemistry: Cyclo voltammetry
Half-wave Potential

\[ E_{1/2} = \frac{E_{pc} + E_{pa}}{2} \]
Half-wave potential: Electron Transfer

\[ \Delta E_{1/2} = E_{1/2}^{II} - E_{1/2}^{I} \]
Half-wave potential: Electron Transfer

In the cyclovoltammogram below, would the $\Delta E_{1/2}$ be relatively large or small?

A) Small  B) Large  C) I dunno  D) None
Half-wave potential: Electron Transfer

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A) Small  ✔️  B) Large  C) I dunno  D) None
Free Energy and Equilibrium Constant

Free Energy of reaction:

$$\Delta G = \Delta G^° + R T \ln Q$$

Free Energy and potential relation:

$$\Delta G = -n F E \quad \Delta G^° = -n F E^°$$
Equilibrium Constant and Potential

Potential in free energy equation:

\[-nFE = -nF E^\circ + RT \ln Q\]

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

Nernst Equation:

\[K = \exp\left(\frac{F E^\circ}{RT}\right)\]
$K_c$ and $\Delta E_{1/2}$

Half-wave potential and Nernst equation

$$\Delta E_{1/2} = E^\circ$$

$$K_c = K$$

$$K_c = \exp\left(\frac{F\Delta E_{1/2}}{RT}\right)$$
Equilibrium

Kept at constant temperature, what does a large $\Delta E_{1/2}$ mean?

A) Equilibrium constant will be large, formation of products favored.

B) Equilibrium constant will be small, formation of reactants favored.

C) Equilibrium constant will be 1, both sides of reaction favored.

D) None of the above.
Equilibrium

Kept at constant temperature, what does a large $\Delta E_{1/2}$ mean?

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C) None of the above.
Robin-Day Classification

The Robin-Day classification scheme divides MV molecules into three different classes (Class I, Class II, Class III) according to the molecule’s equilibrium constant.

Class I. \( K_c < 10^2 \) (low)

Class II. \( 10^2 \leq K_c \leq 10^6 \) (intermediate)

Class III. \( K_c > 10^6 \) (high)
Class III

Class II

Class I

Electrochemistry

In this experiment we will be doing cyclic voltammetry experiments on three different ferrocene compounds.

The first compound is just ferrocene. Ferrocene is composed of a single iron ion that is sandwiched between two cyclopentadienyl ions.
The Ferrocene Dimers you will use

Z

E
The Experiment

The Ferrocene compounds have already been synthesized.

You will prepare their own solution with samples for electrochemical analysis.

You will need to prepare one sample for each ferrocene compound.

You will be required to use potentiostats to run cyclic voltammetry experiments on the compounds.
The Report

You will have two weeks to submit a lab report on today’s experiment.

The format of the lab report should conform to the requirements listed on your class syllabus.

You should focus on the conclusion and the discussion of your results.

Be able to explain your results using your knowledge of electrochemistry and electron transfer.
This material is based upon work supported by the National Science Foundation under Grant Number DUE-1140469.

Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the National Science Foundation.