

Lecture 18 CH131 Summer 1

Monday, June 24, 2019

- Complete: Balancing redox equations, <http://goo.gl/MMEUCs>
- Cell voltage, E_{cell} , and electrical energy
- The Nernst equation determines cell voltage, E_{cell}
- Exploring the Nernst equation

Next lecture: Complete ch17: Electricity from mixing: Concentration cells. Practice problems.

For **oxidation numbers** and **balancing redox equations**, please work through <http://goo.gl/MMEUCs>



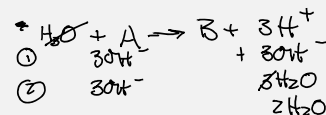
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Balancing oxidation reduction equations

If in **basic solution**, convert $\text{H}^+(aq)$ to $\text{OH}^-(aq)$

1. Add as many $\text{OH}^-(aq)$ as $\text{H}^+(aq)$ to both sides
2. Combining $\text{H}^+(aq)$ and $\text{OH}^-(aq)$ into $\text{H}_2\text{O}(l)$
3. Cancel $\text{H}_2\text{O}(l)$ where possible



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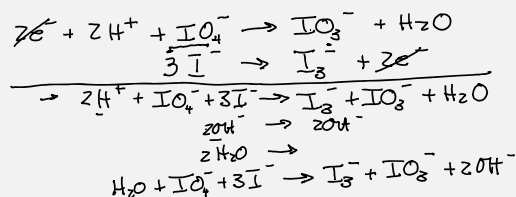
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Balancing oxidation reduction equations

If in **basic solution**, convert $\text{H}^+(aq)$ to $\text{OH}^-(aq)$

Balance $\text{IO}_4^-(aq) + \text{I}^-(aq) \rightarrow \text{IO}_3^-(aq) + \text{I}_3^-(aq)$

Answer: $\text{H}_2\text{O}(l) + \text{IO}_4^-(aq) + 3\text{I}^-(aq) \rightarrow \text{IO}_3^-(aq) + \text{I}_3^-(aq) + 2\text{OH}^-(aq)$



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Balancing half-reactions

For **oxidation numbers** and **balancing redox equations**, please work through <http://goo.gl/MMEUCs>

$\text{O}_2(g)$ **reduced** to hydrogen peroxide, $\text{H}_2\text{O}_2(aq)$



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[TP] Based on the balanced **reduction** half-reaction, how many moles of electrons are **consumed** when 1 mole of $\text{O}_2(g)$ is **reduced** to hydrogen peroxide, $\text{H}_2\text{O}_2(aq)$?

18% 1. 1
82% 2. 2
0% 3. 3
0% 4. 4
0% 5. 6

$$2e^- + 2H^+ + O_2 \rightarrow H_2O_2 + 2OH^-$$

$$2e^- + 2H_2O + O_2 \rightarrow H_2O_2 + 2OH^-$$

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Electrochemistry in a nutshell

- Redox processes **transfer electrons**
- Redox processes **evolve spontaneously** to equilibrium
- Electron transfer can be **harnessed as an electric current**

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Cell voltage, E_{cell} , and electrical energy

Electron flow in a voltage E is able to provide electrical energy

$$w_e = \text{charge that flows} \times \text{voltage}$$

In terms of moles of electrons that flow, n_e , the amount of charge is

$$\text{charge that flows} = n_e \times F$$

where F , known as the Faraday constant, is **96485 C/mol**.

$$w_e = n_e F \text{ voltage.}$$

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

$e^- = 1.6 \times 10^{-19} \text{ C}$
 $1 \text{ mol } e^- = 96485 \text{ C}$

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Cell voltage, E_{cell} , and electrical energy

A typical physiological voltage is $0.150 \text{ V} = 0.150 \text{ J/C}$.

The corresponding energy due to the transfer of 1.00 mol of electron is ...

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Cell voltage, E_{cell} , and electrical energy

A typical physiological voltage is $0.150 \text{ V} = 0.150 \text{ J/C}$.

The corresponding energy due to the transfer of 1.00 mol of electron is ...

$$w_e = \text{charge that flows} \times \text{voltage} = n_e F E_{\text{cell}}$$

$$= 1.00 \text{ mol} \times 96485 \text{ C/mol} \times 0.150 \text{ J/C}$$

$$= 14.5 \text{ kJ}$$

This is a lot of energy!

While each electron contributes a small amount of energy, there are a lot of electrons in a mole!

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What determines cell voltage, E_{cell} ?

The bigger, E_{cell} , the more energy that can be harnessed.

E_{cell} is a measure of free energy change, $Q \text{ vs } K$

$$\Delta G_{\text{cell}} = -n_e F E_{\text{cell}} = RT \ln \left(\frac{Q}{K} \right)$$

Negative values of free energy change mean work is available to be done on the surroundings.

In general, if $\Delta G_{\text{cell}} < 0$, that is, if $E_{\text{cell}} > 0$, then the redox process is able to provide energy to the surroundings.

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What determines cell voltage, E_{cell} ?

We know spontaneity is determined by Q relative to K .

We can simplify things by arranging for $Q = 1$, typically by making reactants and products be in their standard state.

This arrangement defines what we call the standard free energy change,

$$\Delta G_{\text{cell}}^{\circ} = -n_e F E_{\text{cell}}^{\circ} = RT \ln \left(\frac{1}{K} \right)$$

$$\Delta G^{\circ} = RT \ln \left(\frac{Q}{K} \right)$$

$$\Delta G^{\circ} = RT \ln \left(\frac{1}{K} \right) = -RT \ln(K)$$

and so the corresponding standard voltage reflects the value of K ,

$$E_{\text{cell}}^{\circ} = \frac{RT}{n_e F} \ln(K)$$

$K > 1, E_{\text{cell}}^{\circ} > 0$
 $K < 1, E_{\text{cell}}^{\circ} < 0$

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What determines cell voltage, E_{cell} ?

For arbitrary values of Q we can write the cell voltage and standard voltage as

$$E = -\frac{RT}{n_e F} \ln \left(\frac{Q}{K} \right) = E^{\circ} - \frac{RT}{n_e F} \ln(Q)$$

$$\Delta G = -n_e F E = RT \ln \left(\frac{Q}{K} \right)$$

$$E = -\frac{RT}{n_e F} \ln \left(\frac{Q}{K} \right)$$

$$= +\frac{RT}{n_e F} \ln(K) - \frac{RT}{n_e F} \ln(Q)$$

$$E = E^{\circ} - \frac{RT}{n_e F} \ln(Q)$$

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What determines cell voltage, E_{cell} ?

Since $x = 10^{\log(x)}$ we can write $\ln(x) = \log(x) \ln(10) = 2.303 \log(x)$ and so

$$E = -\frac{2.303RT}{n_e F} \log\left(\frac{Q}{K}\right) = E^\circ - \frac{2.303RT}{n_e F} \log(Q)$$

$$E^\circ = \frac{2.303RT}{n_e F} \log(K)$$

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What determines cell voltage, E_{cell} ?

At 25 °C the factor $\frac{2.303RT}{F}$ evaluates to 0.05912 V ≈ 0.06 V

$$E(25^\circ\text{C}) \approx \frac{0.06\text{ V}}{n_e} \log\left(\frac{Q}{K}\right) \approx E^\circ(25^\circ\text{C}) - \frac{0.06\text{ V}}{n_e} \log(Q)$$

$$E^\circ(25^\circ\text{C}) \approx \frac{0.06\text{ V}}{n_e} \log(K)$$

$$E \approx -\frac{0.06\text{ V}}{1} \log\left(\frac{1/100}{1}\right)$$

$$\approx -0.06 \log(10^{-2})$$

$$\approx +0.06 \times 2\text{V} = 0.12\text{ V}$$

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$$E = -(0.06/n_e) \text{ V } \log(Q/K)$$

Calculate the voltage at 25 °C for $n_e = 1$ when $Q = (1/100) \times K$

$$E = 0.12 \text{ V}$$

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$$E = -(0.06/n_e) \text{ V } \log(Q/K)$$

Calculate the voltage at 25 °C for $n_e = 1$ when $Q = (1/10) \times K$

$$E = 0.06 \text{ V}$$

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$$E = -(0.06/n_e) V \log(Q/K)$$

Calculate the voltage at 25 °C for $n_e = 1$ when $Q = (10) \times K$

$$E = -0.06 V$$

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$$E = -(0.06/n_e) V \log(Q/K)$$

At 25 °C for $n_e = 1$, ...

each **order of magnitude** change in Q/K ...
changes voltage by **0.06 V**.

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[TP] The value of E when $Q = 1$ at 25 °C is

$$E(Q = 1) = E^\circ = +(0.06/n_e) V \log(K)$$

For $n_e = 1$, if K is different by a **factor of ten** (say, 17 instead of 1.7),
the **magnitude of standard voltage** will change by ...

0% 1. 10 V
0% 2. 1 V
7% 3. 0.1 V
93% 4. 0.06 V
0% 5. Some other amount

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[TP] The value of E when $Q = 1$ at 25 °C is

$$E(Q = 1) = E^\circ = +(0.06/n_e) V \log(K)$$

For $n_e = 3$, if K is different by a **factor of ten** (say, 17 instead of 1.7),
the **magnitude of standard voltage** will change by ...

0% 1. 0.18 V
7% 2. 0.06 V
93% 3. 0.02 V
0% 4. Some other amount

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[Quiz] The value of E when $Q = 1$ at 25 °C is
 $E(Q = 1) = E^\circ + (0.06/n_e) V \log(K)$
 A typical physiological value of E° is 0.18 V.
 For $n_e = 1$ this corresponds to the value of K equal to ...

0% 1. 0.1
 0% 2. 1
 0% 3. 10
 0% 4. 100
 100% 5. 1000
 0% 6. Some other value

$R \rightarrow P \quad E^\circ = 0.18 V$
 $K = 10^3$

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$E = -(0.06/n_e) V \log(Q/K)$

The value of E when $Q = 1$ at 25 °C is
 $E(Q = 1) = E^\circ + (0.06/n_e) V \log(K)$
 Calculate K corresponding to $E^\circ = 1.8 V$ for $n_e = 1$.
 $K = 10^{30}$. Very large!

$E > 0$
 $E^\circ \neq E$
 $Q = 1 \quad Q = \text{actual}$

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Exploring the Nernst equation

At 25 °C $E(\text{any } Q) \neq E^\circ - (0.06/n_e) V \log(Q)$
 $E^\circ = +(0.06/n_e) V \log(K)$

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[TP] At 25 °C
 $E = E^\circ - (0.06/n_e) V \log(Q) \neq 0$
 What is the value of E when everything is in standard states?
 $Q = 1$

0% 1. $E = \infty$
 13% 2. $E = 0$
 87% 3. $E = E^\circ$
 0% 4. None of the above

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[TP] At 25 °C
 $E = E^\circ - (0.06/n_e) V \log(Q)$
 What is the value of E when everything is **at equilibrium**?

0% 1. $E = \infty$
 93% 2. $E = 0$
 7% 3. $E = E^\circ$
 0% 4. None of the above

$E^\circ = \frac{0.06 \log(K)}{n_e}$
 $Q = K$
 $E = E^\circ - \frac{0.06}{n_e} V \log(K)$
 $= 0$
Dead battery

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[TP] At 25 °C
 $E = E^\circ - (0.06/n_e) V \log(Q)$
 What is the value of E when there are **no products** present?

79% 1. $E = \infty$
 14% 2. $E = 0$
 0% 3. $E = E^\circ$
 7% 4. None of the above

$Q = \frac{0}{\text{some}} = 0 = \frac{1}{10^{10}}$
 $\log(0) = \log(10^{-10})$
 $= -10$

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[Quiz] At 25 °C
 $E = E^\circ - (0.06/n_e) V \log(Q)$
 What is the value of E when there are **only products** present?

0% 1. $E = \infty$
 0% 2. $E = 0$
 0% 3. $E = E^\circ$
 100% 4. None of the above

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[TP] For $A + B \rightleftharpoons 2 C + D$ at 25 °C
 $E^\circ = (0.06/n_e) V \log(K)$
 What is the value of the **equilibrium constant** for
 $2 A + 2 B \rightleftharpoons 4 C + 2 D$?

0% 1. K
 15% 2. $2K$
 85% 3. K^2
 0% 4. $K/2$
 0% 5. \sqrt{K}
 0% 6. None of the above

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[TP] For $A + B \rightleftharpoons 2 C + D$ at 25 °C
 $E^\circ = (0.06/n_e) V \log(K)$
 What is the value of n_e for
 $2 A + 2 B \rightleftharpoons 4 C + 2 D$?

13% 1. n_e
 67% 2. $2 n_e$
 0% 3. n_e^2
 13% 4. $n_e/2$
 7% 5. $\sqrt{n_e}$
 0% 6. None of the above

$(e^- + A \rightarrow B^-)$
 $(C^- \rightarrow D + e^-)$
 $A + C^- \rightarrow B^- + D \quad n_e = 1$
 $2A + 2C^- \rightarrow 2B^- + 2D \quad n_e = 2$

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[Quiz] For $A + B \rightleftharpoons 2 C + D$ at 25 °C
 $E^\circ = (0.06/n_e) V \log(K)$
 What is the value of E° for
 $2 A + 2 B \rightleftharpoons 4 C + 2 D$?

69% 1. E°
 6% 2. $2 E^\circ$
 0% 3. $(E^\circ)^2$
 19% 4. $E^\circ/2$
 6% 5. $\sqrt{E^\circ}$
 0% 6. None of the above

$E^\circ = \frac{0.06}{2n_e} \log(K^2)$
 $= \frac{0.06}{2n_e} \cdot 2 \log(K)$
 $= E^\circ$

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[TP] For $A + B \rightleftharpoons 2 C + D$ at 25 °C
 $E^\circ = (0.06/n_e) V \log(K)$
 What is the value of E° when all concentrations are doubled?

100% 1. E°
 0% 2. $2 E^\circ$
 0% 3. $(E^\circ)^2$
 0% 4. $E^\circ/2$
 0% 5. $\sqrt{E^\circ}$
 0% 6. None of the above

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[Quiz] For $A + B \rightleftharpoons 2 C + D$ at 25 °C, if $E = 3.7 V$, $E^\circ = 2.0 V$, and $n_e = 1$,
 what is the value of E when all concentrations are doubled?

100% 1. $E < 3.7 V$
 0% 2. $E > 3.7 V$
 0% 3. $(E^\circ)^2$
 0% 4. $E^\circ/2$
 0% 5. $\sqrt{E^\circ}$

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Concentration cells: Mixing → electric current

What happens when ink is dropped into water?
 It **disperses spontaneously**

What happens when salt water is dropped into fresh water?
 It **disperses spontaneously**

Let's see how to **harness** such **spontaneity** of mixing ...
 to **generate electricity!**

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[TP] What do you expect to be true about the process
 $\text{Cl}^-(0.0001 \text{ M}) \rightarrow \text{Cl}^-(1 \text{ M})$?

✗ 56% 1. $E > 0$
 0% 2. $E = 0$
 ✓ 44% 3. $E < 0$
 0% 4. More information needed

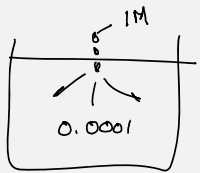
dilute → conc.
 $\Delta G = -n_e F E$
 $= -T \Delta S_{\text{tot}}$

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[TP] What do you expect to be true about the process
 $\text{Cl}^-(1 \text{ M}) \rightarrow \text{Cl}^-(0.0001 \text{ M})$?

100% 1. $E > 0$
 0% 2. $E = 0$
 0% 3. $E < 0$
 0% 4. More information needed



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[TP] What is true about the process
 $\text{Cl}^-(1 \text{ M}) \rightarrow \text{Cl}^-(0.0001 \text{ M})$?

7% 1. $K > 1$
 93% 2. $K = 1$
 0% 3. $K < 1$
 0% 4. More information needed

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[TP] What is true about the process
 $\text{Cl}^- (1 \text{ M}) \rightarrow \text{Cl}^- (0.0001 \text{ M})$?

13% 1. $E^\circ > 0$
87% 2. $E^\circ = 0$
0% 3. $E^\circ < 0$
0% 4. More information needed

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