[TP] Based on the balanced reduction half-reaction, how many moles of electrons are consumed when 1 mole of $O_2(g)$ is reduced to hydrogen peroxide, $H_2O_2(aq)$?

10% 1. 1
10% 2. 2
0% 3. 3
0% 4. 4
0% 5. 6
80% 6. Not sure

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1

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1

Lecture 17 CH131 Summer 1 2021

Tuesday, June 29, 2021

Begin ch17: Electron transfer reactions and electrochemistry.

- Balancing redox equations, http://goo.gl/MMEUCs
- Electrochemical cells harness spontaneous electron flow
- Cell voltage, E_{cell}, and electrical energy
- Nernst equation
- Cell voltage and spontaneity
- Calculating standard cell voltage, $E°_{cell}$
- What determines cell voltage, E_{cell}?

Next: Complete: What determines cell voltage, E_{cell}?; Practice problems; Concentration cells: Mixing → electric current

2

A long, long time ago …

… my chemistry teacher (John Endicott) ended a lecture by asking us to balance a chemical equation like the following.

$$O_2(g) + NO(g) \rightarrow H_2O_2(aq) + NO_3^-(aq)$$

I tried by inspection but could not do it.

3

3

Balancing half-reactions

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

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Balancing oxidation reduction equations

For each oxidation reduction pair (half-reactions)

1. Balance elements other than O and H
2. Balance O with $H_2O(l)$
3. Balance H with $H^+(aq)$
4. Balance charge by adding e^- to the side that is most positive

$A \rightarrow A^+ + e^-$ oxidation

$e^- + B^+ \rightarrow B$ reduction

$A + B^+ \rightarrow A^+ + B$ redox reaction, oxidation-reduction reactions

half-reaction: harness the electron flow to do electrical work

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Balancing oxidation reduction equations

Balance $P_4(s) \rightarrow H_3PO_4(aq)$

Answer: $16\ H_2O(l) + P_4(s) \rightarrow 4\ H_3PO_4(aq) + 20\ H^+(aq) + 20\ e^-$

$16 H_2O + P_4 \rightarrow 4 H_3PO_4 + 20 H^+ + 20 e^-$

oxidation half-reaction

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Balancing oxidation reduction equations

Balance $S_2O_8^{2-}(aq) \rightarrow HSO_4^-(aq)$

Answer: $2\ e^- + 2\ H^+(aq) + S_2O_8^{2-}(aq) \rightarrow 2\ HSO_4^-(aq)$

$(2e^- + 2H^+ + S_2O_8^{2-} \rightarrow 2HSO_4^-)$

balanced reduction half-reaction.

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Balancing oxidation reduction equations

Combine balanced half-reactions

1. Adjust e^- to be the same
2. Combine
3. Cancel where possible

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Balancing oxidation reduction equations

Combine balanced half-reactions

$16\ H_2O(l) + P_4(s) \rightarrow 4\ H_3PO_4(aq) + 20\ H^+(aq) + 20\ e^-$

$(2\ e^- + 2\ H^+(aq) + S_2O_8^{2-}(aq) \rightarrow 2\ HSO_4^-(aq)) * 10$

$16\ H_2O(l) + P_4(s) + 10\ S_2O_8^{2-}(aq) \rightarrow 4\ H_3PO_4(aq) + 20\ HSO_4^-(aq)$

$16\ H_2O(l) + P_4(s) + 10\ S_2O_8^{2-}(aq) \rightarrow 20\ HSO_4^-(aq) + 4\ H_3PO_4(aq)$

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9

[TP] Based on the balanced reduction half-reaction, how many moles of electrons are consumed when 1 mole of $O_2(g)$ is reduced to hydrogen peroxide, $H_2O_2(aq)$?

9%	1.	1
91%	2.	2
0%	3.	3
0%	4.	4
0%	5.	6
0%	6.	Not sure

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

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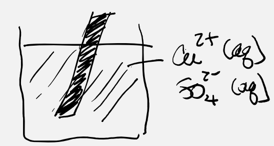
$Cu^{2+}(aq)$ oxidizes $Zn(s)$

Spontaneous flow of electrons from Zn to Cu

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

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

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



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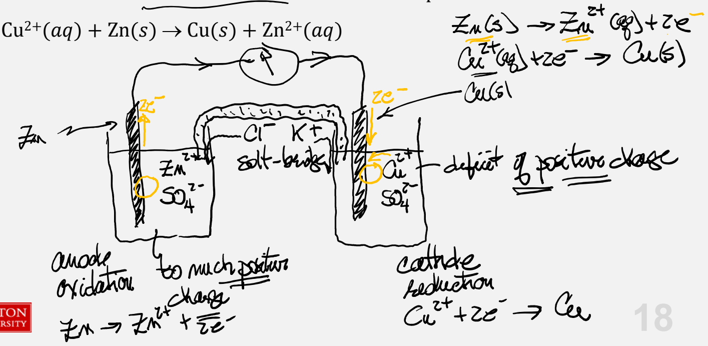
Cu^{2+}(*aq*) oxidizes Zn(*s*) spontaneously

Let's sketch an electrochemical cell to harness the spontaneous electron flow in

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



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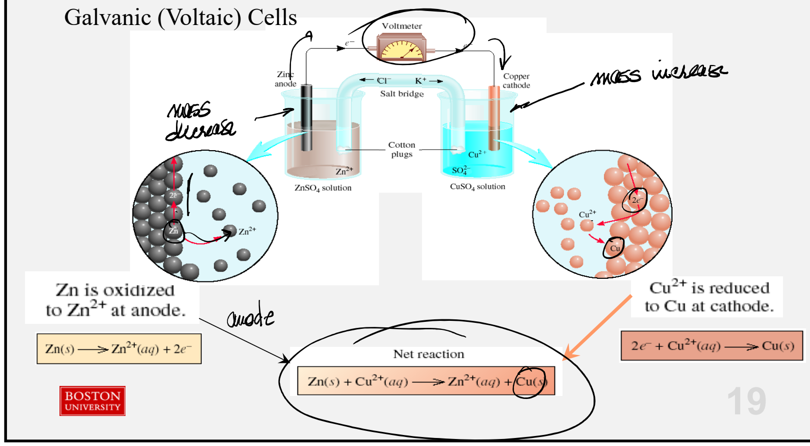
Galvanic (Voltaic) Cells



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Cell voltage, E_{cell}, and electrical energy

A spontaneous redox process means electrons flow spontaneously, from reducing agent to oxidizing agent.

Arranging the flow to take place in an electrochemical cell means the spontaneity of the redox process can be harnessed to do electrical work.

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Cell voltage, E_{cell}, and electrical energy

$1\ V = 1\ J/C$

Electron flow in a voltage E provides electrical energy

w_e = charge that flows × voltage

In terms of moles of electrons that flow, n_e (McQuarrie et al., use ν_e), the charge that flows is

charge that flows = $n_e \times F$

Here F, known as the Faraday constant, is the total charge on one mole of electrons, $F = 96485$ C/mol.

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Cell voltage, E_{cell}, and electrical energy

A typical physiological voltage is 0.150 V = 0.150 J/C.

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

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

= 1.00 mol × 96485 C/mol × 0.150 J/C

= 14.5 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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Nernst equation

$\Delta G = -T\Delta S_{tot}$ Q, K $\Delta U = q + w$

The amount of electrical work done on the system is

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

* But the amount of electrical work is also precisely the free energy change of the redox process,

$w_e = \Delta G_{\text{cell}} = RT \ln\left(\frac{Q}{K}\right)$

Key connection between spontaneity and energy available in electrochemical cells.

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Nernst equation

By our convention that work done on the system corresponds to positive energy change, free energy change is defined with a negative sign …

$\Delta G_{\text{cell}} = -n_e\, F\, E_{\text{cell}}$

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

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

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Nernst equation

Combining these two expressions for electrical work,

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

$w_e = \Delta G_{\text{cell}} = RT \ln\left(\frac{Q}{K}\right)$

we get the Nernst equation, the fundamental equation of electrochemistry,

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

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Nernst equation

Just as it is convenient to tabulate standard free energy change ($Q = 1$),

$$\Delta G°_{\text{cell}} = RT \ln\left(\frac{1}{K}\right) = -RT \ln(K),$$

it is convenient to work with corresponding standard cell voltages,

$$\Delta G°_{\text{cell}} = -n_e F E°_{\text{cell}}$$

$$E°_{\text{cell}} = \frac{RT}{n_e F} \ln(K)$$

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Nernst equation

In terms of standard cell voltages, we can express the Nernst equation

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

as

$$E_{\text{cell}} = -\frac{RT}{n_e F} \ln(Q) + E°_{\text{cell}}$$

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Cell voltage versus spontaneity

Here is the essence of the Nernst equation, $E_{\text{cell}} = -\frac{RT}{n_e F} \ln\left(\frac{Q}{K}\right)$:

- The more the cell is on the reactants side of equilibrium ($Q < K$), the more positive is the cell voltage, E_{cell}.

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Cell voltage versus spontaneity

Here is the essence of the Nernst equation, $E_{\text{cell}} = -\frac{RT}{n_e F} \ln\left(\frac{Q}{K}\right)$:

- The more the cell is on the products side of equilibrium ($Q > K$), the more negative is the cell voltage, E_{cell}.

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Cell voltage versus spontaneity

Here is the essence of the Nernst equation, $E_{\text{cell}} = -\frac{RT}{n_e F}\ln\left(\frac{Q}{K}\right)$:

- Equilibrium ($Q = K$) means $E_{\text{cell}} = 0$, a "dead battery."

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Cell voltage versus spontaneity

Let's explore the relationship between Q, K, and E_{cell}.

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[TP] For the redox process

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

when the ions each are 1 M, Zn(s) is consumed. This means …

100% 1. $K > 1$
0% 2. $K < 1$
0% 3. $Q > 1$
0% 4. $Q < 1$
0% 5. More information needed
0% 6. Not sure

spontaneity, Q, K.

$[Zn^{2+}] = 1 M$, $[Cu^{2+}] = 1 M$

$Q = \frac{[Zn^{2+}]}{[Cu^{2+}]} = \frac{1}{1} = 1$

spontaneous, $Q < K$

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[TP] For the redox process

$$L^{2+}(aq) + M(s) \rightarrow L(s) + M^{2+}(aq)$$

when $Q = x$, M(s) is consumed. This means …

0% 1. $K > 1$
0% 2. $K < 1$
0% 3. $Q > 1$
0% 4. $Q < 1$
100% 5. More information needed
0% 6. Not sure

spontaneous.
$Q < K$

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[TP] For the redox process

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

when $Q = 10$, $Zn(s)$ is consumed. This means over time the cell voltage will …

100% 1. become smaller
0% 2. stay the same
0% 3. become larger
0% 4. More information needed
0% 5. Not sure

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[TP] For the redox process

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

when $Q = 10$, $Zn(s)$ is consumed. Compared to the voltage when $Q = 1$, the voltage when $Q = 10$ is …

100% 1. smaller
0% 2. the same
0% 3. larger
0% 4. More information needed
0% 5. Not sure

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Calculating standard cell voltage, $E°_{cell}$

Since $E°_{cell}$ is proportional to the $\Delta G°_{cell}$,

$\Delta G°_{cell} = -n_e F E°_{cell}$

and because we know how to express a redox process as the sum of its half reactions, we can use Hess's law to express $\Delta G°_{cell}$ as the sum of the standard free energy change for each half reaction,

$\Delta G°_{cell} = \Delta G°_{cathode} + \Delta G°_{anode}$

Let's use this relation to define standard reduction potentials.

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Calculating standard cell voltage, $E°_{cell}$

By convention, reduction half reactions have a standard reduction potential $E°$, whose value is the cell potential relative to the standard hydrogen electrode, SHE,

$2\,H^+(1\,M) + 2\,e^- \rightarrow H_2(1\,atm)$, $E° = 0\,V$

All other reductions defined relative to SHE

$Zn^{2+}(1\,M) + 2\,e^- \rightarrow Zn(s)$, $E° = -0.763\,V$

$Cu^{2+}(1\,M) + 2\,e^- \rightarrow Cu(s)$, $E° = +0.340\,V$

etc.

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Calculating standard cell voltage, $E°_{\text{cell}}$

This means we can write for the cathode (reduction) contribution

$\Delta G°_{\text{cathode}} = -n_e\, F\, E°_{\text{cathode}}$

and for the anode (oxidation) contribution

and $\Delta G°_{\text{anode}} = +n_e\, F\, E°_{\text{anode}}$

The reason for the '+' in the anode expression is because oxidation takes place there — the reverse of reduction — and so the sign of its contribution to free energy change must be reversed.

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Calculating standard cell voltage, $E°_{\text{cell}}$

Combining the three expressions

$\Delta G°_{\text{cathode}} = -n_e\, F\, E°_{\text{cathode}}$ and $\Delta G°_{\text{anode}} = +n_e\, F\, E°_{\text{anode}}$

$\Delta G°_{\text{cell}} = \Delta G°_{\text{cathode}} + \Delta G°_{\text{anode}} = -n_e F E°_{\text{cathode}} + n_e F E°_{\text{anode}}$

$\Delta G°_{\text{cell}} = -n_e\, F\, E°_{\text{cell}} = -n_e F E°_{\text{cell}}$

and canceling the common factor $n_e\, F$, we get the fundamental expression for $E°_{\text{cell}}$ in terms of reduction potentials,

$E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}}$

Note that both $E°_{\text{cathode}}$ and $E°_{\text{anode}}$ are standard reduction potentials.

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Calculating standard cell voltage, $E°_{\text{cell}}$

Here is an example: Does Cu^{2+} oxidize Zn?

$Cu^{2+}(1\text{ M}) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(1\text{ M})$, $E° > 0$?

The standard reduction potentials are

$Zn^{2+}(1\text{ M}) + 2\,e^- \rightarrow Zn(s)$, $E° = -0.763\text{ V}$

$Cu^{2+}(1\text{ M}) + 2\,e^- \rightarrow Cu(s)$, $E° = +0.340\text{ V}$

Therefore, the standard cell potential is

$E°_{\text{cell}} = E°_{\text{cathode}} - E°_{\text{anode}} = +0.340\text{ V} - (-0.763\text{ V}) = +1.103\text{ V} > 0$

Since $E°_{\text{cell}} > 0$, Zn is oxidized by Cu^{2+}

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What determines cell voltage, E_{cell}?

For the purposes of making estimates of the effect of changes in Q on voltage, it convenient to set the temperature to 25°C and to use $\ln(Q) = 2.303\log(Q)$

$E_{\text{cell}} = -\frac{RT}{n_e F}\ln\left(\frac{Q}{K}\right) = -\frac{2.303R \times 298\text{ K}}{n_e F}\log\left(\frac{Q}{K}\right) \approx -\frac{0.06}{n_e}\text{V}\log\left(\frac{Q}{K}\right)$

$E°_{\text{cell}} = \frac{RT}{n_e F}\ln(K) = \frac{2.303R \times 298\text{ K}}{n_e F}\text{V}\log(K) \approx \frac{0.06}{n_e}\text{V}\log(K)$

Let's use these expressions to estimate the effects of Q and K on voltage.

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

$E_{cell} \approx -\frac{0.06}{n_e} \text{V} \log\left(\frac{Q}{K}\right)$

$E°_{cell} \approx \frac{0.06}{n_e} \text{V} \log(K)$

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

$E = 0.12$ V

$E_{cell} = -\frac{0.06V}{1} \log\left(\frac{0.01K}{K}\right)$

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

$= -0.06 * (-2)$

$= +0.12V$

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

$E_{cell} \approx -\frac{0.06}{n_e} \text{V} \log\left(\frac{Q}{K}\right)$

$E°_{cell} \approx \frac{0.06}{n_e} \text{V} \log(K)$

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

$E = 0.06$ V //

$-\frac{0.06}{1} \text{V} \log\left(\frac{0.1K}{K}\right)$

$-0.06V \log(10^{-1})$

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

$E_{cell} \approx -\frac{0.06}{n_e} \text{V} \log\left(\frac{Q}{K}\right)$

$E°_{cell} \approx \frac{0.06}{n_e} \text{V} \log(K)$

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 $\log(Q/K)$

$E_{cell} \approx -\frac{0.06}{n_e} \text{V} \log\left(\frac{Q}{K}\right)$

$E°_{cell} \approx \frac{0.06}{n_e} \text{V} \log(K)$

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

$E_{cell} \approx -\frac{0.06}{n_e} \text{V} \log\left(\frac{Q}{K}\right)$

$E°_{cell} \approx \frac{0.06}{n_e} \text{V} \log(K)$

Write an expression for E when $Q = 1$.

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

$E_{cell} \approx -\frac{0.06}{n_e} \text{V} \log\left(\frac{Q}{K}\right)$

$E°_{cell} \approx \frac{0.06}{n_e} \text{V} \log(K)$

The value of E when $Q = 1$ is called the standard voltage $E°$ and at 25°C it is written as

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

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

$E(Q = 1) = E° = +(0.06/n_e)$ 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
0% 3. 0.1 V
100% 4. 0.06 V
0% 5. Some other amount
0% 6. Not sure

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

$E(Q = 1) = E° = +(0.06/n_e)$ 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
0% 2. 0.06 V
78% 3. 0.02 V
0% 4. Some other amount
22% 5. Not sure

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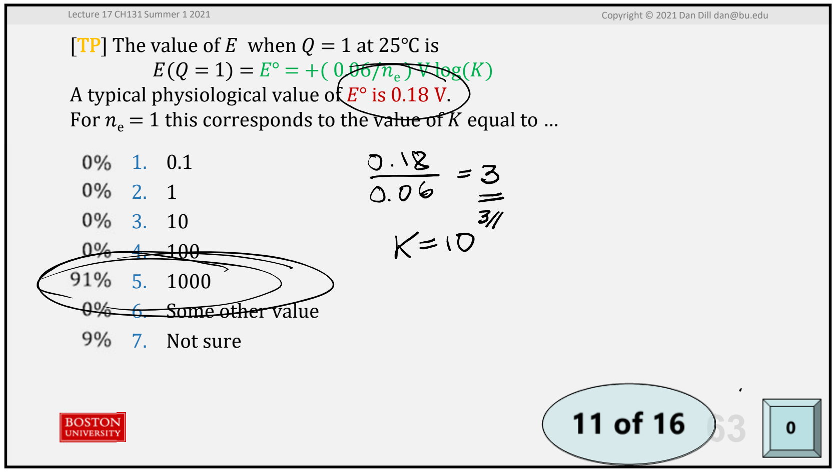
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[TP] The value of E when $Q = 1$ at 25°C is
$E(Q = 1) = E° = +(\ 0.06/n_e\ )\ V \log(K)$
A typical physiological value of $E°$ is 0.18 V.
For $n_e = 1$ this corresponds to the value of K equal to …
0% 1. 0.1
0% 2. 1
0% 3. 10
0% 4. 100
91% 5. 1000
0% 6. Some other value
9% 7. Not sure
$\frac{0.18}{0.06} = 3$
$K = 10^3$
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