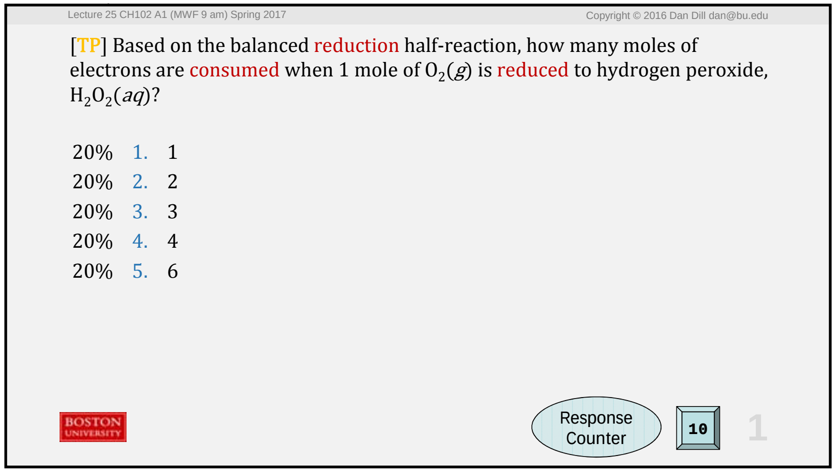

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017

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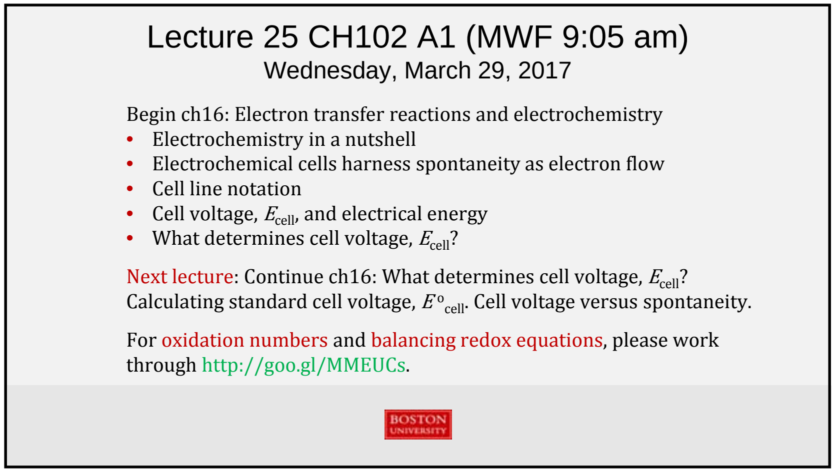
[TP] Based on the balanced reduction half-reaction, how many moles of electrons are consumed when 1 mole of $O_2(g)$ is reduced to hydrogen peroxide, $H_2O_2(aq)$?

20% 1. 1
20% 2. 2
20% 3. 3
20% 4. 4
20% 5. 6

1



## Lecture 25 CH102 A1 (MWF 9:05 am)

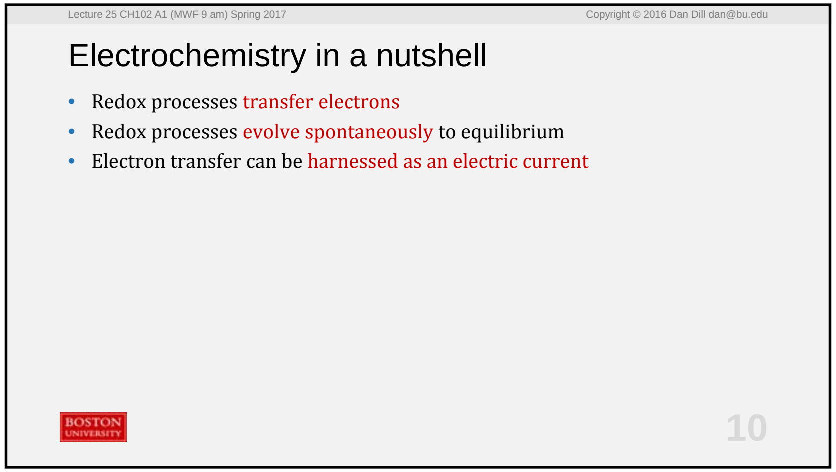
Wednesday, March 29, 2017

Begin ch16: Electron transfer reactions and electrochemistry

- Electrochemistry in a nutshell
- Electrochemical cells harness spontaneity as electron flow
- Cell line notation
- Cell voltage, $E_{\text{cell}}$, and electrical energy
- What determines cell voltage, $E_{\text{cell}}$?

Next lecture: Continue ch16: What determines cell voltage, $E_{\text{cell}}$? Calculating standard cell voltage, $E^{\circ}_{\text{cell}}$. Cell voltage versus spontaneity.

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



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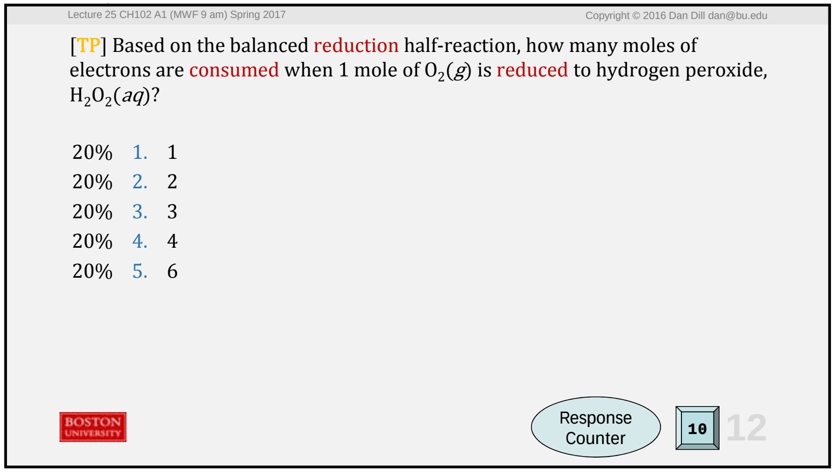
## Electrochemistry in a nutshell

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

10



Lecture 25 CH102 A1 (MWF 9 am) Spring 2017

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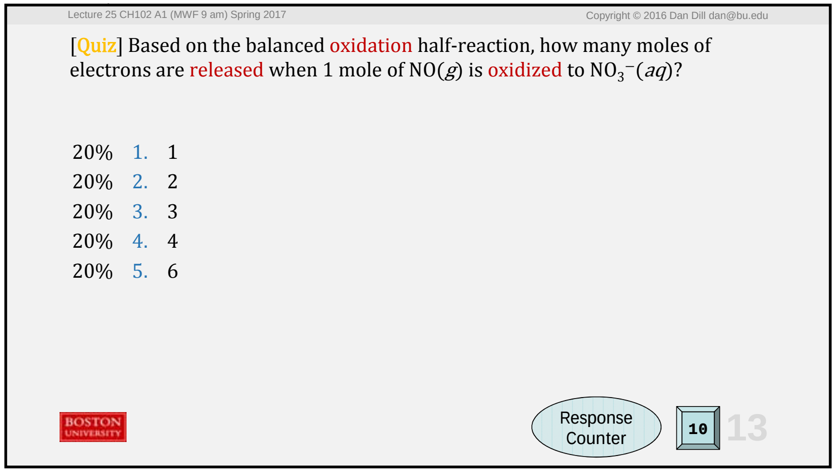
[TP] Based on the balanced reduction half-reaction, how many moles of electrons are consumed when 1 mole of $O_2(g)$ is reduced to hydrogen peroxide, $H_2O_2(aq)$?

20% 1. 1
20% 2. 2
20% 3. 3
20% 4. 4
20% 5. 6

12

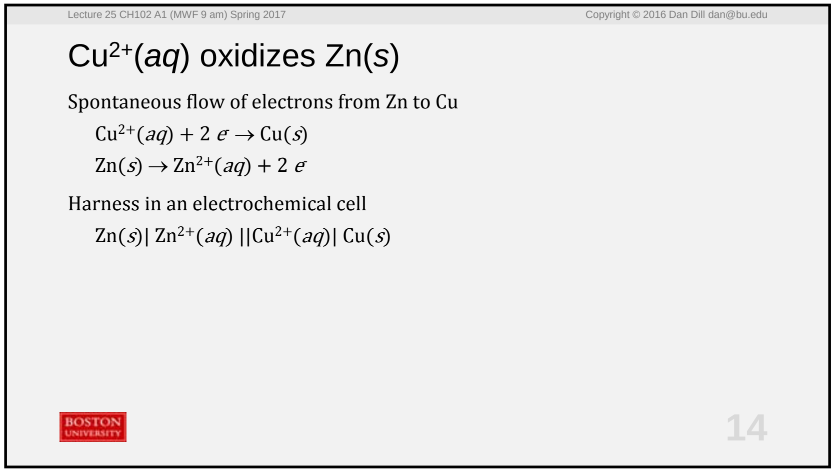


[Quiz] Based on the balanced oxidation half-reaction, how many moles of electrons are released when 1 mole of $NO(g)$ is oxidized to $NO_3^-(aq)$?

| | | |
|---|---|---|
| 20% | 1. | 1 |
| 20% | 2. | 2 |
| 20% | 3. | 3 |
| 20% | 4. | 4 |
| 20% | 5. | 6 |

Response Counter

10



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

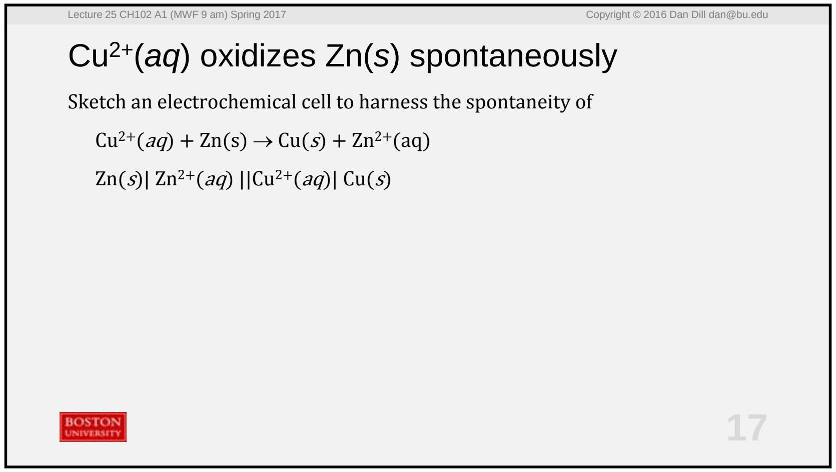
Spontaneous flow of electrons from Zn to Cu

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

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

Harness in an electrochemical cell

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

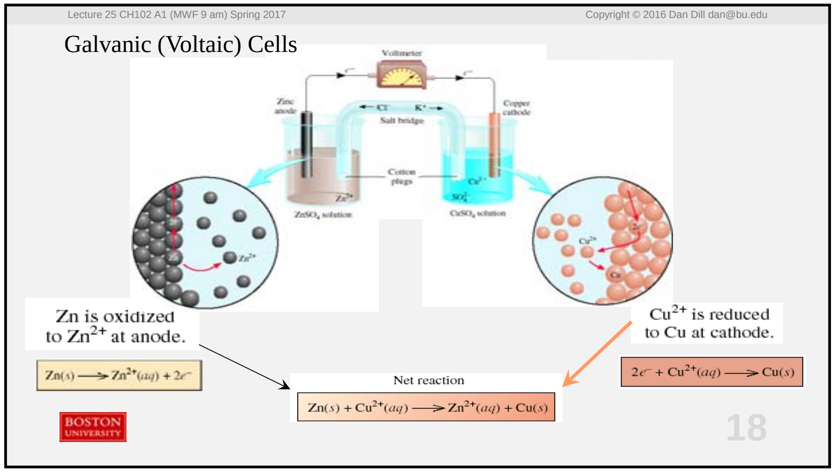


## $Cu^{2+}(aq)$ oxidizes $Zn(s)$ spontaneously

Sketch an electrochemical cell to harness the spontaneity of

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

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



## Galvanic (Voltaic) Cells

Zn is oxidized to $Zn^{2+}$ at anode.

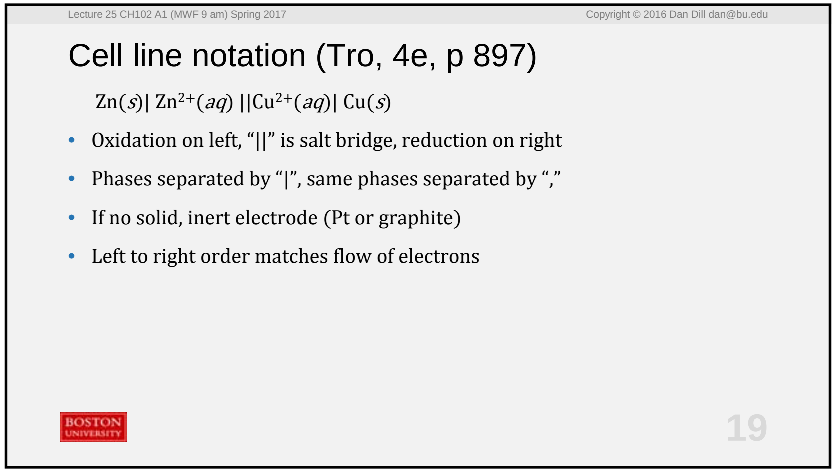
$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cu$^{2+}$ is reduced to Cu at cathode.

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

Net reaction

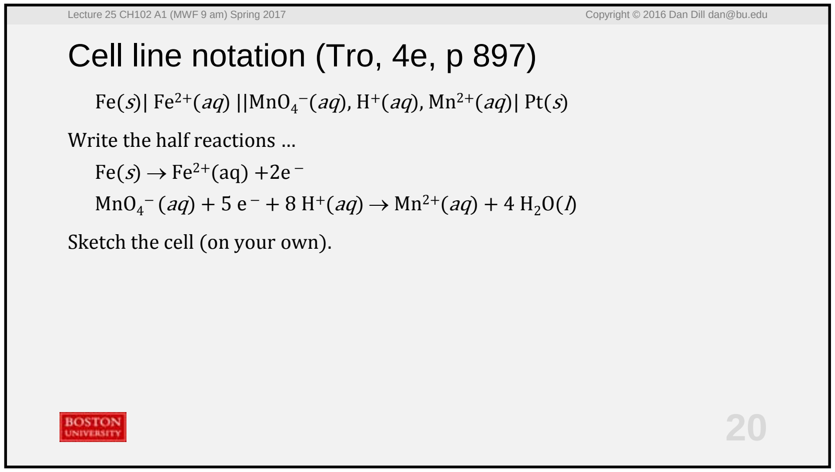
$Zn(s) + Cu^{2+}(aq) \longrightarrow Zn^{2+}(aq) + Cu(s)$



## Cell line notation (Tro, 4e, p 897)

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

- Oxidation on left, "||" is salt bridge, reduction on right
- Phases separated by "|", same phases separated by ","
- If no solid, inert electrode (Pt or graphite)
- Left to right order matches flow of electrons



## Cell line notation (Tro, 4e, p 897)

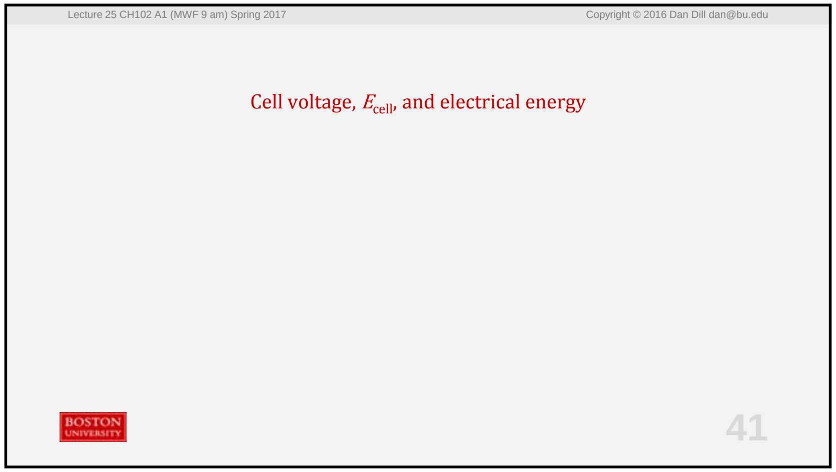
$Fe(s)| Fe^{2+}(aq) || MnO_4^-(aq), H^+(aq), Mn^{2+}(aq)| Pt(s)$

Write the half reactions …

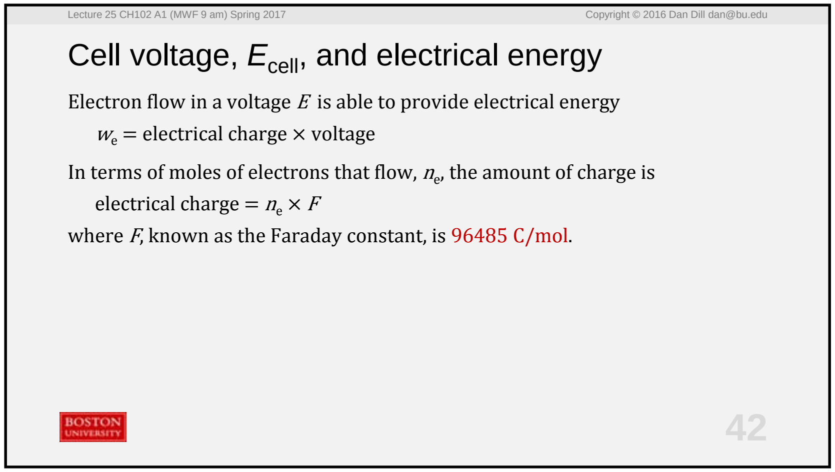
$Fe(s) \rightarrow Fe^{2+}(aq) + 2e^-$

$MnO_4^-(aq) + 5\,e^- + 8\,H^+(aq) \rightarrow Mn^{2+}(aq) + 4\,H_2O(l)$

Sketch the cell (on your own).



Cell voltage, $E_{cell}$, and electrical energy



## Cell voltage, $E_{cell}$, and electrical energy

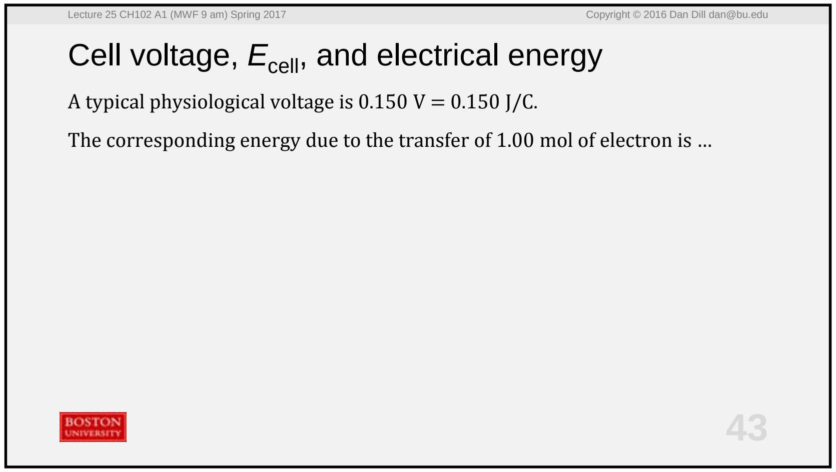
Electron flow in a voltage $E$ is able to provide electrical energy

$w_e$ = electrical charge × voltage

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

electrical charge = $n_e \times F$

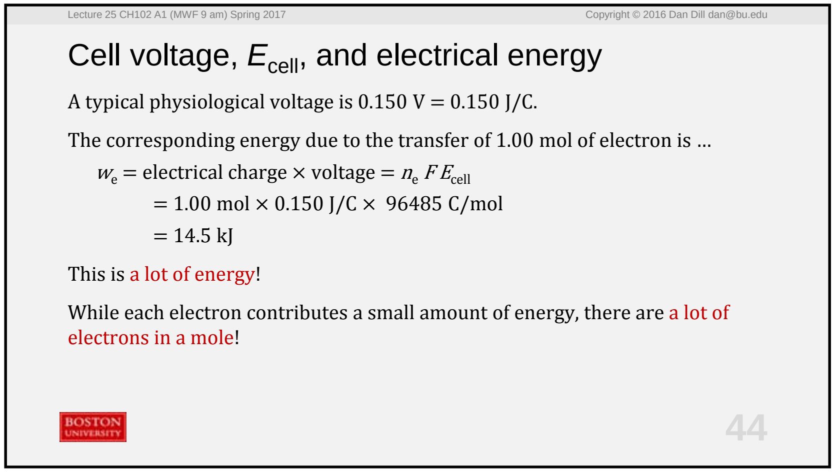
where $F$, known as the Faraday constant, is 96485 C/mol.



## Cell voltage, $E_{\text{cell}}$, 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 …



## Cell voltage, $E_{\text{cell}}$, and electrical energy

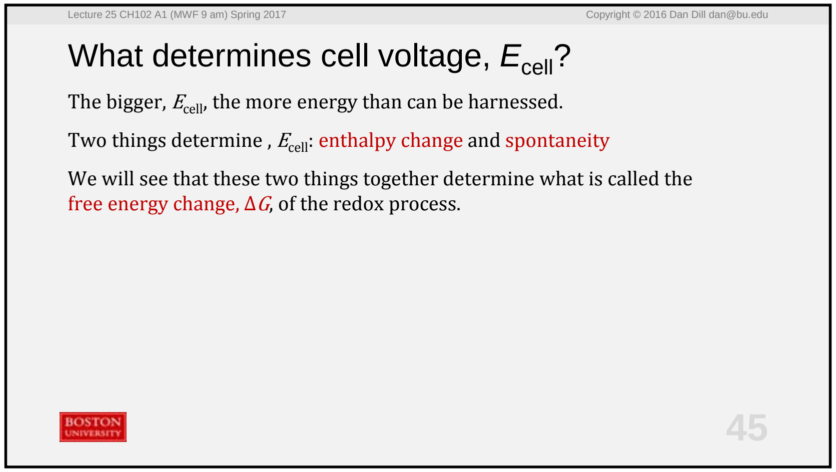
A typical physiological voltage is 0.150 V = 0.150 J/C.

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

$$w_e = \text{electrical charge} \times \text{voltage} = n_e\, F\, E_{\text{cell}}$$
$$= 1.00 \text{ mol} \times 0.150 \text{ J/C} \times \ 96485 \text{ C/mol}$$
$$= 14.5 \text{ kJ}$$

This is a lot of energy!

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

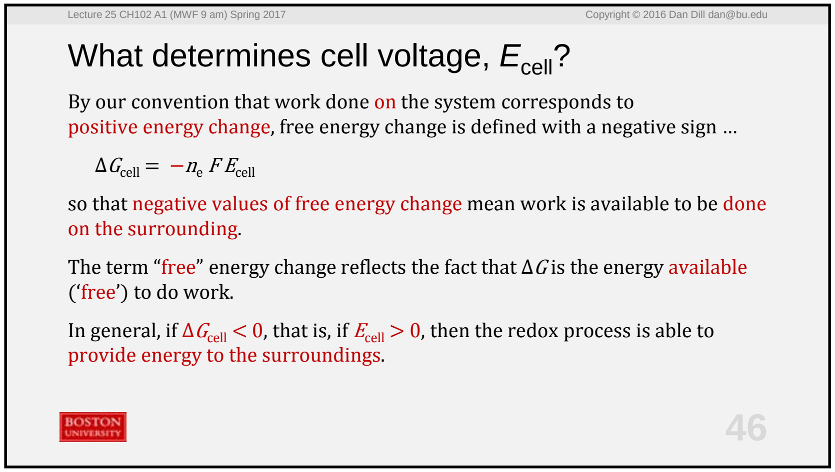


## What determines cell voltage, $E_{\text{cell}}$?

The bigger, $E_{\text{cell}}$, the more energy than can be harnessed.

Two things determine , $E_{\text{cell}}$: enthalpy change and spontaneity

We will see that these two things together determine what is called the free energy change, $\Delta G$, of the redox process.



## What determines cell voltage, $E_{\text{cell}}$?

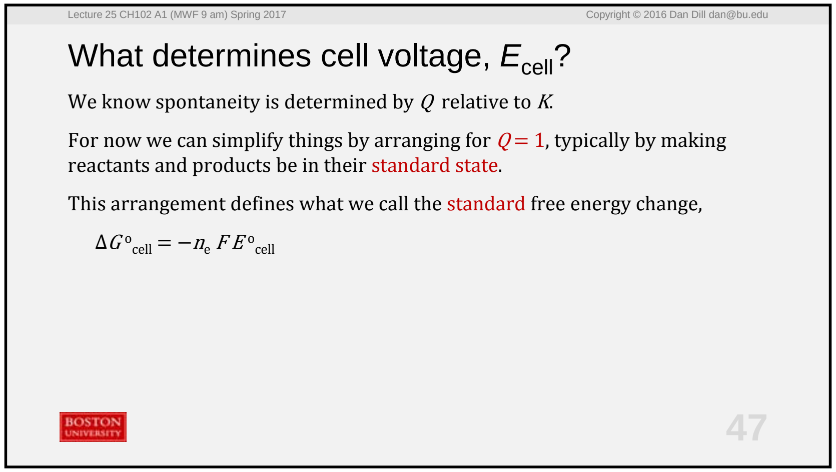
By our convention that work done on the system corresponds to positive energy change, free energy change is defined with a negative sign …

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

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

The term “free” energy change reflects the fact that $\Delta G$ is the energy available (‘free’) to do work.

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.



## What determines cell voltage, $E_{\text{cell}}$?

We know spontaneity is determined by $Q$ relative to $K$.

For now 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,

$$\Delta G^{\circ}_{\text{cell}} = -n_{\text{e}}\, F E^{\circ}_{\text{cell}}$$