

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

[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

BOSTON UNIVERSITY

Response Counter

10 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_{cell} , and electrical energy
- What determines cell voltage, E_{cell} ?

Next lecture: Continue ch16: What determines cell voltage, E_{cell} ?
Calculating standard cell voltage, E°_{cell} . Cell voltage versus spontaneity.

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

BOSTON UNIVERSITY

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

Electrochemistry in a nutshell

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

BOSTON UNIVERSITY

10

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

[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

BOSTON UNIVERSITY

Response Counter

10 12

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

[Quiz] Based on the balanced **oxidation** half-reaction, how many moles of electrons are **released** when 1 mole of $\text{NO}(g)$ is **oxidized** to $\text{NO}_3^-(aq)$?

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

BOSTON UNIVERSITY

Response Counter 10 | 13

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

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

Spontaneous flow of electrons from Zn to Cu

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

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

Harness in an electrochemical cell

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

BOSTON UNIVERSITY

14

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

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

Sketch an electrochemical cell to harness the spontaneity of

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

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

BOSTON UNIVERSITY

17

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

Galvanic (Voltaic) Cells

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

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

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

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

Net reaction

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

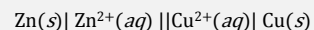
BOSTON UNIVERSITY

18

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017

Copyright © 2016 Dan Dill dan@bu.edu

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



- 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

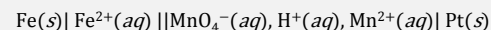


19

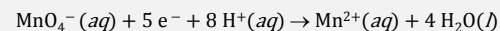
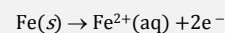
Lecture 25 CH102 A1 (MWF 9 am) Spring 2017

Copyright © 2016 Dan Dill dan@bu.edu

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



Write the half reactions ...



Sketch the cell (on your own).



20

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017

Copyright © 2016 Dan Dill dan@bu.edu

Cell voltage, E_{cell} , and electrical energy



41

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017

Copyright © 2016 Dan Dill dan@bu.edu

Cell voltage, E_{cell} , and electrical energy

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

$$w_e = \text{electrical charge} \times \text{voltage}$$

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

$$\text{electrical charge} = n_e \times F$$

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


42

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

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 ...

 43

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

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 ...


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

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

$$= 14.5 \text{ kJ}$$

This is **a lot of energy!**

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

 44


Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

What determines cell voltage, E_{cell} ?

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

Two things determine E_{cell} : **enthalpy change** and **spontaneity**

We will see that these two things together determine what is called the **free energy change, ΔG** , of the redox process.

 45

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

What determines cell voltage, E_{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 ΔG 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**.

 46

Lecture 25 CH102 A1 (MWF 9 am) Spring 2017

Copyright © 2016 Dan Dill dan@bu.edu

What determines cell voltage, E_{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,

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



47