

Lecture 25 CH102 A2 (MWF 11:15 am) Spring 2019 Copyright © 2019 Dan Dill dan@bu.edu

[TP] For the redox process

$$\text{Cu}^{2+}(\text{aq}) + \text{Zn}(\text{s}) \rightarrow \text{Cu}(\text{s}) + \text{Zn}^{2+}(\text{aq})$$
 when the ions each are 1 M, Zn(s) is consumed. This means ...

20% 1. $K > 1$
 20% 2. $K < 1$
 20% 3. $Q > 1$
 20% 4. $Q < 1$
 20% 5. More information needed

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Lecture 25 CH102 A2 (MWF 11:15 am)
 Friday, March 29, 2019

- Cell voltage, E_{cell} , and electrical energy
- What determines cell voltage, E_{cell}° ?
- Calculating standard cell voltage, E_{cell}°
- Cell voltage versus spontaneity

Next lecture: Cell voltage versus Q/K : The Nernst equation; Exploring the Nernst equation; Concentration cells: Mixing → electric current

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Cell voltage, E_{cell} , and electrical energy

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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.


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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 than can be harnessed.

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

These two things together determine what is called the **free energy change, ΔG** , of the redox process.


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What determines cell voltage, E_{cell} ?

We will see that free energy change, ΔG , is the amount of **energy that can be harnessed**, **excluding any energy associated with pressure-volume work**.

The reason pressure-volume work is excluded is that it is typically lost to the surroundings as a consequence of volume changes that arise to keep pressure constant.

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What determines cell voltage, E_{cell} ?

Since 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 $\Delta G_{\text{cell}} < 0$, 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 .

For now, we can simplify things by arranging for $Q = 1$, typically by making reactants and products be in their **standard states**.

This arrangement, $Q = 1$, defines what we call the **standard** free energy change,

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

indicated by the "°".



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Calculating standard cell voltage, E°_{cell}

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

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

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 $\Delta G^{\circ}_{\text{cell}}$ as

$$\Delta G^{\circ}_{\text{cell}} = \Delta G^{\circ}_{\text{cathode}} + \Delta G^{\circ}_{\text{anode}}$$



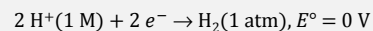
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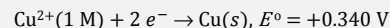
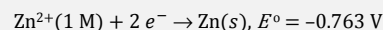
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Calculating standard cell voltage, E°_{cell}

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



All other reductions defined **relative to SHE**



etc.



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Calculating standard cell voltage, E°_{cell}

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

$$\Delta G^\circ_{\text{cathode}} = -n_e F E^\circ_{\text{cathode}}$$

and for the anode (oxidation) contribution

$$\text{and } \Delta G^\circ_{\text{anode}} = +n_e F E^\circ_{\text{anode}}$$

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°_{cell}

Combining the three expressions

$$\Delta G^\circ_{\text{cathode}} = -n_e F E^\circ_{\text{cathode}} \text{ and } \Delta G^\circ_{\text{anode}} = +n_e F E^\circ_{\text{anode}}$$

$$\Delta G^\circ_{\text{cell}} = \Delta G^\circ_{\text{cathode}} + \Delta G^\circ_{\text{anode}}$$

$$\Delta G^\circ_{\text{cell}} = -n_e F E^\circ_{\text{cell}}$$

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

$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}}$$

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



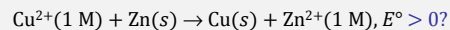
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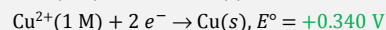
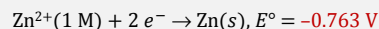
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Calculating standard cell voltage, E°_{cell}

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



The standard reduction potentials are



The standard cell potential is

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

So, Zn is **oxidized** by Cu^{2+}



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Cell voltage versus spontaneity

Spontaneity is proportional to voltage.

Spontaneity is proportional to how far the process is from equilibrium.

Voltage versus Q/K ?





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 0% 3. $Q > 1$
 0% 4. $Q < 1$
 0% 5. More information needed


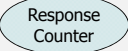

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[Quiz] For the redox process

$$\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$$
 when $Q = x$, Zn(s) is consumed. This means ...

20% 1. $K > 1$
 20% 2. $K < 1$
 20% 3. $Q > K$
 20% 4. $Q < K$
 20% 5. More information needed





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[TP] For the redox process

$$\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$$
 when $Q = 10$, Zn(s) is consumed.
 This means over time the cell voltage will ...

25% 1. become smaller
 25% 2. stay the same
 25% 3. become larger
 25% 4. More information needed





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[TP] For the redox process

$$\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$$
 when $Q = 10$, Zn(s) is consumed.
 Compared to the voltage when $Q = 1$, the voltage when $Q = 10$ is ...

25% 1. smaller
 25% 2. the same
 25% 3. larger
 25% 4. More information needed



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[Group Quiz] For the redox process
$$M^+(aq) + X(s) \rightarrow M(s) + X^+(aq)$$

when $Q = 0.1$, $M(s)$ is **formed**.
Compared to the voltage when $Q = 1$, the **magnitude** of the voltage when $Q = 0.1$ is ...

- 25% 1. smaller
- 25% 2. the same
- 25% 3. larger
- 25% 4. More information needed

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