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[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 24 CH102 A1 (MWF 9:05 am)
 Monday, March 26, 2018

- Cell voltage, E_{cell} , and electrical energy
- Calculating standard cell voltage, E°_{cell}
- Cell voltage versus spontaneity

Next lecture: Continue ch16. 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
 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 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 change that arise to keep pressure constant.

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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**.

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 state**.

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

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



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Calculating standard cell voltage, E_{cell}°

Since E_{cell}° is proportional to the $\Delta G_{\text{cell}}^{\circ}$,

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

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 $\Delta G_{\text{cell}}^{\circ}$ as

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



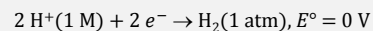
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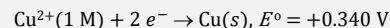
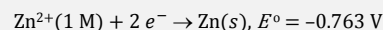
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Calculating standard cell voltage, E_{cell}°

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,

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

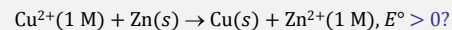
Note that both E°_{cathode} and E°_{anode} are standard **reduction** potentials.



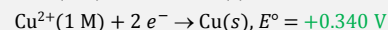
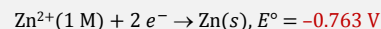
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Calculating standard cell voltage, E°_{cell} Here is an example: Does Cu^{2+} oxidize Zn?

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 away from equilibrium

Voltage versus Q/K ?



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
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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


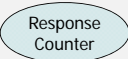

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[Group Quiz] For the redox process
$$M^+(aq) + X(s) \rightarrow M(s) + X^+(aq)$$

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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