

Lecture 26 CH102 A1 (MWF 9 am) Spring 2017 Copyright © 2016 Dan Dill dan@bu.edu

[TP] For the redox process
 $\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$
 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 26 CH102 A1 (MWF 9:05 am)

Friday, March 31, 2017

- Review: What determines cell voltage, E_{cell} ?
- Calculating standard cell voltage, E_{cell}° .
- Cell voltage versus spontaneity.

Next lecture: Complete: Cell voltage versus spontaneity. The Nernst equation. Exploring the Nernst equation. Concentration cells: Mixing → electric current

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

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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

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

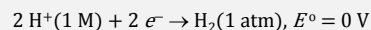
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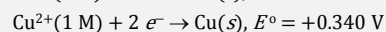
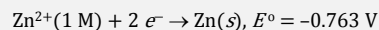
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Calculating standard cell voltage, E°_{cell}

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

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

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

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

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

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

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.



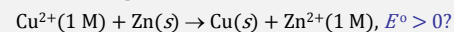
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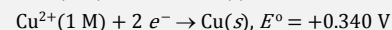
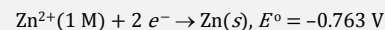
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Calculating standard cell voltage, E°_{cell}

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



The standard reduction potentials are



The standard cell potential is

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

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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[TP] For the redox process

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 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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[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

$$\text{M}^{+}(aq) + \text{X}(s) \rightarrow \text{M}(s) + \text{X}^{+}(aq)$$
 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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[TP] For the redox process

$$\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Cu}(s) + \text{Zn}^{2+}(aq)$$
 when $[\text{Cu}^{2+}] = 0$ and $[\text{Zn}^{2+}] = 4$, the voltage is ...

33% 1. < 0
 33% 2. 0
 33% 3. > 0

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[TP] A redox reaction has $K = 10$. If there are **only products** present, $-\log(Q/K)$ is ...

17% 1. $+\infty$
 17% 2. 2
 17% 3. 1
 17% 4. 0
 17% 5. -1
 17% 6. $-\infty$

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