

Slide 1

Some more advanced redox problems

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Slide 3

**Concentration cells**

I take two beakers, each containing 250 mL of distilled water. Into the left one, I add 10.00 g of  $\text{Cu}(\text{NO}_3)_2$  and into the right one I add 5.00 g of  $\text{Cu}(\text{NO}_3)_2$ . I connect the two beakers with a  $\text{KNO}_3$  salt bridge and then place a copper wire into each beaker. If I put a voltmeter between the two copper wires, what voltage will I measure?

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Slide 4

**If a picture paints a thousand words...then why can't I paint you?**

Is the answer 0 V?

Depends on the question!

10.00 g  $\text{Cu}(\text{NO}_3)_2$   
250 mL  $\text{H}_2\text{O}$

5.00 g  $\text{Cu}(\text{NO}_3)_2$   
250 mL  $\text{H}_2\text{O}$

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Slide 5

All chemistry problems begin with...

...a balanced equation!  
Except for redox reactions that begin with...  
two balanced  $\frac{1}{2}$  reactions.

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

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Slide 6

STANDARD cell potential

Reduction:  $\text{Cu}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Cu}(\text{s})$   $E_{\text{red}}^0 = 0.34 \text{ V}$   
Oxidation:  $\text{Cu}(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2 \text{e}^-$   $E_{\text{ox}}^0 = -0.34 \text{ V}$

$E_{\text{cell}}^0 = E_{\text{red}}^0 + E_{\text{ox}}^0 = 0.34 \text{ V} + (-0.34 \text{ V}) = 0 \text{ V}$

No voltage!!! At STANDARD conditions!  
298 K, 1 atm, and 1 M concentrations!

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Slide 7

Nernst Equation

$E_{\text{cell}} = E_{\text{cell}}^0 - 0.0592 \text{ V}/n \log Q$

$Q = \frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}}$

(anode is where oxidation occurs)

In our example, which one is the anode and which one is the cathode?

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Slide 8

Which one ends up being the anode (oxidation)

- A. The bigger concentration
- B. The smaller concentration
- C. The  $\text{KNO}_3$

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Slide 9

$10.00 \text{ g Cu(NO}_3)_2 \cdot \frac{1 \text{ mol}}{187.6 \text{ g}} = 0.05332 \text{ mol}$

$\frac{0.05332 \text{ mol Cu}^{2+}}{0.250 \text{ L}} = 0.2133 \text{ M}$

$5.00 \text{ g Cu(NO}_3)_2 \cdot \frac{1 \text{ mol}}{187.6 \text{ g}} = 0.02666 \text{ mol}$

$\frac{0.02666 \text{ mol}}{0.250 \text{ L}} = 0.1066 \text{ M}$

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Slide 10

What about me? What about Q?

Only one of the cells can be the anode. Which one?

The one which makes the cell work!

0.2133 M  $\text{Cu(NO}_3)_2$       0.1066 M  $\text{Cu(NO}_3)_2$

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Slide 11

**Nernst Equation**

$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - 0.0592 \text{ V/n log } Q$$
$$Q = \frac{[\text{Cu}^{2+}]_{\text{anode}}}{[\text{Cu}^{2+}]_{\text{cathode}}}$$

$Q = 0.2133 \text{ M}/0.1066 \text{ M} = 2$   
OR  
 $Q = 0.1066 \text{ M}/0.2133 \text{ M} = 0.5$   
 $E_{\text{cell}} = 0 \text{ V} - 0.0592 \text{ V/n log } Q$

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Slide 12

**Nernst Equation**

$$E_{\text{cell}} = 0 \text{ V} - 0.0592 \text{ V/n log } Q$$
$$E_{\text{cell}} = -0.0592 \text{ V}/2 \text{ log } 2 = -0.00891 \text{ V}$$
$$E_{\text{cell}} = -0.0592 \text{ V}/2 \text{ log } (0.5) = 0.00891 \text{ V}$$

Only one of them is spontaneous!

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Slide 13

**What about me? What about Q?**

The lower concentration cell is always the anode.

$0.2133 \text{ M Cu(NO}_3)_2$  Cathode       $0.1066 \text{ M Cu(NO}_3)_2$  Anode

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Slide 14

**Obviously...**

...tough to get too high a voltage out of a concentration cell since  $E_{\text{cell}}^0 = 0$ .

Depends on stoichiometry, but for this cell even if you have 100x the concentration in the cathode...

$Q = 1/100 = 0.01$

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Slide 15

$$E_{\text{cell}} = E_{\text{cell}}^0 - 0.0592 \text{ V}/n \log Q$$
$$= 0 \text{ V} - 0.0592 \text{ V}/2 \log (0.01)$$
  
$$E_{\text{cell}} = 0.0592 \text{ V}$$

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Slide 16

I make a battery (STP) by hooking up the following two half cells:

$\text{MnO}_4^- (\text{aq}) + 8 \text{H}^+ (\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4 \text{H}_2\text{O} (\text{l})$   
 $E_{\text{red}}^0 = 1.51 \text{ V}$

$\text{SO}_4^{2-} (\text{g}) + 4 \text{H}^+ (\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2\text{SO}_3 (\text{aq}) + \text{H}_2\text{O} (\text{l})$   
 $E_{\text{red}}^0 = 0.20 \text{ V}$

The initial concentration of everything is 1 M in a volume of 250 mL.  
After running the cell for a while, the concentration of the permanganate has dropped by 25%. At that point, I apply a voltage of 1.50 V and 2 Amps for 1 hour. What is the cell potential after the hour?

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Slide 17

**Always start with the reaction!**

$\text{MnO}_2(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$   
 $E^\circ_{\text{red}} = 1.51 \text{ V}$

$\text{SO}_4^{2-}(\text{g}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^- \rightarrow \text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
 $E^\circ_{\text{red}} = 0.20 \text{ V}$

Which is the anode? Which is the cathode?

$\text{MnO}_2(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l})$   
 $E^\circ_{\text{red}} = 1.51 \text{ V}$

$\text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_4^{2-}(\text{g}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^-$   
 $E^\circ_{\text{ox}} = -0.20 \text{ V}$

$E^\circ_{\text{cell}} = 1.51 \text{ V} + (-0.20 \text{ V}) = 1.31 \text{ V}$

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Slide 18

**Balance the equation**

Use Appendix II and go straight to step 6 (combine reactions to eliminate electrons):

$2^*(\text{MnO}_2(\text{aq}) + 8 \text{H}^+(\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4 \text{H}_2\text{O}(\text{l}))$

$\frac{5^*(\text{H}_2\text{SO}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightarrow \text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq}) + 2 \text{e}^-)}{2 \text{MnO}_2(\text{aq}) + 16 \text{H}^+(\text{aq}) + 5 \text{H}_2\text{SO}_3(\text{aq}) + 5 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{Mn}^{2+}(\text{aq}) + 8 \text{H}_2\text{O}(\text{l}) + 5 \text{SO}_4^{2-}(\text{aq}) + 20 \text{H}^+(\text{aq})}$

$2 \text{MnO}_2(\text{aq}) + 16 \text{H}^+(\text{aq}) + 5 \text{H}_2\text{SO}_3(\text{aq}) + 5 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{Mn}^{2+}(\text{aq}) + 8 \text{H}_2\text{O}(\text{l}) + 5 \text{SO}_4^{2-}(\text{aq}) + 20 \text{H}^+(\text{aq})$

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Slide 19

**Balance the equation**

$2 \text{MnO}_2(\text{aq}) + 5 \text{H}_2\text{SO}_3(\text{aq}) \rightarrow 2 \text{Mn}^{2+}(\text{aq}) + 3 \text{H}_2\text{O}(\text{l}) + 5 \text{SO}_4^{2-}(\text{aq}) + 4 \text{H}^+(\text{aq})$

$E^\circ_{\text{cell}} = 1.31 \text{ V}$

The initial concentration of everything is 1 M in a volume of 250 mL.

Since the initial concentrations of everything are 1 M, I am at standard conditions and the measured cell potential would be 1.31 V.

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Slide 20

**Balance the equation**

$$2 \text{MnO}_4^- (\text{aq}) + 5 \text{H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 3 \text{H}_2\text{O} (\text{l}) + 5 \text{SO}_4^{2-} (\text{aq}) + 4 \text{H}^+ (\text{aq})$$

$E^\circ_{\text{cell}} = 1.31 \text{ V}$

The initial concentration of everything is 1 M in a volume of 250 mL. After running the cell for a while, the concentration of the permanganate has dropped by 25%. At that point, I apply a voltage of 1.5 V and 2 Amps for 1 hour. What is the cell potential after the hour?

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Slide 21

**ICE ICE, BABY, ICE ICE**

$$2 \text{MnO}_4^- (\text{aq}) + 5 \text{H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 3 \text{H}_2\text{O} (\text{l}) + 5 \text{SO}_4^{2-} (\text{aq}) + 4 \text{H}^+ (\text{aq})$$

|   |        |     |     |   |     |     |
|---|--------|-----|-----|---|-----|-----|
| I | 1 M    | 1 M | 1 M | - | 1 M | 1 M |
| C | -2x    | -5x | +2x | - | +5x | +4x |
| E | 0.75 M |     |     |   |     |     |

So:  $1 - 2x = 0.75$   
 $x = 0.125$

$$2 \text{MnO}_4^- (\text{aq}) + 5 \text{H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 3 \text{H}_2\text{O} (\text{l}) + 5 \text{SO}_4^{2-} (\text{aq}) + 4 \text{H}^+ (\text{aq})$$

|   |        |           |           |   |           |           |
|---|--------|-----------|-----------|---|-----------|-----------|
| I | 1 M    | 1 M       | 1 M       | - | 1 M       | 1 M       |
| C | -0.25  | -5(0.125) | +2(0.125) | - | +5(0.125) | +4(0.125) |
| E | 0.75 M | 0.375     | 1.25      | - | 1.625     | 1.5       |

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Slide 22

**I don't have to, but I could...**

$$2 \text{MnO}_4^- (\text{aq}) + 5 \text{H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 3 \text{H}_2\text{O} (\text{l}) + 5 \text{SO}_4^{2-} (\text{aq}) + 4 \text{H}^+ (\text{aq})$$

|   |        |           |           |   |           |           |
|---|--------|-----------|-----------|---|-----------|-----------|
| I | 1 M    | 1 M       | 1 M       | - | 1 M       | 1 M       |
| C | -0.25  | -5(0.125) | +2(0.125) | - | +5(0.125) | +4(0.125) |
| E | 0.75 M | 0.375     | 1.25      | - | 1.625     | 1.5       |

$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0592/n \log Q$

$$Q = \frac{[\text{H}^+]^4 [\text{SO}_4^{2-}]^5 [\text{Mn}^{2+}]^2}{[\text{MnO}_4^-]^2 [\text{H}_2\text{SO}_3]^5} = \frac{(1.5)^4 (1.625)^5 (1.25)^2}{(0.75)^2 (0.375)^5} = 2.15 \times 10^4$$

$E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0592/n \log Q = 1.31 \text{ V} - 0.0592/10 \log 21500$   
 $E_{\text{cell}} = 1.28 \text{ V}$

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Slide 23

**Balance the equation**

$$2 \text{MnO}_4^- (\text{aq}) + 5 \text{H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 3 \text{H}_2\text{O} (\text{l}) + 5 \text{SO}_4^{2-} (\text{aq}) + 4 \text{H}^+ (\text{aq}) \quad E^\circ_{\text{cell}} = 1.31 \text{ V}$$

The initial concentration of everything is 1 M in a volume of 250 mL. After running the cell for a while, the concentration of the permanganate has dropped by 25%. **At that point, I apply a voltage of 1.5 V and 2 Amps for 1 hour.** What is the cell potential after the hour?

What's going on here?  
I'm running the reaction BACKWARDS!

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Slide 24

**I apply a voltage of 1.5 V and 2 Amps for 1 hour.**

What does this do?

It pumps electrons into the system.  
Electrons with sufficient "energy" to put the system back where it came from...recharge the battery.

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Slide 25

**Still feeling the ICE**

|   |                                |   |  |                                     |                                    |                              |
|---|--------------------------------|---|--|-------------------------------------|------------------------------------|------------------------------|
|   | $2 \text{MnO}_4^- (\text{aq})$ | $+ 5 \text{H}_2\text{SO}_3 (\text{aq})$ | $\rightarrow 2 \text{Mn}^{2+} (\text{aq})$ | $+ 3 \text{H}_2\text{O} (\text{l})$ | $+ 5 \text{SO}_4^{2-} (\text{aq})$ | $+ 4 \text{H}^+ (\text{aq})$ |
| I | 0.75 M                         | 0.375                                   | 1.25                                       | -                                   | 1.625                              | 1.5                          |
| C | +2x                            | +5x                                     | -2x  | -                                   | -5x                                | -4x                          |
| E |                                |   |  |                                     |                                    |                              |

How do I find x?  
Count electrons

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Slide 26

**Clicker questions**

1 apply a voltage of 1.5 V and 2 Amps for 1 hour. How many electrons is that?

- A. 3 mol
- B. 7200 mol
- C. 0.112 mol
- D. 0.0746 mol
- E. 2 mol

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Slide 27

$2 \text{ A} = 2 \text{ C/s}$

$1 \text{ hr} * 60 \text{ min/hr} * 60 \text{ s/min} = 3600 \text{ s}$

$2 \text{ C/s} * 3600 \text{ s} = 7200 \text{ C}$

$7200 \text{ C} * 1 \text{ mol e}^- / 96485 \text{ C} = 0.0746 \text{ mol e}^-$

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Slide 28

**Clicker question**

$2 \text{ MnO}_4^- (\text{aq}) + 5 \text{ H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{ Mn}^{2+} (\text{aq}) + 3 \text{ H}_2\text{O} (\text{l}) + 5 \text{ SO}_4^{2-} (\text{aq}) + 4 \text{ H}^+ (\text{aq})$

How many moles of  $\text{MnO}_4^-$  would be regenerated by the 0.0746 mol  $\text{e}^-$ ?

- A. 0.0746 mol  $\text{MnO}_4^-$
- B. 0.373 mol  $\text{MnO}_4^-$
- C. 0.0149 mol  $\text{MnO}_4^-$
- D. 0.186 mol  $\text{MnO}_4^-$
- E. 0.149 mol  $\text{MnO}_4^-$

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Slide 29

**Need to see the electrons**

$\text{MnO}_4^- (\text{aq}) + 8 \text{H}^+ (\text{aq}) + 5 \text{e}^- \rightarrow \text{Mn}^{2+} (\text{aq}) + 4 \text{H}_2\text{O} (\text{l})$

5 mol e<sup>-</sup>/1 mol MnO<sub>4</sub><sup>-</sup>

$0.0746 \text{ mol e}^- \times \frac{1 \text{ mol MnO}_4^-}{5 \text{ mol e}^-} = 0.0149 \text{ mol MnO}_4^-$

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Slide 30

**Still feeling the ICE**

$2 \text{MnO}_4^- (\text{aq}) + 5 \text{H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 3 \text{H}_2\text{O} (\text{l}) + 5 \text{SO}_4^{2-} (\text{aq}) + 4 \text{H}^+ (\text{aq})$

|   |        |       |      |   |       |     |
|---|--------|-------|------|---|-------|-----|
| I | 0.75 M | 0.375 | 1.25 | - | 1.625 | 1.5 |
| C | +2x    | +5x   | -2x  | - | -5x   | -4x |
| E |        |       |      |   |       |     |

$0.0149 \text{ mol MnO}_4^- = 2x$

0.250 L

$X = 0.00745 \text{ mol}/0.250 \text{ L} = 0.0298 \text{ M}$

$2 \text{MnO}_4^- (\text{aq}) + 5 \text{H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 3 \text{H}_2\text{O} (\text{l}) + 5 \text{SO}_4^{2-} (\text{aq}) + 4 \text{H}^+ (\text{aq})$

|   |         |            |            |   |            |            |
|---|---------|------------|------------|---|------------|------------|
| I | 0.75 M  | 0.375      | 1.25       | - | 1.625      | 1.5        |
| C | +0.0596 | +5(0.0298) | -2(0.0298) | - | -5(0.0298) | -4(0.0298) |
| E | 0.810 M | 0.524 M    | 1.19 M     |   | 1.48 M     | 1.38 M     |

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Slide 31

$2 \text{MnO}_4^- (\text{aq}) + 5 \text{H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 3 \text{H}_2\text{O} (\text{l}) + 5 \text{SO}_4^{2-} (\text{aq}) + 4 \text{H}^+ (\text{aq}) \quad E^\circ_{\text{cell}} = 1.31 \text{ V}$

The initial concentration of everything is 1 M in a volume of 250 mL. After running the cell for a while, the concentration of the permanganate has dropped by 25%. At that point, I apply a voltage of 1.5 V and 2 Amps for 1 hour. **What is the cell potential after the hour?**

Nernst!

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Slide 32

**Still feeling the ICE**

$2 \text{MnO}_4^- (\text{aq}) + 5 \text{H}_2\text{SO}_3 (\text{aq}) \rightarrow 2 \text{Mn}^{2+} (\text{aq}) + 3 \text{H}_2\text{O} (\text{l}) + 5 \text{SO}_4^{2-} (\text{aq}) + 4 \text{H}^+ (\text{aq})$   
 I 0.75 M 0.375 M      1.25 M      -      1.625 M      1.5 M  
 C +0.0596 M      +5(0.0298) M      -2(0.0298) M      -      -5(0.0298) M      -4(0.0298) M  
 E 0.810 M      0.524 M      1.19 M      1.48 M      1.38 M

$E_{\text{cell}} = E^{\circ}_{\text{cell}} - 0.0592/n \log Q$   
 $Q = \frac{[\text{H}^+]^4 [\text{SO}_4^{2-}]^5 [\text{Mn}^{2+}]^2}{[\text{MnO}_4^-]^2 [\text{H}_2\text{SO}_3]^5} = \frac{(1.38)^4 (1.48)^5 (1.19)^2}{(0.810)^2 (0.524)^5} = 1.407 \times 10^3$   
 $E_{\text{cell}} = E^{\circ}_{\text{cell}} - 0.0592/n \log Q = 1.31 \text{ V} - 0.0592/10 \log 1407$   
 $E_{\text{cell}} = 1.29 \text{ V}$

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Slide 33

**Little problem**

You can also use  $E^{\circ}$  in the same way we used  $\Delta G^{\circ}$ ...to determine  $K_{\text{eq}}$ .

This is not that important a tool...because most of the  $K_{\text{eq}}$  are HUGE!!!

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Slide 34

**Consider the following reaction:**

What is the equilibrium constant for the reaction between  $\text{Fe}^{3+}$  and Zn?

$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe} \quad E^{\circ}_{\text{red}} = -0.036 \text{ V}$   
 $\text{Zn} \rightarrow \text{Zn}^{2+} + 2 \text{e}^- \quad E^{\circ}_{\text{ox}} = 0.76 \text{ V}$

$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{ox}}$   
 $= -0.036 \text{ V} + 0.76 \text{ V} = 0.724$

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Slide 35

**Getting K**

$$E_{\text{cell}} = E_{\text{cell}}^0 - (0.0592/n)\log Q$$

At equilibrium  $E_{\text{cell}} = 0$

$$0 = E_{\text{cell}}^0 - (0.0592/n)\log K$$
$$E_{\text{cell}}^0 = (0.0592/n)\log K$$
$$\log K = nE_{\text{cell}}^0/0.0592$$
$$K = 10^{nE/0.0592}$$

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Slide 36

**In our case...**

$$K = 10^{nE/0.0592}$$
$$E_{\text{cell}}^0 = 0.724 \text{ V}$$

What's n?

$$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$$
$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$$

We need the balanced equation for the reaction...straight to Step 6

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Slide 37

**Combine the ½ reactions to eliminate electrons**

$$\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe}$$
$$\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$$
  
$$2^*(\text{Fe}^{3+} + 3\text{e}^- \rightarrow \text{Fe})$$
$$3^*(\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-)$$
$$2\text{Fe}^{3+} + 3\text{Zn} + 6\text{e}^- \rightarrow 2\text{Fe} + 3\text{Zn}^{2+} + 6\text{e}^-$$
  
$$6 = n$$

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Slide 38

In our case...

$$K = 10^{nE/0.0592}$$
$$E_{\text{cell}}^0 = 0.724 \text{ V}$$
$$n=6$$
$$K = 10^{6 \cdot 0.724 / 0.0592}$$
$$K = 2.5 \times 10^{73}$$

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Slide 39

In our case...

$$K = 10^{nE/0.0592}$$

Imagine a smaller K

$$E_{\text{cell}}^0 = 0.100 \text{ V}$$
$$n=1$$
$$K = 10^{1 \cdot 0.199 / 0.0592}$$

K = 49...still pretty big.

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Slide 40

**Redox Chemistry**

1. It all starts with a balanced equation (stick with the 6-1/2 steps)
2.  $E^0$  (Appendix II) tells you whether or not a reaction is spontaneous (happens)
3. Nernst equation corrects  $E^0$  for concentration to get actual E.
4. Electrolysis is forcing a non-spontaneous reaction to happen.
5.  $J = CV$
6.  $A = C/s$

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