| Slide 1 | | |
|---------|--|--|
| | | |
| | Some more advanced redox | |
| | problems | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| 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 Cu(NO ₃) ₂ and into the right one | |
| | I add 5.00 g of Cu(NO ₃) _{2.} I connect the two beakers with a 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? | |
| | | |
| | | |
| | | |
| | | |
| Slide 4 | If a picture paints a thousand | |
| | wordsthen why can't I paint you? | |
| | 0 V? | |
| | Depends on the question! | |
| | KNO ₃ | |
| | $\begin{array}{ccc} 10.00\ \mathrm{g}\ \mathrm{Cu(NO_3)_2} & 5.00\ \mathrm{g}\ \mathrm{Cu(NO_3)_2} \\ 250\ \mathrm{mL}\ \mathrm{H_2O} & 250\ \mathrm{mL}\ \mathrm{H_2O} \end{array}$ | |
| | | |

| Slide | 5 |
|-------|---|
| | |

All chemistry problems begin with...

...a balanced equation!

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

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

| S | ide | 6 |
|--------|-----|------------|
| \sim | ıuc | <i>-</i> U |

STANDARD cell potential

$$\begin{split} & \text{Reduction: Cu$^{2+}$ (aq) + 2 e-$ \rightarrow Cu$ (s) E^0_{red}=$0.34 V$} \\ & \text{Oxidation: } & \text{Cu(s)} \rightarrow \text{Cu$^{2+}$ (aq) + 2 e-$ E^0_{ox}} =-0.34 V \end{split}$$

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

No voltage!!! At STANDARD conditions!

298 K, 1 atm, and 1 M concentrations!

Slide 7

Nernst Equation

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

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

(anode is where oxidation occurs)

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

| | | |
|------|---|------|
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | - | |
| | | |
| | | |

Which one ends up being the anode (oxidation)

- A. The bigger concentration
- B. The smaller concentration
- C. The KNO₃

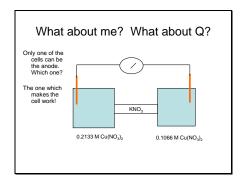
Slide 9

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

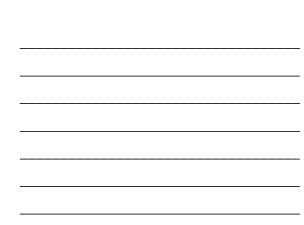
 $\frac{0.05332 \text{ mol Cu}^{2+}}{0.250 \text{ L}}$ = 0.2133 M

 $5.00 \text{ g Cu(NO}_3)_2 * \frac{1 \text{ mol}}{187.6 \text{ g}} = \frac{0.02666 \text{ mol}}{0.250 \text{ L}}$ = 0.1066 M

Slide 10



| | | |
|------|------|--|
| | | |



| Slide | 1 | 1 |
|-------|---|---|
|-------|---|---|

Nernst Equation

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

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

Q = 0.2133 M/0.1066 M = 2

OR

Q = 0.1066 M/ 0.2133 M = 0.5

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

Slide 12

Nernst Equation

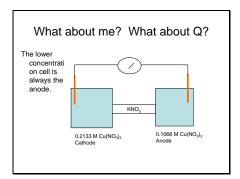
 $E_{cell} = 0 \text{ V} - 0.0592 \text{ V/n log Q}$

 $E_{cell} = -0.0592 \text{ V/2 log 2} = -0.00891 \text{ V}$

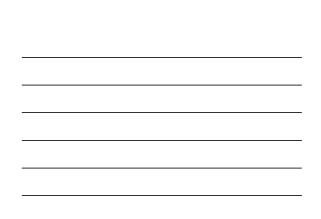
 $E_{cell} = -0.0592V/2 \log (0.5) = 0.00891 V$

Only one of them is spontaneous!

Slide 13



| | | |
|------|------|--|
| | | |
| | | |



| 01 | • | 1 | 4 | 4 |
|----|---|-------------|-----|---|
| SI | 1 | $d\epsilon$ | ۱ د | 4 |

Obviously...

...tough to get too high a voltage out of a concentration cell since $E^0_{cell} = 0$.

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

Q = 1/100 = 0.01

Slide 15

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

 $E_{cell} = 0.0592 \text{ V}$

Slide 16

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

 MnO_4 (aq) + 8 H⁺ (aq) + 5 e- \rightarrow Mn^{2+} (aq) + 4 H₂O (I) E^0 _{red} = 1.51 V

 ${\rm SO_4}^{2\cdot}(\rm g) + 4~H^*~(aq) + 2~e^- \rightarrow H_2 {\rm SO_3}(aq) + H_2 {\rm O}~(\rm I)$ ${\rm E^0}_{\rm red} = 0.20~{\rm V}$

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?

| | | |
|--|------|--|
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |
| | | |

Always start with the reaction!

 $\rm MnO_4{}^{\textstyle \cdot}(aq)$ + 8 H+ (aq) + 5 e- \rightarrow $\rm Mn^{2+}(aq)$ + 4 $\rm H_2O$ (I) $\rm E^0_{\rm red}$ = 1.51 V

 ${\rm SO_4^{2^{-}}}(\rm g)$ + 4 H+ (aq) + 2 e- \rightarrow $\rm H_2SO_3(aq)$ + $\rm H_2O$ (I) $\rm E^0_{\rm red}$ = 0.20 V

Which is the anode? Which is the cathode? $MnO_{c}(a_0) + 8 \ H^+(a_0) + 5 \ e^- \to Mn^{2+}(a_0) + 4 \ H_2O \ (I) \\ E_{o_0}^- = 1.5 \ I^+ V \\ + I_8O_{c}(a_0) + I_2O \ (I) \to SO_{c}^{-2} \ (g) + 4 \ H^+(a_0) + 2 \ e^- E_{o_0}^- = -0.20 \ V \\ E_{o_0}^- = 1.5 \ I^- V + (-0.20 \ V) = 1.31 \ V$

Slide 18

Balance the equation

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

 $2*(MnO_4^-(aq) + 8 H^+ (aq) + 5 e^- \rightarrow Mn^{2+}(aq) + 4 H_2O (I))$

 $\begin{array}{l} \frac{5^{+}(H_{2}SO_{3}(aq)+H_{2}O\ (I) \longrightarrow SO_{2}{}^{2}\cdot (aq)+4\ H^{+}\ (aq)+2\ e^{-})}{2\ MnO_{4}\ (aq)+16\ H^{+}(aq)+5\ H_{2}SO_{3}(aq)+5\ H_{2}O\ (I) \longrightarrow 2} \\ Mn^{2+}(aq)+8\ H_{2}O\ (I)+5\ SO_{4}{}^{2}\cdot (aq)+20\ H^{+}\ (aq) \end{array}$

 $\begin{array}{l} 2\;\text{MnO}_{4}\text{-}(\text{aq}) + 16\;\text{H}^{\text{-}}(\!\!\!\!\text{aq}) + 5\;\text{H}_{2}\text{SO}_{3}(\text{aq}) + 5\;\text{H}_{2}^{\text{-}}0\;(|) \rightarrow 2\\ \text{Mn}^{2\text{-}}(\text{aq}) + 8\;\text{H}_{2}^{\text{-}}0\;(|) + 5\;\text{SO}_{4}^{\text{-}}2\;(\text{aq}) + 20\;\text{H}^{\text{-}}(\!\!\!\!\text{aq})\\ 3 \end{array}$

Slide 19

Balance the equation

2 MnO₄-(aq) + 5 H₂SO₃(aq) \rightarrow 2 Mn²⁺(aq) + 3 H₂O (I) + 5 SO₄²⁻(aq) + 4 H⁺ (aq)

E_{cell} = 1.31 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.

| | | | |
|------|------|------|--|
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |
| | | | |

Balance the equation

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

 $E_{cell}^0 = 1.31 \text{ V}$

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, 1 apply a voltage of 1.5 V and 2 Amps for 1 hour. What is the cell potential after the hour?

Slide 21

ICE ICE, BABY, ICE ICE

I 1 M C -2x E 0.75 M

So: 1-2x=0.75 x = 0.125

Slide 22

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

 $\mathsf{E}_{\mathsf{cell}} = \mathsf{E}^0_{\;\mathsf{cell}} - 0.0592 / \mathsf{n} \; \mathsf{log} \; \mathsf{Q}$

 $Q = \underbrace{[H^+]^4[SO_4^{-2}]^5[Mn^{2+}]^2}_{ [MnO_4]^2[H_2SO_3]^5} = \underbrace{(1.5)^4(1.625)^5(1.25)^2}_{ (0.75)^2(0.375)^5} = 2.15x10^4$

 ${
m E_{cel}} = {
m E_{cel}^0} - 0.0592 / {
m n} \ {
m log} \ {
m Q} = 1.31 \ {
m V} - 0.0592 / {
m 10} \ {
m log} \ 21500$ ${
m E_{cel}} = 1.28 \ {
m V}$

| J | |
|---|--|
| | |
| | |
| | |
| | |
| | |
| 1 | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| _ | |
| | |
| | |
| | |
| | |
| | |
| 1 | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |
| | |

| SI | : | ٦ | _ | 1 | 2 |
|----|----|---|---|----|-----|
| | 11 | a | e | _/ | . 1 |

Balance the equation

2 MnO $_4$:(aq) + 5 H $_2$ SO $_3$ (aq) \rightarrow 2 Mn 2 +(aq) + 3 H $_2$ O (I) + 5 SO $_4$ 2-(aq) + 4 H $^+$ (aq) E $_0$ cell = 1.31 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!

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.

Slide 25

Still feeling the ICE

How do I find x? Count electrons

| |
|------|
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |

| Slide 26 | |
|----------|--|
| | |
| | |
| | |

Clicker questions

I 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

| Sl | i | de | • | 2 | 7 |
|----|---|----|---|---|---|
| N) | ш | u١ | _ | _ | 1 |

2 A = 2 C/s

1 hr * 60 min/hr * 60 s/min = 3600 s

2 C/s * 3600 s = 7200 C

7200 C * 1 mol e-/96485 C = 0.0746 mol e-

Slide 28

Clicker question

 $2~\text{MnO}_4\text{'}(\text{aq}) + 5~\text{H}_2\text{SO}_3(\text{aq}) \rightarrow 2~\text{Mn}^{2*}(\text{aq}) + 3~\text{H}_2\text{O}~(\text{I}) + 5~\text{SO}_4^{2*}(\text{aq}) + 4~\text{H}^*~(\text{aq})$

How many moles of ${\rm MnO_4}^{-}$ would be regenerated by the 0.0746 mol e-?

A. 0.0746 mol MnO₄-

B. 0.373 mol MnO₄

C. 0.0149 mol MnO₄

D. 0.186 mol MnO₄⁻ E. 0.149 mol MnO₄⁻

| |
|------|
| |
| |
| |
| |
| |
| |
| |
| |
| |
| |

Need to see the electrons

5 mol e-/1 mol MnO₄- $0.0746 \text{ mol } e^{-*} \frac{1 \text{ mol MnO}_{\underline{A}^{-}}}{5 \text{ mol } e^{-}} = 0.0149 \text{ mol MnO}_{\underline{A}^{-}}$

 $\mathrm{MnO_4}$ -(aq) + 8 H+ (aq) + 5 e- \rightarrow $\mathrm{Mn^{2+}}(\mathrm{aq})$ + 4 H $_2\mathrm{O}$ (I)

Slide 30

Still feeling the ICE

Slide 31

2 MnO $_4$ -(aq) + 5 H $_2$ SO $_3$ (aq) \rightarrow 2 Mn²⁺(aq) + 3 H $_2$ O (I) + 5 SO $_4$ -2 (aq) + 4 H $^+$ (aq) E $_{\rm cell}^0$ = 1.31 V

The initial concentration of everything is 1 M in a volume of 1250 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!

| S | li | de | 3 | 2 |
|---|----|----|---|---|
| | | | | |

Still feeling the ICE

$$\begin{split} 2\,MnO_{2}(aq) + 5\,H_{2}SO_{3}(aq) &\rightarrow 2\,Mn^{2+}(aq) + 3\,H_{2}O\,(1) + 5\,SO_{3}^{-2}(aq) + 4\,H^{+}(aq) \\ 1\,0.75\,M0.375 & 1.25 & 1.625 \\ C\,+\,0596 & +\,5(0.0298) & 2(0.0298) & -\,5(0.0298) \cdot 4(0.0298) \\ E\,0.810\,M & 0.524\,M & 1.19\,M & 1.48\,M & 1.38\,M \\ \end{split} \\ E_{cell} = E^{0}_{cell} - 0.0592/n \log Q & 0.0042/n M + 1.0042/n M + 1.0042/n$$

| | $\begin{split} E_{cell} &= E^0_{cell} - 0.0592/n \log Q \\ Q &= [H^+]^4[SO_a^2]^5[Mn^2]^2 = (1.38)^4(1.48)^5(1.19)^2 = 1.407x10^3 \end{split}$ | |
|----------|---|---|
| | | |
| | | |
| | | |
| | | |
| | | |
| | | 1 |
| Slide 33 | Little problem | |
| | You can also use E^0 in the same way we used ΔG^0 to determine $K_{\rm eq}.$ | |
| | This is not that important a toolbecause most of the K _{eq} are HUGE!!! | |
| | · | |
| | | |
| | | |
| | | |
| | | |
| | | 1 |
| Slide 34 | Consider the following reaction: | |
| | What is the equilibrium constant for the reaction between Fe ³⁺ and Zn? | |
| | Fe ³⁺ + 3e ⁻ \rightarrow Fe E ⁰ _{red} = -0.036 V Zn \rightarrow Zn ²⁺ + 2 e E ⁰ _{ox} = 0.76 V | |
| | $E^0_{cell} = E^0_{red} + E^0_{ox}$ | |
| | = -0.036 V + 0.76 V = 0.724 | |
| | | |

| α | • | 1 | | \sim | |
|----------|---|-------------|--------|--------|---|
| S | 1 | ~ I. | \sim | - 2 | - |
| ·) | | u | _ | • | , |
| | | | | | |

Getting K

 $\mathsf{E}_{\mathsf{cell}} = \mathsf{E^0}_{\mathsf{cell}} - (0.0592/\mathsf{n}) \mathsf{log}\;\mathsf{Q}$

At equilibrium $E_{cell} = 0$

$$\begin{split} 0 &= E^0_{cell} - (0.0592/n) \log K \\ E^0_{cell} &= (0.0592/n) \log K \\ Log \ K &= n E^0_{cell} / 0.0592 \\ K &= 10^{nE/0.0592} \end{split}$$

Slide 36

In our case...

 $K = 10^{nE/0.0592}$

 $E^0_{cell} = 0.724 \text{ V}$

What's n? $Fe^{3+} + 3e^{-} \rightarrow Fe$ $Zn \rightarrow Zn^{2+} + 2e^{-}$

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

Slide 37

Combine the ½ reactions to eliminate electrons

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

211 / 211 120

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

2 Fe³+ + 3 Zn + 6e- \rightarrow 2 Fe + 3 Zn²+ + 6e-

6 = n

| _ | | | | |
|---|--|--|--|--|
| | | | | |
| - | | | | |
| - | | | | |
| - | | | | |
| - | | | | |
| - | | | | |
| - | | | | |
| | | | | |

| | In our case $K = 10^{nE/0.0592}$ $E^{0}_{cell} = 0.724 \text{ V}$ $n=6$ $K = 10^{6^{\circ}0.724/0.0592}$ $K = 2.5 \times 10^{73}$ | |
|----------|--|--|
| Slide 39 | In our case $K = 10^{nE/0.0592}$ Imagine a smaller K $E^0_{cell} = 0.100 \text{ V}$ n=1 | |
| | K = 101*0.199/0.0592 K = 49still pretty big. | |
| 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 | |