Slide 1

RedOx Chemistry

OK, I balanced the frigging equation, so what?

Slide 2

An example of an Electrochemical Reaction

Oxidation half-reaction: $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^-$

Reduction half-reaction: $Sn^{4+} + 2\ e- \rightarrow Sn^{2+}$

Net: $2\ Fe^{2+} + Sn^{4+} \rightarrow 2\ Fe^{3+} + Sn^{2+}$

So frigging what?

Well a couple things:

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Looking back at our first example..

$2\ Fe^{2+} + Sn^{4+} \rightarrow 2\ Fe^{3+} + Sn^{2+}$

A couple frigging things:

1) It is a different set of compounds. If I mix Fe^{2+} and Mn^{5+} and IF the reaction above happens, the stuff in my beaker is different.
2) Electrons move…think lightning and kites.

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WTFDYMBI?

What do you mean by "IF"?

2 Fe^{2+} + Sn^{4+} → 2 Fe^{3+} + Sn^{2+}

2 Fe^{3+} + Sn^{2+} → 2 Fe^{2+} + Sn^{4+}

2 Fe^{2+} + Sn^{4+} ↔ 2 Fe^{3+} + Sn^{2+}

Is this just another case of equilibrium…?

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Not Usually

Only one of the reactions will happen. That's why your rusty car never de-rusts!

Why is that? Well, I thought you'd never ask?

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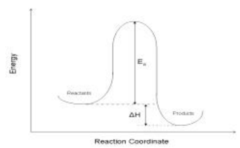
Typical Reaction Energy Diagram



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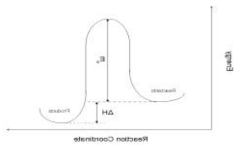
What if you just flip it around?



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So what?

We've seen the reaction diagrams before, what does it mean?

Reactions can only do 4 things:

1) Not happen at all – boring!
2) Proceed as written
3) Proceed in reverse
4) Sit at equilibrium

How do you decide what they do?

Yes, that's right, ΔG!

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WTFIDG?

Well, we don't know what ΔG is yet, but I'll tell you this: it is related to the second frigging thing – electrons are moving around.

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If electrons are going to move…

…somebody needs to give them a push!

Once they've been pushed, they just fall down the hill!

ElectroMotiveForce (emf) is the push.

You know it more by the name of its unit: volts!

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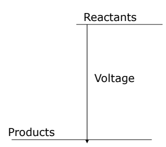
EMF is really the push behind the electrons. The voltage is the potential difference between reactants and products (like altitude).

You can't fall uphill!



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The Cell Potential

The voltage difference is called the "cell potential" and it depends on a number of factors (the usual suspects: temperature, concentration, pressure etc.).

The starting point is STANDARD cell potentials (E^0) – which can be found in the Table in Appendix II

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Ox: $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^-$ $E^0_{red} = 0.77$ V

Red : $Sn^{4+} + 2\ e- \rightarrow Sn^{2+}$ $E^0_{red} = 0.15$ V

Net: $2\ Fe^{2+} + Sn^{4+} \rightarrow 2\ Fe^{3+} + Sn^{2+}$

So, I got the number from the table, what do I do with them?

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They aren't all red!

Ox: $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^-$ $E^0_{red} = 0.77$ V

Ox: $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^-$ $E^0_{ox} = -\ 0.77$ V

Red : $Sn^{4+} + 2\ e- \rightarrow Sn^{2+}$ $E^0_{red} = 0.15$ V

Net: $2\ Fe^{2+} + Sn^{4+} \rightarrow 2\ Fe^{3+} + Sn^{2+}$

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What about the Stoichimetry?

Ox: $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^-$ $E^0_{red} = 0.77$ V

Ox: $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^-$ $E^0_{ox} = -\ 0.77$ V

Ox: $2(Fe^{2+} \rightarrow Fe^{3+} + 1\ e^-)$ $E^0_{ox} = 2(-\ 0.77\ V)$?

Red : $Sn^{4+} + 2\ e- \rightarrow Sn^{2+}$ $E^0_{red} = 0.15$ V

Net: $2\ Fe^{2+} + Sn^{4+} \rightarrow 2\ Fe^{3+} + Sn^{2+}$

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Ignore the Stoichiometry (clutch chest and fake heart attack)

Ox: $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^{-}$ $E^0_{red} = 0.77$ V

Ox: $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^{-}$ $E^0_{ox} = -\ 0.77$ V

~~Ox: $2(Fe^{2+} \rightarrow Fe^{3+} + 1\ e^{-})$ $E^0_{ox} = 2(-\ 0.77\ V)$?~~

Red : $Sn^{4+} + 2\ e^- \rightarrow Sn^{2+}$ $E^0_{red} = 0.15$ V

Net: $2\ Fe^{2+} + Sn^{4+} \rightarrow 2\ Fe^{3+} + Sn^{2+}$

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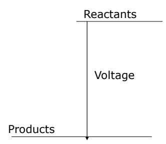
Why no stoichiometry?

It's literally like an altitude. Two hills 100 foot tall aren't the same as 1 hill 200 feet tall.

You have more electrons falling down, but they all fall down the same distance.



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So what does it all mean?

Ox: $Fe^{2+} \rightarrow Fe^{3+} + 1\ e^{-}$ $E^0_{ox} = -\ 0.77$ V

Red : $Sn^{4+} + 2\ e^- \rightarrow Sn^{2+}$ $E^0_{red} = 0.15$ V

Net: $2\ Fe^{2+} + Sn^{4+} \rightarrow 2\ Fe^{3+} + Sn^{2+}$

$E^0_{cell} = E^0_{red} + E^0_{ox}$
$E^0_{cell} = 0.15\ V + -0.77\ V = -0.62\ V$

The cell potential is negative – that means the reaction is NOT spontaneous.

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Looking back at our first example..

$2\ Fe^{2+} + Sn^{4+} \rightarrow 2\ Fe^{3+} + Sn^{2+}$

$E^0_{cell} = -0.62$ V

$2\ Fe^{3+} + Sn^{2+} \rightarrow 2\ Fe^{2+} + Sn^{4+}$

$E^0_{cell} = +0.62$ V

Mixing Fe^{2+} and Sn^{4+} results in nothing happening.
Mixing Fe^{3+} and Sn^{2+} results in electrons moving.

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Another example:

What is the cell potential of:

$2I^-_{(aq)} + Br_{2\ (aq)} \rightarrow I_{2\ (s)} + 2\ Br^-_{(aq)}$

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Split into ½ reactions

$2I^-_{(aq)} \rightarrow I_{2\ (s)} + 2\ e^-$ $E^0_{ox} = -\ E^0_{red} = -\ 0.54$ V

$Br_{2\ (aq)} + 2\ e^- \rightarrow 2\ Br^-_{(aq)}$ $E^0_{red} = 1.09$

$E^0_{cell} = 1.09$ V -0.54 V $= +0.55$ V

So this reaction is spontaneous and there is an exchange of electrons that fall off a 0.55 V cliff.

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What happens after electrons fall…

…they get married and raise quarks!

…nothing unless you catch them!

Think hydroelectric power or just an old mill wheel…if you catch the falling water, you can make it turn a wheel to do useful work.

Catch the falling electrons and use them to do useful work

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Electrochemical cells

You know them as "batteries", although that is only one example.

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To make a battery…

…I need to separate the half-cells!

Why can't I mix them together?

They short-circuit!

If I put everything in a single beaker, they just react and I'm done. I need to separate the reactants from the products so I can "catch" the electrons!

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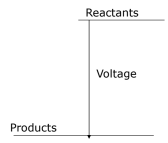
Why no stoichiometry?

If I make the falling electrons pass through my electric device, I can use the energy they release as they fall to do something useful.



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I need to be separate…

…but not too separate.

They need to be chemically isolated but electrically connected.

(see picture on white board! ☺)

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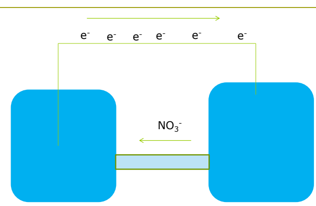
Galvanic cell – battery – electrochemical cell….



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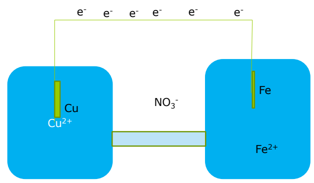
Galvanic cell – battery – electrochemical cell….



Which way does it go?

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Whole bunch of possible reactions

Cu^{2+} + 2 e^- = Cu E_{red} = 0.34 V
Fe^{2+} + 2 e^- = Fe E_{red} = -0.45 V

Fe^{3+} + 1 e- = Fe^{2+} E_{red} = 0.77 V
Cu^{2+} + 1 e^- = Cu^+ E_{red} = 0.16 V

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Whole bunch of possible reactions

Cu^{2+} + 2 e^- = Cu E_{red} = 0.34 V (could be either)
Fe^{2+} + 2 e^- = Fe E_{red} = -0.45 V (could be either)

Fe^{3+} + 1 e- = Fe^{2+} E_{red} = 0.77 V (could only do ox)
Cu^{2+} + 1 e^- = Cu^+ E_{red} = 0.16 V (could only do red)

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E is like delta G is related to "K"…biggest positive voltage wins

$Cu^{2+} + 2\ e^- = Cu$ $E_{red} = 0.34$ V (could be either)

$Fe^{2+} + 2\ e^- = Fe$ $E_{red} = -0.45$ V (could be either)

$Fe^{2+} = 1$ e- + Fe^{2+} $E_{ox} = -0.77$ V (could only do ox)

$Cu^{2+} + 1\ e^- = Cu^+$ $E_{red} = 0.16$ V (could only do red)

Slide 32

E is like delta G is related to "K"…biggest positive voltage wins

$Cu^{2+} + 2\ e^- = Cu$ $E_{red} = 0.34$ V (could be either)

$Fe^{2+} + 2\ e^- = Fe$ $E_{red} = -0.45$ V (could be either)

$Cu^{2+} + 1\ e^- = Cu^+$ $E_{red} = 0.16$ V (smaller than the Cu^{2+} to Cu reaction)

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E is like delta G is related to "K"…biggest positive voltage wins

$Cu^{2+} + 2\ e^- = Cu$ $E_{red} = 0.34$ V (could be either)

$Fe^{2+} + 2\ e^- = Fe$ $E_{red} = -0.45$ V (could be either)

Iron must be oxidized or the E_{cell} would be negative and non-spontaneous.

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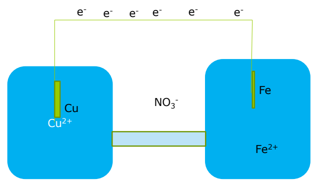
Galvanic cell – battery – electrochemical cell….



Which way does it go?

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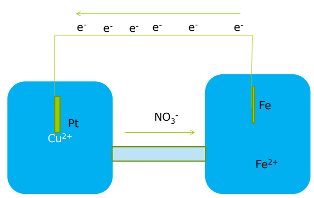
Galvanic cell – battery – electrochemical cell….



Inert reference electrode

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Shorthand notation

$2I^-_{(aq)} + Br_{2\,(aq)} \rightarrow I_{2\,(s)} + 2\,Br^-_{(aq)}$

$2I^-_{(aq)} \rightarrow I_{2\,(s)} + 2\,e^-$ $E^0_{ox} = -\,E^0_{red} = -\,0.54$ V

$Br_{2\,(aq)} + 2\,e^- \rightarrow 2\,Br^-_{(aq)}$ $E^0_{red} = 1.09$

I could write it as a chemical reaction, but an electrochemical cell can also be written in shorthand as:

Ox reactant|ox product||red reactant|reduction product

I^-(1 M,aq) |I_2(s)||Br_2(1 M,aq)|Br^-(1 M,aq)

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Caveat

I^-(1M,aq) |I_2(s)||Br_2(1M,aq)|Br^-(1M,aq)

Of course the I^- and the Br^- might have a counterion present

KI(1M, aq) |I_2(s)||Br_2(1M,aq)|KBr(1M,aq)

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Energy

We normally measure energy in "Joules".

Electron energy is sometimes measured in "electron volts" which kind of implies the connection between cell potentials and energy.

Cell potential is like a cliff. What has more energy, a 1 pound rock falling off a 50 foot cliff or a 10 pound rock?

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Mass is to cliffs as _________is to volts.

The 10 pound rock has more kinetic energy (mgh becomes ½ mv^2)

In an electron potential field, the equivalent concept to mass is the charge.

Charge is measured in "Coulomb"s ("C") and each electron has a charge of 1.602×10^{-19} C

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A Joule is…

…a "Coulomb Volt".

Take the charge (# of electrons x each charge) and multiply it by the voltage.

Energy is, therefore, determined by the cell potential AND the number of electrons falling through it.