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RedOx Chemistry

OK, I balanced the frigging equation,
so what?

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An example of an Electrochemical Reaction

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

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

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

So frigging what?

Well a couple things:

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Looking back at our first example..

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

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"?

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

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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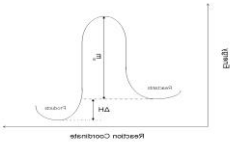
Typical Reaction Energy Diagram

Energy

Reaction Coordinate

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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?
Thermodynamics!

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Thermodynamics

Thermodynamics is the branch of chemistry that determines which of all the possible outcomes for a "system" happens.

What's a system?

Whatever you are studying.

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Condensed Thermodynamics

Thermodynamics is the answer to the question:
what do you want to be?

There are two things driving the universe. You
are familiar with both of them!

1. Laziness
2. Disorder

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“Laziness”

Really just a question of energy.

The universe prefers to be in its lowest energy state possible.

Balls don't roll up hill.

It is a natural inclination of all physical systems to seek the
lowest energy state possible. (On the couch with a beer and
a remote!)

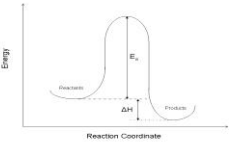
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In terms of reactions?

Reactions like to roll down hill in energy.

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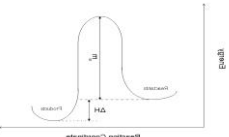
Downhill in energy



My products are lower in energy than my reactants. This is GOOD!
This is called an exothermic reaction (giving off heat/energy).

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What if you just flip it around?



Will this reaction happen? It is uphill in energy.
This is an "endothermic" reaction: absorbing heat/energy from the surrounding universe.

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Energy isn't the whole story.

If energy were the whole story, only exothermic reactions would happen.

And if only exothermic reactions happen...there would be no equilibrium reactions.

The reverse reaction of an exothermic reaction is always endothermic.

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Enter Entropy!

The other pillar of thermodynamics is entropy.

Entropy often gets described as “disorder” or “randomness”. This is not quite accurate.

Entropy represents the number of possible states that a system could be in.

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States

I mix 1 molecule of O_2 and 1 molecule of H_2 in an evacuated 1 L flask. How many different states of this system are there?

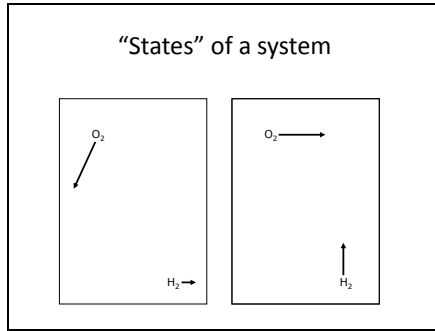
A nearly infinite number of them!

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“States” of a system

O_2	H_2
H_2	O_2

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What the $\&^{\%}$ * can we do?

Thermodynamics deals with statistical analysis of ensembles of states.

In our case, we are usually looking at a single representative state of the system that is the "most probable" state.

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To determine what happens...

We need to balance the energy considerations AND the entropy considerations.

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Reaction Energies

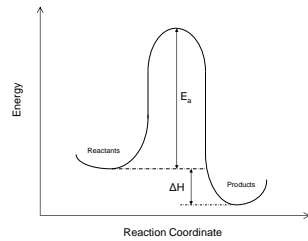
The energy change associated with a chemical reaction is called the **enthalpy of reaction** and abbreviated ΔH .

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

This is the total change in the internal energy of a system. Remember, the system is defined as the process of interest.

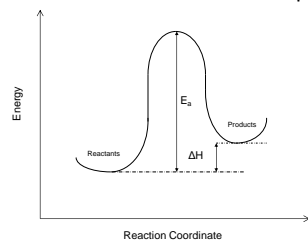
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General Reaction Scheme – “hot pack”



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Endothermic Reaction – “cold pack”



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Where does the Energy go?

In the case of a chemical reaction, you need to keep the different types of energy separate in your mind:

Bond energy – energy INSIDE the molecules

Thermal energy (heat) – kinetic energy of the molecules

Energy of the “bath” – kinetic energy of solvent or other molecules in the system

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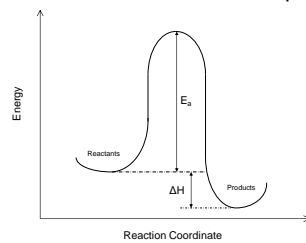
Energy changes

ΔH represents the change in INTERNAL MOLECULAR ENERGY.

$$\Delta H = H_{\text{final}} - H_{\text{initial}}$$

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Exothermic Reaction – “hot pack”



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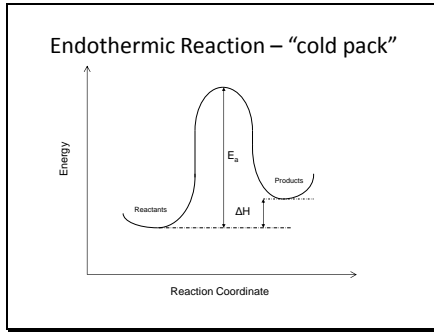
Exothermic energy changes

$\Delta H = H_{\text{final}} - H_{\text{initial}} < 0$

$H_{\text{initial}} > H_{\text{final}}$

This energy is internal to the molecule.
The excess gets absorbed by the rest of the system as heat causing the molecules to move faster (more kinetic energy) and the temperature to increase.

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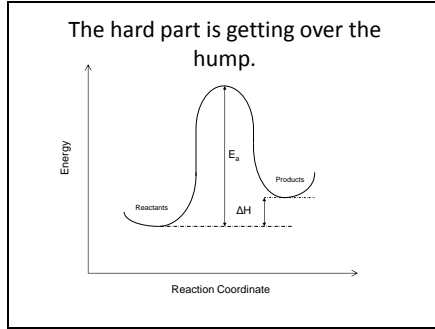
Endothermic energy changes

$\Delta H = H_{\text{final}} - H_{\text{initial}} > 0$

$H_{\text{initial}} < H_{\text{final}}$

This energy is internal to the molecule and must come from somewhere.
The additional energy required by the system gets absorbed from the rest of the system as heat causing the molecules to move slower (less kinetic energy) and the temperature to decrease.

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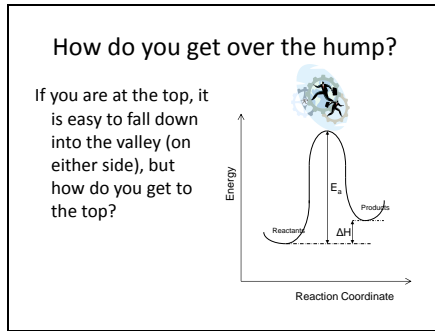
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E_a = Activation Energy

The tale of a reaction is not limited strictly to the identity and energetics of the products and reactants, there is a path (reaction coordinate) that must get followed.

The “hump” represents a hurdle that must be overcome to go from reactants to products.

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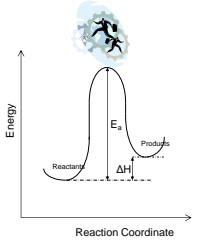


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How do you get over the hump?

The molecules acquire or lose energy the same way: by colliding with each other!

The energy comes from the "bath", the rest of the universe.



Energy

Reaction Coordinate

Reactants

Products

E_a

ΔH

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System vs. Universe

You have to keep the system and universe separate in your mind.

Conservation of Energy implies that ALL processes are a zero sum game. Endothermic vs. exothermic applies to the SYSTEM not the universe. The universe gives or gets the energy change of the system.

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Energy Considerations

Energy is an important consideration in any physical or chemical process.

You need to "climb the hill"!

We've seen that the "hill" (E_a) relates to the rate (k) and the equilibrium position (K).

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If energy were the whole story...

Why would water evaporate?

It is an endothermic process with an activation barrier, so it requires energy to be put into the system. Yet, water spontaneously evaporates even at near freezing temperatures. (And actually sublimates when frozen!)

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BUT...

ENERGY CHANGES AREN'T

THE WHOLE STORY!

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The rest of the story...

The energy of the molecules and their motions are one part of the story – the “thermo part”.

There is also the distribution of atoms within the allowed states. It not only matters what the average energy of the system is, but which molecules have what energies and what positions!

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The rest of the story...

...is **entropy (S)** - is a measure of the distribution of states.

Entropy is sometimes defined as "disorder" or "randomness". It is really more complicated than that and represents the total number of different micro-states available to the system.

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Entropy is...

...a state function.

Entropy gets handled much the same as enthalpy.

There are tables of entropy values, and it is usually the change (ΔS) that matters more than the absolute amount.

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Some examples

What has more entropy: 1 mole of water or 1 mole of steam? Why?

1 mole of steam – the molecules in steam are not associated with each other and are, therefore, free to explore more positions and energy states!

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Some examples

What has more entropy: 1 mole of water or ½ mole of water mixed with ½ mole of methanol? Why?

The mixture – there are the same number of molecules in both systems, but the mixture allows for more possible distributions of the molecules!

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The Laws of Thermodynamics

1st Law – Conservation of Energy

2nd Law – The Entropy of the universe is always increasing for spontaneous changes.

3rd Law – A perfect crystal at 0 K has no entropy.

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Just like the rock needing a shove to get rolling, a reaction needs to get “over the hump” (overcome E_A). But an exothermic reaction is always better than an endothermic reaction because the final state (products) are lower in energy.

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What about entropy and the Universe?

Turns out the Universe likes MORE entropy.
(The little trickster likes "disorder"!)

Increasing entropy means ΔS would be: greater than 0, less than 0?

Greater than 0 (products – reactants)

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NOTE:

There is no law of conservation of entropy.

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If the Universe gets to choose:

It prefers an exothermic reaction ($\Delta H < 0$) that increases entropy ($\Delta S > 0$).

Such a reaction is called "spontaneous" – it happens without you needing to force it.

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Spontaneous change

A spontaneous change is one that happens "naturally", without being forced by an outside agent.

Spontaneous change:
Water evaporating at room temperature.
A rock rolling down hill.

Non-spontaneous change:
Freezing water at room temperature.
Rolling a rock uphill.

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Spontaneous change

A spontaneous change is thermodynamically favorable.

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Spontaneous change

Thermodynamics is all about balancing enthalpy and entropy.

Some processes are enthalpically and entropically favorable. ($\Delta H < 0$ and $\Delta S > 0$). They happen.

Some process are enthalpically and entropically unfavorable. ($\Delta H > 0$ and $\Delta S < 0$). They DON'T happen.

What about when one property is favorable and the other is unfavorable?

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The Universe has a choice:

There are two other cases:

$\Delta H < 0$ and $\Delta S < 0$. Enthalpy good, entropy bad!

$\Delta H > 0$ and $\Delta S > 0$. Enthalpy bad, entropy good!

What's a poor old Universe supposed to do? Find a balance!

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Balancing entropy and enthalpy

Gibb's Free Energy:

$\Delta G = \Delta H - T \Delta S$

If $\Delta G > 0$ then reaction is NOT spontaneous.

If $\Delta G < 0$ then reaction IS spontaneous

If $\Delta G = 0$ then...the reaction is at equilibrium!

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For electrons...

Turns out that electrons will only "spontaneously" move in one direction: downhill in energy.

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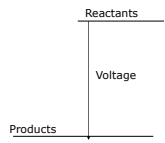
If electrons are going to move...
...somebody needs to give them a push!
Once they've been pushed, they just fall down the hill!
ElectroMotiveForce (emf) is the push.
You know it more by the name of its unit: volts!

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$\Delta G = -nFE$
Where:
n=number of electrons transferred
F=Faraday's constant
E = cell potential
Since a reaction is only spontaneous when $\Delta G < 0$, then E must be positive.

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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!



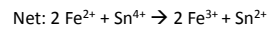
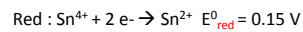
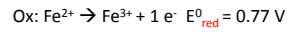
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The Cell Potential

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 a Tables of Standard Reduction potentials.

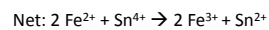
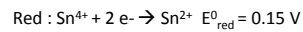
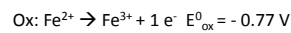
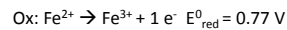
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So, I got the number from the table, what do I do with them?

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They aren't all red!



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What about the Stoichiometry?

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

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

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

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

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

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Ignore the Stoichiometry (clutch chest and fake heart attack)

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

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

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

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

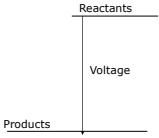
Net: $2 \text{Fe}^{2+} + \text{Sn}^{4+} \rightarrow 2 \text{Fe}^{3+} + \text{Sn}^{2+}$

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

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

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

$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} + E^{\circ}_{\text{ox}}$
 $E^{\circ}_{\text{cell}} = 0.15 \text{ V} + (-0.77 \text{ V}) = -0.62 \text{ V}$

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

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Looking back at our first example..

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

$E^{\circ}_{\text{cell}} = -0.62 \text{ V}$

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

$E^{\circ}_{\text{cell}} = +0.62 \text{ V}$

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:

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

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Split into ½ reactions

$$2\text{I}^-_{(\text{aq})} \rightarrow \text{I}_{2(\text{s})} + 2\text{e}^- \quad E^0_{\text{ox}} = -E^0_{\text{red}} = -0.54\text{ V}$$
$$\text{Br}_{2(\text{aq})} + 2\text{e}^- \rightarrow 2\text{Br}^-_{(\text{aq})} \quad E^0_{\text{red}} = 1.09$$
$$E^0_{\text{cell}} = 1.09\text{ V} - 0.54\text{ V} = +0.55\text{ V}$$

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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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 $\frac{1}{2} mv^2$)

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 $1.609 \times 10^{-19} C$

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A Joule is...

...a "Coulomb Volt".

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

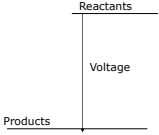
Energy is, therefore, determined by the cell potential AND the number of electrons falling through it.

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Keep in mind what the voltage is:

It's the hill the electrons fall down!

If you catch 'em you can make them do work!



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How much work can an electron do if an electron could do work?

Well, it's all a question of energy.

Joules is energy, volts is electrical potential.

Gravitation equivalent:

Joules is energy, height gravitational potential

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Joule = Coulomb * Volt

The charge * the potential = the energy change in the reaction

If 2 Coulombs falls through a 3 V electric field, 6 Joules of energy are liberated!

$E = q * V$
 $E = \#e * 1.602 \times 10^{-19} C/e * V$

q = charge

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How do I figure out the charge?

The particle that carries charge is the electron.
The total charge is really just the number of electrons multiplied by the charge on each electron.

1 electron has a charge of 1.602×10^{-19} C

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$$E = q * V$$

$$1 \text{ mol e}^- * \frac{6.022 \times 10^{23} \text{ e}^-}{1 \text{ mol e}^-} * \frac{1.602 \times 10^{-19} \text{ C}}{1 \text{ e}^-} = 9.6485 \times 10^4 \text{ C}$$

$$E = 96,485 \text{ C} * 9 \text{ V} = 8.68 \times 10^5 \text{ J}$$

(Remember a Joule = 1 CV)

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96485 C/mol e⁻

That number is soooo important it has a name:
Faraday's constant (F)

It's the conversion factor from moles to
Coulombs.

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V, E, and I

Voltage is the potential the electron can fall through.

Energy ($CV=J$) tells you how much work you can do. It's what you get when an electron falls through the potential.

Current (I) Amperes tells you how many electrons it takes to do it and how long it takes to do it! (It's kind of the electrical equivalent of MOLES! MOLES! MOLES!)

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Non-spontaneous reactions

So, if your $E < 0$ then the reaction is not spontaneous. Are you done?

Not necessarily.

Remember what "spontaneous" means: it happens without a shove.

If it is non-spontaneous, you can always give it a shove!

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Recharging your iPod...

...is just pushing the electrons uphill.

The battery will discharge by itself. To charge it you need to plug it in because the energy from the outlet is sufficient to "carry" the electrons back up the hill in the battery so they can fall down again later.

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Martyrs

Another use of voltages is to decide what happens if there is more than one option.
(That's the whole role of thermodynamics, after all.)

Consider a very common pair of half-reactions:

$$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \rightarrow 2 \text{OH}^- (\text{aq}) \quad E_{\text{red}} = 0.401 \text{ V}$$
$$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s}) \quad E_{\text{red}} = -0.447 \text{ V}$$

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What happens?

$$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \rightarrow 2 \text{OH}^- (\text{aq}) \quad E_{\text{red}} = 0.401 \text{ V}$$
$$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s}) \quad E_{\text{red}} = -0.447 \text{ V}$$

There are two options:

1. Iron gets reduced (and oxygen gets oxidized)
2. Oxygen gets reduced (and iron gets oxidized)

Which one actually happens? How would you know?

E_{cell} must be positive!

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What happens?

$$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \rightarrow 2 \text{OH}^- (\text{aq}) \quad E_{\text{red}} = 0.401 \text{ V}$$
$$\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \quad E_{\text{ox}} = +0.447 \text{ V}$$
$$E_{\text{cell}} = 0.401 \text{ V} + 0.447 \text{ V} = 0.848 \text{ V}$$
$$2 \text{OH}^- (\text{aq}) \rightarrow \text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4 \text{e}^- \quad E_{\text{ox}} = -0.401 \text{ V}$$
$$\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \quad E_{\text{red}} = -0.447 \text{ V}$$
$$E_{\text{cell}} = -0.401 \text{ V} + -0.447 \text{ V} = -0.848 \text{ V}$$

Only the positive one can happen!

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What happens?

$$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 2 \text{OH}^-(\text{aq}) \quad E_{\text{red}} = 0.401 \text{ V}$$
$$\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \quad E_{\text{ox}} = +0.447 \text{ V}$$
$$E_{\text{cell}} = 0.401 \text{ V} + 0.447 \text{ V} = 0.848 \text{ V}$$

Net: $2 \text{Fe}(\text{s}) + \text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{Fe}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq})$

It's rust....(one of several ways to formulate it).

The need for E to be positive chooses the reaction.

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Suppose I've got more stuff in the system...

$$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 2 \text{OH}^-(\text{aq}) \quad E_{\text{red}} = 0.401 \text{ V}$$
$$\text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Fe}(\text{s}) \quad E_{\text{red}} = -0.447 \text{ V}$$
$$\text{Mg}^{2+}(\text{aq}) + 2\text{e}^- \rightarrow \text{Mg}(\text{s}) \quad E_{\text{red}} = -2.37 \text{ V}$$

If I've got iron, magnesium and oxygen all together, what happens?

ΔG (or E) is our guide.

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One thing that could happen...

$$\text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) + 4\text{e}^- \rightarrow 2 \text{OH}^-(\text{aq}) \quad E_{\text{red}} = 0.401 \text{ V}$$
$$\text{Fe}(\text{s}) \rightarrow \text{Fe}^{2+}(\text{aq}) + 2 \text{e}^- \quad E_{\text{ox}} = +0.447 \text{ V}$$
$$E_{\text{cell}} = 0.401 \text{ V} + 0.447 \text{ V} = 0.848 \text{ V}$$

Net: $2 \text{Fe}(\text{s}) + \text{O}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow 2 \text{Fe}^{2+}(\text{aq}) + 2 \text{OH}^-(\text{aq})$

We saw this before. What's the other things that could happen?

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How else could E be positive?

$O_2(g) + 2 H_2O(l) + 4e^- \rightarrow 2 OH^-(aq)$ $E_{red} = 0.401 V$

$Fe^{2+}(aq) + 2 e^- \rightarrow Fe(s)$ $E_{red} = -0.447 V$

$Mg^{2+}(aq) + 2e^- \rightarrow Mg(s)$ $E_{red} = -2.37 V$

Options:

1. Iron gets oxidized and oxygen gets reduced.
2. Magnesium gets oxidized and oxygen gets reduced
3. Magnesium gets oxidized and iron gets reduced.

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How else could E be positive?

$O_2(g) + 2 H_2O(l) + 4e^- \rightarrow 2 OH^-(aq)$ $E_{red} = 0.401 V$

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ $E_{ox} = +2.37 V$

$E_{cell} = 2.771 V$

$Fe^{2+}(aq) + 2 e^- \rightarrow Fe(s)$ $E_{red} = -0.447 V$

$Mg(s) \rightarrow Mg^{2+}(aq) + 2e^-$ $E_{ox} = +2.37 V$

$E_{cell} = 1.923 V$

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The biggest E is most spontaneous.

1. Iron gets oxidized and oxygen gets reduced.
2. Magnesium gets oxidized and oxygen gets reduced
3. Magnesium gets oxidized and iron gets reduced.

So, ranking my options:

2>3>1

In other words, magnesium gets oxidized before iron!!!

This is called a "sacrificial anode".

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Sacrifice is good...unless you're the one doing it.

If you attach a magnesium rod to a steel bridge, the bridge won't rust until the magnesium is completely corroded!

Of all the possible chemical fates of the system, thermodynamics (E) picks the magnesium corrosion to be most likely.

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Let's take a look back...

Chlorine analysis:

Convert all of the Cl_2 to I_2 :
 $\text{Cl}_2 + 2 \text{I}^- \rightarrow \text{I}_2 + 2 \text{Cl}^-$

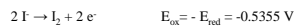
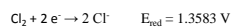
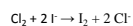
Indicator reaction:
 $\text{I}_2 + \text{starch} \rightarrow \text{I}_2\text{-starch (blue complex)}$

Quantitative Titration:
 $\text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2 \text{I}^-$

This is actually two different redox reactions!

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The Conversion reaction

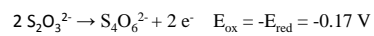
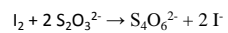


$$E_{\text{cell}} = E_{\text{red}} + E_{\text{ox}} = 1.3583 \text{ V} + (-0.5355 \text{ V}) = 0.8228 \text{ V}$$

No surprise, our reaction is spontaneous. (Kind of hard to do a titration if it isn't!!! ☺)

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The actual titration reaction



$$E_{\text{cell}} = E_{\text{red}} + E_{\text{ox}} = 0.5355 \text{ V} + (-0.17 \text{ V}) = 0.3655 \text{ V}$$

Also spontaneous!
