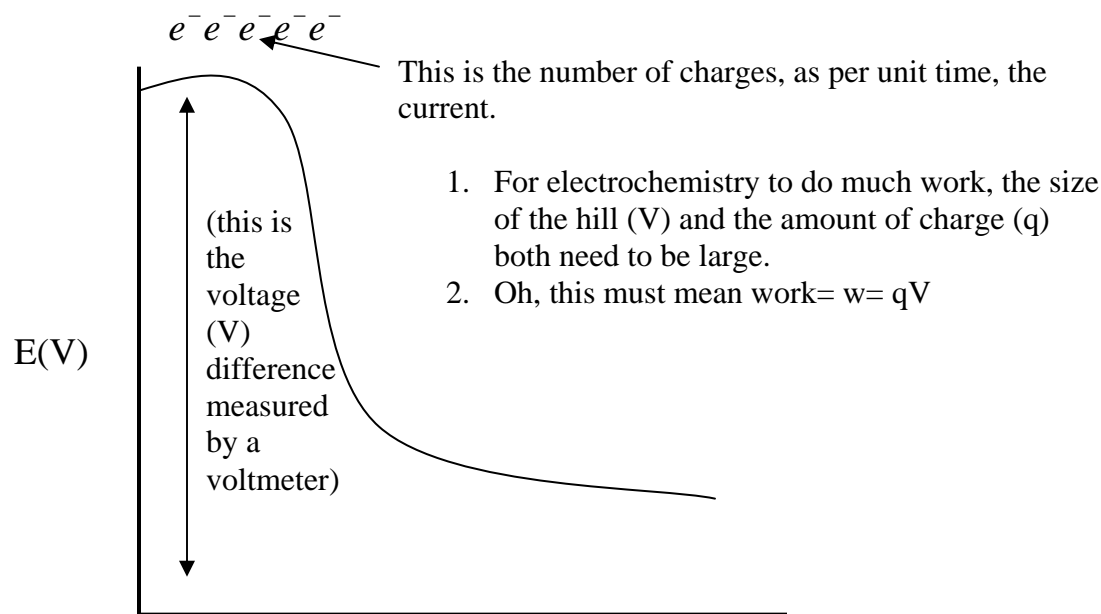


Electrochemistry Part 2: Getting quantitative and looking at electrochemical cells in action

Everything we want to learn in the way of quantitative information about electrochemistry can be found in the familiar diagram below:

- The $e^- e^- e^- e^-$ is the amount of charge, q , and can be related to mass through a simple stoichiometry problem
- The potential hill, E , is the value on your battery—it depends on the half cell potentials and the concentrations
- Thermodynamic values like w and ΔG are realized from q times E .



These three general categories of calculations are examined in order on the following pages:

Everything you wanted to know about measuring charge: basic stuff they should have told you in your high school physics class

Electrical Charge. The fundamental unit of charge, q , is measured in Coulombs. One electron has a charge of 1.602×10^{-19} Coulombs (C). Therefore, one mole of electrons has a special amount of charge

$$F = \text{Faraday (Coulombs/mole)} = q \text{ (Coulombs)} / n \text{ (moles)}$$

$$F = 9.649 \times 10^4 \text{ C/mole}$$

$$\text{So } q = nF$$

So electrons are our currency for electrochemical measurements in the same way that protons were our currency for acid/base reactions. A Faraday is simply an amount of charge in the same way a dozen is an amount of eggs and we can do routine stoichiometry calculations with this charge to mole conversion factor.

Example: In a redox reaction involving the reduction of Fe^{+++} to Fe^{++} , a total of 9.649×10^3 C are used up. How much Fe^{+++} was reduced?

$$(9.649 \times 10^3 \text{ C}) \left(\frac{1 \text{ mole Fe}^{+3}}{9.65 \times 10^4 \text{ C/mol}} \right) \left(\frac{1 \text{ mole Fe}^{+2}}{1 \text{ mole Fe}^{+3}} \right) \left(\frac{55.85 \text{ g}}{1 \text{ mole Fe}^{+2}} \right) = 5.585 \text{ g Fe}^{+3}$$

Note that for this reaction, a single electron is transferred from the Fe^{+2} to the Fe^{+3} . This is analogous to a single H^+ transfer in a monoprotic acid.

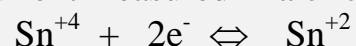
Adding time to the equation and get CURRENT.

The measure of current as a function of time is the ampere:

One Ampere = one Coulomb/second

Having current measured as a function of time means we can talk about a rate of reaction (kinetics stuff, something we haven't considered since we started equilibrium.)

Example: What is the current measured in a circuit involving the half cell reaction



which is occurring at a rate of 4.2×10^{-3} mole/hr?

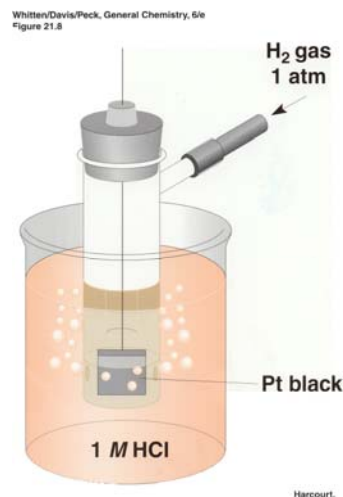
$$i = (4.24 \times 10^{-3} \text{ mole/hr}) \left(\frac{1 \text{ hr}}{3600 \text{ s}} \right) \left(\frac{2 \text{ mole e}^-}{1 \text{ mole Sn}^{+4}} \right) \left(\frac{9.65 \times 10^4 \text{ C}}{\text{mole e}^-} \right) = 0.227 \text{ A}$$

By the way, what do you think about this magnitude of current? Will it kill you? Will it power a small city or a small toy? I'd say, that's a pretty nasty shock—right at the edge of where a DC voltage can kill you.

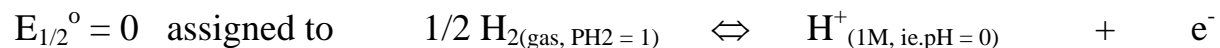
Standard Potentials.

You will recall from our brief detour into physics that you need the difference between TWO potentials to do work. A single half cell reaction is only a figment of your imagination (or an incorrect answer on an exam.) The only value of interest to us is this difference, this CHANGE IN POTENTIAL. Now here is the problem, do you know how many half cell reactions be described as an REFERENCE

the other half cell to each other. Let's let be equal to 0 V, so we reference AGAINST THE STANDARD



there are in the world? Well a lot, since every chemical reaction can oxidation or reduction. So what do we do? We create a STANDARD POTENTIAL (E^0) to which we arbitrarily assign a number. Then all reactions can be compared to the reference and through that reference, our STANDARD REFERENCE POTENTIAL for a half cell reaction can do the math in our head. Now, let's choose a half cell to be our WHICH ALL OTHERS THINGS ARE MEASURED!!! Let's choose HYDROGEN ELECTRODE (SHE).

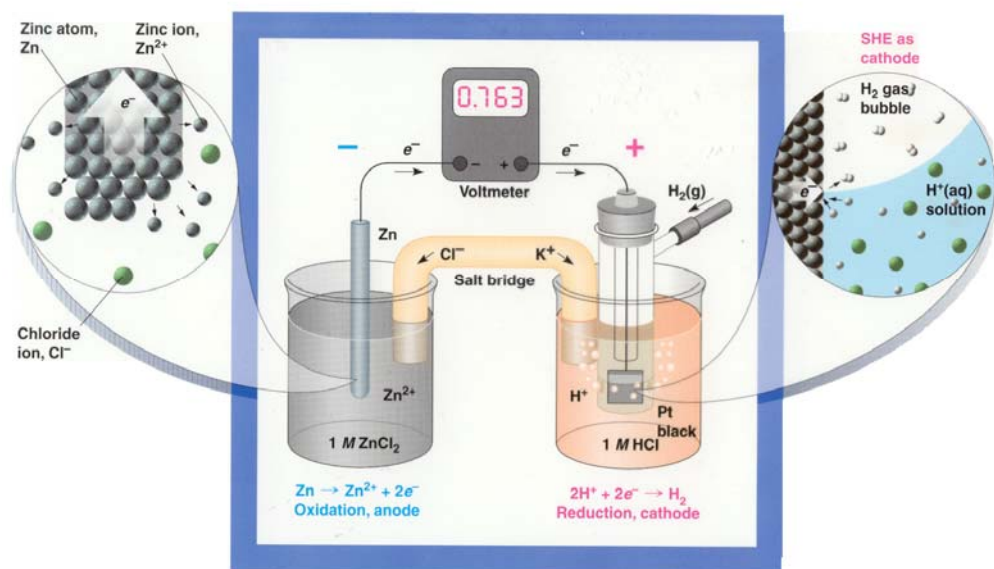


Now looking at this half cell, it doesn't seem to have a lot going for it. To build one you need to have a gas bulb filled with an explosive gas, AND a solution that is at pH = 0. But we don't get to pick, it was already chosen for us. Fortunately we don't have to use this half cell in the lab, we just use it to make the table of standard half cell reactions. In the lab we will use something else as a reference cell, like a STANDARD CALOMEL ELECTRODE (SCE) and we will simply note the difference between the SCE and the SHE when we do our calculations.

TABLES OF STANDARD HALF CELL REACTIONS.

Let's go in the lab, pull out a standard hydrogen electrode, and hook it up in a cell like the one below.

Whitten/Davis/Peck, General Chemistry, 6/e
Figure 21.9



Harcourt, Inc.

Now let's hook up all the half cell reactions in the world and obtain standard reference potentials (E°)—in the case above we started with a zinc solution that was lying around.

But a couple of things to consider before we get too far along....

First, electrochemistry is just thermodynamics, and you may recall from thermodynamics that things like concentration and temperature matter, so we need some standard concentrations and a standard temperature so that our electrochemistry friends can pitch in and help. How about we choose the following standard conditions:

- all reactants and products must be at 1 atm or 1M

- a standard temperature like 298K.

Reduction potentials: One more thing. We need to either write our half reactions as either oxidations or reductions. (We can't switch back and forth or we get our signs mixed up.) Now this may seem no big deal to you, but it sure was worth fighting over among electrochemists. For example, famous UT electrochemists like Al Bard and former President Larry Faulkner were big on writing everything as an oxidation half reaction. But they lost the This means the electrons will appear on the left side of the equation. Anyway, here it is, our very abbreviated table:

Whitten/Davis/Peck, General Chemistry, 6/e
Table 21.2

TABLE 21-2 Standard Aqueous Reduction Potentials in Aqueous Solution at 25°C		
Element	Reduction Half-Reaction	Standard Reduction Potential E° , volts
Li	$\text{Li}^+ + e^- \longrightarrow \text{Li}$	-3.045
K	$\text{K}^+ + e^- \longrightarrow \text{K}$	-2.925
Ca	$\text{Ca}^{2+} + 2e^- \longrightarrow \text{Ca}$	-2.87
Na	$\text{Na}^+ + e^- \longrightarrow \text{Na}$	-2.714
Mg	$\text{Mg}^{2+} + 2e^- \longrightarrow \text{Mg}$	-2.37
Al	$\text{Al}^{3+} + 3e^- \longrightarrow \text{Al}$	-1.66
Zn	$\text{Zn}^{2+} + 2e^- \longrightarrow \text{Zn}$	-0.763
Cr	$\text{Cr}^{3+} + 3e^- \longrightarrow \text{Cr}$	-0.74
Fe	$\text{Fe}^{2+} + 2e^- \longrightarrow \text{Fe}$	-0.44
Cd	$\text{Cd}^{2+} + 2e^- \longrightarrow \text{Cd}$	-0.403
Ni	$\text{Ni}^{2+} + 2e^- \longrightarrow \text{Ni}$	-0.25
Sn	$\text{Sn}^{2+} + 2e^- \longrightarrow \text{Sn}$	-0.14
Pb	$\text{Pb}^{2+} + 2e^- \longrightarrow \text{Pb}$	-0.126
H_2	$2\text{H}^+ + 2e^- \longrightarrow \text{H}_2$	0.000 (reference electrode)
Cu	$\text{Cu}^{2+} + 2e^- \longrightarrow \text{Cu}$	+0.337
I_2	$\text{I}_2 + 2e^- \longrightarrow 2\text{I}^-$	+0.535
Hg	$\text{Hg}^{2+} + 2e^- \longrightarrow \text{Hg}$	+0.789
Ag	$\text{Ag}^+ + e^- \longrightarrow \text{Ag}$	+0.799
Br_2	$\text{Br}_2 + 2e^- \longrightarrow 2\text{Br}^-$	+1.08
Cl_2	$\text{Cl}_2 + 2e^- \longrightarrow 2\text{Cl}^-$	+1.360
Au	$\text{Au}^{3+} + 3e^- \longrightarrow \text{Au}$	+1.50
F_2	$\text{F}_2 + 2e^- \longrightarrow 2\text{F}^-$	+2.87

Harcourt, Inc.

Notice in my small table that the SHE sits pretty much in the middle of things. Half of the reactions when written as reductions are spontaneous (E° is positive) and half are not spontaneous (E° is negative).

There is a much bigger collection of standard reduction potentials half reactions in the appendix of your text. Spend some time looking at them and making sense out of what you see from everyday life. Also, look at the bounds for this table. Does it make sense that Li and F₂ half reactions exhibit the largest absolute magnitudes?

Using the Tables of Standard Reduction Potentials.

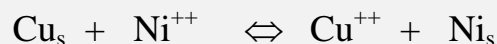
The whole purpose of the reduction potential tables was to avoid writing an exponentially increasing number of reactions between every new half cell reaction and every half cell reaction we already knew. So how do we put two half cell reactions together using the SHE?

By convention:

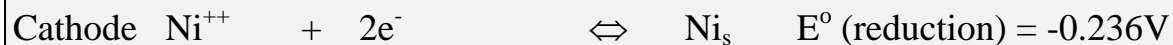
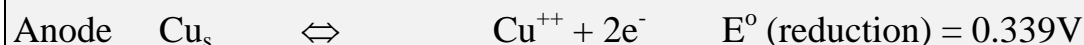
$$E^{\circ}_{\text{(net)}} = E^{\circ}_{\text{(cathode)}} - E^{\circ}_{\text{(anode)}}$$

Use this equation exactly as written, inserting values directly from the table of standard reductions. DON'T switch signs in the half cell reaction and then use this equation or you will mess up.

Example: Given below is an electrochemical cell reaction. Is the reaction spontaneous as written?



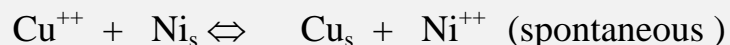
Break it down into the half cell reactions:



Now use the equation

$$\begin{array}{rclcl} E^{\circ} = & (-0.236\text{V}) & - & (0.339\text{V}) & = -0.575 \\ & \text{Cathode} & - & \text{anode} & = \text{net} \end{array}$$

Note that AS WRITTEN, this reaction is not spontaneous. However we can reverse the reaction and $E^{\circ} = +0.575$ and the reaction is spontaneous.



COMPLICATION: THE NERNST EQUATION

If electrochemistry was simply a matter of calculating E° values, life would be easy. But it is not. Do you really think that if we put together a nickel and copper cell and measured the potential, it would be 0.575? If you do, you are probably the same sort of person who believes that the pH of a 0.01M HCl solution is 2 (Go measure it, it is not.) In fact, there are a lot of complications to solution chemistry that need to be addressed if we are going to get a reasonable quantitative handle on the actual potential of an electrochemical cell. We need to deal with CONCENTRATION and how it affects E . We will borrow what we learned back in thermodynamics about relating ΔG to ΔG° through Q

$$\Delta G = \Delta G^\circ + RT \ln Q$$

Deriving the Nernst Equation. You may have noticed that batteries go dead. This means that even when they read 1.5V on the label, the battery's potential to do work is no longer 1.5V. Why is this? The problem is, we aren't accounting for concentration changes in the electrochemical cell. Remember that electrochemistry is just thermodynamics, and thermodynamics always considers relative concentrations. So clearly we will have to add corrections for concentrations to our equation for E .

This is where the Nernst equation comes in. The Nernst equation accounts for the concentration of electroactive species in an electrochemical cell; i.e., the Nernst equation turns E° into E , the actual cell potential. It is easily obtained by combining the above equation with the one on p.131 that relates E to ΔG .

For a reaction:

$$aA + ne^- \rightleftharpoons bB$$
$$Q = \frac{[B]^b}{[A]^a}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{[B]^b}{[A]^a}$$

R = ideal gas constant n = # of e^-
 T = temperature F = Faraday

Here, Q has the same form as an equilibrium constant in that it is equal to products over reactants, but the difference is that Q is used when NOT AT EQUILIBRIUM. (In other words, Q applied back when you added NaOH to your titration flask and things were kind of pink just before the solution went clear.)

It is important to note from the Nernst equation that when $Q = 1$, then $\ln Q = 0$ and $E = E^\circ$. This makes sense, because remember that E° is the standard potential and by definition occurs when all our concentrations are 1 M. If you stick the number 1 into every concentration in Q , obviously you end up with the $\ln Q$ term going away.

A more practical form of the Nernst assumes that $T = 25^{\circ}\text{C}$ and uses $\log_{\text{base } 10}$. In this case a Nernst equation half cell reaction is

$$E_{1/2} = E_{1/2}^{\circ} - \frac{0.05916}{n} \log Q$$

and for the cell reaction

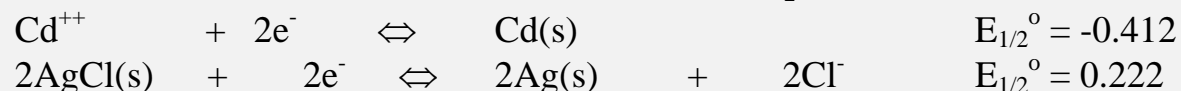
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.05916}{n} \log Q$$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

where Q is the reaction quotient for the balanced redox reaction. Here n is the # of electrons in the balanced reaction.

Example of a Nernst Equation Calculation

Consider a cell formed with the half reactions below and a CdCl_2 solution that is 0.0167M. The two half cell reactions,



yield a standard voltaic cell reaction potential of



the Nernst equation is

$$E_{\text{cell}} = 0.624 - \frac{0.05916}{2} \log [\text{Cl}^{-}]^2 [\text{Cd}^{++}]$$

and for the non-standard concentrations of 0.167M Cd^{++} and 0.0334 Cl^{-}

$$E_{\text{cell}} = 0.624\text{V} - \frac{0.05916}{2} \log [0.0334]^2 [0.0167] = E_{\text{cell}} = 0.764\text{V}$$

Note that as written, by lowering the CdCl_2 concentration from 1M, we are able to make a stronger battery.

Another example of the Nernst equation in action. This one is fun because you get to apply some of what you've learned about acid base chemistry!!

For the two half cell reactions,



which give a cell reaction



the Nernst equation is

$$E_{\text{cell}} = -0.402\text{V} - \frac{0.05916}{2} \log \frac{[\text{H}^+]^2}{[\text{Cd}^{++}]\text{P}_{\text{H}_2}}$$

Now according to the Nernst equation, if all the concentrations were unity (in this case it would mean the pH = 0), then the reaction is not spontaneous. But is it possible to make this reaction spontaneous? According to LeChatelier we can do so by altering the concentrations. What if we left $\text{P}_{\text{H}_2} = [\text{Cd}^{++}] = 1$, what would the pH have to be to make the reaction spontaneous? Mathematically, this means we want to find the pH when E goes from negative to positive:

$$0 = -0.402\text{V} - \frac{0.05916}{2} \log \frac{[\text{H}^+]^2}{(1)(1)}$$

Now solve for H^+ and you get

$$[\text{H}^+] = 1.6 \times 10^{-7} \text{ M or pH} = 6.8$$

So this is an example of a reaction that does not occur in acidic solution but is spontaneous at physiological pH and has a large driving force in base!! This is a startling example of how easily we can manipulate the balance of materials in a chemical system to observe very different types of chemistry. It is also why body pH is so important to all you medical types.

The Dead Battery: What happens at equilibrium.

Galvanic cells (batteries) work when a reaction is NOT at equilibrium. But in a battery, reactants decrease, products increase and then we reach a point where nothing happens. This place is of course, EQUILIBRIUM. While it is the case that EQUILIBRIUM is just one special case for an electrochemical cell, it is an important case at a boundary.

$$\text{when } Q \rightarrow K \quad E_{\text{cell}} \rightarrow 0$$

At that point we can substitute K into the Nernst equation and do a little rearranging

$$0 = E^{\circ} - \frac{0.05916}{n} \log K_{25}$$

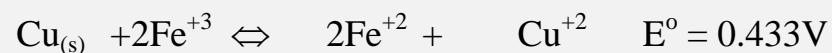
$$E^{\circ} = \frac{0.05916}{n} \log K_{25}$$

$$K_{\text{eq}} = 10^{nE/0.05916}$$

WOW!!! An equation that allows us to use an electrochemical cell to measure equilibrium constants. I'm sure many of you were wondering how we made all those tables of K values, for the most part they were developed from electrochemical measurements of dead batteries!!

Example of a dead battery as an equilibrium problem.

Given the following cell reaction:



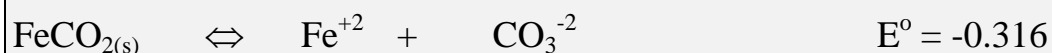
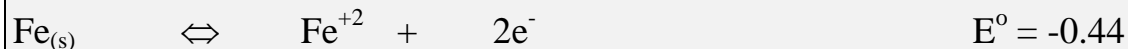
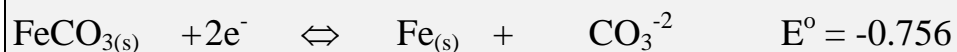
What is the equilibrium constant for the reaction?

$$K_{eq} = 10^{(2)(0.433)/0.05916} = 4 \times 10^{14}$$

Note that when E° is positive, K is greater than 1.

Another example:

Combine the two half cell reactions:



what we have is a K_{sp} equilibrium for FeCO_3 .

$$K_{eq} = K_{sp} = 10^{2(-0.316)/0.05916} = 2 \times 10^{-11}$$

Note that as expected, our K_{sp} is a very small number. This occurs when E° is negative.

Tying Electrochemistry to Thermodynamics—putting q and E together to do electrical work

What is the WORK necessary to move electrons?

In electrochemistry the electric POTENTIAL, E , measured in Volts (V), is the measure of the potential difference between two points. Work is the physical measure of what happens when an amount of charge passes between two points with a potential difference. Work has the units of Joules, and with V and C also in *mks* units, we have then

$$\text{Work (J)} = q E = (\text{volts})(\text{Coulombs})$$

So one Joule of work is done when one Coulomb moves across a potential gradient of one Volt. Now don't blow this off, $w = qE$ is an extremely important concept in any kind of science associated with moving charged particles.

Example. How much work does it take to move over 2.36×10^{-3} moles of electrons across a 1.05 V potential?

$$\text{Work(J)} = (1.05\text{V})q = (1.05\text{V})(2.36 \times 10^{-3}\text{ moles } e^{-})(9.65 \times 10^4\text{C/mol})$$

$$\text{Work} = 239 \text{ J}$$

By the way, is 239 J a lot or a little? Will it power a city, or a flashlight?

We just did a problem in which we used a 1.05 V potential difference. If we had wanted to do more work, we could have used a bigger potential difference; this is the idea behind purchasing a bigger battery, (a 12 V rather than a 1.5 V battery.)

So where did that 0.059 in the Nernst equation come from?

Without going into the reasons why, when dealing with electrochemical cells, we can relate this idea of work done in electrochemistry to the thermodynamic concept of free energy, through the equation:

$$w = \text{free energy} = \Delta G = -q E = -nFE$$

You will also remember that

$$\text{free energy} = \Delta G = -RT \ln K$$

so

$$-RT \ln K = -nFE$$

and

$$E = (RT/nF) \ln K \quad (\text{this is where } 0.059 \text{ in the Nernst comes from})$$

And looking just at the transitions from spontaneous to non-spontaneous reactions, the following must be true:

type of reaction	thermodynamics	electrochemistry	equilibria
spontaneous reaction	ΔG is negative	E is positive	K is > 1
non-spontaneous reaction	ΔG is positive	E is negative	K is < 1

As we leave thermodynamics and head into kinetics, spend a moment reflecting back on the very first day in CH301 when you were told about calorimetry. We haven't look at a subject since then, from enthalpy to entropy to free energy to physical equilibria to chemical equilibria to acids and bases and solubility to batteries and the Nernst equation. Every one of these subjects asked: how has the energy of a system changed from start to finish. Thermodynamics, equilibria and electrochemistry are the tools we have used to answer that question.

And now, the last piece of the puzzle—how the speed with which a reaction happens matters in defining the natural world.