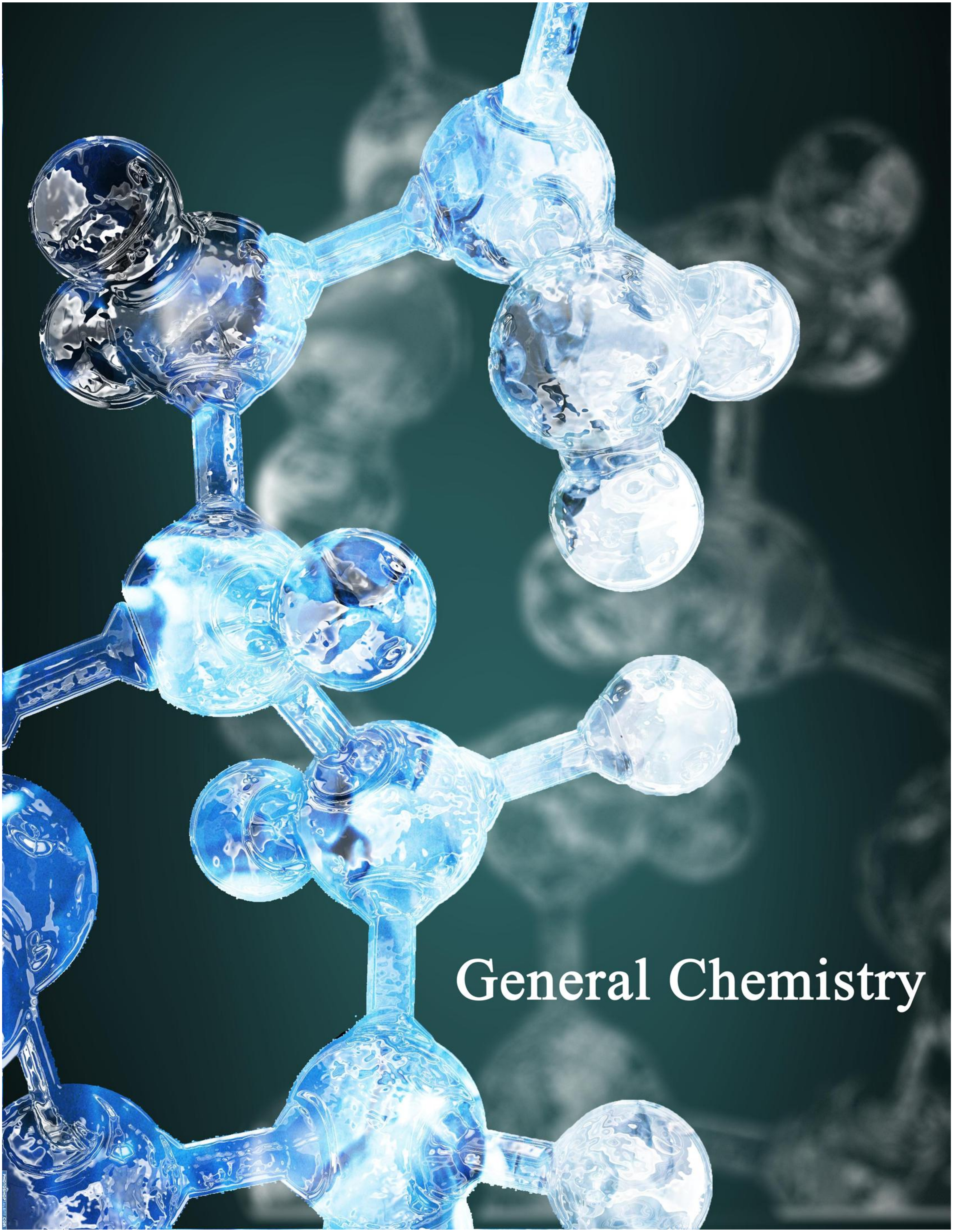

General Chemistry

Introduction

I wrote this book to make up for the deficiencies I have found in other text books. In private, chemists talk about chemistry very differently than the way that they teach it. When chemists do problems they use rules and procedures not often passed on to their students. One day as I was lecturing on a particular topic, I worked a problem for my class one way, but had already worked out the problem in my head using a very different and much easier procedure. I became aware of a disconnect between the way that I was presenting the material to my students and the way I thought about the chemistry myself. As a consequence, my teaching changed. My goal was to teach my students how I thought about chemistry and give them the insights those years in my profession had provided, and not just parrot what was found in the book. This text book is the result.

This book will not be everyone's cup of tea. For some instructors it will force them to see the material in very different ways and this change will be too different for them to adopt. I accept that. For the student, they will find explanations, insights, pictures and graphs not found in other texts. Because of the predictive power of these new explanations students will understand more, and memorize less. Chemistry will be easier for them, as it is meant to be.

Chemistry is meant to be fun. Have fun, and good luck,

Dr. Steven Fawl
PhD. Chemistry
U.C. Davis 1985

While on his death-bed, Michael Faraday was asked, "Have you ever pondered by yourself what will be your occupation in the next world?"

His last words were, "I shall be with Christ, and that is enough."

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Organic Chemistry

Chapter Eleven

Rate Laws, Kinetics, Mechanisms, And Activation Energies

IN this chapter we will explore how reactions occur. The methods used to determine the rate at which a reaction occurs help us understand how the molecules come together and react. Once known, we call these steps a reaction mechanism which can often be inferred from the reaction rate law. When a reaction is allowed to occur at multiple temperatures the change in the rate of the reaction can be used to calculate how much energy, called the activation energy, it takes for the reaction to occur. Finally, it is possible to calculate how much reactant will be left after any given period of time by using the integrated rate law and half-life. These integrated rate laws are particularly useful when measuring radioactive isotopes that are used to measure the age of rocks and bones.

The Rate of a Reaction

Suppose we have the following reaction and we want to describe how fast the reaction occurs,

$$2\,A + 3\,B \rightarrow C$$

We can describe the rate as the change in concentration of one of these ingredients per change in time. It shouldn't matter which component we use to describe the rate so all of the following are equivalent to one another,

$$\text{Rate} = -\frac{1}{2}\cdot\frac{\Delta[A]}{\Delta t} = -\frac{1}{3}\cdot\frac{\Delta[B]}{\Delta t} = \frac{1}{1}\cdot\frac{\Delta[C]}{\Delta t}$$

Since two A molecules disappear for every three B molecules we must multiply each of these rates by the inverse of their stoichiometric coefficient (in this case ½ and ⅓ respectively). The negative sign in the rate appears because we are looking at the rate of disappearance of species A and B so the final concentration will be lower than the initial. This means that the change in concentration for A would be,

$$\Delta A = [A]_{final} - [A]_{initial} = \text{negative number}$$

Since the final concentration is smaller than the initial concentration, the change in concentration would be a negative number. Since a rate should not be negative (it makes no sense to say that you are traveling -25 mph), a negative sign is added to the equation to make this number positive.

In similar fashion, if you are looking at the rate of appearance of C, its rate would look like,

$$\text{Rate} = \frac{\Delta[C]}{\Delta t} \quad \text{(rate of appearance)}$$

In this case, the 1/1 term was left out for convenience. Most often, we monitor the rate of disappearance of a reactant. The general form of this rate would be,

$$\text{Rate} = -\frac{1}{x} \cdot \frac{\Delta[A]}{\Delta t} = k[A]^x$$

Or just,

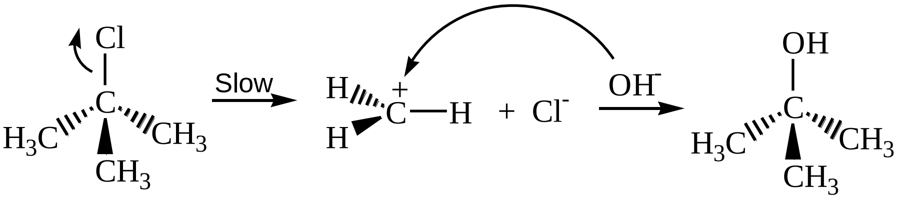
$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = x\,k[A]^x = k[A]^x$$

In virtually all chemistry text books, the value of x is conflated into the rate constant, k. It isn't being ignored. It is assumed that the rate constant includes a value for x. This makes our math a little bit easier and the student isn't left wondering if the k value should be multiplied by x or not (it shouldn't be). It is this last form that will be used in the remainder of this text.

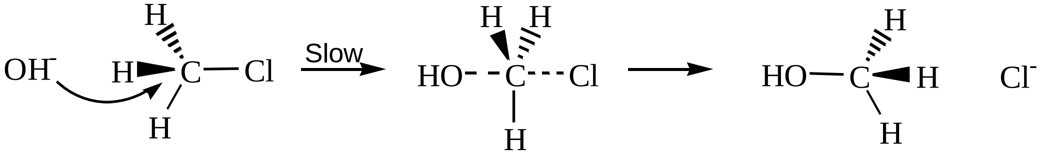
Reaction Order

A reaction rate is determined by the slowest step in a reaction. These steps can only involve one, or at most two, chemical components. When a step in a reaction involves only one molecule or atom, it is called a First Order reaction. If a step in a reaction involves two molecules, it is called a Second Order reaction.

1st Reaction – The molecule blows up and then the OH^- attacks it.



2nd Order Reaction – The OH^- pushes the Cl^- off of the molecule.



A good example of a first order reaction is a rollover accident on a freeway. The car rolls over because of mishandling by its driver. No other cars are involved. It just happens. This is to be distinguished from a head-on collision which is second order. In this case two cars collide, causing an accident. A head-on collision is a second order process. Third order processes are so rare that we may as well say that they do not occur. Imagine three cars hitting each other simultaneously. Have you ever seen this happen, even in the movies? No. The probability that three cars can hit each other simultaneously is exceedingly rare so that, although a few examples exist, we might as well say that they do not occur.

Now imagine that two cars collide, and then a third car hits them. This is not a third order process. The original process involves only two cars, so it is a second order process. The resulting mass of metal in the first accident is then struck by a third car, but this is just another second order process. While it is true that a third order process has occurred, it has not occurred in a single step. In order for this to happen two second order processes had to occur.

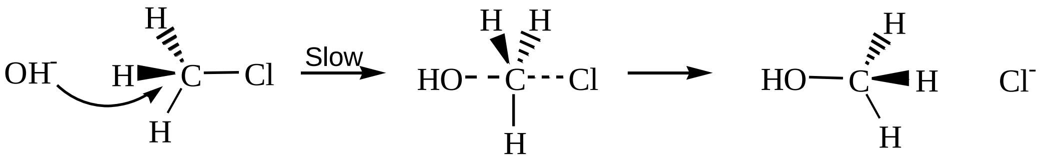
Zero Order Reactions

If first order reactions involve one molecule or atom, and second order reactions involve two atoms or molecules, what about zero order reactions? Do they occur?

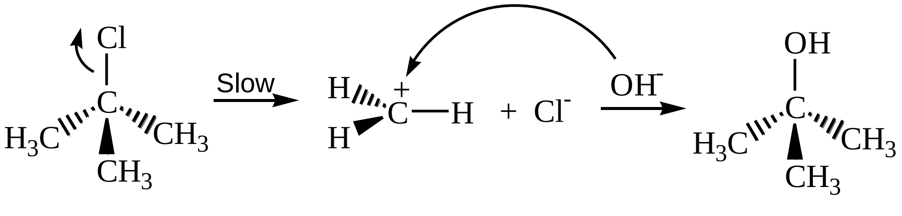
A zero order reaction infers that no molecules are involved in a reaction and if no molecules are involved in a reaction, is a reaction even occurring? The answer is a conditional yes. While it is true that there is no such thing as a zero order reaction, there are many reactions where one or more components of a reaction are zero order.

Every reaction has a slow step and every slow step will involve one, or perhaps two, atoms or molecules. This means that every slow step is either first or second order. There are no exceptions. We can determine the order with respect to any atom, ion, or molecule by seeing how changing their concentration changes the rate of the reaction. If, by changing their concentration the rate changes, then that atom, ion, or molecule is involved in the slow step of the reaction. But there are many reactions where various components are needed, but are not involved in the slow step of the reaction.

Consider the second order reaction that was presented earlier.



The OH⁻ attacks the CH_3Cl but it is impossible to add OH⁻ by itself. You must add NaOH. So what is the Na⁺ ion doing? Nothing, it is a spectator ion. So this reaction is zero order with respect to the Na⁺ ion. The Na⁺ ion is not involved in the slow step of the reaction, in fact, it is not involved at all, so it does not affect the rate of this reaction and is zero order (no ions of sodium are involved). Now consider the first order reaction presented earlier.



In this case, only $(CH_3)_3Cl$ is involved in the slow step of the reaction so the reaction is first order. In the second step of the reaction, the OH⁻ ion attacks the positive charge on the carbon that was made in the first step. Therefore, OH⁻ is a required ingredient for the reaction and it gets consumed, but the rate of the reaction does not depend on it. The rate of the reaction completely depends on how fast $(CH_3)_3Cl$ blows up and not on the amount of OH⁻ that is in solution. So, even though OH^- is required in this reaction, the rate does not depend on it so the reaction is zero order with respect to added OH^-. As noted earlier, since NaOH is actually being used in this reaction, and therefore Na^+ ions are also present, they are not involved in the slow step, so the Na^+ ions are also zero order. So it is possible to be zero order if you are needed but not involved in the slow step (OH^-) or not needed at all (spectator ions like Na^+).

Saturated Catalysts

There is one other way in which a component can be zero order and that is as a saturated catalyst. While catalysis is a very active area of research and the mode of action of catalysts are not well understood, we know that by adding a catalyst we can speed up the rate of a reaction. Generally, catalysts act like any other component in a reaction and their presence is usually first order, that is, the rate of reaction changes in proportion to the change in the amount of catalyst. But there is a condition, particular to catalysts that we need to investigate. What happens when a catalyst cannot make a reaction go any faster? Why would this happen?

Catalysts act by bringing molecules together in such a way that is beneficial for a reaction to occur. In addition, they can weaken or even break bonds that will allow new bonds to form. To do this, the catalyst is surrounded by the molecules that are going to react. If a catalyst is already completely surrounded with reactant molecules and working at full speed, adding more reactant molecules will not increase the speed of the reaction. In this special case, the reactant molecule appears to have no effect on the rate of the reaction. Under these conditions, the reactant appears to be zero order.

So, while there is no such thing as a zero order reaction, there can be components of a reaction that can appear to be zero order. This occurs under the following set of conditions,

1. Spectator ions must be present but do not take part in the reaction.
2. Required components that are not involved in the slow step.
3. A reaction that is limited by a saturated catalyst where the reaction cannot go faster.

Rate Laws

The rate of a reaction is usually written as follows,

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^x$$

Where k is the rate constant for this reaction, [A] is the concentration of species A, and x is the order with respect to species A. For zero order, first order, and second order processes we would write,

Zero order	rate = $k[A]^0$
First order	rate = $k[A]^1$
Second order	rate = $k[A]^2$

Fundamentally, we can see that the power indicates the number of atoms or molecules of species A involved in the slow step of a reaction. We can also see the affect that changing the concentration has on the rate of a reaction. If the concentration of A is doubled, the rate of a zero order reaction would not change ($2^0 = 1$, so doubling the concentration does not change the rate). If a reaction is first order then doubling the concentration of A will cause the rate to double ($2^1 = 2$ so doubling the concentration doubles the rate). And finally, if a reaction is second order with respect to A, doubling the concentration of A quadruples the rate ($2^2 = 4$ time faster rate).

You may be wondering, if a rate is the change in the concentration of A over a change in time, how can this be equal to a constant time the concentration of A? Specifically, how can a rate equal a single concentration of A and not the change in A? The answer is simple – we are looking at the instantaneous rate, that is, we are looking at the rate of change at a single point. This is called the law of initial rates. What this means is that we are going to measure the rate of the reaction over a very short period of time near the start of the experiment. By doing this, the concentration of A has not changed significantly so we can assume it to be constant over a short period of time. This has the effect of having measured the slope of the rate curve at a point along the reaction curve.

Using Rate Laws

To determine the order with respect to any given component of a reaction each component is independently varied and its effect on the rate is determined. Since these concentrations can be any value, they are usually doubled or tripled in order to make it easier to determine the rate law. A simple example is given below.

Problem 11.1

The following experimental data were obtained for the reaction at 250 K,

$$F_2 + 2\ ClO_2 \rightarrow 2\ FClO_2$$

Run	$[F_2]/M$	$[ClO_2]/M$	Rate/(M/s)
1	0.10	0.010	1.2×10^{-3}
2	0.10	0.040	4.8×10^{-3}
3	0.20	0.010	4.8×10^{-3}

Write a rate law consistent with this data.

What is the value and units of the rate constant?

Answer

Begin by writing a preliminary rate law based on the experimental data.

$$\text{Rate} = k\ [F_2]^x\ [ClO_2]^y$$

The values for x and y must be determined. Initially, we will do this by inspection but we will do this more formally later on. Taking Run 1 and 2 we can see that the $[F_2]$ does not change and therefore does not affect the rate of the reaction, but the $[ClO_2]$ changes by a factor of four. Quadrupling the concentration of ClO_2 causes the rate to quadruple therefore the reaction is first order with respect to ClO_2 ($4 \text{ x rate} = [4]^1$).

In similar fashion, if we look at the first and third set of data we can see that the $[ClO_2]$ remains unchanged but the $[F_2]$ doubles. This doubling causes the rate to quadruple, therefore the reaction is second order with respect to F_2 (4 x rate = $[2]^2$).

The rate law is,

$$\text{Rate} = k\,[F_2]^2\,[ClO_2]^1$$

To determine the value of the rate constant, k, you must put a set of data into this equation and solve for k. We will use the first set of data,

$$\text{Rate} = k\,[F_2]^2\,[ClO_2]^1$$
$$1.2\text{x}10^{-3}\,M/\text{s} = k\,[0.1\,M]^2\,[0.01\,M]^1$$
$$k = 12\,\frac{1}{M^2 s}$$

Sometimes it is easy to tell what happens to a rate when a concentration is doubled or quadrupled but sometimes it is not. In those cases a more formal method must be used to determine the order of each component in a rate law. The process can be illustrated using the problem given above. You begin by placing two experimental runs into a ratio.

$$\frac{\text{rate}_2}{\text{rate}_1} = \frac{k\,[F_2]_2^x\,[ClO_2]_2^y}{k\,[F_2]_1^x\,[ClO_2]_1^y}$$

Next, we choose a set of data where the concentration of all but one of the components remains constant. We can see that in Runs 1 and 2, the [F2] remains constant so we will use these data.

$$\frac{4.8\times10^{-3}\,M/s}{1.2\times10^{-3}\,M/s} = \frac{k\,[0.10\text{M } F_2]_1^x\,[0.04\text{M } ClO_2]_1^y}{k\,[0.10\text{M } F_2]_2^x\,[0.01\text{M } ClO_2]_2^y}$$

Since k and the concentration of F_2 are constant on the top and bottom of this equation, they will cancel leaving us with,

$$\frac{4.8\times10^{-3}\,M/s}{1.2\times10^{-3}\,M/s} = \frac{[0.04\text{M } ClO_2]_1^y}{[0.01\text{M } ClO_2]_2^y} \Rightarrow 4 = 4^y \quad \therefore \quad y = 1$$

In similar fashion we can solve for the order with respect to the F_2 by choosing to put Run 1 and 3 into a ratio,

$$\frac{4.8\times10^{-3}\ M/s}{1.2\times10^{-3}\ M/s}=\frac{k\,[0.20\mathrm{M\ F_2}]_1^{\mathrm{x}}\,[0.01\mathrm{M\ ClO_2}]_1^{\mathrm{y}}}{k\,[0.10\mathrm{M\ F_2}]_2^{\mathrm{x}}\,[0.01\mathrm{M\ ClO_2}]_2^{\mathrm{y}}}$$

Since k and the concentration of ClO_2 are now constant, they can be cancelled which leaves us with,

$$\frac{4.8\times10^{-3}\ M/s}{1.2\times10^{-3}\ M/s}=\frac{[0.20\mathrm{M\ F_2}]_3^{\mathrm{x}}}{[0.10\mathrm{M\ F_2}]_1^{\mathrm{x}}}\ \Rightarrow 4=2^{x}\quad\therefore\quad x=2$$

Based on this analysis of the data the rate would be,

$$\text{Rate} = k\,[F_2]^2\,[ClO_2]^1$$

This is the same answer we got by noting how the rates changed when the concentrations changed (working the problem "by inspection").

Thus far, determining the values of x and y have been pretty easy. Most students can determine these values just by looking at the problem but occasionally it will not be obvious what the power might be so you may have to solve for it. The process is not complex but it does require knowledge of how to work with logarithms. Suppose that, after placing the rates and concentrations into a ratio that we get the following result,

$$2.25 = 1.5^{x}$$

To solve for x we would take the $\log_{10}$ of both sides of this equation,

$$\log_{10}(2.25) = \log_{10}(1.5^{x})$$

We will use the following log identity, $\log(A^{x}) = x\log(A)$

$$\log_{10}(2.25) = \log_{10}(1.5^{x}) = x\log_{10}(1.5)$$

so,

$$x = \frac{\log_{10}(2.25)}{\log_{10}(1.5)} = 2$$

We will use this procedure on the next example.

Problem 11.2

Thiosulfate ($S_2O_3^{2-}$) reacts with triiodide (I_3^-) according to the following reaction at 25°C,

$$2\ S_2O_3^{2-} + I_3^- \leftrightarrow S_4O_6^{2-} + 3\ I^-$$

Experimentally the forward rate law can be determined from the following data,

Run	Rate/Msec^{-1}	$[S_2O_3^{2-}]/M$	$[I_3^-]/M$
1	$1.40\text{x}10^{-4}$	0.020	0.12
2	$3.15\text{x}10^{-4}$	0.030	0.12
3	$4.20\text{x}10^{-4}$	0.060	0.04

What is the forward rate law?

What is the value of the rate constant?

Answer

Begin by choosing a run where one of the ingredients remains constant. Runs 1 and 2 satisfy this condition. Place these runs into a ratio,

$$\frac{3.15\times10^{-4}\ M/s}{1.4\times10^{-4}\ M/s}=\frac{k\,[0.030\text{M}\ \text{S}_2\text{O}_3^{2-}]_2^{\text{x}}\ [0.12\text{M}\ I_3^-]_2^{\text{y}}}{k\,[0.020\text{M}\ \text{S}_2\text{O}_3^{2-}]_1^{\text{x}}\ [0.12\text{M}\ I_3^-]_1^{\text{y}}}$$

Since the $[I_3^-]$ and k remain constant in this equation they will cancel which leaves us with,

$$\frac{3.15\times10^{-4}\ M/s}{1.4\times10^{-4}\ M/s}=\frac{[0.030\text{M}\ \text{S}_2\text{O}_3^{2-}]_2^{\text{x}}}{[0.020\text{M}\ \text{S}_2\text{O}_3^{2-}]_1^{\text{x}}}\ \Rightarrow 2.25 = 1.5^x \quad \therefore \quad x = 2$$

It may be possible to solve for x by inspection but if this is not possible then we would use the following procedure,

$$\text{since } 2.25 = 1.5^x \ \text{ then x} = \frac{\log_{10}(2.25)}{\log_{10}(1.5)} = 2$$

Normally, we would now choose a different set of runs where our other ingredient remains constant but in this experiment there are no runs that do this. Instead, since we already know the order with respect to $S_2O_3^{2-}$, we can use this information to solve for our remaining ingredient, I_3^-. Choosing runs 1 and 3, and the known order with respect to $S_2O_3^{2-}$, we put them into a ratio,

$$\frac{4.2\times 10^{-4}\ \mathrm{M/s}}{1.4\times 10^{-4}\ \mathrm{M/s}} = \frac{k\,[0.060\mathrm{M}\ \mathrm{S_2O_3^{2-}}]_3^2\,[0.04\mathrm{M}\ \mathrm{I_3^-}]_3^y}{k\,[0.020\mathrm{M}\ \mathrm{S_2O_3^{2-}}]_1^2\,[0.12\mathrm{M}\ \mathrm{I_3^-}]_1^y}$$

Cancelling the rate constants, k, we can solve for a value of y.

$$\frac{4.2\times 10^{-4}\ M/s}{1.4\times 10^{-4}\ M/s} = \frac{[0.060\mathrm{M}\ \mathrm{S_2O_3^{2-}}]_3^2\,[0.04\mathrm{M}\ I_3^-]_3^y}{[0.020\mathrm{M}\ \mathrm{S_2O_3^{2-}}]_1^2\,[0.12\mathrm{M}\ I_3^-]_1^y} \Rightarrow 3 = 3^2\cdot\left[\frac{1}{3}\right]^y \quad \therefore \quad y = 1$$

$$3 = 3^2\cdot\left[\frac{1}{3}\right]^y \ \Rightarrow\ \frac{3}{9} = \frac{1}{3} = \left[\frac{1}{3}\right]^y \ \therefore\ \ y = 1$$

So, the rate law derived from this data is,

rate = $k[S_2O_3^{2-}]^2\,[I_3^-]^1$

To determine the value of the rate constant, k, you must put a set of data into this equation and solve for k. We will use the first set of data,

rate = $k[S_2O_3^{2-}]^2\,[I_3^-]^1$

$1.4\mathrm{x}10^{-4}\ M/\mathrm{s} = k\ [0.02\ M]^2\ [0.12\ M]^1$

$$k = 2.917\ \frac{1}{M^2 s}$$

In all reactions, the overall order of the reaction is the sum of the order of the individual ingredients. In both cases above, the sum of the individual orders leads to reactions that are overall third order. Earlier in this chapter it was argued that third order reactions do not occur, so does that mean that the reactions in the examples given above do not occur? No, it does not. Both of these reactions occur, but how? The statement regarding the order of a reaction says that third order reactions cannot occur in a single step. Third order reactions can occur as long as it takes more than one step. So how do multistep reactions occur? That is the topic of the next section on reaction mechanisms.

The Mechanism of a Reaction

The purpose of obtaining data on the rate of a reaction and the order with respect to components within the reaction is not really to determine how fast the reaction goes. The purpose is to provide insight into the way the reaction occurs, that is, the step by step way in which the molecules react. These steps are known as the mechanism of the reaction and it provides insight as to how and why a reaction occurs as well as any constraints that might affect the amount of product made.

If a reaction is third order or greater, that reaction must occur in more than one step. To understand why we must begin with a discussion of the slow step of a reaction. Every reaction has precisely one slow step. This slow step acts like a gatekeeper or a toll booth on a bridge. No matter how fast your car can go, it must slow down at the toll booth. How fast a car is able to go through a toll booth determine how fast all the car in line are able to move through the toll booth. So while only one car is actually in the toll booth, multiple cars behind it are slow as a consequence.

Thus far, we have only discussed reactions that move in one direction, that is, reactants become products. These kind of reactions are very familiar to us. We have completed and balanced many reactions like the one given below.

$$F_2 + 2\ ClO_2 \rightarrow 2\ FClO_2$$

Notice that the arrow goes in just one direction, from left to right which indicates that the reaction goes in just one way, from reactants to products. But many, if not most reactions go in both directions and it is best to use a double indicate that the products can combine and remake the starting product.

$$F_2 + 2\ ClO_2 \rightleftarrows 2\ FClO_2$$

This now indicates that there is a reaction going to the right (the forward reaction) and another reaction going to the left (the reverse reaction). Each of these reactions has a rate. If we simplify this reaction by writing just reactants and products we would have,

$$\text{Reactant} \rightleftarrows \text{Product}$$

We can see that as the reactant become product, the product is also becoming reactant and each of them is doing so at its own particular rate that can be written as,

$$\mathrm{Rate}_{\mathrm{forward}} = k_f\,[\mathrm{Reactant}]$$

$$\mathrm{Rate}_{\mathrm{reverse}} = k_r[\mathrm{Product}]$$

At equilibrium, these two rates will become equal to each other. At that point we would have,

$$\mathrm{Rate}_{\mathrm{Forward}} = \mathrm{Rate}_{\mathrm{Reverse}}$$

$$k_F\,[\mathrm{Reactant}] = k_R[\mathrm{Product}]$$

If we rearrange this equation we would get,

$$\frac{k_F}{k_R} = \frac{[\mathrm{Product}]}{[\mathrm{Reactant}]} = K_{eq} = \text{Equilibrium constant}$$

The ratio of the two rate constants, k_F and k_R, is just another constant that we call the equilibrium constant K_{eq}. Equilibriums are a type of balance, if a disturbance is made to one side of the reaction then a compensating reaction must occur to maintain the balance. Therefore, if a small amount of product is removed from an equilibrium, the reactants must compensate by making more. This slow removal of product forces an equilibrium to compensate by having the reactant make more product which causes the reaction to move slowly to the right. Since the slow step of a reaction slowly uses up a reactant, any equilibrium directly preceding this slow step will be forced to move at the same rate as the slow step. Consider the following reaction,

$$2A + B \rightarrow C + D$$

And suppose that the rate law is,

$$\mathrm{Rate} = k\,[A]^2\,[B]$$

We begin by noticing that this rate law is overall third order so the reaction cannot occur in just one step. Therefore, this reaction must occur in at least two steps, possibly more. All reactions have only one slow step. Any additional steps added to a rate law must occur due to equilibriums that directly precede the slow step. For example, we could propose the following mechanism for the reaction above,

$$\begin{array}{l} 2\,A \rightleftarrows E \text{ (equilibrium)} \\ \underline{B + E \rightarrow C + D \text{ (slow)}} \\ 2A + B \rightarrow C + D \ \text{ (overall)} \end{array}$$

We note that, when added together, these two reactions give us our overall reaction and no step is greater than second order (a requirement for all reactions). We also note that, because B reacts with E slowly in the second step, E is slowly being removed from the reaction. As E is slowly removed, the equilibrium slowly shifts to the right to maintain the ratio of products to reactants (the equilibrium). This is how the equilibrium that precedes the slow step becomes a part of the slow step of the reaction.

The analysis of the mechanism involves, as it always does, with the slow step. We begin by writing the rate law based on the slow step of the reaction. Since the slow step involves B and E, we would write the rate law as,

$$\text{Rate} = k[B][E]$$

You will notice that the ingredient [E] is not present as a reactant or product in the overall reaction. It is made in the equilibrium step and then consumed in the slow step. We call ingredients that appear and then disappear during the course of a reaction, reaction **intermediates**. Intermediates are not ingredients that have been added to the reaction, they simply appear and then disappear, so they cannot be in a rate law. A way must be found to remove them from the rate law. Fortunately, this is not a single step mechanism. There is an equilibrium that precedes this slow step that can be used to remove [E] from the rate law. We begin by writing down the equilibrium expression that precedes the slow step,

$$K_{eq} = \frac{[\text{Product}]}{[\text{Reactant}]} = \frac{[E]}{[A]^2}$$

We now solve this equilibrium for [E],

$$K_{eq}\,[A]^2 = [E]$$

And then substitute this result back into our rate law,

$$\text{Rate} = k[B][E] = k[B]\,K_{eq}\,[A]^2$$

If we rearrange the equation, we get,

$$\text{Rate} = k\,K_{eq}\,[A]^2\,[B]$$

Often, the rate constant and the equilibrium constant are combined into a single constant denoted by k', so that,

$$\text{Rate} = k'\,[A]^2\,[B]$$

This rate law matches the experimentally determined rate law given above. That does not mean that this rate law is correct. Since we are proposing the existence of an intermediate, E, we would need evidence of its existence before we could say that this mechanism is correct. The best that we can say is that this mechanism matches our experimentally determined rate law and may possibly be correct.

The important point here is that we were able to propose a series of reactions where no step was greater than second order that produced a rate law that is overall third order. So, do reactions occur that are overall third order? Yes, but they must occur in more than one step. In fact, we should note that this reaction required two step, one step less than the order of the reaction. For reactions greater than second order, the minimum number of steps required is one less than the order. So it would take at least three steps for a 4th order reaction to occur.

Let us turn our attention to a real chemical reaction. Mechanisms always begin with data tables. The following set of experimental data were obtained for the reaction;

$$2\,NO + 2\,H_2 \rightarrow N_2 + 2\,H_2O$$

Initial Rate/$10^{-5}$$M$/s	[NO]/10^{-2} M	[H_2]/10^{-2} M
0.60	0.50	0.20
2.40	1.00	0.20
0.30	0.25	0.40

We begin by analyzing the date in the table and determine the rate law. Using the methods outlined earlier in this chapter the rate law is determined to be,

$$\text{Rate} = k[NO]^2\,[H_2]$$

The first thing that a student must notice is that this reaction is overall third order. Since third order reactions cannot occur in a single step any mechanism that proposes that a third order step must have occurred is automatically wrong.

We now propose a number of ways in which this reaction may occur. Consider the following three mechanisms,

i) $2\,NO + H_2 \rightarrow N_2O + H_2O$ (slow)

ii) $2\,NO \leftrightarrow N_2O_2$ (eq)
$N_2O_2 + H_2 \rightarrow N_2O + H_2O$ (slow)

iii) $NO + H_2 \leftrightarrow H_2O + N$ (equil)
$N + NO \rightarrow N_2O$ (slow)

When analyzing a mechanism, you always begin by writing the rate law based on the ingredients involved in the slow step of reaction. For the first mechanism, the slow step involves 2 NO and an H_2, so we would write the rate law as,

i) $\text{Rate} = k[NO]^2\,[H_2]$

we then look to see if this rate law is the same as our experimentally determined rate law which was rate = $k[NO]^2\,[H_2]$. The answer is yes, it matches but that does not mean that this mechanism is correct. This reaction has just one step that involves three species, two NO's and an H_2. That's a total of three molecules which makes this a one step, third order reaction. That's impossible, so even though the mechanism gives you the correct rate law, this mechanism is not correct.

Turning our attention to reaction ii) we start by writing the rate base on the ingredients involved with the slow step,

ii) $\text{Rate} = k[N_2O_2][H_2]$

This rate law is not the same as the experimentally determined rate law so we might be tempted to say that it is not correct, but we must remember that equilibriums that occur just before a slow step are also slow and must be incorporated into the overall rate law. How do we do this? One clue as to how to proceed is to remember that a rate law can only contain ingredients that are found in the overall reaction. This rate law contains $[N_2O_2]$ and this must be removed in some way. To do this, we use the equilibrium that comes before the slow step.

$$K_{eq} = \frac{[N_2O_2]}{[NO]^2}$$

Solving for $[N_2O_2]$,

$$K_{eq}[NO]^2 = [N_2O_2]$$

Substituting this result into our rate law we get,

$$\text{Rate} = k\ K_{eq}\ [NO]^2\ [H_2]$$

The rate constant and equilibrium constants combine to form a new constant designated as k',

$$\text{Rate} = k'[NO]^2\ [H_2]$$

Comparison to our experimentally determined rate law shows that the proposed mechanism has correctly reproduced our rate law. This means that this mechanism may be correct but more evidence would be required to find evidence that $[N_2O_2]$ was involved in the reaction.

Let's turn our attention to mechanism iii and determine if it is a possible mechanism for this reaction. As before, we begin by writing the rate law based on the slow step,

$$\text{iii)}\quad \text{Rate} = k[NO]\ [N]$$

We notice that there is one ingredient, [N], that is not found in the overall reaction so it cannot be in the mechanism. Fortunately, there is an equilibrium preceding this slow step that allows us to replace the [N] with other ingredients. Following the same procedure as before, we use the preceding equilibrium to solve for [N].

$$K_{eq} = \frac{[H_2O]\ [N]}{[NO]\ [\ H_2]}$$

Solving for [N],

$$K_{eq}\frac{[NO]\ [\ H_2]}{[H_2O]} = [N]$$

Substituting this result into our rate law we get,

$$\text{iii)}\ \text{Rate} = \text{k K}_{\text{eq}}\ [\text{NO}]\frac{[\text{NO}]\ [\text{H}_2]}{[\text{H}_2\text{O}]}$$

Gathering terms and combining the rate law and the equilibrium constant we get,

$$\text{iii)}\ \text{Rate} = \text{k}'\ \frac{[\text{NO}]^2\ [\text{H}_2]}{[\text{H}_2\text{O}]}$$

This rate law does not match the experimentally determined rate law since it includes water in the denominator. This rate law is not correct so the mechanism cannot be correct. The only possible correct mechanism was ii) and more experimental evidence would be required to confirm this as the mechanism for this reaction.

Integrated Rate Laws

Rate law data is used to determine how fast a reaction will occur under any given set of conditions and is most often use to determine the mechanism of a reaction. While useful, sometimes we want to know information that mechanisms and rate laws are incapable of revealing. For example, we may want to know how much of one ingredient may be left after a given period of time or how long it would take for that same ingredient to drop to 10% of its initial value. Rate laws and rate law data cannot be used to answer these questions. Fortunately, we can use the integrated rate laws instead.

To derive the integrated rate laws requires calculus. The math will be presented here but you will not be required to understand how these equations are derived but if you have an understanding of calculus, the following discussion can be helpful.

First Order Integrated Rate Law

We begin with our original discussion of rate,

$$\text{Rate} = -\ \frac{\Delta[\text{A}]}{\Delta\text{t}} = \text{k}[\text{A}]^{\text{x}}$$

As discussed previous the $\Delta[A]$ is read as "the change in the concentration of A" and the Δt should be read as "the change in the time." In calculus we discuss very small changes in both concentration and time and use a different symbol for these changes,

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^x$$

For a first order reaction, $x = 1$ so we would have,

$$-\frac{d[A]}{dt} = k[A]^1 = k[A]$$

Rearranging this equation we get,

$$-\frac{d[A]}{[A]} = kdt$$

Integrating this equation we get,

$$-\int_{A_i}^{A_f} \frac{d[A]}{[A]} = k\int_{t_i}^{t_f} dt$$

Students of calculus will recognize the first integral as giving the natural log function (ln(x)) and the second equation as just time. The result being,

$$-[\ln(A_f) - \ln(A_i)] = k\,(t_f - t_i)$$

Using the properties of logs, the natural log terms can be combined, and noting that the final time minus the initial time is just the change in time (Δt), we get,

$$-\ln\frac{A_f}{A_i} = k\,\Delta t$$

Using the properties of logs again, we can incorporate the negative sign into the natural log to get our final integrated rate law for first order reactions,

$$\ln\frac{A_i}{A_f} = k\,\Delta t$$

This new equation allows us to do calculations that the rate law did not allow us to do. Given an initial amount of an ingredient (A_i), this equation allows us to calculate how much will be left (A_f) after any given length of time (Δt). The only thing we need to know is the rate constant k.

Now that we have our integrated rate law it is useful to define a new term, the half-life, which is given the symbol $t_{½}$. The half-life is defined as the amount of time needed for an initial concentration to drop in half. By this definition, we are looking for the amount of time required for $A_f = ½\, A_i$. Substituting these values into our integrated rate law and redefining Δt as $t_{½}$ we get,

$$\ln\left(\frac{A_i}{\frac{1}{2}A_i}\right) = \ln(2) = 0.693 = k\ t_{1/2} \Rightarrow \quad t_{1/2} = \frac{0.693}{k}$$

We have now derived three equations to use with first order kinetics. They are,

$\text{Rate} = k\,[A]$	For use with rate laws tables to determine a rate law
$\ln\frac{A_i}{A_f} = k\,\Delta t$	Used to determine how much is left over time.
$t_{1/2} = \frac{0.693}{k}$	Used with the integrated rate law to determine the $t_{½}$

We now turn our attention to second order kinetics and derive a similar set of equations.

Integrated Second Order Rate Law

A second order rate law can be written in one of two ways; either two of the same reactant come together or two different reactants come together. These two conditions are shown below.

1) $\text{rate} = k[A]^2$

2) $\text{rate} = k[A]\,[B]$

We will begin by deriving the integrate rate for our first condition; when the two reactants are the same.

Integrated Rate Law for $k[A]^2$

We begin with the definition of rate as presented earlier in the chapter,

$$\text{Rate} = -\frac{\Delta[A]}{\Delta t} = k[A]^x$$

As discussed previously the Δ[A] is read as "the change in the concentration of A" and the Δt should be read as "the change in the time." In calculus we discuss very small changes in both concentration and time and use a different symbol for these changes,

$$\text{Rate} = -\frac{d[A]}{dt} = k[A]^x$$

For a second order reaction, x = 2 so we would have,

$$-\frac{d[A]}{dt} = k[A]^2$$

Rearranging this equation we get,

$$-\frac{d[A]}{[A]^2} = k\,dt$$

Integrating this equation we get,

$$-\int_{A_i}^{A_f} \frac{d[A]}{[A]^2} = k\int_{t_i}^{t_f} dt$$

Students of calculus will recognize the first integral as giving - 1/[A} and the second equation as just time. The result being,

$$-\left[\left(-\frac{1}{A_f}\right) - \left(-\frac{1}{A_i}\right)\right] = k\,(t_f - t_i)$$

Rearranging terms and noting that the final time minus the initial time is just the change in time (Δt), we get our integrated rate law,

$$\frac{1}{A_f} - \frac{1}{A_i} = k\,\Delta t$$

As before, we define a half-life, $t_{1/2}$, as being the time it takes for half of our compound to go away. Under these conditions we would have $A_f = \frac{1}{2} A_i$. Substituting, we would get,

$$\frac{1}{\frac{1}{2}A_i} - \frac{1}{A_i} = k\, t_{1/2}$$

$$\frac{2}{A_i} - \frac{1}{A_i} = k\, t_{1/2}$$

$$\frac{1}{A_i} = k\, t_{1/2} \quad \text{or} \quad t_{1/2} = \frac{1}{k\, A_i}$$

We have now derived three equations to use with second order kinetics. It should be noted that the 2k term that shows up in these equations are most often combined into a single constant that could be called k′ but is most often conflated into the rate constant k.

They are,

$\text{Rate} = k\,[A]^2$	For use with rate laws tables to determine a rate law
$\frac{1}{A_f} - \frac{1}{A_i} = k\,\Delta t$	Used to determine how much is left over time.
$t_{1/2} = \frac{1}{k\,A_i}$	Used with the integrated rate law to determine the $t_{1/2}$

Integrated Rate Law for k[A] [B]

Now, let's turn our attention to the second of our two forms of the second order rate law,

$$\text{rate} = k[A]\,[B]$$

In this case, [A] and [B] need not be equal in concentration. If they are, then we have reduced this problem down to the first form of second order rate laws which has already been solved. When these concentrations are not equal, the mathematics becomes messier but still doable.

To begin, we note that for every A that reacts must also B react. If A_i and B_i are the initial amounts of A and B, and the amount that reacts is x, then the amount of A and B left after any given amount of time is,

$$A = A_i - x \quad \text{and} \quad B = B_i - x$$

Since x is the amount that has reacted, our rate law becomes,

$$-\frac{dx}{dt} = k[A_i - x][B_i - x]$$

Rearranging, we get,

$$\frac{dx}{[A_i - x][B_i - x]} = -k\,dt$$

Integrating this, we get,

$$\int_0^x \frac{dx}{[A_i - x][B_i - x]} = -k \int_0^t dt$$

$$\frac{1}{[B_i] - [A_i]} \ln\frac{[A_i][B]}{[B_i][A]} = k\,\Delta t$$

Or,

$$\ln\frac{[A_i][B]}{[B_i][A]} = ([B_i] - [A_i])\,k\,\Delta t$$

This equation does not have a simple half-life expression. Since $[A] \neq [B]$ the one with the lower concentration will reach its half-life concentration before the other and the half-life will depend on the concentration of the more concentrated ingredient. Overall then,

Rate = k [A][B]	Used with rate law tables to determine a rate law
$\ln\frac{[A_i][B]}{[B_i][A]} = \left([B_i] - [A_i]\right)\,k\,\Delta t$	Used to determine how much is left over time.

Applications of the Integrated Rate Laws

Classically, the integrated rate laws are used to determine how much of a substance is left after a given period of time. Since radioactivity is a first order process, the integrated rate laws for first order kinetics are used to determine how long it will take for an amount of radioactive compound to decay. In other words, we will use these equations to radiometrically date ancient objects.

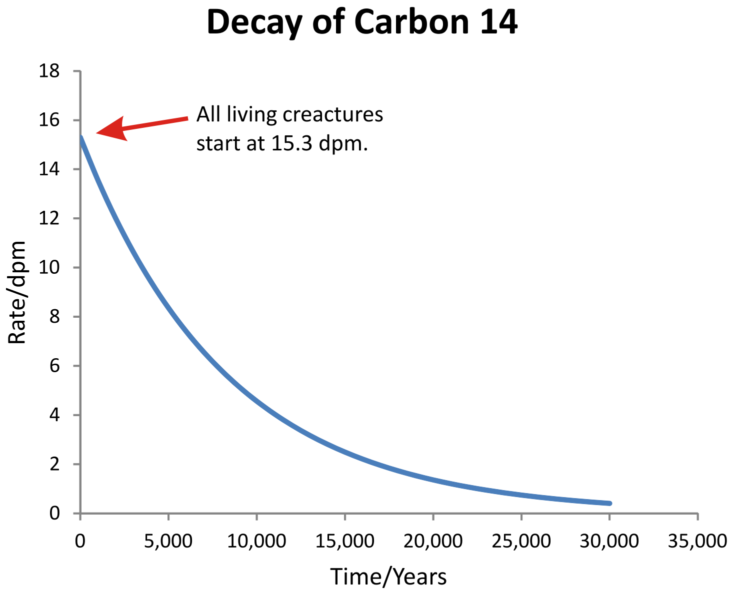
Carbon Dating

Nearly 80% of earth's atmosphere is made of nitrogen gas (N_2). High energy electrons known as cosmic rays coming from the sun constantly bombard our atmosphere and some of these cosmic rays hit a nitrogen atom. The electron combines with a proton to form a neutron which changes the element from nitrogen to carbon by the following reaction;

$$^{14}_{7}N + e^{-} \rightarrow ^{14}_{6}C$$

The new carbon 14 atom is radioactive and it combines with oxygen to form radioactive $^{14}CO_2$. Plants convert CO_2 into the molecules necessary for life. Animals eat the plants and we eat both the plants and the animals so we get this radioactive carbon in us. With some exceptions, all living creatures contain radioactive carbon and as long as they are living and continue to consume other plants and animals, the amount of radioactive carbon in them remains constant and accounts for a decay rate of 15.3 disintegrations per minute per gram of carbon (or just 15.3 dpm) in all of us.

Once a living creature dies, and with no more carbon being taken in, the existing carbon 14 becomes depleted as it decays. According to first order kinetics, the decay occurs logarithmically. The decay of a sample containing carbon 14 can be seen below.



Dating something made from carbon requires knowledge of the initial amount of carbon 14 present. To calibrate this dating method tree rings of ancient trees are analyzed for carbon 14 content and the result compared to the age based on counting the tree rings. Using this method it has been found that, while the carbon 14 content in our atmosphere has fluctuated, it has remained essentially constant at 15.3 disintegrations per minute for at least the past 30,000 years. Using this dating method, scraps of ancient papyrus, old antlers and bones, and scraps of wood from coffins, houses, and wooden bows and arrows have been dated. Ancient artifacts like the Dead Sea Scrolls and the Shroud of Turin have been dated using these techniques.

Problem 11.3

An archaeologist measured the amount of radioactivity of a piece of cloth used to wrap an Egyptian mummy. The cloth was found to have a decay rate of 9.1 dpm. If the decay rate is 15.3 dpm in living tissue, how old is the mummy? $t_{½} = 5730$ years.

Answer

To answer this question we will use the integrated rate law for first order kinetics.

$$\ln\frac{A_i}{A_f} = k\,\Delta t$$

We already know the initial and final concentrations of carbon 14 (15.3 dpm and 9.1 dpm respectively) but to use this equation we will also need to know the rate constant, k. Fortunately, we also know the half-life and we know the relationship between the half-like and the rate constant,

$$t_{1/2} = \frac{0.693}{k} \quad \text{or} \quad k = \frac{0.693}{t_{1/2}}$$

Substituting this result into our integrated rate law we get,

$$\ln\frac{A_i}{A_f} = \frac{0.693}{t_{1/2}}\,\Delta t$$

We can solve this equation for Δt,

$$\ln\frac{15.3\text{ dpm}}{9.1\text{ dpm}} = \frac{0.693}{5730\text{ yrs}}\ \Delta t$$

$$\Delta t = 4296\text{ yrs old}$$

When an object is more than about 70,000 years old, carbon 14 can no longer be used to date the object. To date objects like rocks and dinosaur bones, other, much longer lived radioactive substances must be used. A table of these isotopes is given below.

RADIOACTIVE HALF-LIVES		
Parent Nuclide	Daughter Nuclide	Half-Life
^{238}U	^{206}Pb	$4.47\text{x}10^{9}$ years
^{235}U	^{207}Pb	$7.10\text{x}10^{8}$ years
^{87}Rb	^{87}Sr	$4.9\text{x}10^{10}$ years
^{40}K	^{40}Ar	$1.3\text{x}10^{9}$ years

Dating Rocks and Fossils

To date an object that is millions or even billions of years old one must use radioactive elements whose half-lives are on the same scale as the object being dated. A few of the common isotopes used for dating rocks and fossils is given above. Age dating a rock differs rather significantly from carbon dating a bone or a piece of wood. In the case of bone or wood, the initial amount of carbon 14 is known so all that needs to be done is to figure out how much is left and the age of the object can be calculated. Unfortunately, we don't know how much Uranium, Rubidium, or Potassium might be in a rock or fossil so we can't just measure how much is left since we don't know how much there was to start. But, there is a way to find out.

Long lived radionuclides like ^{238}U decay to form stable products like ^{206}Pb. The ^{238}U is called the parent nuclide and the decay product, ^{206}Pb, is called the daughter nuclide. Overall, when ^{238}U decays, it produces ^{206}Pb and a couple of other products, alpha particles (α) which are helium nuclei ($^{4}_{2}$He) and beta particles (β-) which are electrons ejected from the nucleus of the atom.

$$^{238}U \rightarrow {}^{206}Pb + 8\,\alpha + 6\,\beta^-$$

Since ^{238}U decays into ^{206}Pb, each of the ^{206}Pb atoms present in the sample was once a ^{238}U, so the sum of the number of the ^{238}U and ^{206}Pb atoms present in the sample must be the initial amount of ^{238}U present when the rock was formed. The integrated first order rate law would be,

$$\ln\left[\frac{A_i}{A_f}\right] = \ln\left[\frac{^{238}U_i}{^{238}U_f}\right] = \ln\left[\frac{^{238}U + {}^{206}Pb}{^{238}U}\right] = \frac{0.693}{t_{1/2}}\,\Delta t$$

This equation works for Uranium/Lead dating but can be simplified for any long lived isotope where the parent and daughter products are used for age dating,

$$\ln\left[\frac{\text{Parent} + \text{Daughter}}{\text{Parent}}\right] = \frac{0.693}{t_{1/2}}\,\Delta t$$

Another example of a process used to date very old rocks is K/Ar dating. Potassium 40 decays to form an inert gas, Argon 40. Potassium 40 is found in nearly all rocks and the trick here is to measure the amount of gaseous argon 40 left in a sample due to radioactive decay. The procedure is actually quite simple. The rock is melted and the argon gas is allowed to escape. This argon is then captured and the amount is measured. The potassium 40 in the rock is measured and the age is determined. The problem with the potassium-argon dating method is that it relies on two tenuous assumptions. The first is that the rock had no daughter product present (^{40}Ar) when it was initially deposited and that no argon has infiltrated the rock from the atmosphere (Argon is the fourth most abundant gas in our atmosphere).

Despite these challenges, K/Ar dating is a common technique used to date igneous rocks. Igneous rocks are chosen because argon is not soluble in molten rock and escapes from the magma when the rock is deposited. As long as there is nothing to inhibit the expulsion of gaseous Argon from the molten rock, K/Ar dating works very well, but it is possible to get false dates for igneous rocks deposited far underground or even underwater. If the argon is not allowed to escape, the rock will appear to be much too old. Such was the case in Hawaii where a large amount of magma flowed into the ocean. Depending on the depth of the sample, the age of the rock appeared to change. Only rock near the surface of the water could be used to determine a reliable date for the rock and the lava flow.

Problem 11.4

A piece of zirconium was dated using $^{238}U/^{206}Pb$ dating method. It was found that this rock contained $3.2x10^{-3}$ grams of uranium and $2.2x10^{-5}$ grams of lead. If the half-life of uranium is $4.47x10^{9}$ years how old is the rock?

To answer this question we will use the first order integrated rate law of the form,

$$\ln\left[\frac{Parent + Daughter}{Parent}\right] = \frac{0.693}{t_{1/2}}\,\Delta t$$

In this case, the parent is 238U and the daughter is 206Pb. We begin by calculating the moles of each of these,

$$\frac{3.2\times10^{-3}\text{ g U}}{238\text{ g/mol U}} = 1.3445\times10^{-5}\text{ mol }^{238}\text{U}$$

And,

$$\frac{2.2\times10^{-5}\text{ g Pb}}{206\text{ g/mol Pb}} = 1.0680\times10^{-7}\text{ mol }^{206}\text{Pb}$$

$$\ln\left[\frac{\text{Parent+Daughter}}{\text{Parent}}\right] = \ln\left[\frac{1.3445\times10^{-5}\text{ mol }^{238}\text{U} + 1.0680\times10^{-7}\text{ mol }^{206}\text{Pb}}{1.3445\times10^{-5}\text{ mol }^{238}\text{U}}\right] = \frac{0.693}{4.47\text{x}10^{9}\text{yrs}}\,\Delta t$$

$$\Delta t = 5.10\text{x}10^{7}\text{ yrs old}$$

Applications of Second Order Integrated Rate Laws

A second order rate law implies that there are two reactants coming together to form a product. We have seen plenty examples of these kinds of reactions, neutralizations and double replacement reactions chief among them. Even so, most chemistry texts tend to avoid second order integrated rate laws so they are rarely seen by students. The main reason for this is that one form of the rate law requires both ingredients have the same concentration and for most reactions this is not reasonable, and the other form is complicated and generally avoided.

Any system where two different compounds come together like $H^+ + OH^- \rightarrow H_2O$, second order kinetics can be used. Consider the following example.

Problem 11.5

The reaction between H^+ and OH^- is the world's fastest aqueous reaction. The rate constant is $1.3x10^{11}$ $M^{-1}s^{-1}$. If each of the ions has a concentration of 0.50 M, how long will it take for their concentrations to decrease to 0.01 M?

Use the integrated second order rate law equation,

$$\frac{1}{A_f} - \frac{1}{A_i} = k\ \Delta\mathrm{t}$$

Therefore,

$$\frac{1}{0.01\ M} - \frac{1}{0.50\ M} = 1.3\mathrm{x}10^{11}\ \mathrm{M}^{-1}\mathrm{s}^{-1}\ \Delta\mathrm{t}$$

$$\Delta t = 6.15\times10^{-10}\ \text{sec}$$

Now consider the same second order reaction where the concentration of H^+ does not equal the concentration of OH^-.

Problem 11.6

How long will it take for the OH^- concentration to decrease to 0.01 M when the initial concentration of H^+ = 0.20 M and the OH^- = 0.05 M? The rate constant is $1.3x10^{11}$ $M^{-1}s^{-1}$ (note: the rate constant = 2k)

This is, essentially, a limiting reactant problem. We have the following conditions,

Ion	Initial Concentration	Final Concentration
H+	0.20 M	0.20 M – 0.040 M = 0.16 M
OH-	0.050 M	0.50 M – 0.040 M = 0.010 M

For the concentration of OH^- to drop to 0.01 M, 0.04 M must be consumed. Since this is a second order reaction, both H^+ and OH^- must decrease by 0.04 M. Putting these values into our integrated rate law we have,

$$\ln\frac{[A_i][B]}{[B_i][A]} = ([B_i] - [A_i])\ 2k\ \Delta t$$

$$\frac{\ln\frac{[A_i][B]}{[B_i][A]}}{2k([B_i] - [A_i])} = \Delta t$$

$$\frac{\ln\frac{[0.20\ M\ H^+][0.010\ M\ OH^-]}{[0.050\ M\ OH^-\ ][0.16\ MH^+]}}{1.3x10^{-11}([0.050\ M\ OH^-] - [0.20\ M\ H^+])} = \Delta t$$

$$\Delta t = 7.11x10^{-11}\ sec$$

Note: the assignment of A and B to a particular ion makes no difference to this equation. You will get the same answer if you had assigned A = OH^- and B = H^+.

The Effect of Temperature on a Rate Law

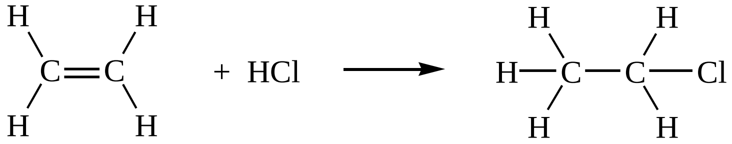
Most people know that one way of speeding up a reaction is by heating it, but what exactly does the heat do to cause the reaction to speed up? On a molecular level, heat provides the energy needed to break bonds and allow new bonds to form. It also increases the rate at which molecules move so molecules run into each other more often, but, not every collision produces a reaction. The molecules must strike one another in just the right orientation and with enough force to allow a reaction to occur. Therefore, there are three factors that influence the rate of a reaction, the energy of the collision, the frequency of collision and the orientation of the molecules when they collide. Each of these factors influence the value of the rate constant, k. We could therefore write,

Rate constant = k = frequency factory × orientation factor × energy factor

Mathematically, we would write,

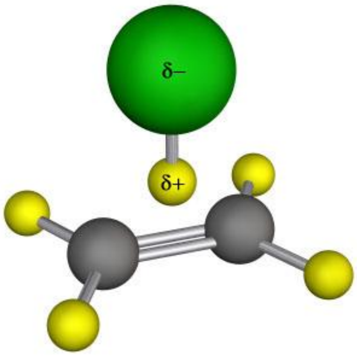
$$k = Z \cdot \rho \cdot e^{-E_a/_{RT}}$$

Where Z is the frequency factor, ϱ is orientation factor, and $e^{-Ea/_{RT}}$, is the energy factor. The more complicated the structure of the reactant, the more likely that the value of the rate constant will depend on the orientation of the collision. For example, a well-known reaction to all students of organic chemistry is the reaction between HCl and ethene to make chloroethane,



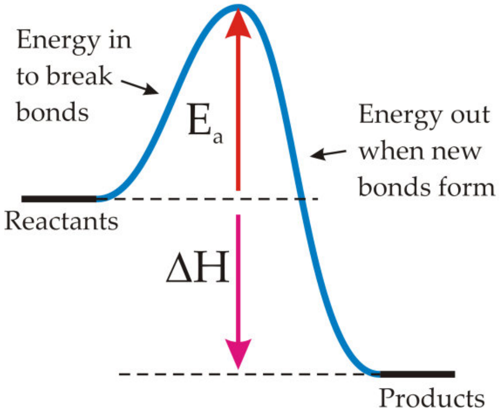
Ethene Chloroethane

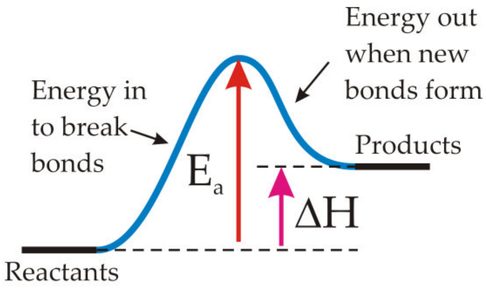
Experiments have shown that the reaction only takes place when the HCl molecule approaches the alkene with its hydrogen-end, and in a direction that is approximately perpendicular to the double bond, as shown below.



The reason for this is that the chlorine is highly electronegative and it pulls electrons away from the hydrogen which makes it slightly positively charged. This positively charged hydrogen is attracted to the electrons in the double bond and reacts with it making chloroethane. If the HCl had attacked the double bond using the chlorine, then the negative charge on the chlorine would be repulsed by the electrons in the double bond and no reaction would have occurred.

We now turn our attention to the last term, the energy factor, $e^{-Ea/RT}$. This term is temperature dependent and it determines the number of molecules with sufficient energy to allow a reaction to occur. Molecules at higher temperature have more energy so that, when they collide, there is a higher probability of a reaction occurring. In any reaction, in order for a reaction to occur, some bonds must break and new bonds must form. This term determines whether there is sufficient energy to break the bonds needed for new bonds to form. This also means that in every reaction we must first put energy into these molecules to break existing bonds before getting any energy out by forming new bonds. The amount of energy put into a reaction to cause the bonds to break is call the activation energy and is given the symbol, E_a.





A typical activation energy is about 60,000 kJ/mol. At room temperature the fraction of molecules having sufficient energy to react is very small, just one chance in 33 billion collisions. Fortunately, with Avogadro's number of molecules present in the typical reaction vessel, there are a very large number of collisions taking place so reactions still occur very fast. As the system is heated two things happen, these molecules move faster and have more energy per collision. Taken together, heating a reaction causes a reaction to speed up.

The frequency and orientation terms are usually multiplied together (Z × ρ) and given the symbol, A, called the pre-exponential frequency factor so that our equation now looks like,

$$k = Ae^{-E_a/RT}$$

This equation is most often used to determine the activation energy of a reaction, but this is not the most convenient way of using this equation. Usually, another form of this equation is used to determine the E_a of a reaction. We begin by taking the natural log of both sides of this equation,

$$\ln(k) = \frac{-E_a}{RT} + \ln(A)$$

Or

$$\ln(k) = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln(A)$$

This new equation is already more convenient since it is in the form,

$$y = mx + b$$

Where,

$$y = \ln(k)$$
$$m = -\frac{E_a}{R}$$
$$x = \frac{1}{T}$$
$$b = \ln(A)$$

A plot of the ln(k) versus 1/T will produce a straight line whose slope is $-E_a/R$ from which the activation energy can be determined.

Problem 11.7

The compound, trans-dichloro-bis-(ethylenediamine)cobalt(III) chloride, is green but when heated in the presence of sulfuric acid it slowly turns red.

$$\underset{\text{(dark green)}}{\text{trans-}[\text{Co(en)}_2\text{Cl}_2]^+} + H_2O \rightarrow \underset{\text{(burgundy to red violet)}}{\text{cis/trans-}[\text{Co(en)}_2(\text{H}_2\text{O})\text{Cl}]^+} + Cl^-$$

At the half way point in this conversion the solution is half green and half red and the combination of colors is best described as a gun-metal grey. When the solution is grey, half of the green compound has been converted to red so the time that it takes for this conversion is the half-life for this compound. If these solutions are heated, it takes less time for this conversion to turn grey. These data of time and temperature can be used to determine the activation energy of this reaction.

Regardless of the order of the reaction, from the first and second order half-life expressions, as long as the concentration remains constant, $t_{½}$ is inversely proportional to the rate constant, k.

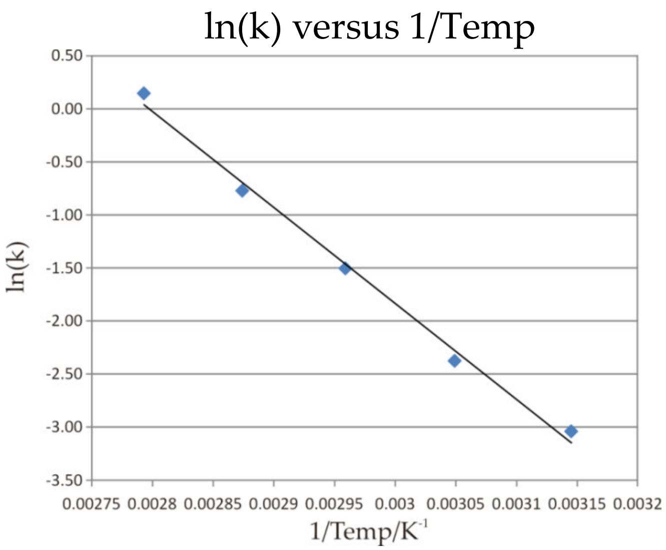
$$t_{1/2} = \frac{0.693}{k} \quad \text{or} \quad t_{1/2} = \frac{1}{k\ A_i}$$

So that, in either case,

$$t_{1/2} \propto \frac{1}{k}$$

Experimental Data		**Calculated Values from Data**			**Data Used in Plot**	
Temp/°C	$t_{1/2}$ Time/min:sec	Temp/K °C + 273	Time/min	$k \propto {}^{1}/_{t_{1/2}}$ /min^{-1}	ln(k)	1/Temp/K^{-1}
85°C	0:50	358 K	0.866	1.1547	0.1438	0.002793
75°C	2:10	348 K	2.166	0.4617	-0.7728	0.002874
65°C	4:30	338 K	4.500	0.2222	-1.5042	0.002959
55°C	10:45	328 K	10.75	0.0930	-2.3752	0.003049
45°C	20:54	318 K	20.90	0.0478	-3.0407	0.003145

From this data you get the following plot



From the slope and intercept of this graph you get,

Slope = -9046.7 = -Ea/R
Intercept = 25.30 = ln(A)

Therefore;

Ea = 75,214.3 J/mol and $A = 9.719 \times 10^{10}\ s^{-1}$

While the equation, $\ln(k) = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln(A)$, is more convenient to use than the exponential form, it is still rather difficult to use because it requires that you plot your data and find the slope and intercept in order to determine the activation energy. Fortunately, we can simplify this equation further. Assume that we have a set of rate data taken at two different temperatures, T_1 and T_2. We would then have two activation energy equations of the form,

$$\ln(k_1) = -\frac{E_a}{R} \cdot \frac{1}{T_1} + \ln(A)$$

And,

$$\ln(k_2) = -\frac{E_a}{R} \cdot \frac{1}{T_2} + \ln(A)$$

If we subtract the bottom equation at T_2 from the top equation at T_1 we would get,

$$\ln(k_1) - \ln(k_2) = \left[-\frac{E_a}{R} \cdot \frac{1}{T_1} + \ln(A)\right] - \left[-\frac{E_a}{R} \cdot \frac{1}{T_2} + \ln(A)\right]$$

Using the properties of logarithm's we can combine the natural log terms and we see that the ln(A) drops out of this equation.

$$\ln\left(\frac{k_1}{k_2}\right) = \left[-\frac{E_a}{R} \cdot \frac{1}{T_1}\right] - \left[-\frac{E_a}{R} \cdot \frac{1}{T_2}\right]$$

Factoring out the E_a/R term and rearranging, we get,

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

This equation is known as the Arrhenius equation and it is commonly used to determine the activation energy of a reaction at two different temperatures. We will find that if we combine the temperature terms there is another form of this equation that is easier to use.

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{E_a}{R}\left[\frac{T_1}{T_1 T_2} - \frac{T_2}{T_1 T_2}\right]$$

So that,

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

We now have two form of the Arrhenius equation and each of them has their use.

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right] \qquad \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Use this version when solving for k's or Ea.

Use this version when solving for T_1 or T_2.

Problem 11.8

Given the following rate data, calculate the rate law at 25°C and the activation energy.

	Rate/10^{-4}	$[I^-]/M$	$[OCl^-]/M$
@ 25°C			
	6.10	0.20	0.050
	12.2	0.40	0.050
	36.6	0.60	0.100
@ 33°C			
	14.4	0.20	0.050

What is the rate law?
What is the value of the rate constant at 25°C and at 33°C?
What is the activation energy for this reaction?

Using the techniques outlined earlier in this chapter, based on the rate law data, the rate law was determined to be,

$$\text{rate} = k\,[I^-]\,[OCl^-]$$

Based on this rate law we can use the experimental data to determine the rate constant for this reaction as 25°C and 33°C.

$$6.1\text{x}10^{-4}\ M/s = k\,[0.20\ M]\,[0.05\ M] \quad \text{so,}\ \ k = 0.061\ 1/Ms\ @\ 25°C = 298\ K$$

$$14.4\text{x}10^{-4}\ M/s = k\,[0.20\ M]\,[0.05\ M] \quad \text{so,}\ \ k = 0.144\ 1/Ms\ @\ 33°C = 306\ K$$

The activation energy can now be determined,

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

$$\ln\left(\frac{0.144\ 1/Ms}{0.061\ 1/Ms}\right) = \frac{E_a}{8.314}\left[\frac{306\text{ K} - 298\text{ K}}{306\text{ K} \times 298\text{ K}}\right]$$

$$E_a = 81{,}399\text{ J/mol}$$

There are other versions of the Arrhenius equation that can be convenient to use. Consider the following rate law used in the example above,

$$\text{rate} = k\,[I^-]\,[OCl^-]$$

We used the rate law to determine the value of the rate constant at two different temperatures. You should notice that the data at 25°C uses the same concentrations for I^- and OCl^- as the rate at 33°C (see below).

	Rate/10^{-4}	$[I^-]/M$	$[OCl^-]/M$
@ 25°C			
	6.10	0.20	0.050
@ 33°C			
	14.4	0.20	0.050

When the concentrations are constant at two different temperatures, rates can be used in the Arrhenius equation rather than the rate constant.

$$\ln\left(\frac{\text{rate}_1}{\text{rate}_2}\right) = \ln\left(\frac{k_1[I^-]_1\,[OCl^-]_1}{k_2[I^-]_2\,[OCl^-]_2}\right)$$

If the concentration of the ions does not change from one temperature to another then they will cancel in this express and we would be left with,

$$\ln\left(\frac{\text{rate}_1}{\text{rate}_2}\right) = \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

Therefore, it is possible to replace the rate for the rate constant as long as the concentrations remain constant. Finally, let's consider the first and second order half life expressions,

$$t_{1/2} = \frac{0.693}{k} \quad \text{and} \quad t_{1/2} = \frac{1}{k\,[A]_i}$$

Or,

$$k = \frac{0.693}{t_{1/2}} \quad \text{and} \quad k = \frac{1}{t_{1/2}\,[A]_i}$$

There is nothing special about a half-life. We could have just as easily defined a one-third life or three-quarter life with equal valid results. The only difference is that our constants will change. For example, let's define a two-thirds life for first and second order kinetics. We would have,

First Order -

The two thirds life is defined as the amount of time needed for an initial concentration to drop to two-thirds of its original value. By this definition, we are looking for the amount of time required for $A_f = 2/3\ A_i$. Substituting these values into our integrated rate law and redefining Δt as $t_{2/3}$ we get,

$$\ln\left(\frac{A_i}{\frac{2}{3}A_i}\right) = \ln\left(\frac{3}{2}\right) = 0.4055 = k\,t_{2/3} \Rightarrow \quad t_{2/3} = \frac{0.4055}{k} \quad \text{or} \quad k = \frac{0.4055}{t_{2/3}}$$

Second Order –

As before, we define a two-thirds life, $t_{2/3}$, as being the time it takes for an initial concentration to drop to two-thirds of its original value. Under these conditions we would have $A_f = 2/3\ A_i$. Substituting, we would get,

$$\frac{1}{\frac{2}{3}A_i} - \frac{1}{A_i} = k\ t_{2/3}$$

$$\frac{3}{2A_i} - \frac{1}{A_i} = k\,t_{2/3}$$

$$\frac{1}{2A_i} = k\,t_{2/3} \quad \Rightarrow \quad t_{2/3} = \frac{1}{2\,k\,A_i} \quad \text{or} \quad k = \frac{1}{2\ t_{2/3}\ A_i}$$

Since we have an equivalence between the rate constant and a half-life or two-thirds life we can substitute these results into the Arrhenius equation.

First Order:

$$\ln\left(\frac{k_1}{k_2}\right) = \ln\left[\frac{\left(\frac{0.4055}{t_{2/3}}\right)_1}{\left(\frac{0.4055}{t_{2/3}}\right)_2}\right] = \ln\left[\frac{\left(t_{2/3}\right)_2}{\left(t_{2/3}\right)_1}\right] = \frac{E_a}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

Second Order: If [A] is constant, then $[A]_1 = [A]_2$

$$\ln\left(\frac{k_1}{k_2}\right) = \ln\left[\frac{\left(\frac{1}{2\ t_{2/3}\ [A]_1}\right)_1}{\left(\frac{1}{2\ t_{2/3}\ [A]_2}\right)_2}\right] = \ln\left[\frac{\left(t_{2/3}\right)_2}{\left(t_{2/3}\right)_1}\right] = \frac{E_a}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

You can see that you get the same result regardless of whether the reaction is first or second order. In fact, you will get the same result regardless of whether you are using the half-life, two-thirds life or any other randomly chosen stopping point for the reaction. So rather than use a half-life or two-thirds life we can use the time it takes to get to any random stopping point into the equation. This gives us the following set of equalities for the Arrhenius equation;

$$\ln\left(\frac{t_2}{t_1}\right) = \ln\left(\frac{\text{rate}_1}{\text{rate}_2}\right) = \ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

Using this form of the Arrhenius equation, we can do some interesting calculations.

Problem 11.9

A cook finds that it takes 30 minutes to boil potatoes at 100°C in an open sauce pan and only 12 minutes to boil them in a pressure cooker at 110°C. Estimate the activation energy for cooking potatoes, which involves the conversion of cellulose into starch.

We begin by assuming that the both potatoes were cooked to the same level of "doneness." In that way we are assuming that we are measuring the time to the same end point for both potatoes. So, we have the following data,

t_2 = 30 min @ 100°C and t_1 = 12 min @ 110°C
Using the Arrhenius equation using time, we have the following

$$\ln\left(\frac{t_2}{t_1}\right) = \frac{E_a}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

$$\ln\left(\frac{30\text{ min}}{12\text{ min}}\right) = \frac{E_a}{8.314\text{ J/mol}\cdot\text{K}}\left[\frac{383\text{ K} - 373\text{ K}}{383\text{ K} \times 373\text{ K}}\right]$$

$$E_a = 108{,}830\text{ J/mol}$$

Problem 11.10

Cryosurgical procedures involve lowering the body temperature of the patient prior to surgery. The activation energy for the beating of the heart muscle is about 30 kJ/mol (30,000 J/mol) A persons normal body temperature is 98.6°F (or 37°C) and most people have a pulse rate of about 75 beats/min. Using this information estimate a person's pulse if their body temperature is dropped to 72°F (22°C).

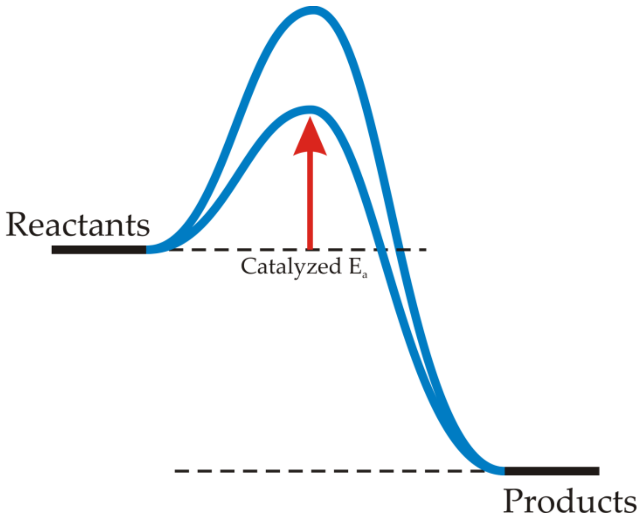
$$\ln\left(\frac{\text{rate}_1}{\text{rate}_2}\right) = \frac{E_a}{R}\left[\frac{T_1 - T_2}{T_1 T_2}\right]$$

$$\ln\left(\frac{75\text{ bpm}}{\text{rate}_2}\right) = \frac{30{,}000\text{ J/mol}}{8.314\text{ J/mol K}}\left[\frac{310\text{ K} - 295\text{ K}}{310\text{ K} \times 295\text{ K}}\right]$$

$$\text{Rate}_2 = 41.5\text{ bpm}$$

Speeding up Reactions: Catalysis

Catalysts are components added to a reaction that help speed it up but are not consumed during the course of the reaction. Catalysts provide an alternate route for a reaction that takes less energy than the reaction without a catalyst. You often hear that catalysts lower the activation energy of a reaction thereby making the reaction go faster, but this statement is not true. Catalysts do not lower the activation energy; they provide an alternate route that requires less energy.



There are a number of different kinds of catalysts but they can be placed into two general categories, homogeneous and heterogeneous catalysis. Homogeneous catalysis occurs when the catalyst is in the same state as the reactants it catalyzes. For example, there is a reaction called the "Iodine Clock" where two reactants, a thiosulfate ion ($S_2O_3^{2-}$) and triiodide ion (I_3^-), come together and turn a solution from the dark brick red color of the triiodide ion to clear. Copper ions (Cu^{2+}) are known catalysts for this reaction. Since all the ingredients are ions in solution, the copper ions are a homogeneous catalyst for this reaction.

Most people are familiar with heterogeneous catalysts without really knowing it. The catalytic converter in your car is an example of heterogeneous catalysis. In this case, hot gases from your car engine travel over a solid catalyst made of platinum, palladium, or rhodium, or a combination of these precious metals. These catalytic metals convert toxic gases like carbon monoxide (CO) into less toxic carbon dioxide (CO_2). Since the catalyst is a solid and the reactants are gases, the catalytic converter in your car is an example of heterogeneous catalysis.

The presence of a catalyst in a reaction adds a term to the uncatalyzed rate. This term is,

$$[k_{cat}[Cat] + 1]$$

So, if you have a rate law that looks like,

$$Rate = k\,[A]$$

Then the catalyzed rate law would look like,

$$\text{Rate}_{cat} = [k_{cat}[\text{Cat}] + 1]\ k\ [A]$$

Or, by multiplying through,

$$\text{Rate}_{cat} = k_{cat}[\text{Cat}]\ k[A]\ +\ k[A]$$

If all of the concentrations were equal to 1 M and the catalyzed rate constant was 10,000 times larger than the uncatalyzed rate constant (kcat >> k), then our rate law would look like,

$$\text{Rate}_{cat} =\ k_{cat}[\text{Cat}]\ k[A]\ +\ k[A]\ = (10{,}000)\ [1M]\ (1)[1M]\ +\ (1)\ [1M]$$

$$\text{Rate}_{cat} = 10{,}000 + 1 = 10{,}001 \approx 10{,}000$$

The catalyzed portion of the rate law is so large that the uncatalyzed portion adds almost nothing to it and is sometimes ignored. One of the things that this equation does for us is to show us that both the catalyzed and uncatalyzed reactions occur simultaneously but the catalyzed portion is so large compared to the uncatalyzed portion that the uncatalyzed portion might as well be ignored. Unfortunately, this leads some books and some instructors to the conclusion that this equation can be used

$$\text{Rate}_{cat} = k_{cat}[\text{Cat}]\ k[A]\ +\ k[A] \approx k_{cat}[\text{Cat}]\ k[A]$$

And you will sometimes see a catalyzed rate law written as,

$$\text{Rate}_{cat} = k_{cat}[\text{Cat}]\ k[A]$$

Unfortunately, while mathematically this equation is approximately true, it imples that when the concentration of the catalyst is zero ([Cat] = 0 *M*) the rate should be zero, but we know that when there is no catalyst the reaction still occurs according to the uncatalyzed rate law so this approximation should not be used in chemistry.

Experimentally, determining a value for the catalyzed rate constant is not difficult. If we rearrange our catalyzed rate law slightly we get,

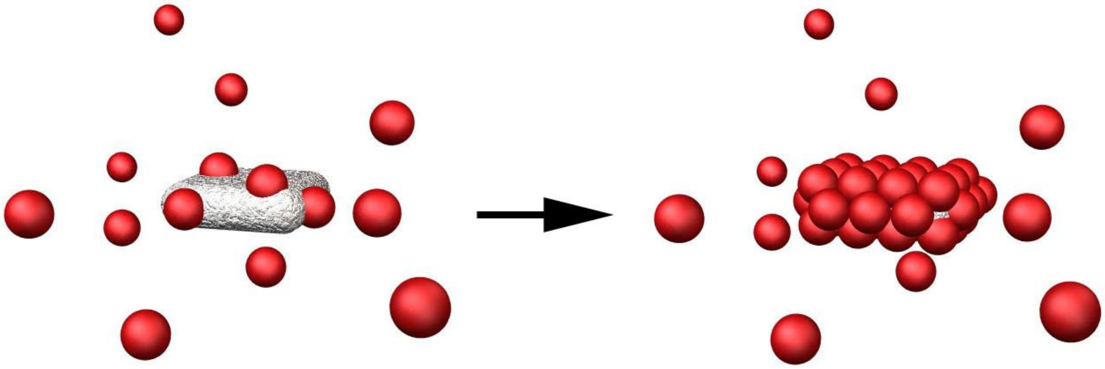
$$\text{Rate}_{cat} = k_{cat}\ k[A]\ [\text{Cat}]\ +\ k[A]$$

This equation is of the form, y = mx + b. A plot of the Rate$_{cat}$ versus [Cat] yields a plot with a slope of k$_{cat}$ k[A] and an intercept of k[A]. By dividing the slope by the intercept we obtain a value for the catalyzed rate constant.

$$\frac{m}{b} = \frac{k_{cat}\ k[A]}{k[A]} = k_{cat}$$

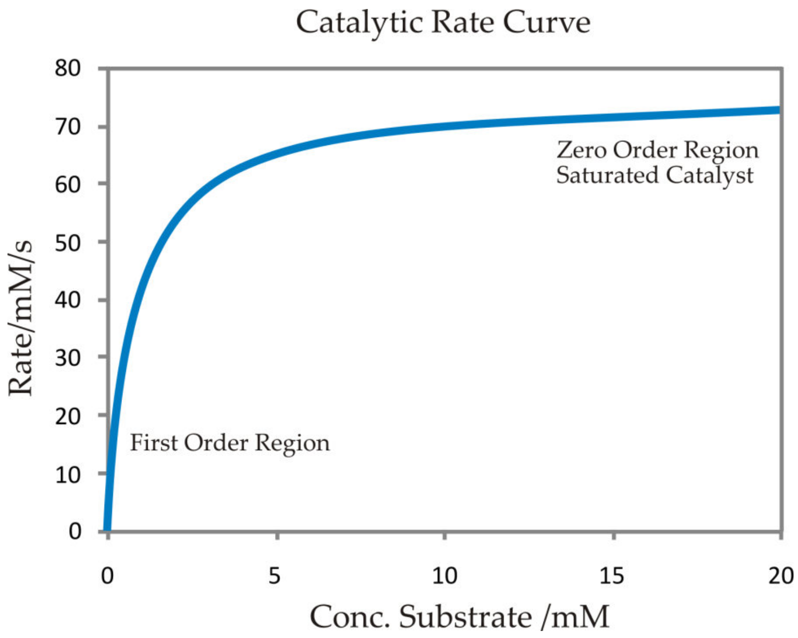
A Saturated Catalyst

Platinum metal is commonly used as a heterogeneous catalyst for many reactions but it suffers from the same problem as most heterogeneous catalysts – it has a limited size. Initially, the catalyst acts upon the substrate (reactant) following first order kinetics. If you double the amount of reactant, the reaction rate doubles. As the amount of substrate increases, the catalyst eventually becomes completely covered in reactant and with no more space to catalyze the reaction, adding more substrate no longer increases the rate.



the rate, the reactant appears to be zero order. There is, therefore, a maximum rate at which a catalyzed reaction can go that is dependent on the total surface area of the catalyst.

When a plot is made of the rate of the reaction and the concentration of reactant the rate initially rises in proportion to the amount of reactant added (first order region), but then levels off when the concentration of the reactant becomes very high (zero order region). This produces a curve and at the top of the curve we can see that there is a maximum rate at which a catalyzed reaction can occur. This behavior is common with catalysts and is also seen with biological catalysts called enzymes. The equations that govern biological catalysts and the rate curve it produces will be explored more thoroughly after we look at enzyme kinetics.



Enzyme Kinetics: The Michaelis-Menton Equation

Enzymes are biological molecules that catalyze chemical reactions. Generally, enzymes are globular proteins but a number of RNA catalysts are also known. Enzymes are very specific in their action. They will bind to only a small number of reactant molecules called "substrates" and usually perform a single chemical reaction. They act as catalysts by orienting the substrate molecules properly to facilitate reaction and provide an environment that is favorable for the reaction to occur. When the enzyme binds to the substrate the result is an enzyme-substrate (ES) complex. We show this using the following equilibrium,

$$E + S \rightleftarrows ES$$

The enzyme then acts on the substrate converting it to product and then releases the product and waits for another incoming substrate.

$$ES \rightleftarrows EP \rightleftarrows E + P$$

Overall, a series of equilibriums between the enzyme, substrate, and enzyme complexes lead to the formation of the product.

$$E + S \rightleftarrows ES \rightleftarrows EP \rightleftarrows E + P$$

For simplicity we can assume that there is only one active complex (ES) and that there is only one equilibrium, the first one between the enzyme and the substrate. With these restrictions, the reaction sequence simplifies to,

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{ES} \overset{k_p}{\rightarrow} \mathrm{E} + \mathrm{P}$$

Biochemists do not talk about the rate of an enzymatic reaction, they use the term velocity, but it has the same meaning as rate. Using the language of a biochemist, the velocity is determined by slow step which is the breakdown of the ES complex to give E + P, so that;

$$\text{velocity} = v = k_p\,[\mathrm{ES}]$$

Where k_p is the rate constant for the slow step of the reaction and in biochemistry it is called the catalytic rate constant. The total amount of enzyme in this reaction is the amount of free enzyme present and the amount bound to the substrate,

$$[\mathrm{E}]_{tot} = [\mathrm{E}] + [\mathrm{ES}]$$

If we divide both side of our velocity equation by the total enzyme concentration we get,

$$\frac{v}{[\mathrm{E}]_{tot}} = \frac{k_p\,[\mathrm{ES}]}{[\mathrm{E}] + [\mathrm{ES}]}$$

In this equation we have a term that is neither a reactant nor a product, the ES complex, so it must be removed. As with other mechanisms, we do this by using the equilibrium that comes before the slow step, but not in the way we might expect. Our focus is on the [ES] complex so we will be looking at the dissociation of this complex. So, we are looking at the following equilibrium,

$$\mathrm{ES} \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} \mathrm{E} + \mathrm{S}$$

Which is the reverse of how it is presented above.

$$\frac{[\mathrm{E}][\mathrm{S}]}{[\mathrm{ES}]} = \frac{k_{-1}}{k_1} = K_s$$

Solving for [ES] we have,

$$[ES] = \frac{[E][S]}{K_S}$$

Substituting this result in for [ES] in our rate law we get,

$$\frac{v}{[E]_{tot}} = \frac{k_P \frac{[E][S]}{K_S}}{[E] + \frac{[E][S]}{K_S}}$$

Cancelling the [E] on the right side we get,

$$\frac{v}{[E]_{tot}} = \frac{k_P \frac{[S]}{K_S}}{1 + \frac{[S]}{K_S}}$$

Dividing both sides by k_P we get,

$$\frac{v}{k_p[E]_{tot}} = \frac{\frac{[S]}{K_S}}{1 + \frac{[S]}{K_S}}$$

If we multiply the right side by K_S/K_S the equation becomes simplified,

$$\frac{v}{k_p[E]_{tot}} = \frac{K_S}{K_S}\frac{\frac{[S]}{K_S}}{1 + \frac{[S]}{K_S}} = \frac{[S]}{K_S+[S]}$$

Also, since v = kp[E], the maximum velocity must be obtained when $[E] = [E]_{tot}$ so that,

$$\frac{v}{v_{max}} = \frac{[S]}{K_S+[S]}$$

This equation is called the Michaelis-Menton equation. It has a couple of properties that should be explored. If the concentration of the substrate is much smaller than the equilibrium constant then $K_s + [S] \approx K_s$ and the equation reduces to,

$$\frac{v}{v_{max}} = \frac{[S]}{K_S}$$

Or,

$$v = v_{max}\frac{[S]}{K_s}$$

This equation says that the velocity (rate) of a reaction is a function of the concentration of the substrate (reactant). Putting it another way, if we double the concentration of S, the rate will double. This behavior is exactly what we expect from first order kinetics, so we see that, while the concentration of substrate is kept low, the enzymatic reaction behaves like it a first order reaction.

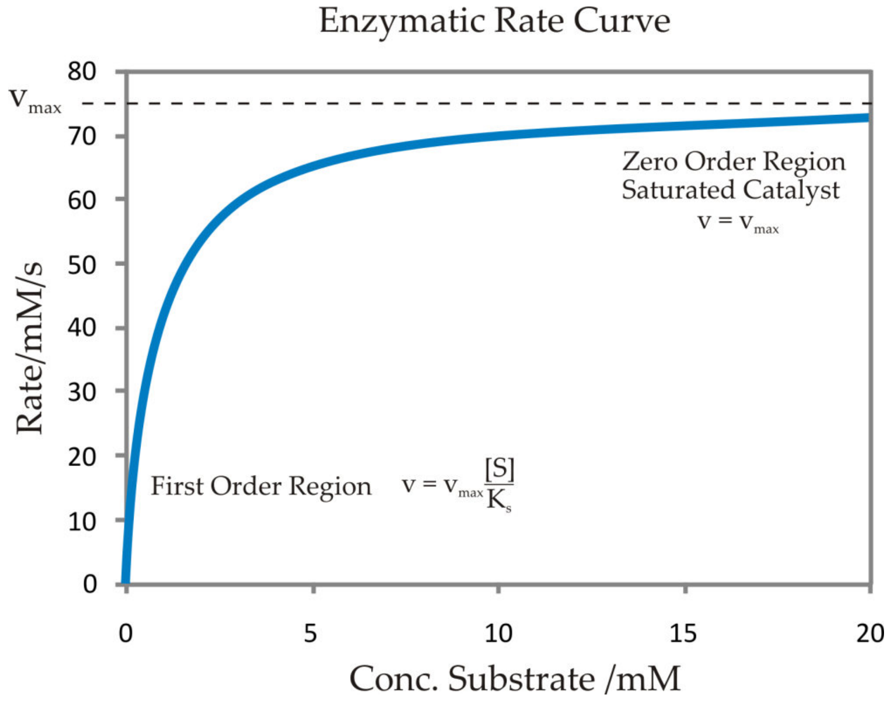
If the concentration of substrate is very much larger than Ks, then Ks + [S] ≈ [S]. Under these conditions our equation reduces to,

$$\frac{v}{v_{max}} = \frac{[S]}{[S]} = 1$$

Or,

$$v = v_{max}$$

Here we see that the velocity (rate) of the reaction is at its maximum, but more importantly, this reaction no longer depends on the concentration of the substrate. This is the same behavior seen in zero order reactions, so at high concentrations, reactions catalyzed by enzymes behave like zero order reactions. So, the equations used for enzyme kinetics model the behavior we predicted earlier for heterogeneous catalysis.



The Lineweaver-Burke Plot

The Michaelis-Menton equation is useful, but difficult to use. We can add substrate to our reaction mixture and measure the reaction rate (v) but this gives us a handle on just two of the four variables in this equation. We still need to know v_{max} and K_s but with only one equation, how can these values be known? We begin by taking the inverse of the Michaelis-Menton equation,

$$\frac{v_{max}}{v} = \frac{K_s+[S]}{[S]}$$

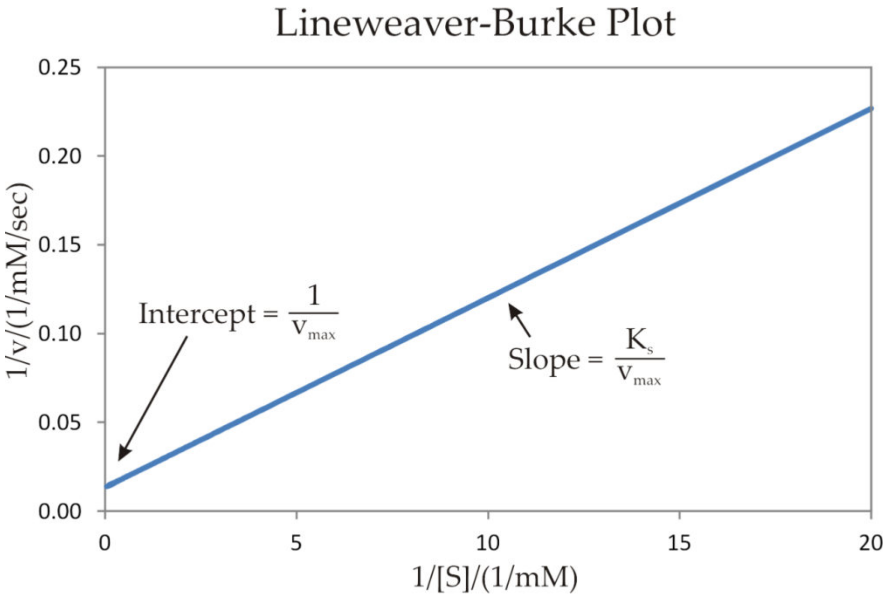
Moving the v_{max},

$$\frac{1}{v} = \frac{K_s+[S]}{v_{max}[S]} = \frac{K_s}{v_{max}[S]} + \frac{[S]}{v_{max}[S]}$$

Simplifying, we get our final equation,

$$\frac{1}{v} = \frac{K_s}{v_{max}[S]} + \frac{1}{v_{max}}$$

This form of the Michaelis-Menton equation is called the Lineweaver-Burke reciprocal plot. This equation is of the form y = mx + b where y = 1/v and x = 1/[S]. If this plot is made, then the slope is K_s/v_{max} and the intercept is $1/v_{max}$. When applied to the data given in our enzymatic rate curve plot, we obtain the following plot;



The slope of this plot is 0.01067 s, and the intercept is 0.01333 s/m*M*. Therefore,

$$\frac{1}{v_{max}} = 0.0133 \text{ s/mM} \qquad v_{max} = 75 \text{ mM/s}$$

And,

$$\frac{K_s}{v_{max}} = 0.01067 \text{ s} \qquad \frac{K_s}{75 \text{ mM/s}} = 0.01067 \text{ sec}$$

$$K_s = 0.01067 \text{ s} \times 75 \text{ mM/s} = 0.80 \text{ mM}$$

Chapter Twelve

Equilibria, pH, Solubility, Titration Curves, and Amphoterism

"Give me a lever long enough, and a fulcrum strong
enough, and I'll move the world" - Archimedes

Chemical equilibria are a natural extension of rate laws, but rather than looking at the rate of a reaction going only in one direction, we will now look at reactions going in the forward and reverse directions. Initially, chemical equilibria give students problems because the student will be forced to look at reactions very differently than the way they were trained in earlier chapters. The idea of "reactants and products" is much more amorphous when discussing equilibria and deciding precisely which of the various forms of a reaction is occurring can take some time to learn. In addition, solubility rules will give way to solubility products and students will find that everything is soluble to some degree which runs contrary to the fundamentals taught to them earlier in the year. But rest assured that many chemistry students have gone before you and have successfully navigated the waters of chemical equilibria.

Introducing Chemical Equilibria

Physically, an equilibrium is established when the forward rate and reverse rate of a reaction become equal. A simplified view of this can shown by the following reaction;

$$\text{Reactant} \rightleftarrows \text{Product}$$

We can see that as the reactant become product, the product is also becoming reactant and each of them is doing so at its own particular rate that can be written as,

$$\text{Rate}_{\text{forward}} = k_f\,[\text{Reactant}]$$

$$\text{Rate}_{\text{reverse}} = k_r[\text{Product}]$$

At equilibrium, these two rates will become equal to each other. At that point we would have,

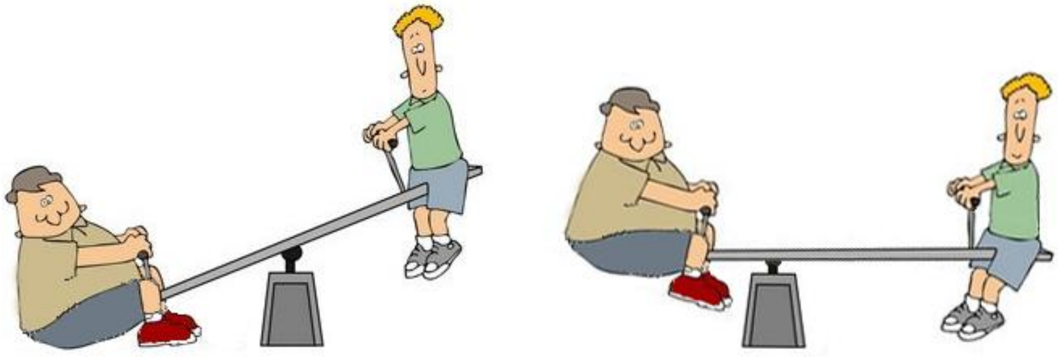
$$\text{Rate}_{\text{Forward}} = \text{Rate}_{\text{Reverse}}$$

$$k_F\,[\text{Reactant}] = k_R[\text{Product}]$$

If we rearrange this equation we would get,

$$\frac{k_F}{k_R} = \frac{[\text{Product}]}{[\text{Reactant}]} = K_{eq} = \text{Equilibrium constant}$$

The ratio of the two rate constants, k_F and k_R, is just another constant that we call the equilibrium constant K_{eq}. The concentration of the reactant and product are rarely, if ever, equal. Usually, though not always, there is more reactant than product. Even so, equilibrium is maintained.



Consider the two kids on the teeter-totter shown above. As can be seen, the kids on the left are out of balance – they are not at equilibrium. To balance them we could make the bigger kid smaller or the smaller kid bigger. Doing this would establish a balance but the two kids would have to weigh the same. This is not how chemical reactions achieve equilibrium. Chemical reactions achieve equilibrium like the two kids on the right. Here, the center stand was moved to compensate for the weight difference between the kids. Now, the bigger kid sits on the shorter part of the teeter totter and the smaller kid sits on the longer. These are compensating effects that bring the two kids into equilibrium. Chemical equilibriums work this way. A faster reaction has a lower concentration (the longer side has the smaller kid) and a slower reaction has a higher concentration (the shorter side has the bigger kid). The net result is that this brings the two reactions into equilibrium.

Equilibrium Types

Equilibriums come in many forms. Solids, liquids, gases, and ions can all be involved in an equilibrium. Equilibriums are categorized into a few different types. These types are outlined below,

Equilibrium Type	Example	Equilibrium Expression	Equilibrium Constant	Meaning Of The Subscript
Water	$H_2O \leftrightarrows H^+ + OH^-$	[H+] [OH-]	K_w	w = water
Acid	$HAc \leftrightarrows H^+ + Ac^-$	$\frac{[H^+]\,[Ac^-]}{[HAc]}$	K_a	a = acid
Base	$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$	$\frac{[NH_4^+]\,[OH^-]}{[NH_3]}$	K_b	b = base
Solid	$AgCl(s) \leftrightarrows Ag^+ + Cl^-$	[Ag+] [Cl-]	K_{sp}	sp = solubility product
Gas	$H_2(g) + Br_2(g) \leftrightarrows 2\ HBr(g)$	$\frac{P^2_{HBr}}{P_{H_2} \cdot P_{Br_2}}$	K_p	p = pressure
Mixed	$CO_2(g) + H_2O \leftrightarrows H_2CO_3(aq)$	$\frac{[H_2CO_3]}{P_{CO_2}}$	K_{eq}	eq = equilibrium (generic)

All equilibriums are written as dissociations whenever possible. In the case of a gas or a mixed equilibrium it is not always possible to make this distinction, but with water, acids, bases and solids, the equilibrium reactions are always written as dissociations (a single compound dissociating into two or more products).

You will notice that the water and mixed equilibriums both include water but water does not appear in the equilibrium expression. Liquids, solvents, and solids do not appear in equilibriums. Solids do not have concentrations and there is so much water in a solution that the concentration of water remains constant so it is moved and made a part of the equilibrium constant. For our purposes, we will ignore the presence of solids and liquids in equilibriums.

Writing Equilibrium Expressions: Part I

Students have difficulty writing equilibrium reactions because, prior to their introduction to equilibriums, all of the single replacement, double replacement, and neutralization reactions they have seen have trained them to make all the ingredients in a problem a reactant, draw an arrow, and then figure out what those ingredients will do. Instructors have spent the better part of an entire semester of chemistry trying to get students to predict the products made when reactants come together and now, with the introduction of equilibriums, all of that work must be undone.

By their nature, equilibriums are reactions that go in both the forward and reverse direction so there is no clear distinction between reactant and product. As a consequence, when a student is given a set of ingredients in an equilibrium, those ingredients may be found on either side of a reaction as either reactant or product, it is up to the student to decide. This is a new and often difficult concept for a student and they struggle to write the equilibrium that is occurring.

Fortunately, there are some guidelines that can be followed that will help. There are a limited number of equilibrium types and each type should be written in a particular way. The student needs to look at what they have been given and then fit these ingredients to one of these basic equilibrium types.

Equilibrium Type	**Example**	**Equilibrium Expression**	**Equilibrium Constant**
Water	$H_2O \leftrightarrows H^+ + OH^-$	[H+] [OH-]	K_w
Acid	$HAc + H_2O \leftrightarrows H_3O^+ + Ac^-$	$\frac{[H_3O^+]\,[Ac^-]}{[HAc]}$	K_a
Base	$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$	$\frac{[NH_4^+]\,[OH^-]}{[NH_3]}$	K_b
Solid	$AgCl(s) \leftrightarrows Ag^+ + Cl^-$	[Ag+] [Cl-]	K_{sp}

Three of these equilibriums are related to one another, acids, bases, and water. Acids contain H^+, bases contain OH^-, and water contains both. It will help us to write equilibriums if we can understand how these substances are related to one another. In the next section we will investigate the relationship between acids, bases and water.

Acids, Bases, and Water

Most people are familiar with chemicals that are acidic and basic. For example, people know that vinegar is an acid and ammonia is a base and if pressed, they could tell you why – acids give off H^+ and bases give off OH^-. This definition for an acid and a base works pretty well in everyday life and is the working definition for most people. Unfortunately, another common experience runs afoul of this definition and should make you think about the definition for an acid and a base.

Suppose that you have heartburn and you want to get rid of that burning sensation in your stomach. What would you do? Most people would take some kind of antacid to relieve the pain, but suppose that you didn't have any, what then? Just check the kitchen cupboard. If you stir a teaspoon of baking soda ($NaHCO_3$) into a cup of water and drink it, the baking soda will neutralize the acid and make you feel better. But the question is, why does this work?

We all know that a base will neutralize and acid. In the case of our heartburn, the acids in our stomach (HCl) are too high and must be neutralized. The reaction is given below.

$$HCl + NaHCO_3 \rightarrow NaCl + H_2O + CO_2(g)$$

By taking baking soda, the HCl is neutralized, salt and water is produced along with CO_2 gas (belch!). So, if a base neutralizes an acid, and baking soda neutralized the acids in your stomach, then baking soda must be a base. So, where is the OH^- in baking soda? There isn't any. The problem isn't with our baking soda. The problem is with our definition of a base.

Definitions for an Acid and a Base

The following table outlines three levels of definition for an acid and a base and in which class you are most likely to use them.

Acid-Base Definition	Acid	Base	Where used
Arrhenius	H^+ donor	OH^- donor	Beginning Chem
Brønsted-Lowrey	H^+ donor	H^+ acceptor	Advanced Chem
Lewis	Electron acceptor	Electron donor	Organic Chem

The simplest definition for an acid and base is the Arrhenius definition where acids donate an H^+ and bases donate an OH^-. This definition works most of the time and is the definition that most people know. But when baking soda neutralizes the acids in our stomach, there was no OH^- present so the Arrhenius definition of a base no longer applies. Baking soda is a Brønsted-Lowery base.

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2(g)$$

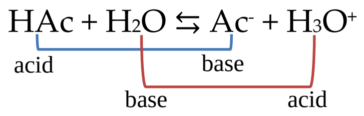
Here we see that the bicarbonate ion (HCO_3^-) accepted the H^+, reacted with it, and produced water and CO_2 gas. By definition, this makes the bicarbonate ion a Brønsted-Lowery base. With this new definition of a base we will now look at the details of an acid base equilibrium.

Conjugate Acid-Base Pairs

Consider the following acid dissociation in water,

$$HAc + H_2O \leftrightarrows Ac^- + H_3O^+$$

We can see that the HAc has donated an H^+ to the water molecule which has accepted it. By the Brønsted-Lowery definition of an acid and a base, this makes the HAc an acid and the H_2O a base. On the other side of the reaction, we see that the H_3O^+ (hydronium ion) donates its H^+ to the Ac^- which accepts it. This makes H_3O^+ an acid and the Ac^- a base. We therefore have conjugate acid-base pairs,



Conjugate acid-base pairs

So what we see is that every acid has its corresponding conjugate base and every base has its corresponding conjugate acid. See the following table for a representative list of conjugate acid-base pairs. Notice that, in the presence of an acid, water is behaving like a base.

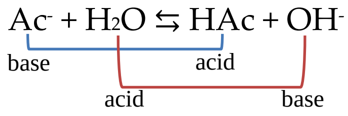
Conjugate Acid-Base Pairs	
Acid	Base
HAc	Ac^-
HCN	CN^-
HF	F^-
H_3O^+	H_2O
H_2CO_3	HCO_3^-
HCO_3^-	CO_3^{2-}
NH_4^+	NH_3

If HA represents any of the acids on the left, and A- represents any of the conjugate bases on the right, then we can write a general acid dissociation reaction that has the following form,

$$HA + H_2O \leftrightarrows A^- + H_3O^+$$

All acid dissociations have this form and should be written this way. Now, let us turn our attention to what happens when we put a base into water.

If it is possible to put acid into water then it is also possible to put a base into water. Normally, we think of a base as being NaOH, but with our new definition of a base (Brønsted-Lowery) then the sodium or potassium salt of any conjugate base is a base. We saw this when we discovered that $NaHCO_3$ (baking soda) was acting as a base when it neutralized the acids in our stomach. We should also note that Na+ and K+ are never a part of any equilibrium. Our solubility rules tell us that all sodium and potassium compounds are soluble and in every reaction we have seen, sodium and potassium ions are always spectator ions. The same thing is true for equilibriums. Sodium and potassium ions are spectator ions and therefore do not take part in the equilibrium. So, when we put Sodium Acetate into water we need only consider the acetate ion and the water (Ac^- and H_2O). What happens when we put these two ingredients together? According to the definitions given earlier, every acid has a conjugate base and every base has a conjugate acid so,



Conjugate acid-base pairs

So what we see is that every base has its corresponding conjugate acid and every acid has its corresponding conjugate base. See the following table for a representative list of conjugate acid-base pairs, but from the perspective of the base. The only difference between this table and the table above is that, in the presence of a base, water behaves like an acid.

Conjugate Acid-Base Pairs Base	 Acid
Ac^-	HAc
CN^-	HCN
F^-	HF
OH^-	H_2O
HCO_3^-	H_2CO_3
CO_3^{2-}	HCO_3^-
NH_3	NH_4^+

If A^- represents any of the bases on the left, and HA represents any of the conjugate acids on the right, then we can write a general base dissociation reaction that has the following form,

$$A^- + H_2O \leftrightarrows HA + OH^-$$

All base dissociations have this form and should be written this way. One careful note about this reaction; the A^- will always be given to you as a sodium or potassium salt (NaA or KA) and not just as the ion. The sodium and potassium ion are spectators so they are not included in the equilibrium, but they are still present in solution.

Writing Equilibrium Expressions: Part II

We have discovered that acid and base equilibriums have one of two related forms,

Acid: $HA + H_2O \leftrightarrows A^- + H_3O^+$
Base: $A^- + H_2O \leftrightarrows HA + OH^-$

Precisely which of these two equilibriums you choose to use will depend on the ingredients given and sometimes the choice will be matter of convenience - it is somewhat easier to solve acid dissociations than base. Before we can continue, it is important to comment about the hydronium ion. Most instructors leave out the hydronium ion when writing equilibriums. Basically, they cancel the water present on both sides of the acid equilibrium so you will see most acid equilibriums written as,

$$HA \leftrightarrows H^+ + A^-$$

Technically, this is incorrect, but water is so ubiquitous that it is understood to be there even if it is not written. This detail simplifies our reactions (which is why it is done) and it does no harm to the overall equilibrium process (water is ignored in equilibriums). So the two forms of equilibrium reaction reduce to,

Acid: $HA \leftrightarrows H^+ + A^-$
Base: $A^- + H_2O \leftrightarrows HA + OH^-$

Water is kept in the base version in order for the reaction to balance. We can now set about to answer the problem proposed earlier in the chapter,

> “How do we know which equilibrium we should choose when given a list of ingredients?”

Let us now answer that question. The list of potential ingredients is pretty small. We have weak acids and bases and strong acids and bases. The list of strong acids and bases is pretty small so it should be committed to memory. They are,

Strong Acids		Strong Bases
HCl		NaOH
H_2SO_4		KOH
HNO_3		

Whenever a strong acid or base are present they are a source of H^+ or OH^- only. The corresponding anions or cations are not involved in the reaction. Anything else added to your ingredient list will be involved in the equilibrium with the exception of sodium and potassium ions that may be present as spectator ions. For example, let's write the equilibrium that occurs when we HAc is added to NaAc.

HAc is not a strong acid so it is involved in the equilibrium and NaAc is involved but we ignore the Na^+ spectator ion. Our two ingredients are, HAc and Ac^-. We now have a choice. Both of these ingredients are found in the acid and base version of our equilibrium so we must choose one. It is best to choose the acid version whenever possible but either version could be chosen. While the best choice is the acid version, both versions are given below (always written as dissociations),

$$\text{Acid: } HAc \leftrightarrows H^+ + Ac^- \qquad \text{Base: } Ac^- + H_2O \leftrightarrows HAc + OH^-$$

There is nothing wrong with the base reaction and you would not have been wrong by choosing it, but solving them can be slightly more complicated so it is usually easier to choose the acid version.

What would we have done had we been given HCN and NaOH as our ingredients? Ignoring the Na^+, or ingredients are HCN an OH^-. Only the base version of our equilibrium includes an OH^- so we choose to write that version,

$$CN^- + H_2O \leftrightarrows HCN + OH^-$$

We recognize that the ingredients we have been given are the products of this base reaction. Since we ALWAYS write our reactions in one of the two basic forms (as dissociations) we place both ingredients on the product side and write our equilibrium. Doing this runs contrary to how most students have been taught about reactions but it is essential that you start seeing ingredients to equilibriums instead of reactants to be added together.

What if we added HCl to NH_3? In this case, HCl is a strong acid so it only contributes an H^+. Ammonia (NH_3) is a weak base willing to accept the H^+, so always writing these reactions as dissociations, we would write,

$$NH_4^+ \leftrightarrows NH_3 + H^+$$

This process gets easier with practice. You cannot solve an equilibrium if you write it down, so it is essential that you learn how to write these equilibriums properly.

Problem 12.1

For each of the following sets of compounds write the equilibrium reaction that would occur when the compounds are mixed together.

a) HNO_3 and NaBenz
b) NH_4Cl and KOH
c) NaCN and NaOH
d) HF and HCl

Answer

a) HBenz ⇆ H+ + Benz-
b) $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$ or $NH_4OH \leftrightarrows NH_4^+ + OH^-$
c) $CN^- + H_2O \leftrightarrows HCN + OH^-$
d) $HF \leftrightarrows H^+ + F^-$

The Water Equilibrium

Water has its own special equilibrium reaction,

$$H_2O \leftrightarrows H^+ + OH^- \qquad K_w = 1\times10^{-14}\ M^2$$

You will notice that this reaction is written as a dissociation like all other equilibrium reactions. When strong acids and strong bases are mixed, this is the equilibrium that is produced. For example, suppose that we mix HCl with NaOH. We already know that strong acids and bases are sources of H+ and OH- so, like all of the other equilibriums we have considered, we can ask, which of the various possible equilibriums would result from mixing HCl and NaOH. The answer is the water equilibrium. It is important to note that, even though we are mixing HCl and NaOH, we are really adding the products of a water dissociation together and would write the resulting equilibrium as the water dissociation.

When pure water dissociates it makes one H^+ and one OH^-. In other words, the concentration of H^+ must equal the concentration of OH^- in pure water. Since these concentrations must be equal, if we consider the water equilibrium,

$$H_2O \leftrightarrows H^+ + OH^- \qquad K_w = 1\times10^{-14}\ M^2$$

Then,

$$K_w = [H^+]\ [OH^-] = [H+]^2 = 1\times10^{-14}\ M^2$$

Solving for the $[H^+]$ we find,

$$[H^+] = 1\times10^{-7} M$$

So the concentration of H^+ in pure water is $1\times10^{-7} M$ H^+.

Calculating pH

It is common to use pH to discuss the acidity or basicity of a solution, but what exactly is pH? By definition,

$$pH = -\log_{10} [H^+]$$

The "p" in pH really means (in words) "take the negative log of…" Therefore we can have pH, pOH, pKw, pKa, and even pCa^{2+} if we were to take the negative log of a calcium concentration.

Students are often misinformed about the range of pH values and often believe that the range is between 1 and 14. This is not true. For example, you will sometimes use concentrated acids in lab experiments. Concentrated HCl is about 12 *M*. If we calculate its pH we find that,

$$pH = -\log_{10}[12\ M\ H^+] = -1.079$$

In similar fashion, we can calculate the pH of a solution that is very basic. Consider a concentrated solution of NaOH which has a concentration of 19.25 M OH^-. To calculate the pH of this solution we must first find the $[H^+]$. To do this we will use the relationship,

$$K_w = [H^+]\ [OH^-] = 1\times10^{-14}\ M^2$$

$$[H^+]\ [19.25\ M\ OH^-] = 1\times10^{-14}\ M^2$$

Solving for $[H^+]$ we have,

$$[H^+] = \frac{1\times10^{-14}\ M^2}{19.25\ M} = 5.195\times10^{-16}\ M\ H^+$$

So, the pH would be,

$$pH = -\log_{10}[5.195\times10^{-16}\ M\ H^+] = 15.28$$

So the actual range of the pH scale goes from about -1 to about 15. If the pH is less than 7 then the solution is acidic and if it is more than 7 then the solution is basic. If the pH = 7 then the solution is considered neutral.

pH of Common Items		
🟥	Pool Acid	0
🟥	Stomach acid	1
🟥	Battery Acid	2
🟧	Vinegar	3
🟧	Orange Juice	4
🟨	Coffee/Soda	5
🟩	Rain	6
🟩	Milk/Blood	7
🟦	Sea Water	8
🟦	Baking Soda	9
🟦	Antacids	10
🟪	Milk of Magnesia	11
🟪	Conc. Ammonia	12
🟪	Conc. Bleach	13
🟪	Lye/Draino	14

As you can tell, sometimes you will be given the $[OH^-]$ and be asked for the pH of the solution. We could use the process outlined above or we could use a helpful relationship between pH and the OH^- concentration. Starting with our water equilibrium expression, we can take the $-\log_{10}$ of both sides,

$$-\log([H^+][OH^-]) = -\log(1\times10^{-14})$$

We can separate the H^+ from the OH^- by using a property of logs,

$$[-\log([H^+])] + [-\log([OH^-])] = -\log(1\times10^{-14})$$

The first term is just pH and, because of the definition that $-\log_{10}$ = ″p″, the second term becomes pOH. Finally, mathematically, the -log (1×10^{-14}) = 14 so we have,

$$pH + pOH = 14$$

or,

$$pH = 14 - pOH$$

While this is convenient, when using a calculator, it is sometimes easier NOT converting to pOH. Using the definition of pOH = -log [OH^-] we see that we can simplify this last equation,

$$pH = 14 - pOH = 14 - (-\log [OH^-])$$

or,

$$pH = 14 + \log[OH^-]$$

In our previous example, to calculate the pH of a 19.25 M NaOH solution, we only need to do the following calculation,

$$pH = 14 + \log[19.25\ M] = 15.28$$

Problem 12.2

What is the pH of an aqueous solution if the [H^+] =

a. 5.5×10^{-3} *M*?
b. 4.2×10^{-5} *M*?
c. 7.5×10^{-8} *M*?

Answer

a. pH = - log [5.5×10^{-3}] = 2.26
b. pH = - log [4.2×10^{-5}] = 4.38
c. pH = - log [7.5×10^{-8}] = 7.12

Problem 12.3

What is the $[H^+]$ in an acid rain sample that has a pH = 3.22?

$[H^+] = 10^{-pH}$ $[H^+] = 10^{-3.22}$ $[H^+] = 6.03\times10^{-4}$ M

What is the $[H^+]$ in a blood sample that has a pH = 7.30?

$[H+] = 10^{-pH}$ $[H^+] = 10^{-7.30}$ $[H^+] = 5.01\times10^{-8}$ M

What is the $[H^+]$ in a bleach sample that has a pH = 9.55?

$[H^+] = 10^{-pH}$ $[H^+] = 10^{-9.55}$ $[H^+] = 2.82\times10^{-10}$ M

Problem 12.4

What is the $[\ OH^-\ ]$ in a seawater sample that has a pH = 8.65?

$[H^+] = 10^{-pH}$ $[H^+] = 10^{-8.65}$ $[H^+] = 2.24\times10^{-9}$ M

$[H^+]\ [OH-] = 1x10^{-14}$ $[2.24\times10^{-9}\ M]\ [OH-] = 1\times10^{-14}$ $[OH-] = 4.46\times10^{-9}$ M

What is the $[\ OH^-\ ]$ in an ammonia solution that has a pH = 10.20?

$[H^+] = 10^{-pH}$ $[H^+] = 10^{-10.20}$ $[H^+] = 6.31\times10^{-11}$ M

$[H^+]\ [OH^-] = 1\times10^{-14}$ $[6.31\times10^{-11}\ M]\ [OH^-] = 1\times10^{-14}$ $[OH^-] = 1.58\times10^{-4}$ M

What is the $[\ OH^-\ ]$ in an oven-cleaning solution that has a pH = 12.35?

$[H^+] = 10^{-pH}$ $[H^+] = 10^{-12.35}$ $[H^+] = 4.47\times10^{-13}$ M

$[H^+]\ [OH^-] = 1\times10^{-14}$ $[4.47\times10^{-13}\ M]\ [OH^-] = 1\times10^{-14}$ $[OH^-] = 0.0224$ M

LeChatlier's Principle

We have shown that equilibriums are a type of balance. LeChatlier's principle states that if a disturbance is made to one side of a reaction then a compensating reaction must occur to maintain the balance. For example, consider the following reaction,

$$HAc \leftrightarrows H^+ + Ac^-$$

This reaction can be affected by adding additional HAc, H^+, or Ac^-, or by adding any reactant capable of removing one of these ingredients like NaOH, which is capable of reacting with, and removing, the H^+. This equilibrium will react to any stress placed on it by shifting its equilibrium to compensate for that stress. Consider the following table.

Added Ingredient	Source of…	$HAc \leftrightarrows H^+ + Ac^-$ Equilibrium Ingredient Stressed			Resulting Shift in Equilibrium
		HAc	H^+	Ac^-	
HAc	HAc	increased			→
HCl	H^+		increased		←
NaAc	Ac^-			increased	←
NaOH*	OH^-		decreased		→
$NaNO_3$	spectators				No effect
$AgNO_3$**	Ag^+			decreased	→
H_2O***	water	diluted	diluted	diluted	→

* by removing H^+ more must be made so the equilibrium shifts to the right

** Ag^+ removes Ac^- by forming AgAc(s). The reaction shifts to the right to make more Ac^-

*** whichever side has the most ingredients feels the effect the most. The equilibrium shifts right.

From this table we can see that when we add an ingredient found on the left side of our equilibrium, then the equilibrium must shift left to compensate for the added ingredient. In life fashion, when we add an ingredient that is found on the right, then the equilibrium shifts to the left to compensate. This behavior is just like a balance where, by adding extra weight to one side of a balance, we must move some of that added weight to the other side to get back to a state of balance. This simple procedure does not mean that you don't have to know any chemistry to do it. As we can see, when we added NaOH to our equilibrium, the equilibrium shifted to the right. This is because the NaOH neutralized the H^+ and turned it into water. This depleted the H^+ concentration on the right so the equilibrium had to shift to the right to replace the missing H^+. We see a similar effect with the addition of silver ions (Ag^+). Silver reacts with the acetate ion (Ac) to form a solid. This removes (Ac-) from solution so the equilibrium shifts to the right to make more.

What is not so obvious is the effect of adding water. Dilutions cause all the ingredients in an equilibrium to decrease and this will very often cause an equilibrium to shift, but not always. The exact effect depends on the reaction, or more specifically, the number of ingredients on each side of the equilibrium. Let us go back to a familiar equilibrium, acetic acid.

$$\mathrm{HAc} \leftrightarrows \mathrm{H^+} + \mathrm{Ac^-}$$

We want to know how this equilibrium will change when one or more ingredients has been added or removed. We begin by defining a value, Q.

$$\frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{HAc}]} = \mathrm{Q}$$

This equilibrium express looks just like a standard equilibrium only we are not going to be using equilibrium concentrations. Instead, we are going to let the concentration of all ingredients be 1 *M*. Doing this we have,

$$\mathrm{Q} = \frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{HAc}]} = \frac{[1M][1M]}{[1M]} = \frac{1}{1} = 1$$

We are now in a position where we can ask what would happen to Q if we changed the concentration of one ingredient, say, the $[\mathrm{H^+}]$. If the $[\mathrm{H^+}]$ changed from 1M to 2M we can calculate a new value for Q.

$$\mathrm{Q} = \frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{HAc}]} = \frac{[2M][1M]}{[1M]} = \frac{2}{1} = 2$$

By increasing the concentration of H+, we have increased the value of Q. More importantly, when we look at the product to reactant ratio, it is now 2:1.

$$\mathrm{Q} = \frac{[\mathrm{Product}]}{[\mathrm{Reactant}]} = \frac{2}{1}$$

If we want to get back to a state where this ratio is 1:1 then we have too much product. Some of the product must become reactant so the equilibrium must shift to the left.

So, what would happen if we were to dilute all of the ingredients in half? Then our Q would be,

$$\mathrm{Q} = \frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{HAc}]} = \frac{\left[\frac{1}{2}M\right]\left[\frac{1}{2}M\right]}{\left[\frac{1}{2}M\right]} = \frac{\left(\frac{1}{2}\right)}{1}$$

If we want to get back to a state where this ratio is 1:1 then we have too much reactant (or not enough product). The equilibrium shifts to the right, makes more product and consumes more reactant until equilibrium is established once again.

Dilution does not always affect an equilibrium. Consider the reaction between bromine and hydrogen,

$$H_2 + Br_2 \leftrightarrows 2\ HBr$$

As before, we can define a Q value by setting all concentrations equal to 1 *M*.

$$Q = \frac{[H_2][Br_2]}{[HBr]^2} = \frac{[1M][1M]}{[1M]^2} = \frac{1}{1} = 1$$

What would happen if we diluted this equilibrium in half?

$$Q = \frac{[H_2][Br_2]}{[HBr]^2} = \frac{[\frac{1}{2}M][\frac{1}{2}M]}{[\frac{1}{2}M]^2} = \frac{(\frac{1}{4})}{(\frac{1}{4})} = 1$$

The Q value is unchanged so dilution would have no effect on this equilibrium. Contrast this to the following reaction,

$$N_2 + 3\ H_2 \leftrightarrows 2\ NH_3$$

What would happen if this equilibrium was diluted? Since the initial Q value will always equal 1, we can move directly to the dilution,

$$Q = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{[\frac{1}{2}M]^2}{[\frac{1}{2}M]\,[\frac{1}{2}M]^3} = \frac{(\frac{1}{2})^2}{(\frac{1}{2})^4} = \frac{1}{(\frac{1}{2})^2} = \frac{1}{(\frac{1}{4})}$$

In this case, there are not enough reactants so the equilibrium shifts to the left. Overall, we have these results,

Equilibrium	Moles of reactants	Moles of products	Shift when diluting
$HAc \leftrightarrows H^+ + Ac^-$	1 (HAc)	2 ($H^+ + Ac^-$)	→
$H_2 + Br_2 \leftrightarrows 2\ HBr$	2 ($H_2 + Br_2$)	2 (2 HBr)	none
$N_2 + 3\ H_2 \leftrightarrows 2\ NH_3$	4 ($N_2 + 3\ H_2$)	2 ($2\ NH_3$)	←

We see that the overall trend is that a dilution causes an equilibrium to shift in the direction of the side with the most number of ingredients. When the numbers of ingredients on both sides are equal, no shift occurs. It should be intuitively obvious that the opposite trend is true if all ingredients become concentrated. Just how this might happen is not obvious, but when considering gases, the concentration can increase simply by making the volume of the container smaller (same number of moles in a smaller volume of gas). How you would concentrate all ingredients in solution is a puzzler, but might be accomplished by boiling the water away.

Comparing Q to K

Deciding how an equilibrium will shift when an ingredient is added is relatively simple, but it assumes that there is an existing equilibrium to shift. What would happen if ALL the ingredients in an equilibrium were changed, could we use the process outlined earlier to determine the direction of equilibrium shift? No. We will require a new standard by which to compare Q. Rather than assume that all concentrations are 1 M and look to see how the Q changes when we change a concentration, we will use the equilibrium constant K as our new standard.

Let's go back to an equilibrium that is becoming familiar to us, the acetic acid equilibrium,

$$\text{HAc} \leftrightarrows \text{H}^{+} + \text{Ac}^{-}$$

The equilibrium express for this is,

$$\frac{[\text{H}^{+}][\text{Ac}^{-}]}{[\text{HAc}]} = \text{K}_{\text{a}} = 1.8 \times 10^{-5}$$

When a chemist looks at this expression, they see something different than a student sees. A chemist looks at this expression and sees this,

$$\frac{[\text{H}^{+}][\text{Ac}^{-}]}{[\text{HAc}]} = \frac{[\text{Products}]}{[\text{Reactants}]} = \frac{1.8\times10^{-5}}{1} = \text{K}_{\text{a}}$$

This expression tells a chemist that the products are very much lower in concentration than the reactants for this equilibrium (1.8×10^{-5} times lower). In fact, this value is so small, it is not a large error to say that there is virtually no H^{+} or Ac^{-} present in solution compared to the amount of HAc. So, when given 1 M concentrations for all of them, it is easy to see that virtually all of the H^+ and Ac^- must shift to the left to lower their concentrations and make HAc. You would come to the same conclusion if we place Q and K in a ratio.

$$\frac{Q}{K}=\frac{1}{1.8\times10^{-5}}=\frac{55{,}556}{1}\Rightarrow\frac{[\text{Products}]}{[\text{Reactants}]}$$

This value, 55,556, has the same meaning as the comparisons made previously with Q alone. This equilibrium has too much product, not enough reactant, and must shift to the left (toward the reactant side of the equilibrium) to compensate. There are three possible values for the Q/K ratio,

$\frac{Q}{K}>1$ The equilibrium shifts to the left

$\frac{Q}{K}=1$ $Q=K \therefore$ the system is at equilibrium

$\frac{Q}{K}<1$ The equilibrium shifts to the right

Perhaps an example might help. Suppose a solution is made so that the concentration of HAc = 1.2 *M*, NaAc = 1.5×10^{-2} *M*, and HCl = 2.4×10^{-3} *M*. If the equilibrium constant, K_a, is equal to $1.8\text{x}10^{-5}$, which direction must the reaction go to achieve equilibrium? You should start by writing the equilibrium reaction,

$$\text{HAc} \leftrightarrows \text{H}^+ + \text{Ac}^-$$

The Q for this reaction is,

$$Q=\frac{[\text{H}^+][\text{Ac}^-]}{[\text{HAc}]}=\frac{[2.4\times10^{-3}M][1.5\times10^{-2}M]}{[1.2\ M]}=\ 3\times10^{-5}$$

Therefore,

$$\frac{Q}{K}=\frac{3\times10^{-5}}{1.8\times10^{-5}}=\ 1.67>0 \text{ so the equilibrium shifts to the left}$$

Solving Equilibriums: Acids

The most common equilibriums occur with acids and bases. These equilibriums are used to solve for the pH of an equilibrium system or to determine the composition of a system of known pH. Using these methods we can create solutions of any given pH. This is particularly important in biology where living systems live in a narrow range of pH. Students should learn how to make buffer solutions, which are solutions that resist changes in pH. These solutions are used to preserve and protect biological systems and are commonly used in chemistry to aid in ion separations and control the shape and function of organic molecules.

When a weak acid is added to water it partially dissociates. The pH of the resulting solution depends on the concentration of the acid and the size of its dissociation constant. For example, lets determine the pH of a 1 M Acetic acid solution. We begin by writing the equilibrium,

$$\mathrm{HAc} \leftrightarrows \mathrm{H^+} + \mathrm{Ac^-} \qquad K_a = 1.8\times10^{-5}$$

Initially, the acetic acid (HAc) is 1 M but, in order to establish its equilibrium, some of it must dissociate. The amount that dissociates is unknown but can be calculated. We will let the amount that dissociates be equal to x.

$$\begin{array}{ccccc} \mathrm{HAc} & \leftrightarrows & \mathrm{H^+} & + & \mathrm{Ac^-} \\ 1\mathrm{M}-x & & x & & x \end{array}$$

For every HAc that dissociates, one H^+ and one Ac^- is made so each of these has a value of x also. Placing these values into the equilibrium expression we have,

$$\frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{HAc}]} = \frac{[x][x]}{[1M - x]} = 1.8\times10^{-5}$$

This equilibrium can be put into quadratic form and then solved using the quadratic formula,

$$x^2 + 1.8\times10^{-5}\,x - 1.8\times10^{-5} = 0$$

$$ax^2 \quad + \quad bx \quad + \quad c \quad = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} = \frac{-(1.8\text{x}10^{-5}) \pm \sqrt{(1.8\text{x}10^{-5})^2 - 4(1)(1.8\text{x}10^{-5})}}{2(1)} = 4.23\times10^{-3}\,M$$

Fortunately, we rarely have to use the quadratic formula to solve these equilibriums. We can use a simplifying assumption. If we assume that x is small compared to 1 M HAc, then [1 *M* – x] ≈ [1 *M*], so that,

$$\frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{HAc}]} = \frac{[x][x]}{[1M - x]} \approx \frac{[x][x]}{[1M]} = 1.8 \times 10^{-5}$$

Under these conditions we find that $x = 4.24\times10^{-3}$ *M*. This simplifying assumption has added a very small error into our calculation but has greatly simplified the solution since we no longer need the quadratic formula to solve the equilibrium. Since x equals the concentration of Ac^- and H^+, we can calculate the pH of this solution from our answer,

$$\mathrm{pH} = -\log[\mathrm{H^+}] = -\log[4.24\times10^{-3}\ M\ \mathrm{H^+}] = 2.37$$

ICE Tables

To organize our understanding of equilibriums and help solve them, it can be helpful to use ICE tables. ICE is a simple acronym for the titles of the first column of the table.

- I stands for the initial concentrations given in the problem.
- C stands for the change in concentration. This is the concentration change needed to get the reaction to equilibrium.
- E is for the concentration when the reaction is at equilibrium. It is the sum of the initial and change rows.

For example, consider the following problem.

What is the pH of a solution that is 0.150 M HF and 0.200 M NaF? The Ka for HF is $6.76\text{x}10^{-4}$.

The equilibrium is, $HF \leftrightarrows H^+ + F^-$ so we have three ingredients,

Reaction	**HF**	**H^+**	**F^-**
I (initial)	0.150 *M*	0 *M*	0.200 *M*
C (change)	-x	+x	+x
E (equilibrium)	0.150 – x *M*	x *M*	0.200 + x *M*

We begin by putting the INITIAL concentrations of ingredients in the appropriate box of our ICE table. Now, we have a missing ingredient, H^+, so the equilibrium must shift to make some. Its source is HF, so HF dissociates to makes some H^+. We let the amount of HF that dissociates be equal to x and since every HF that dissociates makes one H^+ and one F^-, each of these is x also. So the HF concentration goes down (-x), some H+ is made (+x), and some additional F- is made (+x). We place these values into the CHANGE row of our ICE table. At equilibrium the new concentration for each component in the equilibrium will be the sum of the initial concentration and the amount of change, so the first two entries in each column are summed and placed into the EQUILIBRIUM row of our ICE table.

Placing this information into our equilibrium expression we have,

$$\frac{[H^+][F^-]}{[HF]} = \frac{[x][0.200 + x]}{[0.150 - x]} \approx \frac{[x][0.200]}{[0.150]} = 6.76 \times 10^{-4}$$

$$x = 5.07\text{x}10^{-4}\ \text{M}\ H^+ \quad \text{pH} = -\log[5.07\text{x}10^{-4}\ \text{M}\ H^+] = 3.29$$

To solve this equilibrium we used another simplifying assumption, we assumed that the amount of H^+ made was so small that it did not significantly change the amount of HF or F^- present in our initial solution. We ignored the value of x as a contributor to the existing concentration. This greatly simplifies our math by not requiring the use of the quadratic formula and the error introduced is small.

MICE Tables

Thus far, we have solved equilibriums that are convenient and easy. These equilibriums were given a set of initial ingredients that allowed us to solve them using a simplifying assumption that x was small and could be ignored. Unfortunately, this will not always be the case. There is something more that a trained chemist sees in these problems that is rarely related to students. We are looking at the Q/K values for each of these equilibriums.

$$Q = \frac{[H^+][Ac^-]}{[HAc]} = \frac{[0\ M][0\ M]}{[1M]} = 0$$

$$Q = \frac{[H^+][F^-]}{[HF]} = \frac{[0\ M][0.200\ M]}{[0.150\ M]} = 0$$

In both cases, regardless of the value of K, Q/K < 1 so the equilibrium shifts to the right. In addition, each of these equilibriums has a small equilibrium constant,

$$\frac{[\mathrm{H^+}][\mathrm{Ac^-}]}{[\mathrm{HAc}]} = \frac{[\mathrm{Products}]}{[\mathrm{Reactants}]} = \frac{1.8 \times 10^{-5}}{1}$$

$$\frac{[\mathrm{H^+}][\mathrm{F^-}]}{[\mathrm{HF}]} = \frac{[\mathrm{Products}]}{[\mathrm{Reactants}]} = \frac{6.76 \times 10^{-4}}{1}$$

In both cases, the products have a much smaller overall concentration than the reactants. If one or more product is missing then the reaction does not have to shift very much to make the missing product. This means that the x value in our ICE table will be small and can generally be ignored. This is the perfect setup for solving equilibriums. So, when a chemist sees that the equilibrium constant is small, and the missing ingredient is a product, they are happy because the equilibrium can be quickly and easily solved. Such was the case in the two previous examples. Both of them had one or more missing products, very small equilibrium constants, and were solved by ignoring x.

So, what happens if the equilibrium is small and a reactant is missing? A chemist sees the problem this way, assume that we have some acid called HA whose equilibrium constant is small, say Ka = $1\text{x}10^{-6}$

$$\mathrm{HA} \leftrightarrows \mathrm{H^+} + \mathrm{A^-}$$

The equilibrium expression would be,

$$\frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{[\mathrm{Products}]}{[\mathrm{Reactants}]} = \frac{1x10^{-6}}{1}$$

But, the reactant, HA has no concentration, so,

$$\frac{[\mathrm{H^+}][\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{[\mathrm{H^+}][\mathrm{A^-}]}{[0\ \mathrm{M}]} = \infty\ (infinity)$$

In this case, regardless of the value of K, Q/K >> 1 so the reaction must go toward the left (toward the products). Of course, we already knew this. Any time we have a missing ingredient an equilibrium must shift to make it. But this shift is different. As given, the concentration of the reactant is low (in fact, it is zero) but according to the equilibrium constant, the products are supposed to be low. If anything, the products should be so low in concentration they should be nearly zero. In order to achieve this condition the equilibrium would not only have to shift to the left (toward the reactants), it would have to shift nearly all of the product over to the reactant side leaving very little product on the right. If this were an ICE table, the x value in the CHANGE box would have to nearly as large as the INITIAL concentrations. In other words, x would not be small and could not be ignored. If nothing were done to fix this problem, we would have to use the quadratic equation to solve for the value of x. Fortunately for us, we will not have to resort to the use of the quadratic equation. We can solve this problem in other ways.

Problem 12.5

Let's see what happens when we solve an equilibrium using the methods shown in previous examples where a reactant is missing and the equilibrium constant is small. Consider the following acid dissociation,

$$HCN \leftrightarrows H^+ + CN^- \quad K_a = 5.8\times10^{-10}$$

What is the concentration of HCN in a solution that is initially 0.20 M HCl and 0.60 M NaCN?

Reaction	HCN	H^+	CN^-
I (initial)	0 *M*	0.20 *M*	0.60 *M*
C (change)	+x	-x	-x
E (equilibrium)	x *M*	0.20 - x *M*	0.60 - x *M*

Putting these values into the equilibrium,

$$\frac{[H^+][CN^-]}{[HCN]} = \frac{[0.20 - x][0.60 - x]}{[x]} \approx \frac{[0.20][0.60]}{[x]} = 5.8 \times 10^{-10}$$

$$x = [HCN] = 206{,}896{,}551.7 \text{ M}$$

Obviously, this cannot be correct. The error was the assumption that x is small.

A chemist knows that the easiest way to solve an equilibrium with a small equilibrium constant is to set up the conditions so that one or more of the products have zero concentration. In that way, the reactant need only dissociate a tiny amount to make enough product to come to equilibrium. This means that x would be small, can be ignored, and the equations easily solved.

Let's consider the problem presented in 12.5. We discovered that the problem with this solution was in the assumption that x was small. In this case, x is not small so most of the product must move to the reactant side in order to establish the equilibrium. Since this must be true, why don't we help by moving the entire reaction to the reactant side as far as possible? This will make one of the products zero concentration and allow us to solve this equilibrium more easily.

$$HCN \leftrightarrows H^+ + CN^- \quad K_a = 5.8\times10^{-10}$$

What is the concentration of HCN and the pH of a solution that is initially 0.20 M HCl and 0.60 M NaCN?

Reaction	**HCN**	**H^+**	**CN^-**
M (move) ←	0 *M*	0.20 *M*	0.60 *M*
	+ 0.20 *M*	- 0.20 *M*	- 0.20 *M*
I (initial)	0.20 *M*	0.0 *M*	0.40 *M*
C (change)	-x	+x	+x
E (equilibrium)	0.20 - x *M*	x *M*	0.40 + x *M*

Putting these values into the equilibrium,

$$\frac{[H^+][CN^-]}{[HCN]} = \frac{[x\ M][0.40 + x\ M]}{[0.20 - x\ M]} \approx \frac{[x\ M][0.40\ M]}{[0.20\ M]} = 5.8\times10^{-10}$$

$$x = [H^+] = 2.9\times10^{-10}\ M \qquad pH = 9.54$$

Since we are ignoring the small contribution of x, the [HCN] = 0.20 M.

You will notice that in the previous example the equilibrium constant is very small ($K_a = 5.8\times10^{-10}$). This tells us that the ingredients on the right side of the reaction must be very small. We use this observation to help us solve the equilibrium by making the ingredients on the small side (product side) as small as possible, that is, zero concentration by moving everything as far to the left as possible. We then allow the equilibrium to become established and solve the equilibrium like all the others, by assuming that x is small.

Solving Equilibriums: Bases

Although a base equilibrium is somewhat different from an acid, base equilibriums are solved exactly the same way as an acid. What makes base reactions different is that they occur when the conjugate base of a weak acid is added to water. For example, the conjugate base of acetic acid (HAc) is the acetate ion (Ac^-). When sodium acetate is added to water, the sodium acetate dissolves and the acetate ion reacts with water in a reaction called a hydrolysis (literally hydro = water and lysis = to break down). Hydrolysis breaks water down into its two component parts, an H^+ and an OH^-, and the acetate ion reacts with the H^+ to produce acetic acid according to the following reaction,

$$Ac^- + H_2O \leftrightarrows HAc + OH^-$$

The resulting solution is basic. Bases are most often formed when weak acids are neutralized with strong bases. Consider the neutralization reaction between acetic acid and sodium hydroxide,

$$HAc + NaOH \rightarrow NaAc + H_2O$$

The resulting solution contains sodium acetate (NaAc) and water. We already showed that adding sodium acetate to water produces a hydrolysis reaction that makes the solution basic. So the result of the neutralization between a weak acid and strong base is a solution that is basic.

It is important to note that the term "neutralization" does not mean that the resulting solution is pH = 7. Neutralization occurs when equal amounts of acid and base have been added together. The resulting solution could be acidic, basic, or neutral depending on the acid and bases used. The following table outlines all possible combination of acids and bases and the pH of the resulting solution.

Acid	**Base**	**pH of resulting solution**
Strong	Strong	pH = 7 (neutral)
Weak	Strong	pH > 7 (basic)
Strong	Weak	pH < 7 (acidic)
Weak	Weak	The weakest one determines the pH

The equilibriums of acids and their conjugate bases are related to one another. Consider the acid dissociation of a generic acid, HA, and its conjugate base, A^-,

$$\begin{array}{lcl}
\text{Acid:} & \cancel{HA} \leftrightarrows H^+ + \cancel{A^-} & K_a \\
\text{Base:} & \cancel{A^-} + H_2O \leftrightarrows \cancel{HA} + OH^- & K_b \\
\hline
 & H_2O \leftrightarrows H^+ + OH^- & K_a \cdot K_b = K_w
\end{array}$$

When two equilibriums are added, the equilibrium constants are multiplied together. When we add these two reactions we also see that the HA and the A- will cancel leaving us with just the water dissociation reaction. Using the relationship, $K_a \cdot K_b = K_w = 1x10^{-14}$, we can quickly calculate the K_b for the hydrolysis of the conjugate base if the K_a is known ($K_b = K_w/K_a$).

Let's do an example of a base calculation. Sodium benzoate (NaBenz) is the conjugate base of benzoic acid (HBenz) and is commonly used a preservative in foods. What is the pH of 0.100 M NaBenz if the K_a for HBenz is $4.5x10^{-5}$? To solve this we need to know the hydrolysis reaction for sodium benzoate and the K_b for the reaction. The hydrolysis for sodium benzoate is,

$$Benz^- + H_2O \leftrightarrows HBenz + OH^-$$

And the K_b for this reaction is,

$$K_b = \frac{K_w}{K_a} = \frac{1\times10^{-14}}{4.5\times10^{-5}} = 2.22\times10^{-10}$$

Using the standard ICE table, we can solve this equilibrium and calculate the pH.

Reaction	$Benz^-$	HBenz	OH^-
I (initial)	0.100 *M*	0 *M*	0 *M*
C (change)	-x	+x	+x
E (equilibrium)	0.100 - x *M*	x *M*	x *M*

Putting these values into the equilibrium,

$$\frac{[HBenz][OH^-]}{[Benz^-]} = \frac{[x\,M][\,x\,M]}{[0.100 - x\,M]} \approx \frac{[x\,M]^2}{[0.100\,M]} = 2.22\times10^{-10}$$

$$x = [OH^-] = 4.71\times10^{-6}\,M \qquad pH = 14 + \log[4.71\times10^{-6}\,M] = 8.67$$

Large Equilibrium Constants

Before we move on to other topics, we should consider what happens when an equilibrium constant is very large. We don't run into many of these but it is certainly possible that we could. If the equilibrium constant is large, then we would do the opposite of what we did when it was small and, if possible, shift the reaction as far to the right as possible.

A common air pollutant, ozone (O_3), is known to be equilibrium with O_2 according the following reaction,

$$2\ O_3(g) \leftrightarrows 3\ O_2(g)$$

At 25°C the K_{eq} for this reaction is known to be $1.8 x 10^{57}$. If $[O_3]$ is 1.20 M, what is the concentration of O_2?

Since the equilibrium constant is large, the product side of this equilibrium should have a large concentration while the reactant side should be small. Since we were given a concentration for the reactant and no concentration for the product we need to move the equilibrium as far as possible to the product side.

Reaction	**O_3(g)**	**O_2(g)**
M (move) →	1.20 *M*	0.0 *M*
	- 1.20 *M*	+ 1.80 *M**
I (initial)	0.0 *M*	1.80 *M*
C (change)	+x	-x
E (equilibrium)	x *M*	1.80 - x *M*

*Note that the stoichiometry demands that there be a 2:3 relationship between O_3 and O_2, so 1.20 *M* O_3 will make 1.80 *M* O_2.

Putting these values into the equilibrium,

$$\frac{[O_2]^3}{[O_3]^2} = \frac{[1.80\ -\ x\ M]^3}{[x\ M]^2} \approx \frac{[1.80\ M]^3}{[x\ M]^2} = 1.8\times10^{57}$$

$$x = [O_3(g)] = 5.69\times10^{-29}\ M \text{ and } [O_2(g)] = 1.8\ M$$

Based on this result we can conclude that ozone is unstable and will nearly completely convert to oxygen. What we may not say is that this reaction occurs fast. Knowing that an equilibrium lies "far to the right" is not the same as saying that it gets their fast. Without rate law data, we don't know how long it would take for this system to achieve equilibrium.

Problem 12.6

Nitrous acid (HNO_2) is a weak acid with a $K_a = 4.6\text{x}10^{-4}$. What is the pH of a solution whose initial composition is 1.2 M HNO_2, 0.8 M $NaNO_2$, and 0.6 M HCl?

$$HNO_2 \leftrightarrows H^+ + NO_2^- \quad K_a = 4.6\times10^{-4}$$

In this case, the equilibrium is small and all ingredients have a concentration. To solve the equilibrium we should make the products as small as possible by moving the reaction as far to the left as possible.

Reaction	HNO_2	H^+	NO_2^-
M (move) ←	1.2 *M*	0.6 *M*	0.8 *M*
	+0.6 *M*	-0.6 *M*	-0.6 *M*
I (initial)	1.8 *M*	0.0 *M*	0.20 *M*
C (change)	-x	+x	+x
E (equilibrium)	1.8 - x *M*	x *M*	0.20 + x *M*

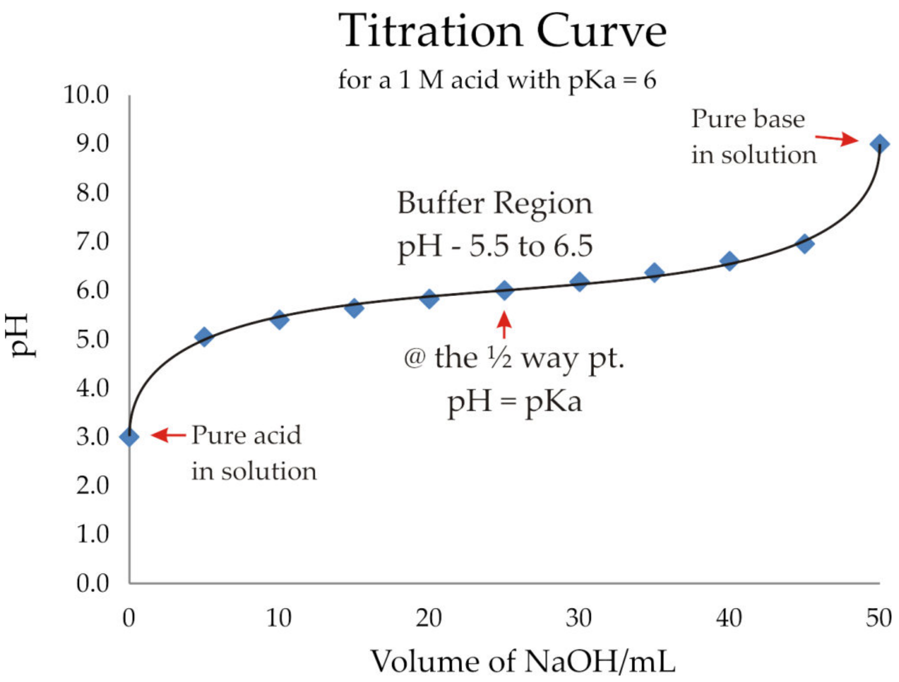
Putting these values into the equilibrium,

$$\frac{[H^+][NO_2^-]}{[HNO_2]} = \frac{[x\text{ M}][0.20 + x\text{ M}]}{[1.8 - x\text{ M}]} \approx \frac{[x\text{ M}][0.20\text{ M}]}{[1.8\text{ M}]} = 4.6\times10^{-4}$$

$$x = [H^+] = 4.14\times10^{-4}\text{ M} \qquad pH = 3.38$$

Titrating an Acid

When a weak acid is put into water, the acid partially dissociates which makes the solution slightly acidic. As the acid is titrated with NaOH, it is neutralized and makes its conjugate base. This base makes the solution more basic so the pH of the solution rises. This rise is not linear; it is curved, with a somewhat flat area in the center known as the buffer region. Eventually, all of the acid is neutralized so that all that remains in solution is the conjugate base. This base hydrolyzes with the water and this makes the solution basic. A typical titration curve is shown below.



There are a number of features of this curve that warrant discussion but they can be broken down into three parts, initial pH, final pH and all the pH's in between. Even so, the first step in drawing a titration curve is figuring out how much NaOH must be added to completely neutralize the acid. This calculation will help us later on when we want to know the final pH and will help us to know where we are when we calculate the pH at other points along the titration curve.

The Amount of NaOH Needed

This calculation should not require much explanation. As with all titrations, an acid is neutralized when the moles of acid equal the moles of added base. Mathematically, we will use a familiar equation,

$$M_1V_1 = M_2V_2$$

We can modify this equation slightly by changing the subscripts to be more descriptive of the titration process,

$$M_{H+}V_{H+} = M_{OH-}V_{OH-}$$

If the molarity and volume of the acid are known along with the molarity of the base, then this equation can be rearranged to solve for the volume of base needed to titrate the acid.

$$\frac{M_{H+}V_{H+}}{M_{OH-}} = V_{OH-}$$

This equation should be familiar to you, but there is an important detail that must be explained. This calculation gives you the volume of base (typically, NaOH) needed to titrate each H^+ in the acid. If the acid is diprotic (has two H^+'s) then you would multiply by two, or if the acid were triprotic (has three H^+'s), you would multiply by three. These values give you the total volume needed to neutralize the acid but they also tell you how much base must be added for each of the H^+'s present in the acid. This allows you to break up the titration curve into sections, one section for each H^+, and know where you are along the titration curve after the addition of any given amount of base.

Problem 12.7

How much 0.25 M NaOH must be added to 50.0 mL of 0.60 M H_2A to completely neutralize the acid? How much NaOH must be added to remove the first H^+? How much NaOH must be added to remove the second H^+?

We begin by using the equation,

$$M_{H+}V_{H+} = M_{OH-}V_{OH-}$$

$$(0.60\ M\ H_2A)\ (0.050\ L) = (0.25\ M\ NaOH)\ (V_{OH-})$$

$$V_{OH-} = 0.12\ L\ NaOH\ or\ 120.0\ mL\ NaOH$$

The acid being neutralized is a diprotic acid (there are two H^+'s in H_2A) so we will need 120 mL of NaOH to neutralize the first H^+ and an additional 120 mL of NaOH to neutralize the second H^+. Therefore, we will need a total of 240 mL NaOH to completely neutralize all of the H^+'s in this acid. Because there are two H^+'s present in this acid, the titration curve will have two sections. These sections, or regions, will become important later.

The Initial pH

The initial pH of any titration curve requires solving for the pH when the pure acid has been put into water and before any titration has been done. If this were an ICE table and the initial concentration of the acid was [HA], then the table would look like this,

Reaction	HA	H+	A-
I (initial)	[HA]	0 *M*	0 *M*
C (change)	-x	+x	+x
E (equilibrium)	[HA] - x	x	x

Putting these values into the equilibrium would require solving the following equation for x,

$$\frac{[H^+][A^-]}{[HA]} = \frac{[x][x]}{[HA - x]} \approx \frac{[x]^2}{[HA]} = K_a$$

Since all acids dissociate when dissolved in water, this equation becomes a general expression for the initial dissociation of acids and should be used to calculate the $[H^+]$ and the pH of the solution.

$$[H^+] = \sqrt{K_a\,[HA]} \;\Rightarrow\; pH = -\log[H^+]$$

The Final Endpoint

At the final endpoint of the titration, all of the acid (HA) has been neutralized and only this acid's conjugate base (A^-) remains in solution. Weak bases undergo hydrolysis according to the following reaction,

$$A^- + H_2O \leftrightarrows HA + OH^-$$

If we want to calculate the pH of this solution we need to know the concentration of the conjugate base $[A^-]$ and the K_b for the reaction. Generally, neither of these values are given to you in the problem, but you will be given enough information to find both of them.

Let's start by calculating the concentration of the conjugate base $[A^-]$. By definition, the concentration of the conjugate base will be the moles of conjugate base divided by the total volume of solution. So we need to know two things, the moles of conjugate base and the total volume of solution.

When one mole of acid is neutralized, one mole of conjugate base is produced. There is a 1:1 relationship between the moles of acid and the moles of conjugate base. So, if we know the moles of acid we were given, we also know the moles of conjugate base produced (they are the same). To calculate the moles of conjugate base we would do the following calculation,

$$\text{moles of acid} = \text{moles of conjugate base}$$
$$\text{moles of acid} = M_{acid}V_{acid} = \text{moles of conjugate base}$$

With the moles of base in hand, we turn our attention to the volume. This is where our initial volume calculation comes in handy. We have already calculated the total volume of base needed to neutralize our acid and we know the initial volume of acid that we titrated. The total volume is just the sum of these two numbers,

$$\text{Total volume} = \text{Volume of Acid} + \text{Volume of added base}$$

So, the molarity of the conjugate base would be,

$$\text{Molarity of Conjugate Base} = [A^-] = \frac{\text{moles of conjugate base}}{\text{total volume}} = \frac{\text{moles of acid}}{\text{vol. acid+vol. base}}$$

Now that we know the concentration of conjugate base, we need to the equilibrium constant for the reaction. Usually, this is not given to you. Normally, you would be given the acid dissociation constant, K_a. Fortunately, there is a simple relationship between the K_a and K_b for a reaction, and that is,

$$K_a \cdot K_b = K_w$$

Using this relationship we can solve for the Kb and now we have all the information we need to determine the pH of this base solution. We can now proceed to our ICE table. Based on our hydrolysis reaction,

$$A^- + H_2O \leftrightarrows HA + OH^-$$

We would fill in our ICE table.

Reaction	A-	HA	OH-
I (initial)	$[A^-]$	0 *M*	0 *M*
C (change)	-x	+x	+x
E (equilibrium)	$[A^-]$ - x	x	x

Putting these values into the equilibrium would require solving the following equation for x,

$$\frac{[HA][OH^-]}{[A^-]} = \frac{[x][x]}{[A^- - x]} \approx \frac{[x]^2}{[A^-]} = \frac{K_w}{K_a} = K_b$$

Solving for the value of x yields a value for $[OH^-]$ from which pH can be calculated,

$$[OH^-] = \sqrt{K_b\,[A^-]} \;\Rightarrow\; pH = 14 + \log[OH^-]$$

Problem 12.8

Calculate the pH at the endpoint of the titration of 50 mL of 0.6 *M* acetic acid (HAc) with 1.0 *M* NaOH. $K_a = 1.8\text{x}10^{-5}$ for acetic acid.

Answer

Begin by calculating the volume of NaOH needed to completely neutralize the acetic acid.

$$M_{H+}V_{H+} = M_{OH-}V_{OH-}$$

$$(0.60\ M\ \text{HAc})\ (0.050\ \text{L}) = (1.0\ M\ \text{NaOH})\ (V_{OH-})$$

$$V_{OH-} = 0.030\ \text{L NaOH or } 30.0\ \text{mL NaOH}$$

The total volume of solution at the endpoint would be,

Total volume = vol. acid + vol. base = 0.050 L HAc + 0.030 L NaOH = 0.080 L

The number of moles of conjugate base = moles of initial acetic acid

$$\text{Moles HAc} = M_{HAc}V_{HAc} = (0.60\ \text{M})\ (0.050\text{L}) = 0.030\ \text{moles Ac}^-$$

The molarity of the conjugate base at the end of the titration is,

$$[Ac^-] = \frac{\text{moles Ac}^-}{\text{liters of solution}} = \frac{0.030\ \text{mole Ac}^-}{0.080\ \text{L}} = 0.375\ \text{M Ac}^-$$

Filling in our ICE table,

Reaction	Ac-	HAc	OH-
I (initial)	0.375 *M*	0 *M*	0 *M*
C (change)	-x	+x	+x
E (equilibrium)	0.375 - x M	x M	x M

Putting these values into the equilibrium would require solving the following equation for x,

$$\frac{[\mathrm{HAc}][\mathrm{OH}^-]}{[\mathrm{Ac}^-]} = \frac{[\mathrm{x}][\mathrm{x}]}{[0.375 - \mathrm{x}]} = \mathrm{K_b} = \frac{\mathrm{K_w}}{\mathrm{K_a}} = \frac{1\times10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10}$$

$$\frac{[\mathrm{x}][\mathrm{x}]}{[0.375 - \mathrm{x}]} \approx \frac{[\mathrm{x}]^2}{[0.375]} = 5.56\times10^{-10}$$

Solving for the value of x yields a value for [OH$^-$] from which pH can be calculated,

$$[\mathrm{OH}^-] = \sqrt{5.56\times10^{-10}\,[0.375]} = 1.44\times10^{-5}\ M$$

$$\mathrm{pH} = 14 + \log[1.44\times10^{-5}\ M] = 9.16$$

The pH's in Between: The Henderson-Hasselbach Equation

To solve the equilibrium for the pH values between the initial and final endpoints using the methods described thus far can be tedious. Fortunately, there is a simpler way to calculate these pH values and that is by using the Henderson-Hasselbach equation (H-H equation). Before we derive the H-H equation, let's consider the standard ICE table method for solving these equilibriums. Doing so will teach us something about why the H-H equation works.

Suppose we have an acid called HA and we have partially titrated it so that some of the HA has been neutralized and some A- has been made. The equilibrium reaction would look like this,

$$HA \leftrightarrows H^+ + A^-$$

Regardless of the actual concentrations of HA and A^-, an ICE table would be set up that looked like this,

Reaction	HA	H^+	A^-
I (initial)	[HA]	0 *M*	$[A^-]$
C (change)	-x	+x	+x
E (equilibrium)	[HA] - x	x	$[A^-]$ + x

When we put these values into an equilibrium, we would do the following,

$$\frac{[H^+][A^-]}{[HA]} = \frac{[x][A^- - x]}{[HA + x]} \approx \frac{[x][A^-]}{[HA]} = K_a$$

Since x is assumed to be small, it is ignored, so the concentrations of HA and A^- are assumed to remain unchanged which makes this equilibrium very easy to solve for pH. The H-H equation begins where this equilibrium leaves off and makes it even easier to solve for pH.

Let's begin by making our simplified equilibrium more generic. Let's call the [HA] = "Acid" or just "A" and the [A-] = "Base" or just "B." Also, let's substitute x = $[H^+]$. Doing this our equilibrium remains pretty much the same,

$$\frac{[x][A^-]}{[HA]} = \frac{[H^+][B]}{[A]} = K_a$$

If we take the $-\log_{10}$ of both sides of this equation we get,

$$-\log_{10}\left[\frac{[H^+][B]}{[A]}\right] = -\log_{10}(K_a)$$

The properties of logs allows us to separate the H+ from the rest of the terms,

$$-\log_{10}[H^+] - \log_{10}\frac{[B]}{[A]} = -\log_{10}(K_a)$$

Rearranging, we get,

$$-\log_{10}[H^{+}] = -\log_{10}(K_a) + \log_{10}\frac{[B]}{[A]}$$

By definition, $-\log_{10}[H^{+}] = pH$ and $-\log_{10}(K_a) = pK_a$. Making these substitutions (and dropping the need to show $\log_{10}$) we get the Henderson-Hasselbach equation,

$$pH = pK_a + \log\frac{[B]}{[A]}$$

Just like the solution to our standard ICE table, this equation assumes that x is small but it allows us to calculate the pH of a solution very quickly so using it is the preferred method of solving for points in a titration curve, although an ICE table calculation would give you the same answer. This equation cannot be used to solve for the pH at the initial or final points in a titration curve. To use this equation we must have an initial value for both A and B. At the initial and final points in a titration curve, we only have a value for one of them so this equation cannot be used.

It is important to note an important aspect of the H-H equation. Because both the acid and base are present in the same solution, they share the same volume, as a consequence, the volume term in their concentrations cancel and we are left with a ratio of their moles. So the H-H equation could have been just as easily written as,

$$pH = pK_a + \log\frac{\text{moles of B}}{\text{moles of A}}$$

In fact, this is the most common version of the H-H equation and is the version we will use.

Problem 12.9

Calculate the pH of a solution that is made by adding 50 mL of 0.2 M HCN to 75 mL of 0.3 M NaCN. $K_a = 5.8\times10^{-10}$

Answer

Begin by calculating the moles of HCN and NaCN.

$$\text{Moles HCN} = (0.2\text{ M HCN})\ (0.050\text{ L}) = 0.010\text{ mole HCN}$$
$$\text{Moles NaCN} = (0.3\text{ M NaCN})\ (0.075\text{ L}) = 0.0225\text{ mole NaCN}$$

Calculate the pKa,

$$\text{pKa} = -\log(\text{Ka}) = -\log(5.8\text{x}10^{-10}) = 9.24$$

Use the H-H equation to solve for pH,

$$\text{pH} = 9.24 + \log\left(\frac{0.0225\text{ mole CN}^-}{0.010\text{ mole HCN}}\right) = 9.59$$

Using the H-H Equation to Draw Titration Curves

Even though the H-H equation makes it easier to calculate the pH of solutions, there is still some work that needs to be done to calculate the pH's along a titration curve. Typically, NaOH is used to titrate the acid. This is convenient because one mole of NaOH will neutralize one mole of acid. Consider the following neutralization reaction,

$$\text{HF} + \text{NaOH} \rightarrow \text{NaF} + \text{H}_2\text{O}$$

For every NaOH added, one HF is neutralized and one NaF is produced. In terms of the H-H equation, this would look like,

$$\text{pH} = \text{pK}_\text{a} + \log\left(\frac{\text{mol base}}{\text{mol acid} - \text{mol base}}\right)$$

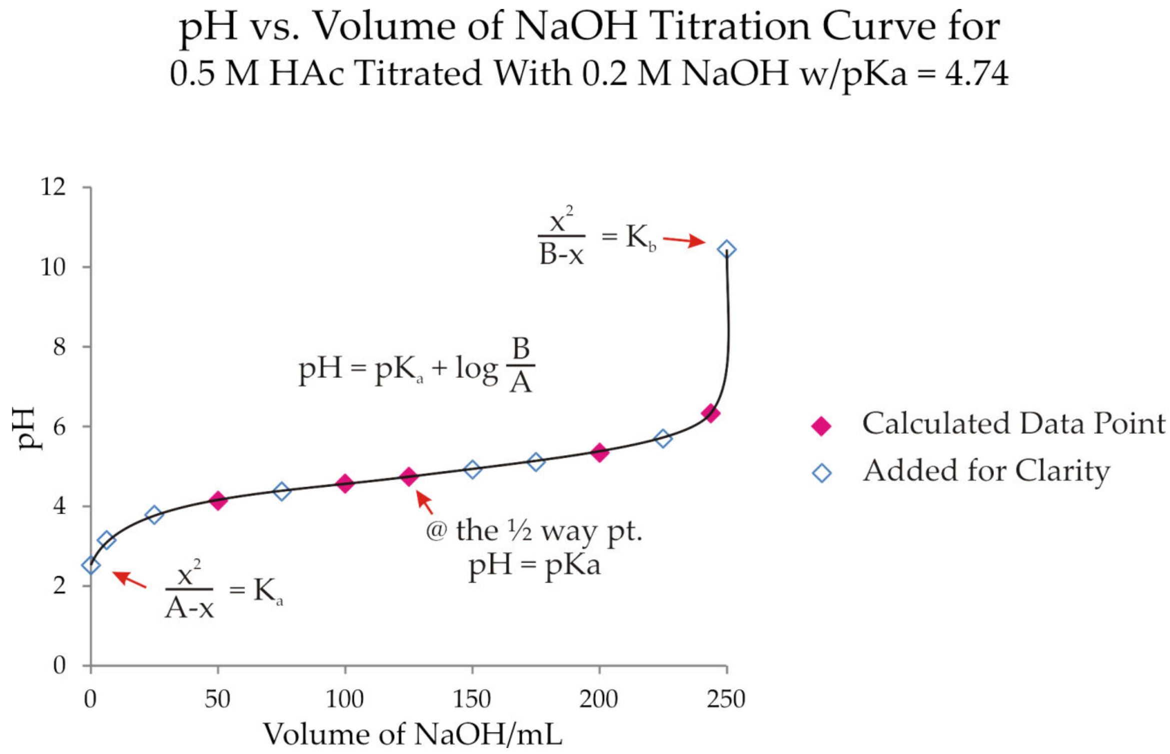
If A = moles of acid and x = moles of added NaOH then we would write,

$$\text{pH} = \text{pK}_\text{a} + \log\left(\frac{\text{x}}{\text{A} - \text{x}}\right)$$

During a titration, the value of A never changes, but as more NaOH is added to the solution, the value of x changes and so does the pH. This can be readily seen in the following table.

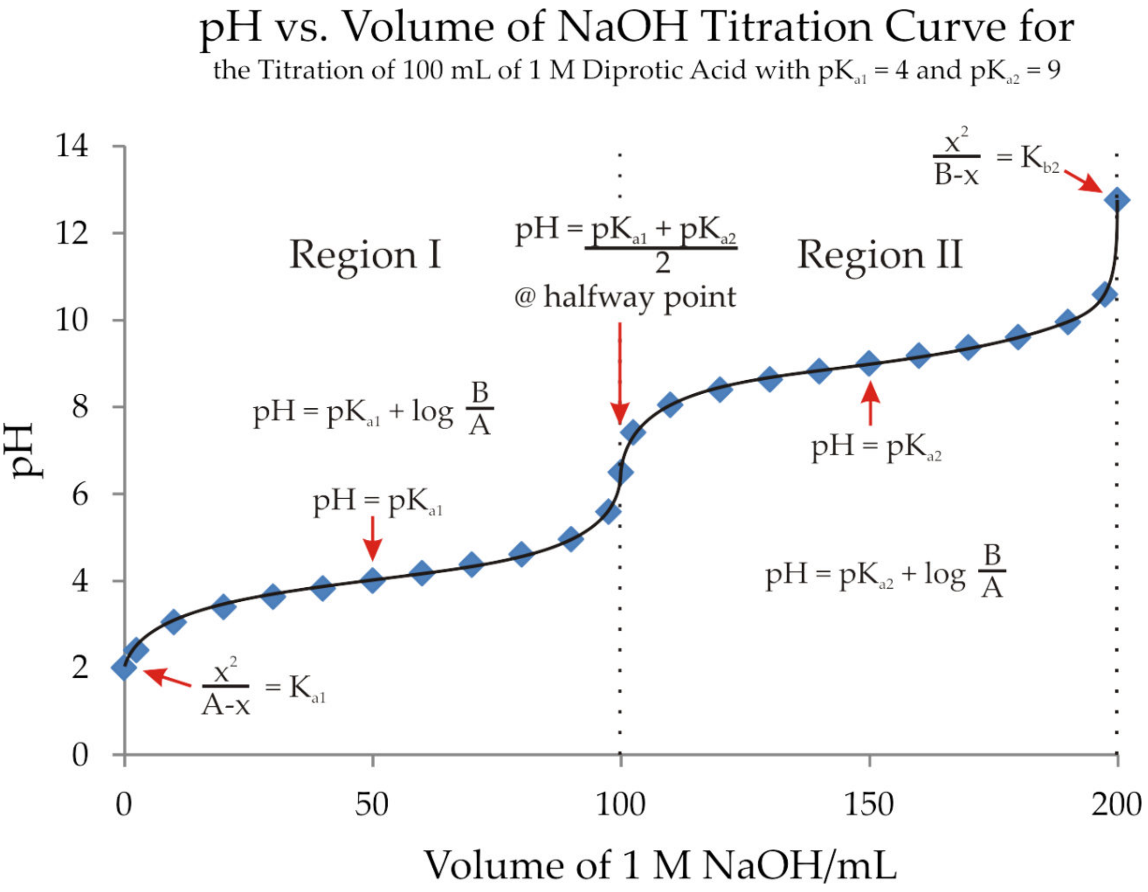
Titration of 100 mL of 0.5 M HAc with various volumes of 0.2 M NaOH pKa of HAc = 4.74. Total volume of NaOH needed = 250 mL				
Vol of NaOH	Mol of NaOH	Mol of Acid (0.5M HAc) (0.100L) = 0.05 mol HAc	H-H - Equation	pH
0	Cannot use H-H equation on initial point. Use $\frac{[x]^2}{[A - x]} = K_a$			
50	(0.2 M) (0.050L) = 0.01 mol NaOH	0.05 mol HAc	$pH = 4.74 + \log\left(\frac{0.01}{0.05 - 0.01}\right)$	4.14
100	(0.2 M) (0.100L) = 0.02 mol NaOH	0.05 mol HAc	$pH = 4.74 + \log\left(\frac{0.02}{0.05 - 0.02}\right)$	4.56
125	(0.2 M) (0.125L) = 0.025 mol NaOH	0.05 mol HAc	$pH = 4.74 + \log\left(\frac{0.025}{0.05 - 0.025}\right)$	4.74
200	(0.2 M) (0.200L) = 0.04 mol NaOH	0.05 mol HAc	$pH = 4.74 + \log\left(\frac{0.04}{0.05 - 0.04}\right)$	5.34
225	(0.2 M) (0.225L) = 0.045 mol NaOH	0.05 mol HAc	$pH = 4.74 + \log\left(\frac{0.045}{0.05 - 0.045}\right)$	5.69
250	Cannot use H-H equation on final end point. Use $\frac{[x]^2}{[B - x]} = K_b$			

One point on the titration curve requires some comment. You will notice that the pH at the 125 mL mark is the same as the pKa. This is not by accident. At the halfway point in the titration, the moles of acid and the moles in base are equal so they cancel in the H-H equation and pH = pKa.



Titration Curves of Polyprotic Acids

Thus far we have only been concerned with monoprotic acids which are acids that have only one H^+ available for titration. There are many more acids with two or more H+'s available for titration. These are called diprotic (two H^+'s) or triprotic acids (three H^+'s) or collectively, polyprotic acids (many H^+'s). The titration curve of a polyprotic acid is not significantly different from the titration curve for the monoprotic acids we have already considered. In fact, the easiest way to think about a polyprotic acid is to simply stack two or more of our already familiar titration curves on top of each other to create a titration curve for a polyprotic acid.



This curve should look very familiar and all the points along this curve use the same equations that we have seen already, except one. The pH at the midway point of the titration is calculated using a new formula. It is,

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

Polyprotic acids have some unique features not found in simple monoprotic acids, so to understand how this equation came to be, we must explore the chemistry of polyprotic acids further.

The Chemistry of Polyprotic Acids

Polyprotic acids have more than one H^+ and because they are weak acids, these H^+'s are released one at a time. A chemist would say that these H^+'s are released stepwise, that is, first one and then the other, like going up a set of stairs. A common diprotic acid is carbonic acid (H_2CO_3). The stepwise dissociation of carbonic acid is given below,

$$H_2CO_3 \leftrightarrows H^+ + HCO_3^- \qquad K_{a1} = 4.3\times10^{-7}$$
$$HCO_3^- \leftrightarrows H^+ + CO_3^{2-} \qquad K_{a2} = 4.7\times10^{-11}$$

The nature of an equilibrium is that, if one component of an equilibrium is present, all components of all its equilibriums are also present. Therefore, a solution of H_2CO_3 will also contain H^+, HCO_3^-, and CO_3^{2-}, and because we are working in water, if H^+ is present, so is OH^-. So solutions of polyprotic acids are a complex mixture of many different molecules and ions whose concentrations are governed by the size of their respective equilibrium constants.

Initially, this may seem overwhelming. There is so much going on in solutions of polyprotic acids it would seem impossible to get a handle on the concentration of each of these ions and molecules. Fortunately, this is not the case. Most of the time, we can treat each of these equilibriums independently of the others. Putting it simply, if we are working with an equilibrium, we can ignore any of the others that come before or after. Why is this so? Let's take a look at our carbonic acid equilibrium. Let's assume that we have a 0.03 M H_2CO_3 solution and we want to know its pH. We can set up an ICE table for H_2CO_3.

Reaction	H_2CO_3	H^+	HCO_3^-
I (initial)	0.03 *M*	0 *M*	0 *M*
C (change)	-x	+x	+x
E (equilibrium)	0.03 – x *M*	x	x

Putting these values into the equilibrium we can solve for the value of x.

$$\frac{[x][x]}{[0.030 - x]} \approx \frac{[x]^2}{[0.03]} = 4.3\times10^{-7}$$

$$x = 1.14\text{x}10^{-4}\ \text{M H}^{+} \quad \text{so} \quad \text{pH} = 3.94$$

The important point here is NOT that the pH = 3.94 but that in setting up the problem we let the $[H^+] = [HCO_3^-]$ so both of them are equal to $1.14\text{x}10^{-4}$ M. Now, consider the second equilibrium for carbonic acid,

$$HCO_3^- \leftrightarrows H^+ + CO_3^{2-} \qquad K_{a2} = 4.7\times10^{-11}$$

Let's set up an ICE table for this equilibrium, but we have to remember that the initial concentration of both $[H^+]$ and $[HCO_3^-]$ were already determined in the previous calculation, so we have,

Reaction	HCO_3^-	H^+	**CO_3^{2-}**
I (initial)	1.14×10^{-4} *M*	1.14×10^{-4} *M*	0 *M*
C (change)	-x	+x	+x
E (equilibrium)	1.14×10^{-4} – x *M*	1.14×10^{-4} + x *M*	x M

When we put this data into our equilibrium, we will do the following,

$$\frac{[1.14\times10^{-4} + \text{x M}]\,[x]}{[1.14\times10^{-4} - \text{x M}]} \approx \frac{[1.14\times10^{-4}]\,[x]}{[1.14\times10^{-4}]} = x = 4.7\times10^{-11}$$

When we ignored the small contribution of x to our existing concentration of H^+ and HCO_3^- , the concentrations of H^+ and HCO_3^- cancelled, and we were left with $x = 4.7\times10^{-11}$. That alone is not important. The important point is that, by ignoring x, we are saying that the second equilibrium does not contribute any H^+ to the solution so the pH remains unchanged. The only thing that the second equilibrium did was contribute a very small amount of CO_3^{2-} in created in order to establish the second equilibrium. This contribution was so small that, compared to the concentration of ingredients in the first equilibrium, it could be ignored. So, the underlying idea of this section is that when dealing with equilibriums, we can deal with them one at a time and not be concerned about how equilibriums before or after affect our calculations.

This simplifying idea makes dealing with polyprotic acids much easier. Generally, we can deal with the equilibriums one at a time and treat them just as we would the equilibrium of monoprotic acids. There are, of course, times when both equilibriums MUST be considered. When would we have to do that? If we take another look at the carbonic acid equilibrium, we can see that the end point of the first equilibrium is the beginning point of the second (both are HCO_3^-).

$$\begin{array}{ll} H_2CO_3 \leftrightarrows H^+ + HCO_3^- & K_{a1} = 4.3\times10^{-7} \\ HCO_3^- \leftrightarrows H^+ + CO_3^{2-} & K_{a2} = 4.7\times10^{-11} \end{array}$$

At this point, both equilibriums contribute equally. If you look back at our diprotic titration curve you will see that this point in the curve is where Region I ends and Region II begins. This special place is often called the "first endpoint" in a titration curve since it occurs at the point where the first H^+ in a polyprotic acid has been completely neutralized.

The pH at the First Endpoint

In the carbonic acid equilibrium, we have two equilibriums occurring simultaneously,

$$\begin{array}{ll} H_2CO_3 \leftrightarrows H^+ + HCO_3^- & K_{a1} \\ HCO_3^- \leftrightarrows H^+ + CO_3^{2-} & K_{a2} \end{array}$$

If we are considering only HCO_3^- as our starting reactant, then the first equilibrium has been written backwards. If we reverse it, we must invert its equilibrium constant.

$$\begin{array}{ll} H^+ + HCO_3^- \leftrightarrows H_2CO_3 & 1/K_{a1} \\ HCO_3^- \leftrightarrows H^+ + CO_3^{2-} & K_{a2} \\ \hline 2\ HCO_3^- \leftrightarrows H_2CO_3 + CO_3^{2-} & K_{a2}/\ K_{a1} \end{array}$$

When we add these reactions together we must multiply the equilibrium constants. The result is the equilibrium that is occurring when pure HCO_3^- is added to water. We note that this equilibrium does not have any H^+'s in it so we cannot use it directly to calculate a pH, but we can use this equilibrium to understand what must be happening when HCO_3^- is added to water. For example, suppose we wanted to calculate the concentration of CO_3^{2-} in a 1 M $NaHCO_3$ solution (sodium bicarbonate = baking soda). To do this, we would set up an ICE table.

Reaction	2 HCO_3^-	H_2CO_3	**CO_3^{2-}**
I (initial)	1 *M*	0 *M*	0 *M*
C (change)	-2x	+x	+x
E (equilibrium)	1 – 2x *M*	x *M*	x M

First, note that it takes two HCO_3^-'s to make one H_2CO_3 and one CO_3^{2-}, therefore the "change" in our ICE table is 2x in order to make x amount of our products. We can solve this equilibrium without assuming that x is small and without using the quadratic formula.

$$\frac{[x][x]}{[1-2x]^2} = \frac{[x]^2}{[1-2x]^2} = \frac{K_{a2}}{K_{a1}} = \frac{4.7\times10^{-11}}{4.3\times10^{-7}} = 1.093\times10^{-4}$$

$$\frac{[x]^2}{[1-2x]^2} = 1.093\times10^{-4}$$

$$\frac{[x]}{[1-2x]} = \sqrt{1.093 \times 10^{-4}} = 0.01045$$

$$x = (1-2x)(0.01045)$$

$$x = 0.01045 - 0.02090x$$

$$1.02090x = 0.01045$$

$$x = \frac{0.01045}{1.02090} = 0.0102 \text{ M } CO_3^{2-} = 0.0102 \text{ M } H_2CO_3$$

The actual solution to this problem is not important. The important point is that, when the equilibrium is solved, the concentration of H_2CO_3 and CO_3^{2-} are equal to one another.

Earlier we noted that, if one part of an equilibrium is present, then all associated equilibriums are occurring simultaneously. So, while the HCO_3^- equilibrium is being established, so are the following equilibriums,

$$\begin{array}{ll} H_2CO_3 \leftrightarrows H^+ + HCO_3^- & K_{a1} \\ HCO_3^- \leftrightarrows H^+ + CO_3^{2-} & K_{a2} \\ \hline H_2CO_3 \leftrightarrows 2\ H^+ + CO_3^{2-} & K_{a1} \cdot K_{a2} \end{array}$$

The equilibrium expression for this equilibrium is,

$$\frac{[H^+]^2[CO_3^{2-}]}{[H_2CO_3]} = K_{a1} \cdot K_{a2}$$

But, we have already shown that for a solution of pure aqueous HCO_3^-, the H_2CO_3 and CO_3^{2-} concentrations are equal, so they cancel each other. This leaves us with the following relation,

$$\frac{[H^+]^2\cancel{[CO_3^{2-}]}}{\cancel{[H_2CO_3]}} = [H^+]^2 = K_{a1} \cdot K_{a2}$$

Taking the –log of both sides of this equation we get (and using the properties of logs),

$$2\left(-\log[H^+]\right) = [-\log(K_{a1})] + [-\log(K_{a2})]$$

$$2\ pH = pK_{a1} + pK_{a2}$$

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

So, at the endpoint of a multi-region titration, the pH can be determined with very little effort. This equation cannot be used at the final endpoint of any titration, but for polyprotic acids with multiple regions, this equation can be used to calculate the pH of the intermediate endpoints.

Titrating Polyprotic Acids

Titrating a polyprotic acid should not present any great challenge as long as you are aware of where you are along the titration curve. Even so, there are a couple of tricks that you will want to use to make these calculations go easier. Suppose that we want to titrate 100 mL of 0.9 M phthalic acid with 1.2 M NaOH. We will abbreviate this acid as H_2P. We may or may not be given the equilibrium reactions but we would certainly be given the Ka's for this acid. Even without the equilibrium reactions, we should be able to write them down.

$$H_2P \leftrightarrows H^+ + HP^- \qquad K_{a1} = 1.05\text{x}10^{-3}$$
$$HP^- \leftrightarrows H^+ + P^{2-} \qquad K_{a2} = 5.25\text{x}10^{-6}$$

While the order of operation is not important, two tasks should be undertaken immediately.

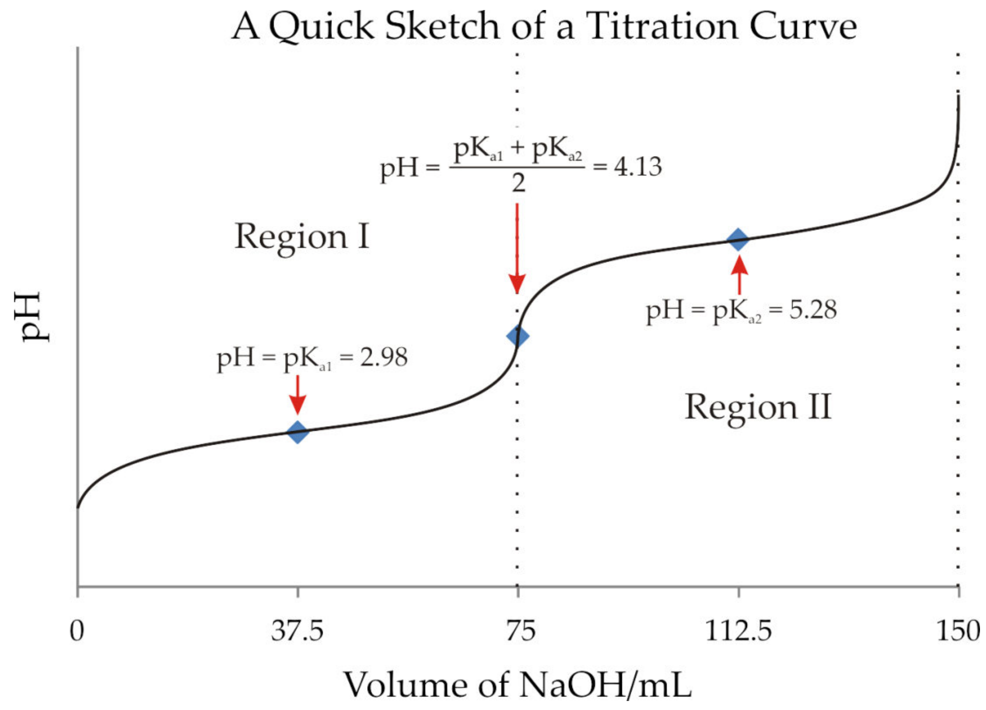
1. Determine the volume of NaOH needed to reach each endpoint
2. Draw a quick sketch of the titration curve and put in the pKa's

Begin by determining the volume of NaOH needed to complete the titration.

$$M_1V_1 = M_2V_2$$
$$(0.90 \text{ M } H_2P)\ (0.100 \text{ L}) = (1.2 \text{ M NaOH})\ (V_{NaOH})$$
$$V_{NaOH} = 0.075 \text{ L or } 75 \text{ mL}$$

Since there are two H^+'s in H_2P it will take a total of 2 x 75 mL = 150 mL of NaOH to complete this titration. The first end point will be at 75 mL and the final end point at 150 mL of NaOH.

Drawing a quick sketch of the titration curve will help orient you when asked the pH at other various points along the curve. It should only take a few seconds to draw the curve.



We now calculate the pKa's for H_2P and use them to calculate the intermediate midpoints and endpoints (which have already been placed on our quick sketch).

$$pK_{a1} = -\log(1.05\times10^{-3}) = 2.98$$
$$pK_{a2} = -\log(5.25\times10^{-6}) = 5.28$$

Intermediate Midpoint and End Point Calculations			
Vol NaOH	Position on Curve	Equation	pH
37.5 mL	1st midpoint	$pH = pK_{a1}$	2.98
75 mL	1st endpoint	$pH = \frac{pK_{a1} + pK_{a2}}{2}$	$4.13 = \frac{2.98 + 5.28}{2}$
112.5 mL	2nd midpoint	$pH = pK_{a2}$	5.28

Now that these initial points have been calculated and placed on our titration curve we now turn our attention to the initial and final pH. Assuming that we do not have to use the quadratic formula to solve for x, these two positions use very similar formulas to calculate their pH.

$$\text{initial pH} = \frac{x^2}{A - x} \approx \frac{x^2}{A} = K_{a1}$$

$$\text{final pH} = \frac{x^2}{B - x} \approx \frac{x^2}{B} = \frac{K_w}{K_{a2}} = K_{b2}$$

For the initial pH,

$$\frac{x^2}{0.9\ M\ H_2P} = 1.05\times10^{-3}$$

$$x = [H^+] = \sqrt{(0.9)\left(1.05\times10^{-3}\right)} = 0.0307\ M\ H^+$$

$$pH = -\log[0.0307\ M\ H^+] = 1.51$$

The final pH is a bit more difficult to calculate. At the final end point, the following equilibrium is occurring,

$$P^{2-} + H_2O \leftrightarrows HP^- + OH^- \qquad K_{b2}$$

To solve this equilibrium, we need to know the final concentration of base (P^{2-}) and the K_{b2} for the equilibrium. Fortunately, we have already done most of the work needed to calculate the concentration of P^{2-}. We need to remember that the definition of concentration (molarity) is,

$$\text{Molarity} = \frac{\text{moles}}{\text{Liters}}$$

The moles of P^{2-} are going to equal the moles of acid (H_2P) in our original solution. So,

$$(0.9\ \text{M}\ H_2P)\ (0.100\ \text{L}) = 0.09\ \text{mole}\ H_2P \Rightarrow 0.09\ \text{mole}\ P^{2-}$$

Now that we know the number of moles of P^{2-}, what is the volume? The volume will be the sum of the initial volume of H_2P and the volume of the added NaOH. We already know both of these values; we just need to add them together.

Total Volume = Volume of H_2P + Volume of added NaOH
Total Volume = 100 mL of H_2P + 150 mL of NaOH = 250 mL total

We can now calculate the molarity of our P^{2-} (after converting our volume to liters),

$$\text{Molarity} = \frac{0.09\ \text{mol}\ P^{2-}}{0.250\ \text{L}} = 0.36\ \text{M}\ P^{2-}$$

We can now calculate the pH at the final end point of our titration.

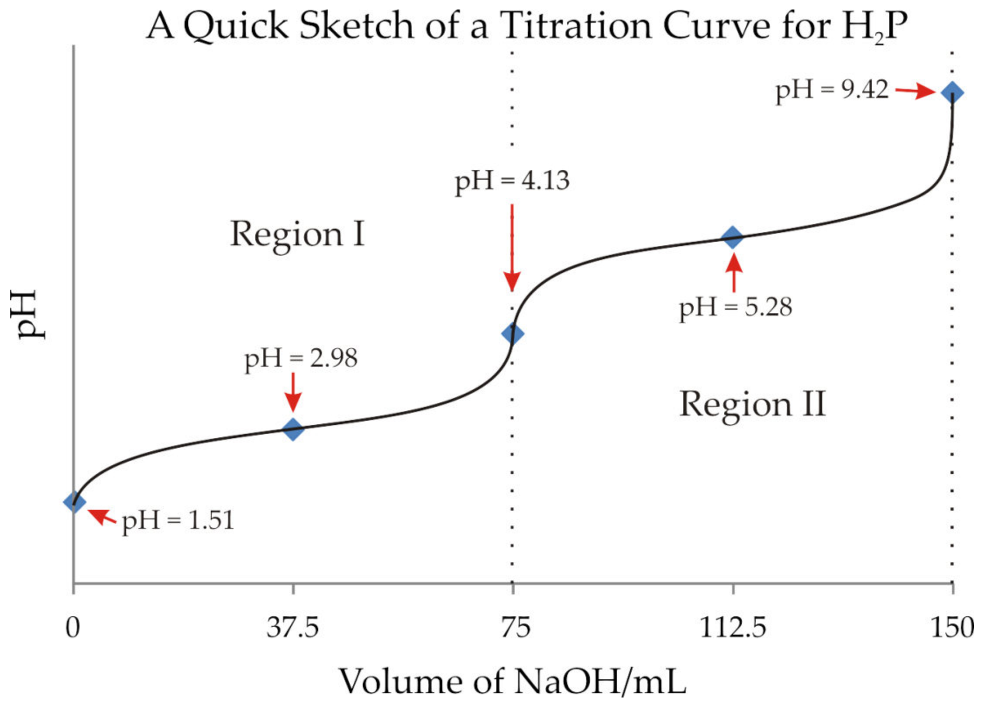
$$\frac{x^2}{B - x} \approx \frac{x^2}{B} = K_{b2}$$

$$\frac{x^2}{0.36\ \text{M}\ P^{2-}} = \frac{1\times10^{-14}}{5.26\times10^{-6}} = 1.90\times10^{-9}$$

$$x = [OH^-] = \sqrt{(0.36)\left(1.90\times10^{-9}\right)} = 2.62\times10^{-5}\ \text{M OH}^-$$

$$\text{pH} = 14 + \log[2.62\times10^{-5}\ \text{M OH}^-] = 9.42$$

Our titration curve is looking pretty good. We have calculated the pH of the initial and final points along with all the intermediate points. We can now turn our attention to some of the points in between. To determine the pH at other points along this curve, we will use the H-H equation.


A Quick Sketch of a Titration Curve for H_2P

Calculating pH Values in Region I

Calculating the pH of a solution in Region I is exactly the same as any monoprotic acid. Choosing a set of volumes between 0 and 75 mL of NaOH we calculate the pH as shown in the following table.

Titration of 100 mL of 0.9 M H_2P with various volumes of 1.2 M NaOH				
Vol of NaOH	Mol of NaOH	Mol of Acid (0.9M H_2P) (0.100L) = 0.09 mol H_2P	H-H - Equation	pH
15	(1.2 M) (0.015L) = 0.018 mol NaOH	0.09 mol H_2P	$\mathrm{pH} = 2.98 + \log\left(\frac{0.018}{0.09 - 0.018}\right)$	2.38
25	(12 M) (0.025L) = 0.030 mol NaOH	0.09 mol H_2P	$\mathrm{pH} = 2.98 + \log\left(\frac{0.030}{0.09 - 0.030}\right)$	2.68
35	(01.2 M) (0.035L) = 0.042 mol NaOH	0.09 mol H_2P	$\mathrm{pH} = 2.98 + \log\left(\frac{0.042}{0.09 - 0.042}\right)$	2.92
45	(1.2 M) (0.045L) = 0.054 mol NaOH	0.09 mol H_2P	$\mathrm{pH} = 2.98 + \log\left(\frac{0.054}{0.09 - 0.054}\right)$	3.16
55	(1.2 M) (0.055L) = 0.066 mol NaOH	0.09 mol H_2P	$\mathrm{pH} = 2.98 + \log\left(\frac{0.066}{0.09 - 0.066}\right)$	3.42
65	(1.2 M) (0.065L) = 0.078 mol NaOH	0.09 mol H_2P	$\mathrm{pH} = 2.98 + \log\left(\frac{0.078}{0.09 - 0.078}\right)$	3.79

Calculating pH Values in Other Regions

When you get beyond Region I and into Region II or III, the first thing that changes is the pKa. The pKa should match the titration Region. We use pK_{a1} for Region I and will use pK_{a2} or pK_{a3} for Regions II or III respectively.

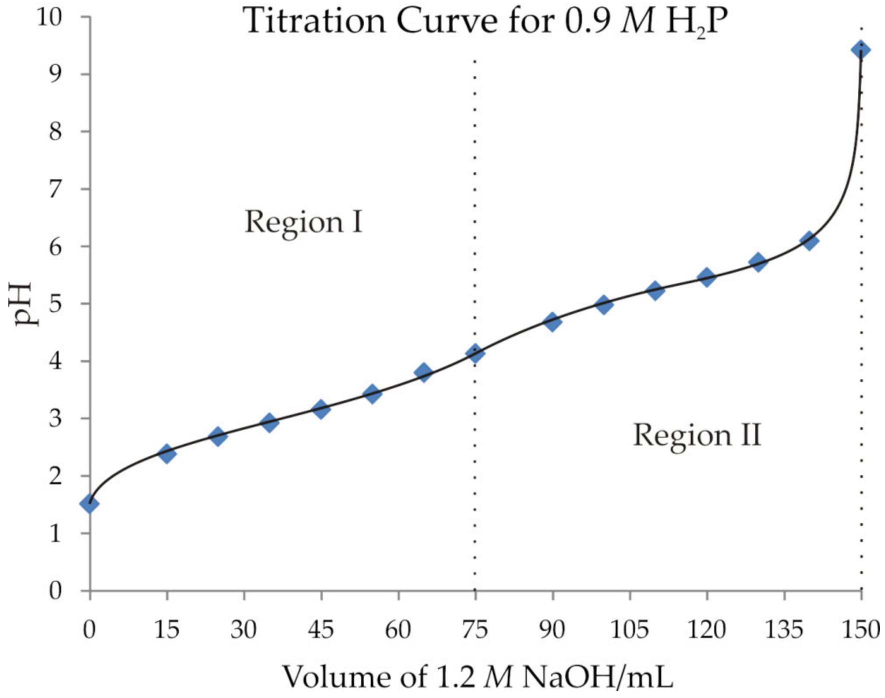
Another change is how we treat the volumes of added NaOH. Once we get past an intermediate endpoint, a new titration begins with new acids. For H_2P, this means that we are now titrating HP^-. We must remember that it took a significant amount of NaOH just to get to the starting point in this titration (in this case, 75 mL of NaOH) and that any additional NaOH moves us further into this region. So, if we add 90 mL of NaOH, it took 75 mL to get to our starting point so we are really moving just 15 mL into Region II. So, in our calculations, we will subtract the amount of base used to get us to the beginning of the region and use only the amount that moves us into the region (in this case, 15 mL). Other than this change, our calculations will look just like those for a monoprotic acid. Choosing a set of volumes between 75 and 150 mL we calculate the pH of the solution as shown in the following table.

Titration of 100 mL of 0.9 M H_2P with various volumes of 1.2 M NaOH

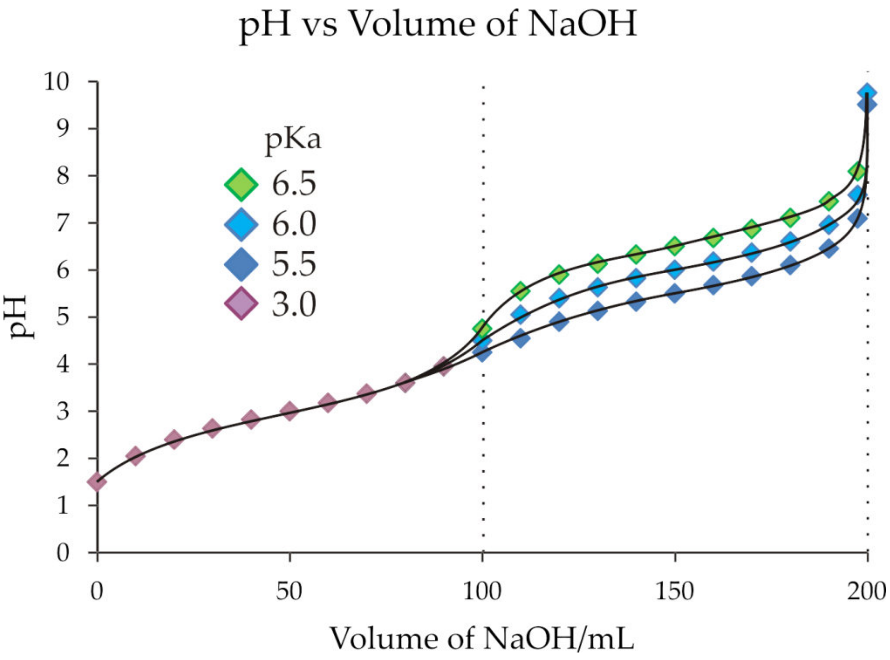
Vol of NaOH	Vol Used In Calc. (- 75 mL)	Mol of NaOH Past 1st End Point	Mol of Acid (0.9M H_2P) (0.100L) = 0.09 mol H_2P = mol HP^-	H-H - Equation	pH
90	15	(1.2 M) (0.015L) = 0.018 mol NaOH	0.09 mol HP^-	$pH = 5.28 + \log\left(\frac{0.018}{0.09 - 0.018}\right)$	4.68
100	25	(12 M) (0.025L) = 0.030 mol NaOH	0.09 mol HP^-	$pH = 5.28 + \log\left(\frac{0.030}{0.09 - 0.030}\right)$	4.98
110	35	(01.2 M) (0.035L) = 0.042 mol NaOH	0.09 mol HP^-	$pH = 5.28 + \log\left(\frac{0.042}{0.09 - 0.042}\right)$	5.22
120	45	(1.2 M) (0.045L) = 0.054 mol NaOH	0.09 mol HP^-	$pH = 5.28 + \log\left(\frac{0.054}{0.09 - 0.054}\right)$	5.46
130	55	(1.2 M) (0.055L) = 0.066 mol NaOH	0.09 mol HP^-	$pH = 5.28 + \log\left(\frac{0.066}{0.09 - 0.066}\right)$	5.72
140	65	(1.2 M) (0.065L) = 0.078 mol NaOH	0.09 mol HP^-	$pH = 5.28 + \log\left(\frac{0.078}{0.09 - 0.078}\right)$	6.09

If we were titrating a triprotic acid we would follow the same procedure. We would subtract the volume needed to get to Region III from the volumes given and change our pK_a to pK_{a3} when using the H-H equation.

Combining all of this data we can draw the titration curve for phthalic acid. The curve looks different from the quick sketch that we drew. The curve is less "curvy" and the first endpoint is not as obvious as our quick sketch. The titration curve of H_2P is fairly typical of real titration curves. Whenever you get two pKa's that differ by just three units or less (2.98 compared to 5.28, a difference of 2.3) your curve will be less curvy.



As can be seen below, as the difference between pK_{a1} and pK_{a2} grows, the titration curve shows more curvature at the first endpoint.



Over-Titrating: pH Past the Final Endpoint

Occasionally, an acid may be over titrated. Too much NaOH was added and the titration went past the end point. When this happens, what is the pH of the resulting solution?

The NaOH that is used to titrate the acid is a strong base. It is so strong that it is generally assumed that the pH is completely controlled by the excess NaOH and the effect of the weak base can be ignored. Strictly speaking, this is not true. Some acids, particularly triprotic acids have conjugate bases that are so strong that they can compete with NaOH and significantly change the pH. Even so, most of the time, we ignore the weak base and determine the pH of an over titrated solution by calculating the concentration of excess base added to the solution.

Problem 12.10

If 100 mL of 0.2 M HBenz (benzoic acid) was over titrated by 10 mL with 0.5 M NaOH, what is the pH of this solution? $K_a = 4.5\times10^{-5}$

Answer

First, calculate the amount of NaOH needed to complete the titration of benzoic acid,

$$M_1V_1 = M_2V_2$$

$$(0.2\text{ M HBenz})\ (0.100\text{ L}) = (0.50\text{ M NaOH})\ (V_2)$$

$$V_2 = 0.040\text{ L or 40 mL of NaOH}$$

If the solution is over titrated by 10 mL then 50 mL of NaOH must have been added. The total volume must be 100 mL HBenz + 50 mL NaOH = 150 mL total.

Moles of NaOH past the endpoint = (0.5 M NaOH) (0.010 L) = 0.0050 mole NaOH

$$\text{Molarity NaOH} = \frac{\text{moles NaOH}}{\text{total volume}} = \frac{0.0050\text{ mole NaOH}}{0.150\text{ L total}} = 0.0333\text{ M NaOH}$$

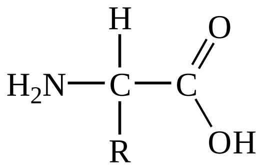
$$\text{pH} = 14 + \log[\text{OH}^-] = 14 + \log[0.0333\text{ M NaOH}] = 12.52$$

Amino Acids

Amino acids are the essential building blocks of proteins. The human body can make most of the amino acids it needs but there are twenty of them that cannot be made and must be consumed in our daily diet. These are given below.

Amino Acid	Abbreviation		-COOH	$-NH_3^+$	R Group	pI
	3 Letter Symbol	1 Letter Symbol	pK_{a1}	pK_{a2}	pK_{a3}	
Alanine	Ala	A	2.34	9.69	–	6.00
Arginine	Arg	R	2.17	9.04	12.48	10.76
Aspartic acid	Asn	N	2.02	8.80	–	5.41
Asparagine	Asp	D	1.88	9.60	3.65	2.77
Cysteine	Cys	C	1.96	10.128	8.18	5.07
Glutamic acid	Glu	E	2.19	9.67	4.25	3.22
Glutamine	Gln	Q	2.17	9.13	–	5.65
Glycine	Gly	G	2.34	9.60	–	5.97
Histidine	His	H	1.82	9.17	6.00	7.59
Isoleucine	Ile	I	2.36	9.60	–	6.02
Leucine	Leu	L	2.36	9.60	–	5.98
Lysine	Lys	K	2.18	8.95	10.53	9.74
Methionine	Met	M	2.26	9.21	–	5.74
Phenylalanine	Phe	F	1.83	9.13	–	5.48
Proline	Pro	P	1.99	10.60	–	6.30
Serine	Ser	S	2.01	9.15	–	5.58
Threonine	Thr	T	2.09	9.10	–	5.60
Tryptophan	Trp	W	2.83	9.39	–	5.89
Tyrosine	Tyr	Y	2.20	9.11	10.07	5.66
Valine	Val	V	2.32	9.62	–	5.96

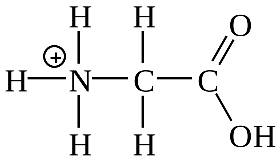
Most amino acids are diprotic acids and a few are triprotic. The general structure of an amino acid is given below,



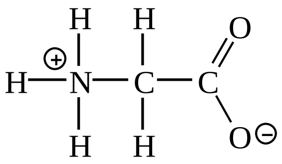
A generic amino acid

The "R" group differs from one amino acid to the other which makes each amino acid unique. If "R" = H, then the amino acid is glycine. If "R" = CH_3 then the amino acid is alanine.

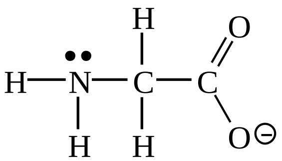
The COOH is the acid portion and the NH_2 is the amino portion of an amino acid. The COOH group behaves like any normal weak acid and the NH_2 like any normal weak base. But, as we know, an NH_2 can accept an H^+ making it a weak acid (NH_3^+), and this makes amino acids diprotic acids. Occasionally, an R group will include nitrogen which makes the amino acid a triprotic acid. Although amino acids are often written in the generic form shown above, they are never found that way in solution. In solution, amino acids take on one of three forms,



In Acid



@pH = 5.97

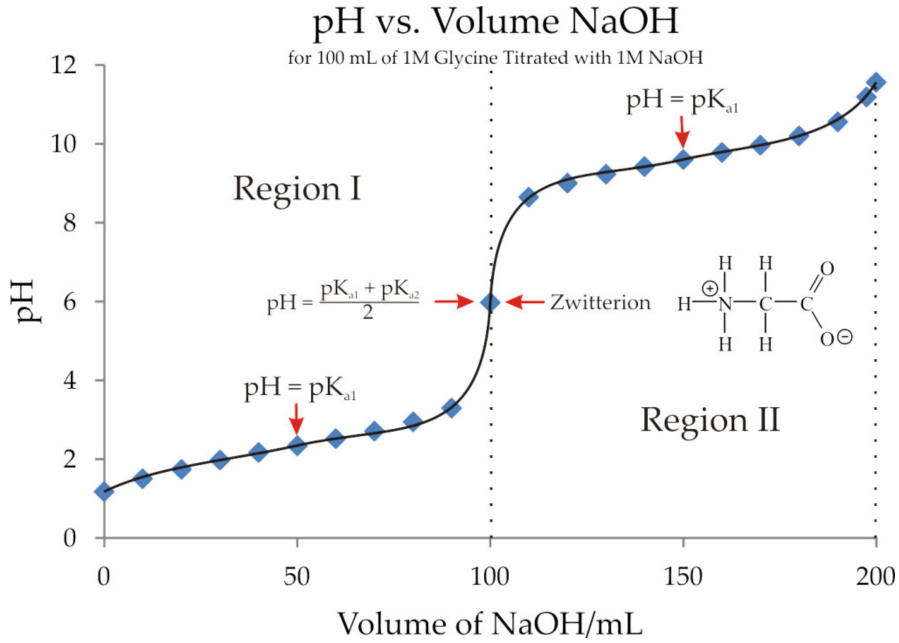


In Base

We could write the equilibriums for glycine as follows,

$$H_2Gly^+ \leftrightarrows H^+ + HGly \qquad pK_{a1} = 2.34$$
$$HGly \leftrightarrows H^+ + Gly^- \qquad pK_{a2} = 9.60$$

The titration curve for glycine looks like any normal titration curve for a diprotic acid.



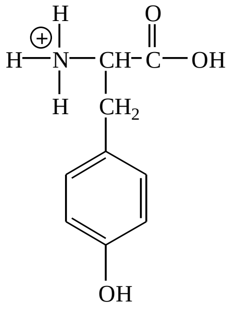
The main difference between an ordinary diprotic acid and an amino acid is that an amino acid is always charged. At the half-way point in the titration, the acidic H+ is removed this produces an ion with a positive charge on NH_3^+ end and a negative charge on the COO^- end. Since these charges balance on another, overall, the amino acid is uncharged. This form of the amino acid is known as a "zwitterion" and is called the isoelectric point for this amino acid. The term "zwitter" is a German word meaning "hybrid", "two", "between", or "hermaphrodite." In this context it describes an ion that has both positive and negative charges. Since this ion sits at the half-way point in a titration, the pH at which this ion exists is where,

$$pH = \frac{pK_{a1} + pK_{a2}}{2} = pI$$

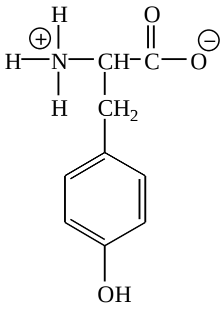
For amino acids this pH is known as the pI, where "I" stands for isoelectric point. For diprotic amino acids, the pI is just the average of the two pKa's as it is with any normal diprotic acid. For amino acids with three pKa's the relationship is a bit more complicated. Since the isoelectric point is the point at which the amino acid must be electrically neutral, the isoelectric point will depend on the nature of the side group. In normal diprotic amino acids, there is an acid that contributes a negative charge and an amine that contributes a positive charge and they must be equal. In triprotic amino acids, the side group will add another positive or negative charge depending on the nature of the side group. If the side group is another amine (like arginine, histidine or lysine) then the positive charge must be equally shared between the amine and the amine on the side group so the pI is the average of the pKa's for the two amines.

This contrasts with amino acids with side groups containing acids (glutamic acid and aspartic acid) which contribute negative charges. The pI for these two amino acids is the average of the acid group and the acid side group.

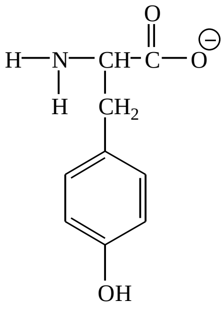
Of the two remaining triprotic amino acids, cysteine's side group has an SH bond that behaves like an acid, so its pI is the average of the acid pKa and the side group pKa. The last triprotic amino acid is tyrosine whose side group is a phenol (OH). This side group remains uncharged but it can be ionized in relatively strong base solutions. Although tyrosine is a triprotic acid, most often its side chain is uncharged so it behaves like a normal diprotic amino acid whose pI is the average of its pK_{a1} and pK_{a2}. The three forms of tyrosine are shown below.



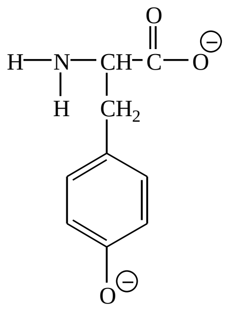
In Acid



@ pH = 5.66
(Zwitterion)



In Base

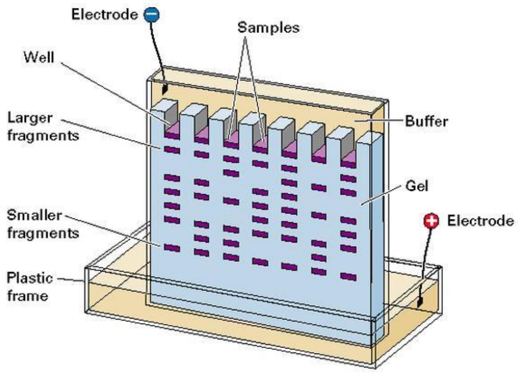


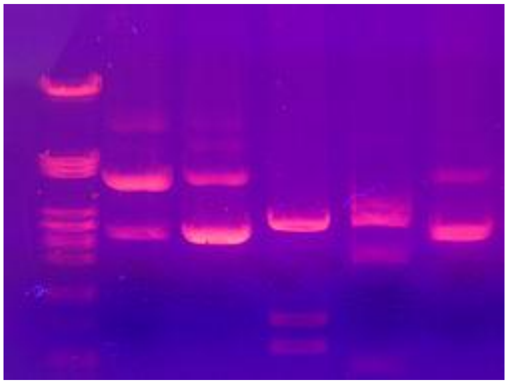
Very Basic

Gel Electrophoresis

Electrophoresis is a method used to separate amino acids. Amino acids are injected into an immobilized pH gradient (IPG) gel and a current is applied. The electric current passes through the gel, creating a "positive" anode and "negative" cathode end. Negatively charged amino acids migrate through the pH gradient in the gel toward the "positive" end while positively charged amino acids move toward the "negative" end. Eventually, the amino acid finds itself in an environment where the pH matches its pI and the isoelectric point is reached. The amino acid is no longer charged so it stops moving through the gel. As a result, the amino acids become focused into sharp stationary bands with each amino acid positioned at a point in the pH gradient corresponding to its pI. The technique is capable of extremely high resolution with proteins differing by a single charge being fractionated into separate bands.

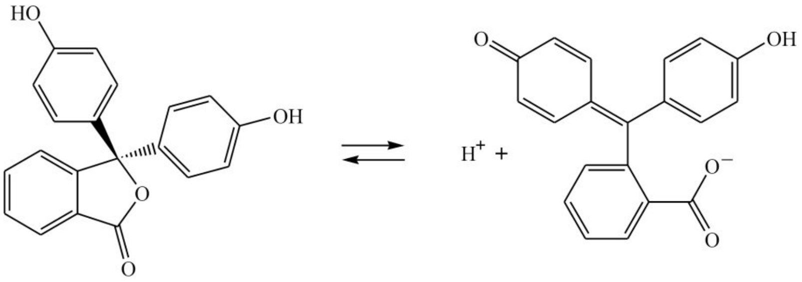
The method is applied particularly often in the study of proteins, whose amino acids separate based on their relative content of acidic and basic residues, whose value is represented by the pI. Proteins are introduced into an Immobilized pH gradient gel composed of polyacrylamide, starch, or agarose where a pH gradient has been established. Isoelectric focusing can resolve proteins that differ in pI value by as little as 0.01.





Indicators

Indicators are organic compounds, usually acids, which are added in small amounts to a solution to indicate when a particular pH has been reached. Indicators are usually colored, or they change in color as the pH of a solution changes. A common indicator used in titrations is phenolphthalein (HPh).



$$\mathrm{HPh} \rightleftharpoons \mathrm{H^+} + \mathrm{Ph^-}$$

(Clear) (Pink)

In acid solution, HPh predominates and the solution is clear, but as NaOH is added, the solution becomes more basic and Ph^- is formed and the solution turns magenta (pink). This behavior is predicted by LeChatlier's principle. According to the equilibrium shown above, as NaOH is added, H^+ is consumed. This forces the equilibrium to shift to the right, making more Ph-. As a consequence, the solution turns pink.

Indicators are chosen so that they change color just after the endpoint of a titration. For example, phenolphthalein changes color at pH = 8.2 but is often used as the indicator for titrations between strong acids and bases whose endpoint is pH = 7.

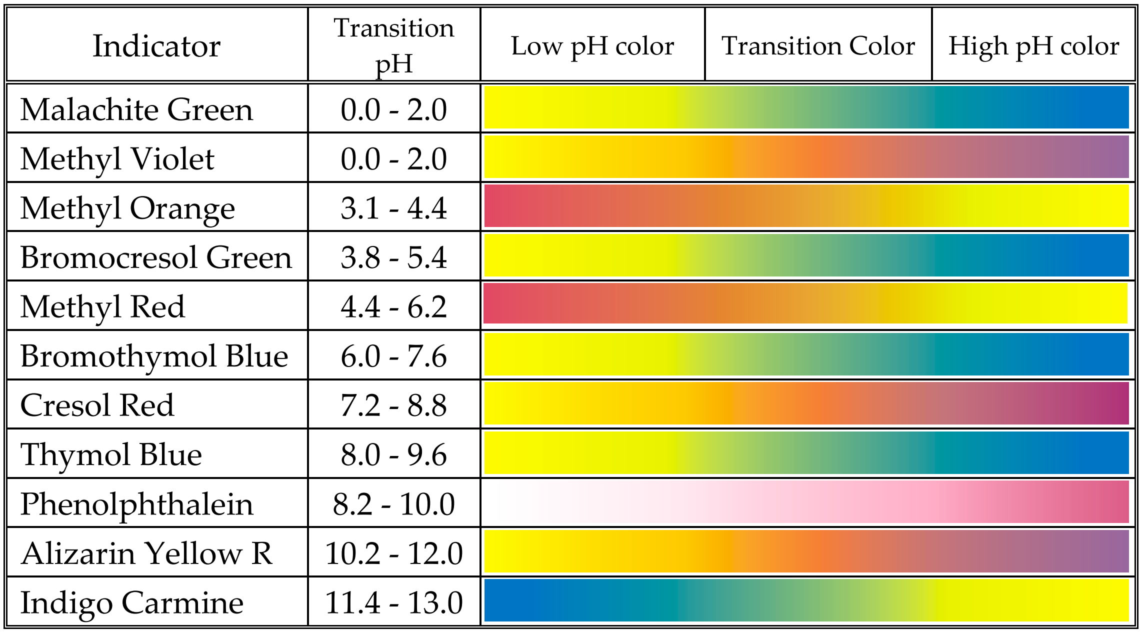
At the endpoint of a titration, the pH curve is very steep and the pH changes rapidly with small amounts of added base. A single drop of added base can produce large changes in pH. For example, there are about 20 drops of water in 1 mL of water, so each drop is about 0.05 mL. If 1 drop of 0.1 M NaOH is added to 100 mL of pure water, what is the pH of the resulting solution?

Water starts at a pH = 7. One drop of 0.1 M NaOH adds (0.1 M) x (0.00005 L) = 1×10^{-5} mole of NaOH. Adding this much NaOH to 100 mL of water produces a solution that is,

$$pH = 14 + \log\left[\frac{0.00005 \text{ mole NaOH}}{0.10005 \text{ L total}}\right] = 10.7$$

So the water changes from pH = 7 to pH = 10.7 with the addition of one drop of 0.1 M NaOH. A half drop would have changed the pH to 10.39. The error introduced by over titrating the solution by a half drop (0.025 mL) is smaller than the error in the reading of the buret used to deliver it (±0.03 mL). If phenolphthalein was used as our indicator, it would have changed from clear to decidedly pink leaving no doubt that the titration was finished, which is the point of using the indicator. It is little wonder that students are told to titrate their solutions to a faint pink phenolphthalein end point. Doing so insures a near perfect titration.

Some of the more common indicators are given below along with the colors on either side of their transition pH.



Indicator	Transition pH	Low pH color	Transition Color	High pH color
Malachite Green	0.0 - 2.0			
Methyl Violet	0.0 - 2.0			
Methyl Orange	3.1 - 4.4			
Bromocresol Green	3.8 - 5.4			
Methyl Red	4.4 - 6.2			
Bromothymol Blue	6.0 - 7.6			
Cresol Red	7.2 - 8.8			
Thymol Blue	8.0 - 9.6			
Phenolphthalein	8.2 - 10.0			
Alizarin Yellow R	10.2 - 12.0			
Indigo Carmine	11.4 - 13.0			

Buffers

Buffers are solutions that resist changes in pH when strong acids or bases are added to them. They are made by mixing portions of a weak acid with its conjugate base. The use of buffers is common in the biological science where living systems live in narrow ranges of pH usually around a pH of 7. As shown previously, while water itself is pH = 7, it is not a buffer and small amounts of added acid or base can change its pH significantly. So when a solution of pH = 7 is required, solutions are made consisting of combinations of weak acids and bases. A chemist might use solutions consisting of NaH_2PO_4 and Na_2HPO_4 (pK_{a2} = 7.20) to make a buffer of pH = 7, but a biologist would not. High phosphate concentrations can be detrimental to living systems so a phosphate buffer may not be appropriate. Biologists commonly use tris (hydroxymethyl) methylamine (Tris or THAM) whose pK_a = 8.07 to make buffers of pH = 7.

The best buffer is a buffer that is prepared with a pH right in the center of its buffer range, or close to it. This is where the pH = pK_a for that acid/base combination. The higher the concentration of acid and base (within limits) the more capable the buffer is to resist changes in pH.

To make a buffer of any given pH, we always choose a conjugate acid/base system whose pK_a is closest to the pH of the buffer we are trying to make. A selection of acid/base pairs and their pKa's are given below.

Acid/Base Systems Useful for Making Buffers		
Conjugate Acid	Conjugate Base	pKa of System
H_2PO_4	NaH_2PO_4	2.12
H_3Cit	NaH_2Cit	3.14
HAc	NaAc	4.74
NaH_2Cit	Na_2HCit	4.77
H_2CO_3	$NaHCO_3$	6.37
Na_2HCit	Na_3Cit	6.39
NaH_2PO_4	Na_2HPO_4	7.20
NH_4Cl	NH_4OH	9.26
$NaHCO_3$	Na_2CO_3	10.33
Na_2HPO_4	Na_3PO_4	12.33

It is common to use the H-H equation to calculate the amount of conjugate acid and base needed to make a buffer of any particular pH. In some cases, buffers are made by titrating an acid or a base in which case the H-H equation is used to calculate the amount of acid or base needed to create the buffer.

Making a Buffer

The two most common ways to make a buffer is by "scratch", where you are allowed to add as much of the ingredients as you need, or by titration where you are given an existing solution of an acid or base and you titrate it to the proper pH. Neither of these buffers are particularly difficult to make. They both use the H-H equation but in very different ways.

Making a Buffer from "Scratch"

Suppose you are told to make 100 mL of buffer of pH = 4.5 and that is all the information you have been given. How would you make it? The first thing you should do is consult a table of pKa's and decide on which acid/base pair is appropriate to make this buffer. We have a couple of choices. We can make this buffer using acetic acid and sodium acetate (HAc/NaAc) or using sodium dihydrogen citrate and disodium hydrogen citrate (NaH_2Cit/ Na_2HCit), it's our choice. Let's use sodium dihydrogen citrate and disodium hydrogen citrate (an arbitrary choice), but since they are both solids and easily weighed out, it will be easier to make this buffer than using a solution of concentrated acetic acid (vinegar) and have to measure volumes.

Now that we know which acid/base system we are going to use, we turn our attention to the H-H equation and use it to determine how much of each ingredient we need. We already know the pH that we want (pH = 4.5) and we know the pKa of this acid/base system (pKa = 4.77) so we can use the H-H equation to calculate how much NaH_2Cit and Na_2HCit we will need.

$$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{\text{mol base}}{\text{mol acid}}\right)$$

$$4.5 = 4.77 + \log\left(\frac{\text{mol Na}_2\text{HCit}}{\text{mol NaH}_2\text{Cit}}\right)$$

Solving for the base/acid ratio we have,

$$0.537 = \left(\frac{\text{mol Na}_2\text{HCit}}{\text{mol NaH}_2\text{Cit}}\right) = \frac{0.537\text{ mol Na}_2\text{HCit}}{1\text{ mol NaH}_2\text{Cit}}$$

Although the math just gives us a number (0.537) we must realize that this means that for every mole of NaH_2Cit we will need 0.537 moles of Na_2HCit. Unfortunately, we cannot just weigh out 1 mole of NaH_2Cit and 0.537 moles of Na_2HCit and expect this buffer to work. We must also consider the volume. We are making 100 mL of buffer. Putting 1 mole of NaH_2Cit into 100 mL of water will make the solution 10 M in NaH_2Cit (and 5.37 M in Na_2HCit). It is unlikely that a solution of NaH_2Cit can be made this concentrated. It is more reasonable to make the solution 1 M in NaH_2Cit but this means using only 0.10 mole of NaH_2Cit rather than 1 mole. As long as the ratio between NaH_2Cit and Na_2HCit remain constant, the solution will be pH = 4.5. So, if we add 0.10 mole of NaH_2Cit and 0.0537 moles of Na_2HCit to 100 mL of water our ratio will remain constant, our concentrations will be reasonable, and the solution will be pH = 4.5. We need only to weigh out the appropriate amounts of acid and base and make our buffer solution.

Making a Buffer by Titration

The other most common way to make a buffer is by titration. Starting with one or the other of an acid/base pair the other is created by titration. This means that the H-H will take one of two forms,

$$pH = pK_a + \log\left(\frac{x}{A - x}\right) \quad \text{if titrating an acid with a base}$$

or,

$$pH = pK_a + \log\left(\frac{B - x}{x}\right) \quad \text{if titrating a base with an acid}$$

For example, suppose that we want to make a buffer of pH = 9. A logical choice would be to use the NH_4Cl/NH_4OH acid/base pair. Starting with 100 mL of 1.5 *M* NH_4OH, how much 0.6 *M* HCl must be added to make a buffer of pH = 9? The K_b for the dissociation of NH_4OH is $1.8\text{x}10^{-5}$.

It is important to note that NH_4OH can be written in many different ways; $NH_3(aq)$, $NH_3 + H_2O$, and NH_4OH are all equivalent ways of writing the formula of this compound. For convenience, we will choose the following,

Base version: $NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$
Acid version: $NH_4^+ \leftrightarrows NH_3 + H^+$

It is usually easiest to work with the acid version of reactions when making buffers (more about this later) so we will choose the acid version as the equilibrium we will use. We can calculate the K_a from the K_b using the following relation,

$$K_a = \frac{K_w}{K_b} = \frac{1\times10^{-14}}{1.8\times10^{-5}} = 5.55\times10^{-10}$$

$$pK_a = -\log[5.55\text{x}10^{-10}] = 9.26$$

The initial number of moles of NH_3 (NH_4OH) are;

$$(1.5\ M\ NH_4OH)\ (0.100\ L) = 0.15\ \text{mol}\ NH_4OH\ (NH_3)$$

Putting these values into the H-H equation we can solve for the number of moles of acid that must be added to make this buffer,

$$pH\ = pK_a + \log\left(\frac{B - x}{x}\right)$$

$$9.0\ = 9.26 + \log\left(\frac{0.15\ \text{mol}\ NH_3 - x}{x}\right)$$

$$-0.26\ = \log\left(\frac{0.15\ \text{mol}\ NH_3 - x}{x}\right)$$

$$10^{-0.26} = 0.5495 = \left(\frac{0.15 - x}{x}\right)$$

$$0.5495x = 0.15 - x$$

$$1.5495x = 0.15$$

$$x = \frac{0.15}{1.5495} = 0.09681\ \text{mol}\ H^+\ \text{must be added}$$

These moles of H^+ come from the addition of 0.6 M HCl to the ammonia solution. To calculate the volume of HCl needed we do the following calculation,

$$M_{H+}V_{H+} = \text{moles}\ H^+$$

$$(0.6\ M\ HCl)\ (V_{HCl}) = 0.09681\ \text{mole HCl}$$

V_{HCl} = 0.1614 L or 161.4 mL of 0.6 M HCl must be added to make this buffer.

Making a Buffer by Titration of a Polyprotic Acid

Buffers of pH = 7 are often made using phosphates, specifically, the second equilibrium of phosphoric acid whose pK_a is close to 7.0,

$$H_3PO_4 \leftrightarrows H^+ \; H_2PO_4^- \qquad pK_{a1} = 2.12$$
$$H_2PO_4^- \leftrightarrows H^+ + HPO_4^{2-} \qquad pK_{a2} = 7.20$$
$$HPO_4^{2-} \leftrightarrows H^+ + PO_4^{3-} \qquad pK_{a3} = 12.33$$

The main difference between creating buffers with monoprotic acids and polyprotic acids is that we will often have to add a significant amount of base just to get to the beginning of the appropriate pH region for a polyprotic acid. This is certainly true for buffers made with phosphoric acid. To make a buffer of pH = 7 we must titrate through Region I and then titrate part way into Region II. Once we are at the beginning of Region II, the calculations are the same as those used for a monoprotic acid but we must remember to add the additional amount of base needed to get to the start of this region.

For example, suppose we have 150 mL of 0.2 M H_3PO_4 and we are going to make a buffer of pH = 7 by titrating this H_3PO_4 with 0.5 M NaOH. How much NaOH do we need to add? Like we did for our titration curves, we will begin by calculating the volume of NaOH needed to titrate the H_3PO_4 and then proceed as we would with any other monoprotic acid.

Begin by determining the volume of NaOH needed to complete the titration.

$$M_1V_1 = M_2V_2$$
$$(0.2\text{ M } H_3PO_4)\ (0.150\text{ L}) = (0.5\text{ M NaOH})\ (V_{NaOH})$$
$$V_{NaOH} = 0.060\text{ L or 60 mL of 0.5 M NaOH for each } H^+ \text{ in } H_3PO_4$$

Now, proceed as with any other monoprotic acid. We are working in Region II of a triprotic acid. The equilibrium for this region is,

$$H_2PO_4^- \leftrightarrows H^+ + HPO_4^{2-} \qquad pK_{a2} = 7.20$$

All of the H_3PO_4 has been neutralized and has become $H_2PO_4^-$, therefore the moles of H_3PO_4 must equal the moles of $H_2PO_4^-$ at the beginning of this region.

The initial number of moles of H_3PO_4 are;

$$(0.2 \text{ M } H_3PO_4)\ (0.150 \text{ L}) = 0.030 \text{ mol } H_3PO_4 = H_2PO_4^-$$

Putting these values into the H-H equation we can solve for the number of moles of acid that must be added to make this buffer,

$$\text{pH} = \text{p}K_a + \log\left(\frac{x}{A - x}\right)$$

$$7.0 = 7.20 + \log\left(\frac{x}{0.030 \text{ mol } H_2PO_4^- - x}\right)$$

$$-0.20 = \log\left(\frac{0.030 - x}{x}\right)$$

$$10^{-0.20} = 0.631 = \left(\frac{0.030 - x}{x}\right)$$

$$0.631x = 0.030 - x$$

$$1.631x = 0.030$$

$$x = \frac{0.030}{1.631} = 0.01839 \text{ mol OH}^- \text{ must be added}$$

These moles of OH^- come from the addition of 0.5 M NaOH. To calculate the volume of NaOH needed we do the following calculation,

$$M_{OH-}V_{OH-} = \text{moles OH}^-$$

$$(0.5\ M \text{ NaOH})\ (V_{NaOH}) = 0.01839 \text{ mole NaOH}$$

V_{HCl} = 0.03679 L or 36.79 mL of 0.5 M NaOH must be added, but this measures how far we want to titrate into Region II, not the total volume. The total volume will be,

60 mL to the start of Region II + 36.79 mL into Region II = 96.79 mL total

So, it will take 96.79 mL of 0.5 M NaOH to titrate 150 mL of 0.2 M H_3PO_4 to a pH = 7.

There are many ways to make a buffer and all the various methods cannot be explored here. The following table outlines most methods and the form of the H-H equation that should be used.

Form of the H-H Equation	Comments Note: "acid" and "base" refer to strong acids and strong bases unless otherwise indicated. The "x" denotes a missing variable for which the equation will be solved
$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{B}{A}\right)$	You are free to add both A and B. Solve this equation for the $\frac{B}{A}$ ratio.
$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{x}{A}\right)$	Given A, how much B should you add?
$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{B}{x}\right)$	Given B, how much A should you add?
$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{x}{A - x}\right)$	Given A, how much base should you add?
$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{B - x}{x}\right)$	Given B, how much acid should you add?
$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{B + x}{A - x}\right)$	Given an existing buffer, how much base should you add to make the buffer more basic?
$\mathrm{pH} = \mathrm{p}K_a + \log\left(\frac{B - x}{A + x}\right)$	Given an existing buffer, how much acid should you add to make the buffer more acidic?

Solubility Products

In earlier chapters you learned a set of solubility rules that allowed you to determine if a compound was soluble or insoluble, but the truth is, all compounds are soluble; some compounds are just more soluble than others. This section takes another look at compounds that were earlier found to be insoluble and provides quantitative methods to determine the degree of solubility of these compounds.

All compounds are soluble but some are more soluble that others. Transition metal sulfides are particularly insoluble. Compounds like CuS, Ag2S, and HgS are so insoluble that virtually none of it dissolves. Even so, some of it does and the degree of solubility can be expressed as a solubility product.

$$\mathrm{HgS(s)} \leftrightarrows \mathrm{Hg^{2+}} + \mathrm{S^{2-}} \qquad \mathrm{Ksp} = 2\mathrm{x}10^{-54}$$

Solubility products are just like any other equilibrium except that they include a solid, indicated by an (s) in the equilibrium. Solids do not have concentrations so they are left out of the equilibrium expression. For HgS(s), the equilibrium expression, called a solubility product, would be,

$$K_{sp} = [Hg^{2+}]\,[S^{2-}] = 2x10^{-54}$$

If we want to determine the $[Hg^{2+}]$ and $[S^{2-}]$ for HgS(s) we need to realize that when HgS dissolves, one Hg^{2+} and one S^{2-} is produced. We set these values equal to x,

$$[Hg^{2+}]\,[S^{2-}] = [x]\,[x] = x^2 = 2x10^{-54}$$

$$x = \sqrt{2\times10^{-54}} = 1.41\times10^{-27}\ M\ Hg^{2+}\text{ and }S^{2-}$$

To get a grasp on just how small this number really is, we realize that, by the definition of molarity, we have,

$$1.41\times10^{-27}\ M = \frac{1.41\times10^{-27}\text{ mole}}{1\text{ liter of solution}}$$

There are $6.02x10^{23}$ atoms or ions in a mole of this compound so we have,

$$1.41x10^{-27}\text{ moles x }6.02x10^{23}\text{ ions/mole} = 0.000851\text{ atoms in 1 Liter of solution}$$

Or we could say that we would need 1174.6 liters of water to dissolve one molecule of HgS. This is more than 300 gallons of water. Some hot tubs are smaller than this.

From this we can see that HgS(s) is extremely insoluble as are most transition metal sulfides. Even so, using solubility products we can calculate the concentration of even the most insoluble compound.

Solubility in Water

When solids dissolve in water, their ions move into solution. The solubility expression for a few compounds will illustrate the point.

$AgCl(s) \leftrightarrows Ag^{+} + Cl^{-}$	$K_{sp} = [Ag^{+}]\,[Cl^{-}] = 1.8x10^{-10}$
$PbI_2(s) \leftrightarrows Pb^{2+} + 2\ I^{-}$	$K_{sp} = [Pb^{2+}]\,[I^{-}]^2 = 9.8\times10^{-9}$
$Fe(OH)_3(s) \leftrightarrows Fe^{3+} + 3\ OH^{-}$	$K_{sp} = [Fe^{3+}]\,[OH^{-}]^3 = 2.79\times10^{-39}$
$Ca_3(PO_4)_2(s) \leftrightarrows 3\ Ca^{2+} + 2\ PO_4^{3-}$	$K_{sp} = [Ca^{2+}]^3\,[PO_4^{3-}]^2 = 2.07\times10^{-33}$

Like all equilibriums, the coefficient on the ion becomes the exponent in the solubility product. This is no different than what we saw when working with acids and bases.

Let's take a closer look that the solubility product for $PbI_2(s)$. We can set up an ICE table to calculate the solubility of PbI_2 in water.

Reaction	$PbI_2(s)$	Pb^{2+}	**2 I^{-}**
I (initial)	Not applicable	0 *M*	0 *M*
C (change)	Not applicable	+x	+ 2x
E (equilibrium)	Not applicable	x *M*	2x *M*

We note that, for every PbI_2 that dissolves, one Pb^{2+} is produced and two I^{-} are produced. So, if $Pb^{2+} = x$ then $I^{-} = 2x$. We put these into our equilibrium expression and solve for x,

$$K_{sp} = [Pb^{2+}]\,[I^{-}]^2 = [x]\,[2x]^2 = 4x^3$$

For many students there is a disconnect that occurs here. The solubility product demands that the I^{-} concentration be squared and the solubility of PbI_2 demands that the concentration of $I^{-} = 2x$, so you must do both; double the I^{-} concentration and square it. With this illuminating idea, we can look at the other compounds shown above,

$AgCl(s) \leftrightarrows Ag^{+} + Cl^{-}$	$[Ag^{+}]\,[Cl^{-}] = [x][x] = x^2 = 1.8x10^{-10}$	$x = 1.348\times10^{-3}\ M$
$PbI_2(s) \leftrightarrows Pb^{2+} + 2\ I^{-}$	$[Pb^{2+}]\,[I^{-}]^2 = [x][2x]^2 = 4x^3 = 9.8\times10^{-9}$	$x = 1.342\times10^{-5}\ M$
$Fe(OH)_3(s) \leftrightarrows Fe^{3+} + 3\ OH^{-}$	$[Fe^{3+}]\,[OH^{-}]^3 = [x][3x]^3 = 27x^4 = 2.79\times10^{-39}$	$x = 1.008\times10^{-10}\ M$
$Ca_3(PO_4)_2(s) \leftrightarrows 3\ Ca^{2+} + 2\ PO_4^{3-}$	$[Ca^{2+}]^3\,[PO_4^{3-}]^2 = [3x]^3\,[2x]^2 = 108x^5 = 2.07\times10^{-33}$	$x = 1.139\times10^{-7}\ M$

It is a common error to believe that the relative solubility of two compounds can be determined by looking at the size of their solubility products. For example, consider PbCrO4 and $Mg_3(PO_4)_2$. Their solubility products are given below.

$PbCrO_4$ $K_{sp} = 3\times10^{-13}$
$Mg_3(PO_4)_2$ $K_{sp} = 1.04\times10^{-24}$

Based on the solubility products alone, we might guess that $PbCrO_4$ is more soluble than $Mg_3(PO_4)_2$, but a check of the math reveals that the opposite is true, $Mg_3(PO_4)_2$ is more soluble than PbCrO4.

For $PbCrO_4$

$PbCrO_4\ (s) \leftrightarrows Pb^{2+} + CrO_4^{2-}$
$[Pb^{2+}]\ [CrO_4^{2-}] = [x][x] = x^2 = 3\times10^{-13}$ $x = 5.48\text{x}10^{-7}\ M$

For $Mg_3(PO_4)_2$

$Mg_3(PO_4)_2(s) \leftrightarrows 3\ Mg^{2+} + 2\ PO_4^{3-}$
$[Mg^{2+}]^3\ [PO_4^{3-}]^2 = [3x]^3\ [2x]^2 = 108x^5 = 1.04\times10^{-24}$ $x = 6.26\text{x}10^{-6}\ M$

Since $6.26\text{x}10^{-6}\ M$ is greater than $5.48\text{x}10^{-7}\ M$, $Mg_3(PO_4)_2$ is more soluble than $PbCrO_4$. Never depend on the size of the solubility product to determine relative solubility. Do the math and compare the answers. It is the only dependable way to compare.

The Common Ion Effect

The common ion effect is an application of LeChatlier's principle. If a solution is in equilibrium, adding one of its ions to the solution will force the equilibrium to shift in such a way as to make more solid. In similar fashion, a solid will not dissolve as much in a solution that already contains one of its ions. For example, a saturated solution of AgCl will form more solid if NaCl is added to it and less AgCl will dissolve in a solution containing NaCl than in a sample of pure water.

For example, what is the solubility of $BaSO_4$ in 0.100 *M* H_2SO_4? The K_{sp} for BaSO4 is 1.08×10^{-10}. Begin by setting up an ICE table for this reaction

$$BaSO_4(s) \leftrightarrows Ba^{2+} + SO_4^{2-}$$

Reaction	$BaSO_4(s)$	Ba^{2+}	SO_4^{2-}
I (initial)	Not applicable	0 *M*	0.100 *M*
C (change)	Not applicable	+x	+ x
E (equilibrium)	Not applicable	x *M*	0.100 + x *M*

$$[Ba^{2+}]\ [SO_4^{2-}] = [x\ M][0.100 + x\ M] \approx\ [x\ M][0.100\ \mathrm{M}] = 1.08\times10^{-10}$$

$$x = 1.08\times10^{-9}\ M\ Ba^{2+}$$

Care must be taken to make sure we answer the question being asked. For example, if $Ag_2Cr_2O_7$ is added to 100 mL of 0.200 M $K_2Cr_2O_7$ what is the concentration of Ag^+ in the solution? The K_{sp} for $Ag_2Cr_2O_7$ is 2.0×10^{-7}.

Begin by setting up an ICE table for this reaction

$$Ag_2Cr_2O_7(s) \leftrightarrows 2\ Ag^+ + Cr_2O_7^{2-}$$

Reaction	$Ag_2Cr_2O_7$ (s)	2 Ag^+	$Cr_2O_7^{2-}$
I (initial)	Not applicable	0 *M*	0.200 *M*
C (change)	Not applicable	+ 2x	+ x
E (equilibrium)	Not applicable	2x *M*	0.200 + x *M*

$$[Ag^+]^2\ [Cr_2O_7^{2--}] = [2x]^2\,[0.200 + x] \approx\ [2x]^2\,[0.200] = 1.08\times10^{-10}$$

$$x = 1.16\times10^{-5}\ M$$

In this case, solving for x does not solve the problem. The question asks for the concentration of Ag^+ ions and these are equal to 2x, so the actual concentration of Ag^+ ions are,

$$2x = 2(1.16\times10^{-5}\ M) = 2.32\times10^{-5}\ M\ Ag^+$$

Henry’s Law

In 1803 William Henry formulated a gas law that eventually was named after him. It states that:

> *"At a constant temperature, the amount of a given gas that dissolves in a given type and volume of liquid is directly proportional to the partial pressure of that gas in equilibrium with that liquid."*

This law states that the solubility of a gas in a liquid is directly proportional to the partial pressure of that gas over the liquid. The most common example of Henry's Law is given by carbonated soft drinks. A can of soda is under pressure due to an excess of CO_2 that has been added to it. When the can is opened, the pressure is released and the CO_2 begins to escape. As a consequence, the can of soda fizzes. Over time, the CO_2 escapes and reaches equilibrium with the atmosphere causing the soda to go flat.

Since we are considering gases being dissolved in water, we could write a general reaction showing the equilibrium that must be occurring,

$$\text{Gas(g)} + H_2O \leftrightarrows \text{Gas(aq)}$$

The equilibrium expression for this reaction would be,

$$K_H = \frac{M_{\text{gas}}}{P_{\text{gas}}}$$

Where K_H is the Henry's law equilibrium constant, P_{gas} is the pressure of the gas in atmospheres and M_{gas} is the molarity of the gas dissolved in water. This equation is frequently rearranged to give us the general form of the Henry's Law equation,

$$K_H \cdot P_{\text{gas}} = M_{\text{gas}}$$

All gases dissolve in water to some degree; some better than others. Fish rely on dissolved oxygen in water to breath. Divers get "The Bends" if they come to the surface too quickly which allows dissolved nitrogen to create bubbles in the blood much like a soda can with CO_2.

Our atmosphere is made up of four major gas components (in order), N_2 (78 %), O_2 (21%), Ar (1%), and CO_2 (390.9 ppm in 2012 = 0.03909% or 0.0003909 atm) and a number of other trace gases*. Of these, CO_2 is particularly soluble in water. As a consequence, water that has been left in contact with the air for any length of time will absorb CO_2 according to the following reaction,

Henry's Law Constants	
Gas	K_H M/atm
O_2	1.3×10^{-3}
H_2	7.8×10^{-4}
CO_2	0.034
N_2	6.1×10^{-4}
He	3.7×10^{-4}
Ne	4.5×10^{-4}
Ar	1.4×10^{-3}
CO	9.5×10^{-4}
H_2S	0.10

$$CO_2(g) + H_2O \leftrightarrows H_2CO_3(aq)$$

Water in contact with the air will rather quickly equilibrate. Using Henry's law we can calculate the concentration of CO_2 of water in contact with the air.

$$K_H \cdot P_{gas} = M_{gas}$$

$$(0.034\ \text{M/atm}) \cdot (0.0003909\ \text{atm}) = 1.329\times10^{-5}\ M\ H_2CO_3(aq)$$

We have already seen the H_2CO_3 equilibrium and have become aware that the first dissociation of this acid completely determines the pH of the solution, so what would the pH of the water be that is in contact with the CO_2 in air? The H_2CO_3 dissociates according to the following equilibrium.

$$H_2CO_3(aq) \leftrightarrows H^+ + HCO_3^- \qquad K_{a1} = 4.3\times10^{-7}$$

Using an ICE table, we can solve for the pH,

Reaction	H_2CO_3	H^+	CO_3^{2-}
I (initial)	1.33×10^{-5} *M*	0 *M*	0 *M*
C (change)	-x	+ x	+ x
E (equilibrium)	1.33×10^{-5} – x *M*	x *M*	x *M*

$$\frac{[H^+][CO_3^{2-}]}{[H_2CO_3]} = 4.3 \times 10^{-7}$$

$$\frac{[x][x]}{[1.33x10^{-5}\text{-}x]} \approx \frac{[x]^2}{[1.33x10^{-5}]} = 4.3\times10^{-7}$$

$$x = [H^+] = \sqrt{(1.33x10^{-5})\,(4.3\times10^{-7})} = 2.39x10^{-6}\ M\ H^+$$

$$pH = -\log[2.39x10^{-6}\ M\ H+] = 5.62$$

So, even “pure” water will have a pH ≈ 5.6 when left in contact with the air. This can cause problems in lab when the anticipated pH of water is 7.0. Instructors will have students boil water to remove the dissolved CO_2 if the pH of the water needs to be determined.

At least one prestigious western United States private university sent their expensive water purification system out for repair because its graduate students reported that the water had a pH of about 5.6. They had poured the water into a clean beaker and then, after leaving it sit for a short while, measured its pH. Discovering the water had a pH of 5.6 they became concerned about the quality of the water. Had they had a better chemistry background, they would have saved themselves a lot of time, trouble and money. Now they put lids on the bottles and the problem has disappeared.

pH Controlled Solubility

If the pH of a solution is controlled properly, it is possible to separate metal ions from one another by selective precipitation. To do this properly, an anion must be used that makes both metals insoluble and whose concentration can be controlled by changes in pH. Two anions are commonly used that fulfill these criteria, sulfide (S^{2-}) and carbonate (CO_3^{2-}). Both of these anions share similar chemistry. They are both the conjugate base of diprotic acids and the acids are made by bubbling the gas through water. Therefore, both gases follow Henry’s Law. In addition, they form precipitates with a wide variety of metal ions. The important equilibriums are given below, For H_2S:

$$\begin{array}{ll}
H_2S(g) + H_2O \leftrightarrows H_2S(aq) & K_{eq} = 0.1\ M/\text{atm} \\
H_2S(aq) \leftrightarrows H^+ + HS^- & K_{a1} = 9.1\times10^{-8} \\
HS^- \leftrightarrows H^+ + S^{2-} & K_{a2} = 1.1\text{x}10^{-12} \\
\hline
H_2S(g) \leftrightarrows 2\ H^+ + S^{2-} & K_{eq}\cdot K_{a1}\cdot K_{a2} = 1\text{x}10^{-20}
\end{array}$$

For H_2CO_3

$$\begin{array}{ll}
CO_2(g) + H_2O \leftrightarrows H_2CO_3(aq) & K_{eq} = 0.034\ M/\text{atm} \\
H_2CO_3\ (aq) \leftrightarrows H^+ + HCO_3^- & K_{a1} = 4.3\times10^{-7} \\
HCO_3^- \leftrightarrows H^+ + CO_3^{2-} & K_{a2} = 4.7\text{x}10^{-11} \\
\hline
CO_2(g) + H_2O \leftrightarrows 2\ H^+ + CO_3^{2-} & K_{eq}\cdot K_{a1}\cdot K_{a2} = 6.87\text{x}10^{-19}
\end{array}$$

When a gas is bubbled into water, it is generally assumed that the pressure of this gas equals atmospheric pressure which, in most cases, means 760 torr or 1 atm (the normal pressure around us). This means that these equilibriums reduce to,

For H_2S,

$$\frac{[H^+]^2[S^{2-}]}{P_{H_2S}} = \frac{[H^+]^2[S^{2-}]}{1\ \text{atm}} = 1\times10^{-20}$$

$$[H^+]^2[S^{2-}] = 1\times10^{-20}$$

For H_2CO_3,

$$\frac{[H^+]^2[CO_3^{2-}]}{P_{CO_2}} = \frac{[H^+]^2[CO_3^{2-}]}{1\ \text{atm}} = 6.87\times10^{-19}$$

$$[H^+]^2[CO_3^{2-}] = 6.87\times10^{-19}$$

If we rearrange the final two equations slightly,

$$[S^{2-}] = \frac{1\times10^{-20}}{[H^+]^2} \quad \text{and} \quad [CO_3^{2-}] = \frac{6.87\times10^{-19}}{[H^+]^2}$$

We can see that the $[S^{2-}]$ and $[CO_3^{2-}]$ can be adjusted by changes in pH. If these solutions are buffered, then the pH is fixed and these ions can have only one concentration which is set by the pH of the solution.

What is the concentration of copper ions in a solution of CuS that has been saturated with H_2S at pH = 3? $K_{sp} = 8\text{x}10^{-37}$.

The solubility product for CuS is,

$$CuS(s) \leftrightarrows Cu^{2+} + S^{2-}$$

The solubility expression is,

$$[Cu^{2+}]\,[S^{2-}] = 8x10^{-37}$$

Rearranging,

$$\left[Cu^{2+}\right] = \frac{8\times10^{-37}}{[S^{2-}]}$$

As shown earlier, under these conditions, the relationship between $[S^{2-}]$ and the $[H^{+}]$ is,

$$[S^{2-}] = \frac{1\times10^{-20}}{[H^{+}]^{2}}$$

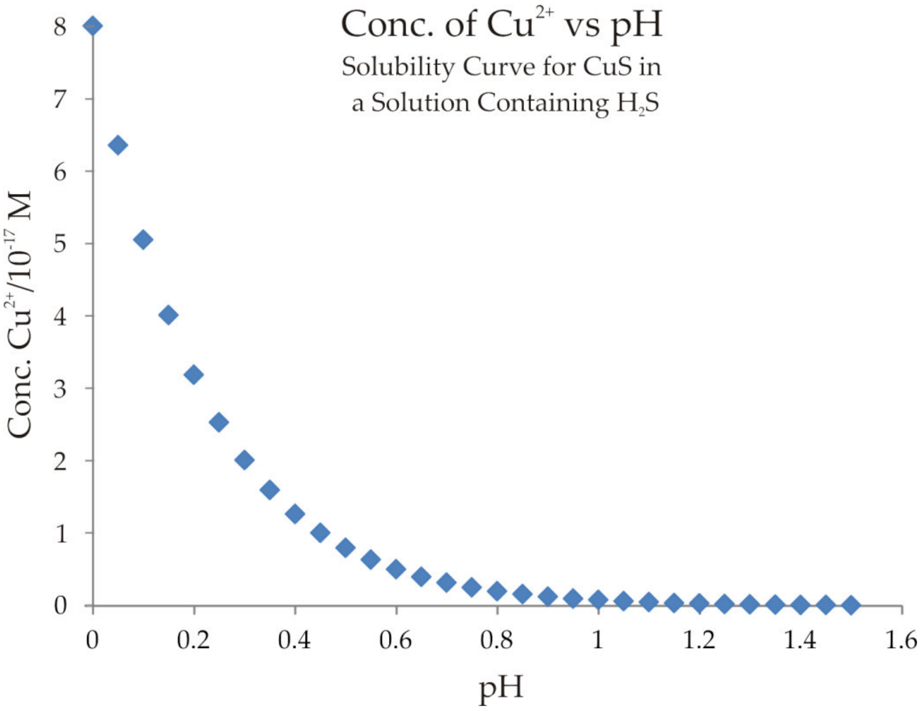
Substituting this into our solubility product expression for CuS we get,

$$\left[Cu^{2+}\right] = \frac{8\times10^{-37}}{[S^{2-}]} = \frac{8\times10^{-37}}{\left[\frac{1\times10^{-20}}{[H^{+}]^{2}}\right]} = \frac{8\times10^{-37}[H^{+}]^{2}}{1\times10^{-20}} = 8\times10^{-17}[H^{+}]^{2}$$

We can use this equation so calculate the concentration of copper ions at pH = 3 ($1x10^{-3}$ M H^{+}),

$$\left[Cu^{2+}\right] = 8\times10^{-17}[H^{+}]^{2} = 8\times10^{-17}\left[1\times10^{-3}\right]^{2} = 8\times10^{-23}\text{ M }Cu^{2+}$$

The equation can also be used to show how the concentration of copper ions changes with pH. Doing so creates a solubility curve for Cu^{2+} in saturated solutions of H_2S.



From this curve we can see that the concentration of Cu^{2+} decreases as the solution becomes more basic (pH increases). The concentration of Cu^{2+} is never very large ($\approx 10^{-17}$ *M*) even in very acidic solutions (1 *M* H^+) so it is safe to assume that Cu^{2+} is essentially insoluble at all values of pH in solutions containing H_2S.

Controlling the H_2S concentration using pH allows for the separation of ions. An example of how this might be done can be shown using zinc and iron(II) ions. The solubility products of zinc sulfide and iron (II) sulfide are given below,

$$ZnS(s) \leftrightarrows Zn^{2+} + S^{2-} \quad K_{sp} = 2\times10^{-25}$$

$$FeS(s) \leftrightarrows Fe^{2+} + S^{2-} \quad K_{sp} = 8\times10^{-19}$$

Following the procedure used above, we get for zinc sulfide,

$$[Zn^{2+}]\,[S^{2-}] = 2\times10^{-25}$$

$$[Zn^{2+}] = \frac{2\times10^{-25}}{[S^{2-}]} = \frac{2\times10^{-25}}{\left[\dfrac{1\times10^{-20}}{[H^+]^2}\right]} = \frac{2\times10^{-25}[H^+]^2}{1\times10^{-20}} = 2\times10^{-5}[H^+]^2$$

And for iron (II) sulfide,

$$[Fe^{2+}]\,[S^{2-}] = 8\times10^{-19}$$

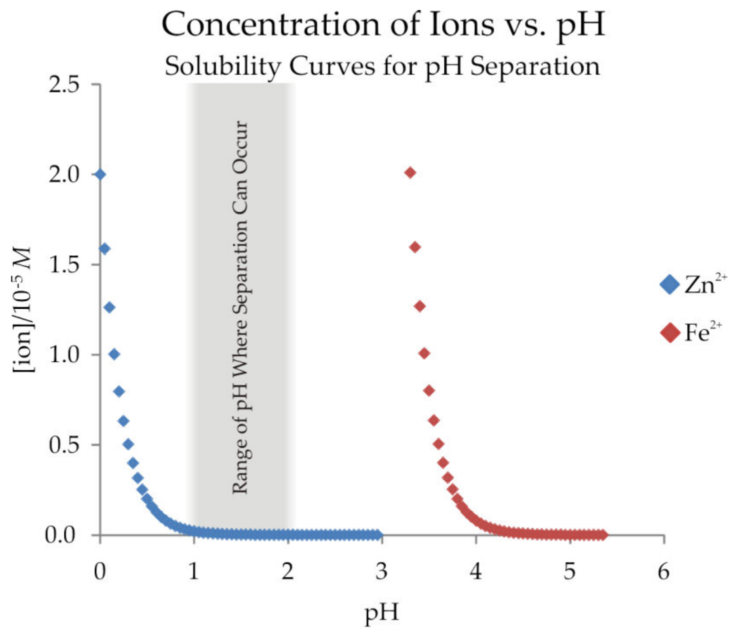
$$\left[Fe^{2+}\right] = \frac{8\times10^{-19}}{[S^{2-}]} = \frac{8\times10^{-19}}{\left[\dfrac{1\times10^{-20}}{[H^{+}]^{2}}\right]} = \frac{8\times10^{-19}[H^{+}]^{2}}{1\times10^{-20}} = 80\,[H^{+}]^{2}$$

When these equations are used to calculate the concentration of zinc and iron (II) ions in solutions of various pH, we obtain a pair of solubility curves as shown below. Between these two curves is a region of pH where zinc sulfide is not soluble but iron (II) sulfide is soluble. A mathematical comparison shows that, at pH = 1 (0.1 M H^{+}) we have the following condition,

$$\left[Zn^{2+}\right] = 2\times10^{-5}[H^{+}]^{2} = 2\times10^{-5}[0.1\,M\,H^{+}]^{2} = 2\times10^{-7}\,M\,Zn^{2+}$$

$$\left[Fe^{2+}\right] = 80\,[H^{+}]^{2} = 80\,[0.1\,M\,H^{+}]^{2} = 0.80\,M\,Fe^{2+}$$

There are virtually no zinc ions in solution because they are all found in the solid zinc sulfide. The iron (II) ions are in solution and have a 0.8 M concentration. By pouring off the liquid we would leave the solid ZnS behind and these two ions will now be separated.



Amphoterism

The word "amphoterism" derives its meaning from the Greek word "amphi" which means "both" or "two." The most common use of this Greek word is found in the word "amphibian" which is a creature at home on land and in the water. In chemistry, this word means molecules that are at home in both and acid and a base. Of course, in chemistry, we don't actually say that a compound feels at home, we would say that the compound is soluble in both an acid and a base. The implication is that the compound is insoluble in-between.

For a metal to be soluble it must be in ionic form. Amphoteric metals are found in their natural ionic form in acid solutions but as hydroxide complexes in solutions that are very basic.

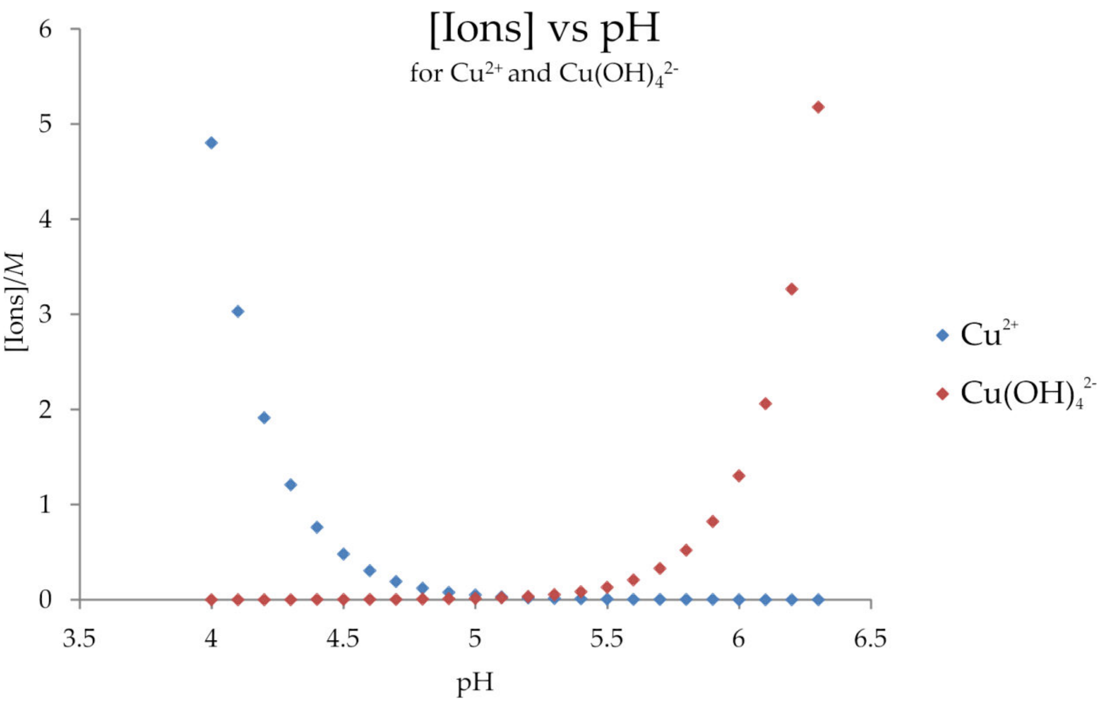
Amphoteric Metal Ions

Acid Form	Insoluble Solid	Basic Complex
Al^{3+}	$Al(OH)_3$	$Al(OH)_4^-$
Cu^{2+}	$Cu(OH)_2$	$Cu(OH)_4^{2-}$
Zn^{2+}	$Zn(OH)_2$	$Zn(OH)_4^{2-}$
Cr^{3+}	$Cr(OH)_3$	$Cr(OH)_4^-$
Be^{2+}	$Be(OH)_2$	$Be(OH)_4^{2-}$
Pb^{2+}	PbO	$Pb(OH)_4^{2-}$
Sn^{2+}	SnO	$Sn(OH)_4^{2-}$

Consider the equilibriums for copper (II),

$$Cu^{2+} + 2\,OH^- \leftrightarrows Cu(OH)_2(s) \qquad K_{sp} = 4.8\times10^{-20}$$
$$Cu(OH)_2(s) + 2\,OH^- \leftrightarrows Cu(OH)_4^{2-} \qquad K_{eq} = 1.3\text{x}10^{16}$$

Initially, copper (II) is soluble but as hydroxide is added, the insoluble precipitate $Cu(OH)_2(s)$ is formed. As more hydroxide is added, the excess OH^- reacts with the solid to form the complex ion, $Cu(OH)_4^{2-}$ and the solid dissolves. These reactions occur within a fairly narrow range of pH's as shown on the following plot. Below a pH of 4.5, Cu^{2+} is soluble and above pH of 5.5, $Cu(OH)_4^{2-}$ is soluble, but in the narrow range between pH 4.5 and 5.5, copper (II) is insoluble; there are virtually no ionic forms of copper left in solution.



The shape of this curve is the general shape for all amphoteric metal ions. The metal ions are in their natural ionic form in acid solutions but as the solution is made more basic, they become insoluble. Eventually, when sufficient hydroxide has been added, the complex ions that are formed increase the solubility of the metal ion.

Distribution Coefficients

A common technique used in organic chemistry to extract a component from a mixture of components is liquid-liquid extraction using a separatory funnel. The technique usually involves separating a mixture of compounds that are soluble in water but more soluble in an immiscible organic compound like octanol, methylene chloride, diethyl ether, or some other organic compound that does not mix with water. The distribution coefficient (P) is just the ratio of the extracted compounds solubility in the organic phase versus its solubility in the aqueous phase. It is generally assumed that organic compounds will be more soluble in the organic phase so the distribution coefficient is always greater than 1.

$$\text{Distribution Coefficient} = P = \frac{[\text{solute}]_{\text{organic phase}}}{[\text{solute}]_{\text{aqueous phase}}}$$

Since these values are greater than 1, and often very much greater than 1, the logP is often reported rather than the distribution coefficient itself. Octanol is the standard organic phase by which most distribution coefficients are measured although, for extraction purposes, nearly any immiscible organic solvent can be used.

The distribution coefficient is often used as a measure of the hydrophilicity and hydrophobicity of a compound. Ionic compounds like organic acids, amines, and some small alcohols are not particularly soluble in hydrophobic solvents like octanol (logP < 0) while non-ionic compounds like benzene, halogenated hydrocarbons, ethers, ketones and aldehydes, can be very soluble (logP > 0).

Component	**Solvent**	**log P_{OW}**	**T (°C)**
Acetone	Octanol	-0.24	25
Methanol	Octanol	-0.82	19
Formic acid	Octanol	-0.54	25
Diethyl ether	Octanol	0.83	20
Benzene	Octanol	2.16	25
Benzoic acid	Octanol	1.87	25
Methylene Chloride	Octanol	1.25	25
Caffeine	CH_2Cl_2	0.662	25
Caffeine	Benzene	-0.32	25
Caffeine	Chloroform	0.992	25

For example, it is common practice in organic chemistry to use methylene chloride to extract caffeine from a sample of tea, coffee, or tablet containing caffeine. Suppose that you dissolve a tablet that contains 0.200 grams of caffeine (NoDoz©, Vivarin©, etc.) in 100 mL of water. Using 60 mL of methylene chloride, how much caffeine can you expect to extract?

$$\log P_{ow} = 0.662 \text{ so } P_{ow} = 10^{0.662} = 4.6$$

This tells us that the caffeine is 4.6 times more soluble in methylene chloride than in water. Using the definition for the distribution coefficient we have,

$$P_{ow} = \frac{[\text{solute}]_{CH_2Cl_2}}{[\text{solute}]_{H_2O}} = 4.6$$

We should note that we can set up an ICE table to solve this equation,

Reaction	g Caff in H_2O	g Caff in CH_2Cl_2
I (initial)	0.200 g	0
C (change)	–x	+ x
E (equilibrium)	0.200 – x g	x g

$$\frac{[\text{x g}_{\text{caff}}/60\text{ mL CH}_2\text{Cl}_2]}{[(0.200\text{ g}_{\text{caff}} - \text{x g}_{\text{caff}})/100\text{ mL H}_2\text{O}]} = 4.6$$

x g caff = 0.1468 g caffeine were extracted from the water

This means that in a single extraction we obtained,

$$\frac{0.1468\text{ g Caffeine}}{0.200\text{ g Caffeine total}} = 72.34\%\text{ of the caffeine}$$

Organic chemists rarely do a single extraction when removing an organic compound from an aqueous solution. Normally, they would do two or three extractions, but what is counter-intuitive is that they will not use two or three 60 mL extraction volumes; they will divide this volume three times and use three 20 mL extractions instead. The same volume of methylene chloride is being used but more caffeine will be extracted. To see this, consider the following; assume that we have the same 0.200 grams of caffeine dissolved in 100 mL of water, but now we do our extraction using three 20 mL samples of methylene chloride. We would get,

First extraction,

$$\frac{[\text{x g}_{\text{caff}}/20\text{ mL CH}_2\text{Cl}_2]}{[(0.200\text{ g}_{\text{caff}} - \text{x g}_{\text{caff}})/100\text{ mL H}_2\text{O}]} = 4.6$$

x g caff = 0.0958 g caffeine were extracted from the water so 0.1042 g are left.

Second extraction,

$$\frac{[\text{x g}_{\text{caff}}/20\text{ mL CH}_2\text{Cl}_2]}{[(0.1042\text{ g}_{\text{caff}} - \text{x g}_{\text{caff}})/100\text{ mL H}_2\text{O}]} = 4.6$$

x g caff = 0.0499 g caffeine were extracted from the water so 0.0543 g are left.

Third extraction,

$$\frac{[\text{x g}_{\text{caff}}/20 \text{ mL CH}_2\text{Cl}_2]}{[(0.0543 \text{ g}_{\text{caff}} - \text{x g}_{\text{caff}})/100 \text{ mL H}_2\text{O}]} = 4.6$$

x g caff = 0.0260 g caffeine were extracted from the water so 0.0283 g are left.

If we add these extractions together, we have extracted a total of 0.1717 grams of caffeine. This gives us,

$$\frac{0.1717 \text{ g Caffeine}}{0.200 \text{ g Caffeine total}} = 85.85\% \text{ of the caffeine}$$

So, by doing three 20 mL extractions rather than a single 60 mL extraction we have extracted about 13.5% more caffeine from the sample and have used the same amount of extracting solvent, methylene chloride.

In theory, it would be better to do four 15 mL extractions or five 12 mL extractions in order to retrieve more of your sample, but the amount of work required to retrieve this last bit of caffeine is not generally worth the added effort.

Chapter Thirteen

Thermodynamics, Heat Capacities, Enthalpy, Entropy, and Gibbs Energy

"Thermodynamics is a funny subject. The first time you go through it, you don't understand it at all. The second time you go through it, you think you understand it, except for one or two small points. The third time you go through it, you know you don't understand it, but by that time you are so used to it, it doesn't bother you anymore."

Arnold Sommerfeld - German Physicist

Thermodynamics is all about energy; how it is generated, what can be done with it, and how it can be converted from one form to another. Oddly, we don't know what energy is. We define energy by what it does.

"Energy is the ability to do work."

Not all energy does useful work. We are aware of this every time we fill up our car. Some of our gas moves our car down the road, but some of the energy is lost as heat and can never be retrieved. That work, that energy, has been lost forever. Cars are getting more efficient. They are able to extract more energy out of each tankful of gas and electric cars are more efficient yet. Even so, there are losses and no system is ever perfect.

Thermodynamics teaches us that, since no system is perfect, perpetual motion will never exist. There will always be losses and these loses will cause systems to run down. In the same way, a cup of water cannot hold more than a cup of water. You cannot pour two cups of water out of a cup that holds only one cup. In the same way, you cannot extract more energy out of system than it contains. So, not only will you not have perpetual motion (you can't get ALL of the water out of the cup), you can't use a perpetual motion machine to create energy (you can't remove water from a cup of water and still have a cup of water). Here is some advice for aspiring scientists, Don’t argue with Einstein – you can’t go faster than the speed of light.

Don’t argue with the Laws of Thermodynamics – energy is never “free.”

The Laws of Thermodynamics

There are four laws of thermodynamics but, oddly, they start at zero.

> **Zeroeth Law** – If two systems are in thermal equilibrium with a third system, they are in thermal equilibrium with each other.
>
> **First Law** – Energy is neither created nor destroyed but it can be converted from one form to another.
>
> **Second Law** – All naturally occurring reactions become more disordered with time.
>
> **Third Law** – At absolute zero, the disorder of a system becomes zero.

C.P. Snow, the British scientist and author offered a humorous way to remember the Three Laws. With reference to gambling, he said,

> (1) You cannot win (you can’t get something for nothing).
>
> (2) You cannot break even (you can’t get back to your original position)
>
> (3) You cannot get out of the game (you have to play because thermodynamics runs your life).

The First Law of Thermodynamics

The first law of thermodynamics can be written as,

$$dU = dq + dw$$

Where dU is a small change in internal energy, dq is a change in the heat energy, and dw is the change in work. The International Union of Pure and Applied Chemistry defines work as pressure-volume work, or more specifically,

$$dw = -PdV$$

From this we define a new form of energy that is called Enthalpy (ΔH),

$$dH = dq + VdP$$

If the pressure is kept constant, then,

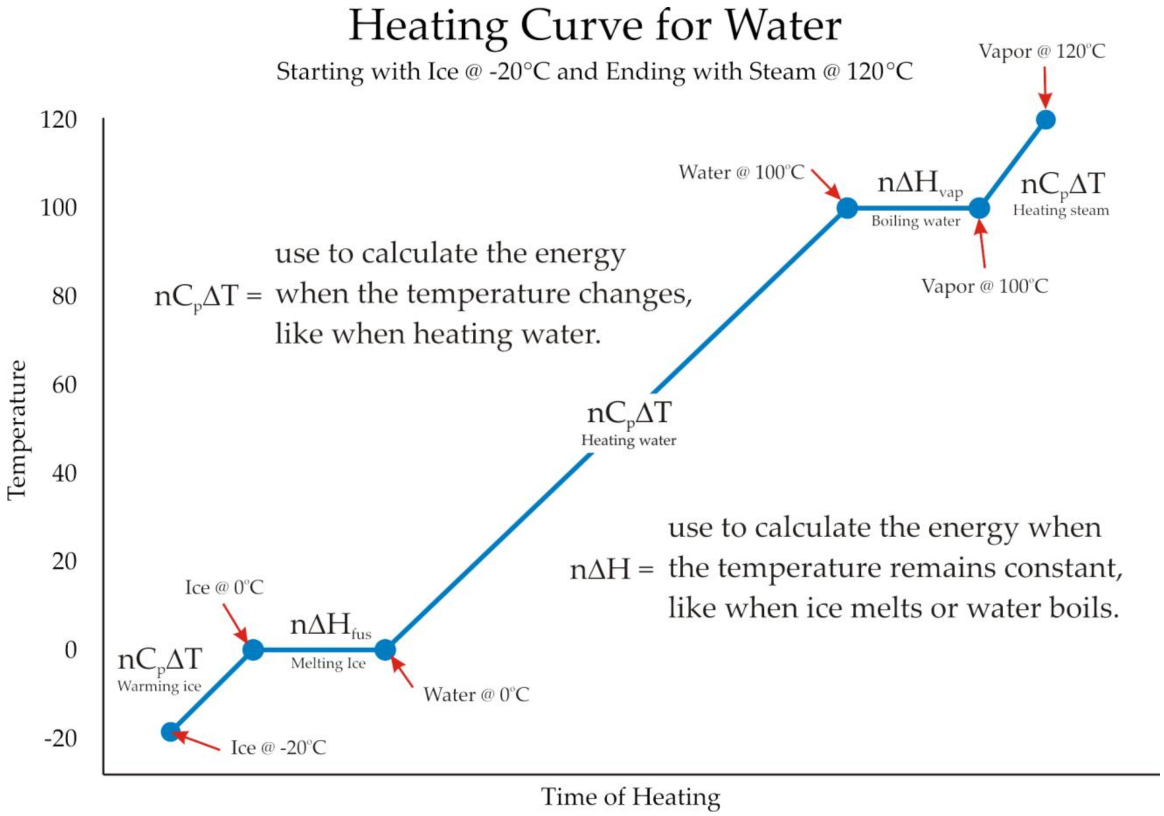
$$dH = dq_P$$

where dq_P is the heat energy measured under constant pressure. Since the atmospheric pressure around us stays reasonably constant, when we do experiments in open beakers and test tubes that measure changes in heat content of a reaction we are measuring the enthalpy of those reactions. If we were to attempt to measure the internal energy of a reaction we would need to keep the volume constant and this, as it turns out, is very difficult to do. Liquids, gases, and even solids, want to expand and contract when energy is transferred in and out of them but if internal energy is measured, the volume cannot be allowed to change. So, rather than measure internal energy, most often we measure enthalpies because of the convenience.

Measuring Changes in Energy

It should be intuitively obvious that one way to measure energy is to measure the change in temperature of some substance, most often, water. Hot water contains more energy than cold water, but not all energy changes require a change in temperature. For example, if you put energy into ice, the ice will melt, but its temperature doesn't change. Ice melts at 0°C and the water that forms is also at 0°C. All of the energy being put into the ice causes the bonds between the frozen water molecules to break, but it does not cause the water to heat up. So we see that there are two distinct processes that can occur with water; putting energy into ice melts it but doesn't change its temperature but after the ice has melted, putting more energy into it raises its temperature.

We have identified two distinct effects that energy can have on our water system. Energy can melt the ice (called a phase change) and it can cause a rise in temperature (the water gets hot). We can represent these changes that occur to water by drawing a heating curve.



This diagram shows what happens when you take a block of very cold ice at -20°C and begin heating it. At first the ice begins to warm up (but doesn't melt) until it reaches 0°C. At 0°C all the energy goes into breaking the ice bonds which converts the ice to water but does not heat it. Once the ice has melted, the cold water begins to heat up until it reaches its boiling point (100°C). Adding more energy does not change the temperature of the hot water, rather, all of the energy is used to break the bonds between the water molecules and turn the water into vapor. Once this happens, any additional energy added will cause the temperature of the water vapor to continue to rise.

A logical question would be to ask why we care about the heating curve of water? The reason is that we often measure the energy released by a reaction by measuring how the reaction changes the temperature of water. In most of the lab work that you will do, you will measure the amount of energy given off by a reaction by measuring the amount of ice that melts or by measuring the change in temperature of a container of water. Understanding how much energy it takes to melt ice or how much energy it takes to raise the temperature of water is critical in measuring the energy changes in chemical reactions.

The Basis for Thermodynamics

At its heart, thermodynamics starts with the ideal gas law equation,

$$PV = nRT$$

It isn't obvious, but pressure times volume equals work. This equivalence can be shown mathematically,

$$P = \frac{\text{force}}{\text{area}} = \frac{\text{mass x acceleration}}{\text{area}} = \frac{\text{kg} \cdot \frac{\text{m}}{\text{s}^2}}{\text{m}^2}$$

$$PV = \left[\frac{\text{kg} \cdot \frac{\text{m}}{\text{s}^2}}{\text{m}^2}\right](\text{m}^3) = \frac{\text{kg}\cdot\text{m}^2}{\text{s}^2} = \text{Joule} = \text{Energy}$$

Since R is the gas law constant, there are four variables that can be used to find energy, P, V, n, and T. Normally, we assume that the number of moles remains constant, so this reduces our variables to just P, V, and T, but we must add one back, entropy (S). Precisely how entropy, which measures the disorder in a system, can be used to create energy isn't obvious, but a simple example might help to explain it.

Osmosis

It is the natural tendency of things to fall apart. Vases fall off of tables and break, but it would be extraordinary to see a broken vase suddenly leap up off the floor and reassemble itself on the table. In like fashion, if we put a drop of blue dye into a container of water, over time, the water will become uniformly blue. We do not expect a container of uniformly blue water to spontaneously bring that dye back together and form a drop of blue dye at its center. It is the natural consequence of the law of entropy (the 2nd law) that the dye spread out into the container of water and become more dilute. In fact, the desire for the blue dye to become dilute is governed by the second law of thermodynamics. But this is not limited to dilution of a dye, it applies to all solutions.

Consider for a moment, the cell shown below. On one side we have pure water and on the other side we have a solution of salt water. Between the two, is a membrane with pores so small that only the water can pass through it. The second law of thermodynamics demands that, if possible, the salt solution should become more dilute. As a consequence, water begins to move from the pure water side, through the membrane, to the side containing the salt. This causes the water on the side containing the salt to rise while the pure water side drops. If we were to put a small wheel on the salt side, the rising water could turn that wheel and create a small amount of electricity. Work would be done and energy would be created. The driving force for this creation of energy was the requirement that the solution become more dilute as demanded by the second law of thermodynamics. A chemist would say that this process was entropically driven. It is therefore reasonable to say that a natural variable of energy is entropy, so we add it to our list,

Variables that govern the production of energy = P, V, T, and S

There are a number of different kinds of energy in thermodynamics that differ from one another by the variables used to determine their value. These energies are,

	Symbol	Natural Variables		
Internal Energy	ΔU	S	V	n
Enthalpy	ΔH	S	P	n
Helmholtz Energy	ΔA	T	V	n
Gibbs Energy	ΔG	T	P	n

Volume is notoriously difficult to keep constant. It requires the use of very rigid containers that are inconvenient to use. As a consequence, Internal and Helmholtz Energies are not usually measured. The two most common energies measured are Enthalpy and Gibbs energies both of which have pressure as natural variables. We can keep this variable constant by doing a reaction in an open container exposed to the atmosphere. Since most of the reactions are done in beakers and open containers, Enthalpy and Gibbs energies are the most common forms of energy measured and will be the focus of this section.

Enthalpy

The enthalpy of a reaction is determined by measuring the amount of energy taken in or given off by a chemical reaction. This usually means that the reaction is allowed to happen and the energy measured by heating or cooling a volume of water. Knowing the temperature change on the water allows for the calculation of the amount of energy transferred.

Heat Capacities - C_p

A heat capacity measures the amount of energy (Joules) needed to raise one mole of a compound or element by 1 Kelvin (1°C). The unit on heat capacity is therefore,

$$C_p = \frac{J}{mol \cdot K}$$

The "p" in C_p indicates that this value has been measured at constant pressure. In the lab, C_p is commonly used to determine the amount of energy given off in a reaction since the reaction can be done in an open beaker exposed to the atmosphere. A table of common heat capacities is given below,

Common Heat Capacities	
Substance	Cp/J/mol·K
$H_2O(s)$	37.7
$H_2O(\ell)$	75.2
$H_2O(g)$	35.2
Ethanol	112
Copper	24.78
Zinc	25.5
Iron	25.69
Nickle	31.69
Lead	27.04

To use a heat capacity of measure the amount of energy given off by a reaction we note that,

$$nC_p\Delta T = mol \cdot \frac{J}{mol \cdot K} \cdot K = Joules = Energy$$

When heat is supplied to a reaction vessel, heat flows from the source of the heat to the reaction vessel. The source of the heat cools off while the surroundings heat up. These are opposite effects, so we could write,

Heat given off = (-) Heat taken in

This assures us that both sides of this equation will have the same mathematical sign. So, if a reaction causes 100 grams of water to rise in temperature by 1.4°C (1.4 K) then the final temperature is going to be higher than the initial temperature so that $T_{final} - T_{initial} = \Delta T$ = positive value. The source has given off the energy that produced this change in energy and whenever energy is given off it is defined as being negative, so,

$$-nCp\Delta T = \text{Energy}$$

$$-nC_p\Delta T = -\frac{100\ g}{18\ g/mol} \cdot 75.2\ \frac{J}{mol \cdot K} \cdot 1.4\ K = -584.9\ \text{Joules} = \text{Energy}$$

The reaction gave off energy so it is exothermic and the sign on this energy must be negative.

Problem 13.1

A family owned a pool and a hot tub but the pool was not heated. Two boys in the family wanted to go swimming in the middle of October but, finding the pool to be a very cold 52°F, they asked their father if they could empty the contents of their hot tub into the pool to warm the water so they could go swimming. The pool contained 20,000 gallons of water and the hot tub was 400 gallons but was kept at a toasty 104°F. Should the father let his sons dump the hot tub water into the pool and let them go swimming?

In this case, the water from the hot tub will cool off (be negative) and the water in the pool will heat up (be positive) so we have the following condition,

$$-\text{Energy from hot tub} = \text{Energy of the pool}$$

$$-nCp\Delta T_{hot\ tub} = nCp\Delta T_{pool}$$

We don’t need to know the heat capacity of the water since it is the same on both sides of this equation and cancel, so we are left with,

$$-n\Delta T_{hot\ tub} = n\Delta T_{pool}$$

Also we do not have to convert the gallons of water into moles of water since the conversion would be the same on both sides and this conversion would also cancel. In either case, the water from the hot tub and water in the pool must come to some common temperature that we will call T_{final}. So our equation is,

$$-(400 \text{ gallons})(T_{final} - 104) = (20{,}000 \text{ gallons})(T_{final} - 50)$$

$$(T_{final} - 104) = -50\,(T_{final} - 50)$$

$$T_{final} - 104 = -50T_{final} + 2500$$

$$51\,T_{final} = 2604$$

$$T_{final} = 51.06°\text{F}$$

The appropriate thing to do would be to say “No.” The temperature of the pool water will rise only 1.06°F which would hardly be noticeable. Of course, the boys could still go swimming if they wanted.

What would happen if we included a phase change in our problem? For example, suppose we put some ice into water. The ice will melt and the water will get cold, but how cold?

Problem 13.2

Most water comes out of the household tap at 22°C. Suppose that we fill a glass with 500 mL of water (about 2 cups) and add to it 4 ice cubes that weigh 20 grams each. The ice cubes are at 0°C. Once the ice melts, what will be the final temperature of the water?

The difficulty here is envisioning what will happen. There are three processes occurring, the ice melts and becomes water, the glass of water cools, and then the ice water and the glass of water mix, which heats the ice water, cools the glass of water and the entire mixture comes to a final temperature. Schematically, we would write,

$$\text{Ice melts} + \text{Ice water heats up} = \text{Glass of water cools}$$

This equation is not quite complete. The source of the energy for the melting of the ice and the warming of the ice water comes from the glass of water, so one side of this equation heats up while the other side cools. This makes them opposites of one another so we must add a negative sign to one side of this equation. Which side we choose is not important, but it makes most sense to put the negative sign on the right side, where the water is cooling, so that both sides are positive.

Ice melts + Ice water heats up = – Glass of water cools

Thermodynamically, melting ice is a phase change that requires the use of the ΔH_{fus} of ice ($\Delta H_{fus} = 6.01$ kJ/mol) and the heating of water requires the use of a heat capacity ($Cp_{water} = 75.2$ J/mol·K). Putting these into our equation we have,

$$n\Delta H_{fus} + nCp_{water}\Delta T = -\, nCp_{water}\Delta T$$

$$\left(\frac{80\text{ g}}{18\text{g/mol}}\right) 6010\text{ J/mol} + \left(\frac{80\text{ g}}{18\text{g/mol}}\right)(75.2\text{ J/mol·K})\left(T_f - 0^{\circ}\text{C}\right) = -\left(\frac{500\text{ g}}{18\text{g/mol}}\right)(75.2\text{ J/mol·K})\left(T_f - 22^{\circ}\text{C}\right)$$

$$26{,}711.11\text{ J} + 334.22\text{ J/K }(T_f) = -2088.88\text{ J/K }(T_f) + 45{,}955.55\text{ J}$$

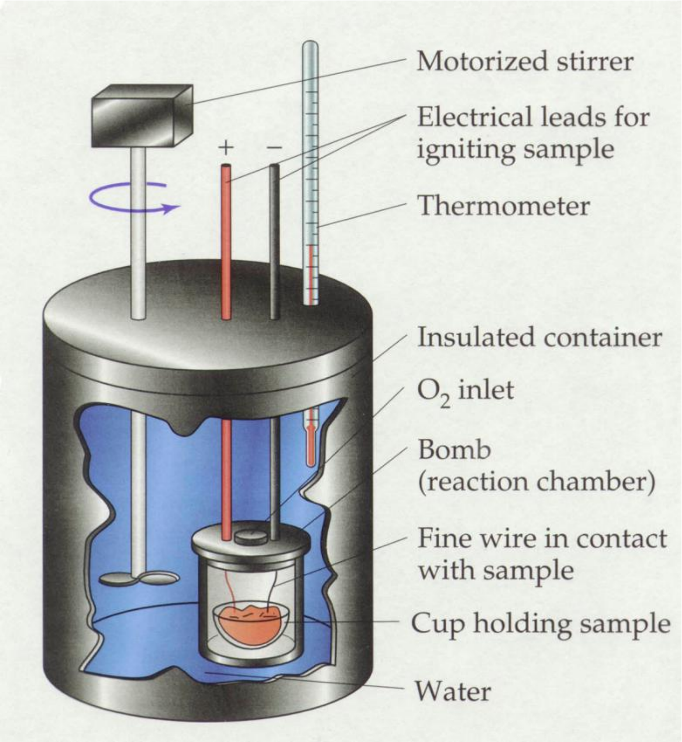
$$2423.1\text{ J/K }(T_f) = 19{,}244.44\text{ J}$$

$$T_f = 7.94\ ^{\circ}\text{C}$$

Our glass of water would be satisfyingly cool to drink.

Calorimetry

A calorimeter is a device that is used to measure the energy taken in or given off in a chemical reaction. Usually, it is insulated so that the energy lost to the surroundings will be kept to a minimum. A calorimeter can be as simple as a Styrofoam cup or as complicated as a bomb calorimeter that is extremely well insulated and calibrated for very precise measurements of energy. Regardless of the complexity of the device itself, all calorimeters share something in common; they all use water to trap and measure the energy given off by a reaction. A picture of a very simple bomb calorimeter is given below.



Typically, a sample is loaded into the reaction chamber and then pressurized to 30 atm of pure oxygen. Thin electrical leads go through the sample. These electrical leads glow like a light bulb when electricity is passed through them which ignites the sample and causes it to burn. The energy given off during the burning of the sample is collected by the water surrounding the reaction chamber and, using a very precisely calibrated thermometer, the change in temperature of the water is noted. Using the change in temperature and the heat capacity of the water and the calorimeter, the energy is calculated. A "bomb" calorimeter gets its name because of the extreme pressure inside of the reaction chamber (known as the bomb). This pressure serves a greater purpose than just supplying sufficient oxygen for the combustion reaction. The amount of oxygen in the reaction chamber far exceeds the amount of oxygen needed for the reaction. There is so much oxygen present that the amount used does not significantly change the pressure inside the reaction chamber. Therefore, the pressure remains constant, which is a requirement if an enthalpy is to be measured. For example, if 1.5 grams of Benzoic acid were combusted in a 1 liter bomb calorimeter pressurized to 30 atm of oxygen, the pressure in the container after reaction would be 29.85 atm. Technically, the pressure changes but the volume remains constant because of the size and strength of the stainless steel calorimeter. This means that a bomb calorimeter is actually measuring the internal energy of a reaction and not its enthalpy. The relationship between ΔH and ΔU is given below,

$$\Delta H = \Delta U + \Delta(PV)$$

Since the container is rigid, the volume remains constant so the only potential source of work is by the change in pressure, but since this change in pressure is due to the change in moles of gas we have (from the ideal gas law),

$$\Delta H = \Delta U + \Delta n_{gas}RT$$

The balanced combustion reaction for benzoic acid is,

$$C_7H_6O_2 + \frac{15}{2}\,O_2(g) \rightarrow 7\ CO_2(g) + 3\ H_2O(\ell)$$

The change in the number of moles of gas for each mole of benzoic acid is,

$$(n_{final} - n_{initial}) = (7 \text{ mole } CO_2 - 7.5 \text{ mole } O_2) = -0.50 \text{ mole gas} = \Delta n_{gas}$$

The standard heat of combustion (ΔH_c) for benzoic acid is -3228 kJ/mol or -3,228,000 J/mole. If we remember that R = 8.314 J/mol K then for each mole of benzoic acid,

$$\Delta n_{gas}RT = (-0.5 \text{ mol})\ (8.314 \text{ J/molK})\ (298) = -1238.8 \text{ J of energy}$$

So, the difference between the enthalpy and the internal energy for the combustion of benzoic acid is,

$$\Delta H_c = -3228.0 \text{ kJ/mol}$$
$$\Delta U_c = -3226.8 \text{ kJ/mol}$$

There is less than 0.04% difference between these two numbers. As a consequence, unless very precise values are desired, the distinction between Enthalpy and Internal Energy is lost when it comes to bomb calorimetry and it is generally assumed that the energy data coming from bomb calorimeters represents enthalpy data.

Various Forms of Enthalpy

All chemical compounds can be made from the individual elements from which they are composed. When a compound is made from the elements the amount of heat taken in or released during that reaction is called the heat of formation and is designated as ΔH_f. Compounds can also be measured under a standard set of conditions. For thermodynamics, those conditions are,

Standard State Conditions	
Condition	Value
Temperature	25°C or 298.15 K
Pressure	1 atm
Concentration	1 *M*
Amount	1 mole

So, when a compound is made from the elements and is also made under standard conditions, we designate this by adding a degree sign to the thermodynamic value. Therefore the $\Delta H°_f$ is the enthalpy of formation of a compound from the elements under standard conditions. The ° sign in this designation is not pronounced "degree;" we call it "zero". We would say "delta H zero of formation" and not "delta H degree of formation." There are, in fact, several forms of enthalpy that will be used in this text and it is useful to be able to understand the difference between them.

Definition of Various Forms of Thermodynamic Values	
Value	Definition
ΔH	The amount of heat given off or taken in by a reaction.
$\Delta H°$	The amount of heat given off or taken in by a reaction under standard state conditions.
$\Delta H°_f$	The amount of heat given off or taken in by a reaction under standard state conditions when 1 mole of a compound is made from the elements.
$\Delta H°_c$	The amount of heat given off or taken in by a reaction under standard state conditions when 1 mole of a compound is combusted in oxygen.

Most of the work done by students in a lab is done in open containers at room temperature using amounts of chemicals that only approximate 1 mole.

Therefore, most student labs in thermodynamics are measuring a ΔH. In order to measure any of the other values, careful work must be done under very controlled conditions.

The Standard Heat of Formation

The standard heat of formation, ΔH°_f, measures the amount of energy released or taken in when a compound is made from the elements. This requires that the elements be in their natural state as found in nature. For example, for oxygen this means gaseous $O_2(g)$ and for carbon this mean C(s) and not diamond or graphite which are compounds made from carbon. The standard heat of formation of some the common compounds are given below,

1. $H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(\ell)$ $\Delta H^\circ_f = -285.8$ kJ/mol
2. $C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ_f = -393.5$ kJ/mol
3. $C(s) + 2\ H_2(g) + \frac{1}{2} O_2 \rightarrow CH_3OH(\ell)$ $\Delta H^\circ_f = -239.2$ kJ/mol
4. $2\ Fe(s) + {}^3/_2\ O_2(g) \rightarrow Fe_2O_3(s)$ $\Delta H^\circ_f = -824.2$ kJ/mol
5. $\frac{1}{2} N_2(g) + {}^3/_2\ H_2(g) \rightarrow NH_3(g)$ $\Delta H^\circ_f = -45.9$ kJ/mol

The main features that these reactions share in common is that all the compounds are being made for elements and that precisely on mole of each compound is being made. If only one mole of each compound is being made, it is absolutely necessary to balance some of these reactions using fractions.

By definition, the ΔH°_f of any element equals zero.

Hess's Law

Using heats for formation, it is possible to calculate the enthalpy of any reaction for which heat of formation data is available. To do so, we must add and subtract various reactions together. The addition and subtraction of reactions to obtain a new reaction is Hess's Law. For example, consider combustion of methanol to form carbon dioxide and water,

$$CH_3OH(\ell) + {}^3/_2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(\ell)$$

Using the first three reactions given above, we can add and subtract them in such a way as to obtain a value for the enthalpy of combustion of methanol. By comparison of the reactions we have been given to the one that we need we can tell that we need to make two waters so we must multiply our water reaction by two. We can also see that are given a methanol reaction that makes methanol but we need methanol as a reactant so that reaction must be reversed. Reversing a reaction changes the sign on an enthalpy so the enthalpy of the methanol reaction changes from -239.2 kJ/mol to +239.2 kJ/mol. Doubling a reaction double the amount of energy it will give off so, if we double the water reaction we must also double its enthalpy.

$$\begin{array}{ll}
\cancel{2\ H_2(g)} + \cancel{1}\ ½\ O_2(g) \rightarrow 2\ H_2O(\ell) & 2(\Delta H^\circ_f = -285.8\ \text{kJ/mol}) \\
\cancel{C(s)} + 1\ O_2(g) \rightarrow CO_2(g) & \Delta H^\circ_f = -393.5\ \text{kJ/mol} \\
CH_3OH(\ell) \rightarrow \cancel{C(s)} + \cancel{2\ H_2(g)} + \cancel{½}\ O_2 & \Delta H^\circ_f = +239.2\ \text{kJ/mol} \\
\hline
CH_3OH(\ell) + {}^3/_2\ O_2(g) \rightarrow CO_2(g) + 2\ H_2O(\ell) & \Delta H^\circ_c = -725.3\ \text{kJ/mol}
\end{array}$$

You will notice that the overall enthalpy is not a heat of formation even though it was calculated from heats of formation. The term "heat of formation" has a specific meaning. It requires that a compound be made from the elements, but this reaction does not do that so we have to change the designation. Therefore, this reaction becomes a standard heat of combustion for methanol, which is the amount of heat given off when 1 mole of methanol is combusted with oxygen. We therefore designate our enthalpy as a ΔH°_c where the "c" indicates that it is a combustion and it is being done under standard conditions (°).

Problem 13.3

Using Hess' Law and the following information calculate the heat of formation of the plant hormone ethylene, C_2H_4.

$$\begin{array}{ll}
C_2H_4(g) + 3\ O_2(g) \rightarrow 2\ CO_2(g) + 2\ H_2O(l) & \Delta H^\circ_c = -1411\ \text{kJ/mol} \\
C(s) + O_2(g) \rightarrow CO_2(g) & \Delta H^\circ_f = -393.5\ \text{kJ/mol} \\
H_2(g) + ½\ O_2(g) \rightarrow H_2O(l) & \Delta H^\circ_f = -285.8\ \text{kJ/mol}
\end{array}$$

By definition, the reaction for the heat of formation of $C_2H_4(g)$ is,

$$2\ C(s) + 2\ H_2(g) \rightarrow C_2H_4(g)$$

We need to add the reactions given above in such a way that we obtain the reaction for the formation of $C_2H_4(g)$.

$$\begin{array}{ll}
2\ CO_2(g) + 2\ H_2O(l) \rightarrow C_2H_4(g) + 3\ O_2(g) & \Delta H^\circ_c = +1411\ kJ/mol \\
2\ C(s) + 2\ O_2(g) \rightarrow 2\ CO_2(g) & 2(\Delta H^\circ_f = -393.5\ kJ/mol) \\
2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(l) & 2(\Delta H^\circ_f = -285.8\ kJ/mol) \\
\hline
2\ C(s) + 2\ H_2(g) \rightarrow C_2H_4(g) & \Delta H^\circ_f = 52.4\ kJ/mol
\end{array}$$

The ΔH°_f for $C_2H_4(g)$ is 52.4 kJ/mol.

There is an easier in which to use Hess's Law. Sometimes you will see Hess's Law written formally as,

$$\Delta H^\circ_{reaction} = \sum \Delta H^\circ_{f_{products}} - \sum \Delta H^\circ_{f_{reactants}}$$

But most often this is simplified to just,

$$\Delta H^\circ_{reaction} = \Delta H^\circ_{f_{products}} - \Delta H^\circ_{f_{reactants}}$$

where it is understood that we are talking about the sum of the products and the sum of the reactants. There is negative sign on the ΔH°_f for the reactants because it is necessary to reverse these reactions. Heats for formation are always written so that compounds are made from the elements. When the reaction is reversed, the product becomes a reactant and the enthalpy changes sign. The negative sign in from the ΔH°_f for the reactants has the effect of reversing this reaction for us.

If we apply this to the combustion of methanol we would have the following reaction and set of data,

$$\begin{array}{lccccccc}
 & CH_3OH(\ell) & + & {}^3/_2\ O_2(g) & \rightarrow & CO_2(g) & + & 2\ H_2O(\ell) \\
\Delta H^\circ_f = & -239.2\ kJ/mol & & 0\ kJ/mol & & -393.5\ kJ/mol & & -285.8\ kJ/mol
\end{array}$$

We note that oxygen, $O_2(g)$, does not have an enthalpy since it is an element and it takes no energy to create elemental oxygen from elemental oxygen. In addition, since there are two $H_2O(\ell)$ being made, we must multiply the enthalpy by two. Doing this we have,

$$\Delta H^\circ_{\text{reaction}} = \sum \Delta H^\circ_{f_{\text{products}}} - \sum \Delta H^\circ_{f_{\text{reactants}}}$$

$$\Delta H^\circ_{\text{reaction}} = \left[\left(-393.5\ \text{kj/mol}\right) + 2\,(-285.8\ \text{kj/mol})\right] - \left[(-230.2\ \text{kJ/mol}) + \tfrac{3}{2}\,(0\ \text{kJ/mol})\right]$$

$$\Delta H^\circ_{\text{reaction}} = 52.4\ \text{kj/mol}$$

This process is far easier than adding all of the reactions together and making sure that common components cancel in a reaction, and it is the method that will be used throughout the rest of this text.

Problem 13.4

When nitroglycerin explodes, it releases a tremendous amount of energy. It does not require oxygen to explode, rather, it converts itself from liquid nitroglycerin to several gases by the following reaction,

$$4\ C_3H_5N_3O_9(\ell) \rightarrow 12\ CO_2(g) + 6\ N_2(g) + 10\ H_2O(g) + O_2(g)$$

Its tremendous destructive power comes from the rapid conversion of the liquid into several gases expand rapidly when heated by the energy of the reaction. What is the energy released by the rapid decomposition of 100 grams of nitroglycerin?

$3\ C(s) + {}^5/_2\ H_2(g) + {}^3/_2\ N_2(g) + {}^9/_2\ O_2(g) \rightarrow C_3H_5N_3O_9(\ell)$ $\Delta H^\circ_f = -370.9$ kJ/mol
$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H^\circ_f = -393.5$ kJ/mol
$H_2(g) + \frac{1}{2}\ O_2(g) \rightarrow H_2O(g)$ $\Delta H^\circ_f = -241.8$ kJ/mol

Ignoring the elements, O_2 and N_2 in the products (0 kj/mol),

$$\Delta H^\circ_{\text{reaction}} = \left[12\left(-393.5\ \text{kj/mol}\right) + 10\,(-241.8\ \text{kj/mol})\right] - [(-370.9\ \text{kJ/mol})]$$

$$\Delta H^\circ_{\text{reaction}} = -6769.1\ \text{kj/mol}$$

To calculate the energy released by 100 gram of nitroglycerin we must multiply our answer by the number of moles of nitroglycerin.

$$\text{Energy} = \frac{100\ \text{g Nitroglycerin}}{227.1\ \text{g/mol}} \times (-\,6769.1\ \text{kj/mol}) = -\,2980.67\ \text{kJ}$$

This is enough energy to instantly boil a liter of room temperature water.

Gibbs Energy

Gibbs energy measures the maximum amount of work that can be done by a chemical reaction. More importantly, the sign on the Gibbs energy determines whether a reaction will occur or not. Mathematically, we would say that,

If $\Delta G = (+)$ then the reaction does not occur as written.

If $\Delta G = (-)$ then the reaction occurs as written.

It is important to note that a negative ΔG only says that the reaction will occur but it does not tell you how fast. It may take millions of years for the reaction to make appreciable amounts of product. For example, consider the reaction between hydrogen and oxygen,

$$H_2 + \frac{1}{2} O_2 \rightarrow H_2O \qquad \Delta G^\circ = -228.6 \text{ kJ/mol}$$

A balloon containing hydrogen and oxygen could sit comfortably for many years with no appreciable amount of water formed but, if a small amount of energy is added, then these gases will combine rapidly in a violent explosion. One should not assume that a reaction occurs fast just because the ΔG is negative. The rate at which a chemical reaction occurs is determined by kinetics, not thermodynamics and the two should not be confused.

Gibbs energy has two components, enthalpy and entropy. It begins with enthalpy as the source of the energy but not all of this energy can be used to do useful work. Some of energy is lost to random processes that do not produce useful work. This lost energy is due to disorder and is called Entropy.

Understanding the relationship between energy and disorder can be difficult so imagine a container full of unpopped colored popcorn. The kernels are neatly layered in yellow, blue and red popcorn. To pop the corn, the corn is heated on a stove. Some of this energy does something useful, it pops the corn, but some of the energy does something that is not useful, it mixes the corn. If desired, the popcorn could be reordered into neat layers again but that would require even more energy. The amount of energy that did something useful is the difference between the amount of energy put into the corn minus the amount of energy used to mix the corn. We could write this as an equation, Energy used to pop the corn = Energy from stove – Energy used to mix the corn

Mathematically, this is written as,

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

So, enthalpy is the source of the energy but entropy causes some of this energy to become lost due to random processes like mixing. Entropy is often described as being a measure of the disorder, or conversely, the order of a system depending on your point of view.

Entropy

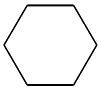
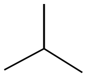
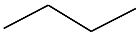
Entropy is a measure of the disorder of system. In general, all naturally occurring reactions become more disordered with time. It is our natural experience that things fall apart with time. It is not unusual to see a vase fall off of a table and smash into a million bits, but nobody has ever seen a broken vase spontaneously leap up off the floor and reassemble itself on the table. In similar fashion, if you put a drop of blue die into a vat of water it will slowly dissipate and color the entire vat of water. But it would be rare and unusual to watch a vat of blue water spontaneously form a deep blue drop of dye in its center and have all the rest of the water clear.

Entropy is often called "Times Arrow." A more disordered system always comes after a more ordered system. All you have to do to make your house messy is nothing. Furniture gets dusty, cobwebs form, and the house eventually decays and falls apart. If things become more disordered with time, it is clear that things were more ordered in the past than they are today. This concept fueled the idea that there must be a beginning to our universe. If the universe is eternal then the second law predicts that the universe must have fallen apart long ago. The fact that it has not fallen apart is evidence that the universe is not eternal and must have had a beginning.

There are many thermodynamic principles that are also common experience. Solids are more ordered than liquids and liquids are more ordered than gases. Consider the following reaction,

$$C_4H_9OH(\ell) + 6\ O_2(g) \rightarrow 4\ CO_2(g) + 5\ H_2O(g)$$

We can predict that the entropy of this reaction should increase. There are only 7 reactants compared to 9 products and one of the reactants is a liquid which has lower entropy than a gas. The entropy change for this reaction is +342.2 J/mol·K. The positive value tells you that the entropy has increased, as predicted.

Substance	Entropy/ $S°_f$		Substance
$I_2(s)$	116.1	260.7	$I_2(g)$
$H_2O(\ell)$	70.0	188.8	$H_2O(g)$
$SO_2(g)$	248.2	256.8	$SO_3(g)$
$C_5H_{12}(\ell)$	263.37	295	$C_6H_{14}(\ell)$
$C_6H_{12}(\ell)$ 	204.0	295.2	$C_6H_{12}(\ell)$ 
$C_4H_{10}(\ell)$ 	200.79	229.7	$C_4H_{10}(\ell)$ 

As the table above illustrates, large molecules have more entropy than smaller molecules ($SO_3 > SO_2$ and $C_6H_{14} > C_5H_{12}$). Gases have more entropy than liquids which have more entropy than solids ($I_2(g) > I_2(s)$ and $H_2O(g) > H_2O(\ell)$) and more compact molecules (rings and branched chains) have lower entropy than less compact molecules (linear chains) with the same formula.

In a manner similar to Gibbs energy and Enthalpy, the sign on Entropy is important.

If $\Delta S = (+)$ then the entropy increases and the system becomes more disordered.
If $\Delta S = (-)$ then the entropy decreases and the system becomes more ordered.

It is important to note that, unlike our previous discussion where all the elements are defined as having zero enthalpy, the elements do not have zero entropy. In fact, if you look at a table of values for entropy, you will find that all elements and compounds have positive entropies. This is because entropy is measured differently from other thermodynamic values. For ΔH and ΔG we are comparing the energy of the compound to the energy of the elements from which it is made, but that is not how entropy is measured. Entropy is a measure of disorder so the standard against which it is measured is one of perfect order or zero entropy. This occurs at absolute zero. The values we find in tables tell us how much entropy a compound has at 25°C. The entropy is always positive because entropy always increases with increasing temperature. This also means that entropy values are written as $S°_f$ and not $\Delta S°_f$. Entropy values do not have a delta (Δ) sign because we are not looking at the change in entropy but the entropy itself. It is very much the same as a temperature reading. There is a big difference between saying that it is 25°C outside and saying that the change in temperature is 2°C. Entropy tables give us absolute values of entropy and not the difference in entropy compared to some other state so there is no delta (Δ) sign. This does not mean that there will never be a $\Delta S°$. We will obtain a $\Delta S°$ when we take the sum or difference between two $S°_f$.

When combined with enthalpy, we can see how entropy and enthalpy influence the sign on the Gibbs energy. Common experience tells us that a reaction is occurring when a solution heats up and when solutions heat up, they also fall apart. For these reactions, the enthalpy will be exothermic and negative (energy is given off so they heat up) and the entropy will be positive (the system is becoming more disordered). Under these conditions, ΔG is negative and the reaction occurs. You will note the use of $\Delta S°_f$ rather than $S°_f$ in the following table. This is because we are looking at a reaction so we are taking the difference in entropies of the various components in the reaction.

	Enthalpy $\Delta H°_f$	Entropy $\Delta S°_f$	Gibbs Energy $\Delta G°_f$	Comments
1	− (exothermic)	+ (more disordered)	− (rxn occurs)	Most reactions occur this way.
2	− (exothermic)	− (more ordered)	− (rxn occurs)	The reaction occurs only if $\Delta H > T\Delta S$ The reaction is driven by Enthalpy
3	− (exothermic)	− (more ordered)	+ (rxn doesn't occur)	Only if $\Delta H < T\Delta S$ But the reverse reaction does occur.
4	− (exothermic)	− (more ordered)	0 (at equlibirium)	Only if $\Delta H = T\Delta S$ Equilibrium systems cannot do work.
5	+ (endothermic)	− (more ordered)	+ (rxn doesn't occur)	But the reverse reaction does occur.
6	+ (endothermic)	+ (more disordered)	− (reaction occurs)	The reaction occurs only if $\Delta H < T\Delta S$ The reaction is driven by Entropy
7	+ (endothermic)	+ (more disordered)	+ (rxn doesn't occur)	Only if $\Delta H > T\Delta S$ But the reverse reaction does occur.
8	+ (endothermic)	+ (more disordered)	0 (at equlibirium)	Only if $\Delta H = T\Delta S$ Equilibrium systems cannot do work.

You will note that there is only one set of conditions that insures that a reaction will occur as written and that is condition number 1 where the reaction is exothermic (ΔH is negative) and entropy increases (ΔS is positive). These conditions will always produce a negative Gibbs energy which means that these reactions always occur.

The sign on the Gibbs energy for the rest of these conditions will depend on the relative size of the enthalpy and entropy. Generally speaking, a positive enthalpy and negative entropy conspire to keep a reaction from occurring (5). When working together, a reaction does not occur, but sometimes they compete against one another for dominance. A positive enthalpy will try to keep a reaction from occurring but if the entropy is large and positive it can overcome the enthalpy and cause the reaction to occur. In this case, the reaction occurs because of the large entropy so the reaction is said to be “entropically driven.” On the other hand, sometimes the entropy is negative but is overcome by a very large and negative enthalpy. When this happens the reaction occurs only because of the size of the enthalpy and is said to be “enthalpically driven.”

On rare occasions the enthalpy and entropy terms are equal and opposite to one another and neither of them wins. In this case, the reaction is at equilibrium and no work can be done. Thermodynamically, equilibrium is death. A battery only produces electricity when it is far from equilibrium. Once a battery reaches equilibrium it is dead and no more work can be done. This is true of all thermodynamic systems and will become the focus of our discussion. Work can be done by chemical reactions that are far from equilibrium. As the reaction goes toward equilibrium we can harness the energy and do work. A battery works because it is far from equilibrium. When a battery runs down we recharge it. The process of charging the battery moves the chemical reaction back to a position that is far from equilibrium so that the battery can produce electricity again.

It may not seem obvious but, in order to know how much energy we can get out of a system, we must know where the equilibrium point is and how far away from equilibrium we are. Only then can we calculate how much energy there is in a system.

The Gibbs Equation

The Gibbs equation for any set of conditions (temperature and pressure) is,

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

Or, if the experiment is run under standard conditions,

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

The values of ΔG°, ΔH°, and ΔS° are found in thermodynamic tables. We use the same principles used with enthalpy to determine a value for each of these.

$$\Delta H^\circ_{\text{reaction}} = \sum \Delta H^\circ_{f_{\text{products}}} - \sum \Delta H^\circ_{f_{\text{reactants}}}$$

$$\Delta S^\circ_{\text{reaction}} = \sum S^\circ_{f_{\text{products}}} - \sum S^\circ_{f_{\text{reactants}}}$$

$$\Delta G^\circ_{\text{reaction}} = \sum \Delta G^\circ_{f_{\text{products}}} - \sum \Delta G^\circ_{f_{\text{reactants}}}$$

As stated previously, Gibbs energy has a relationship to the equilibrium. The ΔG° of a reaction determines the equilibrium position of the system. Mathematically, we write this relationship as,

$$\Delta G^\circ = -RT\ln(K)$$

Where R is 8.314 J/mol·K. If the ΔG° is known, the equilibrium constant for the reaction can be calculated. The equilibrium constant can be a K_{sp}, K_a, or any other type of K_{eq}.

Problem 13.5

Given the following set of thermodynamic data calculate the ΔH°, ΔS°, and ΔG° and the solubility product (K_{sp}) for the following reaction at 25°C (Enthalpies are in kJ/mol and entropies are in J/mol·K).

$$CoCl_2(s) \leftrightarrows Co^{2+}(aq) + 2\,Cl^-(aq)$$

	ΔH°	S°
$CoCl_2(s)$	-312.5	109.2
$Co^{2+}(aq)$	-67.36	-155.2
$Cl^-(aq)$	-167.4	55.1

$\Delta H°_{\text{reaction}} = \sum \Delta H°_{f_{\text{products}}} - \sum \Delta H°_{f_{\text{reactants}}}$
$\Delta H° = [(-67.36 \text{ kJ/mol}) + 2(-167.4 \text{ kJ/mol})] – [(-312.5 \text{ kj/mol})]$
$\Delta H° = -89.66 \text{ kJ/mol}$ (exothermic)

$\Delta S°_{\text{reaction}} = \sum S°_{f_{\text{products}}} - \sum S°_{f_{\text{reactants}}}$
$\Delta S° = [(-155.2 \text{ J/mol·K}) + 2(55.1 \text{ J/molK})] – [(109.2 \text{ J/mol·K})]$
$\Delta S° = -154.2 \text{ J/mol·K}$ (entropy decreases)

$\Delta G° = \Delta H° - T\Delta S°$
$\Delta G° = -89{,}660 \text{ J/mol} - (298 \text{ K})(-154.2 \text{ J/molK})$
$\Delta G° = -43{,}708.4 \text{ J/mol}$ (reaction is spontaneous as written)

$\Delta G° = – RT \ln(K_{sp})$
$K_{sp} = e^{-\Delta G°/RT} = e^{-\frac{(-43{,}708.4 \text{ J/mol})}{(8.314 \text{ J/molK})(298\text{K})}}$
$K_{sp} = 4.59 \times 10^{7}$

Since enthalpy and entropy have different units, we must convert one of them. Generally, it is easier to convert the enthalpy unit (kJ/mol) into J/mol by multiplying by 1000J/kJ.

These results tell us that this reaction is exothermic ($\Delta H°$ is negative), it becomes more ordered ($\Delta S°$ is negative) and the reaction is spontaneous ($\Delta G°$ is negative). This is condition 2 in the table above. The enthalpy and entropy are in competition but this reaction occurs because the enthalpy is more strongly negative than the entropy, therefore this reaction is driven by enthalpy.

Gibbs Energy Far from Equilibrium

Thus far, we have only considered equilibrium systems. As stated earlier, a battery at equilibrium is a dead battery. Work can only be obtained when a system is far from equilibrium. The Gibbs equation can be modified to account for systems far from equilibrium. We begin with the relationship between Gibbs energy and the equilibrium constant,

$$\Delta G° = – RT \ln(K)$$

Rearranging we get,

$$0 = \Delta G^\circ + RT\ \ln(K)$$

The equation says that a system at equilibrium can do no work. No useful energy is produced. So what happens when we move far from equilibrium? When this happens our equilibrium constant K, becomes a Q. This is the same Q used when we considered equilibriums. It looks just like an equilibrium but without the equilibrium concentrations,

$$Q = \frac{\text{Non-equilibrium concentration of Products}}{\text{Non-equilibrium concentration of Reactants}}$$

If we replace the K in our Gibbs equation with a Q, the ΔG° will no longer equal the –RT ln(Q) term so energy will be produced,

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

The ΔG in this equation gives us a value of how much energy can be extracted from a system when it is far from equilibrium (Q). Eventually, the system reaches equilibrium (Q = K) and no more energy can be extracted. When this happens, ΔG = 0 and ΔG° = – RT ln(K), back to our original equation.

Problem 13.6

What is the ΔG for the following reaction when the concentration of all ions is 0.5 *M*?

$$PbI_2(s) \leftrightarrows Pb^{2+}(aq) + 2\ I^-(aq)$$

	ΔG°
$PbI_2(s)$	-173.6 kJ/mol
$Pb^{2+}(aq)$	-24.31 kJ/mol
$I^-(aq)$	-51.67 kJ/mol

$$\Delta G^\circ_{\text{reaction}} = \sum \Delta G^\circ_{f_{\text{products}}} - \sum \Delta G^\circ_{f_{\text{reactants}}}$$

$$\Delta G^\circ = [(-24.31\ \text{kJ/mol}) + 2(-51.67\ \text{kJ/mol})] - [(-173.6\ \text{kj/mol})]$$

$$\Delta G^\circ = 45.95\ \text{kJ/mol (not spontaneous)}$$

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

$$Q = [Pb^{2+}]\ [I^-]^2$$

$$\Delta G = 45{,}950\ \text{J/mol} + (8.314\ \text{J/molK})(298\ \text{K})\ \ln\left([0.5\ \text{M}][0.5\ \text{M}]^2\right)$$

$$\Delta G = 40{,}798\ \text{J/mol}$$

Calculating ΔG°

There are some interesting details about the Gibbs equation that are worthy of note. One of the more important is the use of the standard state to measure the ΔG° of a reaction. The standard state (the ° in ΔG°) means that the reaction conditions are at 1 atmosphere pressure, 1 *M* concentration[1] and at 25°C. When all of the reactants and products of a reaction are 1 *M* the Q term will equal one (1). Since the natural log of one equals zero the Gibbs equation reduces to,

$$Q = \frac{\text{Products}}{\text{Reactants}} = \frac{(1)}{(1)} = 1$$

$$\Delta G = \Delta G^\circ + RT\ \ln(Q) = \Delta G^\circ + RT\ \ln(1)$$

$$\Delta G = \Delta G^\circ$$

Therefore, we can see that by setting all the ingredients in a reaction to 1 *M* or 1 atmosphere allows us to measure ΔG° directly. While this method works as a first approximation, in practice, another method is used to calculate ΔG°.

If we rearrange the Gibbs equation only slightly, we get,

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

This equation is of the form, $y = mx + b$ where,

$y = \Delta G$
$m = RT$
$x = \ln(Q)$
$b = \Delta G^\circ$

---

[1] While most texts use 1 *M* as the standard condition for concentration, the actual value is 1 unit activity. The value of 1 *M* is used here for convenience and consistency but will be appended later in the text.

A plot of ΔG versus ln(Q) should have a slope equal to RT and an intercept equal to $\Delta G°$. Using this method you can tell if the system used is "well behaved." A well behaved system will have a slope of RT. If the slope is not RT then there is a problem with the system that must be investigated and fixed. This gives you double check on the system to make sure that it is working correctly. There is no way to double check a calculation of $\Delta G°$ using one set of data at 1 *M*, so the graphing method is a superior way of determining the $\Delta G°$.

Unfortunately, even this method will not give you the values for $\Delta G°$ found in the CRC Handbook. This is because 1 *M* solutions do not actually behave like 1 *M* solutions. They behave as though they were less concentrated. To account for this behavior and to obtain the best value for $\Delta G°$, we must determine how the solution actually behaves by calculating the activity of its ions.

Activities

Solutions behave a lot like gases and like gases; there are concentrations where solutions behave in an ideal manner and concentrations where they do not. When a compound like NaCl dissolves in water, it produces an Na^+ and a Cl^- ion. Since these ions have equal and opposite charges they are attracted to one another and can "clump" together in solution. Positive ions tend to be surrounded by negative ions and negative ions are surrounded by positive ions. This is like the "stickiness" of gasses that keeps them from behaving ideal. Ions with double or triple charges attract more ions of the opposite charge so they tend to behave less ideal than singly charged ions.

To account for the ions present in solution and their charge, an ionic strength is calculated. To calculate the ionic strength of a solution, the following formula is used,

$$\text{Ionic strength} = \mu = \sum_{i=1}^{\infty} \frac{1}{2} Z_i^2 M_i$$

Where Z is the ionic charge and *M* is the molarity. A simple example will explain how this equation is used. Consider the calculation of the ionic strength for a 0.1 M $CaCl_2$ solution. This solution contains two ions, Ca^{2+} and Cl^- and their concentrations are 0.1 *M* and 0.2 *M* respectively. The charge on the calcium ion (Z) is 2+ and the charge on the chloride ion (Z) is -1. So, the ionic strength is,

$$\mu = \frac{1}{2}\,(+2)^2\ (0.1\text{ M})\ +\ \frac{1}{2}\,(-1)^2(0.2\text{M}) = 0.3\text{ M}$$

Now that we know the ionic strength we need to calculate the behavior of each of these ions in solution. We call the actual behavior these ions in solution their "activities." To calculate the activity of each ion we introduce a multiplier, a correction factor, called the activity coefficient that is used to scale the concentration and turn it into an activity.

$$a_i = f_i\, M_i$$

where a_i is the activity (the effective concentration) of the ion, f_i is the correction factor called the activity coefficient, and M_i is the molarity of the ion of interest. As might be guessed, the activity of an ion is strongly influenced by its charge, its size, and the ionic strength of the solution around it. These factors are all part of the Debye-Hückel equation that gives us a way to calculate the activity coefficient, f_i. The Debye-Hückel equation is,

$$\log f_i = \frac{-\,0.511\ Z_i^2\sqrt{\mu}}{1 + 3.29\ \alpha_i\sqrt{\mu}}$$

The only new term in this equation is a_i with is a measure of the effective size of the hydrated ion in nanometers. A table of these diameters is given below.

Effective hydrated diameters of ions in aqueous solution (25°C).		
Cations	Anions	α_i /nm
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+		0.25
K^+	Cl^-, Br^-, I^-, NO_3^-, $HCOO^-$	0.3
	OH^-, F^-, HS^-, ClO_4^-, MnO_4^-	0.35
Na^+	HCO_3^-, $H_2PO_4^-$, HSO_3^-, CH_3COO^-	0.4 – 0.45
Hg_2^{2+}	HPO_4^{2-}, SO_4^{2-}, CrO_4^{2-}	0.4
Pb^{2+}	CO_3^{2-}, SO_3^{2-}	0.45
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}	S^{2-}	0.5
Li^+, Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}	Phthalate^{2-}, $C_6H_5COO^-$	0.6
Mg^{2+}, Be^{2+}		0.8
H^+, Al^{3+}, Cr^{3+}, Fe^{3+}, La^{3+}		0.9
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}		1.1

If we continue with our previous example using 0.1 M $CaCl_2$, we are now in a position to calculate the effective concentration of the calcium and the chloride ion. Using 0.3 M as our ionic strength, 2+ as the charge and 0.6 nm as the effective size, we would calculate the activity coefficient for Ca^{2+} to be,

$$\log f_{Ca^{2+}} = \frac{-0.511\,(+2)^2_{Ca^{2+}}\sqrt{0.3\text{ M}}}{1 + 3.29\,(0.6\text{ nm})\,\sqrt{0.3\text{ M}}} = -0.5379$$

$$f_{Ca^{2+}} = 10^{-0.5379} = 0.2898$$

The activity of the Ca^{2+} in 0.1 M $CaCl_2$ would be,

$$a_i = f_i\,M_i$$

$$a_{Ca} = (0.2898)\,(0.10\,M\text{ Ca}^{2+}) = 0.02898\,M\text{ Ca}^{2+}$$

The activity for the calcium ion is less than a third of its concentration. The solution is not behaving ideally otherwise the activity and the concentration would have been the same. Let's do the same calculation for the chloride ion where the ionic strength is 0.3 M, the charge is –1, and effective size is 0.3 nm.

$$\log f_{Cl^-} = \frac{-0.511\,(-1)^2_{Cl^-}\sqrt{0.3\text{ M}}}{1 + 3.29\,(0.3\text{ nm})\,\sqrt{0.3\text{ M}}} = -0.1817$$

$$f_{Ca^{2+}} = 10^{-0.1817} = 0.6582$$

The activity of the Cl^- in 0.1 M $CaCl_2$ would be,

$$a_i = f_i\,M_i$$

$$a_{Cl} = (0.6582)\,(0.20\,M\text{ Cl}^-) = 0.1354\,M\text{ Cl}^-$$

The activity coefficient for Cl^- (0.6582) is much larger than for Ca^{2+} (0.2898). This means that the chloride ion is behaving more ideally than the calcium ion. The calcium ion is less ideal because of its larger charge and associated larger hydration diameter. As stated previously, ions with double or triple charges will behave less ideally than ions with a single charge.

As can be seen in the following table, as a solution of calcium chloride becomes more dilute, the activity coefficient approaches 1.00 and the solution behaves more ideal.

Activity Coefficient of Calcium and Chloride Ions at Decreasing Concentrations

Molarity $CaCl_2$	$f_{Ca^{2+}}$	f_{Cl^-}
1	0.1581	0.4714
0.1	0.2898	0.6582
0.01	0.5447	0.8403
0.001	0.7924	0.9407
0.0001	0.9242	0.9802
0.00001	0.9748	0.9936
0.000001	0.9919	0.9980

You will sometimes hear an instructor say that a solution has unit activity. This is a code word for a very dilute solution where the ions are behaving ideally. At high concentration, the concentration and the activity are not the same; in fact, the activity may be a small fraction of the concentration. But as the solution becomes more and more dilute the activity and the concentration become equal. It is under the condition of unit activity, where concentrations and activities are equal, that we can expect that $\Delta G = \Delta G°$. Most books do not make this distinction and would have you believe that these two are equal at 1 M concentrations.

Gibbs Energy and Activities

As described earlier, the relationship between ΔG and ΔG° can be described by the equation,

$$\Delta G = RT \ln(Q) + \Delta G°$$

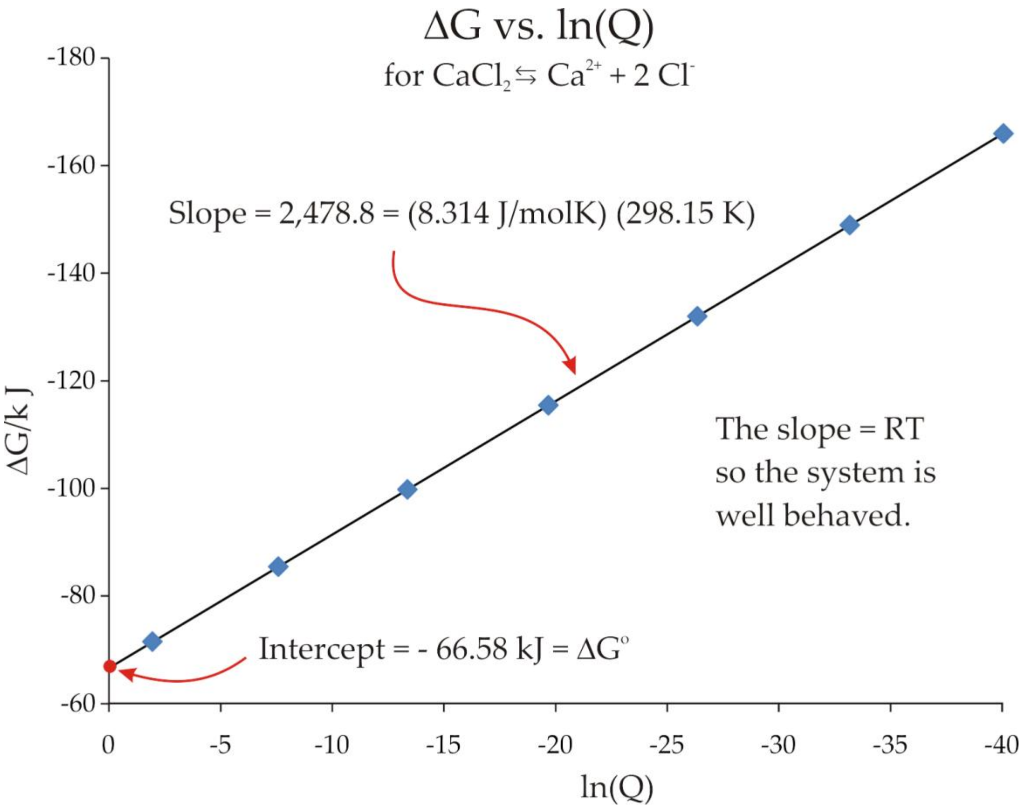
And ΔG° can be calculated by plotting ΔG versus ln(Q) as long as the Q value is calculated using activity coefficients rather than molarities. The intercept of this plot gives a value for ΔG° and the slope should equal RT as long as the system is well behaved. We can use our previous data to determine the ΔG° for the reaction,

$$CaCl_2(s) \leftrightarrows Ca^{2+}(aq) + 2\ Cl^-(aq)$$

Data Table for the Reaction: $CaCl_2(s) \leftrightarrows Ca^{2+}(aq) + 2\ Cl^-(aq)$

Molarity $CaCl_2$	$f_{Ca^{2+}}$	f_{Cl^-}	Q = $(\alpha_{Ca^{2+}})(\alpha_{Cl^-})^2$	ln(Q)	Measured ΔG
1	0.1581	0.4714	1.40×10^{-1}	-1.96	-71,445
0.1	0.2898	0.6582	5.02×10^{-4}	-7.60	-85,410
0.01	0.5447	0.8403	1.53×10^{-6}	-13.38	-99,758
0.001	0.7924	0.9407	2.80×10^{-9}	-19.69	-115,393
0.0001	0.9242	0.9802	3.55×10^{-12}	-26.36	-131,931
0.00001	0.9748	0.9936	3.85×10^{-15}	-33.19	-148,854
0.000001	0.9919	0.9980	3.95×10^{-18}	-40.07	-165,912

A plot of ΔG versus ln(Q) reveals a well behaved system with an intercept (ΔG°) equal to -66.58 kJ/mol. This value is the same as the accepted value calculated from data found in thermodynamic tables like those in the CRC Handbook of Chemistry and Physics. The system is said to be well behaved because the slope is equal to RT. Had a similar plot been made that substituted a Q value based on concentrations an incorrect value of -72.72 kJ/mol for ΔG° would have been obtained. This result is not considered close enough to the actual value. It is best to use activities when attempting to find values for ΔG°.



Systems at Equilibrium

When a system is at equilibrium no energy can be produced but that does not mean that there is nothing to be learned. According to the Gibbs Equation,

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

But at equilibrium $\Delta G = 0$ so that,

$$0 = \Delta H - T\Delta S$$

Or,

$$\Delta H = T\Delta S$$

This means that the enthalpy and entropy of a reaction is intimately connected to one another. As an example, consider the enthalpy of fusion for water. When water melts it turns to water but this is an equilibrium system so that,

$$\frac{\Delta H_{fus}}{T} = \Delta S_{fus}$$

The heat of fusion for water is 6.01 kJ/mol and water melts at 273.15 K so that,

$$\frac{6{,}010 \text{ J/mol}}{273.15 \text{ K}} = 22.0 \text{ J/mol}\cdot\text{K} = \Delta S_{fus}$$

We see that the change in entropy when ice melts is a positive value. This result is not surprising. Any time a solid melts and becomes a liquid, entropy increases and is positive.

The van’t Hoff Equation

The Gibbs equation shows us that,

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

Gibbs energy is also related to the equilibrium constant by,

$$\Delta G° = -RT \ln(K)$$

So it follows that,

$$-\text{RT}\ln(\text{K}) = \Delta\text{H}^\circ - \text{T}\Delta\text{S}^\circ$$

Rearranging we get,

$$\ln(\text{K}) = -\frac{\Delta\text{H}^\circ}{\text{RT}} + \frac{\Delta\text{S}^\circ}{\text{R}}$$

Let's assume that we measured the equilibrium constant at two different temperatures. Under these conditions we would have two equations,

$$\ln(\text{K}_1) = -\frac{\Delta\text{H}^\circ}{\text{RT}_1} + \frac{\Delta\text{S}^\circ}{\text{R}}$$
$$\ln(\text{K}_2) = -\frac{\Delta\text{H}^\circ}{\text{RT}_2} + \frac{\Delta\text{S}^\circ}{\text{R}}$$

Assuming that both ΔH° and ΔS° remain constant, if we subtract the bottom equation from the top equation the entropy terms would cancel and we would get,

$$\ln(\text{K}_1) - \ln(\text{K}_2) = -\frac{\Delta\text{H}^\circ}{\text{RT}_1} - \left(-\frac{\Delta\text{H}^\circ}{\text{RT}_2}\right)$$

Rearranging, we would get,

$$\ln\left(\frac{\text{K}_1}{\text{K}_2}\right) = -\frac{\Delta\text{H}^\circ}{\text{R}}\left(\frac{1}{\text{T}_1} - \frac{1}{\text{T}_2}\right)$$

We can simplify this a bit more by combining the temperatures and multiplying them by the negative sign,

$$\ln\left(\frac{\text{K}_1}{\text{K}_2}\right) = \frac{\Delta\text{H}^\circ}{\text{R}}\left(\frac{\text{T}_1-\text{T}_2}{\text{T}_1\text{T}_2}\right)$$

This equation is identical in form to the Arrhenius equation with some important differences. First, the Arrhenius equation uses rate constants and the van't Hoff equation uses equilibrium constants. Second, the van't Hoff equation uses the enthalpy of the reaction rather than the activation energy, but the overall form of the equation is identical.

Problem 13.6

Given the following set of thermodynamic data what is the concentration of $Ag^{+}(aq)$ at 40°C?

$$AgCl(s) \leftrightarrows Ag^{+}(aq) + Cl^{-}(aq)$$

	ΔH°	S°
AgCl (s)	-127.0	96.3
$Ag^{+}(aq)$	105.9	73.9
$Cl^{-}(aq)$	-167.4	55.1

$$\Delta H^\circ_{reaction} = \sum \Delta H^\circ_{f_{products}} - \sum \Delta H^\circ_{f_{reactants}}$$

$$\Delta H^\circ = [(105.9\text{ kJ/mol}) + (-167.4\text{ kJ/mol})] – [(-127.0\text{ kj/mol})]$$

$$\Delta H^\circ = 65.5\text{ kJ/mol (endothermic)}$$

$$\Delta S^\circ_{reaction} = \sum S^\circ_{f_{products}} - \sum S^\circ_{f_{reactants}}$$

$$\Delta S^\circ = [(73.9\text{ J/mol}\cdot\text{K}) + (55.1\text{ J/molK})] – [(96.3\text{ J/mol}\cdot\text{K})]$$

$$\Delta S^\circ = 32.7\text{ J/mol}\cdot\text{K (entropy increases)}$$

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

$$\Delta G^\circ = 65{,}500\text{ J/mol} - (298\text{ K})(32.7\text{ J/molK})$$

$$\Delta G^\circ = 55{,}755.4\text{ J/mol (reaction is not spontaneous as written)}$$

$$\Delta G^\circ = – RT\ln(K_{sp})$$

$$K_{sp} = e^{-\Delta G^\circ/RT} = e^{-\frac{(55{,}755.4\text{ J/mol})}{(8.314\text{ J/molK})(298\text{K})}}$$

$$K_{sp} = 1.69\times10^{-10}$$

Now that we have a value for the equilibrium constant at 25°C, we can use the ΔH° to calculate the new equilibrium constant at 40°C.

$$\ln\left(\frac{K_1}{K_2}\right) = \frac{\Delta H^\circ}{R}\left(\frac{T_1 - T_2}{T_1 T_2}\right)$$

$$\ln\left(\frac{1.69\times10^{-10}}{K_2}\right) = \frac{65{,}500\text{ J/mol}}{8.314\text{ J/mol}\cdot\text{K}}\left(\frac{298\text{ K} - 313\text{ K}}{(298\text{ K})(313\text{ K})}\right)$$

$$K_2 = 6.0\times10^{-10}\text{ @ }40^\circ\text{C}$$

$$Ksp = [Ag+]\ [Cl-]$$

$$6.0\times10^{-10} = [x]\ [x] = x^2$$

$$x = 2.45x10^{-5}\ M\ Ag^+$$

Notice that the K_{sp} increased when the temperature increased. This means that AgCl is more soluble when the water gets hotter.

Gibbs Energy of Dilution

Ions in solution want to become more dilute. This driving force is so strong that energy can be extracted while it takes place. The driving force of dilution is entropy. Consider the following "reaction."

$$6\ M\ \text{NaCl} \rightarrow 0.1\ M\ \text{NaCl}$$

Using the Gibbs equation, it is possible for us to calculate the ΔG for this reaction.

$$\Delta G = \Delta G° + RT\ \ln(Q)$$

Where,

$$Q = \frac{\text{Products}}{\text{Reactants}} = \frac{0.1\ \text{M NaCl}}{6\ \text{M NaCl}}$$

All that is required to calculate the ΔG of this reaction is knowing the ΔG°. Any time a reaction has the same ingredients on both side of the reaction but at different concentrations the ΔG° will be zero. This is because a 6 *M* and 0.1 *M* NaCl solution share the same standard state (ΔG°), and if the standard states are the same, then the difference between them is zero. Therefore the ΔG for the dilution of NaCl is,

$$\Delta G = 0 + (8.314\ \text{J/mol}\cdot\text{K})\ (298.15\ \text{K})\ \ln\left(\frac{0.1\ \text{M NaCl}}{6\ \text{M NaCl}}\right) = -10{,}140\ \text{J/mol}$$

Notice that the ΔG is negative which indicates that this reaction is spontaneous.

Problem 13.7

What is the ΔG for the formation of 0.5 *M* $CuSO_4$ from solid $CuSO_4$?
$CuSO_4$(sat'd) = 1.28 *M*

This question should be done in two parts. First, solid $CuSO_4$ is used to make a saturated solution of $CuSO_4$ and then the saturated solution is diluted to 0.5 *M* $CuSO_4$.

1) $CuSO_4(s) \leftrightarrows CuSO_4(\text{sat'd})$
2) $CuSO_4(\text{sat'd}) \rightarrow 0.5\ M\ CuSO_4$

The ΔG = 0 for the first part of this reaction because the system is at equilibrium. The second part is a dilution so ΔG° = 0 and ΔG = RT ln(Q). Putting these two together we get,

1) $\Delta G = 0$
2) $\Delta G = (8.314\ \text{J/mol}\cdot\text{K})\ (298.15\ \text{K})\ \ln\left(\frac{0.5\ M\ CuSO_4}{1.28\ M\ CuSO_4}\right) = -2330.1\ \text{J/mol}$

Summing these two, the ΔG for the formation of 0.5 *M* $CuSO_4$ from solid $CuSO_4$ is -2330.1 J/mol.

Chapter Fourteen

Oxidation and Reduction, Electrochemical Cells, Batteries, Electroplating and The Goldman–Hodgkin–Katz Equation

"In arranging the bodies in order of their electrical nature, there is formed an electrochemical system which, in my opinion, is more fit than any other to give an idea of chemistry."

Jöns Jacob Berzelius- 1819

The study of chemical thermodynamics includes a study of electrochemical cells, but this area of chemistry is so large that it deserves a chapter of its own. Electrochemistry is the area of study that delves into the chemistry of electron flow which includes explanations as to why batteries work, how solubility and pH are measured, how to chrome a bumper and how and why a nerve causes an electrical impulse. Fundamentally, it is the study of how systems gain and lose electrons and, if set up properly, how those electrons can be made to do work.

Electrochemistry has its own language so this study will necessarily begin with some definitions.

Oxidation and Reduction

The fundamental basis of electrochemistry is the concept of oxidation and reduction. At its most basic level, oxidation means "reacts with oxygen" but this idea over-simplifies a complexity of oxidation and reduction.

Very early in your chemistry career you learned how to do combination reactions and some, not all, involved oxygen. Some representative combination reactions are given below,

$$2\ S + 3\ O_2 \rightarrow 2\ SO_3$$
$$N_2 + 3\ H_2 \rightarrow 2\ NH_3$$
$$2\ Al + 3\ S \rightarrow Al_2S_3$$
$$4\ P + 5\ O_2 \rightarrow 2\ P_2O_5$$

When we learned how to combine these elements to make compounds we used their position on the Periodic Table to predict their charge, then we combined them in such a way to make sure that all of the charges cancelled. We noted that one of the two elements was positively charged and the other would be negative and we decided whether they would be positive or negative based on their proximity to the most electronegative element, Fluorine.

Without actually saying so, you were learning oxidation and reduction. Take, for example, our first compound, SO_3. We can make SO_3 by combining sulfur with oxygen, but to do so, we note the following; based on their position on the Periodic Table, sulfur and oxygen take on these charges,

S becomes S^{6+}
O becomes O^{2-}

When they combine, these charges must balance so we end up making,

$$S^{6+} + 3\ O^{2-} \rightarrow SO_3$$

Now that we know the formula of the product that will be made, we can complete and balance our reaction,

$$2\ S + 3\ O_2 \rightarrow 2\ SO_3$$

But, we should carefully consider how this reaction occurred. If the sulfur must give off 6 electrons to become S^{6+}, where did those electrons go? They must have been given to the oxygen. Three oxygens must have gained two electrons each to become O^{2-}. Sulfur must have given its electrons to the oxygens. By definition, a transfer of electrons from element or compound to another is an oxidation-reduction reaction.

So, which is which? Which of these reactions is the oxidation and which is the reduction? Let's take another look at our reaction. In this case, let's take a look at each reaction but include the electrons that are needed to complete the reaction

$$\mathrm{S} \rightarrow \mathrm{S}^{6+} + 6\ \mathrm{e}^-$$

$$\mathrm{O_2} + 4\ \mathrm{e}^- \rightarrow 2\ \mathrm{O}^{2-}$$

We can see that the sulfur gave up 6 electrons and the oxygen took in 4 electrons. If we were to balance these two reactions in such a way that the electrons will cancel, we would multiply the top reaction by 2 (giving us 12 electrons) and bottom one by 3 (giving us 12 electrons) so that these electrons will now cancel.

$$\begin{array}{c} 2\ \mathrm{S} \rightarrow 2\ \mathrm{S}^{6+} + \cancel{12\ \mathrm{e}^-} \\ \underline{3\ \mathrm{O_2} + \cancel{12\ \mathrm{e}^-} \rightarrow 6\ \mathrm{O}^{2-}} \\ 2\ \mathrm{S} + 3\ \mathrm{O_2} \rightarrow 2\ \mathrm{S}^{6+} + 6\ \mathrm{O}^{2-} \rightarrow 2\ \mathrm{SO_3} \end{array}$$

By definition, the loss of electrons is an oxidation, so the sulfur was oxidized. This makes sense since it reacted with oxygen. By contrast, the definition of reduction is the gain of electrons so the oxygen was reduced. There are many ways to remember the definitions for oxidation and reduction but the simplest is probably the acronym, OIL RIG.

OIL = oxidation is loss
RIG = reduction is gain

It seems counterintuitive that to reduce something you must gain something, but we are talking about electrons. When you gain an electron, your charge is reduced, that is, it is made more negative. So to reduce your charge you must gain electrons. In this way, reduction is gain makes sense.

Problem 14.1

In each of the following reactions, determine whether the highlighted at is being oxidized or reduced.

1. $\mathrm{Zn} + \underline{\mathbf{Cu}}\mathrm{SO_4} \rightarrow \mathrm{ZnSO_4} + \underline{\mathbf{Cu}}$
2. $2\ \mathrm{K}\underline{\mathbf{Cl}}\mathrm{O_3} \rightarrow 2\ \mathrm{K}\underline{\mathbf{Cl}} + 3\ \mathrm{O_2}$
3. $2\ \underline{\mathbf{Al}} + 3\ \mathrm{S} \rightarrow \mathit{Al}_2\mathrm{S_3}$
4. $\underline{\mathbf{Mn}}_2\mathrm{O_3} + 4\ \mathrm{Fe}^{2+} + 5\ \mathrm{H_2O} \rightarrow 2\ \underline{\mathbf{Mn}}\mathrm{O_4}^- + 4\ \mathrm{Fe} + 10\ \mathrm{H}^+$

In each case, we will check to see how the charge has changed on the highlighted atom and from this, determine whether this represents an oxidation or a reduction.

1. $Cu^{2+} \rightarrow Cu$ – copper gained 2 electrons. This is a reduction.
2. $Cl^{5+} \rightarrow Cl^{-}$ – chlorine gained 6 electrons. This is a reduction.
3. $Al \rightarrow Al^{3+}$ – aluminum lost 3 electrons. This is an oxidation.
4. $Mn^{3+} \rightarrow Mn^{7+}$ – manganese lost 4 electrons. This is an oxidation.

For every oxidation there must always be a reduction and vice-versa. Electrons cannot be given up if there is nothing to accept them. So in each reaction above, there must be a corresponding oxidation or reduction. What is the corresponding oxidation or reduction for each reaction above?

1. $Zn \rightarrow Zn^{2+}$ – zinc lost two electrons. This is an oxidation.
2. $O^{2-} \rightarrow O_2$ – oxygen lost two electrons. This is an oxidation.
3. $S \rightarrow S^{2-}$ – sulfur gained two electrons. This is a reduction.
4. $Fe^{2+} \rightarrow Fe$ – iron gained two electrons. This is a reduction.

Balancing Oxidation-Reduction Reactions

Oxidation-reduction reactions can be very complicated to balance and are one of the few reactions that use a set of rules for balancing. There are seven steps in the balancing process and perhaps as many as nine depending on the solutions used. The steps are not complicated, and in fact are quite easy, and by the time you are done even the most complicated reaction can be easily balanced. We will begin by balancing the following oxidation-reduction reaction,

$$Cr_2O_7^{2-} + I^{-} \rightarrow Cr^{3+} + I_3^{-}$$

Step One: Split the reaction into two half-reactions.

Every reaction will have two parts, one that is an oxidation and another that is a reduction. You do not need to know which is which. When we are finished balancing you will be able to determine which reaction is the oxidation and which is the reduction. For now it is enough to know that there is one of each and each of them has a reaction. When separated, they are called half-reactions. Which atoms, molecules, or ions to use in each half-reaction should be intuitively obvious,

1st half-reaction: $Cr_2O_7^{2-} \rightarrow Cr^{3+}$

2nd half-reaction: $I^- \rightarrow I_3^-$

These have now been split into two half-reactions.

Step Two: Balance the central atom.

The next step is to balance the central atom. This is the atom that changes charge. In the first half-reaction, the central atom is the chromium, and in the second half-reaction it is the iodine. There are two chromium atoms on the left side of the 1st half-reaction so we must multiple the Cr^{3+} by two. There are three iodines on the right side of the 2nd half-reaction so we must multiply the the I^- by three.

1st half-reaction: $Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+}$

2nd half-reaction: $3\ I^- \rightarrow I_3^-$

The central atom in each reaction is now balanced.

Step Three: Add water to the side deficient in oxygen.

If one side of a reaction has more oxygens than the other, then waters are added to the opposite side to make up for the deficiency. If there no oxygens present in the reaction, this step is skipped.

For the first half-reaction, there are 7 oxygens present on the left hand side and none on the right, so we must add 7 H_2O's to the right side to make up for the deficiency. The second half-reaction has no oxygens so we do nothing.

1st half-reaction: $Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$

2nd half-reaction: $3\ I^- \rightarrow I_3^-$

The oxygens in both half-reactions have now been balanced.

Step Four: Add H^+ to the side opposite of the added water.

In step three we added water to the first half-reaction. Doing so adds extra hydrogens and these must be balanced by adding H+ to the side opposite to the side to which water was added.

1st half-reaction: $14\,H^+ + Cr_2O_7^{2-} \rightarrow 2\,Cr^{3+} + 7\,H_2O$

2nd half-reaction: $3\,I^- \rightarrow I_3^-$

We add enough H^+'s to balance the number of hydrogens present on both sides of the reaction. In this case, we added 14 H^+ to balance the hydrogens present from the 7 H_2O's.

The hydrogens are now balanced.

Step Five: Balance the charge by adding electrons.

These two half-reactions already have a material balance, that is, all the atoms balance but the charges do not. To balance the charge electrons are added to the side that is most positive to make both sides equal in charge. To start, we must know the charge on each side of our half-reactions

1st half-reaction: $\underbrace{\underset{+14}{14\,H^+} + \underset{-2}{Cr_2O_7^{2-}}}_{+12} \rightarrow \underbrace{\underset{+6}{2\,Cr^{3+}}}_{+6} + 7\,H_2O$

We must add 6 electrons to the left side of this reaction to reduce the +12 charge to a +6 charge so that both sides will have a +6 charge.

2nd half-reaction: $\underbrace{\underset{-3}{3\,I^-}}_{-3} \rightarrow \underbrace{\underset{-1}{I_3^-}}_{-1}$

We must add 2 electrons to the right side of this reaction to reduce the -1 charge to a -3 charge so that both sides will have a -3 charge.

The result of adding the electrons as described above is that the two half-reactions are now materially and electrically balanced,

$$\text{1}^{\text{st}}\text{ half-reaction: } 6\ e^- + 14\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$$

$$\text{2}^{\text{nd}}\text{ half-reaction: } 3\ I^- \rightarrow I_3^- + 2\ e^-$$

There are two important observations to make at this point. First, we can now determine which reaction is the oxidation and which is the reduction. The first half-reaction is a reduction since it is gaining electrons (electrons are a reactant). This means that the second reaction must be an oxidation. We can see this because the second half-reaction loses electrons (electrons are a product). The second important point is that we have both an oxidation and a reduction reaction occurring. If at the end of this process we had two oxidations or two reductions we would know that something must have gone wrong. This is an important check on our work. For every oxidation reaction there must also be a reduction reaction.

Step Six: Add the two reactions together, multiplying them in such a way that the electrons will cancel.

Oxidation-reduction reactions occur because of an exchange of electrons. There can never be a deficiency or surplus of electrons in an oxidation-reduction reaction. Overall, the electrons must cancel. This means that we must multiply our reactions in such a way that, when added together, the electrons will cancel. In this example, we must multiply the 2nd half-reaction so that, when these reactions are added together, the electrons will cancel.

$$\text{1}^{\text{st}}\text{ half-reaction: } \cancel{6\ e^-} + 14\ H^+ + Cr_2O_7^{2-} \rightarrow 2\ Cr^{3+} + 7\ H_2O$$

$$\text{2}^{\text{nd}}\text{ half-reaction: } 3\ (3\ I^- \rightarrow I_3^- + 2\ e^-) \Longrightarrow 9\ I^- \rightarrow 3\ I_3^- + \cancel{6\ e^-}$$

When added together, we get,

$$14\ H^+ + Cr_2O_7^{2-} + 9\ I^- \rightarrow 2\ Cr^{3+} + 7\ H_2O + 3\ I_3^-$$

Step Seven: Cancel any H_2O's and H^+'s that appear on both sides of the reaction.

When H_2O and H^+ is used to balance both half-reactions they will both appear on both sides of the reaction and should be cancelled. The example given here does not have this condition so this step can be skipped, but it is an important final step in the balancing process and should not be ignored. Overall, our balanced oxidation-reduction reaction is,

Start: $Cr_2O_7^{2-} + I^- \rightarrow Cr^{3+} + I_3^-$

$$\downarrow$$

Finish: $14\ H^+ + Cr_2O_7^{2-} + 9\ I^- \rightarrow 2\ Cr^{3+} + 7\ H_2O + 3\ I_3^-$

The reaction has been balanced materially and electrically. Attempting to balance this reaction without the use of these rules would have been virtually impossible, but the rules, when applied correctly allow you to balance oxidation-reduction reactions very quickly.

Although this reaction has been properly balanced, we are not quite finished learning how to balance oxidation-reduction reactions. Without actually saying so, it is implied by the presence of H^+ that this reaction was balanced in an acid, but what if the reaction conditions were basic, how would we balance it then? This is the subject of our next section.

Balancing in a Base

To balance a reaction in a base is actually the conversion of an oxidation-reduction after the reaction has already been balanced in an acid. To convert an acid reaction to a base reaction requires adding enough OH^- to both sides of an acid reaction to neutralize the H^+ ions present.

Step Eight: Add an equivalent number OH^- ions to the number of H^+ ions present to both sides of the reaction.

Using our balanced oxidation-reduction reaction as an example, we add 14 OH^- ions to both side of our reaction to convert it from an acid to a base.

$$\begin{array}{c} 14\,H^+ + Cr_2O_7^{2-} + 9\,I^- \rightarrow 2\,Cr^{3+} + 7\,H_2O + 3\,I_3^- \\ \underline{\qquad\qquad 14\,OH^- \rightarrow 14\,OH^- \qquad\qquad} \\ 14\,OH^- + 14\,H^+ + Cr_2O_7^{2-} + 9\,I^- \rightarrow 2\,Cr^{3+} + 7\,H_2O + 3\,I_3^- + 14\,OH^- \end{array}$$

The H^+ and OH^- ions are incompatible in the same solution and will combine to form water which is the next step.

Step Nine: Combine the H^+ and OH^- to make water and cancel any existing waters that appear on both sides of the reaction.

$$\boxed{14\,OH^- + 14\,H^+} + Cr_2O_7^{2-} + 9\,I^- \rightarrow 2\,Cr^{3+} + 7\,H_2O + 3\,I_3^- + 14\,OH^-$$

$\Big\downarrow$ Combine to make water

$$\overset{7}{\cancel{14}}\,H_2O + Cr_2O_7^{2-} + 9\,I^- \rightarrow 2\,Cr^{3+} + \cancel{7\,H_2O} + 3\,I_3^- + 14\,OH^-$$

$\Big\downarrow$ Cancelling waters

$$7\,H_2O + Cr_2O_7^{2-} + 9\,I^- \rightarrow 2\,Cr^{3+} + 3\,I_3^- + 14\,OH^-$$

The result is a new reaction that has been balanced in a base.

Problem 14.2

Please balance each of the following redox reactions;

1. $MnO_4^- + Fe^{2+} \rightarrow Fe^{3+} + Mn^{2+}$ (in acid)
2. $CrO_4^{2-} + I^- \rightarrow I_2 + Cr^{3+}$ (in base)
3. $Co^{2+} + NO_3^- \rightarrow Co_2O_3 + NO$ (in base)
4. $I_3^- + S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}$ (in acid)
5. $H_2S + Cr_2O_7^{2-} \rightarrow Cr^{3+} + S$ (in acid)
6. Fe^{2+} + NiOOH —> Fe^{3+} + $Ni(OH)_2$ (in base)

Answer: Note: Each reaction was balanced in acid and then converted to base as needed.

1. $MnO_4^- + Fe^{2+} \rightarrow Fe^{3+} + Mn^{2+}$

   $5(Fe^{2+} \rightarrow Fe^{3+} + e^-)$
   $5e^- + 8 H^+ + MnO_4^- \rightarrow Mn^{2+} + 4 H_2O$
   $5 Fe^{2+} + 8 H^+ + MnO_4^- \rightarrow Mn^{2+} + 4 H_2O + 5 Fe^{3+}$

2. $CrO_4^{2-} + I^- \rightarrow I_2 + Cr^{3+}$

   $2(3 e^- + 8 H^+ + CrO_4^{2-} \rightarrow Cr^{3+} + 4 H_2O)$
   $3(2 I^- \rightarrow I_2 + 2 e^-)$
   $6 I^- + 16 H^+ + 2 CrO_4^{2-} \rightarrow 2 Cr^{3+} + 8 H_2O + 3 I_2$
   $16 OH- \rightarrow 16 OH-$
   $6 I^- + 8 H_2O + 2 CrO_4^{2-} \rightarrow 2 Cr^{3+} + 8 OH^- + 3 I_2$

3. $Co^{2+} + NO_3^- \rightarrow Co_2O_3 + NO$

   $3(3 H_2O + 2 Co^{2+} \rightarrow Co_2O_3 + 6 H^+ + 2e^-)$
   $2(3 e^- + 4 H^+ + NO_3^- \rightarrow NO + 2 H_2O)$
   $8 H+ + 2 NO_3^- + 9 H_2O + 6 Co^{2+} \rightarrow 3 Co_2O_3 + 18 H^+ + 2 NO + 4 H_2O$
   $2 NO_3^- + 5 H_2O + 6 Co^{2+} \rightarrow 3 Co_2O_3 + 10 H^+ + 2 NO$
   $10 OH^- \rightarrow 10 OH^-$
   $2 NO_3^- + 5 OH^- + 6 Co^{2+} \rightarrow 3 Co_2O_3 + 5 H_2O + 2 NO$

4. $I_3^- + S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}$

   $2 e^- + I_3^- \rightarrow 3 I^-$
   $S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2 e^-$
   $I_3^- + S_2O_3^{2-} \rightarrow 3 I^- + S_4O_6^{2-}$

5. $H_2S + Cr_2O_7^{2-} \rightarrow Cr^{3+} + S$

   $3(H_2S \rightarrow S + 2 H^+ + 2 e^-)$
   $6 e^- + 14 H^+ + Cr_2O_7^{2-} \rightarrow 2 Cr^{3+} + 7 H_2O$
   $14 H^+ + Cr_2O_7^{2-} + 3 H_2S \rightarrow 3 S + 6 H^+ + 2 Cr^{3+} + 7 H_2O$
   $8 H^+ + Cr_2O_7^{2-} + 3 H_2S \rightarrow 3 S + 2 Cr^{3+} + 7 H_2O$

6. $Fe^{2+} + NiOOH \rightarrow Fe^{3+} + Ni(OH)_2$

   $Fe^{2+} \rightarrow Fe^{3+} + e^-$
   $e^- + H^+ + NiOOH \rightarrow Ni(OH)_2$
   $H^+ + NiOOH + Fe^{2+} \rightarrow Fe^{3+} + Ni(OH)_2$
   $OH^- \rightarrow OH^-$
   $H_2O + NiOOH + Fe^{2+} \rightarrow Fe^{3+} + Ni(OH)_2 + OH^-$

Electrochemical Cells

An electrochemical cell is an apparatus that makes it possible to harness the electrons that are given off and taken in during an oxidation-reduction reaction and do useful work with them. In this case, create electricity. For example, consider the reaction between metallic zinc and copper ions,

$$\mathrm{Zn(s)} + \mathrm{Cu^{2+}} \rightarrow \mathrm{Zn^{2+}} + \mathrm{Cu(s)}$$

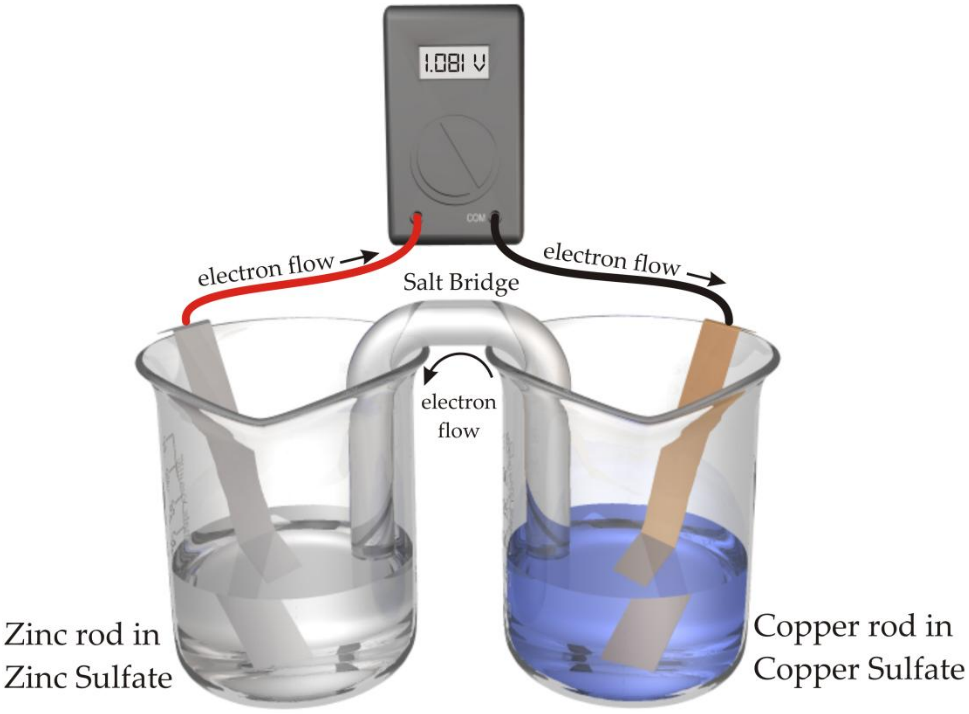
The balanced half-reactions are,

$$\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}} + 2\ \mathrm{e^-}\ \text{(oxidation)}$$
$$2\ \mathrm{e^-} + \mathrm{Cu^{2+}} \rightarrow \mathrm{Cu(s)}\ \text{(reduction)}$$

We can separate these two reactions and force the electrons created by the oxidation reaction to flow to the reduction reaction.

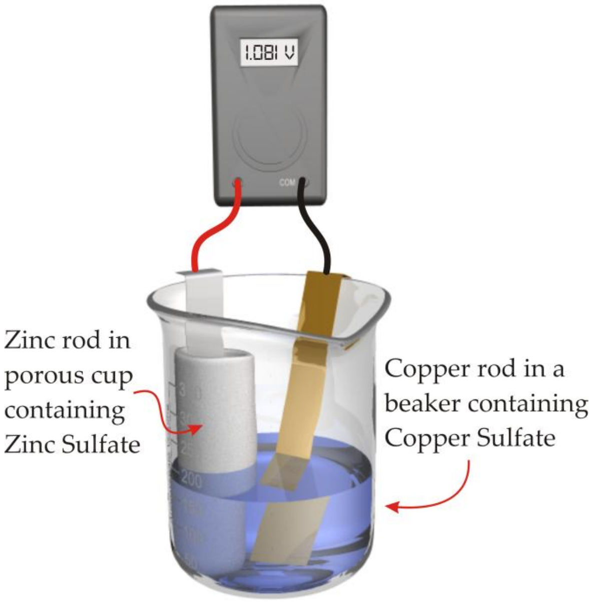
$$\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}} + \underbrace{2\ \mathrm{e^-}\ \mid\ 2\ \mathrm{e^-}}_{\text{Link these with a wire}} + \mathrm{Cu^{2+}} \rightarrow \mathrm{Cu(s)}$$

We start by placing two beakers side-by-side and putting a zinc rod and a solution of $\mathrm{ZnSO_4}$ in one and the copper rod and a solution of $\mathrm{CuSO_4}$ in the other.

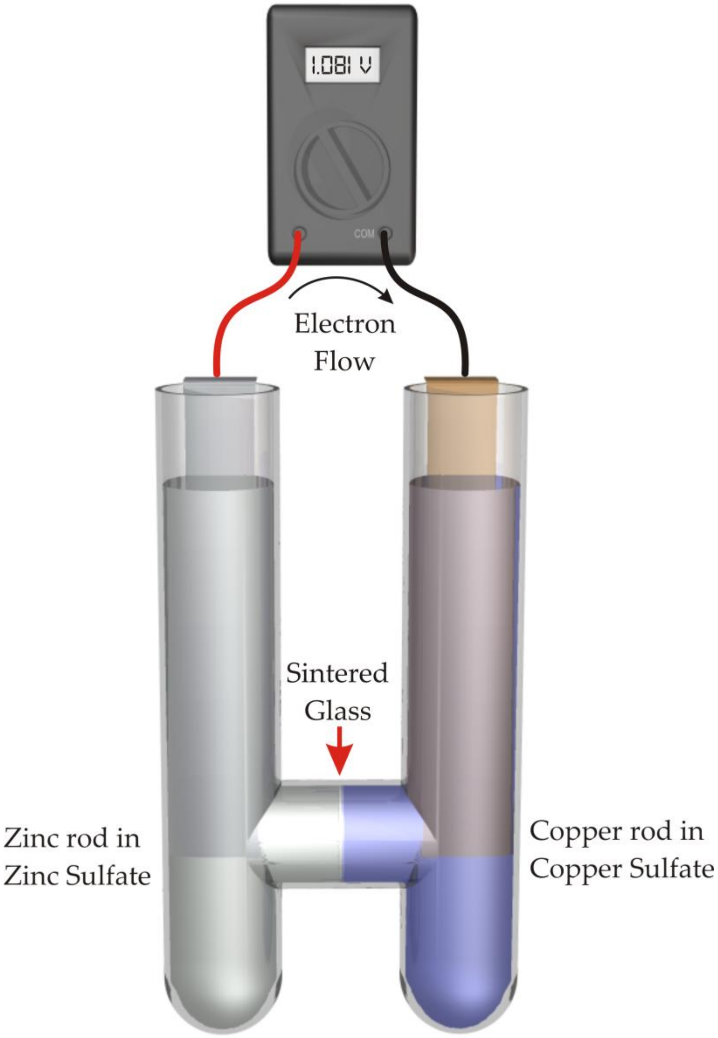


You will notice that the electrons flow from the zinc electrode, which is the source of the electrons, to the copper electrode where they are consumed. You will also notice that we have added a salt bridge to act as a connection between the two beakers. As the electrons flow out of zinc electrode, zinc ions are being produced. Left unabated, the zinc beaker would become positively charged with a surplus of positive zinc ions. By contrast, as the electrons flow to the copper side they combine with the copper ions to make elemental copper. This leaves the corresponding sulfate ion behind so the copper side becomes negatively charged. The salt bridge prevents a buildup of charge on both sides of the electrochemical cell. The salt bridge acts as a conduit to allow negative ions to flow toward the zinc cell and positive ions to flow toward the copper cell so that both sides remain electrically neutral. Usually, the salt bridge is filled with a thick gel or agar that has a high concentration of potassium nitrate or potassium chloride. If potassium chloride is used in the salt bridge, chloride ions move into the zinc cell to neutralize the charges on the zinc and potassium moves into the copper cell to neutralize the charge on the sulfate ion. The salt bridge “completes the circuit” and allows the electrons to flow. Without the salt bridge, no voltage could be created by the electrochemical cell.

The electrochemical cell shown above works well but the salt bridge makes it messy to use. For most lab situations a simpler setup can be used to create an electrochemical cell. Rather than use a salt bridge, a porous cup can be used to contain one of the two solutions. A porous cup has very small holes in it that allow for some mixing of the solution, but the mixing is very slow. More importantly, ions are allows to transport across the porous cup to complete the circuit and keep both parts of the cell electrically neutral.



Electrochemical cells come in many shapes and sizes. One of the most popular cells is the H-cell, so called because of its shape. It behaves in many ways like a beaker and a porous cup but it uses sintered that allows for ion flow rather than a porous ceramic. Because the connection between the two half-cells is made of glass, it is easily cleaned, but there are other advantages.



Sometimes, it is desired to use mercury as one of the two electrodes, but mercury, being a liquid, cannot be used like the zinc or copper rods that we have seen. Instead, a pool of mercury must be used and either side of an H-cell provides a perfect reservoir for the mercury. When mercury is used, the electrical connection comes in the form of a platinum wire that is sealed through the bottom of the H-cell.

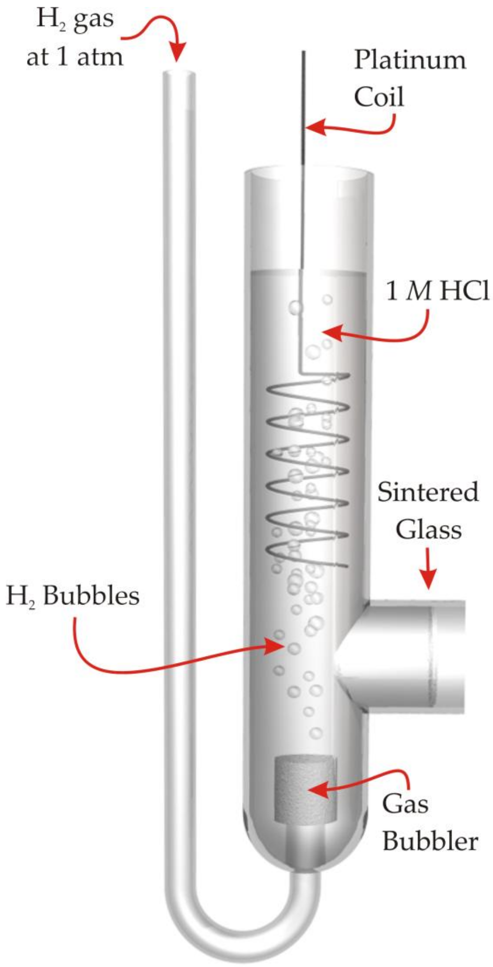
Specialized Cells

The Standard Hydrogen Electrode (SHE)

The standard hydrogen electrode (SHE) is the standard by which all other cell reactions are measured. By definition SHE has a voltage of exactly 0.000 volts. The half-reaction for SHE is,

$$2\ H^+\ (1\ M) + 2\ e^- \rightarrow H_2(g) \quad \mathscr{E}° = 0.000 \text{ volts}$$

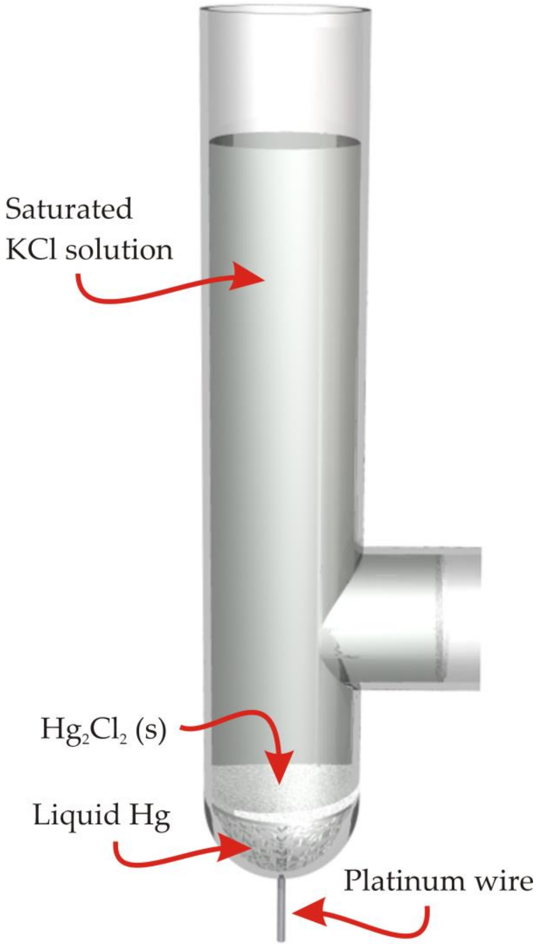
Classically, 1 atmosphere of hydrogen gas is bubbled through sintered class diffuser into a solution of 1 M HCl. The reaction takes place on a coil of platinum that has been activated by depositing platinum crystals on its surface. For this reason, the coil is black in color (called platinum black) rather than the normal silver color associated with platinum.



Calomel Electrode

A calomel electrode is often used as a substitute for SHE as a standard by which other voltages are measured. The cell consists of a pool of mercury in contact with solid Hg_2Cl_2 (call calomel, thus, the name of this cell) in a solution of saturated KCl. The calomel half-reaction is,

$$Hg_2Cl_2(s) + 2\ e^- \rightarrow 2\ Hg(\ell) + 2\ Cl^- \quad \mathscr{E}° = 0.2444 \text{ volts @ } 25°C$$



Although this electrode is very stable, its use suffers from the toxic effects of mercury. It has been largely replaced by the much less toxic and inexpensive Ag/AgCl electrode.

Ag/AgCl Electrode

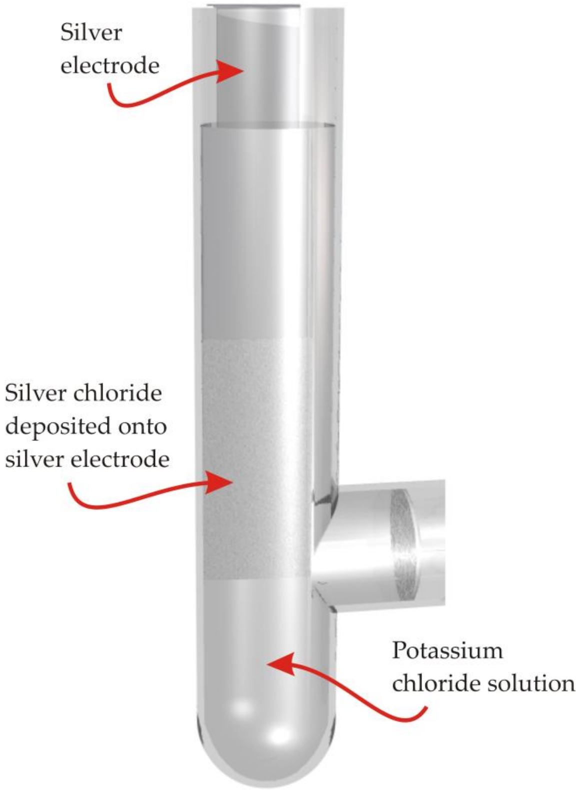
The Ag/AgCl electrode is commonly used as the reference electrode in pH meters. It has the advantage of being inexpensive, non-toxic, and extremely stable. The Ag/AgCl half-reaction is,

$$AgCl(s) + e^{-} \rightarrow Ag(s) + Cl^{-} \quad \mathscr{E}^{\circ} = 0.2225 \text{ volts}$$

The concentration of the Cl^{-} will determine the voltage of this cell.

Reference Electrode Potentials*	
Electrode	Voltage
Ag/AgCl/Sat. KCl	0.197
Ag/AgCl/3.5 mol/kg KCl	0.205
Ag/AgCl/3.0 mol/kg KCl	0.210
Ag/AgCl/1.0 mol/kg KCl	0.235
Ag/AgCl/0.6 mol/kg KCl	0.250
Ag/AgCl (Seawater)	0.266

*Taken from NACE International CP Specialist Course Manual



Building Electrochemical Cells

The foregoing electrochemical cells were not presented as a stroll down the road of electrochemical history. They were presented to show possible ways in which electrochemical cells can be constructed using gases, liquids, solids and precipitates. These details are important when designing a working electrochemical cell.

Cell construction begins with the half-reactions. Everything found in a half-reaction must also be in the half-cell. Certain rules apply that aid in the making of a cell. These are outlined below.

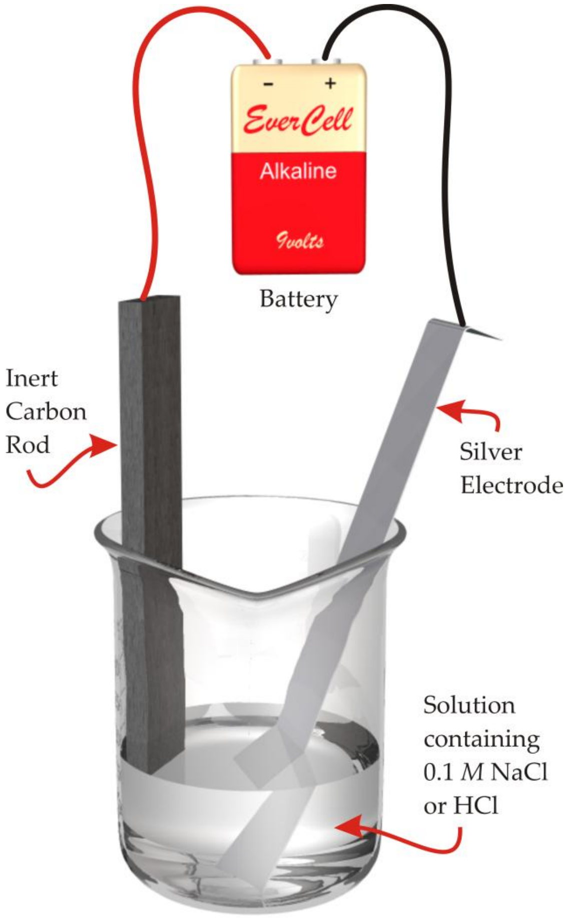
The Electrodes: If the solid metal is in the half-reaction, it is used as the electrode in the cell. If mercury is used, then a pool of mercury must be used. The electrical connection for a mercury pool is a platinum wire that sticks out the bottom of the half-cell. Electrodes cannot be made of ions or non-metallic solids. If a metal is not present in the half-reaction then an inert electrode like a carbon rod or platinum wire is used.

Half-reaction	Appropriate Electrode
$Fe^{3+} + 3\ e^- \rightarrow Fe(s)$	Fe(s)
$Cu^{2+} + e^- \rightarrow Cu^+$	Platinum or Carbon
$I_2(s) + 2\ e^- \rightarrow 2\ I^-$	Platinum or Carbon
$NO_3^- + 4\ H^+ + 3\ e^- \rightarrow NO + 2\ H_2O$	Platinum or Carbon
$PbI_2 + 2\ e^- \rightarrow Pb(s) + 2\ I^-$	Pb(s)

Ions in Solution: All the ions present in the half-reaction must also be present in the half-cell, but ions do not exist by themselves, compounds must be used. If an ion is negatively charged then Na^+ or K^+ must be added to it to make it a soluble compound. If an ion is positively charged then a corresponding negative charge must be found that makes the compound soluble. The most common choice is the nitrate ion (NO_3^-) since all nitrate compounds are soluble, but nitrate suffers from being very reactive and is not always a good choice. Sulfate, chloride, and perchlorate (SO_4^{2-}, Cl^-, ClO_4^-) compounds are good choices if the compound is soluble so it is important that you remember your solubility rules.

Acids and Bases in Solution: Acids are common ingredients in half-cells since they are used to balance oxidation-reduction reactions. When an acid is needed, HCl is often a good choice unless the chloride ion interferes by making unwanted precipitates. Again, knowing your solubility rules is important. Bases have fewer problems. Sodium rarely interferes with a reaction so using NaOH is always a safe choice.

Solids and Precipitates: Very often, a solid or precipitate must be present in the cell. It is always best that these solids have a direct contact with the electrode but their mere presence in the cell will suffice. Small amounts of these solids can be added to the bottom of the cell, but a better strategy is to electrodeposit them onto the electrode itself. This is not nearly as difficult as might be guessed. All it takes is a battery, a couple of wires, the electrode and a solution containing needed ions.



To make a Ag/AgCl electrode some AgCl must be deposited onto the silver electrode. To do this, a small amount of a dilute source of chloride ion (NaCl or HCl) is put into a beaker and the silver electrode is dipped into it. The silver electrode is made positively charged by attaching it to the positive terminal of a battery. The negative pole of the battery is attached to a carbon rod and it is placed into the beaker of solution. The chloride ion (Cl^-) is attracted to the positive charge of the silver electrode, reacts with the silver and becomes AgCl. The entire process takes just a few seconds.

How to Build a Cell

All electrochemical cells begin with a balanced oxidation-reduction reaction but as a student, most likely you will be given an oxidation-reduction reaction that must be balanced. A sample reaction is given below,

$$Cu(s) + HgO(s) \rightarrow Cu^{2+} + Hg(\ell)$$

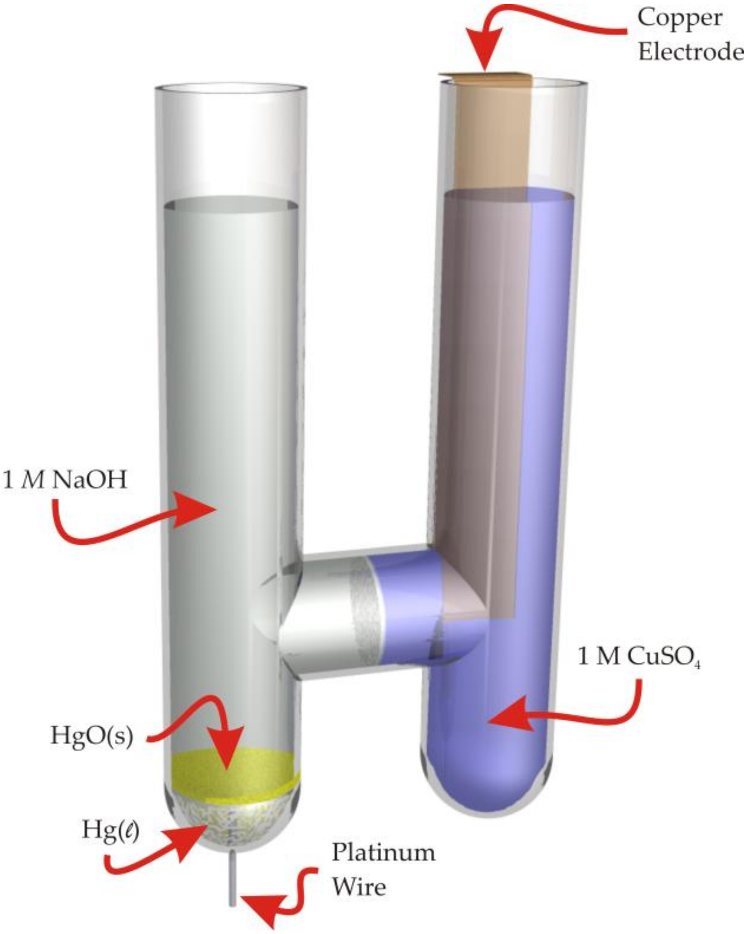
Oxides like HgO(s) must be balanced in a base, so the balanced half-reactions would be,

$$Cu(s) \rightarrow Cu^{2+} + 2\ e^-$$
$$2\ e^- + H_2O + HgO(s) \rightarrow Hg(\ell) + 2\ OH^-$$

Everything found in a half reaction must also be present in the half cell so each of the cells must have the following ingredients,

Copper Cell	Mercury Cell
$Cu(s)$	$HgO(s)$
Cu^{2+} (1 *M* $CuSO_4$)	$Hg(\ell)$
	OH^- (1 *M* NaOH)

Using an H-Cell as our glassware of choice, we would make the cell as shown on the right. You will note that all the ingredients are present. We have an electrode made of solid copper in a solution containing $CuSO_4$ because it is soluble and a source of Cu^{2+} ions. The yellow HgO(s) is made by putting a few drops of $Hg(NO_3)_2$ into the 1 M NaOH. The precipitate forms automatically and sits on top of the pool of mercury in the bottom of the cell. Except for a volt meter, this cell is complete.



Electron Flow

It is impossible to know the direction of electron flow without knowing the voltage of the cell. The value is not important. It is the sign of the voltage that will determine the direction of electron flow. The reason for this is that the voltage, $\mathscr{E}°$, is related to the Gibbs energy, $\Delta G°$, by the following equation,

$$\Delta G° = -\, n\, \mathscr{F}\mathscr{E}°$$

Where,

n = the number of electrons transferred in the reaction
$\mathscr{F}$ = Faraday's constant, 96,485 coulombs/mole e^-
$\mathscr{E}°$ = voltage = Joules/coulomb

It should be noted that a coulomb is a measure of charge and there are 96,485 coulombs of charge on one mole of electrons. Therefore, when put together, these three values give us joules,

$$(\text{moles of } e^-)\ (\text{coulomb/mole } e^-)\ (\text{joules/coulomb}) = \text{joules}$$

When a reaction is spontaneous, the $\Delta G°$ is negative. So, because of the negative sign in the conversion of volts to joules, a spontaneous reaction is one whose voltage is positive.

$$\begin{array}{lr}
Cu(s) \rightarrow Cu^{2+} + 2\,e^- & -\,0.34 \text{ volts} \\
2\,e^- + H_2O + HgO(s) \rightarrow Hg(\ell) + 2\,OH^- & 0.0984 \text{ volts} \\
\hline
Cu(s) + H_2O + HgO(s) \rightarrow Cu^{2+} + Hg(\ell) + 2\,OH^- & -\,0.2416 \text{ volts}
\end{array}$$

The sum of these two voltages is – 0.2416 volts. This negative sign tells us that the reaction does not occur as written. Instead, the opposite reaction occurs,

$$\begin{array}{lr}
Cu^{2+} + 2\,e^- \rightarrow Cu(s) & 0.34 \text{ volts} \\
Hg(\ell) + 2\,OH^- \rightarrow 2\,e^- + H_2O + HgO(s) & -\,0.0984 \text{ volts} \\
\hline
Cu(s) + H_2O + HgO(s) \rightarrow Cu^{2+} + Hg(\ell) + 2\,OH^- & +\,0.2416 \text{ volts}
\end{array}$$

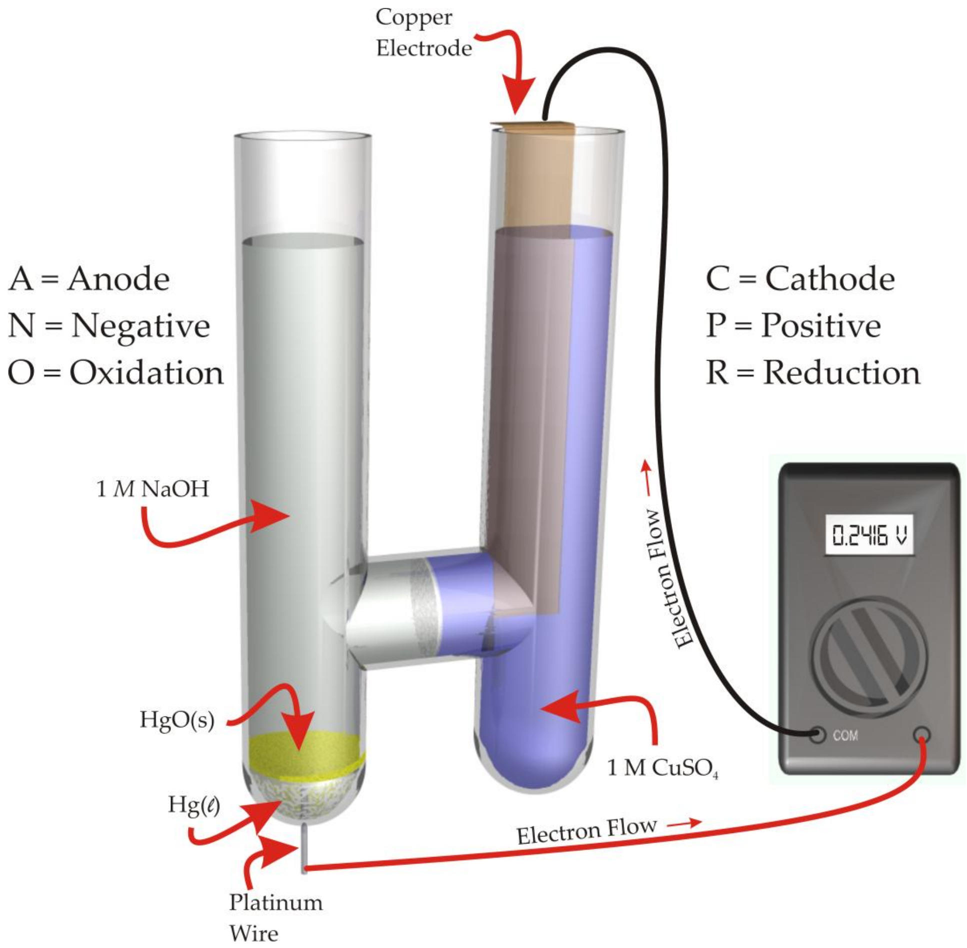
By reversing the reaction we change the sign on the voltages, but we also change which reaction is the oxidation and which is the reduction. Now, the mercury electrode is the source of the electrons and the copper consumes them. This makes the reaction occurring on the mercury electrode the oxidation and the reaction occurring on the copper electrode the reduction. Electrons flow from the oxidation reaction to the reduction reaction so the electrons flow from the mercury to the copper.

By definition, the electrode that produces electrons is negatively charged and the electrode that consumes them is positively charged. The negative electrode is called the "anode" and the positive electrode is called the "cathode." Electrons flow from the anode to the cathode. These are easy to remember, especially if you have ever learned CPR (cardiopulmonary resuscitation),

A = Anode
N = Negative
O = Oxidation

C = Cathode
P = Positive
R = Reduction

We are now prepared to completely label our electrochemical cell including the anode, cathode and direction of electron flow.



Calculating Voltages

When the voltages of two half-reactions are added together, it appears like the process is simple addition. The simplicity of adding voltages hides the underlying process that actually occurs. Consider for a moment Gibbs energy. We add the Gibbs energy of reactions to obtain an overall energy.

$$\Delta G^\circ_1 + \Delta G^\circ_2 = \Delta G^\circ_3$$

We also know that Gibbs energy is "extensive", that is, it scales with size. For example, there is twice as much energy in two gallons of gas than there is one gallon. Also, we note that when we need to double a reaction, we also double the Gibbs energy for that reaction.

None of this is true for voltage. Voltage is intensive, that is, it doesn't scale with size. A "D" cell battery is many times larger than a "AAA" battery but they both give off 1.5 volts. So, although our experience tells us that we can add and subtract energy, we cannot add and subtract voltage in the same way.

The relationship between Gibbs energy and voltage has already been given. It is,

$$\Delta G^\circ = -\, n\mathscr{F}\mathscr{E}^\circ$$

So, if we want to add voltages the same way that we add Gibbs energy we must use this equation so that,

$$\Delta G^\circ_1 + \Delta G^\circ_2 = \Delta G^\circ_3$$

By substitution,

$$(-\, n_1\mathscr{F}\mathscr{E}^\circ_1) + (-\, n_2\mathscr{F}\mathscr{E}^\circ_2) = (-\, n_3\mathscr{F}\mathscr{E}^\circ_3)$$

Getting rid of all the negative signs and cancelling Faraday's constant, $\mathscr{F}$, we get,

$$n_1\mathscr{E}^\circ_1 + n_2\mathscr{E}^\circ_2 = n_3\mathscr{E}^\circ_3$$

So, to add two voltages together we do the following operation,

$$\frac{n_1\mathscr{E}^\circ_1 + n_2\mathscr{E}^\circ_2}{n_3} = \mathscr{E}^\circ_3$$

In our previous example, we had the following half-reactions,

$$\begin{array}{lr}
Cu^{2+} + 2\,e^- \rightarrow Cu(s) & 0.34\text{ volts} \\
Hg(\ell) + 2\,OH^- \rightarrow 2\,e^- + H_2O + HgO(s) & -\,0.0984\text{ volts} \\
\hline
Cu(s) + H_2O + HgO(s) \rightarrow Cu^{2+} + Hg(\ell) + 2\,OH^- & +\,0.2416\text{ volts}
\end{array}$$

The mercury electrode produced two electrons and the copper electrode consumed two electrons. So, n_1 and n_2 both equal 2 for these reactions and the overall number of electrons transferred is also $n_3 = 2$ so that,

$$\frac{n_1\mathscr{E}^\circ_1 + n_2\mathscr{E}^\circ_2}{n_3} = \frac{2(0.34\text{ volts})+2(-0.0984\text{ volts})}{2} = 0.2416\text{ volts}$$

In a reaction where all the electrons cancel, as in the above example, it will appear as though the voltages have just been added together, but the reality is that our addition formula was used. This formula is particularly important when electrons do not cancel. Consider the following example,

$$\begin{array}{lr}
Fe^{3+} + e^- \rightarrow Fe^{2+} & 0.771\text{ volts} \\
Fe^{2+} + 2\,e^- \rightarrow Fe(s) & -0.441\text{ volts} \\
\hline
Fe^{3+} + 3\,e^- \rightarrow Fe(s) & ?\quad\text{volts}
\end{array}$$

Simple addition would put the voltage at 0.771 + (– 0.441) = 0.33 volts, but, as we will find out, this voltage is very wrong. The actual voltage has to be calculated using our formula,

$$\frac{n_1\mathscr{E}^\circ_1 + n_2\mathscr{E}^\circ_2}{n_3} = \frac{1(0.771\text{ volts})+2(-\,0.441\text{ volts})}{3} = -\,0.037\text{ volts}$$

It should be noted that there is one electron transferred in the first reaction, two electrons in the second reaction, and three electrons transferred overall. When applied properly, not only did simple addition give us the wrong answer, but it gave us the wrong sign on the voltage.

The Nernst Equation

The Gibbs equation can be converted its voltage equivalent using the relationship we have been using between energy and voltage. We begin with the Gibbs equation,

$$\Delta G = \Delta G^\circ + RT\,\ln(Q)$$

And then substitute the equivalent expression using voltage,

$$\Delta G^\circ = -\,n\mathscr{F}\mathscr{E}^\circ$$

If we rearrange this a bit we would get,

$$\frac{\Delta G^\circ}{-n\mathscr{F}} = \mathscr{E}^\circ$$

If we take the Gibbs equation and divide by - $n\mathscr{F}$, we get,

$$\frac{\Delta G}{-n\mathscr{F}} = \frac{\Delta G^\circ}{-n\mathscr{F}} + \frac{RT\ln(Q)}{-n\mathscr{F}}$$

Because of the equivalence between ΔG° and $\mathscr{E}^\circ$ we would have,

$$\mathscr{E} = \mathscr{E}^\circ + \frac{RT}{-n\mathscr{F}}\ln(Q)$$

Finally, we get the Nernst equation,

$$\mathscr{E} = \mathscr{E}^\circ - \frac{RT}{n\mathscr{F}}\ln(Q)$$

At 25°C, the $RT/\mathscr{F}$ term becomes a constant whose value is,

$$\frac{RT}{\mathscr{F}} = \frac{(8.314\ \mathrm{J/mol\cdot K})(298.15\ \mathrm{K})}{(96{,}485\ \mathrm{C/mol})} = 0.02569\ \mathrm{J/C} = 0.02569\ \text{volts}$$

So the Nernst equation is often rewritten as,

$$\mathscr{E} = \mathscr{E}^\circ - \frac{0.02569\ \text{volts}}{n}\ln(Q)$$

Most books don't use natural log in the Nernst equation, rather, the natural log is converted to $\log_{10}$ using the following formula,

$$\ln(x) = 2.3026\ \log_{10}(x)$$

Using this conversion, we obtain the final form of the Nernst equation,

$$\mathscr{E} = \mathscr{E}^\circ - \frac{0.02569 \text{ volts}}{\text{n}} \; (2.3026) \log_{10}(\text{Q})$$

Combining constants we get,

$$\mathscr{E} = \mathscr{E}^\circ - \frac{0.05915 \text{ volts}}{\text{n}} \log_{10}(\text{Q})$$

This is the Nernst equation found in most books and will be the version used here.

Using the Nernst Equation

The rules that applied to the Gibbs equation also apply to the Nernst equation. Specifically, at equilibrium the voltage of an electrochemical cell is zero; the battery is dead. But, like the Gibbs equation this means that when Q = K,

$$0 = \mathscr{E}^\circ - \frac{0.05915 \text{ volts}}{\text{n}} \log_{10}(\text{K})$$

Or,

$$\mathscr{E}^\circ = \frac{0.05915 \text{ volts}}{\text{n}} \log_{10}(\text{K})$$

In addition, if the concentration of all cell contents are 1 *M* (technically, 1 unit activity), then Q = 1 and $\log_{10}(\text{Q}) = 0$ so that, $\mathscr{E} = \mathscr{E}^\circ$. Under these conditions, if the cell contents are all 1 *M*, then,

$$\mathscr{E} = \frac{0.05915 \text{ volts}}{\text{n}} \log_{10}(\text{K})$$

That is, the measured voltage ($\mathscr{E}$) of the cell gives direct access to the equilibrium constant. It is this form of the equation that is used to determine the solubility product of extremely insoluble compounds. No matter how insoluble a compound might be, an electrochemical cell can be built that will allow for the calculation of its solubility product.

Determining a Solubility Product

Some of the most insoluble binary compounds known are sulfides. Copper sulfide (CuS) has a solubility product of just 8.8×10^{-45}. Even though this is a very small number, its value is easily calculated using an electrochemical cell. For the student, the difficult part of setting up a cell to measure an solubility product is determining the two half-reactions that will be used. We can start with the solubility product itself,

$$CuS(s) \leftrightarrows Cu^{2+} + S^{2-}$$

The two half-reactions that we use MUST add to give us exactly this overall reaction. The first half-reaction seems obvious, it involves copper,

$$Cu(s) \rightarrow Cu^{2+} + 2\ e^{-}$$

It is the second half reaction that causes the trouble. Students wrongly assume that the other half reaction will be,

$$S + 2\ e^{-} \rightarrow S^{2-}$$

What makes this half-reaction wrong is that, when added to our first half-reaction we do not get the reaction we want,

$$Cu + S \leftrightarrows Cu^{2+} + S^{2-}$$

The problem is that, Cu + S is NOT CuS and we cannot wave our hands and say that they will make CuS when added together. This is the wrong approach. We must find another half-reaction that, when added to our copper half reaction we get the correct overall reaction. It is sometime useful to pair up the metal half reaction with the overall solubility product to see what we need,

$$\begin{array}{c} Cu(s) \rightarrow Cu^{2+} + 2\ e^{-} \\ \underline{\text{(missing reaction)}} \\ CuS(s) \leftrightarrows Cu^{2+} + S^{2-}\ \text{(overall)} \end{array}$$

So, what is missing? Well, we need some CuS as a reactant and we need some S^{2-} as a product. We also need to get rid of the solid Cu present in the oxidation reaction as well as the electrons. Combining these observations we get,

$$\cancel{\mathrm{Cu(s}})\ \rightarrow \mathrm{Cu^{2+}} + \cancel{2\ e^-}$$
$$\mathrm{CuS(s)} + \cancel{2\ e^-} \leftrightarrows \cancel{\mathrm{Cu(s}}) + \mathrm{S^{2-}}$$
$$\overline{\mathrm{CuS(s)} \leftrightarrows \mathrm{Cu^{2+}} + \mathrm{S^{2-}}\ \text{(overall)}}$$

Everything found in the half-reaction must also be in the half-cell. In addition, to make sure that Q = 1, all ingredients must be 1 M where appropriate. Finally, and perhaps most importantly, it was argued earlier that we cannot know the direction of electron flow until we know the voltage of the cell. In this case, we cannot know for certain which of these reactions is the oxidation and which is the reduction because we do not know the overall voltage of the cell. We may have to reverse this reaction for it to be spontaneous. But, because this is a solubility product, we can make some predictions that might help us.

Compounds with solubility products are, by definition, not very soluble, and since they are not very soluble we do not expect the concentration of the ions to be very large. But, when we set up our electrochemical cell we are going to use 1 *M* concentrations for all ions in solution. If this were a question about LeChatlier's principle and we asked which direction the reaction would go if both $\mathrm{Cu^{2+}}$ and $\mathrm{S^{2-}}$ were 1 *M*, we would say "to the left" and we would be correct.

$$\underleftarrow{\mathrm{CuS(s)} \leftrightarrows \overset{1M}{\mathrm{Cu^{2+}}} + \overset{1M}{\mathrm{S^{2-}}}}$$

The reaction shifts to the left
based on LeChatlier's Principle

This means that, when the cell is moving in the spontaneous direction and has a positive voltage, we are actually measuring the reverse of our solubility product, or $1/K_{sp}$. Our Nernst equation becomes,

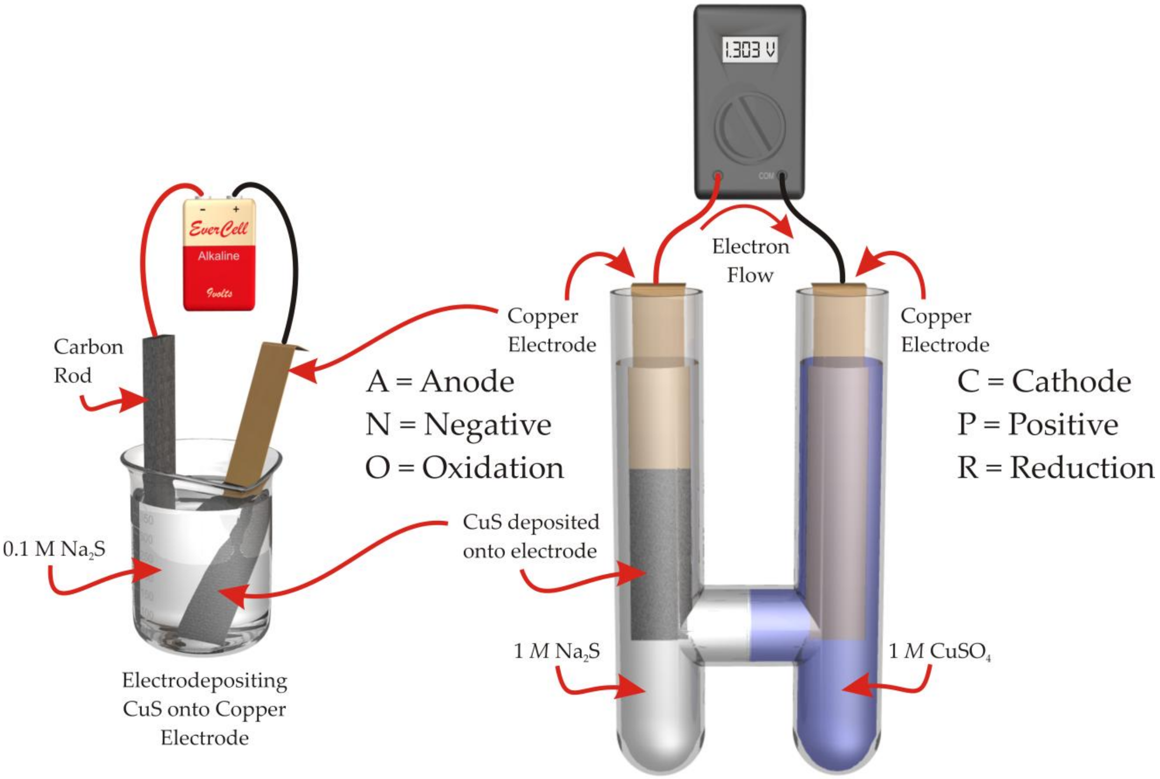
$$\text{Positive voltage} = \mathscr{E} = \frac{0.05915\ \text{volts}}{\text{n}}\ \log_{10}\left(\frac{1}{K_{sp}}\right)$$

This also means that the CuS cell has become our oxidation cell, and the copper cell is our reduction cell, the opposite of what we have written.

Now that we have our half-reactions, know the concentration of all cell ingredients, and can anticipate the direction of the reaction when the cell goes in the spontaneous direction ($\mathscr{E}$ = + voltage) we can begin building our cell.

We can make a list of ingredients needed to build the cell and build it.

Ingredient	Copper Cell (Reduction)	Cu/CuS Cell (Oxidation)
Electrode	Cu(s)	Cu(s) with CuS(s) deposited on it.
Solution	Cu^{2+} (1 *M* $CuSO_4$)	S^{2-} (1 M Na_2S)



The voltage for this cell is 1.303 volts. Using the Nernst equation we can solve for the solubility product. We should note that the total number of electrons transferred is 2.

$$1.303 \text{ volts} = \frac{0.05915 \text{ volts}}{2} \log_{10}\left(\frac{1}{K_{sp}}\right)$$

$$K_{sp} = 8.76\text{x}10^{-45}$$

This is a very satisfactory result and was easily obtained using an electrochemical cell.

Cell Diagrams

A cell diagram is a shorthand way of representing an electrochemical cell so that it can be typed out easily and appears as a single line of text. It is not a drawing the cell like those shown above.

Cell diagrams follow the flow of electrons from the anode to the cathode, but through the salt bridge, porous cup, or sintered glass. Each part of the cell is separated by a slash (/) and the salt bridge, sintered glass, or porous cup is indicated by a double-slash (//).

For example, suppose that we have the following set of reactions,

$$Zn \rightarrow Zn^{2+} + 2\ e^- \qquad \mathscr{E}^\circ = +\ 0.763 \text{ volts}$$
$$PbSO_4 + 2\ e^- \rightarrow Pb(s) + SO_4^{2-} \qquad \mathscr{E}^\circ = -\ 0.356 \text{ volts}$$

The reaction is spontaneous as written (the sum of the voltages is positive) so the zinc reaction is the oxidation (anode) and the lead reaction is the reduction (cathode). The cell diagram, going from the anode to the cathode would be,

$$Zn(s)/\ 1\ M\ ZnSO_4\ //\ 1\ M\ H_2SO_4\ /\ PbSO_4(s)/\ Pb$$

Starting at the zinc electrode we move through a solution of 1 *M* $ZnSO_4$ until we get to the sintered glass that separates the cells. After moving through the sintered glass we are in a solution of 1 *M* H_2SO_4 until we get to the electrode that is coated in $PbSO_4(s)$ and then through this precipitate to the lead electrode. If you are given a cell diagram you should be able to reproduce the two half reactions used to create the cell. In this case you would read the cell diagram as,

Zn(s) becomes zinc ions in solution.
$PbSO_4$ solid becomes Pb(s) in the presence of H_2SO_4.

This should be enough information to reproduce the two half reactions shown above.

Another example might be helpful. Suppose we have the following half-reactions,

$$Zn(s) + 2\ OH^- \rightarrow ZnO(s) + H_2O + 2\ e^-$$
$$HgO(s) + H_2O + 2\ e^- \rightarrow Hg(\ell) + 2\ OH-$$

The cell diagram would be,

$$Zn(s) / ZnO(s) / 1\ M\ NaOH / HgO(s) / Hg(\ell)$$

You will notice that this cell does not have a double-slash because no salt-bridge or sintered glass is needed. Both half-reactions have the same ingredient in solution, 1 M NaOH, and since one of the functions of the salt bridge is to prevent mixing of the solutions, it is not needed in this cell so it is omitted.

How about a more complicated cell?

$$3\ e^- + 4\ H^+ + NO_3^- \rightarrow NO(g) + 2\ H_2O$$
$$2\ I^- \rightarrow I_2(s) + 2\ e^-$$

Since neither of the half-reactions has solid metal present, we must choose an inert electrode for each of them. Either carbon or platinum is appropriate, and these act as both the anode and the cathode. The cell diagram would be,

$$Pt / I_2(s) / 1\ M\ KI // 1\ M\ HNO_3 / 1\ atm\ NO(g) / Pt$$

In this case, we have chosen platinum for our electrodes though carbon rods would have worked equally well. Since both H^+ and NO_3^- must be in the reduction cell, we have combined them to make HNO_3 and used this in solution rather than HCl and $NaNO_3$, though using those two ingredients would have worked also.

Batteries

Batteries are nothing more than electrochemical cells that have been conveniently packaged for our daily use. Batteries differ from the electrochemical cells we have been building; they never use 1 *M* solutions. In fact, solutions are rarely used at all, though exceptions do exist. Our interest has been to use electrochemical cells to calculate equilibrium constants but if a cell is going to be used as a power source there is no need to limit cell concentrations to 1 M. Rather, it is more convenient to move the reaction far from equilibrium so that the battery will last as long as possible. As a consequence we will find that the cells ingredients will be highly concentrated thick pastes rather than aqueous solutions.

Nickel-Cadmium (Ni-Cad)

Mercury

Alkaline

Storage Battery

Lithium Ion

Fuel Cell

Electrolysis and Electroplating

The Goldman–Hodgkin–Katz Equation

$$\mathscr{E} = \frac{RT}{\mathscr{F}} \ln \frac{pK\,[K^+]_{out} + pNa\,[Na^+]_{out} + pCl\,[Cl^-]_{in}}{pK\,[K^+]_{in} + pNa\,[Na^+]_{in} + pCl\,[Cl^-]_{out}}$$

Since we are considering only ions that are monovalent (+1 or -1), n = 1 and doesn't show up in the equation.