

Chapter 12 A deeper look at chemical Equilibrium

Problems: 9, 10, 14, 21, 22, 23, 26, 28, 31, 33

In Gen Chem we wrote that

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where [A] was a concentrations. In chapter 6, I corrected this to say that what we actually should be using is activity, and not concentration. In this chapter we will focus on what **activity** actually means.

11-1 The Effect of Ionic Strength on solubility

Back in chapter 5 we used an example of $\text{Mg}(\text{OH})_2$ and calculated its solubility. We found that it has a K_{sp} of 7.1×10^{-12} and that when dissolve ion water we could get a solution of 0.12 mM Mg and 0.24 mM OH. We talked about the common ion effect, that is if we add either OH or Mg, MgOH becomes even less soluble.

In this chapter we want to talk about what happened if we add an “inert” salt, one that doesn’t interact with either the Mg Or the OH. In this case the solubility of the complex actually rises. This occurs because the salt adds other ions to the solution and these ions interfere with the interaction that makes the MgOH precipitate.

You can think of it this way. In the dilute solution we have so many + and - ions in solution. If they get too close to each other, they interact ionically are attracted together and fall out of solution. Now what happens if we add 10x as much NaCl? We now have 10x as many other ions and what do they do? They cluster around out Mg and OH ions, lowering their ability to ‘see’ each other, thus making them less prone to find each other and precipitate out. We call this charged environment around a given ion it’s ‘Ionic Atmosphere’ The fact that it takes a higher concentration of Mg and OH to form a precipitate means that the ions are being less ‘active’ hence this is where the term activity comes from, ions being less (or more) ‘active’ that you expect.

One way to measure the ‘ionic atmosphere’ is through a parameter called the **ionic strength** (μ). This is simple a measure of total ion concentration that is weighted by the square of the ionic charge.

$$\mu = 1/2(c_1z_1^2 + c_2z_2^2 + \dots) = 1/2 \sum c_i z_i^2$$

Where the summation is over all ions in the solution.

Let's do two simple examples.

What is the ionic strength of .1M NaCl

.1M Na Cl will completely dissociate to .1M Na and .1M Cl

So we have

$$=1/2[(0.1)1^2 + 0.1(-1)^2] = 0.1M$$

How about .1M Na₂SO₄?

This dissolves to 0.2M Na⁺¹ and 0.1M SO₄⁻² Right??

$$=1/2[(.2)1^2 + .1(-2)^2]$$

$$=1/2[.2+.4] = .3M!$$

Note this math assumes that the salt undergoes 100% dissociation. This is not necessarily always true. (Van't Hoff factors from Chem 114) Particularly with multivalent ions. Fortunately for you, the math in these cases is too complicated for me so we won't deal with it in this class.

12-2 Activity Coefficients

How do we change our equilibrium constant to take this factor into effect? We use Activity *A* instead of concentration where:

$$A_c = [C]/(1M) \times \gamma_c$$

and the activity of a species is its concentration times its activity coefficient(γ). (Having reminded you about the 1M division by the standard state, let's forget that factor for the rest of the discussion) The correct form of the equilibrium expression is:

$$K = \frac{A_C^c A_D^d}{A_A^a A_B^b} = \frac{[C]^c \gamma_C^c [D]^d \gamma_D^d}{[A]^a \gamma_A^a [B]^b \gamma_B^b}$$

The γ factors vary with the charge of the ion (figure 12-4), and with the ionic strength of the solution (Figure 12-5)

Calculating Activity Coefficients.

Once we think about the ions in a solution we can develop models that tell us how to calculate activity. The model we will use in class is called the **extended Debye-Hückel model**. With this system we can derive the following equation

$$\log \gamma = \frac{-0.51z^2\sqrt{\mu}}{1+(\alpha\sqrt{\mu}/305)}$$

You do not need to memorize this equation, I will give it to you on a test

where z is the charge on the ion, μ is the ionic strength and α is the hydrated radius of the ion in pm (10^{-12}m). The later term you don't have to memorize, I will give you in a table. Let's look at the hydrated radius for a bit (Table 12-1 Page 248) If you look at the periodic table, what is the trend for atomic radius? (Bottom larger than top, left larger than right) Now look at some of the hydrated radii $\text{H} > \text{Li} > \text{Na} > \text{K} > \text{Rb}$, $\text{Be} > \text{Li}$, $\text{Mg} > \text{Na}$, Just the opposite What is happening? The smaller the radius and the larger the charge the more tightly the ion binds the solvent water through dipole interactions. The smaller ions bind water more tightly, and have a larger hydrated radius reflecting the tightly bond water molecules

Knowing the hydrated radius of an ion and the ionic strength of a solution you can calculate the activity of any ion. Here are some general trends you can observe

1. As ionic strength increases, activity decreases, up to a point. (Figure 12.-5)
2. The greater the charge the greater the activity correction
3. The smaller the hydrated radius the more important the activity becomes

At this point the book gives you a table of values and then spends some time showing you how to extrapolate values. Don't spent lots of time on this, because I will have you calculate correct values directly from the equation.

Some additional notes

1. Assume activity coefficient of non-ionic (neutral) molecules are 1 (No charge, so the equation give you $\gamma=1$)
2. The extended Debye Huckle only work up to about 0.1M ionic strength, then things flatten out, finally activity starts to rise when the ionic strength is $>1\text{M}$. This is because you aren't dealing with a dilute solution anymore so the solvent isn't truly water, but a water/salt mixture. Won't do things in this region for this class (unless I make a mistake) about 1M activity starts going up again. Reasons for this beyond scope of class.
3. For gases there is a similar term that you may have seen in P-Chem. Here the activity is called Fugacity, $A = P\gamma$, and the γ is called the fugacity coefficient.
4. The real definition of pH
When you measure pH with a pH meter, you are actually measuring the $-\log(\text{activity of } \text{H}^+)$ rather than $-\log$ of $[\text{H}^+]$ or $-\log([\text{H}^+] \gamma_{\text{H}})$

With that in mind lets calculate the pH and pOH of pure water and of .1M NaCl

Pure water $[H^+] = [OH^-] = 1 \times 10^{-7}$; $\mu = 1 \times 10^{-7}$, $\gamma = 1$

.1M NaCl $\mu = .1$

$\log \gamma_H = (-.51(1)\sqrt{.1}) / (1 + (900\sqrt{.1})/305) = -.08$; $\gamma = .825$

$\log \gamma_{OH} = (-.51(1)\sqrt{.1}) / (1 + (350\sqrt{.1})/305) = -.118$; $\gamma = .761$

$1 \times 10^{-14} = X^2(.825).761$

$X = 1.59 \times 10^{-7}$ $[H^+] = [OH^-] = 1.26 \times 10^{-7}$ or about 26% higher!

However, since $pH = -\log$ activity

$pH = -\log 1.26 \times 10^{-7} (.825) = 6.98$

$pOH = -\log 1.26 \times 10^{-7} (.761) = 7.02$

12-3 Charge and Mass Balances

So far we have looked at equilibrium problems fairly simply, and have ignored some of the harder problems because we didn't have all the tools. Now I will introduce two additional tools that you can use to help solve more difficult equilibrium problems.

In physics you learned about conservation of energy and mass. In chemical system we have the same kinds of guiding principles in that some things cannot change. Let's start with charge

Charge Balance

In any solution the sum of the positive charges is equal to the sum of the negative charges. The idea here is that your beaker you never has a net charge, it is always neutral. The sum of the charges is just a little bit trickier and has the form

$$n_1[C_1] + n_2[C_2] + \dots = m_1[D_1] + m_2[D_2] + \dots$$

The Charge Balance equation can be a use equation in solving equilibria problems. The idea of the charge balance equation is simple - Since solutions, as a whole, are electrically neutral, the sum of the + charges in a solution = sum of negative charges.

Thus in a strong acid (HCl), strong base (NaOH) titration, what are the ions in solution?

H^+ , OH^- , Cl^- , and Na^+

and our charge balance equation is

$$[Na^+] + [H^+] = [OH^-] + [Cl^-]$$

How about a weak acid (HA) and NaOH titration

$$[Na^+] + [H^+] = [A^-] + [OH^-]$$

Now how about something a little more interesting
 H_3PO_4 and NaOH ?

H_3PO_4 is polyprotic so it can undergoes 3 different equilibria
 $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- + \text{H}^+ \rightleftharpoons \text{HPO}_4^{2-} + \text{H}^+ \rightleftharpoons \text{PO}_4^{3-} + \text{H}^+$

Your first attempt at writing a charge balance equation for this system might be

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}]$$

But you would be WRONG Why?

Say you had 1L of 1M $[\text{HPO}_4^{2-}]$ How many moles of -charges would you have?

1L of 1M means 1mole of HPO_4^{2-} but , because HPO_4^{2-} has a -2 charge your total negative charge is -2 mole! $[\text{HPO}_4^{2-}] \times 2 \text{ mole charge/1 mole } \text{HPO}_4^{2-}$

The PO_4^{3-} is even worse because it has a -3 charge.

Bottom line the equation should be

$$[\text{H}^+] + [\text{Na}^+] = [\text{OH}^-] + [\text{H}_2\text{PO}_4^-] + 2 [\text{HPO}_4^{2-}] + 3[\text{PO}_4^{3-}]$$

Mass Balance (or material balance)

The quantity of all species in a solution containing a particular atom (or group of atoms) must equal the amount of that atom (or group) delivered to the solution.

This similar to conservation of mass. In our beaker no mass can appear or disappear, so total amount of material in the beaker has to equal the sum of everything we placed in the beaker.

This is a little different, however, because we will apply it to one kind of atom, or one chemical group. Take the example of a phosphate buffer. To make a phosphate buffer you might start off with 1 mole of H_3PO_4 , phosphoric acid in 1 liter, so you have a 1M solution.

Phosphoric acid is polyprotic, so once it is in solution it can change to several different forms: H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} . What the mass balance equation says is that if you started with 1 mole H_3PO_4 , then in the final solution you will still have 1 mole of the phosphate group in the solution, but it may be spread out into several different chemical forms, H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , and PO_4^{3-} . Thus moles of H_3PO_4 (initial) = moles H_3PO_4 (final) + moles H_2PO_4^- (final) + moles HPO_4^{2-} (final) + moles

PO_4^{-3} (final). Notice one nice thing. We are still in our 1 l of solution, so we can divide all of our mole by the total volume and get Molarity of H_3PO_4 (initial) = $[\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^{-1}] + [\text{HPO}_4^{-2}] + [\text{PO}_4^{-3}]$ (final).

This was a mass balance equation where you focused on various ionic forms of a single chemical species. Another kind of mass balance equation you will see involves that balance between the cation and the anion of an ionic compound.

Suppose I told you I made a solution that was 1F Na_2SO_4 . What is the M of Na^+ and SO_4^{2-} in that solution?

Hopefully you recognized that Na_2SO_4 is ionic and will ionize in the chemical reaction $\text{Na}_2\text{SO}_4(\text{s}) \rightleftharpoons 2\text{Na}^+ + 1\text{SO}_4^{2-}$. So for every mole of Na_2SO_4 you put into the solution you get 2 Moles of Na^+ and 1 mole of SO_4^{2-} so the solution is 2M Na^+ and 1M SO_4^{2-} .

Now let's push this a bit farther. If I made a solution that contained only Na_2SO_4 , but I didn't tell you what the formality of the solution was, could you still come up with an equation that relates the $[\text{Na}^+]$ to $[\text{SO}_4^{2-}]$?

YES from the chemical equation, $\text{Na}_2\text{SO}_4(\text{s}) \rightleftharpoons 2\text{Na}^+ + 1\text{SO}_4^{2-}$ you see that I have 2 moles of Na^+ for every mole of SO_4^{2-} thus:

$$\text{moles Na}^+ = 2 \times \text{moles of SO}_4^{2-}$$

and again, dividing by the total volume to convert into concentrations

$$[\text{Na}^+] = 2[\text{SO}_4^{2-}]$$

So this is a second kind of mass balance, where you look at the concentrations of the anion and cation of an ionic species.

12-4 Systematic approach to Equilibrium problems

Now we can attack **any** complex chemical problem if we take the following approach

1. Write down all Pertinent reactions
2. From these equations identify all species in solution.
3. Write down the Charge Balance Equation
4. Write down all pertinent mass balance equations
5. Write down the equilibrium constant for each reaction

A. This is the only equation where activity coefficients are used! Even then they are usually ignored.

6. Count number of unknowns and equations. If you have as many unknowns as equations you can begin to solve the system. If you have more unknowns than equations then you must go back and dig up more equilibria or fix some concentrations

7. Now start solving the equations

Steps 1-5 are chemistry and may involve some chemical intuition

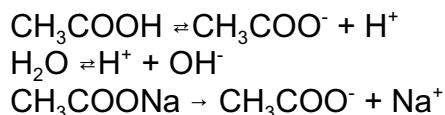
Step 6 is pure mathematics, although sometime chemical intuition will tell you what number you can ignore to simplify the problem to make the mathematics easier to solve.

PROBLEM

I have a 1L solution that contains both sodium acetate and acetic acid, and has a pH of 6. If the total (Formal) concentration of acetate is 1M, what is the actual molar concentration of all species in solution.

Systematic approach to equilibrium attack

1. Reactions:



2. Find species:

From above equations can see that we have the following species in solution
 CH_3COOH , CH_3COO^- , CH_3COONa , H^+ , H_2O , OH^- , Na^+

3. Charge Balance Equation:

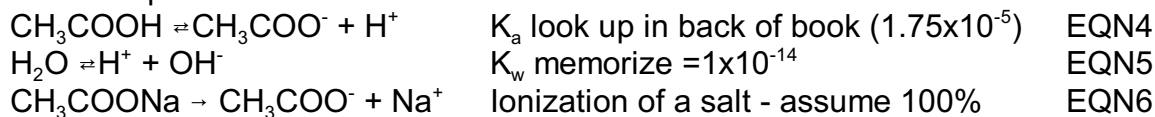
$$1[\text{Na}^+] + 1[\text{H}^+] = 1[\text{CH}_3\text{COO}^-] + 1[\text{OH}^-] \quad \text{EQN 1}$$

4. Mass balance equation:

$$[\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-] = 1\text{M} \quad \text{EQN 2}$$

$$\text{We also have pH}=6, \text{ so } [\text{H}^+] = 1 \times 10^{-6} \quad \text{EQN 3}$$

5. Equilibrium equations:



6. Count

7 species, 6 equations

We either need 1 more equations or get rid of 1 species

We will assume that sodium acetate dissociated completely so

$$[\text{CH}_3\text{COONa}] = 0$$

and $[\text{H}_2\text{O}] \approx 55\text{M}$ and is a constant.

Thus we are trying to solve the above system for 5 unknowns and we have 6 equations! So we have more than enough equations, solving should be easy.

7. Start solving

Well if $[H^+] = 10^{-6}$, the easy one is to use EQN 5 to solve for $[OH^-]$

$$K_w = [H^+][OH^-]; 1 \times 10^{-14} = 1 \times 10^{-6}[OH^-];$$

$$[OH^-] = 1 \times 10^{-8}$$

The remaining species are more difficult because they are all tied together. Recognizing that we know $[H^+]$ you can see that in equations 2 and 4 we have two equations with two unknowns.

$$[CH_3COOH] + [CH_3COO^-] = 1M \quad \text{EQN 2}$$

$$K_a = [CH_3COO^-]1 \times 10^{-6} / [CH_3COOH] \quad \text{EQN 4}$$

And filling in $K_a = 1.75 \times 10^{-5}$, $X = [CH_3COOH]$ and $Y = [CH_3COO^-]$ we have

$$X + Y = 1$$

$$1.75 \times 10^{-5} = Y(1 \times 10^{-6})/X$$

This should be solvable

$X + Y = 1$; $X = 1 - Y$ substitute this in to the other equation

$$1.75 \times 10^{-5} = Y(1 \times 10^{-6})/1 - Y$$

$$(1 - Y) \times 1.75 \times 10^{-5} = 1 \times 10^{-6} Y$$

$$1.75 \times 10^{-5} - 1.75 \times 10^{-5} Y = 1 \times 10^{-6} Y$$

$$1.75 \times 10^{-5} = (1.75 \times 10^{-5} + 1 \times 10^{-6}) Y$$

$$1.75 \times 10^{-5} = 1.85 \times 10^{-5} Y$$

$$Y = 1.75 / 1.85 = .946 \text{ M} = [CH_3COO^-]$$

and since $1 = X + Y$; $X = [CH_3COOH] = 1 - .946 = .054 \text{ M}$

We have got 4 of 5 let's go for it using the only equation we haven't yet used eqn 1.

$$1[Na^+] + 1[H^+] = 1[CH_3COO^-] + 1[OH^-]$$

$$1[Na^+] + 1(1 \times 10^{-6}) = 1(.946) + 1(1 \times 10^{-8})$$

$$[Na^+] = 1(.946) + 1(1 \times 10^{-8}) - 1(1 \times 10^{-6})$$

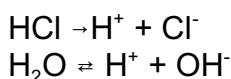
Notice that for all practical purposes $[Na^+] = 1(.946)$ and you can ignore the rest of the terms in this equation.

Now lets try some more difficult problems

What is the pH of $.5 \times 10^{-7}$ M HCl?

If you remember this is a very dilute HCl, so the way we were handling it before was by assuming that the H^+ from the HCl could simply be added to the H^+ from water, so $H^+ = .5 \times 10^{-7}$ (acid) + 1×10^{-7} (water) = 1.5×10^{-7} ; pH= 6.82

But this is a quick and dirty estimate because the H^+ from the acid will push the water equilibrium backwards, so the two numbers aren't independent of each other. Let's solve it correctly



Species: H^+ , Cl^- , OH^- , H_2O (HCL completely ionizes so cocentration =0)
 $H_2O = 55.5M$

3 species need three equations:

$$\text{Charge Balance: } H^+ = Cl^- + OH^- \quad (1)$$

$$\text{Mass balance: } Cl^- = 0.5 \times 10^{-7} \quad (2)$$

$$K_w = 1 \times 10^{-14} = [H^+][OH^-] \quad (3)$$

Plug 2 into 1

$$[H^+] = 0.5 \times 10^{-7} + [OH^-] \quad (4)$$

Plug 4 into 3

$$\begin{aligned} 1 \times 10^{-14} &= (0.5 \times 10^{-7} + [OH^-]) \times [OH^-] \\ &= 0.5 \times 10^{-7} [OH^-] + [OH^-]^2 \end{aligned}$$

Either use quadratic or solver

$$[OH^-] = 7.81 \times 10^{-8}$$

$$\text{Then } [H^+] = 10^{-14} / 7.81 \times 10^{-8} = 1.28 \times 10^{-7}; \text{ pH} = 6.89$$

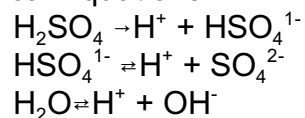
What is the pH of 0.001M H_2SO_4 ?

If only 1 H^+ dissociates $H^+ = .001$, pH =3

If both H^+ dissociate, $H^+ = .002$, pH = 2.699

Actually the first H^+ dissociates 100%, but the second has a K_a of 1.03×10^{-2} so somewhere in between. This is a potentially complicated systems so let's try the systematic approach

Chemical Equations:



Total number of species: 5 H_2SO_4 , HSO_4^{1-} , SO_4^{2-} , H^+ , OH^-

Equations:

Charge Balance

$$[\text{H}^+] = [\text{HSO}_4^{1-}] + 2[\text{SO}_4^{2-}] + [\text{OH}^-]$$

Mass Balance of sulfuric acid

$$.001\text{M} = [\text{H}_2\text{SO}_4] + [\text{HSO}_4^{1-}] + [\text{SO}_4^{2-}]$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$K_a = [\text{H}^+][\text{SO}_4^{2-}] / [\text{HSO}_4^{1-}]$$

Right now don't have enough equations, but if you remember your first ionization of H_2SO_4 is complete, then $[\text{H}_2\text{SO}_4] = 0$ so you only really have 4 unknowns, HSO_4^{1-} , SO_4^{2-} , H^+ , OH^- , and 4 equations so you can solve the system. And the mass balance equation becomes

$$.001\text{M} = [\text{HSO}_4^{1-}] + [\text{SO}_4^{2-}]$$

I will make 1 assumption here. Since this is an acid solution, the $[\text{OH}^-]$ will be negligible, so I will drop it out of my charge balance equation:

$$[\text{H}^+] = [\text{HSO}_4^{1-}] + 2[\text{SO}_4^{2-}]$$

With this in mind I will focus on the three equations

$$.001\text{M} = [\text{HSO}_4^{1-}] + [\text{SO}_4^{2-}] \quad \text{I}$$

$$[\text{H}^+] = [\text{HSO}_4^{1-}] + 2[\text{SO}_4^{2-}] \quad \text{II}$$

$$K_a = 1.03 \times 10^{-2} = [\text{H}^+][\text{SO}_4^{2-}] / [\text{HSO}_4^{1-}] \quad \text{III}$$

Start by rearranging equation I to:

$$[\text{HSO}_4^{1-}] = .001 - [\text{SO}_4^{2-}]$$

I will now plug this value for $[\text{HSO}_4^{1-}]$ into equations II and III

$$[\text{H}^+] = .001 - [\text{SO}_4^{2-}] + 2[\text{SO}_4^{2-}] \quad \text{II}$$

$$[\text{H}^+] = .001 + [\text{SO}_4^{2-}] \quad \text{II}$$

$$1.03 \times 10^{-2} = [\text{H}^+][\text{SO}_4^{2-}] / (.001 - [\text{SO}_4^{2-}]) \quad \text{III}$$

I will now rearrange II to get $[\text{SO}_4^{2-}]$ on 1 side of the equation

$$[\text{SO}_4^{2-}] = [\text{H}^+] - .001 \quad \text{II}$$

And substitute this into equation III

$$1.03 \times 10^{-2} = [\text{H}^+][\text{SO}_4^{2-}] / (.001 - [\text{SO}_4^{2-}]) \quad \text{III}$$

$$1.03 \times 10^{-2} = [\text{H}^+]([\text{H}^+] - .001) / (.001 - ([\text{H}^+] - .001)) \quad \text{III}$$

$$1.03 \times 10^{-2} = [\text{H}^+]([\text{H}^+] - .001) / (.002 - [\text{H}^+]) \quad \text{III}$$

I don't see any way to simplify, so I am going to plug this into the solver on my calculator, and I get **X = .00185 M pH = 2.733**

In this case then **$[\text{OH}^-] = 5.40 \times 10^{-12}$, $\text{pOH} = 11.267$**

(and we were justified in taking this out of the charge balance early on)

To get $[\text{SO}_4^{2-}]$ I will use equation III in the form

$$1.03 \times 10^{-2} = [\text{H}^+][\text{SO}_4^{2-}] / (.001 - [\text{SO}_4^{2-}]) \text{ and substitute in } .00185 \text{ for } [\text{H}^+]$$

$$1.03 \times 10^{-2} = .00185[\text{SO}_4^{2-}] / (.001 - [\text{SO}_4^{2-}])$$

$$1.03 \times 10^{-2} = .00185X / (.001 - X)$$

$$1.03 \times 10^{-2} (.001 - X) = .00185 X$$

$$1.03 \times 10^{-5} - 1.03 \times 10^{-2} X = .00185 X$$

$$1.03 \times 10^{-5} = .00185 X + .0103 X$$

$$1.03 \times 10^{-5} = .01215 X$$

$$X = 1.03 \times 10^{-5} / .01215$$

$$\mathbf{X = .000848 M = [\text{SO}_4^{2-}]}$$

$$\mathbf{\text{So } [\text{HSO}_4^-] = .001 - .000848 = .000152 \text{ M}}$$

Now let's just double check

$$K_a = .00185(.000848) / .000152 = 1.03 \times 10^{-2} \text{ so my answers check out}$$

12-5 Fractional Composition

One final subject to look at Fraction composition

Back when talking about acids (Chapter 7- page 153) talked about something call 'Fraction Dissociation' Anybody remember what that was?

$$\text{Fraction dissociation} = [\text{A}^-] / ([\text{HA}] + [\text{A}^-])$$

I want to take that idea and extent it a bit

It is often useful to define the fraction of every form of a chemical species in solution. For instance the in the $\text{H}_3\text{PO}_4 \rightleftharpoons \text{H}_2\text{PO}_4^- \rightleftharpoons \text{HPO}_4^{2-} \rightleftharpoons \text{PO}_4^{3-}$ system it is

sometimes useful to know

$$\text{fraction of } \text{H}_3\text{PO}_4 = [\text{H}_3\text{PO}_4] / ([\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}])$$

or, similarly

$$\text{fraction of } \text{H}_2\text{PO}_4^- = [\text{H}_2\text{PO}_4^-] / ([\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}])$$

etc

we refer to these fractional compositions as α 's

$$\text{Thus } \alpha_{\text{H}_3\text{PO}_4} = \text{fraction } \text{H}_3\text{PO}_4 = [\text{H}_3\text{PO}_4] / ([\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}])$$

$$\text{and } \alpha_{\text{H}_2\text{PO}_4^-} = \text{fraction of } \text{H}_2\text{PO}_4^- = [\text{H}_2\text{PO}_4^-] / ([\text{H}_3\text{PO}_4] + [\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] + [\text{PO}_4^{3-}])$$

Many times these fractional equations can be derived from the formal (total concentrations and the pH of the solution. For instance, for a simple monoprotic acid $\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^-$

you can derive (as shown in the book)

$$\alpha_{\text{HA}} = [\text{HA}] / F = [\text{H}^+] / ([\text{H}^+] + K_a)$$

And

$$\alpha_{\text{A}^-} = [\text{A}^-] / F = K_a / ([\text{H}^+] + K_a)$$

These equations are usually derived without and assumptions and can be very useful. We will probably see them a few more times in the next few chapters, although we won't stop to derive them.