

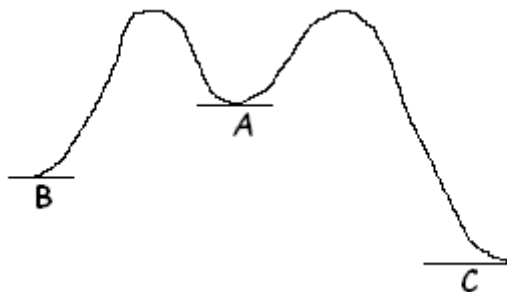
Chem 260 Course Manual

Fall 2012

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

$$\Delta H = \left[\sum_i n_i \Delta H_{ac,i} \right]_{\text{products}} - \left[\sum_j n_j \Delta H_{ac,j} \right]_{\text{reactants}}$$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]}$$



$$\text{pH} = \text{p}K_a + \log \frac{[\text{A}^-]}{[\text{HA}]}$$

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

$$\ln[R]_t = \ln[R]_0 - kt$$

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Welcome to Chem 260: Thermodynamics, Equilibria and Kinetics

In designing our curriculum we referred to this course as “The Big Three.” Although said jokingly, the course’s topics – thermodynamics, equilibria and kinetics – are three of the most important theoretical ideas in chemistry.¹

The remaining courses in our introductory core (Chem 120, Chem 130 and Chem 240) focus on the structure and properties of organic molecules, inorganic compounds, and biomolecules, respectively. The focus in these courses, for obvious reasons, is on individual molecules and compounds; thus, you learn, among other topics, how to name compounds and molecules, study their three-dimensional structures, and explore, in a limited way, their chemical reactivities or biochemical functions.

Our focus in Chem 260 shifts from individual molecules and compounds to a theoretical study of chemical reactivity. Our interest here is not with the specific chemical reactions of organic molecules, inorganic compounds or biomolecules, although we use illustrative examples from these areas. Instead, our interest is in understanding the basic driving forces for chemical reactivity. More important, we will begin to develop useful theoretical tools to help us predict and model chemical reactivity, and to provide insight into how we can control that reactivity.

Course Pre-requisites. The pre-requisites for this course are Chem 170 and either Chem 120 or 130. These pre-requisites are critical. Chemists divide the broader discipline of chemistry into five narrower areas: analytical chemistry, biochemistry, inorganic chemistry, organic chemistry, and physical chemistry. Not surprisingly, our introductory core (Chem 120, 130, 240, and 260) provides coverage in each of these areas, with Chem 260 providing an introduction to physical chemistry and analytical chemistry. Of course, much that is interesting in chemistry occurs at the interface between these areas. It is impossible, therefore, to discuss the topics at the heart of Chem 260 without applying them to examples drawn from biochemistry, inorganic chemistry and/or organic chemistry. We require either Chem 120 or Chem 130 so that you have some practical experience with thinking about chemical reactivity. Don’t worry, however, if you have not yet completed both courses, or if you haven’t taken Chem 240; you don’t need to have completed all three classes to appreciate the examples.

Unlike other courses in our introductory core, Chem 260 is very quantitative. Success in Chem 170 (our self-paced course covering stoichiometric calculations) is critical; we assume that you have mastered these calculations and that you can perform them quickly and with few, if any errors. In fact, this is a good time to go back and review the modular materials for that course.

¹ A fourth important theoretical concept is quantum chemistry, which is introduced in Chem 130.

Chem 260 Abbreviated Syllabus

Instructor: David Harvey

Office: Julian 323 and Julian 377

Phone: 658-4359 (Academic Affairs office)

E-Mail: harvey@depauw.edu

Course Goals: Chem 260 provides an introduction to the disciplines of physical and analytical chemistry. These fields are, of course, too broad to cover in a single semester. Our goals, therefore, are to:

- predict the favorability of chemical reactions
- characterize the extent to which a chemical reaction occurs, including the final composition of the reaction mixture
- evaluate a reaction's temporal feasibility
- elucidate possible pathways for a chemical reaction
- study reactions quantitatively in the laboratory
- design, carry out and evaluate experiments involving chemical reactivity
- appreciate the importance of physical and analytical chemistry in other disciplines

In addition to these discipline-specific goals, we have some broader goals; these are to:

- appreciate the utility of developing models as predictive tools
- learn how to think critically about conceptual or abstract ideas
- improve your skills at solving problems
- gain comfort working and thinking in the laboratory
- become more adept at evaluating and processing large amounts of information
- gain experience working with others as part of a research team

Course Web-Site. Many useful materials, including a detailed schedule, copies of course materials, and answer keys to worksheets, suggested problems, and exams, are available at the course's web site. The link to the site is:

http://dpuadweb.depauw.edu/harvey_web/Chem260/index.html

Course Evaluation. Your evaluation in this course is based on three regular exams, a cumulative final exam, quizzes (both in class and lab), and lab work.

Official Syllabus. A more detailed, official syllabus is available on the course's web site. You are responsible for reading and understanding the syllabus.

What Do We Mean By a Mole_{rxn}?

The unit “mol_{rxn}” in Bodner, Spencer and Rickard’s text is unusual. Nevertheless, a mol_{rxn} is a useful way to clarify the importance of stoichiometry when calculating a reaction’s ΔH .

Suppose you and a classmate perform separate calorimetry experiments to determine ΔH for the reaction



Your classmate performs the experiment using 0.75 mol of A and 1.00 mol of B, determining that q_{rxn} is -1000 kJ. She calculates ΔH by dividing q_{rxn} by the moles of limiting reagent (in this case B), obtaining

$$\Delta H = \frac{q_{\text{rxn}}}{\text{mol B}} = \frac{-1000 \text{ kJ}}{1 \text{ mol B}} = -1000 \text{ kJ/mol B}$$

You, on the other hand, perform the experiment using 0.75 mol of A and 3.00 mol of B, obtaining a q_{rxn} of -1500 kJ. Because A is the limiting reagent you report ΔH as

$$\Delta H = \frac{q_{\text{rxn}}}{\text{mol A}} = \frac{-1500 \text{ kJ}}{0.75 \text{ mol A}} = -2000 \text{ kJ/mol A}$$

Both results are correct even though their respective numerical values are different. It is troublesome, however, that the value of ΔH depends on which compound is the limiting reagent. If we multiply each value of ΔH by the limiting reagent’s stoichiometry in the balanced reaction

$$\left[\frac{-1000 \text{ kJ}}{\text{mol B}} \times \frac{2 \text{ mol B}}{\text{mol}_{\text{rxn}}} \right] = \frac{-2000 \text{ kJ}}{\text{mol}_{\text{rxn}}} = \left[\frac{-2000 \text{ kJ}}{\text{mol A}} \times \frac{1 \text{ mol A}}{\text{mol}_{\text{rxn}}} \right]$$

we obtain the same value of ΔH

$$\Delta H = \frac{-2000 \text{ kJ}}{\text{mol}_{\text{rxn}}}$$

where mol_{rxn} indicates that the value of ΔH is reported for the reaction, not for one of the reactants. Reporting enthalpy in this way ensures that for any reaction we report the same result for ΔH .

Some Thoughts on Solving Equilibrium Problems

The secret to solving equilibrium problems is organization and planning. Most equilibrium problems begin by stating the initial amount of each reactant and product and either the concentration or change in concentration for one reactant or product. From this information you can deduce all remaining changes in concentrations and the final equilibrium concentrations. As shown in the following worked examples, using a table to organize this information helps guide this process.

Beginning an equilibrium problem without planning a method of attack can turn a relatively easy problem into one that becomes difficult. As discussed below, many problems can be simplified if the problem is correctly redefined. Look carefully at the value of the equilibrium constant with an eye toward using this information to redefine the problem.

There are two basic approaches to solving equilibrium problems: a rigorous solution based on an exact algebraic solution to the problem and an approximate solution based on one or more simplifying assumptions. This tutorial reviews these approaches and provides some hints on making and evaluating simplifying assumptions. The example used in this tutorial is identical to that discussed in class, which will help you in sorting through your notes.

Rigorous Solution. Consider the reaction $\text{PCl}_3 + \text{Cl}_2 \rightleftharpoons \text{PCl}_5$, for which the equilibrium constant is 1000 at an unspecified temperature. If the initial concentration for each component is known, then we can evaluate whether the system is at equilibrium by calculating the reaction quotient, Q , and comparing it to the equilibrium constant, K . If the system is not at equilibrium, we can determine the direction in which the reaction will move to reach equilibrium.

Example 1. The initial concentrations of PCl_3 , Cl_2 , and PCl_5 are, respectively 0.0220 M, 0.00400 M, and 0.0400 M. Determine if the mixture is at equilibrium. If the system is not at equilibrium, in which direction will it react?

Solution. The reaction quotient is

$$Q = \frac{(\text{PCl}_5)_o}{(\text{PCl}_3)_o(\text{Cl}_2)_o} = \frac{(0.0400)}{(0.0220)(0.00400)} = 454.5$$

Because $Q < K$, the system is not at equilibrium. Furthermore, the reaction must proceed from reactants \rightarrow products to reach the equilibrium position. As the concentration of PCl_5 increases and the concentrations of PCl_3 and Cl_2 decrease, the value of Q increases until $Q = K$ and equilibrium is established.

Having established the direction in which the equilibrium position lies, we now need to determine the concentration of each species when equilibrium is reached. With only one equation relating the concentrations of reactants and products (the reaction's equilibrium

constant expression), we must rewrite the equilibrium concentration so that it includes only a single variable.¹ We accomplish this by assigning a variable, such as X , to the change in concentration for any one component and use the reaction's stoichiometry to find the change in concentration for the remaining components. A table is a good way to keep this organized.

Example 2. Continuing with Example 1, express the equilibrium concentrations for all three components using X as the sole variable.

Solution. A table helps us organize information as we work through the problem (we begin knowing the numbers shown in **bold**; all other entries are developed as part of the solution):

	PCl_3	+	Cl_2	\rightleftharpoons	PCl_5
Initial	0.0220		0.00400		0.0400
Change	$-X$		$-X$		$+X$
Equilibrium	$0.0220-X$		$0.00400-X$		$0.0400+X$

The first row of this table, which we call an ICE table, provides the initial concentrations for each component. We know from the previous example that the mixture will move toward its equilibrium position by shifting to the right. Because we don't know by how much the concentration of any one species will change, we arbitrarily pick one component and assign it a change of $+X$ if it is known to increase, or $-X$ if it is known to decrease. The change in concentration for the remaining components will be some multiple of X , depending on the reaction's stoichiometry. Although X can be assigned to any component, a judicious choice at this point makes the problem easier by avoiding the possibility that one or more species have a change in concentration that is fractional multiple of X . For this example, where the stoichiometry is 1:1:1, the assignment is straightforward. Letting $-X$ be the decrease in concentration for PCl_3 , we find that the change in concentration for Cl_2 is $-X$ and that for PCl_5 is $+X$.

After defining the equilibrium concentration for each component in terms of the variable X , we are ready to finishing solving the problem. In the rigorous approach to solving equilibrium problems we accomplish this by substituting the equilibrium concentrations

¹ Recall that a single equation with a single variable has a unique solution, but that a single equation with more than one variable has an infinite number of possible solutions. Thus, the equation

$$5x + 2 = -8$$

has a unique solution ($x = -2$), but the equation

$$5x + y = -8$$

has many possible solutions (e.g., $x = -2, y = 2$; $x = 0, y = -8$). Although this is a trivial point, it is important. Should you become stuck when solving an equilibrium problem because you find that there is more than one unknown term, stop and ask yourself whether you do, in fact, know the value for one of the unknown terms. Reread the problem carefully because the missing information must be there.

into the equilibrium constant expression and solving for the variable X . In almost all equilibrium problems, finding a rigorous solution is complicated by the presence of an equation that is a second-order (quadratic) or higher-order polynomial equation in the variable X . Although quadratic equations are relatively easy to solve, higher-order polynomials present a more difficult problem. For now, we will limit problems to those that are second-order in the variable X .

Example 3. Continuing with Example 2, determine the concentration for each component when equilibrium is reached. The equilibrium constant for the reaction is 1000.

Solution. Begin by substituting into the equilibrium constant expression the equilibrium concentrations defined in terms of the variable X (the last row of the table in Example 2); thus

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.0400 + X)}{(0.0220 - X)(0.00400 - X)} = 1000$$

Next, manipulate the equation until it is in the general form of a second-order polynomial (i.e., $aX^2 + bX + c = 0$)

$$\frac{0.0400 + X}{8.8 \times 10^{-5} - 0.026X + X^2} = 1000$$

$$0.0400 + X = 0.088 - 26X + 1000X^2$$

$$1000X^2 - 27X + 0.048 = 0$$

The solutions (roots) for a second-order polynomial are given by the equation

$$X = \frac{-b \pm \sqrt{(b)^2 - 4ac}}{2a}$$

Note that there are two solutions to a second-order polynomial. Only one of these solutions, however, has any chemical significance; the other solution must, therefore, lead to a chemically meaningless result. Continuing, we find

$$X = \frac{27 \pm \sqrt{(-27)^2 - (4)(1000)(-0.048)}}{(2)(1000)} = \frac{27 \pm 23.173}{2000}$$

$$X = 0.0251 \text{ or } X = 0.00191$$

Of these two results, only one can be correct. A value for X of 0.0251 leads to a contradiction as it gives a negative concentration for both reactants¹; thus, the correct value for X is 0.00191 and the equilibrium concentrations for the three components are

$$[\text{PCl}_3]_{\text{eq}} = [\text{PCl}]_0 - X = 0.0220 - 0.00191 = 0.0201 \text{ M}$$

$$[\text{Cl}_2]_{\text{eq}} = [\text{Cl}_2]_0 - X = 0.00400 - 0.00191 = 0.00209 \text{ M}$$

$$[\text{PCl}_5]_{\text{eq}} = [\text{PCl}_5]_0 + X = 0.0400 + 0.00191 = 0.0419 \text{ M}$$

Although algebraically intensive, this approach always leads to the correct answer. Keep in mind that many good scientific calculators have built in subroutines for finding the roots of polynomial equations. Additionally, with many calculators you can graph the function and find the roots by looking for the x-intercepts. These latter two approaches, however, do not always lead to useful answers and, therefore, must be used cautiously.

Approximate Solutions. An alternative approach to solving equilibrium problems is to find a way to simplify the second-order (or higher-order) polynomial equation into one that is first-order in the variable X . This is possible if there is an approximation that introduces only a small error into the calculation. An error of less than $\pm 5\%$ generally is considered acceptable due to the uncertainty in published equilibrium constants.

A simplifying assumption may be possible if there is a term in which the variable X is added to or subtracted from a number. If the value of the variable X is significantly smaller than the number to which it is added or subtracted, then the variable X can safely be ignored; if not, then it must be retained. For example, consider this equilibrium constant expression from Example 3

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.0400 + X)}{(0.0220 - X)(0.00400 - X)} = 1000$$

which includes three terms in which the variable X is added to or subtracted from a number. If X is significantly smaller than 0.0220, but larger than 0.00400, then the first term in the denominator can be simplified to 0.0220 and the numerator simplified to 0.0400 without introducing any significant error; thus

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.0400)}{(0.0220)(0.00400 - X)} = 1000$$

This equation is first-order in X and, therefore, it is easy to solve.

¹ For example, if X is 0.0251 then the concentration of PCl_3 becomes $0.0220 - 0.0251 = -0.0031$. A negative concentration is impossible.

How do we know whether a simplifying assumption might be reasonable? The short answer is “We don’t.”, but we can make an educated guess by carefully examining the values for Q and K . If $Q \approx K$, then we are close to equilibrium and the changes in concentration needed to reach equilibrium will be small. On the other hand, if the difference between Q and K is large, then the changes in concentration as the system moves toward equilibrium must be significant.

Example 4. Evaluate the example shown below and decide whether the value of X is likely to be insignificant for any of the three terms in the equilibrium constant expression.

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.0400 + X)}{(0.0220 - X)(0.00400 - X)} = 1000$$

Solution. In Example 1 we showed that the value of Q for this system’s initial conditions is 454.5 compared to an equilibrium constant, K , of 1000. Because this difference is quite large we can assume that X must be relatively large and that it probably cannot be excluded from any of the three terms.

The fact that we can’t make any simplifying assumptions at this point doesn’t mean that we should give up searching for a way to simplify the problem. Here is where planning helps. If the equilibrium constant for the reaction is quite large, then we might treat the reaction as one that goes to completion and then let it move back to its equilibrium position.

Example 5. Return to Example 2 and allow the reaction to go to completion, reporting the new set of initial concentrations.

Solution. Begin by using a table to organize information (as before, the values in **bold** are the initial information):

	PCl_3	+	Cl_2	\rightleftharpoons	PCl_5
Initial	0.0220		0.00400		0.0400
Change	−0.00400		−0.00400		+0.00400
New Initial	0.0180		0		0.0440

The first row, of course, provides the initial concentrations of the reactants and products. The changes in concentration shown in the second row are determined by assuming that the reaction goes to completion. The limiting reagent in this case is Cl_2 , so we assume that its concentration decreases to zero and assign the change in concentration for the remaining components using the reaction’s stoichiometry.

Having made this adjustment, we let the reaction move back to its equilibrium position using the variable X to define the extent of that movement.

Example 6. Continue with Example 5 by expressing the equilibrium concentration for each species in terms of a single variable, X .

Solution. Continuing with our table as a means for organizing information, we have

	PCl_3	$+ \text{Cl}_2$	$\rightleftharpoons \text{PCl}_5$
Initial	0.0220	0.00400	0.0400
Change	-0.00400	-0.00400	+0.00400
New Initial	0.0180	0	0.0440
Change	$+X$	$+X$	$-X$
Equilibrium	$0.0180 + X$	X	$0.0440 - X$

and an equilibrium expression of

$$K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{(0.0440 - X)}{(0.0180 + X)(X)} = 1000$$

If, as in our example, the equilibrium constant in the forward direction is 1000, then the equilibrium constant in the reverse direction is 0.001. With such a small value, we might reasonably expect that equilibrium will be reached with only a very small change in the concentrations of all three species. If true, then we may be able to remove the term X from the numerator and the first term in the denominator by assuming that

$$0.0440 - X \approx 0.0440$$

and that

$$0.0180 + X \approx 0.0180$$

Applying these assumptions reduces the problem to one that is first-order in X .

Example 7. Continue with Example 6 by making the assumptions described above and completing the algebraic solution.

Solution. Having made the assumptions we find that

$$\frac{(0.0440)}{(0.0180)(X)} = 1000$$

$$X = 2.444 \times 10^{-3}$$

Note how much easier the calculation is! Based on these results, we find that the equilibrium concentrations are:

$$[\text{PCl}_3]_{\text{eq}} = 0.0180 + X = 0.0180 + 2.444 \times 10^{-3} = 0.0204 \text{ M}$$

$$[\text{Cl}_2]_{\text{eq}} = X = 2.444 \times 10^{-3} \text{ M}$$

$$[\text{PCl}_5]_{\text{eq}} = 0.0440 - X = 0.0440 - 2.444 \times 10^{-3} = 0.0416 \text{ M}$$

Of course, making an assumption introduces the possibility of error so we must evaluate whether the errors in this case are acceptable. Errors are determined by comparing the calculated concentrations at equilibrium to those assumed in making the calculation, with the error equal to

$$\% \text{Error} = \frac{\text{assumed concentration} - \text{calculated concentration}}{\text{assumed concentration}} \times 100$$

If any single percent error is greater than 5%, then the assumptions are invalid.

Example 8. Continuing with Example 7, determine the percent errors and determine if the assumptions are acceptable.

Solution. The percent errors are:

$$\text{For } \text{PCl}_5 \text{ the error is } \frac{0.0440 - 0.0416}{0.0440} \times 100 = 5.6\%$$

$$\text{For } \text{PCl}_3 \text{ the error is } \frac{0.0180 - 0.204}{0.0204} \times 100 = -13.3\%$$

Both errors are too large; thus, the assumptions were not valid.

So, what do you do if the simplifying assumptions fail? One solution, of course, is to return to the rigorous solution and solve the problem exactly. Another solution, which often is the better choice, is to continue making approximations. We know, for example, that the assumed equilibrium concentration for PCl_5 of 0.0440 M is too high and that its original concentration of 0.0400 M is too low. Clearly the equilibrium concentration must lie within these limits and the calculated result from Example 8 of 0.0416 M is as good a choice as any.

Example 9. Continue with Example 8, making a new set of simplifying assumptions based upon the results of the first set of assumptions.

Solution. This time we assume that the calculated concentrations for PCl_3 and PCl_5 from Example 8 are better estimates of their respective equilibrium concentrations than the initial assumptions; thus, for our second iteration we assume that

$$\begin{aligned} 0.0440 - X &\approx 0.0416 \\ 0.180 + X &\approx 0.0204 \end{aligned}$$

Continuing, we find that

$$\frac{(0.0416)}{(0.0204)(X)} = 1000$$

$$X = 2.039 \times 10^{-3}$$

For PCl_5 , the equilibrium concentration and error are

$$0.0440 - X = 0.0444 - 2.039 \times 10^{-3} = 0.0420$$

$$\frac{0.0416 - 0.0420}{0.0416} \times 100 = -1.0\%$$

For PCl_3 , the equilibrium concentration and error are

$$0.0180 + X = 0.0180 + 2.039 \times 10^{-3} = 0.0200$$

$$\frac{0.0204 - 0.0200}{0.0204} \times 100 = 2.0\%$$

These are reasonable errors! Comparing the exact concentrations from the rigorous solution to those from this approximate solutions, we find

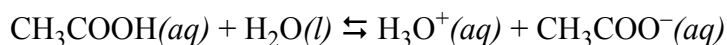
$$[\text{PCl}_3]_{\text{eq}} = 0.0201 \text{ M vs. } 0.0200 \text{ M}$$

$$[\text{Cl}_2]_{\text{eq}} = 0.00209 \text{ M vs. } 0.00204 \text{ M}$$

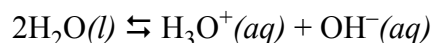
$$[\text{PCl}_5]_{\text{eq}} = 0.0419 \text{ M vs. } 0.0420 \text{ M}$$

Can We Ignore Water's Dissociation When Solving pH Problems?

Our treatment of equilibrium chemistry at this point includes several simplifications. For example, when finding the pH of a solution of acetic acid, CH_3COOH , we ignored the contribution of water's dissociation to the total concentration of H_3O^+ ; that is, in setting up an ICE table, we assumed that the initial concentration of H_3O^+ was zero, which clearly is not true. We argued that this is a reasonable assumption because the H_3O^+ from the dissociation of acetic acid



shifts the equilibrium dissociation of water



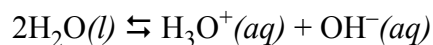
to the left, decreasing its contribution from that of $1.0 \times 10^{-7} \text{ M}$ for neutral water to a value which is insignificant when compared to that from the dissociation of acetic acid. Let's show that this is reasonable by solving for the pH without making any approximations.

A Rigorous Solution to the pH of 0.100 M Acetic Acid¹

When acetic acid dissolves in water it undergoes the dissociation reaction shown above, for which the acid dissociation constant is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

This equation has three terms – $[\text{H}_3\text{O}^+]$, $[\text{CH}_3\text{COO}^-]$, and $[\text{CH}_3\text{COOH}]$ – whose values are unknown. With three variables and only one equation, there is no unique algebraic solution. There is, of course, another equilibrium reaction of importance in any aqueous solution – the dissociation of water



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Although this adds a second equation, it also introduces a new unknown – $[\text{OH}^-]$. We still need, therefore, to find at least two additional equations.

¹ Although it is useful to understand why we can ignore water as a significant source of H_3O^+ , you do not need to know how to do the sort of rigorous calculation outlined here. This is covered in greater detail in Chem 352.

One useful equation is a charge-balance equation, which is simply a statement that the solution must be electrically neutral; that is, the total concentration of positive charge must equal the total concentration of negative charge. For a solution of acetic acid, the charge-balance equation is

$$[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-] + [\text{OH}^-]$$

Another useful equation is a mass-balance equation, which is simply a statement that mass must be conserved. We know, for example, that any acetic acid in solution must be present as either CH_3COOH or CH_3COO^- ; thus

$$0.10 \text{ M} = [\text{CH}_3\text{COOH}] + [\text{CH}_3\text{COO}^-]$$

Now there are four equation – K_a , K_w , charge balance, mass balance – and four unknowns – $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, $[\text{CH}_3\text{COOH}]$, $[\text{CH}_3\text{COO}^-]$. The problem, therefore, is solvable.

To solve, we first substitute $K_w/[\text{H}_3\text{O}^+]$ for $[\text{OH}^-]$ in the charge balance equation

$$[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-] + \frac{K_w}{[\text{OH}^-]}$$

and solve for the equilibrium concentration of acetate

$$[\text{CH}_3\text{COO}^-] = [\text{H}_3\text{O}^+] - \frac{K_w}{[\text{H}_3\text{O}^+]}$$

Next, we solve the mass balance equation for the equilibrium concentration of acetic acid

$$[\text{CH}_3\text{COOH}] = 0.1 - [\text{CH}_3\text{COO}^-] = 0.1 - [\text{H}_3\text{O}^+] + \frac{K_w}{[\text{H}_3\text{O}^+]}$$

Now, we substitute these equations for the equilibrium concentrations of acetic acid and acetate into the K_a expression, giving

$$K_a = \frac{[\text{H}_3\text{O}^+] \left([\text{H}_3\text{O}^+] - \frac{K_w}{[\text{H}_3\text{O}^+]} \right)}{0.1 - [\text{H}_3\text{O}^+] + \frac{K_w}{[\text{H}_3\text{O}^+]}}$$

Further manipulation produces a third-order polynomial equation in $[\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+]^3 + K_a [\text{H}_3\text{O}^+]^2 - (0.1K_a + K_w)[\text{H}_3\text{O}^+] - K_a K_w = 0$$

that is a mess to solve, but for which we obtain

$$[\text{H}_3\text{O}^+] = 1.333 \times 10^{-3} \quad \text{pH} = 2.875$$

The Approximate Solution to the pH of 0.100 M Acetic Acid

Now, let's approach this problem by assuming that the dissociation of water can be ignored as a significant source of H_3O^+ . Because we know that the pH of any weak acid solution must be less than 7 we can reasonably assume that

$$[\text{OH}^-] \ll [\text{H}_3\text{O}^+]$$

This allows us to simplify the charge balance equation, as shown here

$$[\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-] + [\text{OH}^-] \approx [\text{CH}_3\text{COO}^-]$$

Now, we substitute $[\text{H}_3\text{O}^+]$ for $[\text{CH}_3\text{COO}^-]$ in the mass balance equation

$$0.10 \text{ M} = [\text{CH}_3\text{COOH}] + [\text{H}_3\text{O}^+]$$

giving

$$[\text{CH}_3\text{COOH}] = 0.1 - [\text{H}_3\text{O}^+]$$

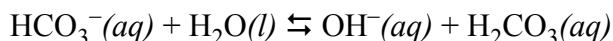
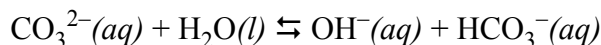
Finally, substituting back into the K_a expression gives

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{H}_3\text{O}^+]}{0.1 - [\text{H}_3\text{O}^+]} = \frac{X^2}{0.1 - X}$$

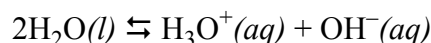
which matches the simplified solution developed in class. Solving the quadratic equation gives $[\text{H}_3\text{O}^+] = 1.333 \times 10^{-3}$ and a pH of 2.875, which are the same results obtained with the more rigorous approach. Thus, we can ignore the contribution of water as a source of H_3O^+ in this problem (and in any problem of interest to us in this course).

Polyprotic Acid-Base Systems

Polyprotic acids or bases present a further complication because they have more than one dissociation reaction controlling the solution's pH. Consider, for example, a solution of 0.10 M Na_2CO_3 for which we wish to calculate the pH. Because CO_3^{2-} has two basic sites, the following two equilibria must be considered¹



along with the dissociation of water



These three equilibria include the concentrations for five species that are unknown to us

$[\text{OH}^-]$, $[\text{H}_3\text{O}^+]$, $[\text{H}_2\text{CO}_3]$, $[\text{HCO}_3^-]$, $[\text{CO}_3^{2-}]$

To solve this system of equations we need five equations; these include the three equilibrium constant expressions

$$K_{b1} = \frac{[\text{OH}^-][\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = \frac{K_w}{K_{a2}} = \frac{1.00 \times 10^{-14}}{4.7 \times 10^{-11}} = 2.1 \times 10^{-4}$$

$$K_{b2} = \frac{[\text{OH}^-][\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} = \frac{K_w}{K_{a1}} = \frac{1.00 \times 10^{-14}}{4.5 \times 10^{-7}} = 2.2 \times 10^{-8}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

a mass balance equation for carbonate

$$0.10 \text{ M} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{H}_2\text{CO}_3]$$

and a charge balance equation

$$[\text{Na}^+] = 2 \times [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{OH}^-]$$

¹ Here, again, we use a rigorous approach to solving equilibrium problems to help understand the general conclusion stated at the end of this tutorial. You do not need to know how to do the sort of rigorous calculations outlined here. This is covered in greater detail in Chem 352.

Note that the concentration of CO_3^{2-} in the charge balance equation is multiplied by 2 as this equation balances the concentration of charge not the concentration of ions. Finally, we know that the $[\text{Na}^+]$ is 0.20 M.

Five equations and five unknowns is a mess. Given that the rigorous treatment of a monoprotic weak acid leads to a third-order polynomial, we can reasonably expect that the solution will be a fourth-order polynomial. To simplify the problem we make some assumptions. Our first assumption starts by noting that $K_{b2} \ll K_{b1}$, suggesting that the concentration of H_2CO_3 is probably very small; thus

$$[\text{H}_2\text{CO}_3] \approx 0$$

This reduces the mass balance equation to

$$0.10 = [\text{CO}_3^{2-}] + [\text{HCO}_3^-]$$

Solving for the equilibrium concentration of carbonate give

$$[\text{CO}_3^{2-}] = 0.10 - [\text{HCO}_3^-]$$

which we then substitute into the charge balance equation

$$[\text{Na}^+] = 0.20 = 2 \times (0.10 - [\text{HCO}_3^-]) + [\text{HCO}_3^-] + [\text{OH}^-]$$

Reducing this equation leaves us with

$$0.20 = 0.20 - 2 \times [\text{HCO}_3^-] + [\text{HCO}_3^-] + [\text{OH}^-]$$

$$0 = -[\text{HCO}_3^-] + [\text{OH}^-]$$

$$[\text{HCO}_3^-] = [\text{OH}^-]$$

Now, we substitute the equilibrium concentrations for OH^- and CO_3^{2-} into K_{b1}

$$K_{b1} = \frac{[\text{HCO}_3^-][\text{HCO}_3^-]}{0.10 - [\text{HCO}_3^-]} = 2.1 \times 10^{-4}$$

Note that we have reduced this problem to one that is equivalent to finding the pH of a monoprotic weak base. To solve we replace $[\text{HCO}_3^-]$ with X

$$K_{b1} = \frac{X^2}{0.10 - X} = 2.1 \times 10^{-4}$$

and proceed as before by assuming that $0.10 - X \approx 0.10$. Solving, we find that

$$X = 4.58 \times 10^{-3}$$

To check the assumption we calculate the percent error, finding that

$$\% \text{error} = \frac{0.10 - 0.0954}{0.10} \times 100 = 4.6\%$$

This error is within reason. We now know some of the equilibrium concentrations; these are

$$[\text{HCO}_3^-] = 4.6 \times 10^{-3} \text{ M}$$

$$[\text{OH}^-] = 4.6 \times 10^{-3} \text{ M}$$

$$[\text{CO}_3^{2-}] = 0.095 \text{ M}$$

There is, of course, one last assumption to check: that the concentration of H_2CO_3 is essentially zero. The calculated equilibrium concentration for H_2CO_3 is

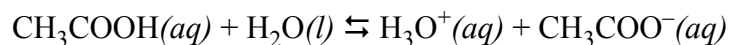
$$[\text{H}_2\text{CO}_3] = \frac{K_{b2}[\text{HCO}_3^-]}{[\text{OH}^-]} = 2.2 \times 10^{-8} \text{ M}$$

which is close enough to zero to suggest that our first assumption is reasonable.

You don't want or need to go through this lengthy process when working with polyprotic weak acids and bases. Instead, use the general "rule-of-thumb" that this treatment works if $K_{a1}/K_{a2} \geq 500$ or $K_{b1}/K_{b2} \geq 500$. Under these conditions, you can safely treat a polyprotic acid or base as if it were monoprotic.

Relative Importance of a Conjugate Acid and its Conjugate Base

Every weak acid has a conjugate weak base (and, of course, every weak base has a conjugate weak acid). Acetic acid, for example, is in equilibrium with its conjugate weak base, the acetate ion, as shown by the following reaction



According to Le Châtelier's principle, adding a source of acid shifts this equilibrium to the left, increasing the concentration of CH_3COOH . Adding a source of base, such as OH^- , consumes H_3O^+ and shifts the equilibrium to the right, increasing the concentration of CH_3COO^- . Clearly there are pH levels favoring acetic acid and pH levels favoring the acetate ion. Exactly what these pH levels are, however, is not clear from this simple treatment.

A weak acid's acid dissociation constant is a good starting point for considering the affect of pH on the relative amount of a weak acid and its conjugate weak base. For acetic acid the K_a expression is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Taking the log of both sides

$$\log K_a = \log[\text{H}_3\text{O}^+] + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

and multiplying through by -1 gives

$$-\log K_a = -\log[\text{H}_3\text{O}^+] - \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

which we rewrite as

$$pK_a = \text{pH} - \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

Solving for the ratio of weak base-to-weak acid, we obtain

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 10^{\text{pH} - pK_a}$$

This equation shows us that the relative amount of CH_3COOH and CH_3COO^- is determined by how close the solution's pH is to acetic acid's pK_a value, which is 4.74. Some actual values are shown in the following table:

pH	$\text{pH} - \text{pK}_a$	$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$	Important Form(s) of Acetic Acid
1.74	-3.00	0.001	CH_3COOH only
2.74	-2.00	0.01	CH_3COOH only
3.74	-1.00	0.1	both CH_3COOH and CH_3COO^-
4.74	0	1	both CH_3COOH and CH_3COO^-
5.74	1.00	10	both CH_3COOH and CH_3COO^-
6.74	2.00	100	CH_3COO^- only
7.74	3.00	1000	CH_3COO^- only

We can use these results to make some general statements about the relative importance of acetic acid's conjugate weak acid and conjugate weak base forms as a function of pH. At a pH of 3.74, for example, there is 1 acetate ion for every 10 molecules of acetic acid; thus, for all practical purposes, at pH levels < 3.74 , CH_3COOH accounts for more than 90% of the mass balance on acetic acid and is the only important form of acetic acid in solution. At a pH of 5.74, there are 10 acetate ions for every 1 molecule of acetic acid; thus, at pH levels > 5.74 , CH_3COO^- accounts for more than 90% of the mass balance on acetic acid and is the only important form of acetic acid in solution. Between these two pH levels, both CH_3COOH and CH_3COO^- are important forms of acetic acid in solution.

More generally, for the weak acid HA we can state that

- when $\text{pH} < \text{pK}_{a,\text{HA}} - 1$, HA is the only important species in solution
- when $\text{pH} > \text{pK}_{a,\text{HA}} + 1$, A^- is the only important species in solution
- when $\text{pK}_{a,\text{HA}} - 1 \leq \text{pH} \leq \text{pK}_{a,\text{HA}} + 1$, both HA and A^- are important species in solution

These general statements about the relative importance of a conjugate weak acid and its conjugate weak base are quite useful when it comes to understanding the behavior of buffers and when writing chemical reactions. Both of these topics are explored in greater detail in other tutorials.

Ladder Diagrams – A Pictorial View of Equilibrium Chemistry

In the previous tutorial we concluded that CH_3COOH is the only significant form of acetic acid in solutions with pH levels less than 3.74 and that CH_3COO^- is the only important species at pH levels greater than 5.74. In between these two pH levels a solution of acetic acid contains relatively similar concentrations of CH_3COOH and CH_3COO^- with the ratio

$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

being 0.1 at a pH of 3.74 and 10 at a pH of 5.74. More generally, for any weak acid, HA

when $\text{pH} < \text{pK}_{\text{a,HA}} - 1$, HA is the only important species

when $\text{pH} > \text{pK}_{\text{a,HA}} + 1$, A^- is the only important species

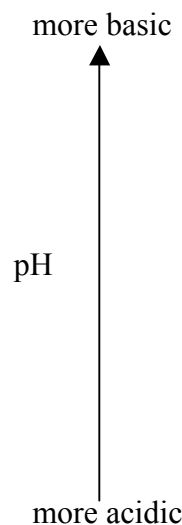
when $\text{pK}_{\text{a,HA}} - 1 \leq \text{pH} \leq \text{pK}_{\text{a,HA}} + 1$, both HA and A^- are important species

Sometimes it is helpful to think about equilibrium chemistry more qualitatively. In such cases a ladder diagram is a useful tool.

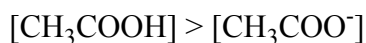
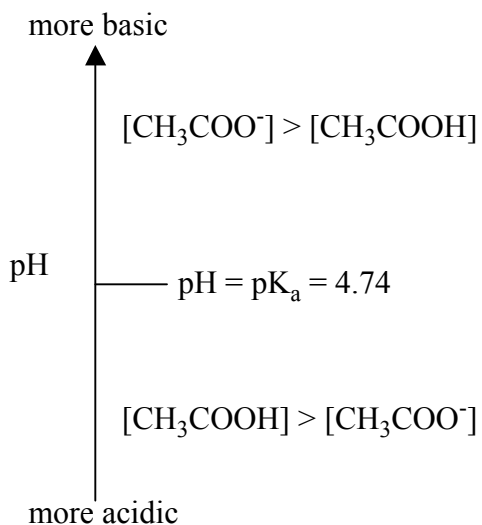
Drawing a Ladder Diagram. Let's begin by drawing a ladder diagram for acetic acid, the pK_{a} of which is 4.74. We begin by drawing a vertical arrow representing pH. As shown to the right, the top of the arrow represents solutions that are more basic and the bottom of the arrow represents solutions that are more acidic.

The second step is to draw a horizontal line at a pH value corresponding to the weak acid's pK_{a} value. This line is a step on the ladder. What is the meaning of this step? In the previous tutorial we derived the following relationship between the relative amounts of CH_3COOH and CH_3COO^-

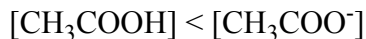
$$\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 10^{\text{pH} - \text{pK}_{\text{a}}}$$



When the pH and the pK_{a} have the same value, the right side of this equation is equal to 1 and the concentrations of CH_3COOH and CH_3COO^- are equal. Below the step, that is for pH levels less than acetic acid's pK_{a} value, we know that

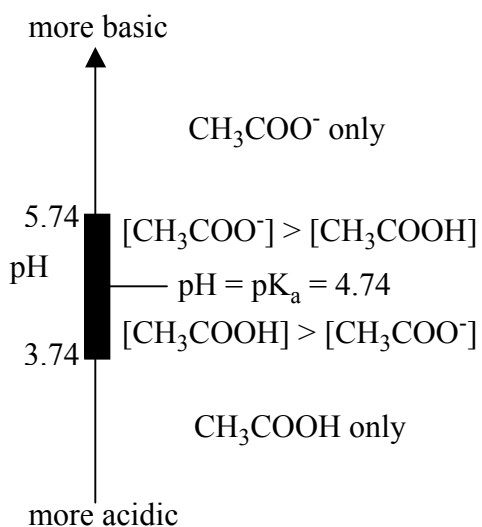


and that for pH levels above the step



The step, therefore, divides the pH axis into two regions, as shown on the figure to the right.

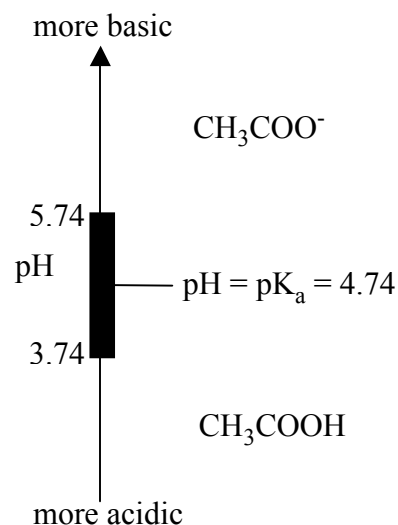
Finally, we can add a rectangular box along the pH axis extending from a pH value of $\text{pK}_a + 1$ to a pH value of $\text{pK}_a - 1$. This box spans the pH levels for which the $[\text{CH}_3\text{COOH}]$ and the $[\text{CH}_3\text{COO}^-]$ are relatively similar (that is, the concentrations are within a factor of 10 of each other). This completes the ladder diagram for acetic acid, a copy of which is shown to the left.



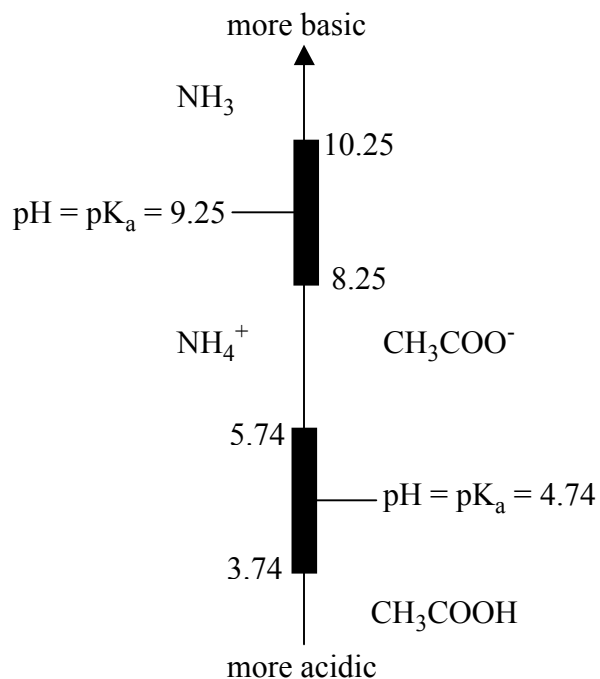
To summarize, the ladder diagram for acetic acid shows that above a pH of 5.74 the only important form of acetic acid is CH_3COO^- and that below a pH of 3.74 the only important form of acetic acid is CH_3COOH . For pH levels between 5.74 and 4.74 both CH_3COOH and CH_3COO^- are present, but there is more CH_3COO^- . For pH levels between 4.74 and 3.74 both CH_3COOH

and CH_3COO^- are present, but there is more CH_3COOH . More often than not we will draw the ladder diagram without including the information about the relative concentrations of species. This simpler form of the ladder diagram is shown to the right.

Extending a ladder diagram to a multiprotic weak acid or to a mixture of weak acids is easy; just add additional steps as needed. An example is shown on the following page for a mixture of acetic acid ($\text{pK}_a = 4.74$) and ammonium, NH_4^+ ($\text{pK}_a = 9.25$). Looking at the diagram you should be able to convince yourself that at a pH of 7, a mixture of acetic acid and ammonium will contain mostly NH_4^+ and CH_3COO^- and only insignificant amounts of



NH_3 and CH_3COOH . You also should be able to convince yourself that it is impossible to prepare a solution that contains significant amounts of both NH_3 and CH_3COOH as these two species do not share a common pH range.

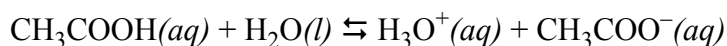


Calculating a Buffer's pH and Evaluating Its Effectiveness

A buffer is a solution with the ability to resist a change in pH upon the addition of a strong acid or a strong base. For a buffer to exist it must satisfy two conditions: (1) the solution must contain a weak acid and its conjugate weak base and (2) the concentrations of the weak acid and the conjugate weak base must be reasonably similar. This tutorial discusses in more detail how to calculate the pH of a buffer, how to evaluate the change in a buffer's pH upon the addition of strong acid or strong base and how to evaluate a buffer's capacity to neutralize the addition of strong acid or strong base.

The Standard Equilibrium Approach to Calculating a Buffer's pH Level

Thus far our standard approach to finding the pH of a buffer is to write the equilibrium reaction responsible for controlling pH and use an ICE table to organize information. For example, to find the pH of a buffer consisting of 3.39×10^{-2} M CH_3COOH and 1.00×10^{-2} M CH_3COO^- we first write the acid dissociation reaction for acetic acid



for which the equilibrium constant is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

Next, we use an ICE table to organize the problem

	CH_3COOH	+	H_2O	\rightleftharpoons	H_3O^+	+	CH_3COO^-
Initial	3.39×10^{-2}		-		0		1.0×10^{-2}
Change	$-X$		-		$+X$		$+X$
Equilibrium	$3.39 \times 10^{-2} - X$		-		X		$1.0 \times 10^{-2} + X$

Note that this table includes the initial concentrations for CH_3COOH and CH_3COO^- , which were given to us, and assumes that the presence of H_3O^+ from water can be ignored (our standard assumption). Defining the change in acetic acid's concentration as X , we then filled in the remainder of the table. Next, we substitute the terms in the row labeled "Equilibrium" into the equilibrium constant expression.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{X(1.0 \times 10^{-2} + X)}{3.39 \times 10^{-2} - X} = 1.8 \times 10^{-5}$$

To simplify the problem, we assume that

$$3.39 \times 10^{-2} - X \approx 3.39 \times 10^{-2} \text{ and } 1.0 \times 10^{-2} + X \approx 1.0 \times 10^{-2}$$

Substituting these assumptions into the K_a expression and solving gives

$$\frac{X(1.0 \times 10^{-2})}{3.39 \times 10^{-2}} = 1.8 \times 10^{-5}$$

$$X = 6.10 \times 10^{-5}$$

Before accepting this solution, we verify the assumptions by calculating the errors introduced into the calculation, finding that they are

$$3.39 \times 10^{-2} - 6.10 \times 10^{-5} = 3.383 \times 10^{-2}$$

$$1.0 \times 10^{-2} + 6.10 \times 10^{-5} = 1.006 \times 10^{-2}$$

$$\% \text{error} = \frac{3.39 \times 10^{-2} - 3.383 \times 10^{-2}}{3.39 \times 10^{-2}} \times 100 = 0.21\%$$

$$\% \text{error} = \frac{1.0 \times 10^{-2} - 1.006 \times 10^{-2}}{1.0 \times 10^{-2}} \times 100 = -0.6\%$$

Clearly the assumptions are within reason; thus, we know that

$$[\text{H}_3\text{O}^+] = X = 6.10 \times 10^{-5}$$

and that the buffer's pH is 4.21.

The Henderson-Hasselbalch Equation

Now, let's look at buffers in a slightly different way. When first discussing buffers we wrote the K_a expression in a logarithmic form called the Henderson-Hasselbalch equation. For an acetic acid/acetate buffer this equation is

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

There are two important things to note about this equation. First, the equation shows us that the pH of an acetic acid/acetate buffer is always going to be at a pH level similar to the $\text{p}K_a$ value for acetic acid. Given that K_a for CH_3COOH is 1.8×10^{-5} , the pH of an acetic acid/acetate buffer will always be near

$$\text{pH} \approx \text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.74$$

The actual pH will deviate from this, being more acidic when the concentration of CH_3COOH is greater than that for CH_3COO^- and more basic when CH_3COO^- is present at a concentration greater than that for CH_3COOH .

Second, for a buffer to exist the concentrations of the conjugate acid and conjugate base cannot differ from each other by too much. As a guideline, we will adopt the following convention: a buffer exists when the relative amount of conjugate base-to-conjugate acid is within a range of 0.1 and 10; that is

$$0.1 \leq \frac{[\text{conjugate base}]}{[\text{conjugate acid}]} \leq 10$$

Under these conditions, a buffer's pH will fall within the limits of

$$\text{pK}_a - 1 \leq \text{pH} \leq \text{pK}_a + 1$$

Another Way to Calculate the pH Level of a Buffer

The Henderson-Hasselbalch equation provides us with a second method for calculating a buffer's pH. In our previous approach we used an ICE table to find the equilibrium concentrations of CH_3COOH , CH_3COO^- and H_3O^+ in an acetic acid/acetate buffer. This led us to write

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{X(1.0 \times 10^{-2} + X)}{3.39 \times 10^{-2} - X} = 1.8 \times 10^{-5}$$

where X is the equilibrium concentration of H_3O^+ . If we rewrite this in the form of the Henderson-Hasselbalch equation, we get

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]_o + [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]_o - [\text{H}_3\text{O}^+]}$$

where $[\text{CH}_3\text{COO}^-]_o$ and $[\text{CH}_3\text{COOH}]_o$ are, respectively, the initial concentrations of the acetate ion and acetic acid, and $[\text{H}_3\text{O}^+]$ is X . This equation leads us to a significant simplification that will apply to almost any buffer problem (or at least to any such problems that you will see in this course). Here is the simplification. As long as the $[\text{H}_3\text{O}^+]$ is much smaller than $[\text{CH}_3\text{COO}^-]_o$ or $[\text{CH}_3\text{COOH}]_o$, then we can drop the $[\text{H}_3\text{O}^+]$ terms, leaving us with the following equation in which all values except for the pH are known

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]_0}{[\text{CH}_3\text{COOH}]_0}$$

Why is this approximation so universal? Having defined a buffer as a solution whose pH level must fall within the limits

$$\text{pK}_a - 1 \leq \text{pH} \leq \text{pK}_a + 1$$

we can see that the buffer's smallest possible pH is $\text{pK}_a - 1$. This, in turn, defines the largest possible $[\text{H}_3\text{O}^+]$. For an acetic acid/acetate buffer, therefore, the smallest possible pH is 3.74 and the largest possible value for $[\text{H}_3\text{O}^+]$ is 1.8×10^{-4} . As long as we are willing to tolerate errors of 5% in our calculations, this means that the concentration of H_3O^+ is negligible as long as

$$[\text{CH}_3\text{COOH}]_0 \text{ or } [\text{CH}_3\text{COO}^-]_0 \geq \frac{1.8 \times 10^{-4}}{0.05} = 0.0036 \text{ M}$$

Because the initial concentrations of acetic acid and acetate determine a buffer's ability to neutralize a strong base or acid (see further discussion below), it is unlikely that we would create an acetic acid/acetate buffer with concentrations this small. For acids that are weaker than acetic acid, this minimum concentration will be even smaller.

Having determined that we can calculate the pH using the equation

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]_0}{[\text{CH}_3\text{COOH}]_0}$$

we make one more simplification. Because both CH_3COO^- and CH_3COOH are in the same solution, we can multiply their respective molar concentrations by the volume, V

$$\text{pH} = \text{pK}_a + \log \frac{[\text{CH}_3\text{COO}^-]_0 \times V}{[\text{CH}_3\text{COOH}]_0 \times V}$$

which simplifies to

$$\text{pH} = \text{pK}_a + \log \frac{(\text{moles CH}_3\text{COO}^-)_0}{(\text{moles CH}_3\text{COOH})_0}$$

This equation is nice because it allows us to calculate the buffer's pH without having to first calculate the concentrations of the buffering species. As we will see shortly, this is useful when determining how the addition of strong acid or strong base will change a buffer's pH.

Example 1. What is the pH of a buffer prepared by dissolving 25.0 g of K_2HPO_4 and 25.0 g of KH_2PO_4 in 250 mL of water?

Solution. First, we determine which species is the weak acid and which is the conjugate weak base. Both compounds are ionic and will dissociate in water. The K^+ ions have no effect on the solution's pH, so they can be ignored. The remaining anions are amphoteric, meaning that they have both acidic and basic properties. Because dihydrogen phosphate has one more proton than monohydrogen phosphate, H_2PO_4^- is the weak acid. To find the pH of the resulting buffer, we find the initial moles of weak acid

$$25.0 \text{ g KH}_2\text{PO}_4 \times \frac{1 \text{ mol KH}_2\text{PO}_4}{136.1 \text{ g KH}_2\text{PO}_4} = 0.1837 \text{ mol KH}_2\text{PO}_4 = (\text{mol H}_2\text{PO}_4^-)_0$$

and the initial moles of weak base

$$25.0 \text{ g K}_2\text{HPO}_4 \times \frac{1 \text{ mol K}_2\text{HPO}_4}{174.2 \text{ g K}_2\text{HPO}_4} = 0.1435 \text{ mol K}_2\text{HPO}_4 = (\text{mol HPO}_4^{2-})_0$$

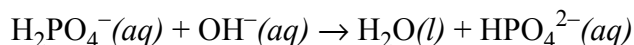
Although the recipe contains information on the amount of water used in preparing the buffer, we don't need to include this in our calculation (although we will use it in the next example).

Knowing the moles of H_2PO_4^- and HPO_4^{2-} , we complete the calculation using the pK_a value for H_2PO_4^- ; thus

$$\text{pH} = \text{pK}_a + \log \frac{(\text{mol HPO}_4^{2-})_0}{(\text{mol H}_2\text{PO}_4^-)_0} = 7.20 + \log \frac{0.1435}{0.1837} = 7.09$$

Finding a Buffer's pH After Adding a Strong Acid or Strong Base

When a strong base is added to a buffer it reacts with some of the conjugate weak acid converting it into the conjugate weak base. For example, the following reaction takes place when we add a strong base, OH^- , to the buffer from the Example 1



Note that we've written this as a reaction that goes to completion. If you look at the reaction in reverse (from right-to-left), you will see that it shows a weak base, HPO_4^{2-} , reacting with water to form its conjugate weak acid, H_2PO_4^- , and hydroxide ion, which is the standard form for a base dissociation reaction. The equilibrium constant for the reverse reaction, therefore, is K_b for HPO_4^{2-} , or 1.59×10^{-7} . This means that the equilibrium con-

stant for the reaction of H_2PO_4^- and OH^- is $(1.59 \times 10^{-7})^{-1}$ or 6.3×10^6 . Clearly the reaction essentially goes to completion.

Knowing that the reaction goes to completion makes it easy to find the moles of H_2PO_4^- and HPO_4^{2-} after the addition of OH^- ; these are

$$\text{moles H}_2\text{PO}_4^- = (\text{moles H}_2\text{PO}_4^-)_0 - \text{moles OH}^-$$

$$\text{moles HPO}_4^{2-} = (\text{moles HPO}_4^{2-})_0 + \text{moles OH}^-$$

Substituting into the Henderson-Hasselbalch equation gives

$$\text{pH} = \text{pK}_a + \log \frac{\text{mol HPO}_4^{2-} + \text{mol OH}^-}{\text{mol H}_2\text{PO}_4^- - \text{mol OH}^-}$$

If we add a strong acid instead of a strong base, the result is

$$\text{pH} = \text{pK}_a + \log \frac{\text{mol HPO}_4^{2-} - \text{mol H}_3\text{O}^+}{\text{mol H}_2\text{PO}_4^- + \text{mol H}_3\text{O}^+}$$

because adding H_3O^+ converts some of the HPO_4^{2-} to H_2PO_4^- .

Example 2. What is the pH after adding 10.00 mL of 1.00 M NaOH to the buffer from Example 1?

Solution. The moles of NaOH added is

$$10.00 \text{ mL NaOH} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{1 \text{ mol OH}^-}{1 \text{ L NaOH}} = 0.0100 \text{ mol OH}^-$$

Substituting into the Henderson-Hasselbalch equation gives

$$\text{pH} = \text{pK}_a + \log \frac{\text{mol HPO}_4^{2-} + \text{mol OH}^-}{\text{mol H}_2\text{PO}_4^- - \text{mol OH}^-} = 7.20 + \log \frac{0.1435 + 0.01}{0.1837 - 0.01} = 7.15$$

Note that adding NaOH raises the pH by only 0.06 pH units, demonstrating that the buffer can neutralize a strong base with only a small change in pH. Adding a similar quantity of NaOH to an equivalent amount of water (250.0 mL) gives

$$[\text{OH}^-] = \frac{\text{moles NaOH}}{\text{total volume}} = \frac{0.0100 \text{ mol}}{0.250 \text{ L} + 0.0100 \text{ L}} = 0.0385 \text{ M}$$

or a pOH of 1.41 and a pH of 12.59. With the water initially at a pH of 7 (neutral), the change in pH for this unbuffered solution is 5.59 pH units.

Evaluating a Buffer's Capacity

Adding a strong acid or a strong base slowly destroys a buffer's ability to do its job because the ratio

$$\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}$$

in the Henderson-Hasselbalch equation changes. Once this ratio falls outside of the range 0.1 to 10 a buffer ceases to exist. We define the buffer's maximum buffer capacity, therefore, as the moles of strong acid or strong base that can be neutralized before reaching the end of the buffer's range.¹ When adding a strong acid this means that the buffer capacity is defined by

$$\frac{\text{mol weak base} - \text{mol H}_3\text{O}^+}{\text{mol weak acid} + \text{mol H}_3\text{O}^+} = 0.1$$

and when adding a strong base the buffer capacity is given by

$$\frac{\text{mol weak base} + \text{mol OH}^-}{\text{mol weak acid} - \text{mol OH}^-} = 10$$

Example 3. How many mL of 6.0 M NaOH can be added to the buffer in Example 1 before it reaches its limit?

Solution. Letting the moles of NaOH be X , we write

$$\frac{\text{mol HPO}_4^{2-} + \text{mol NaOH}}{\text{mol H}_2\text{PO}_4^- - \text{mol NaOH}} = \frac{0.1435 + X}{0.1837 - X} = 10$$

$$0.1435 + X = 1.837 - 10X$$

$$11X = 1.6935$$

$$X = 0.154 \text{ mol NaOH}$$

This corresponds to a volume of 6.0 M NaOH equal to

¹ There is a more quantitatively accurate description of buffer's maximum capacity; however, in the context of this course, this definition is sufficient.

$$0.154 \text{ mol NaOH} \times \frac{1 \text{ L}}{6.0 \text{ mol NaOH}} \times \frac{1000 \text{ mL}}{\text{L}} = 25.7 \text{ mL}$$

Thus, we can add 25.7 mL of 6.0 M NaOH before exceeding the buffer's capacity to neutralize strong base.

At times we may wish to define a buffer's capacity more narrowly. For instance, in Example 1 we showed that a solution containing 0.1837 moles of H_2PO_4^- and 0.1435 moles of HPO_4^{2-} has a pH of

$$\text{pH} = \text{pK}_a + \log \frac{(\text{mol HPO}_4^{2-})_o}{(\text{mol H}_2\text{PO}_4^-)_o} = 7.20 + \log \frac{0.1435}{0.1837} = 7.09$$

For this buffer the maximum capacity to neutralize strong acid is set by the buffer's lower pH limit of 6.20 ($\text{pK}_a - 1$). Suppose, however, that for a particular experiment the buffer's pH must not fall below 6.90. Example 4 shows how to determine this more narrowly defined buffer capacity.

Example 4. How many moles of strong acid can be absorbed by the buffer in Example 1 without the pH drifting below 6.90?

Solution. When adding a strong acid to a buffer the relevant form of the Henderson-Hasselbalch equation is

$$\text{pH} = \text{pK}_a + \log \frac{\text{mol HPO}_4^{2-} - \text{mol H}_3\text{O}^+}{\text{mol H}_2\text{PO}_4^- + \text{mol H}_3\text{O}^+}$$

Letting X be the moles of H_3O^+ and substituting known values for the pK_a of H_2PO_4^- and the moles of H_2PO_4^- and HPO_4^{2-} gives

$$6.90 = 7.20 + \log \frac{0.1435 - X}{0.1837 + X}$$

$$-0.30 = \log \frac{0.1435 - X}{0.1837 + X}$$

$$0.5012 = \frac{0.1435 - X}{0.1837 + X}$$

$$0.09207 + 0.5012X = 0.1435 - X$$

$$1.5012X = 0.5143$$

$$X = 3.43 \times 10^{-2} \text{ mol H}_3\text{O}^+$$

Thus, the buffer capacity for this scenario is 3.43×10^{-2} moles of strong acid.

Designing Buffers

The purpose of using a buffer in an experiment is to limit any significant change in pH that might occur. For example, when using an enzyme in a biochemistry experiment the solution must be carefully buffered because the enzyme will function over a narrow range of pH levels. If the pH drifts too far from the optimal range, then the enzyme ceases to function and the experiment is doomed to failure. Similar problems are found in all areas of chemistry. An aqueous synthetic reaction in inorganic chemistry, for instance, may produce acid as a byproduct. If the reaction becomes very slow under acidic conditions, then a buffer is included to prevent the pH from drifting too low. In both of these examples a suitable buffer is the difference between a useful experiment and one that is a failure.

So, what does it mean to “design a buffer” for a particular experiment? There are several important considerations. What is the buffer’s desired pH? Does the buffer need to be better at neutralizing acid or base? What is the desired buffer capacity? What other considerations are there; for example, is there a maximum concentration of dissolved ions that can be tolerated? Each of these issues is discussed in this tutorial.

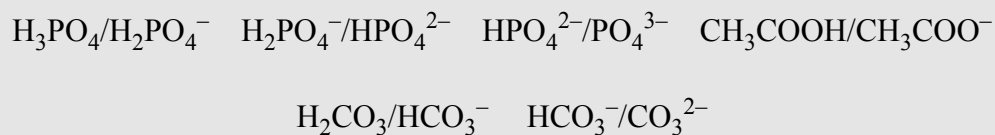
Question 1: What is the Buffer’s Desired pH of the Buffer?

This question is the first one to consider because it limits the possible choices for the conjugate weak acid/weak base pair. Recall that a buffer can be made for any pH within ± 1 pH units of the weak acid’s pK_a ; that is, the pH range for a buffer is

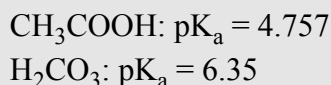
$$\text{pH} = \text{pK}_a \pm 1$$

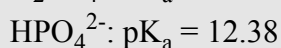
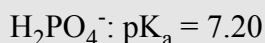
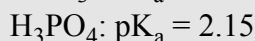
For example, if a buffer needs to have a pH of 7.00, then the weak acid must have a pK_a between 6.00 and 8.00. If the weak acid has a pK_a of 6.00, then a buffer can be prepared with a pH between 5.00 and 7.00. For a weak acid with a pK_a of 8.00, buffers with pH levels between 7.00 and 9.00 are possible.

Example 1. A buffer with a pH of 9.87 is needed. Which of the following conjugate weak acid/weak base pairs can be used?



Solution. Given a target pH of 9.87, the conjugate weak acid’s pK_a must be between 8.87 and 10.87. The pK_a values for the possible conjugate weak acids are:





The only conjugate weak acid in this list with a suitable pK_a is HCO_3^- ; thus, the buffer must use HCO_3^- and CO_3^{2-} .

Question 2: Does the buffer need to be better at neutralizing acid or base?

If only one conjugate weak acid/weak base is available, then this question is of no importance. However, in many circumstances several possible buffering agents are possible. For example, if our target pH is 7.00, we can prepare a buffer using a weak acid with a pK_a as small as 6.00 or as large as 8.00. If the buffer is for a system where it is necessary to protect against the addition of a strong acid only, then we want the buffer to have more of its conjugate weak base than of its conjugate weak acid (because it is the conjugate weak base that reacts with the strong acid). Using the Henderson-Hasselbalch equation as a guide

$$\text{pH} = \text{pK}_a + \log \frac{[\text{conjugate weak base}]}{[\text{conjugate weak acid}]}$$

we see that any buffer where the concentration of conjugate weak base is greater than the conjugate weak acid will have a $\text{pH} > \text{pK}_a$. Thus, if we want a buffer to provide better protection against a strong acid, then the conjugate weak acid's pK_a must be less than the buffer's desired pH. This suggests the following simple guidelines:

To protect against the addition of a strong acid, choose a buffer whose pK_a is less than desired pH.

To protect against the addition of a strong base, choose a buffer whose pK_a is greater than desired pH.

Example 2. Using the same list of possible buffers from Example 1, what is the best choice if you need a buffer with a pH of 6.85 that must be able to protect against the addition of strong base?

Solution. With a target pH of 6.85, the weak acid must have a pK_a between 5.85 and 7.85. Both H_2CO_3 and $\text{H}_2\text{PO}_4^{2-}$ meet this condition. To protect against the addition of strong base, we want the buffer to have more of its conjugate weak acid than its conjugate weak base. We need, therefore, to use a weak acid whose pK_a is greater than the desired pH. Of

the two choices, only H_2PO_4^- meets this condition. A $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer is the best choice.

Question 3: What is the desired buffer capacity?

Given that a buffer's purpose is to maintain a solution's pH against the addition of strong acid or strong base, a useful buffer must be able to neutralize whatever quantity of acid or base we might reasonably expect to enter the system. The amount of strong acid or strong base that can be neutralized is called the buffer's buffer capacity. What determines the buffer capacity is the concentration of the conjugate weak acid and conjugate weak base used to prepare the buffer. A higher concentration of these buffering reagents leads to a greater buffer capacity.

Example 3. Suppose you are carrying out an aqueous reaction in which the solution's pH must remain within the limits of 6.8 ± 0.2 pH units. The buffer of choice is made using H_2PO_4^- ($\text{pK}_a = 7.2$) and HPO_4^{2-} . During the reaction, no more than 0.0010 mol of strong acid will be released. What are the minimum concentrations of H_2PO_4^- and HPO_4^{2-} necessary to prevent the solution's pH from drifting below 6.6? Assume that the desired initial pH is 7.0 and that the buffer's volume is 100.0 mL.

Solution. Using the Henderson-Hasselbalch equation, the initial buffer must have a mole ratio of HPO_4^{2-} to H_2PO_4^- equaling

$$7.0 = 7.2 + \log \frac{(\text{mol HPO}_4^{2-})_o}{(\text{mol H}_2\text{PO}_4^-)_o}$$

$$\frac{(\text{mol HPO}_4^{2-})_o}{(\text{mol H}_2\text{PO}_4^-)_o} = 0.631$$

to obtain the desired pH of 7.0. At the most acidic allowed pH (6.6), the smallest allowed mole ratio is

$$6.6 = 7.2 + \log \frac{(\text{mol HPO}_4^{2-})_o}{(\text{mol H}_2\text{PO}_4^-)_o}$$

$$\frac{\text{mol HPO}_4^{2-}}{\text{mol H}_2\text{PO}_4^-} = 0.251$$

Adding strong acid to the buffer changes the pH because some of the conjugate weak base, HPO_4^{2-} , is converted to the conjugate weak acid, H_2PO_4^- . Knowing that the maximum amount of strong acid is 0.0010 mol, means that

$$\frac{(\text{mol HPO}_4^{2-})_o - 0.001}{(\text{mol H}_2\text{PO}_4^-)_o + 0.001} = 0.251$$

From the initial mole ratio, we know that $(\text{mol HPO}_4^{2-})_o = 0.631 \times (\text{mol H}_2\text{PO}_4^-)_o$. Substituting into the equation above and solving for the initial moles of H_2PO_4^- gives

$$\frac{0.631 \times (\text{mol H}_2\text{PO}_4^-)_o - 0.001}{(\text{mol H}_2\text{PO}_4^-)_o + 0.001} = 0.251$$

$$(\text{mol H}_2\text{PO}_4^-)_o = 0.0033$$

$$(\text{mol HPO}_4^{2-})_o = 0.0021$$

Because the buffer's volume is 100.0 mL, the minimum initial concentrations of the buffer reagents are 0.033 M H_2PO_4^- and 0.021 M HPO_4^{2-} .

Question 4: Why shouldn't we just make the buffer capacity really large to avoid having the buffer fail?

In the previous sections we considered how to prepare a buffer by selecting a suitable conjugate weak acid and conjugate weak base and ensuring that their respective concentrations are capable of neutralizing a specified amount of strong acid or strong base. You might reasonably ask why it is necessary to design the buffer to have a specific buffer capacity. It would, after all, be easier to just prepare the buffer with high concentrations of the buffering agents, knowing that the resulting buffer capacity will be far greater than needed. Unfortunately, this can present significant problems.

Another important consideration when designing a buffer is the total concentration of ions in solution, a property of a solution called its ionic strength. Many systems, particularly in biology and biochemistry, can tolerate only a limited range of ionic strengths. The reason for this is that large differences in ionic strength on two sides of a cell membrane causes fluids to move across the membrane in an attempt to even out the concentrations of dissolved ions (a process known as osmotic flow). The result is catastrophic for cells; thus, the effect of pouring salt on slugs (which many of you have probably seen or done).

Example 4. A $\text{H}_2\text{PO}_4^-/\text{HPO}_4^{2-}$ buffer is needed with a pH of 7.0. To maintain a low ionic strength, the maximum total concentration of phosphate species is limited to 1.0 mM. What concentrations of H_2PO_4^- and HPO_4^{2-} are needed?

Solution. From Example 3, we know that the buffer must have a concentration ratio of

$$\frac{[\text{mol HPO}_4^{2-}]}{[\text{mol H}_2\text{PO}_4^-]} = 0.631$$

Knowing that

$$[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^{2-}] = 1.0 \text{ mM}$$

we have

$$\frac{1.0 \text{ mM} - [\text{mol H}_2\text{PO}_4^-]}{[\text{mol H}_2\text{PO}_4^-]} = 0.631$$

and

$$[\text{H}_2\text{PO}_4^-] = 0.61 \text{ mM}$$

$$[\text{HPO}_4^{2-}] = 1.0 \text{ mM} - 0.61 \text{ mM} = 0.39 \text{ mM}$$

Three Ways to Prepare a Buffer

Suppose you are asked to prepare 500 mL of a $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffer subject to the following conditions: the buffer must have a pH of 9.87 and the total concentration of HCO_3^- and CO_3^{2-} must be 0.200 M. How might you prepare this buffer?

We begin by determining the relative amount of weak base (CO_3^{2-}) and weak acid (HCO_3^-) needed to give the desired pH; thus, using the Henderson-Hasselbalch equation

$$\text{pH} = 9.87 = \text{pK}_a + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 10.33 + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$

we find that

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = 0.3467$$

We then calculate the total moles of CO_3^{2-} and HCO_3^- needed

$$\frac{0.200 \text{ mol}}{\text{L}} \times 0.500 \text{ L} = 0.100 \text{ mol} = \text{mol HCO}_3^- + \text{mol CO}_3^{2-}$$

Next, we calculate the exact moles of CO_3^{2-} and HCO_3^- that we will need. Letting X be the moles of CO_3^{2-} , we know that the moles of HCO_3^- are

$$0.100 \text{ mol} - X = \text{mol HCO}_3^-$$

Substituting back gives

$$\frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{X}{0.1 - X} = 0.3467$$

$$X = 0.02574 \text{ mol CO}_3^{2-}$$

$$0.100 - X = 0.07426 \text{ mol HCO}_3^{2-}$$

Now that we know how many moles of CO_3^{2-} and HCO_3^- are needed, we can determine the amounts of each reagent to use. Here we have three choices: (i) we can use solid Na_2CO_3 and solid NaHCO_3 ; (ii) we can use solid NaHCO_3 and convert some of it to CO_3^{2-} by adding a strong base, such as 6 M NaOH; or (iii) we can use solid Na_2CO_3 and

convert some of it to HCO_3^- by adding a strong acid, such as 6 M HCl. All three approaches are outlined below.

Using Na_2CO_3 and NaHCO_3

The moles of Na_2CO_3 and NaHCO_3 needed are just the same as the moles of CO_3^{2-} and HCO_3^- calculated above; thus

$$0.02574 \text{ mol Na}_2\text{CO}_3 \times \frac{105.988 \text{ g}}{\text{mol}} = 2.73 \text{ g Na}_2\text{CO}_3$$

$$0.07426 \text{ mol NaHCO}_3 \times \frac{84.0059 \text{ g}}{\text{mol}} = 6.24 \text{ g NaHCO}_3$$

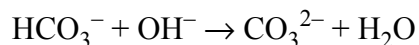
To prepare the buffer, therefore, we add these amounts of the solid reagents to a 500-mL volumetric flask and dilute to volume.

Using NaHCO_3 and NaOH

In this approach we begin by weighing out an amount of NaHCO_3 equivalent to the total moles of HCO_3^- and CO_3^{2-} needed; thus, we begin with 0.100 moles of NaHCO_3 , or

$$0.100 \text{ mol NaHCO}_3 \times \frac{84.0059 \text{ g}}{\text{mol}} = 8.40 \text{ g NaHCO}_3$$

Next, we add NaOH , converting 0.02574 moles of the HCO_3^- to CO_3^{2-} as shown by the following reaction



Thus, we need 0.02574 moles of NaOH , or

$$0.02574 \text{ mol NaOH} \times \frac{1 \text{ L}}{6 \text{ mol}} \times \frac{1000 \text{ mL}}{\text{L}} = 4.29 \text{ mL NaOH}$$

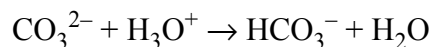
To prepare the buffer we add 8.40 g of NaHCO_3 to a 500-mL volumetric flask and dissolve it with some water. We then add 4.29 mL of 6 M NaOH and dilute to volume.

Using Na_2CO_3 and HCl

In this approach we begin by weighing out an amount of Na_2CO_3 equivalent to the total moles of HCO_3^- and CO_3^{2-} needed; thus we begin with 0.100 moles of Na_2CO_3 , or

$$0.100 \text{ mol Na}_2\text{CO}_3 \times \frac{105.988 \text{ g}}{\text{mol}} = 10.60 \text{ g Na}_2\text{CO}_3$$

Next, we add HCl, converting 0.07426 moles of the CO_3^{2-} to HCO_3^- as shown by the following reaction



Thus, we need 0.07426 moles of HCl, or

$$0.07426 \text{ mol HCl} \times \frac{1 \text{ L}}{6 \text{ mol}} \times \frac{1000 \text{ mL}}{\text{L}} = 12.38 \text{ mL HCl}$$

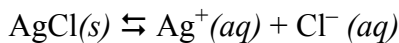
To prepare the buffer we add 10.60 g of Na_2CO_3 to a 500-mL volumetric flask and dissolve it with some water. We then add 12.38 mL of 6 M HCl and dilute to volume.

A Final Comment of Preparing Buffers

For reasons we will discuss later, a buffer prepared following one of these approaches probably will not produce a solution whose pH level matches exactly the desired value. When preparing a buffer in the laboratory it often is necessary to adjust the buffer's pH level to the desired value by adding small amounts of either a strong acid or a strong base while monitoring the pH with a pH electrode.

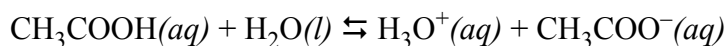
Finding the Equilibrium Constant for a New Reaction

Although every equilibrium reaction has an equilibrium constant, values for these constants are tabulated for only a few specific types of reactions. As we've seen, equilibrium constants are provided for: **solubility** reactions



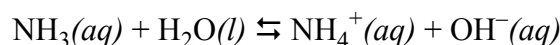
$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

where K_{sp} is the solubility product; for **acid dissociation** reactions



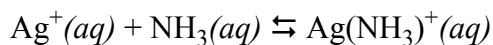
$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$

where K_a is the acid dissociation constant; for **base dissociation** reactions

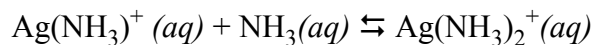


$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

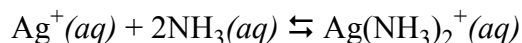
where K_b is the base dissociation constant; and for **complexation** reactions



$$K_1 = \frac{[\text{Ag}(\text{NH}_3)^+]}{[\text{Ag}^+][\text{NH}_3]} = 2040$$



$$K_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}(\text{NH}_3)^+][\text{NH}_3]} = 8130$$



$$\hat{a}_2 = \frac{[\text{Ag}(\text{NH}_3)_2^+]}{[\text{Ag}^+][\text{NH}_3]^2} = K_1 \times K_2 = 1.66 \times 10^7$$

where K_1 and K_2 are step-wise formation constants and β_2 is an overall formation constant. In addition, a few special reactions have equilibrium constants whose values are readily available. The most important of these is that for **water's dissociation**

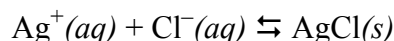


$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.00 \times 10^{-14}$$

The equilibrium constant for any other reaction, therefore, must be determined by finding ways to combine the equilibrium constant expressions for reactions such as those outlined above. To do so we take advantage of two important observations

- if an equilibrium reaction is reversed its new equilibrium constant is the reciprocal of the original equilibrium constant
- if two equilibrium reactions are added together, the equilibrium constant for the new reaction is the product of the two original equilibrium constants

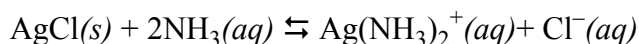
For example, consider the equilibrium constant for the precipitation of AgCl. The reaction



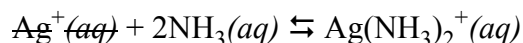
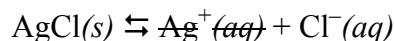
is the reverse of the solubility reaction for AgCl. The equilibrium constant, therefore, is the reciprocal of silver chloride's solubility product; thus

$$K = \frac{1}{[\text{Ag}^+][\text{Cl}^-]} = \frac{1}{K_{\text{sp}}} = \frac{1}{1.8 \times 10^{-10}} = 5.6 \times 10^9$$

Or, consider the solubility of AgCl in a solution of NH_3



This reaction is the sum of the solubility reaction for AgCl and the overall formation constant for $\text{Ag}(\text{NH}_3)_2^+$



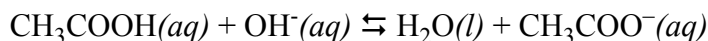
thus, the equilibrium constant is just the product of K_{sp} and β_2

$$K = K_{sp} \times \beta_2 = [Ag^+][Cl^-] \times \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2} =$$

$$\frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2} = (1.8 \times 10^{-10}) \times (1.66 \times 10^7) = 3.0 \times 10^{-3}$$

Recognizing how to combine standard equilibrium constant reactions to make a new equilibrium reaction takes some practice. Here are a few examples that you will encounter in this course:

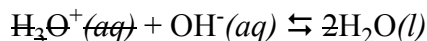
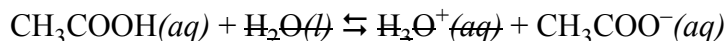
- Reaction of a weak acid, such as acetic acid, with a strong base



If we look at this reaction in reverse we see that it is the reaction of a weak base with water; that is, the reverse reaction is the base dissociation reaction for the acetate ion. The equilibrium constant for this reaction, therefore, is

$$K = \frac{[CH_3COO^-]}{[CH_3COOH][OH^-]} = \frac{1}{K_b} = \frac{1}{5.7 \times 10^{-10}} = 1.75 \times 10^9$$

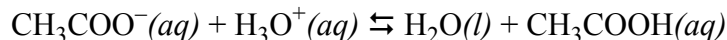
Alternatively, we can see this reaction as the sum of the acid dissociation reaction for acetic acid and the inverse of water's dissociation reaction



giving

$$K = \frac{K_a}{K_w} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \times \frac{1}{[H_3O^+][OH^-]} = \frac{1.75 \times 10^{-5}}{1.00 \times 10^{-14}} = 1.75 \times 10^9$$

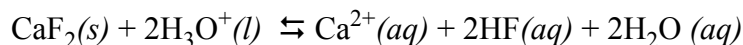
- Reaction of a weak base, such as the acetate ion, with a strong acid



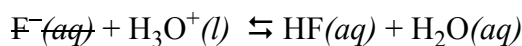
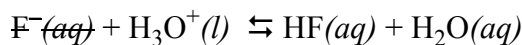
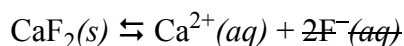
If we look at this reaction in reverse we see that it is the reaction of a weak acid with water; that is, the reverse reaction is the base dissociation reaction for the acetic acid. The equilibrium constant for this reaction, therefore, is

$$K = \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]} = \frac{1}{K_a} = \frac{1}{1.75 \times 10^{-5}} = 5.71 \times 10^4$$

- Solubility of a salt whose anion is a weak base, such as CaF_2 , under conditions where the weak base is protonated



If we look at this reaction we see that it is a summation of the solubility reaction for CaF_2 and the reverse of the acid dissociation reaction for HF; thus

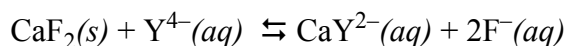


The equilibrium constant, therefore, is

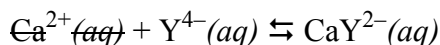
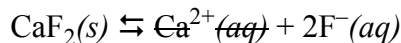
$$K = \frac{[\text{Ca}^{2+}][\text{HF}]^2}{[\text{H}_3\text{O}^+]^2} = K_{\text{sp}} \times (K_a)^{-1} \times (K_a)^{-1} =$$

$$[\text{Ca}^{2+}][\text{F}^-]^2 \times \left\{ \frac{[\text{F}^-][\text{H}_3\text{O}^+]}{[\text{HF}]} \right\}^{-2} = (3.9 \times 10^{-11}) \times (7.2 \times 10^{-4})^{-2} = 7.5 \times 10^{-5}$$

- Solubility of a salt, such as CaF_2 , in the presence of a ligand, such as EDTA (which is abbreviated as Y^{4-})



This reaction is the summation of the solubility reaction for CaF_2 and the metal-ligand complexation reaction between Ca^{2+} and EDTA; thus



The equilibrium constant, therefore, is

$$K = \frac{[\text{CaY}^{2-}][\text{F}^-]^2}{[\text{Y}^{4-}]} = K_{\text{sp}} \times K_1 =$$

$$[\text{Ca}^{2+}][\text{F}^-]^2 \times \frac{[\text{CaY}^{2-}]}{[\text{Ca}^{2+}][\text{Y}^{4-}]} = (3.9 \times 10^{-11}) \times (4.9 \times 10^{10}) = 1.9$$