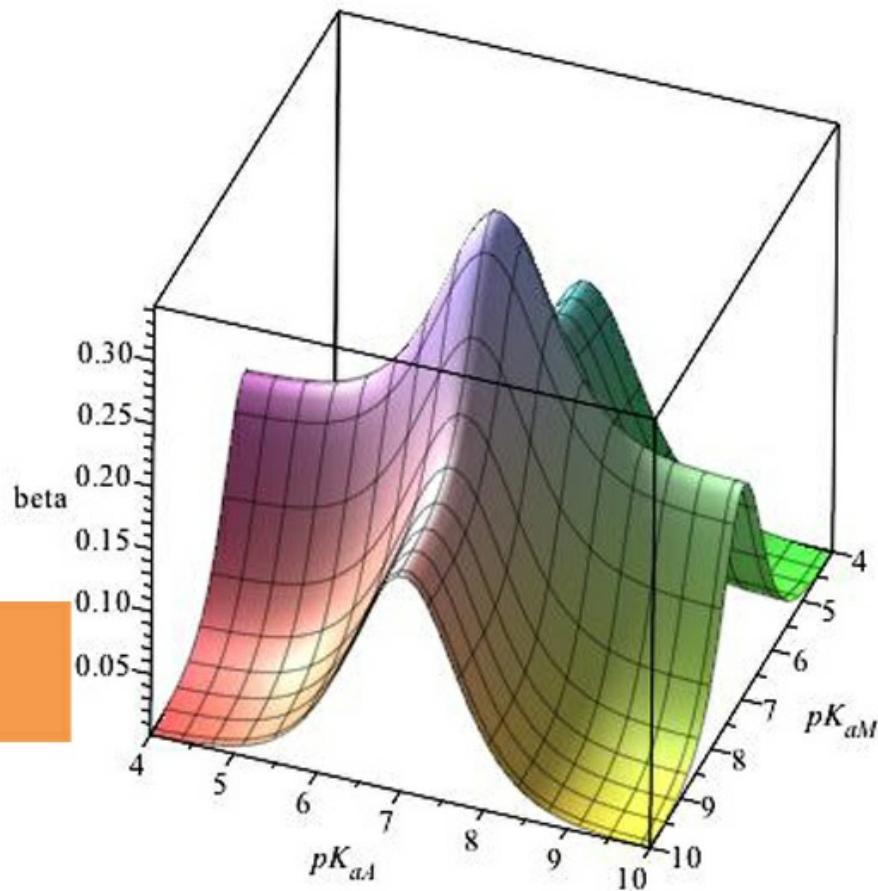


# Equilibrium in Analytical Chemistry Using Maple®

An emphasis on Ionic Equilibrium - Part I

Prof. R.V. Whiteley

Part I



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Prof. R.V. Whiteley, Jr., Pacific University Oregon

# **Equilibrium in Analytical Chemistry Using Maple<sup>®</sup>**

An emphasis on Ionic Equilibrium – Part I



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# Preface

There was once a limit to the rigor of ionic equilibrium calculations because the mathematics to the most interesting problems were intractable. In 1964, J.N. Butler published *Ionic Equilibrium A Mathematical Approach*.<sup>1</sup> In the three decades that followed Butler's masterpiece, most of the work he presented still could not be exploited because the algebra was unmanageable. When desktop computers began to appear in the eighties, a few scholars were able to address more of the interesting problems in ionic equilibrium. In the nineties, computer algebra became available for those desktop computers and all of Butler's work became "doable." However, there are few publications and fewer, still, books where commercially available computer algebra is applied to problems in ionic equilibrium. The work presented here does exactly that, and it does it completely! Moreover, it presents ionic equilibrium in the context of analytical chemistry where it has special applications.

The study of ionic equilibrium is central to the understanding of most processes in chemical analysis. The basic concepts are introduced in general chemistry, but because of time constraints and because students at that level often lack mathematical sophistication, simplifying approximations are required. These simplifications severely restrict the applicability of what is learned, and so the student acquires only a superficial understanding of the topic. The serious presentation of ionic equilibrium is usually deferred to a first course in quantitative analysis where its principles are applied. Even at that level, problems are often solved using simplifications and holes remain in the students' grasp of ionic equilibrium.

If one can write a mass balance, a charge balance and equilibrium expressions, one can, with the help of computer algebra, unravel the makeup of some spectacularly complicated solutions. The reader can generate fascinating titration curves and predict the completeness of precipitation within some bizarre mixtures. A level of sophistication omitted, for simplicity, in other books will be found here: this work comprehensively addresses the effects of ionic strength on all ionic reactions. Ionic strength is covered in detail early and carried throughout the work. These ionic strength effects, however, are ignored where they make problems unnecessarily confusing.

This book is likely to find strong appeal among hard-core analytical chemists. Although it is not a textbook, it will appeal to chemistry and environmental faculty and students. It is rich in its presentation of first principles as it methodically illustrates the use of Maple for solving problems in the context of analytical chemistry. Those who wish to understand the issues of incomplete reaction and the difference between an equivalence point and an endpoint should be especially pleased. Some who are less comfortable with computer algebra might be reluctant to embrace this approach, at first, but they will find that they come up to speed quickly because the instruction presumes no prior knowledge of Maple. Yet, within two chapters the reader is calculating and graphically illustrating important points.

# 1 The Fundamentals of Chemical Equilibrium

Consider the hypothetical chemical reaction:



A and B are the reactants, and C is the product. How far does this reaction ultimately proceed? How do we express this completeness? First, we need to understand that many reactions can run in both directions, *albeit* sometimes to an imperceptibly small degree. To address this contingency we write the reaction:



The completeness is expressed as a reaction quotient, Q. It is the product of the products divided by the product of the reactants. How the products and reactants are expressed in Q can be a little complicated, but in some cases, each reaction component can be expressed as a molarity, *i.e.* in moles per liter.<sup>2</sup> For this designation, square brackets are used. So [C] implies a concentration of product C in moles per liter, and this gives a reaction quotient for our reaction:

$$Q = \frac{[\text{C}]}{[\text{A}][\text{B}]} \quad \text{1-1}$$

Before any C has formed, Q will equal zero, but as C is produced and A and B are consumed, Q will increase until it reaches a steady state value. This is its equilibrium value and it is designated  $K_{\text{eq}}$ . So to describe equilibrium conditions we replace Q in the previous expression with  $K_{\text{eq}}$ . Unlike Q,  $K_{\text{eq}}$  is a constant.<sup>3</sup> A reaction that equilibrates with relatively little product, C, that is, which lies largely to the left, will have a small  $K_{\text{eq}}$  always less than 1, and a reaction that does not proceed at all to the right would have  $K_{\text{eq}}$  equal to zero. So if a reaction proceeding 0% to the right corresponds to  $K_{\text{eq}} = 0$ , then what about a reaction that proceeds completely (100%) to the right? A reaction that proceeds far to the right would be characterized by a large  $K_{\text{eq}}$  because [C] would be much larger than [A] and [B], but 100% to the right implies that [A] or [B], or both [A] and [B] must equal zero. If a zero is substituted into the expression for  $K_{\text{eq}}$  the value for the equilibrium constant is undefined, essentially infinitely large.

Consideration of the “100%” reaction is especially important in analytical applications because calculations are based on the presumption that the reactants are completely consumed. Suppose that A is the analyte, that is, the agent which is to be quantified. Two scenarios are common. In a titration, for example, one might measure out exactly enough B to consume A and form C. From the balanced equation, knowing just the amount of B required for complete consumption of A gives the amount of A. Or, one might add an excess of B and determine the amount of A from the amount of C that is produced, as in a gravimetric analysis where C is weighed.<sup>4</sup> In either scenario it will not do to have the reaction equilibrate where an appreciable amount of C has reverted to A + B. That is, where an appreciable amount of A remains unreacted.

The conventional approach in analytical chemistry is to define “complete” as more than 99.9%. And so analytical chemists require that a reaction like  $A + B \rightleftharpoons C$  be driven at least 99.9% to the right. That would imply that out of every 1000 A atoms, molecules, or ions, 999 would be converted to C and only one would remain unreacted. This is an acceptable error in terms of determining the amount of A. It also makes it possible to express completeness in terms of  $K_{eq}$ .

Suppose that we begin with a solution that is 1.00 M in A and 1.00 M in B and which contains no C. On equilibration of the “complete” reaction 99.9% of A and B have been consumed. By definition, this is a complete reaction. So what is its  $K_{eq}$ ? At equilibrium, assuming no volume change, [A] and [B] would each decrease to  $1.00 \times 10^{-3}$  M, and from the balance equation we can see that [C] would increase to  $0.999 \text{ M} \approx 1.00 \text{ M}$ . Using  $[C] = 1.00 \text{ M}$ ,

$$K_{eq} = \frac{[C]}{[A][B]} = \frac{(1.00)}{(1.00 \times 10^{-3})(1.00 \times 10^{-3})} = 1.00 \times 10^6 \quad 1-2$$

*Caution is required here!* One cannot infer  $K_{eq}$  from the completeness of a reaction at equilibrium or infer the completeness of a reaction from  $K_{eq}$  without a knowledge of concentrations of the reactants and products. Consider for example if [A] and [B] had been 0.0100 M at the onset, and if 99.9% of these had been converted to C, the final concentrations of A and B would have been  $1.00 \times 10^{-5}$  M, and the equilibrium concentration of C would be  $\approx 0.0100$  M. So in this case achieving 99.9% consumption of A and B would require a  $K_{eq} \geq 10^8$ . In general, for a reaction of the type  $A + B \rightleftharpoons C$ , a larger and larger  $K_{eq}$  is required to achieve 99.9% completeness as the reaction mixture becomes more and more dilute.

We will engage this issue in later chapters where completeness of a titration is addressed, but we will illustrate this point here by substituting *any* values (except zero!) for [A], [B], and [C] into the expression for  $K_{eq}$ . With these values, calculate the  $K_{eq}$ . Now suppose that the volume of this mixture suddenly doubled. This will cut *every* concentration in half and upset the equilibrium of the reaction. From these new, “half concentrations,” notice that the non-equilibrium quotient, Q, is now twice the  $K_{eq}$ . Recall that a reaction will proceed until its reaction quotient equals  $K_{eq}$ . Because, in this case, Q is greater than  $K_{eq}$ , the reaction will proceed in the direction that will cause Q to decrease. This requires that [A] and [B] must increase and [C] must decrease. That is, the reaction will proceed to the left, or backwards from our intent. And so, however complete (far to the right) the reaction was before the dilution, it will be less complete after the dilution. This is a consequence of Le Châtelier’s Principle and it haunts analytical chemists because so much analytical work is based on the  $A + B \rightleftharpoons C$  type of reaction.

Not all reactions are affected this way when the reaction mixture is diluted. When the moles of reactant equal the moles of product, equilibrium is not affected by dilution. Consider the reaction:



or



We can show that a  $K_{eq} = 10^3$  (1-3) or =  $10^6$  (1-4), respectively, is sufficiently large that the reaction of 1.00 M reactants would proceed  $\geq 99.9\%$  to the right.

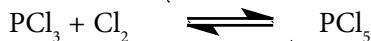
$$K_{eq} = \frac{(1.00)}{(1.00 \times 10^{-3})} = 1.00 \times 10^3 \quad 1-3$$

$$K_{eq} = \frac{(1.00)(1.00)}{(1.00 \times 10^{-3})(1.00 \times 10^{-3})} = 1.00 \times 10^6 \quad 1-4$$

Moreover, diluting either solution *any* amount would affect [A], [B], [C] and [D] equally, so that equilibrium would not be affected. Unfortunately, neither of these reaction types is particularly useful in analytical chemistry.

### Example Problems

1. Consider the reaction of phosphorus trichloride with chlorine to produce phosphorus pentachloride:



- a) Write the expression for the reaction quotient, Q.
- b) Suppose that on equilibration it was found that  $[PCl_3] = 0.109 \text{ M}$ ,  $[Cl_2] = 0.109 \text{ M}$ , and  $[PCl_5] = 0.555 \text{ M}$ . Calculate  $K_{eq}$ .
- c) Consider the following reaction mixture concentrations and from each predict which way the reaction would proceed (left or right) based on the  $K_{eq}$  calculated in 1b.

	$[PCl_3]$	$[Cl_2]$	$[PCl_5]$
i	0.0532	0.244	0.555
ii	0.0235	0.155	0.438
iii	0.0333	0.0333	0.370

- d) Show that doubling the volume of the reaction mixture will upset the equilibrium of this reaction at the conditions described in b above and cause the reaction to flow towards the left.
- 2. Consider the reaction of fluorine and hydrogen to form hydrogen fluoride:



- a) Write the expression for Q.
- b) Suppose that on equilibration it was found that  $[H_2] = 2.00 \times 10^{-3} \text{ M}$ ,  $[F_2] = 4.39 \times 10^{-4} \text{ M}$ , and  $[HF] = 0.100 \text{ M}$ . Calculate  $K_{eq}$ .

- c) Show that reducing the volume of the reaction mixture by half will not upset the equilibrium of this reaction at the conditions described in b above.
- d) Consider the following reaction mixture concentrations and from each predict which way the reaction would proceed (left or right).

	[H <sub>2</sub> ]	[F <sub>2</sub> ]	[HF]
i	0.0250	0.00500	0.100
ii	0.0215	0.0455	0.150
iii	0.0033	0.0033	0.370

### Solutions to Example Problems

1.

a)  $Q = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$

b)  $K_{\text{eq}} = \frac{(0.555)}{(0.109)(0.109)} = 46.7$

c) i  $Q = \frac{(0.555)}{(0.0532)(0.244)} = 42.8$

$Q < K_{\text{eq}}$  requires that Q must increase and this requires that the denominator (reactants) decrease and the numerator (product) increase. So the reaction moves left to right.

ii  $Q = 120 > K_{\text{eq}}$  and so Q must decrease and this requires that the denominator (reactants) increase and the numerator (product) decrease. So the reaction moves right to left.

iii  $Q = 334 > K_{\text{eq}}$  same result as ii above.

- d) Doubling the reaction volume (without changing the quantity of reactants or products) will halve each of the reactant *and* product concentrations. And so:

$$Q = \frac{(0.555 \div 2)}{(0.0532 \div 2)(0.244 \div 2)} = 23.4$$

As in 1.c.i above,  $Q < K_{\text{eq}}$ . This requires that Q must increase. So the denominator (reactants) must decrease and the numerator (product) must increase. Consequently the reaction must run left to right (forward) to reestablish equilibrium.

2.

a)  $Q = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]}$

$$\text{b) } K_{\text{eq}} = \frac{(0.100)^2}{(2.00 \times 10^{-3})(4.39 \times 10^{-4})} = 1.14 \times 10^4$$

- c) Cutting the reaction volume in half (without changing the quantity of reactants or products) will double each of the reactant and product concentrations. And so:

$$Q = \frac{(0.100 \times 2)^2}{(2.00 \times 10^{-3} \times 2)(4.39 \times 10^{-4} \times 2)} = 1.14 \times 10^4$$

- d) See problem #1 for a more complete explanation of consequences

	Q	Consequence
i	= 80 < K <sub>eq</sub>	Q must increase: Reaction flows to right.
ii	= 23 < K <sub>eq</sub>	Q must increase: Reaction flows to right.
iii	= 1.26 × 10 <sup>4</sup> > K <sub>eq</sub>	Q must decrease: Reaction flows to left.

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# 2 Ionic Strength, Activity Coefficients and an Introduction to Maple

In the introduction to chemical equilibrium in Chapter 1, care was taken to avoid addressing reactions with reactants or products that carry a charge. Such ionic equilibria were deferred to this chapter because there can be a substantial error in expressing the equilibrium constant,  $K_{\text{eq}}$ , in terms of concentrations. A correction to this expression of  $K_{\text{eq}}$  is provided here.

Consider again the first reaction addressed in Chapter 1, but here, provide that at least two agents carry a charge. For example,  $z_A$  is the integer charge on ion A (its ionic valence).<sup>5</sup>



Using concentrations to express  $K_{\text{eq}}$  would give:

$$K_{\text{eq}} = \frac{[C^{z_A+z_B}]}{[A^{z_A}][B^{z_B}]} \quad 2-1$$

This, however, is only a crude approximation of the equilibrium constant because the concentration terms are only a crude depiction of the way that *charged* agents behave in solution. The behavior of an ionic agent is especially disposed to the effects of the solvent and other solutes. A solvent's ability to dissipate an electric field will affect the degree to which ions interact with other solutes. Also, in a solution with a high ionic content, ionic agents will be shielded from one another and this too will affect interactions, and so the  $K_{\text{eq}}$  will not be adequately expressed by the concentrations of reactants and products.

It is outside the scope of this work to examine the effects of solvent and solutes on the behavior of ions in solution. The Debye-Hückel Theory of Interionic Interactions (1923), however, describes these effects quantitatively, and it is discussed in countless physical chemistry textbooks. The results of that theory and subsequent work are used here to provide corrections to the concentration-based equilibrium constant.

The correct way to express an agent's behavior thermodynamically is with *activity* not concentration. Activity is denoted with braces so that the activity of  $A^{z_A}$  would be written as  $\{A^{z_A}\}$ . The thermodynamic equilibrium constant,  $K^{\circ}_{\text{eq}}$ , for the reaction written above is, therefore, written

$$K^{\circ}_{\text{eq}} = \frac{\{C^{z_A+z_B}\}}{\{A^{z_A}\} \{B^{z_B}\}} \quad 2-2$$

The work of Debye and Hückel and those who followed has provided a correlation between activity and concentration.<sup>6</sup> To this end they have created the activity coefficient,  $\gamma$ , a factor that when multiplied by an agent's concentration will produce this more accurate depiction of the way that an agent behaves in solution. The relationship between an agent's molarity and its activity is simply

$$\{A^{z_A}\} = \gamma_{A^+} [A^{z_A}] \quad 2-3$$

The dependence of the activity coefficient on the electrical properties of the solvent and the composition of the solution is expressed in the *extended* form of Debye's and Hückel's equation.<sup>7</sup>

$$\log \gamma = -A \cdot z^2 \frac{\sqrt{\mu}}{1 + B \cdot a \sqrt{\mu}} \quad 2-4$$

The constants **A** and **B** each contain several constants including temperature and dielectric constant of the solvent. These values, for water, are found in Appendix I.  $\mu$  is the ionic strength of the solution,

$$\mu = \frac{1}{2} \sum M_i \cdot z_i^2 \quad 2-5$$

where  $M_i$  is the molarity of ion  $i$  in the solution.  $\mu$ , therefore, is somewhat a measure of charge density of the solution. Taking the solvent to be water and the temperature to be 25° C<sup>8</sup> and using values for **A** and **B** in Appendix I provides:

$$\log \gamma = -0.5115 \cdot z^2 \frac{\sqrt{\mu}}{1 + 0.3291 \cdot a \sqrt{\mu}} \quad 2-6$$

The remaining parameter in the equation is **a** which is the estimated, effective ionic radius of the solute ion expressed in Å (Appendix II). The values for **a** are typically given to one significant figure; they are, after all, estimates. This might seem to compromise the precision to which  $\gamma$  can be expressed, but not so. This point is illustrated in Example Problem 3.

Notice that **z** appears in two places: it is in the equation itself and is also embedded in  $\mu$  (2-5). For neutral (non ionic) agents **z** is zero;  $\log \gamma$ , therefore becomes zero and  $\gamma$  becomes exactly 1. This leads to an identity between molarity and activity for neutral solutes.

$$\{A^0\} = [A^0] \quad 2-7$$

For all reactions addressed in Chapter 1, where the reactants and products were neutral,  $K_{eq}$  was correctly expressed in terms of reactant and product molarities.

Although both the original and extended Debye-Hückel equations show that  $\gamma$  approaches 1 as  $\mu$  approaches zero, neither can adequately predict the relationship between  $\gamma$  and  $\mu$  when  $\mu$  exceeds about 0.1. An empirical equation, 2-8, has been offered by C.W. Davies.<sup>9</sup>

$$\log \gamma = -0.5 \cdot z^2 \left\{ \frac{\sqrt{\mu}}{1 + \sqrt{\mu}} - 0.15\mu \right\} \quad 2-8$$

This is a general equation with no adjustments for effective radius of the solute ions, but it does predict the increase in  $\gamma$  with increasing  $\mu$  which is observed for many ions. Equation 2-8 becomes decidedly more suitable than the extended Debye-Hückel equation when  $\mu$  exceeds about 0.2.

Given the relationship between concentration and activity, a relationship between  $K_{eq}$  and  $K_{eq}^\circ$  can be deduced. Combining 2-2 and 2-3 for the  $A + B \rightleftharpoons C$  reaction gives:

$$K_{eq}^\circ = \frac{\gamma_C [C^{zA+zB}]}{\gamma_A [A^{zA}] \gamma_B [B^{zB}]} \quad 2-9$$

and using 2-1 gives:

$$K_{eq}^\circ = \frac{\gamma_C K_{eq}}{\gamma_A \gamma_B} \quad 2-10$$

An outcome of the Debye-Hückel and Davies equation is that as  $\mu$  approaches zero,  $\gamma$  approaches 1, leading again to the identity between activity and molarity at low ionic strength. From 2-10, it should be apparent that in dilute solutions where  $\gamma \approx 1$ ,  $K_{eq}$  is a reasonable approximation to  $K_{eq}^\circ$ . This point will be illustrated near the end of this chapter.

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Inasmuch as thermodynamic tables typically report  $K_{eq}$  at  $\mu \leq 0.001$  where  $\gamma \approx 1$ , they are effectively reporting  $K^o_{eq}$ . It will be shown in Chapter 3 and every chapter thereafter that it is  $K_{eq}$ , not  $K^o_{eq}$  that is required to carry out ionic equilibrium calculations, and so, the necessary operation is to transform  $K^o_{eq}$  into  $K_{eq}$ . By rearranging 2-10, this transformation is

$$K_{eq} = \frac{\gamma_A \gamma_B K^o_{eq}}{\gamma_C} \quad 2-11$$

$\mu$ ,  $\gamma$  and ultimately  $K_{eq}$  can be calculated using Maple simply as a calculator. But Maple has the advantage over a common calculator in that it allows one to create an expression before making substitutions into that expression.

Before beginning to demonstrate the use of Maple for these calculations, a few of the most basic points on the operation of Maple are provided:

- Maple can operate in either of two modes, the document mode or the worksheet mode. They are switched by going to **File** in the menu, sliding down to **New** and then over to **Worksheet Mode or Document Mode**. The document mode is the default setting, probably because it is easier to use and it is prettier, but it is not conducive to instruction in Maple because it hides a lot of the details necessary for many operations. And so, the reader is asked to set Maple to default to the worksheet mode. To do this, in the menu, click on **Maple 17** (or whatever version of Maple that is running) and drag down to **Preferences**. On releasing the mouse a preferences window will open (Figure 2-1). Click on the **Interface** tab and from the new window select Worksheet Mode at the **Default format for new worksheets:** line. At the bottom of the window click on the [Apply Globally] button. Now, whenever Maple is opened or a new worksheet is requested, it will open in the worksheet mode.

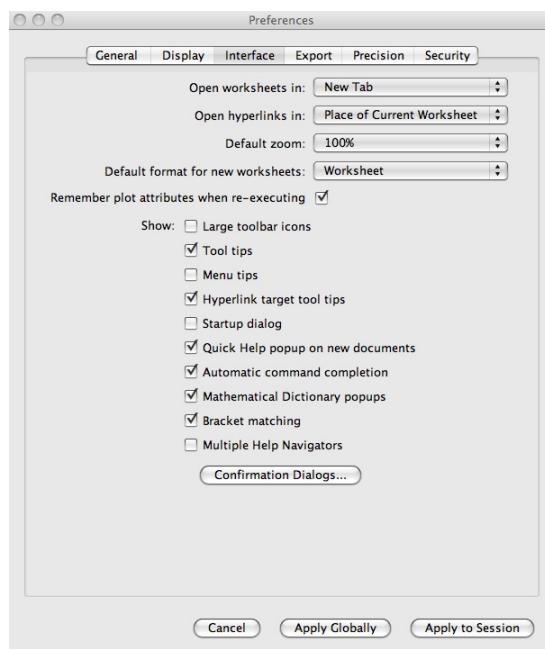


Figure 2-1

The worksheet mode is evident because it shows a [ > prompt for input (Figure 2-2) while the document mode is just a blank sheet with a flashing cursor.

Operating in the worksheet mode is not, alone, sufficient to make instruction clear. Within either mode there are two choices for input. These are Text and Math as seen as two buttons in Figure 2-2. Math is the default input and with that input, typing  $x^2$  will directly show  $x^2$ . This is fine for those who are familiar with programming input, but if this book were to instruct you to enter  $x^2$ , would you know to type  $x^2$ ? Would you know that  $x_a$  is achieved by typing  $x[a]$ ? In order to see input exactly as it must be entered rather than the *consequence* of what is entered, click on the Text button.



Figure 2-2

One can switch between Text and Math modes with the F5 key. Better yet, the default can be globally reset in the **Preferences** (described above) by going to the **Display** tab (Figure 2-3), changing **Input** display to Maple Notation.

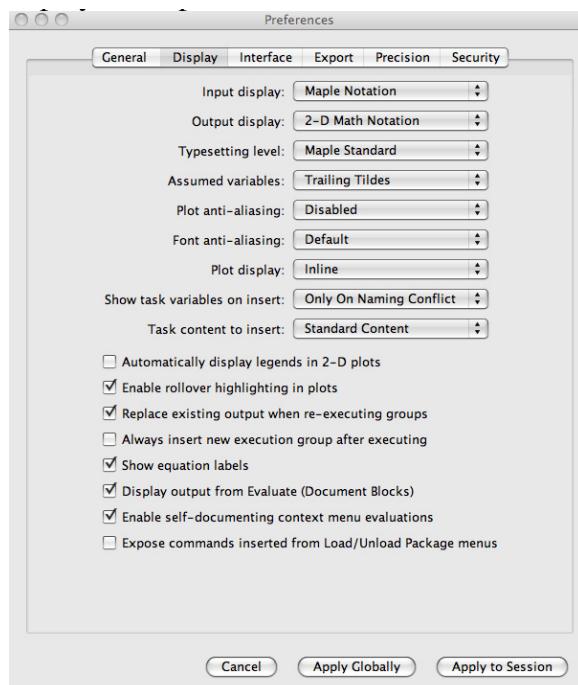


Figure 2-3

- In the worksheet mode, input is typed into Maple following its input prompt, >. You will notice that all input text illustrated throughout this book is red. This is a characteristic of Maple Input.

- Substitutions or definitions of terms are effected by using the assign operation “`:=`” which means “becomes.”<sup>10</sup> So `μ := 0.1` means that  $\mu^{11}$  becomes 0.1, and this will cause the value 0.1 to be substituted for *every* entry of  $\mu$  subsequent to execution of this statement. Even if the user should return to a point in the list of operations prior to this statement, Maple will “remember” that  $\mu$  is 0.1 and it will use that value wherever  $\mu$  is called. There are two ways to clear this definition: first, to undefine  $\mu$  by entering `μ := 'μ'`, or more generally by entering “restart.” Indeed, it is wise to begin every Maple session with the restart command to clear any unwanted definitions.
- Maple is case sensitive. So X and x will represent *different* parameters.
- In the worksheet mode, each input expression (definition, calculation *etc.*) must be followed by a semicolon or colon. If a semicolon is used, the subsequent output will be displayed in blue, standard math notation directly below its input. Using a colon after an expression will suppress the output display. The colon is used to save room on the page and is appropriate where the output is trivial or uselessly complicated. In programming, it is sometimes necessary to suppress what can be several pages of output. More on this in Chapter 7.  
By the way, the document mode does *not require* the colon or semicolon at the end of an input.
- Several statements can be strung together in one input paragraph as long as each is separated by a colon or semicolon. Then, with the [RETURN]<sup>12</sup> key, input is sent to Maple’s mathematical engine for interpretation.

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- Maple (in the text input mode) ignores spaces. So the space bar can (and should) be used to make input more intelligible. *One important exception* is encountered when  $e$  is used as an exponent:  $1e-14$  which means  $1\times 10^{-14}$  *cannot* be entered as  $1e -14$ .

Consider a calculation of the ionic strength (Equation 2-5) of a 0.025 M CaCl<sub>2</sub> solution. Presume that this is a strong electrolyte and therefore that it dissociates completely.



The mathematics of strong electrolyte equilibrium will be addressed in Chapter 3, but for now, suffice it to say that from a 0.025 M CaCl<sub>2</sub> solution, [Ca<sup>2+</sup>] will equal 0.025 M and [Cl<sup>-</sup>] will equal 0.050 M. Applying Equation 2-5 to this condition would produce:

$$\mu = \frac{1}{2} \{(0.025)(+2)^2 + (0.050)(-1)^2\} \quad 2-12$$

This is a trivial calculation by any means, but it will be carried out with Maple as demonstration and because it can be embedded in more extensive Maple worksheets where it is not so trivial. From a new worksheet we might begin:

```
> restart; [RETURN]13
> mu := (1/2)*(M[Ca]*z[Ca]^2 + M[Cl]*z[Cl]^2);14

$$\mu := \frac{1}{2} M_{\text{Ca}} z_{\text{Ca}}^2 + \frac{1}{2} M_{\text{Cl}} z_{\text{Cl}}^2$$

> M[Ca]:= 0.025; z[Ca]:= 2; M[Cl]:= 0.05; z[Cl]:= -1; mu;

$$M_{\text{Ca}} := 0.0250000000$$


$$z_{\text{Ca}} := 2$$


$$M_{\text{Cl}} := 0.0500000000$$


$$z_{\text{Cl}} := -1$$


$$0.0750000000$$

```

Several Maple operations and features are compiled in Appendix (VIII). In this example, notice that the braces in 2-12 were not used in the Maple input. This is because Maple uses braces specifically to enclose sets. Notice that the (square) brackets used for Maple input are not part of a mathematical operation: here, they simply produce a subscript to a parameter, but we shall see also that they are used to enclose lists. Finally, although the components of Equation 2-12 are ionic, it is impractical to attach + and - charges in the input because these are mistaken for arithmetic operations.

Speaking of operations, the most common errors in creating input are using `=` where `:=` is required and forgetting to insert `*` in the multiplication operation.<sup>15</sup>

Notice the excessive, ten decimal place, precision given for  $M_{Ca}$ ,  $M_{Cl}$  and  $\mu$ . The remedy is to access the **Precision** tab (Figure 2-4 which is found under **Maple Preferences**). From that tab change *only the display* (Round screen display to) to four decimal places, and while this tab is open go ahead and change (Round calculations to), to *at least* 14 significant digits, and then [Apply Globally]. Given the precision of any input presented here, this screen display is *more* than adequate, but with some calculations that follow (Problem 3, Chapter 3), rounding calculations to “only” ten significant figures will cause round off errors. Output precision should not be set with the “**Digits := n**” command which sets the number,  $n$ , of digits Maple uses to carry out calculations with software floating point numbers. (The default value for Digits is 10.)

To see how this change affects the output, we can enter `mu := mu`<sup>16</sup> rather than  $\mu$ ; alone.

```
> mu := mu;
```

$$\mu := 0.07500$$

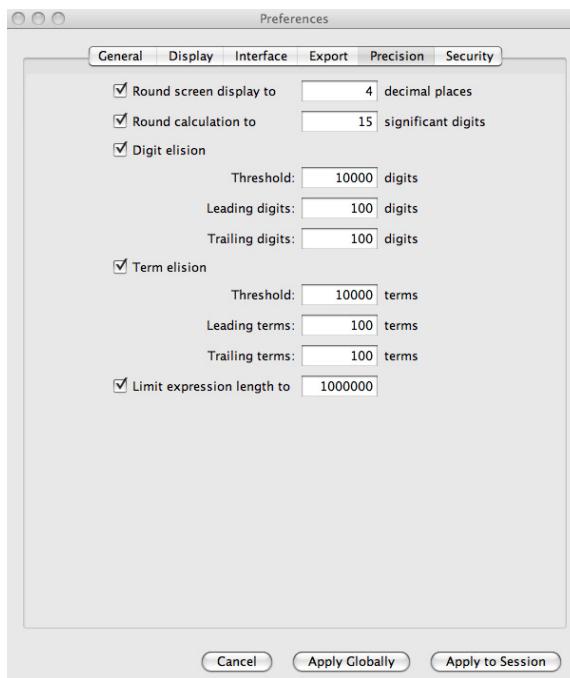


Figure 2-4

Continuing the worksheet from here, the activity coefficients, and activities for  $Ca^{2+}$  and  $Cl^-$  can be calculated. The extended Debye-Hückel equation (2-6) will be used, but it requires a knowledge of the estimated ionic radii. From Appendix II,  $a$  for  $Ca^{2+}$  is 6, and  $a$  for  $Cl^-$  is 3. From here there are many possible approaches: one could first enter an  $a_{Ca}$  and  $a_{Cl}$  and then later assign numerical values to them the same way  $z_{Ca}$  and  $z_{Cl}$  were handled in the previous example. Also, one could “do the algebra” to express each  $\gamma$  explicitly, for example as

$$\gamma = 10 \quad \left\{ \frac{-0.511 \cdot z^2 \sqrt{\mu}}{1 + 0.329 \cdot a \sqrt{\mu}} \right\} \quad 2-13$$

but the example below will assign  $a_{Ca}$  and  $a_{Cl}$  and  $\gamma$  will not be written explicitly. By this approach we will illustrate the consequences of assigning values to parameters *a priori*, and we can demonstrate how  $\gamma$  can be extracted from its implicit expression (2-6). So, continuing with the worksheet:

```
> Gamma[Ca]:= log[10](g[Ca]) = -0.511*z[Ca]^2*sqrt(mu) /  
(1+ 0.329*6*sqrt(mu)); Gamma[Cl]:= log[10](g[Cl]) = -0.5115*z[Cl]  
^2*sqrt(mu) / (1+0.3291*3*sqrt(mu));
```

$$\Gamma_{Ca} := \frac{\ln(g_{Ca})}{\ln(10)} = -0.3634$$

$$\Gamma_{Cl} := \frac{\ln(g_{Cl})}{\ln(10)} = -0.1103$$

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Because  $\gamma$  (*i.e.* gamma in lower case) is a mathematical function, it is not possible, in Maple, to use lower case gamma[ ] for activity coefficients. Notice that it is necessary to stipulate the base of the logarithmic operation. The square brackets [10] are not required, but are recommended for clarity. `Gamma[Ca]:=log(g[Ca]) = -0.511*z[Ca]^2*sqrt(mu)/(1+0.329*6*sqrt(mu));` would have returned  $\Gamma_{\text{Ca}} := \ln(g_{\text{Ca}}) = -0.3634$ . Finally, notice how Maple automatically did the necessary arithmetic with the 0.511, 0.329, a, z and  $\sqrt{\mu}$  to give **-0.3634** and **-0.1102**.

The final calculation will require a *value* for each  $\Gamma$ . So each  $\Gamma$  is solved for its “g.” The `fsolve` function will generate a numerical (floating point arithmetic) solution to its argument. Here, Maple is instructed that  $\Gamma_{\text{Ca}}$  (and  $\Gamma_{\text{Cl}}$ ) are to *become* the floating point solutions to the expressions that were previously assigned. Of course, these are numerical values, because `fsolve` can produce only numeric solutions (*i.e.* no symbolic solutions).

```
> Gamma[Ca] := fsolve(Gamma[Ca], g[Ca]); Gamma[Cl] := fsolve(Gamma[Cl], g[Cl]);
```

$$\begin{aligned}\Gamma_{\text{Ca}} &:= 0.4332 \\ \Gamma_{\text{Cl}} &:= 0.7758\end{aligned}$$

With numerical values for the  $\gamma$ s, the activity of  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  can be obtained with one more input line (two expressions)

```
> A[Ca]:= Gamma[Ca]*M[Ca]; A[Cl]:= Gamma[Cl]*M[Cl];
```

$$\begin{aligned}A_{\text{Ca}} &:= 0.0108 \\ A_{\text{Cl}} &:= 0.0388\end{aligned}$$

At this point we will regress to the suggestion that the algebra be carried out to convert the implicit expression for  $\gamma$  into an explicit form like 2-13. For that, it will be necessary to express  $\Gamma_{\text{Ca}}$  and  $\Gamma_{\text{Cl}}$  explicitly in terms of  $\mu$ , and that will require unassigning  $\mu$  (from 0.07500). First,  $\mu$  is unassigned; then each  $\gamma$  is assigned (becomes) the solution of the expression for that  $\gamma$  ( $\Gamma$ ) in terms of  $\mu$  which is now a variable. Then it will be possible to demonstrate the plotting feature of Maple.

```
> mu := 'mu'; Gamma[Ca] := solve(log[10](g[Ca]) = -0.511*z[Ca]^2*sqrt(mu)/(1+0.329*6*sqrt(mu)), g[Ca]); Gamma[Cl] := solve(log[10](g[Cl]) = -0.511*z[Cl]^2*sqrt(mu)/(1+0.329*3*sqrt(mu)), g[Cl]);
```

$$\mu := \mu$$

$$\Gamma_{\text{Ca}} := e^{-\frac{2353.2420 \sqrt{\mu}}{500.0000 + 987.0000 \sqrt{\mu}}}$$

$$\Gamma_{\text{Cl}} := e^{-\frac{1176.6210 \sqrt{\mu}}{1000.0000 + 987.0000 \sqrt{\mu}}}$$

The second expression in the input says that  $\Gamma_{\text{Ca}}$  “becomes” the solution of:

$$\log_{10}\gamma_{\text{Ca}} = \frac{-0.511X^2 X \sqrt{\mu}}{1 + 0.329 \cdot 6 \sqrt{\mu}} \quad 2-14$$

for  $\gamma_{\text{Ca}}$  in terms of  $\mu$ .<sup>17</sup> The `solve` command was used here because the equation to be solved (for `g[Ca]`) contains a symbolic variable ( $\mu$ ) which `fsolve` cannot handle. While `fsolve` numerically solves an equation, `solve` symbolically solves equations and that allows for symbolic variables in equations.

With each  $\Gamma$  explicitly expressed, it is simply a matter of plotting  $\Gamma_{\text{Ca}}$  (and  $\Gamma_{\text{Cl}}$ ) as a function of  $\mu$  over a specified range. To plot these expressions one might enter:

```
> plot([Gamma[Ca], Gamma[Cl]], mu=0..0.5, color =[blue, red]);
```

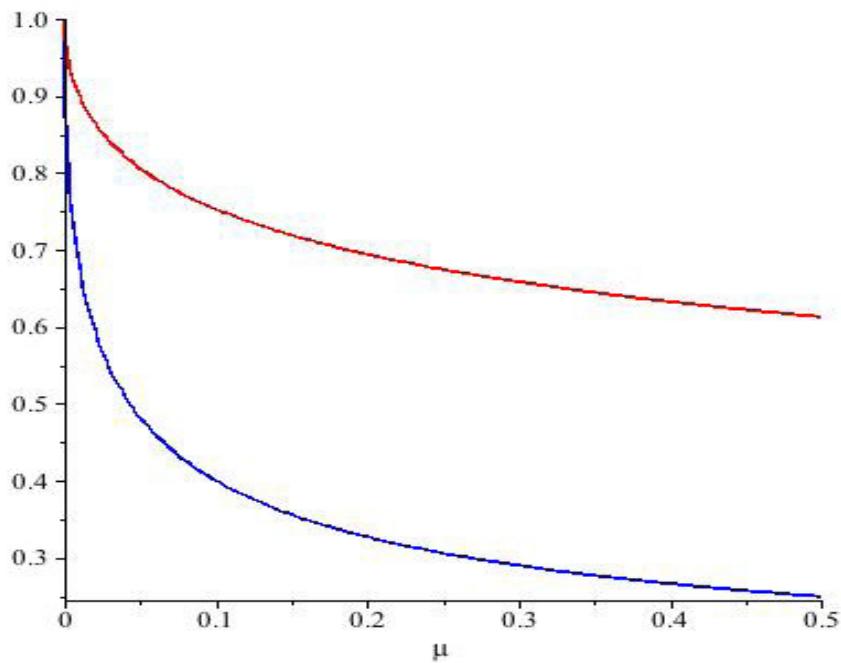


Figure 2-5

More details on the plotting function are contained in Appendix VIII and in examples below. Notice that square brackets are used in this function to enclose lists, the list of expressions to be plotted and the list of colors to be used for those plots. The list of colors is unnecessary because Maple will, by default, use multiple colors when multiple expressions are plotted. However, when Maple chooses the colors, which expression goes with which color is not indicated. When the user chooses colors and places the list of colors in square brackets, the list of colors follows (corresponds to) the list of expressions.<sup>18</sup>

Most of the plot manipulations can be handled after the plot is rendered. Use the mouse to move the cursor into the plot field where it will change to a circle with vertical and horizontal ticks.<sup>19</sup> Clicking the mouse within the plot will cause a menu to appear at the top of the worksheet as shown in Figure 2-6. From these icons one can manipulate the plot without returning to the worksheet to change parameters.



Figure 2-6

The final point of this chapter is to demonstrate how equilibrium constants can be corrected for ionic strength. In order to mimic the  $A + B \rightleftharpoons C$  reaction at the beginning of this chapter, consider:



The equilibrium constant for this reaction is 501. This value refers to a solution of “zero” ionic strength, and therefore it is  $K_{eq}^\circ$ . The conversion, therefore, requires:

$$K_{eq}^\circ = \frac{\{AgCl\}}{\{Ag^+\}\{Cl^-\}}$$
 2-15

$$K_{eq}^\circ = \frac{\gamma_{AgCl}[AgCl]}{\gamma_{Ag}[Ag^+]\gamma_{Cl}[Cl^-]}$$
 2-16

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$$K_{\text{eq}}^{\circ} = \frac{\gamma_{\text{AgCl}}}{\gamma_{\text{Ag}} \gamma_{\text{Cl}}} K_{\text{eq}} \quad 2-17$$

$$K_{\text{eq}} = \frac{\gamma_{\text{Ag}} \gamma_{\text{Cl}}}{\gamma_{\text{AgCl}}} K_{\text{eq}}^{\circ} \quad 2-18$$

Inasmuch as AgCl is neutral,  $\gamma_{\text{AgCl}}$  will be exactly 1 according to 2-4 or 2-8, and it can be left out of the conversion altogether. What follows is the derivation of an expression for  $K_{\text{eq}}^{\circ}$  in terms of  $\mu$  and a plot of that expression *vs.*  $\mu$ . From Appendix II it can be found that for  $\text{Ag}^+$   $a = 2.5$ , and as already noted  $a = 3$  for  $\text{Cl}^-$ . There are countless ways to derive this expression, but what follows will preview the approach that will be used in chapters to come: it will allow the expression to evolve. We begin:

```
> restart; K[eq] := K[eq]^21 * Gamma[Ag] * Gamma[Cl];
```

$$K_{\text{eq}} := K_{\text{eq}}^{\circ} \Gamma_{\text{Ag}} \Gamma_{\text{Cl}}$$

```
> Gamma[Ag] := solve(log[10](Gamma[Ag]) = -0.511*(1)^2*sqrt(mu) / (1 + 0.329*2.5*sqrt(mu)), Gamma[Ag]); Gamma[Cl] := solve(log[10](Gamma[Cl]) = -0.511*(-1)^2*sqrt(mu) / (1 + 0.329*3*sqrt(mu)), Gamma[Cl]); K[eq]:= 501; K[eq];
```

$$\begin{aligned} \Gamma_{\text{Ag}} &:= e^{-\frac{470.6484 \sqrt{\mu}}{400.0000 + 329.0000 \sqrt{\mu}}} \\ \Gamma_{\text{Cl}} &:= e^{-\frac{1176.6210 \sqrt{\mu}}{1000.0000 + 987.0000 \sqrt{\mu}}} \\ K_{\text{eq}}^{\circ} &:= 501 \\ 501 e^{-\frac{470.6484 \sqrt{\mu}}{400.0000 + 329.0000 \sqrt{\mu}}} &- \frac{1176.6210 \sqrt{\mu}}{1000.0000 + 987.0000 \sqrt{\mu}} \end{aligned}$$

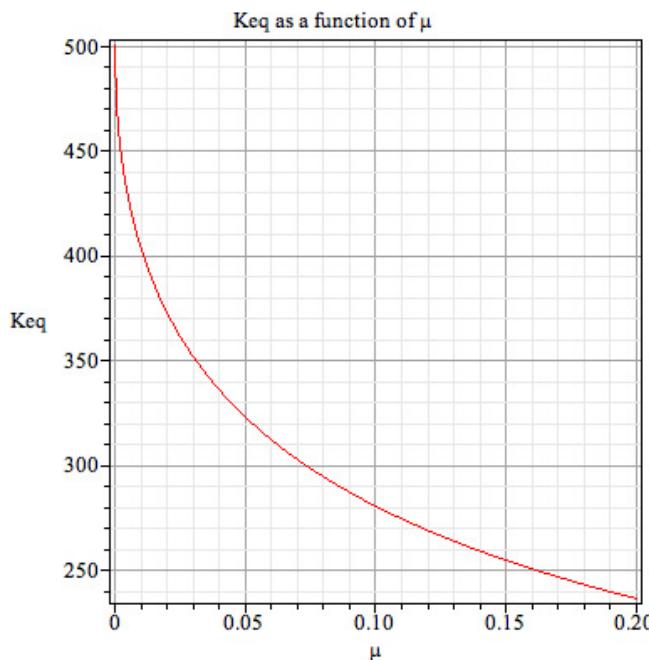
The last output (above) can be expressed more simply by using the simplify ( $K_{\text{eq}}$ ) input rather than  $K_{\text{eq}}$  that was used.

```
> simplify(K[eq]);
```

$$501 e^{-\frac{1.0000 \cdot 10^{-19} \sqrt{\mu} (9.4130 \cdot 10^{24} + 8.5164 \cdot 10^{24} \sqrt{\mu})}{(400.0000 + 329.0000 \sqrt{\mu}) (1000.0000 + 987.0000 \sqrt{\mu})}}$$

Either form of  $K_{eq}$  will work in the following exercise. It will show more features of the plot command, for example the ability to customize the axes and to specify axes labels and a title from the worksheet (rather than from the plot menu described above). The order of these specifications is flexible, but the order of the axes labels must be abscissa first and ordinate second.

```
> plot(K[eq], mu=0..0.2, labels = ["μ", "Keq"], title= "Keq as a function of μ", axes = box, gridlines = true22);
```



**Figure 2-7**

Before proceeding to worked examples of these problems, a few comments should be made regarding the plot of  $K_{eq}$  vs.  $\mu$ . Recall from Chapter 1, that a  $K_{eq} \gg 1$  implies that, at equilibrium, there is a preponderance of products and so reactants are largely consumed. As  $K_{eq}$  increases further, the further the reaction lies further to the right and reactants are even more thoroughly consumed. The plot above shows that this equilibrium constant, when the ionic strength reaches 0.16, is about half as large as it was when the ionic strength was zero. Specifically, then the association of  $\text{Ag}^+$  and  $\text{Cl}^-$  to  $\text{AgCl(aq)}$  is impaired in the presence of (spectator) ions in solution because those spectator ions increase  $\mu$  and that diminishes  $K_{eq}$ .

Does this make sense? Consider: if the solution becomes more crowded with ions (increasing  $\mu$ ), the  $\text{Ag}^+$  and  $\text{Cl}^-$  ions can be shielded from each other. This makes it more difficult for them to combine, thereby impairing their association. This creates an effectively smaller  $K_{eq}$ .

### Example Problems

- Calculate the ionic strength of a solution that is 0.015 M in  $\text{Na}_2\text{SO}_4$  and 0.025 M in  $\text{NaNO}_3$  assuming that both solutes are strong electrolytes.
- Compare the extended Debye-Hückel model (2-6) with the Davies model (2-8) by plotting  $\gamma$  vs.  $\mu$  from  $\mu = 0$  to 0.50. For  $\gamma$ , presume that  $z = \pm 2$  and that  $a = 5$ .
- Illustrate the effect of the uncertainty in  $a$ , the estimated ionic radius, by calculating  $\gamma$  at  $a = 2.0$  and 2.5, at  $\mu = 0.25$  and 0.001, and at  $z = \pm 1$ , using Debye-Hückel.
- Consider the association of  $\text{Zn}^{2+}$  with  $\text{OH}^-$  to form the  $\text{ZnOH}^{1+}$  complex,  
$$\text{Zn}^{2+} + \text{OH}^- \rightleftharpoons \text{ZnOH}^+$$

Taking  $a_{\text{Zn}} = 6$ ,  $a_{\text{OH}} = 3.5$ ,  $a_{\text{ZnOH}} = 4.5$  and  $K_{\text{eq}}^\circ = 2.5 \times 10^4$  and using the extended Debye-Hückel equation (2-6),

- calculate  $\gamma_{\text{Zn}}$  and  $\gamma_{\text{OH}}$  at  $\mu = 0.045$
- calculate the  $K_{\text{eq}}$  for this reaction at  $\mu = 0.045$ .
- create a plot of  $K_{\text{eq}}$  vs.  $\mu$  for  $\mu = 0$  to 0.030.

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## Solutions to Example Problems

1. Because these are strong electrolytes, each will dissociate  $\approx 100\%$ . Consequently,  $[Na^+] = (2 \times 0.015 \text{ M}) + (1 \times 0.025 \text{ M}) = 0.055 \text{ M}$ ,  $[SO_4^{2-}] = 1 \times 0.015 \text{ M} = 0.015 \text{ M}$ , and  $[NO_3^-] = 0.025 \text{ M}$ .

$$\mu = \frac{1}{2} \{ [(0.055)(+1)^2] + [(0.015)(-2)^2] + [(0.025)(-1)^2] \} = 0.070.$$

Solving this with Maple might look like the following.

```
> restart; C[Na2SO4]:= 0.015; C[NaNO[3]]:= 0.025; mu := (1/2)
  * (M[Na]* (1)^2 + M[SO[4]]*2^2 + M[NO[3]]*(-1)^2);23

C_Na2SO4 := 0.0150
C_NaNO3 := 0.0250
mu := 1/2 M_Na + 2 M_SO4 + 1/2 M_NO3

> M[Na] := 2*C[Na2SO4] + C[NaNO[3]]; M[SO[4]] := C[Na2SO4];
M[NO[3]] := C[NaNO[3]]; mu := mu;

M_Na := 0.0550
M_SO4 := 0.0150
M_NO3 := 0.0250
mu := 0.0700
```

This solution might seem a bit circuitous, but it is intended to offer flexibility: by assigning  $M_{Na}$  etc. in terms of  $C_{Na2SO4}$  etc. it is possible to recalculate  $\mu$  by entering new values for  $C_{Na2SO4}$  and  $C_{NaNO_3}$ . *But be advised:* it will not suffice to enter simply:

```
> C[Na2SO4]:= 0.050; C[NaNO[3]]:= 0.075;
mu:=(1/2) * (M[Na]* (1)^2 + M[SO[4]]*2^2 + M[NO[3]]*(-1)^2);
```

Why not? Because  $\mu$  is calculated not from  $C_{NaNO_3}$  and  $C_{Na2SO4}$  but rather from  $M_{Na}$ ,  $M_{SO_4}$  and  $M_{NO_3}$  which Maple has been previously told to set at 0.055, 0.015 and 0.025 M, and it will not forget that until new values are provided. This can be done by inserting<sup>24</sup>

```
M[Na]:= 2*C[Na2SO4] + C[NaNO[3]]; M[SO[4]]:= C[Na2SO4];
M[NO[3]]
:= C[NaNO[3]]; before mu:=(1/2) * (M[Na]* (1)^2 + M[SO[4]]*2^2 +
M[NO[3]]*(-1)^2);
```

So, using the colon to prevent *some* of the output, try:

```
> C[Na2SO4]:= 0.050: C[NaNO[3]]:= 0.075: M[Na] := 2*C[Na2SO4]
+ C[NaNO[3]]; M[SO[4]] := C[Na2SO4]; M[NO[3]] :=
C[NaNO[3]]; mu := (1/2)*(M[Na]* (1)^2 + M[SO[4]]^2 + M
[NO[3]])^(-1)^2;
```

2. This approach is like that used to illustrate the effect of  $\mu$  on  $K_{eq}$  for AgCl(aq) formation. But here, we will write each gamma directly as an exponent (of 10). For example 2-13 for the extended Debye-Hückel.

```
> restart; Gamma[DH]:= 10^(-0.511*2^2*sqrt(mu)/(1 + 0.329*5*
sqrt(mu))); Gamma[Dvs]:= 10^(0.5*2^2*((sqrt(mu)/(1 +
sqrt(mu)) + 0.15*mu));25
```

$$\Gamma_{DH} := 10^{-\frac{2.0440 \sqrt{\mu}}{1 + 1.6450 \sqrt{\mu}}}$$

$$\Gamma_{Dvs} := 10^{-\frac{2.0000 \sqrt{\mu}}{1 + \sqrt{\mu}} - 0.3000 \mu}$$

```
> Gamma[DH]:= solve(Gamma[DH], g[DH]); Gamma[Dvs]:= solve
(Gamma[Dvs], g[Dvs]);
```

We can now create a plot of these two models.

```
> plot([Gamma[DH], Gamma[Dvs]], mu = 0..0.5);
```

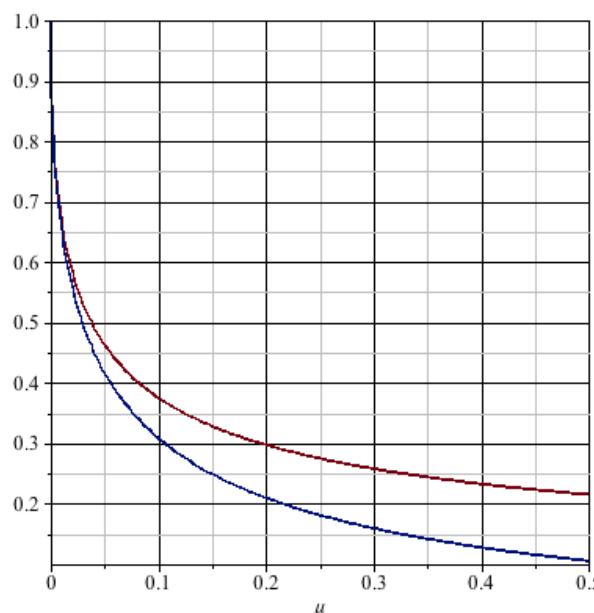


Figure 2-8

Grid lines can be added from the **Plot** menu.

The apparent discrepancy between the two models is remarkable: The Davies equation projects  $\gamma$  at  $\mu = 0.5$  to be more than twice what it would be according to extended Debye-Hückel! This point can be verified by clicking on the graph, setting the cursor to the point probe (the default which is a circle with cross hairs), and from the plot menu selecting the function of the point probe as shown below. With this setting the  $x$  and  $y$  coordinates are displayed for any location of the cursor on the plot.

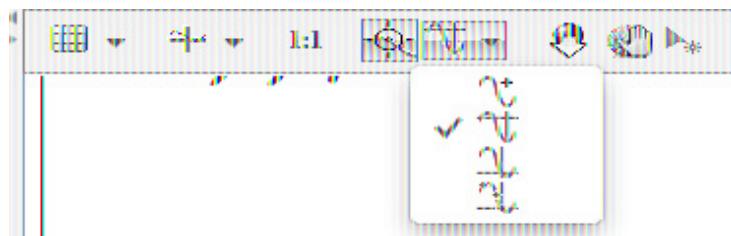


Figure 2-9

The difference between the models is magnified by the ionic valence: replacing  $z = 2$  with  $z = 1$  will illustrate this point. Also, the Davies equation presumes that  $a = 4.6$  for all ions. So using  $a = 5$  which is  $\approx 4.6$  mitigated the difference between the two models.

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2. This calculation is simply the application of the **Gamma [DH]** part of Problem 3 but with four specific pairs of  $a$  and  $\mu$ . But here we will directly assign each Gamma explicitly, that is, by extracting them from the log expression. In Chapter 3 we will streamline Maple operations by learning to substitute values into input expressions, but at this point we will replicate an expression for  $\gamma$  (by cutting and pasting, of course) and then add the appropriate values for  $a$  and  $\mu$ . We will use subscripts to differentiate the four gammas

```
> restart; Gamma[a=2, mu=0.25] := 10^(-0.511*1*sqrt(.25)/(1+0.329*2.0*sqrt(.25))); Gamma[a=2.5, mu=0.25] := 10^(-0.511*1*sqrt(.25)/(1+0.329*2.5*sqrt(.25))); Gamma[a=2, mu=0.001] := 10^(-0.511*1*sqrt(.001)/(1+0.329*2.0*sqrt(.001))); Gamma[a=2.5, mu=0.001]:=10^(-0.511*1*sqrt(.001)/(1+0.329*2.5*sqrt(.001)));
```

$$\begin{aligned}\Gamma_{a=2, \mu=0.2500} &:= 0.6423 \\ \Gamma_{a=2.5, \mu=0.2500} &:= 0.6591 \\ \Gamma_{a=2, \mu=0.0010} &:= 0.9642 \\ \Gamma_{a=2.5, \mu=0.0010} &:= 0.9644\end{aligned}$$

$a$  set equal to 2.0 or 2.5 implies an eleven percent uncertainty (*i.e.*  $a = 2.25 \pm 0.25$ ), but the resulting  $\gamma$ s differ by only 2.6% at  $\mu = 0.25$  and at  $\mu = 0.001$ , they differ by only 0.02%.

The point here is that it is not necessary to know  $a$  to more than one decimal place because  $\gamma$  is not significantly affected.

3. a.  $\gamma_{Zn}$  and  $\gamma_{OH}$  can be calculated in two illustrative steps as shown in a previous example.

```
> restart; g[Zn]:=10^(-0.511*2^2*sqrt(mu)/(1+0.329*6*sqrt(mu))); g[OH]:=10^(-0.511*(-1)^2*sqrt(mu)/(1+0.329*3.5*sqrt(mu)));
```

$$\begin{aligned}g_{Zn} &:= 10^{-\frac{2.0440\sqrt{\mu}}{1+1.9740\sqrt{\mu}}} \\ g_{OH} &:= 10^{-\frac{0.5110\sqrt{\mu}}{1+1.1515\sqrt{\mu}}}\end{aligned}$$

Seeing that each expression is correctly entered, we proceed with:

```
> mu := 0.045; g[Zn] := g[Zn]; g[OH] := g[OH];
```

$$\begin{aligned}\mu &:= 0.0450 \\ g_{\text{Zn}} &:= 0.4947 \\ g_{\text{OH}} &:= 0.8182\end{aligned}$$

Of course a lot of input and output could have been saved at the price of being able to check the expressions for accuracy. For example, the  $\gamma$ s can be obtained with only one paragraph of input.

```
> restart; mu := 0.045; g[Zn] := 10^(-0.511*2^2*sqrt(mu)) / (1 + 0.329*6*sqrt(mu)); g[OH] := 10^(-0.511*(-1)^2 *sqrt(mu)) / (1 + 0.329*3.5*sqrt(mu));
```

$$\begin{aligned}g_{\text{Zn}} &:= 0.4947 \\ g_{\text{OH}} &:= 0.8182\end{aligned}$$

4. b. Modifying the **2-18** expression to suit this  $\text{ZnOH}^+$  problem gives:

$$K_{\text{eq}} = \frac{\gamma_{\text{Zn}^{2+}} \gamma_{\text{OH}^-} K^{\circ}_{\text{eq}}}{\gamma_{\text{ZnOH}^+}}$$

In this problem, unlike what is shown in Equation **2-18**, all agents are charged. So none of the activity coefficients can be taken to be 1. That is,  $\gamma_{\text{ZnOH}}$  will be needed along with  $\gamma_{\text{Zn}^{2+}}$  and  $\gamma_{\text{OH}^-}$ . To continue with the economical input above:

```
> g[ZnOH] := 10^(-0.511*(1)^2 *sqrt(mu)) / (1 + 0.329*4.5*sqrt(mu)); K^{\circ}[\text{eq}] := 2.5e4; K[\text{eq}] := g[Zn]*g[OH]*K^{\circ}[\text{eq}]/g[ZnOH];
```

$$\begin{aligned}g_{\text{ZnOH}} &:= 0.08270 \\ K^{\circ}_{\text{eq}} &:= 25000.0000 \\ K_{\text{eq}} &:= 12237.5103\end{aligned}$$

4.c. In order to create a plot of  $K_{\text{eq}}$  vs.  $\mu$  with  $K_{\text{eq}}$  and  $\mu$  already assigned to an expression and value, respectively, it is more efficient to start over altogether.<sup>26</sup> So begin the next paragraph with restart and proceed. **Fctr**<sup>27</sup> will become the ratios of the three  $\gamma$ s.

```
> restart; K[eq]:= Fctr*K°[eq]; g[Zn] :=10^(-0.511*2^2*sqrt
(μ)/(1 + 0.329*6*sqrt(μ))); g[OH] := 10^(-0.511*(-1)^2*sqrt(μ)/
(1 + 0.329*3.5*sqrt(μ))); g[ZnOH] := 10^(-0.511*(1)^2*sqrt(μ)/(
1 + 0.329*4.5*sqrt(μ))); Fctr := g[Zn]*g[OH]*K°[eq]/g[ZnOH];
```

$$K_{eq} := Fctr \ K°_{eq}$$

$$g_{Zn} := 10^{-\frac{2.0440 \sqrt{\mu}}{1 + 1.9740 \sqrt{\mu}}}$$

$$g_{OH} := 10^{-\frac{0.5110 \sqrt{\mu}}{1 + 1.1515 \sqrt{\mu}}}$$



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$$Fctr := \frac{10^{-\frac{2.0440 \sqrt{\mu}}{1 + 1.9740 \sqrt{\mu}}} 10^{-\frac{0.5110 \sqrt{\mu}}{1 + 1.1515 \sqrt{\mu}}} K^{\circ}_{eq}}{10^{-\frac{0.5110 \sqrt{\mu}}{1 + 1.4805 \sqrt{\mu}}}}$$

And for a little clarity:

```
> K°[eq]:= 2.5e4: Fctr:= simplify(Fctr);
```

*Fctr := 2.50*

$$\times 10^4 - \frac{1.00 \times 10^{-15} \sqrt{\mu} (9.41 \times 10^{24} + 2.55 \times 10^{25} \sqrt{\mu} + 1.76 \times 10^{25} \mu)}{e^{(5.00 \times 10^2 + 9.87 \times 10^2 \sqrt{\mu}) (2.00 \times 10^3 + 2.30 \times 10^3 \sqrt{\mu}) (2.00 \times 10^3 + 2.96 \times 10^3 \sqrt{\mu})}}$$

Arguably, this is *not* a simplified representation of *Fctr*. Notice the change in the numeric formatting. This was done to clarify the output. It was achieved by clicking on the output; going to **Format** at the top of the screen; dragging down to **Numeric Formatting...**<sup>28</sup> and making the changes illustrated below. The **Minimum Exponent Digits** can be set to 0 in some cases. This adjustment to numeric formatting was also used after the plot in Figure 2-11 was created, by clicking on the plot and going to **Format** as described above.

Figure 2-12

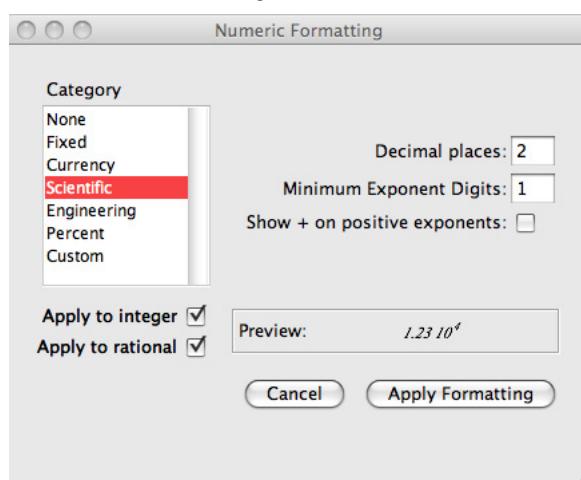


Figure 2-10

Now to create the plot:

```
> plot(K[eq], mu = 0..0.03);
```

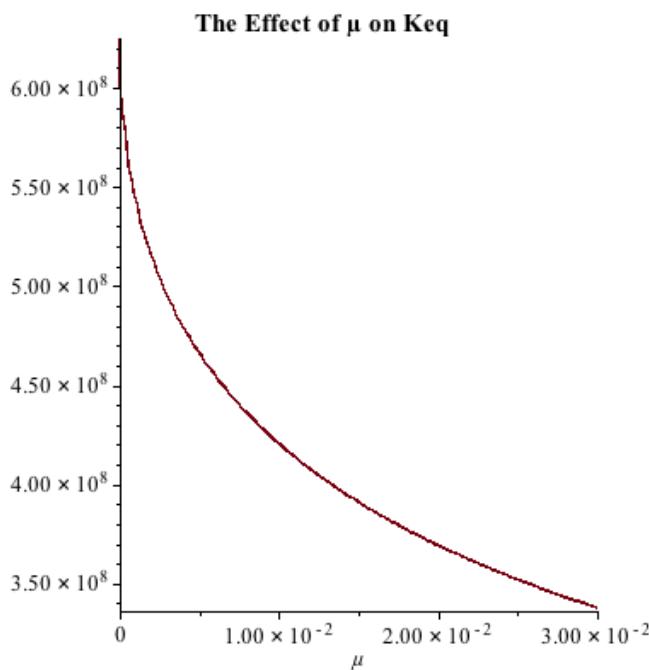


Figure 2-11

Clearly,  $K_{eq}$  is strongly affected by  $\mu$ .

The title was added *after* the plot was rendered by accessing the **Plot** menu, sliding down to **Title** and over to **Add Title** where, for input, a New Title box opens above the plot. While editing that box, the font formatting tools in the menu bar can be used on the title.

# 3 Strong Electrolytes, pH and the Mathematics of Ionic Equilibrium

The first step in solving an ionic equilibrium problem is recognizing the nature of a solute. Consider again the association / dissociation reaction from Chapter 2.



Although not expressly stated, the presumption is that this reaction occurs in solution.<sup>29</sup> The degree to which the association proceeds (*i.e.* to the right) is expressed with an equilibrium constant,  $K_{eq}$ , where

$$K_{eq} = \frac{[C^{zA+zB}]}{[A^{zA}][B^{zB}]} \quad 3-1$$

The relationship between the magnitude of  $K_{eq}$  and the degree to which the reaction proceeds to the right or left was discussed in Chapter 1. But for some ionic solutes, dissociation (right to left) is presumed to be so complete that  $K_{eq}$  is not needed to calculate the concentrations of  $A^{zA}$  and  $B^{zB}$ : it is simply and accurately presumed that “all” of  $C^{zA+zB}$  is converted to  $A^{zA}$  and  $B^{zB}$ . First, when is this presumption safe, and second, how is the extent dissociation articulated mathematically?

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Many ion pairs have been observed to form compounds that “totally” dissociate in aqueous solutions.<sup>30</sup> The list of cations is simple: it includes the ions of the Group IA and Group IIA elements, less Be<sup>2+</sup> and Mg<sup>2+</sup>. Charge density appears to be the defining criterion, because the smaller ions with higher charges are less likely to exist in solution in their ionic form.<sup>31</sup> This factor prevails as well with anions; for example Cl, Br, and I<sup>-</sup> are on the list, but not F<sup>-</sup>. The list below is not exhaustive: it is restricted to those ions most commonly encountered in analytical applications.

Cations	Anions
Ba <sup>2+</sup>	Br <sup>-</sup>
Ca <sup>2+</sup>	Cl <sup>-</sup> , ClO <sub>3</sub> <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup>
H <sup>+</sup>	HSO <sub>4</sub> <sup>-</sup> , SO <sub>4</sub> <sup>2-</sup>
K <sup>+</sup>	I <sup>-</sup> , IO <sub>3</sub> <sup>-</sup>
Li <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>
Mg <sup>2+</sup>	OH <sup>-</sup>
Na <sup>+</sup>	

**Table 3-1**

From this list of seven *common* cations and ten *common* anions seventy, simple combinations can be created and nearly all are strong electrolytes. The most important exception is H<sup>+</sup> + OH<sup>-</sup>. This constitutes H<sub>2</sub>O, a molecule that shows much less than 0.001% dissociation into H<sup>+</sup> and OH<sup>-</sup>, a point that will be explored later in this chapter. Another exception with H<sup>+</sup> is its association with SO<sub>4</sub><sup>2-</sup> to form the HSO<sub>4</sub><sup>-</sup> ion which does not “completely” dissociate back into H<sup>+</sup> and SO<sub>4</sub><sup>2-</sup> when it is dissolved in water.

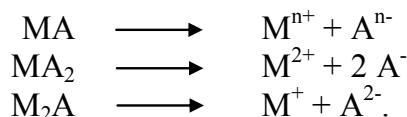
Eight other combinations lead to compounds that also are not strong electrolytes. They are weak electrolytes because, in even modest concentrations, they are not freely soluble. The following table identifies those combinations from the previous table that are insoluble (I) or sparingly soluble (SS).<sup>32</sup>

	ClO <sub>4</sub> <sup>-</sup>	IO <sub>3</sub> <sup>-</sup>	OH <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
Ba <sup>2+</sup>		I		I
Ca <sup>2+</sup>	SS	SS		I
Mg <sup>2+</sup>			I	
K <sup>+</sup>	SS	SS		

**Table 3-2**

This leaves sixty strong electrolytes, but of course there are many more when less common cations and anions are considered. Nevertheless, these sixty compounds are the answer to the question, when is it safe to presume total dissociation.

All sixty examples can be characterized by one of the following reactions:



The simple arrow is used because the reaction is taken to be 100% to the right, even at large concentrations of these solutes. The three, respective, equilibrium constants would be:

$$K_{\text{eq}} = \frac{[\text{M}^{n+}][\text{A}^{n-}]}{[\text{MA}]} \quad 3-2$$

$$K_{\text{eq}} = \frac{[\text{M}^{2+}][\text{A}^-]^2}{[\text{MA}_2]} \quad 3-3$$

and,

$$K_{\text{eq}} = \frac{[\text{M}^+][\text{A}^{2-}]}{[\text{M}_2\text{A}]} \quad 3-4$$

Notice that these are inverted with respect to the  $K_{\text{eq}}$  expression for the  $\text{A} + \text{B} \rightleftharpoons \text{C}$  reaction described above. This is because we are expressly addressing the *dissociation* process, and the  $\text{A} + \text{B}$  is an association process. Also, “total” dissociation implies that  $K_{\text{eq}}$  is infinitely large for 3-2 through 3-4. It is for this reason that total dissociation is better described in another way.

This alternative expression is based on mass balance. Consider, for example, dissolving 0.10 mole of MA in enough solvent to make 1 L of solution. The concentration of MA, that is  $[\text{MA}]$ , would be 0.10 M *only* if MA does not appreciably dissociate, but if MA is a strong electrolyte, and therefore dissociates about 100%, then  $[\text{MA}]$  is approximately zero. How can one express the concentration of the electrolyte MA without consideration of the degree to which MA dissociates? The answer is analytical concentration,  $C_{\text{MA}}$  in this case. This expression for concentration, conventionally in  $\text{mole/L}$ , makes no presumption regarding the fate of the solute. So

$$C_{\text{MA}} = [\text{MA}] + [\text{M}^{n+}] \quad 3-5$$

$$C_{\text{MA}} = [\text{MA}] + [\text{A}^{n-}]. \quad 3-6$$

Mass balance requires that all of the  $\text{M}^{n+}$  in the solution exists associated as MA or dissociated as  $\text{M}^{n+}$ . Likewise, all of the  $\text{A}^{n-}$  is either associated or dissociated.<sup>33</sup> If MA is a strong electrolyte,  $[\text{MA}] \approx 0$  and  $[\text{M}^{n+}] \approx C_{\text{MA}}$ , but if MA is a *very* weak electrolyte, then  $[\text{M}^{n+}] \approx 0$  and so  $C_{\text{MA}} \approx [\text{MA}]$ .

Electrolytes like  $\text{MA}_2$  and  $\text{M}_2\text{A}$  will be covered throughout several chapters to come because their mass balance expressions (3-7 through 3-10) are too complicated for the purpose of this chapter. Consider:

$$C_{MA_2} = [MA_2] + [MA^+] + [M^{2+}] \quad 3-7$$

$$C_{MA_2} = [MA_2] + [MA^+] + \frac{1}{2}[A^-] \quad 3-8$$

and

$$C_{M_2A} = [M_2A] + [MA^-] + \frac{1}{2}[M^+] \quad 3-9$$

$$C_{M_2A} = [M_2A] + [MA^-] + [A^{2-}] \quad 3-10$$

(In Chapter 2 we took  $[CaCl^+]$  i.e.  $[MA^+]$  to be zero and this is not strictly true.)

Returning to the strong electrolyte MA, with  $n = 1$ , and given that MA is strong electrolyte,  $[MA]$  can be taken as zero. From Equations 3-5 and 3-6 the concentration of both ionic species can be expressed in terms of analytical concentration:

$$C_{MA} = [M^+] \quad 3-11$$

$$C_{MA} = [A^-] \quad 3-12$$

This makes the calculation of  $\mu$  trivial:

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$$\begin{aligned}\mu &= \frac{1}{2}\{[M^+](+1)^2 + [A^-](-1)^2\} \\ \mu &= \frac{1}{2}\{C_{MA} + C_{MA}\} \\ \mu &= C_{MA}\end{aligned}\tag{3-13}$$

There is an important category of reactions like



when  $M^{1+} = H^+$ . This is the acid dissociation process,<sup>34</sup>



where  $A^-$  is any of the anions in Table 1. With any of the monovalent (-1) anions, the ion pair HA is a strong acid, and can be expected to dissociate entirely in aqueous solution even when the concentration is high,<sup>35</sup> and that is why the single headed arrow is used.

The concentration and degree of dissociation of HA is manifest in an increase in the  $H^+$  activity of the solution. This is measured by potentiometric methods as pH.<sup>36</sup>

$$pH = -\log\{H^+\}\tag{3-14}$$

Using the relationship between molarity and activity given in 2-3, produces a more useful definition of pH.

$$pH = -\log(\gamma_{H^+}[H^+]) = -\log\gamma_{H^+} - \log[H^+]\tag{3-15}$$

Equations 2-6 and 2-8, showed that  $\gamma_{H^+}$  is a function of  $\mu$ , and 3-13 provides that  $\mu = C_{HA}$ <sup>37</sup> when  $n = 1$ , as is the case for HA. And finally, 3-11 allows that  $[H^+] = C_{HA}$ , when HA is a strong electrolyte. So combining 2-8, 3-11, and 3-15, would yield:

$$pH = 0.5 \cdot 1^2 \left\{ \frac{\sqrt{C_{HA}}}{1 + \sqrt{C_{HA}}} - 0.15C_{HA} \right\} - \log C_{HA}\tag{3-16}$$

Or using extended Debye-Hückle for an aqueous solution at 25° C (2-6) in place of 2-8 would give:

$$pH = \frac{0.511 \cdot 1^2 \sqrt{C_{HA}}}{1 + 0.329 \cdot 9 \sqrt{C_{HA}}} - \log C_{HA}\tag{3-17}$$

These models are limited at the higher values of  $C_{HA}$  by the effectiveness of the Davies and extended Debye-Hückel equations at  $\mu$  greater than about 0.5, and both 3-16 and 3-17 are *incorrect* at very low concentrations of HA.

How are they incorrect for low concentrations of acid? Consider  $C_{\text{HA}} = 0$ ; this would produce an undefined, at least very large pH because  $-\log(0)$  is undefined. But an aqueous solution wherein  $C_{\text{HA}} = 0$  would constitute pure water, and the pH of pure water at 25°C should be 7.00.

The error originates in the mass balance expressions 3-5 and 3-6 which are rewritten here expressly for an acid, HA as

$$C_{\text{HA}} = [\text{HA}] + [\text{H}^+] \quad 3-18$$

$$C_{\text{HA}} = [\text{HA}] + [\text{A}^-]. \quad 3-19$$

When the solvent is water, or any other proton donor, HA is *not* the sole source of  $\text{H}^+$ , and so 3-18 incorrectly predicts that  $[\text{H}^+] = 0$  when  $C_{\text{HA}} = 0$ . The correction requires consideration of the dissociation of the proton donor solvent (water).



This reaction is so important that its equilibrium constant is given a special designation,  $K_w^{38}$ . Because  $[\text{H}_2\text{O}]$  and  $\{\text{H}_2\text{O}\}$  are effectively unchanged in all but the most concentrated solutions, these terms are not included in the respective  $K_w$  and  $K_w^\circ$  expressions.

$$K_w = [\text{H}^+][\text{OH}^-] \quad 3-20$$

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

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

$$K_w^\circ = \gamma_{\text{H}^+}\gamma_{\text{OH}^-}K_w \quad 3-21$$

The dissociation of water is addressed by considering the charge balance requirement for any solution:

$$\sum [M^{zM^+}] \cdot z_M = \sum [A^{zA^-}] \cdot z_A \quad 3-22$$

That is, the sum of the positive charges must equal the sum of the negative charges. Applying this requirement to the HA problem, and considering that water dissociates to produce  $\text{H}^+$  and  $\text{OH}^-$  yields:

$$[\text{H}^+] = [\text{A}^-] + [\text{OH}^-]. \quad 3-23$$

3-20 can be rearranged to provide an expression for  $[\text{OH}^-]$  in terms of  $K_w$  thereby addressing the dissociation of water.

$$K_w / [\text{H}^+] = [\text{OH}^-] \quad 3-24$$

Applying this expression to 3-23 creates a charge balance expression with only two variables.

$$[\text{H}^+] = [\text{A}^-] + K_w / [\text{H}^+] \quad 3-25$$

The  $[\text{A}^-]$  variable can be transformed into the parameter  $C_{\text{HA}}$  by considering 3-19 and the proviso that HA is a strong acid; that means that  $[\text{HA}] = 0$ , and therefore  $[\text{A}^-] = C_{\text{HA}}$  as in 3-12. Making that substitution into 3-25 and rearranging the expression produces a quadratic equation.

$$[\text{H}^+]^2 - [\text{H}^+]C_{\text{HA}} - K_w = 0 \quad 3-26$$

This equation, of course, has real two roots,

$$[\text{H}^+] = \frac{C_{\text{HA}} + \sqrt{C_{\text{HA}}^2 + 4K_w}}{2} \quad 3-27$$

and,

$$[\text{H}^+] = \frac{C_{\text{HA}} - \sqrt{C_{\text{HA}}^2 + 4K_w}}{2} \quad 3-28$$

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but 3-28 has no real meaning because it implies a hydrogen ion concentration less than zero! This leaves 3-27 as the correction to the approximation  $[H^+] \approx C_{HA}$ . Notice that in 3-27,  $[H^+]$  is not found to be zero when  $C_{HA} = 0$ . Indeed, the lower limit on  $[H^+]$  is acquired with this expression; it is  $\sqrt{K_w}$  which is appropriate for the  $[H^+]$  in a solution containing no HA.

We first illustrate how Maple can be used to derive 3-27 and 3-28, and then use Maple to illustrate the difference between the “accurate” expression and the “approximate” expression. The derivation follows with operations introduced in Chapter 2. The ChBal statement is Equation 3-23 restated; the A:= statement is a restatement of 3-19 with the presumption that  $[HA] \approx 0$ ; next, OH “becomes” the solution of 3-20 when it is solved for  $[OH^-]$ . (We could just as well have written 3-24.) To see how this all turns out we conclude with a call for the charge balance expression with ChBal;. Finally we solve this charge balance expression for  $[H^+]$  and define H<sub>quad</sub> as the solution of that expression.

```
> restart; ChBal := H = A + OH; A := C[HA]; OH := solve(K[w] = H*OH, OH); ChBal; H[quad] := solve(ChBal, {H});
```

$$ChBal := H = A + OH$$

$$A := C_{HA}$$

$$OH := \frac{K_w}{H}$$

$$H = C_{HA} + \frac{K_w}{H}$$

$$H_{quad} := \left\{ H = \frac{1}{2} C_{HA} + \frac{1}{2} \sqrt{C_{HA}^2 + 4 K_w} \right\}, \left\{ H = \frac{1}{2} C_{HA} - \frac{1}{2} \sqrt{C_{HA}^2 + 4 K_w} \right\}$$

Notice the use of braces in the `solve(ChBal, {H})` command. These braces instruct that the output is to be in the form of a *set* (of solutions here). By creating a set of outputs, a specific output can be selected for future execution. The first of these two outputs would be `H[quad][1]`, and the second (obviously) `H[quad][2]`. Without these braces, (*cf.* page 50) that output would have been:

$$H_{quad} := \frac{1}{2} C_{HA} + \frac{1}{2} \sqrt{C_{HA}^2 + 4 K_w}, \frac{1}{2} C_{HA} - \frac{1}{2} \sqrt{C_{HA}^2 + 4 K_w}$$

but these two solutions are *not* separate equations and would be treated as a single element. Using only one of the solutions would require carefully cutting and pasting the desired solution into the next input line<sup>39</sup> or the desired output could be re-typed into the next input line.

With a list of outputs, the next step requires only a substitution operation, `subs(s, expr)`. *s* can be an equation or even a list of equations, (*s<sub>1</sub>*, *s<sub>2</sub>*), and *expr* is an expression. With this command, if *s* is an equation, every occurrence of the left hand side of equation *s* that appears in *expr* is replaced by the right hand side of the equation. Here we will define the approximate solution for [H<sup>+</sup>] from 3-18 when we take [HA] ≈ 0, and we will define the accurate solution using the `subs` command.

```
> H[approx]:= C[HA]; H[accurate] := subs(H[quad][1], H);
```

$$H_{\text{approx}} := C_{\text{HA}}$$

$$H_{\text{accurate}} := \frac{1}{2} C_{\text{HA}} + \frac{1}{2} \sqrt{C_{\text{HA}}^2 + 4 K_w}$$

Now to compare the approximate and accurate solutions. The accurate solution has one constant, K<sub>w</sub>, that requires defining before the comparison can be made.

```
> K[w] := 1e-14; H[accurate];
```

$$\begin{aligned} K_w &:= 1.0000 \cdot 10^{-14} \\ \frac{1}{2} C_{\text{HA}} + \frac{1}{2} \sqrt{C_{\text{HA}}^2 + 4.0000 \cdot 10^{-14}} \end{aligned}$$

With H<sub>accurate</sub> and H<sub>approx</sub> expressed exclusively in terms of C<sub>HA</sub> we will make the comparison as we introduce a new feature of the plot output, the `style=`.

```
> plot([H[accurate], H[approx]], C[HA] = 0..1e-6, color = blue, style = [line, point]);
```

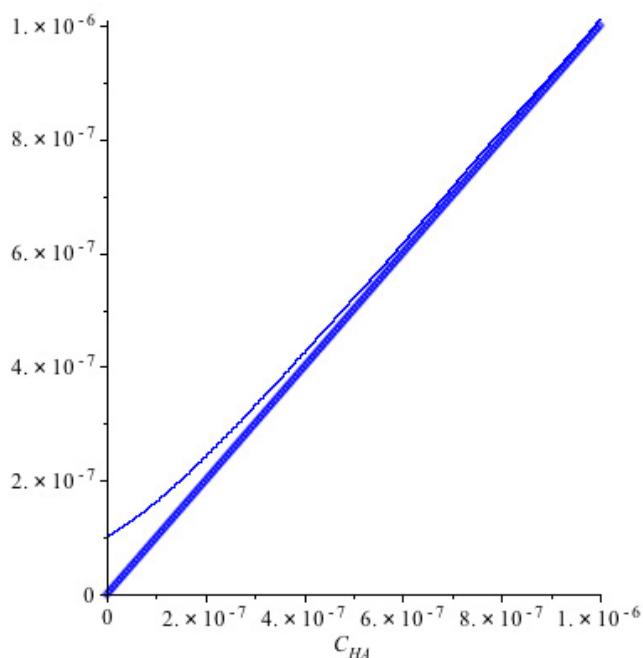


Figure 3-1

This graph shows that when  $C_{HA}$  is greater than about  $5 \times 10^{-7}$  it is difficult to tell the difference between the expressions, but when  $C_{HA} < 1 \times 10^{-7}$  the difference is profound.

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While we are using Maple to explore the consequences of making approximations to describe  $[H^+]$ , let us return to the problem of calculating pH at a large  $C_{HA}$ , that is, where there is an appreciable ionic strength and  $\gamma_{H^+}$  is decidedly less than 1.000. The simplistic approximation for pH is:

$$pH \approx -\log[H^+] \approx -\log C_{HA} \quad 3-29$$

How does this compare to 3-16 which we will call  $pH_{\text{accurate}}$ ? Recall that it entailed a combination of Equations 2-8, 3-11 and 3-15 and that 2-8 is reasonably legitimate to  $\mu = 0.5$ .

```
> restart; pH[approx] := -log[10](C[HA]); pH[accurate] :=
0.5*((sqrt(C[HA]) / (1 + sqrt(C[HA]))) - 0.15*C[HA]) - log[10]
(C[HA]);40
```

$$pH_{\text{approx}} := -\frac{\ln(C_{HA})}{\ln(10.00)}$$

$$pH_{\text{accurate}} := \frac{.50 \sqrt{C_{HA}}}{1.00 + \sqrt{C_{HA}}} - .08 C_{HA} - \frac{\ln(C_{HA})}{\ln(10.00)}$$

```
> plot([pH[approx], pH[accurate]], C[HA] = 0.001..0.2, color =
black, style = [line, point]);
```

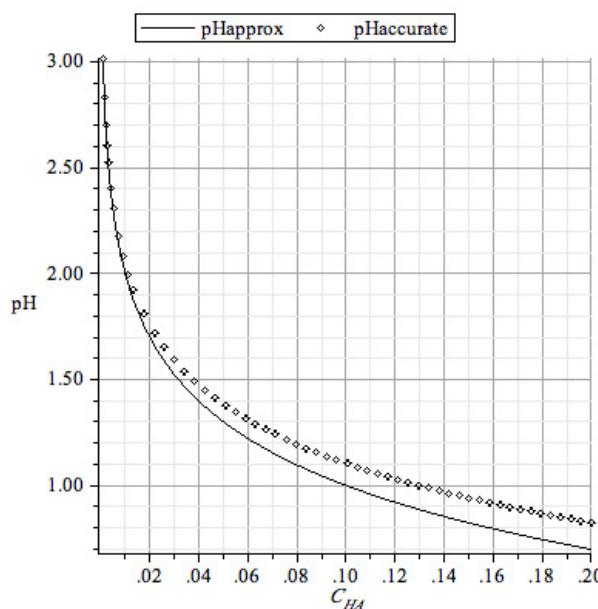


Figure 3-2<sup>41</sup>

The lesson here is that  $\text{pH} \approx -\log[\text{C}_{\text{HA}}]$  is a good approximation for a strong acid when  $\text{C}_{\text{HA}} < 0.01 \text{ M}$ . That is, the effects of ionic strength are invisible at these low concentrations.<sup>42</sup> It has already been illustrated that when  $\text{C}_{\text{HA}} > 5 \times 10^{-7}$ , the effect of  $\text{H}_2\text{O}$  autoprotolysis is invisible, and  $[\text{H}^+] \approx \text{C}_{\text{HA}}$ . So, between  $5 \times 10^{-7}$  and  $1 \times 10^{-2}$ , 3-29 is reasonable for strong acids.

With the need to consider ionic strength and the autoprotolysis of water for rigorous pH calculations, it is appropriate to reflect on the meaning of neutrality: it is *not* necessarily pH 7.00. Indeed, neutrality is not defined by *any* given pH. **A neutral aqueous solution is one in which the activity of  $\text{H}^+$  (actually  $\text{H}_3\text{O}^+$ ) equals the activity of  $\text{OH}^-$ .** That is,

$$\{\text{H}^+\} = \{\text{OH}^-\}. \quad 3-30$$

In pure water, the only ions are  $\text{H}^+$  and  $\text{OH}^-$ . Charge balance requires that  $[\text{H}^+]$  equals  $[\text{OH}^-]$ , and because the ionic strength of pure water is so low (recall that it is a very weak electrolyte with < 0.001% dissociation),  $\mu \approx 0$ . This makes  $\gamma_{\text{H}^+}$  and  $\gamma_{\text{OH}^-}$  very nearly 1.00, but more important, it makes them essentially equal. So, if  $[\text{H}^+] = [\text{OH}^-]$ , and  $\gamma_{\text{H}^+} \approx \gamma_{\text{OH}^-}$ , then  $\{\text{H}^+\} \approx \{\text{OH}^-\}$ . Little surprise here that pure water is neutral!

Returning to 3-21, the definition of  $K_w^\circ$ , and replacing  $\{\text{OH}^-\}$  with  $\{\text{H}^+\}$  because they are equal, gives

$$\{\text{H}^+\} = \sqrt{K_w^\circ}. \quad 3-31$$

At  $25^\circ \text{ C}$ ,  $K_w^\circ = 1.007 \times 10^{-14}$ , and so  $\{\text{H}^+\} = 1.003 \times 10^{-7}$ . With the negligible ionic strength, 3-15 can be applied without regard to  $\mu$  and  $\gamma_{\text{H}^+}$ . This leaves  $-\log[\text{H}^+] = 6.9985$ , or as we are accustomed to saying, the pH is seven. But the point here is that this result came from two subtle presumptions: that  $K_w^\circ \approx 1.00 \times 10^{-7}$  (because  $T \approx 25^\circ \text{C}$ ) and that  $\mu \approx 0$  so that  $\gamma_{\text{H}^+} \approx 1.00$ . Two points can be made of these presumptions.

First, certainly hot water can be neutral, but its pH is not nearly seven. At  $60^\circ \text{C}$ ,  $K_w^\circ = 9.62 \times 10^{-14}$ . So using 3-31 and 3-14 yields a pH = 6.509. Second, salt water at any *appreciable* concentration, *cannot* be neutral by our  $\{\text{H}^+\} = \{\text{OH}^-\}$  requirement, even though  $[\text{H}^+]$  and  $[\text{OH}^-]$  remain equal. The reason is that the addition of an appreciable amount of strong electrolyte will render  $\mu > 0$  and  $\gamma_{\text{H}^+}$  and  $\gamma_{\text{OH}^-} < 1$ . More important,  $\gamma_{\text{H}^+} \neq \gamma_{\text{OH}^-}$  becomes key to the claim that the solution is *not* neutral.

Let us illustrate that adding a strong electrolyte like NaCl does not disrupt the  $[\text{H}^+] = [\text{OH}^-]$  presumption. Charge balance would require that

$$[\text{H}^+] + [\text{Na}^+] = [\text{Cl}^-] + [\text{OH}^-]. \quad 3-32$$

Mass balance for a strong electrolyte like NaCl would allow  $C_{\text{NaCl}} = [\text{Na}^+]$  and  $C_{\text{NaCl}} = [\text{Cl}^-]$  because  $[\text{NaCl}] = 0$ . The important point here is that  $[\text{Na}^+] = [\text{Cl}^-]$  allowing their cancellation in Equation 3-32 leaving  $[\text{H}^+] = [\text{OH}^-]$ . Having illustrated this point, Equation 3-21 can be modified by replacing  $[\text{OH}^-]$  with  $[\text{H}^+]$ , because they too are equal:

$$K_w^\circ = \gamma_{\text{H}^+}[\text{H}^+]\gamma_{\text{OH}^-}[\text{OH}^-] = \gamma_{\text{H}^+}[\text{H}^+]\gamma_{\text{OH}^-}[\text{H}^+][\text{H}^+] = \sqrt{(K_w^\circ/\gamma_{\text{H}^+}\gamma_{\text{OH}^-})}$$

From  $\{\text{H}^+\} = \gamma_{\text{H}^+}[\text{H}^+]$ , it can be shown that

$$\{\text{H}^+\} = \sqrt{(K_w^\circ/\gamma_{\text{OH}^-})} \quad 3-33$$

When  $\gamma_{\text{H}^+} = \gamma_{\text{OH}^-} \approx 1.00$ , we have Equation 3-31, but not in the presence of an appreciable amount of electrolyte.<sup>43</sup> By replacing  $[\text{H}^+]$  with  $[\text{OH}^-]$  in 3-21, one could, likewise show that

$$\{\text{OH}^-\} = \sqrt{(K_w^\circ/\gamma_{\text{H}^+})} \quad 3-34$$

Is  $\{\text{H}^+\}$  equal to  $\{\text{OH}^-\}$ ? Consider a 0.0500 M NaCl solution. Because it is a strong electrolyte,  $C_{\text{NaCl}} = 0.05 = \mu$ . Equation 2-13 can be used to find  $\gamma_{\text{H}^+}$  and  $\gamma_{\text{OH}^-}$  at this ionic strength.  $a_{\text{H}^+}$  and  $a_{\text{OH}^-}$  are found in Appendix II (9 and 3.5 respectively). With these values,  $\gamma_{\text{H}^+} = 0.854$  and  $\gamma_{\text{OH}^-} = 0.811$ . So substituting these values back into 3-33 and 3-34 gives:

$$\{\text{H}^+\} = \sqrt{(0.854 \cdot 1.007 \times 10^{-14}/0.811)} = 1.03 \times 10^{-7}$$

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The pH of the solution is  $-\log\{\text{H}^+\} = 6.98$ , not quite seven and certainly not quite neutral because  $\{\text{H}^+\} > \{\text{OH}^-\}$ .

The second, important category of reactions like



is found when  $\text{A}^{1-}$  represents  $\text{OH}^-$ . This represents the dissociation of a strong base. To be a strong base  $\text{M}^{1+}$  can be any of the monovalent cations of Table 3-1 less the exception of  $\text{H}^+$  as previously described and the (two,  $\text{K}^+$ ) exceptions of Table 3-2.

Some divalent ions like  $\text{Ba}^{2+}$  also constitute strong bases, but here there is a caveat: in an aqueous solution



This is to say that in solution,  $\text{Ba}(\text{OH})_2$  is a strong electrolyte (base) because it completely dissociates to produce the proton acceptor,  $\text{OH}^-$ , but the product of this dissociation does not itself further dissociate appreciably to produce still more hydroxide. For simplicity, it is better to remember that the *really* common, strong bases are  $\text{NaOH}$  and  $\text{KOH}$ ; there are many other strong bases, even beyond Table 3-1, but they are not important, at least in analytical applications. Treatment of the strong base equilibrium is deferred to the Example Problem 3 below.

### Example Problems

1. Calculate the pH of the following  $\text{HNO}_3$  solutions.
  - a)  $5.5 \times 10^{-7} \text{ M}$
  - b)  $5.5 \times 10^{-1} \text{ M}$
  - c)  $5.5 \times 10^{-5} \text{ M}$
  - d)  $1.6 \times 10^{-6} \text{ M HNO}_3$  and  $3.8 \times 10^{-2} \text{ M KNO}_3$ .
2. Illustrate the difference between the expressions,  $\text{pH} = -\log C_{\text{HA}}$  and  $\text{pH} = -\log\{\text{H}^+\}$ , over the range  $C_{\text{HA}} = 0.005 \text{ M}$  and  $0.050 \text{ M}$ , using the Debye-Hückel equation to calculate  $\gamma_{\text{H}^+}$ .
3. Calculate the pH of the following  $\text{NaOH}$  solutions.
  - a)  $4.8 \times 10^{-7} \text{ M}$
  - b)  $5.2 \times 10^{-1} \text{ M}$
  - c)  $7.5 \times 10^{-5} \text{ M}$
  - d)  $2.7 \times 10^{-6} \text{ M NaOH}$  and  $3.9 \times 10^{-2} \text{ M NaCl}$ .
4. Calculate the  $\text{HClO}_4$  concentration that would be needed to produce a pH 2.00 solution.

## Solutions to Example Problems

- The  $C_{HA}$  values listed in this problem *allow* but do not require four<sup>44</sup> approaches to finding the pH: in Part **a**, the ionic strength will be  $\ll 0.001$  so that  $\gamma_{H^+} \approx 1$ , but the autoprotolysis of  $H_2O$  which will augment  $[H^+]$  must be considered; in Part **b**,  $C_{HA}$  is sufficiently large that the autoprotolysis of  $H_2O$  can be ignored, but  $\mu$  will be significant and  $\gamma_{H^+} \neq 1$ ; in Part **c**,  $C_{HA}$  is one hundred times larger than it was in **a** so that autoprotolysis can be ignored, and yet  $C_{HA}$  is sufficiently small that  $\mu \ll 0.001$  and again  $\gamma_{H^+} \approx 1$ ; finally, in Part **d**, autoprotolysis and ionic strength must both be considered.

All four approaches are illustrated below. Certainly they can be executed with a calculator, but Maple is used in order to provide more practice with its use. Then, a one-equation-fits-all approach will be derived and applied to all four solutions. The approaches can be compared.

- a.

```
> restart: ChargeBalance:= H = NO[3] + OH; OH:= K[w]/H;
NO[3] :=C[HA]; ChargeBalance;
```

$$\begin{aligned} ChargeBalance &:= H = NO_3 + OH \\ OH &:= \frac{K_w}{H} \\ NO_3 &:= C_{HA} \\ H &= C_{HA} + \frac{K_w}{H} \end{aligned}$$

$H_a$  will be the solutions (in  $[H^+]$ ) to *ChargeBalance*.

```
> H[a]:= solve(ChargeBalance,H);
```

$$H_a := \frac{1}{2} C_{HA} + \frac{1}{2} \sqrt{C_{HA}^2 + 4 K_w}, \frac{1}{2} C_{HA} - \frac{1}{2} \sqrt{C_{HA}^2 + 4 K_w}$$

Typical of a quadratic, *ChargeBalance* has two roots, but as discussed above, only one will have physical reality. Notice that the brackets, {H} were not used in the *solve* command as they were on page 43. This was to illustrate the need to cut and paste the desired solution into the next operation.

```
> K[w]:= 1.007e-14; C[HA]:= 5.5e-7; H[a];
```

$$\begin{aligned} K_w &:= 1.0070 \cdot 10^{-14} \\ C_{HA} &:= 5.5000 \cdot 10^{-7} \\ &5.6774 \cdot 10^{-7}, -1.7737 \cdot 10^{-8} \end{aligned}$$

Certainly, the  $[H^+]$  is not less than zero. So only the  $5.6774 \cdot 10^{-7}$  will be cut and pasted into the next input line for computation.<sup>45</sup>

```
> H[a] := 5.6774*10^(-7); pH[a] := -log[10](H[a]);
```

$$H_a := 5.6774 \cdot 10^{-7}$$

$$pH_a := 6.2459$$

1. b. Continuing with the Maple worksheet created for Part a and using Debye-Hückel rather than the Davies equation and writing Debye-Hückel in the exponential form gives:

```
> C[HA]:= 0.55; H[b]:= C[HA]; Gamma[H]:= 10^(-0.511*sqrt(C[HA]) / (1 + (0.329*9*sqrt(C[HA]))));
```

$$C_{HA} := 0.5500$$

$$H_b := 0.5500$$

$$\Gamma_H := 0.7611$$

```
> Activity['H[b]']:= Gamma[H]*H[b]; pH:= -log[10](Activity['H[b]']);
```

$$Activity_{Hb} := 0.4186$$

$$pH := 0.3782$$



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Notice the use of single quotation marks around `H[b]`; without these, Maple would have printed `Activity.55` because  $H_b$  has been defined as .55, and Maple will make that literal interpretation *everywhere!*

1. c. Continuing further with the worksheet, we need only reassign  $C_{HA}$ . The presumption is that  $\gamma_{H^+}$  will be essentially one because  $\mu \ll 0.001$ .

```
> C[HA]:= 5.5e-5; H[c]:= C[HA]; pH:=-log[10](H[c]);
```

$$\begin{aligned}C_{HA} &:= 5.50 \times 10^{-5} \\H_c &:= 5.50 \times 10^{-5}\end{aligned}$$

```
> pH:=-log[10](H[c]);
```

$$pH := 4.260$$

It might seem peculiar that two, separate input lines were used here; certainly one would have done, except that we have set the output format to four decimal places (see page 20). This automatically gives  $C_{HA} := 0.0001$  and  $H_c := 0.0001$ . If `pH := -log[10](H[c]);` had been included in the same execution group with these two commands, and the output had been reformatted to two decimal place scientific notation, all three outputs would have had this same format and  $pH := 4.26 \times 10^0$  would have appeared. So the pH operation was separated.

1. d. Here it is necessary to recognize that  $\mu \neq C_{HA}$  because HA is not the only source of ions. First, using 2-5 to find  $\mu$  leads to

$$\mu = \frac{1}{2} \{ [H^+] + [K^+] + [\text{OH}^-] + [NO_3^-] \}.$$

Inasmuch as  $HNO_3$  has been added to the solution,  $[OH^-]$  must be  $< 10^{-7} M^{46}$ , and so it can safely be omitted as a contributor to  $\mu$ .  $[K^+]$  will equal  $C_{KNO_3}$ , and  $[NO_3^-]$  will equal  $C_{KNO_3}$  plus  $C_{HNO_3}$ . If we ignore the autoprotolysis of water, then  $[H^+]$  will equal  $C_{HNO_3}$ .<sup>47</sup> These substitutions bring us to:

$$\mu = C_{KNO_3} + C_{HNO_3}.$$

We can cut and paste the Debye-Hückel expression from Part b of the Maple worksheet and replace  $\mu$  with  $C_{KNO_3} + C_{HNO_3}$ , and with a few input lines to label the output and afterwards a little formatting inside the **Preferences > Precision** tab (see page 16 *et seq.*):

```
> restart; Gamma[H]:= 10^(-0.511*sqrt(mu)/(1 +
(0.329*9*sqrt(mu)))); Gamma[OH]:= 10^(-0.511*sqrt(mu)/
(1 + (0.329*3.5*sqrt(mu)))); mu:= C[KNO[3]] + C[HNO[3]];
C[KNO[3]]:= 3.8e-2; C[HNO[3]]:= 1.6e-6;
```

$$\Gamma_H := 10^{-\frac{0.511 \sqrt{\mu}}{1 + 2.961 \sqrt{\mu}}}$$

$$\Gamma_{OH} := 10^{-\frac{0.511 \sqrt{\mu}}{1 + 1.152 \sqrt{\mu}}}$$

$$\mu := C_{KNO_3} + C_{HNO_3}$$

We can return to Part **a** in the worksheet and lift the solution for  $H_a$ . We will replace  $C_{HA}$  with  $C_{HNO_3}$ , but remember that  $C_{HNO_3}$  and  $K_w$  have been defined. So Maple will make those substitutions, and the substitution for  $K_w$  will be incorrect because  $K_w \neq K_w^\circ$ . What follows is a correction to  $K_w$  while  $[H^+]$  is extracted from the expression.

```
> K[w[0]]^48:= 1.007e-14; K[w]:= K[w[0]]/(Gamma[H]*Gamma[OH]);
H[d]:= (C[HNO[3]] + sqrt(C[HNO[3]]^2 + 4*K[w]))/2; pH:=
-log [10] (Gamma[H] * H[d]);
```

$$K_w := 1.0070000 \cdot 10^{-14}$$

$$K_w := 1.4045610 \cdot 10^{-14}$$

$$H_d := 0.0000016$$

$$pH := 5.8566749$$

Notice that  $K_w$  is  $1.405 \times 10^{-14}$  compared to  $1.007 \times 10^{-14}$  for  $K_w^\circ$  (A 40% increase). The  $H_d$  is used to denote that this is  $[H^+]$  for Part **d** of this problem, but an interesting consequence is seen if  $H$  alone (*i.e.* not  $H_d$ ) is used: for **Gamma[H]**, again, one gets the literal substitution,  $\Gamma_{.1608e-5}$  which has no numeric value!

Was it appropriate to presume  $H[d] := (C[HNO[3]] + sqrt(C[HNO[3]]^2 + 4*K[w]))/2$ ? That is,

$$H_d = \frac{1}{2} C_{HNO_3} + \frac{1}{2} \sqrt{C_{HNO_3}^2 + 4 K_w}$$

This expression is based on the derivation from mass and charge balance conditions that produced 3-27, but those conditions did *not* consider the presence of MA in addition to HA. Revisiting the charge balance will show that 3-27 is still appropriate, with or without MA. Recall,

$$[\text{H}^+] + [\text{M}^+] = [\text{OH}^-] + [\text{A}^-].$$

Inasmuch as all  $\text{M}^+$  must come from MA, and  $\text{A}^-$  comes from either MA or HA,

$$[\text{M}^+] = C_{\text{MA}}$$

and

$$[\text{A}^-] = C_{\text{HA}} + C_{\text{MA}}.$$

So, returning to the charge balance gives:

$$[\text{H}^+] + \epsilon_{\text{MA}} = [\text{OH}^-] + C_{\text{HA}} + \epsilon_{\text{MA}}$$

$$[\text{H}^+] = [\text{OH}^-] + C_{\text{HA}}.$$

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Using 3-24 to replace  $[\text{OH}^-]$  with  $K_w/[H^+]$ , and then multiplying through by  $[H^+]$  gives

$$[H^+]^2 = K_w + [H^+]C_{\text{HA}}$$

which leads directly to 3-26 and on to 3-27.

This expression for  $H_d$  very nearly achieves the one-equation-fits-all approach that could be used to solve all four parts of this problem. With a little Maple programming the problem could be automated altogether. We will defer this more sophisticated approach until Chapter 7 where titration plots will be addressed. For now, the strategy will be simply to trudge through the four problems, but with some new Maple commands that will simplify the task of substituting into expressions.

We begin by recreating the Debye-Hückel expression (in the exponential form) for  $\gamma_{H^+}$  just as we did in Part b above but we will add  $\gamma_{\text{OH}^-}$ , and we will write these in general terms so that they can be adjusted from problem to problem.

```
> restart; Gamma[H]:= 10^(-0.511*sqrt(mu)/(1 +
(0.329*9*sqrt(mu)))); Gamma[OH]:= 10^(-0.511*sqrt(mu)/(1 +
(0.329*3.5*sqrt(mu))));


$$\Gamma_H := 10^{-\frac{0.51100 \sqrt{\mu}}{1 + 2.96100 \sqrt{\mu}}}$$


$$\Gamma_{OH} := 10^{-\frac{0.51100 \sqrt{\mu}}{1 + 1.15150 \sqrt{\mu}}}$$

```

So that we can calculate  $\mu$  from  $C_{\text{HNO}_3}$  and  $C_{\text{KNO}_3}$  we will make that substitution here, and we will do it with the command `algsubs` which is an *algebraic* substitution. It allows one to replace one element in an expression with another element, in this case  $\mu$  with  $C_{\text{HNO}_3} + C_{\text{KNO}_3}$ . So, we will replace  $\Gamma_H$  with  $g_H$  wherein  $\mu$  has been replaced with the sum of the analytical concentrations of  $\text{HNO}_3$  and  $\text{KNO}_3$ . Using the more generally defined  $g_H$  and  $g_{\text{OH}}$ ,  $K_w$  will be defined. The process might be something like:

```
> g['H]:= algsubs(mu=C[HNO[3]] + C[KNO[3]], Gamma[H]);
g['OH]:= algsubs(mu = C[HNO[3]] + C[KNO[3]], Gamma[OH]);
K[w]:= 1.007e-14/(g['H']*g['OH']);
```

$$g_H := 10 \cdot \frac{0.51100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 2.96100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.51100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.15150 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}{1 + 2.96100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.51100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.15150 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}$$

$$g_{OH} := 10 \cdot \frac{0.51100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 2.96100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.51100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.15150 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}{1 + 1.15150 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.51100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.15150 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}$$

$$K_w := \frac{1.00700 \cdot 10^{-14}}{10 \cdot \frac{0.51100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 2.96100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.51100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.15150 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}{1 + 2.96100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.51100 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.15150 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}}$$

Finally, we use the expression for  $[H^+]$  (3-27) that accounts for autoprotolysis of water. In this way we have an expression that is applicable to very small concentrations of  $HNO_3$ . On the same input line we will then calculate the activity of  $H^+$  as defined by 2-3, so that pH can be correctly calculated as *minus log{H<sup>+</sup>}* (3-15) thereby making the calculations appropriate for high concentrations of  $HNO_3$  (and  $KNO_3$ ). As we define H,  $K_w$  will automatically be replaced with the output given (above).

```
> H := (C[HNO[3]] + sqrt(C[HNO[3]]^2 + (4*K[w]))) / 2;
Activity['H'] := g['H'] * H; pH := -log[10](Activity['H']);
```

$$H := \frac{1}{2} C_{HNO_3} + \frac{1}{2} \left( C_{HNO_3}^2 + \frac{4.028 \cdot 10^{-14}}{\frac{0.511 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 2.961 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.511 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.152 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}{1 + 2.961 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.511 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.152 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}} \right)$$

$$Activity_H := 10^{-\frac{0.511 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 2.961 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.511 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.152 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}{1 + 2.961 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.511 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.152 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}}}$$

$$pH := -\ln \left( \frac{0.511 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 2.961 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.511 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.152 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}{1 + 2.961 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 0.511 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.152 \sqrt{\frac{C_{HNO_3} + C_{KNO_3}}{1 + 1.00700 \cdot 10^{-14}}}}}}}}}} \right)$$

This frightful expression for pH is complete for any mixture of  $\text{HNO}_3$  and  $\text{KNO}_3$  within the limits of Debye-Hückel at 25°C; it remains only to make the desired substitutions for  $C_{\text{HNO}_3}$  and  $C_{\text{KNO}_3}$ . This follows with still another method for making simple substitutions, the evaluate command, `eval`. With this command an expression will be evaluated, and as long as numeric values are assigned to all of its parameters, a numeric value is returned. (Notice that the list of parameters that are assigned for *this* evaluation is enclosed in braces.) The numerical value returned by Maple is *exact* but not always in the form scientists desire! However, a floating point evaluation, `evalf`, will produce an answer that is more conventional. These are compared below. The % tells Maple to use the most recent output for this floating point evaluation.<sup>49</sup>

```
> eval(pH, {C[HNO[3]]=5.5e-7, C[KNO[3]]=0}); evalf(%);
```

$$\frac{14.382}{\ln(10)}$$

6.246

This has instructed Maple to evaluate the pH expression with  $C_{\text{HNO}_3}$  set equal to  $5.5 \times 10^{-7}$  and  $C_{\text{KNO}_3}$  set equal to 0 (only for *this* evaluation). The output from this command is indeed unconventional. So its output was evaluated by a floating point operation, `evalf`.



Although the input data ( $C_{\text{HNO}_3}$  and  $C_{\text{KNO}_3}$ ) would allow only three significant figures in the answer (three places in the mantissa), Maple will produce answers with the format (decimal places) set in **Preferences** or through the **Format** tab in the menu. (The perils of the **Format** were addressed on page 20.) For the output for *this* problem, the user might consider setting the Round screen display to 3 digits and [Apply to Session] in the Precision tab under **Preferences**.

Applying expression above to Parts **b**, **c**, and **d** requires only an reevaluation of pH at the new  $C_{\text{HNO}_3}$  and  $C_{\text{KNO}_3}$ , but anticipating the unorthodox numerical output of Maple, we will directly request a floating point evaluation of the “`eval`” of pH.<sup>50</sup> That is, for **b**:

```
> evalf(eval(pH, {C[HNO[3]] = 0.55, C[KNO[3]] = 0})); pH_b := %;
pH_b := 0.378
```

Here we use `%` again but for the sake of labeling. One might be inclined to use `pH[b]` to get  $pH_b$ , but with pH defined (the enormous expression on page 56) Maple will attempt to create a table from that command. For **c** and **d** we cut directly to each pH calculation.

For **c**

```
> pH_c := evalf(eval(pH, {C[HNO[3]] = 5.5e-5, C[KNO[3]] = 0}));
pH_c := 4.263
```

and for Part d.

```
> pH_d := evalf(eval(pH, {C[HNO[3]] = 1.6e-6, C[KNO[3]] = 3.8e-2}));
pH_d := 5.857
```

Just how necessary was this one-equation-fits-all approach to problem 1? A tabulation of results by two approaches shows the following.

	Customized Approach	One-Equation Approach
<i>a</i>	6.246	6.246
<i>b</i>	0.378	0.378
<i>c</i>	4.260	4.263
<i>d</i>	5.857	5.857

Notice that the results are within 0.003 pH units for all answers. So the customized approach, *when properly chosen* is certainly acceptable; the one-equation approach, although more difficult to create, requires no judgement on which issues like autoprotolysis or ionic strength need to be considered.

2. The consequence of neglecting ionic strength is illustrated in this problem. It is similar to the illustration made on page 46 where the Davies equation was used to provide activity coefficients. Here, Debye-Hückel is used for that. We can cut and paste from the current Maple worksheet with a few modifications like  $\mu = C_{\text{HA}}$  rather than  $C_{\text{HNO}_3} + C_{\text{KNO}_3}$ , and by using ":" in place of ";" will preempt some of the outputs that have been given frequently in the previous examples. Recall also that the output has been set at 3 digits.

```
> restart; Gamma[H] := 10^(-0.511 *sqrt(C[HA])) / (1+(0.329*9*sqrt(C[HA])))); Activity[H]:=Gamma[H]*C[HA]; pH[simple]:= -log[10](C[HA]); pH[DH]:= -log[10](Activity[H]);
```

$$pH_{\text{simple}} := -\frac{\ln(C_{\text{HA}})}{\ln(10)}$$

$$pH_{\text{DH}} := -\frac{\ln\left(10 \cdot \frac{\frac{0.511}{\sqrt{C_{\text{HA}}}}}{1 + 2.961 \cdot \frac{\sqrt{C_{\text{HA}}}}{C_{\text{HA}}}}\right)}{\ln(10)}$$

The two pH calculations will be compared using a plot of each over the  $C_{\text{HA}} = 0.005$  to 0.05 M interval. For the sake of review, a few features illustrated in Chapter 2 will be resurrected. The `titlefont` option is added: it requires a list that is enclosed in square brackets. The list allows specification of the font, the style of that font and its size. Two new, color options are added as well.

```
> plot([pH[DH], pH[simple]], C[HA] = 0.005..0.05, color = [magenta, cyan], title = "Comparison of pH Calculations", titlefont = [TIMES, BOLD, 14], axes = box);
```

The difference (next page) between a simplistic pH calculation (cyan) and a calculation using activity coefficient corrections (magenta) is evident, even when  $C_{\text{HA}}$  is only 0.01 M. An interesting extension of this problem is a comparison between the use of the Davies and Debye-Hückel equations to provide the activity coefficients. This is left to the curious.

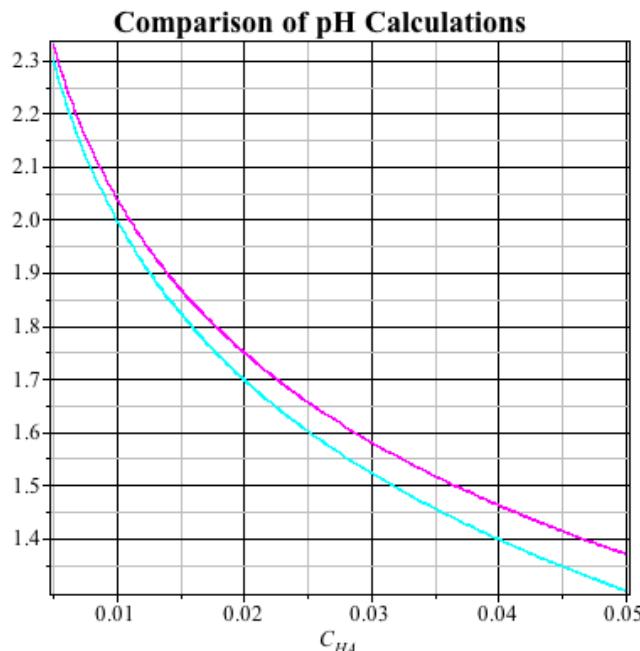


Figure 3-3

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3. This problem is a compliment to problem 1 in that it addresses solutions in which ionic strength and autoprotolysis of water might not be factors. The approach is the same, but an important difference is that these solutions are alkaline because  $\{H^+\} < \{OH^-\}$ .  $C_{HA}$  is not relevant: it is replaced with  $C_{MOH}$ . Because M is  $Na^+$ , MOH is a strong base, NaOH, that will completely dissociate to  $M^+$  ( $Na^+$ ) and  $OH^-$ .

Where  $C_{MOH}$  is significant, autoprotolysis of water can be ignored, and where  $C_{MOH}$  is small, ionic strength of the solution can be ignored and  $\gamma_{H^+}$  can be taken as 1.00; adding  $C_{MA}$  will make ionic strength a factor even when  $C_{MOH} \approx 0$ . As in Problem 1, we could use four approaches to solve these four problems, but instead we will use the one-equation approach. This will require an expression for  $[H^+]$  that is sensitive to autoprotolysis of water, and this will come from charge balance and mass balance requirements like those used to create 3-27. Here, charge balance requires:

$$[H^+] + [Na^+] = [OH^-]. \quad 3-35$$

Because all of the  $Na^+$  comes from the NaOH,  $[Na^+] = C_{NaOH}$ , and from 3-24,  $[OH^-] = K_w/[H^+]$ . So

$$[H^+] + C_{NaOH} = K_w/[H^+]. \quad 3-36$$

and,

$$[H^+]^2 + [H^+]C_{NaOH} - K_w = 0. \quad 3-37$$

Notice the sign change in the coefficient for  $[H^+]$  in 3-26 compared to 3-37. When this quadratic is solved, as in 3-26 it too has two solutions, and only one has a real, physical meaning.

$$[H^+] = \frac{-C_{NaOH} + \sqrt{C_{NaOH}^2 + 4K_w}}{2} \quad 3-38$$

With the exception of this new expression for  $[H^+]$ , one could go back to the “one-equation” worksheet for Problem #1, replace  $C_{HNO_3}$  with  $C_{NaOH}$  and  $C_{KNO_3}$  with  $C_{NaCl}$  and generate the four solutions to this problem, a worthwhile exercise! But in order to demonstrate the variety in which problems can be solved, this problem will be solved a little differently, of course using what has already been presented. Most of the output is *not* shown below for the sake of space, but the input is written so that one can watch the evolution of  $H_{NaOH}$  from:

$$H_{NaOH} := -\frac{1}{2} C_{NaOH} + \frac{1}{2} \sqrt{C_{NaOH}^2 + 4 K_w}$$

to

$$\sqrt{-\frac{1}{2} C_{NaOH} + \frac{1}{2} \left( C_{NaOH}^2 + \frac{\frac{4.028 \cdot 10^{-14}}{0.511 \sqrt{C_{NaOH} + C_{NaCl}}} - \frac{0.511 \sqrt{C_{NaOH} + C_{NaCl}}}{10^{1+2.961 \sqrt{C_{NaOH} + C_{NaCl}}}} \right) }$$

Also, the next steps:  $\text{Activity}_{H_{NaOH}} := \text{Gamma}[\text{H}] * H_{NaOH}$  and  $\text{pH} := -\log_{10}(\text{Activity}_{H_{NaOH}})$  should be apparent. So their outputs, also, are not provided below. Finally, the problem has been reduced to two, *albeit* complex, steps to demonstrate an economy of inputs.

```
> restart; Gamma[H]:=10^(-0.511 *sqrt(C[NaOH]+C[NaCl])/(1+(0.329*9*sqrt(C[NaOH]+C[NaCl])))); Gamma[OH]:=10^(0.511*sqrt(C[NaOH]+C[NaCl])/(1+(0.329*3.5*sqrt(C[NaOH]+C[NaCl])))); H[NaOH]:=(-C[NaOH] +sqrt(C[NaOH]^2+4*K[w]))/2; K[w]:=1.007e-14; H[NaOH]; K[w]:=K[w]/(Gamma[H]*Gamma[OH]); H[NaOH]; Activity['H[NaOH]']:=Gamma[H]*H[NaOH]; pH[NaOH]:= -log[10](Activity['H[NaOH]']);
```

$$pH_{NaOH} := -\frac{\ln \left( \frac{0.511 \sqrt{C_{NaOH} + C_{NaCl}}}{1 + 2.961 \sqrt{C_{NaOH} + C_{NaCl}}} \left( -\frac{1}{2} C_{NaOH} + \frac{1}{2} \sqrt{C_{NaOH}^2 + \frac{\frac{4.028 \cdot 10^{-14}}{0.511 \sqrt{C_{NaOH} + C_{NaCl}}} - \frac{0.511 \sqrt{C_{NaOH} + C_{NaCl}}}{10^{1+2.961 \sqrt{C_{NaOH} + C_{NaCl}}}}}{\ln(10)} \right) \right)}{\ln(10)}$$

With an expression for pH written exclusively in terms of  $C_{NaOH}$  and  $C_{NaCl}$  it is a simple matter of evaluating this expression at the desired concentrations, just as in Problem #1. This is done here with a single input, cutting and pasting the `evalf(eval(pH...))` command three times, making the appropriate substitutions for each problem. In coming chapters, more convenient ways to carry out multiple evaluations will be introduced.

The floating point calculations for part b are especially sensitive to “digits” because of the  $-C_{NaOH}$  term. So, on the **Preferences > Precision** tab, it is *necessary* to set Round calculation to 15 significant digits. At fewer than 13 significant digits, Maple will return `pH_b := Float(∞)`.

```

> pH_a:=evalf(eval(pH[NaOH], {C[NaOH]= 4.8e-7,C[NaCl]=0}));  

pH_b:=evalf(eval(pH[NaOH],{C [NaOH]=0.52,C[NaCl]=0}));pH_c:=  

evalf(eval(pH[NaOH],{C [NaOH]= 7.5e-5,C[NaCl]=0})); pH_d  

:= evalf( eval(pH[NaOH], {C[NaOH] = 2.7e-6,C[NaCl] = 3.9e-  

2}));  

pH_a := 7.696  

pH_b := 13.914  

pH_c := 9.876  

pH_d := 8.511

```

4. The simplistic calculation of pH, 3-29, is useful in *estimating* the answer here. Given

$$\text{pH} \approx -\log C_{\text{HA}}$$

leads to:

$$C_{\text{HA}} \approx 10^{-\text{pH}}.$$

So, for pH = 2.00, an analytical concentration of 0.010 M strong acid would seem appropriate. We will now show that this is significantly incorrect. However, if this answer (0.010 M HClO<sub>4</sub>) is even remotely correct, it would imply that the autoprotolysis of water is insignificant in this problem. That is true *and* it simplifies the problem. The other issue in rigorous pH calculations is ionic strength concerns. Inasmuch as C<sub>HA</sub> ≈ 0.01, and from 3-13, C<sub>HClO<sub>4</sub></sub> = μ = 0.01. So γ<sub>H<sup>+</sup></sub> will be decidedly less than 1.00 because 2-13 would give 0.913.



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If the autoprotolysis of water is neglected, then

$$[\text{H}^+] = C_{\text{HClO}_4}.$$

Setting Round screen display to 3, replacing  $\mu$  with  $C_{\text{HClO}_4}$  in the Debye-Hückel equation and  $[\text{H}^+]$  with  $C_{\text{HClO}_4}$  in 3-15, the computation might be carried out with Maple something like:

```
> restart; pH:=-log[10](H*Gamma[Hyd]): H := C[HClO[4]]:
Gamma[Hyd] := 10^((-0.511*sqrt(C[HClO[4]]))/(1+0.329*9*
sqrt(C[HClO[4]]))); 'pH' = pH;
```

$$\begin{aligned}\Gamma_{\text{Hyd}} &:= 10^{-\frac{0.511 \sqrt{C_{\text{HClO}_4}}}{1 + 2.961 \sqrt{C_{\text{HClO}_4}}}} \\ \text{pH} &= -\frac{\ln\left(\frac{0.511 \sqrt{C_{\text{HClO}_4}}}{1 + 2.961 \sqrt{C_{\text{HClO}_4}}} \cdot 10\right)}{\ln(10)}\end{aligned}$$

```
> fsolve(pH = 2, C[HClO[4]]);
```

$$0.011$$

Notice the peculiar use of `Hyd` for `H` in `Gamma[Hyd]`. This is because `['H']` is only partially effective in protecting `H` from being substituted with  $C_{\text{HClO}_4}$ .  $\Gamma_H$  is returned, not  $\Gamma_{\text{HClO}_4}$ , but within the pH expression,  $\Gamma_{\text{HClO}_4}$  is somehow included. Above, the expression `pH = 2` is so simple that it is included directly within the `fsolve` command rather than naming it and then including that name in `fsolve` something like what was necessary in Problem 3.

The computed  $C_{\text{HClO}_4}$  is ten percent larger than the estimated (0.010 M) value. One can check the output by assigning the most recent output, `%` to  $C_{\text{HClO}_4}$ .

```
> evalf(eval(pH,C[HClO[4]] = %));
```

$$2.0000$$

# 4 Weak Acids and Weak Bases

In Chapter 3 we described the properties of strong electrolytes. If MA is a strong electrolyte, it will entirely dissociate into  $M^{n+}$  and  $A^{n-}$ , even when the concentration of MA is large. That is, even when  $C_{MA}$  is large. Also in Chapter 3, we introduced the concept of the acid and base: recall that an acid<sup>51</sup> would have  $M^{n+} = H^+$  and a base would require that  $A^{n-} = OH^-$ . Soon enough we will broaden these criteria, but for now let us consider the characteristics of a weak acid or weak base of these respective formulae.



and



When HA and MOH do not *completely* dissociate, we have a weak acid and weak base, respectively. *Then, it is no longer appropriate to presume that*

$$[A^-] = C_{HA}$$

or that

$$[M^+] = C_{MOH}$$

as was the case for a strong electrolyte.

Now it becomes necessary to revisit Chapter 1 where equilibrium was first addressed. For HA dissociation, the product is  $H^+$  and  $A^-$  and the reactant is HA. The equilibrium constant,  $K_{eq}$  would be the product of the products divided by the reactant. Because the products are ions, we can assume that the dissociation reaction occurs in solution.<sup>52</sup> HA,  $H^+$ , and  $A^-$  are expressed as molarities, and so square brackets are used. Finally,  $K_{eq}$  is a general notation for an equilibrium constant, but when the equilibrium is the dissociation of an acid,  $K_{eq}$  is replaced with  $K_a$ . When  $K_a$  appears, the reader will *know* that one of the reaction products is  $H^+$ !

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad 4-1$$

$K_a$  is called the acid dissociation constant. This convention leads to the base dissociation constant,  $K_b$ , for MOH.

$$K_b = \frac{[M^+][OH^-]}{[MOH]} \quad 4-2$$

While there is not a lot of variation in the way we might express  $K_a$ ,<sup>53</sup>  $K_b$  can take other forms. In fact,  $K_b$  as defined in 4-2, is limited because if MOH is not a *strong* base, it is probably insoluble, or likely to dissociate to  $H^+ + MO^-$ , *i.e.* act as an acid. This form of a weak base is typically addressed as a compleximetric equilibration which is deferred to Chapter 9. Consider, however, the hydrolysis (water splitting) reaction:



In order to abstract the  $H^+$ , from  $H_2O$  it seems only logical that  $n \leq 0$  because a positively charged  $M^n$  would be more inclined to bind to the  $OH^-$  moiety of water. Generally  $M^n$  is an organic molecule (when  $n = 0$ ) or an anion<sup>54</sup> ( $n < 0$ ), and the  $K_b$  for 4-3 is written:

$$K_b = \frac{[MH^{n+1}][OH^-]}{[M^n]} \quad 4-4$$

A common example of this hydrolysis has  $M^{n+} = NH_3$  ( $n = 0$ ) so that  $MH^{n+1} = NH_4^+$ . Notice that either expression for  $K_b$  (4-2 or 4-4) has  $[OH^-]$  in the numerator just as  $K_a$  has  $[H^+]$  in the numerator.

---

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Before proceeding to make use of  $K_a$  and  $K_b$ , the form of these expressions requires some clarification.  $[H_2O]$  is conspicuously absent in 4-4 despite its appearance in 4-3. As a reactant,  $H_2O$  would be expected to be expressed in the denominator, but it is not because it is effectively, itself, a constant, and so it can be embedded in  $K_b$ . Consider this:  $H_2O$  has a molecular weight of 18.02 g and a density of 1000 g / L. That means that pure water has a concentration of 55.5 mole per L. Virtually all ionic equilibrium problems (at least of analytical interest) pertain to solutions of less than one or two molar. Suppose that for the reaction depicted in 4-3  $[M^{n+}] = 2$  Molar. Even if the reaction proceeds to completeness, only 2 moles of  $H_2O$  could be consumed, and this would constitute less than a four percent change in  $[H_2O]$ .

The thermodynamic expression for the equilibrium constant for 4-3,  $K^o_b$  uses activities in place of concentrations as described in Chapter 2. Here too,  $H_2O$  is not included in the expression, and this is because  $\{H_2O\}$  is effectively constant.

$$K^o_b = \frac{\{MH^{n+}\}\{OH^-\}}{\{M^n\}} \quad 4-5$$

Recalling Endnote 31 in Chapter 3,  $H^+$  is not the correct depiction of the dissociation of HA: it should be  $H_3O^+$ , and the dissociation is more correctly written:



But again by the argument given above,  $[H_2O]$  and  $\{H_2O\}$  are essentially constant throughout this dissociation reaction and so these can be embedded in  $K_a$  and  $K^o_a$ , respectively.

For a strong acid, HA, pH could be calculated based on the premise that

$$C_{HA} = [A^-],$$

and this allowed us to rewrite Equation 3-23 as

$$[H^+] = C_{HA} + [OH^-]$$

which became Equation 3-26

$$[H^+]^2 - [H^+]C_{HA} - K_w = 0.$$

This followed from the mass balance requirement that the acid is either associated (HA) or dissociated ( $A^-$ ), and so

$$C_{HA} = [HA] + [A^-], \quad 4-6$$

and that because HA “totally” dissociates,  $[HA]$  must be zero. Conversely, if HA is a weak electrolyte, it will not fully dissociate and  $[HA]$  will not equal zero. Indeed, HA can be so weak that it is  $[A^-]$  that approaches zero. But the point here is to write a general expression independent of the degree of dissociation of HA. For this purpose we rearrange 4-1 so that  $[HA]$  can be expressed in terms of  $K_a$ ,  $[H^+]$  and  $[A^-]$ .

$$[HA] = \frac{[H^+][A^-]}{K_a} \quad 4-7$$

Substituting this into 4-6 gives:

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

and then after factoring out  $[A^-]$ ,

$$C_{HA} = [A^-] \left\{ \frac{[H^+] + K_a}{K_a} \right\} \quad 4-8$$

A strong acid, by definition, requires total dissociation of HA, and that requires that  $K_a$  be a very large value (approaching infinity). With a large  $K_a$ ,  $\{([H^+] + K_a)/K_a\}$  approaches 1.00, and that leaves  $C_{HA} \approx [A^-]$ . A weak acid, on the other hand, requires that  $K_a$  be a small value. Equation 4-8 is not conducive to showing the effects of  $K_a \rightarrow 0$ , but by rearranging 4-1 to:

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

and substituting this into 4-6 gives:

$$C_{HA} = [HA] \left\{ \frac{[H^+] + K_a}{[H^+]} \right\} \quad 4-9$$

Now, it is evident that as  $K_a$  approaches zero,  $[H^+] + K_a$  will approach  $[H^+]$  and so  $C_{HA} \approx [HA]$ . This also provides another mathematical illustration of Le Châtelier’s Principle as discussed in Chapter 1: Looking again at the dissociation of HA,



it is apparent that increasing  $[H^+]$ , that is adding  $\text{H}^+$ , would drive the equilibrium to the left thereby decreasing  $[A^-]$  and increasing  $[HA]$ . Substituting different values for  $[H^+]$  into Equations 4-8 and 4-9 illustrates this point. That is, with large values for  $[H^+]$ , 4-9 gives  $[HA] \approx C_{HA}$ , and as  $[H^+]$  approaches zero, 4-8 gives  $[A^-] \approx C_{HA}$ .

Before addressing the mass and charge balance requirements of weak bases (page 80), we will proceed to use these new mass balance expressions (4-8 and 4-9) to create an expression for  $[H^+]$  as a function of  $C_{HA}$  when HA is a weak electrolyte with a dissociation constant equal to  $K_a$ . The key is the charge balance requirement as described by Equation 3-23, renumbered here:

$$[H^+] = [A^-] + [OH^-]. \quad 4-10$$

As we did for 3-25 we replace  $[OH^-]$  with  $K_w/[H^+]$ , but instead of replacing  $[A^-]$  with  $C_{HA}$  we rearrange 4-8 to

$$[A^-] = \frac{C_{HA}K_a}{[H^+] + K_a} \quad 4-11$$

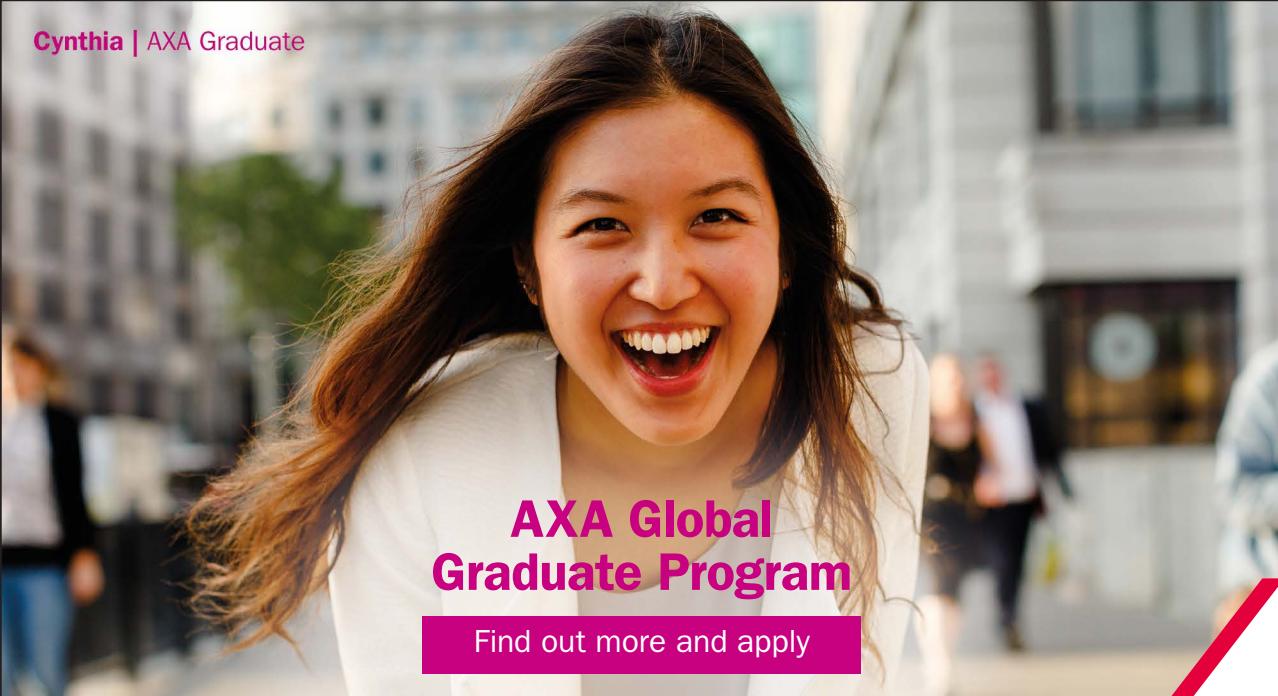
and replace  $[A^-]$  with this term, appropriate for a weak electrolyte. This gives:

$$[H^+] = \frac{C_{HA}K_a}{[H^+] + K_a} + \frac{K_w}{[H^+]} \quad 4-12$$

which can be converted into a cubic equation by multiplying through by  $[H^+]$  and then by  $([H^+] + K_a)$ .

$$[H^+]^3 + K_a[H^+]^2 - (K_a C_{HA} + K_w)[H^+] - K_a K_w = 0 \quad 4-13$$

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One of the roots to this cubic equation will provide the hydrogen ion concentration for an aqueous solution of the weak acid HA. It is not immediately evident how this compares to the strong acid, quadratic expression derived in Chapter 3 (Equation 3-26). We will pause here to illustrate how Equation 4-13 might be derived on Maple, and then to use Maple to show how this expression for  $[H^+]$  behaves at critical values for  $C_{HA}$  and  $K_a$ , and finally discuss how this compares to the performance of 3-26.

Be advised that the exercise that follows is not strictly necessary, that indeed, Maple is more than able to extract  $[H^+]$  ( $H$ ) from an implicit expression like 4-12. (See the solution to Problem 2b of this chapter.) This exercise does, however, illustrate Maple's acuity with computer algebra. This derivation will begin by stating charge balance and mass balance requirements and defining the equilibrium constants,  $K_w$  and  $K_a$ .

```
> restart; ChBal:= H = A + OH; MassBal:= C[WeakAcid]55 = HA + A;
EqCon:= K[a] = (H*A)/HA; Water:= K[w] = H*OH;

ChBal := H = A + OH
MassBal := C[WeakAcid] = HA + A
EqCon := K_a =  $\frac{HA}{H}$ 
Water := K_w = H OH
```

The process of substituting  $A$  ( $[A^-]$ ) and  $OH$  ( $[OH^-]$ ) into the charge balance expression is achieved by defining  $A$  as the solution to the `ChBal` expression for  $A$ , and  $OH$  as a solution to `Water` expression. `MassBal;` is entered to show that the substitutions have been made.

```
> A := solve(ChBal, A); OH := solve(Water, OH); HA := solve (EqCon, HA);
MassBal;

A := H - OH
OH :=  $\frac{K_w}{H}$ 
HA :=  $\frac{H^2 - K_w}{K_a}$ 
C[WeakAcid] =  $\frac{H^2 - K_w}{K_a} + H - \frac{K_w}{H}$ 
```

It is from this mass balance expression that the cubic polynomial will be created, but in order to do that, this expression will require some manipulation to render it in the form of Equation 4-13. Maple provides many commands to effect these manipulations, and often it is a matter of trial and error to discover the appropriate approach.

```
> normal(MassBal);

C[WeakAcid] = 
$$\frac{-HK_w + H^3 - K_w K_a + K_a H^2}{K_a H}$$

```

This is close to 4-13; multiplying through by the denominator,  $K_a H$  will bring the expressions closer together.

```
> MassBal := H*K[a]*MassBal;
```

$$\text{MassBal} := K_a H C_{\text{WeakAcid}} = K_a H \left( \frac{-K_w + H^2}{K_a} - \frac{K_w}{H} + H \right)$$

Notice that the form of the right hand side of the expression has been complicated by the operation, but using the `simplify` command will restore this to form.

```
> MassBal := simplify (MassBal);
```

$$\text{MassBal} := K_a H C_{\text{WeakAcid}} = -HK_w + H^3 - K_w K_a + K_a H^2$$

Finally, the expression we are seeking has the right hand side (`rhs`) of `MassBal` minus the left hand side (`lhs`) of `MassBal` equal to zero. We will rename the expression and carry out this algebra in one operation.<sup>56</sup>

```
> Cubic := rhs(MassBal) - lhs (MassBal) = 0;
```

$$\text{Cubic} := -HK_w + H^3 - K_w K_a + K_a H^2 - K_a H C_{\text{WeakAcid}} = 0$$

We need only to collect the terms to achieve the desired *form* of the cubic equation.

```
> Cubic := collect(Cubic, H);
```

$$\text{Cubic} := H^3 + K_a H^2 + (-K_w - K_a C_{\text{WeakAcid}}) H - K_w K_a = 0$$

This produces, in Maple Text, the expression describing the relationship between  $[H^+]$  and the concentration and dissociation constant for the weak acid solute. It is equivalent to Equation 4-13. Certainly, one could simply have entered this expression directly and then proceeded to the analysis of its behavior from here. The behavior of this expression is particularly important at  $C_{\text{WeakAcid}} = 0$ , and at  $K_a = 0$ . Recall that for a strong acid solution, one can sometimes presume that  $[H^+] = C_{\text{HA}}$ , but that this approximation fails when  $C_{\text{HA}}$  approaches zero.<sup>57</sup> When mass and charge balance were addressed rigorously, Equation 3-27 is created, and it correctly shows that the lower limit to  $[H^+]$  is  $\sqrt{K_w}$ , i.e. at  $C_{\text{HA}} = 0$ .

We will modify the Maple output (above) to create two, specific expressions for the weak acid  $[H^+]$ : one for  $C_{\text{WeakAcid}} = 0$  and the other for  $K_a = 0$  using the substitute operation.

```
> ZeroC[WeakAcid] := subs(C[WeakAcid] = 0, Cubic); ZeroK[a] :=  
subs(K[a] = 0, Cubic);
```

$$\begin{aligned}ZeroC_{WeakAcid} &:= -HK_w + H^3 - K_w K_a + K_a H^2 = 0 \\ZeroK_a &:= -HK_w + H^3 = 0\end{aligned}$$

Both are 3° polynomials but each is restricted to a specific condition. The roots of each will reveal the  $[H^+]$  at these specific conditions. For clarity, a string (text) is added to the input, and this is done by using quotation marks.

```
> "Roots for C[WeakAcid] = 0"; solve(ZeroC[WeakAcid], H); "Roots for  
Ka = 0"; solve(ZeroK[a], H);
```

"Roots for C[WeakAcid] = 0"  
 $\sqrt{K_w}, -\sqrt{K_w}, -K_a$   
 "Roots for Ka = 0"  
 $0, \sqrt{K_w}, -\sqrt{K_w}$

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Exactly as with 3-26, we have multiple roots, but only one of which represents a physically realistic solution. For these cubic equations only one root is greater than zero. Obviously a solution implying that  $[H^+]$  is less than zero is not grounded in reality,<sup>58</sup> but implying that  $[H^+] = 0$  is also impossible in an aqueous solution<sup>59</sup> because of the auto-protolysis of water. So, when there is *no* weak acid present,  $[H^+] = \sqrt{K_w}$ , and if the weak acid is so weak that it does *not* dissociate at all, again  $[H^+] = \sqrt{K_w}$ .

In order to explore the behavior of the weak acid expression for  $[H^+]$  at high concentrations and large  $K_a$ s, it will be necessary to resurrect the issue of activity and activity coefficients because under either of these conditions, the ionic strength is likely to be appreciable. This will affect  $\gamma_{H^+}$ ,  $\gamma_{A^-}$ ,  $K_a$  and  $K_w$ . This problem is unlike the problems addressed in Chapter 3 for strong acids, because there,  $K_a$  was not a factor. Here,  $K_a$  is a factor: it will affect  $[H^+]$ , and that will affect  $\mu$ , and that will affect the  $\gamma$ s which will ultimately affect  $K_a$ . This circular problem must be addressed by reiteration.

How  $K_a$  and  $C_{HA}$  affect the ionic strength can be illustrated by making appropriate substitutions into the expression for ionic strength. Applying 2-5 to a solution of HA gives:

$$\mu = \frac{1}{2} \{ [H^+] + [A^-] + [OH^-] \} \quad 4-14$$

Because HA is a weak acid, we cannot replace  $[A^-]$  with  $C_{HA}$ , but we can use 4-11 which includes a  $K_a$  term to address the limited dissociation. Again, we can replace  $[OH^-]$  with  $[H^+]/K_w$  as described in 3-24. So, the ionic strength can be expressed in terms of  $C_{HA}$ ,  $K_a$  and  $K_w$  as:

$$\mu = \frac{1}{2} \left\{ [H^+] + \frac{C_{HA}K_a}{[H^+] + K_a} + \frac{K_w}{[H^+]} \right\} \quad 4-15$$

Now  $\mu$  can be adjusted with  $K_a$  and  $C_{HA}$ . Finding  $K_a$  is the next problem because it depends directly upon  $\gamma_{H^+}$ ,  $\gamma_{A^-}$  and indirectly upon  $\mu$ . Modifying 2-11 to pertain to the dissociation of  $HA \rightleftharpoons H^+ + A^-$  gives:

$$K_a = \frac{\gamma_{HA}}{\gamma_{H^+}\gamma_{A^-}} K_a^\circ \quad 4-16$$

This ties  $K_a$  to a true constant,<sup>60</sup> its thermodynamic dissociation constant,  $K_a^\circ$ . Because HA is neutral (*i.e.*  $z = 0$ )  $\gamma_{HA} = 1$ , according to Debye-Hückel (2-4, or 2-13) or Davies (2-8). So,

$$K_a = \frac{K_a^\circ}{\gamma_{H^+}\gamma_{A^-}} \quad 4-17$$

Still, there is no clear starting point to the problem; even if  $C_{\text{HA}}$  and  $K_a^\circ$  are known,  $K_a$  cannot be found without  $\mu$  and that cannot be found without  $[\text{H}^+]$  and  $[\text{H}^+]$  cannot be found without  $K_a$ . So the problem is begun with a guess! The simplest guess is that  $K_a = K_a^\circ$  (and  $K_w = K_w^\circ$ ). From this and Equation 4-13,  $[\text{H}^+]$  can be found. With  $[\text{H}^+]$ , the approximation of  $K_a (= K_a^\circ)$  and 4-15,  $\mu$  can be found. From  $\mu$  and either Debye-Hückel or Davies, the required activity coefficients are found. These activity coefficients are used in 3-21 and 4-17 to find  $K_w$  and  $K_a$ , respectively. And now the process is begun again (reiterated). The  $[\text{H}^+]$  found on this second pass will change very little on a third or fourth iteration. This will be illustrated below.

What follows is a demonstration of Maple for determining the pH of an aqueous solution of HF, a weak acid with  $K_a^\circ = 6.6 \cdot 10^{-4}$ .  $C_{\text{HF}}$  will be set at 1.00 M. The Davies Equation (2-8) will be used to find the activity coefficients. This will be a little simpler than Debye-Hückel because, recall that by Davies, all  $z = \pm 1$  ions will have the same  $\gamma$ . Finally, most of the derivation of expressions will be eliminated and expressions will be entered directly, and the “uninteresting” output will be suppressed to minimize distraction. Explanations will be provided throughout, however. We begin by defining the parameters that will not change throughout the problem. We add the cubic expression for  $[\text{H}^+]$  for a weak acid. (We will again use the  $\text{K}[a[0]]$  designation for  $K_a^\circ$  and  $\text{K}[w[0]]$  designation for  $K_w^\circ$ .)

```
> restart; K[w[0]] := 1.007e-14; K[a[0]] := 6.6e-4; H[WeakAcid]
:= H^3 + K[a]*H^2 - (K[a]*C[HF] + K[w])*H - K[a]*K[w] = 0;
```

$$H_{\text{WeakAcid}} := H^3 + K_a H^2 - (K_a C_{\text{HF}} + K_w) H - K_a K_w = 0$$

Next, the parameters for  $H_{\text{WeakAcid}}$  are given values and the expression is displayed again to make sure that it contains H as the only variable.

```
> K[a] := K[a[0]]; K[w] := K[w[0]]; C[HF] := 1.0; H[WeakAcid];
```

$$H^3 + 0.0007 H^2 - 0.0007 H - 6.6462 \cdot 10^{-18} = 0$$

We complete the first iteration by solving this simple 3° polynomial for H. Inasmuch as we can expect a numeric solution, we can request a floating point solution. This provides an added feature over `solve`: with `fsolve` we can define the range over which the solution will be sought, and thereby generate only one solution for future operations. This is achieved with the, `0..C[HF])` portion of the command. Providing a range over which to search for a floating point solution can be beneficial because `fsolve` has been known to “miss” solutions!<sup>61</sup> One has the option of stating this range as a pair of values, something like `,0..1E-2`. So, why is 0 to  $C_{\text{HF}}$  chosen? We have already explained that  $[\text{H}^+]$  must be greater than zero, but why should it be less than or equal to  $C_{\text{HF}}$ ? Recall that the source of  $\text{H}^+$  is  $\text{H}_2\text{O}$  and HF, and because autoprotolysis of  $\text{H}_2\text{O}$  is very small (small  $K_a$ ), HF is effectively the only source of  $\text{H}^+$ . So  $C_{\text{HF}}$  is a reasonable limit.<sup>62</sup> By establishing this range, only one solution is returned and it will be a realistic solution. By having only one solution, we can define H as the solution to the expression, and then immediately use this value in subsequent calculations without substitution.

```
> H := fsolve(H[WeakAcid], H, 0..C[HF]);
```

$$H = 0.0254$$

We now have  $[H^+]$  so that  $\mu$  and the  $\gamma$ s and then  $K_a$  and  $K_w$  can be found.

```
> Gamma := 10^(-0.5 * ((sqrt(mu) / (1 + sqrt(mu))) + 0.15 * mu)); mu := 0.5 * (H
+ (C[HF] * K[a]) / (H + K[a])) + (K[w] / H); 'Gamma' = Gamma;
```

$$\Gamma := 10^{-\frac{0.5000 \sqrt{\mu}}{1+\sqrt{\mu}} - 0.0750 \mu}$$

$$\mu := 0.0254$$

$$\Gamma := 0.8463$$

The first, symbolic *output* for  $\Gamma$  might have been omitted, but the equation entails a lot of algebra and it is wise to make sure that it is properly expressed. Compare it to the *logarithmic* form of 2-8; it is equivalent!

It might have been surprising that ultimately  $\mu = [H^+]$ , but consider this: charge balance required that

$$[H^+] = [F^-] + [OH^-].$$

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So the expression for  $\mu$  (4-14) could have been rewritten:

$$\mu = \frac{1}{2} \{ [H^+] + [\text{H}^+] \} = [H^+]$$

With an estimation for  $[H^+]$  and  $\gamma_{H^+}$ , it is now possible to make a first estimation of the pH of this solution.

```
> pH := -log[10] (Gamma*H);
```

$$pH := 1.6664$$

Normally this first calculation for pH is omitted because it is rarely sufficiently close to the value found on the second iteration. The reiteration process is begun by using the newly-found activity coefficients to find  $K_a$  from  $K^o_a$  and  $K_w$  from  $K^o_w$ . Then, H is unassigned and  $H_{\text{WeakAcid}}$  is recreated, and solved for H and the entire calculation process is recycled.

```
> K[a]:=K[a[0]]/(Gamma*Gamma); K[w]:=K[w[0]]/(Gamma*Gamma); H:='H':  
H[WeakAcid]:= H^3 + K[a]*H^2 - (K[a]*C[HF] + K[w])*H - K[a]*K[w]  
= 0; H:= fsolve(H[WeakAcid], H, 0..1); mu:= 0.5*(H + (C[HF]*K[a]/(H  
+ K[a])) + (K[w]/H)); Gamma:= 10^(-0.5*((sqrt(mu)/(1 + sqrt(mu))) +  
0.15*mu)); pH:=-log[10] (Gamma*H);
```

$$K_a := 0.0009$$

$$K_w := 1.3938 \cdot 10^{-14}$$

$$H_{\text{WeakAcid}} := H^3 + 0.0009 H^2 - 0.0009 H - 1.2733 \cdot 10^{-17} = 0$$

$$H := 0.0298$$

$$\mu := 0.0298$$

$$\Gamma := 0.8398$$

$$pH := 1.6020$$

An appreciably different pH is found on this first reiteration.  $\mu$  has increased and  $\gamma$  has decreased. The previous input paragraph can be cut and pasted as the next input paragraph following this output and when it is executed it will provide an even more accurate assessment of  $[H^+]$  etc. Indeed it is a simple matter to paste the same input paragraph as several subsequent input paragraphs, and when executed, the evolution of  $[H^+]$  etc. can be illustrated. Four such executions showed the following:

Condition	$\gamma$	$[H^+]$	pH
$K = K^o$	0.8463 <sup>63</sup>	0.0254	1.668 <sub>3</sub>
2 <sup>nd</sup>	0.8352	0.0299	1.602 <sub>5</sub>
3 <sup>rd</sup>	0.8343	0.0303	1.597 <sub>4</sub>
4 <sup>th</sup>	0.8343	0.0303	1.597 <sub>0</sub>

Within three iterations a stable pH is returned. Considering that the  $K_a^o$  for HF was provided to only two significant figures, the pH should be reported to only three decimal places, and this is achieved on the third iteration.

Calculation of the pH of a solution of a weak acid or weak base is only the beginning of studying these solutions. Often, of greater interest is the distribution of the forms of the weak acid or weak base. It was shown that  $[A^-]$  could be expressed in terms of  $[H^+]$  and  $C_{HA}$  ( 4-11). Likewise 4-9 can be rearranged for the same effect.<sup>64</sup>

$$[HA] = \frac{C_{HA}[H^+]}{[H^+] + K_a} \quad 4-18$$

We introduce here two new definitions,  $\alpha_{A^-}$  and  $\alpha_{HA}$ . These are the *fractions* of  $C_{HA}$  which exist in the deprotonated form and protonated form, respectively. From this, each component's concentration can be expressed more simply as:

$$[A^-] = \alpha_{A^-} C_{HA} \quad 4-19$$

$$[HA] = \alpha_{HA} C_{HA} \quad 4-20$$

By comparing 4-11 with 4-19 and 4-18 with 4-20, it should be evident that:

$$\alpha_{A^-} = \frac{[A^-]}{C_{HA}} = \frac{K_a}{[H^+] + K_a} \quad 4-21$$

and

$$\alpha_{HA} = \frac{[HA]}{C_{HA}} = \frac{[H^+]}{[H^+] + K_a} \quad 4-22$$

Because this weak acid is either protonated or deprotonated, it is only logical that the fraction of protonated acid plus the fraction of deprotonated acid must equal exactly 1. Adding 4-21 to 4-22 confirms that!

These alpha terms are also a convenient way to discuss Le Châtelier's Principle. From that principle, one would expect that a large  $[H^+]$  would lead to a large  $[HA]$ , and as  $[H^+]$  approaches zero,  $[A^-]$  should become the predominant form of the weak acid. Notice, finally, that neither alpha can reach zero or one unless  $[H^+]$  is zero (impossible in water) or unless  $K_a$  is zero (so HA is not an acid!).

The last output from Maple provided an excellent estimation of  $[H^+]$  and  $K_a$ . So it would be informative to add an input line requesting  $\alpha_{A^-}$  and  $\alpha_{HA}$ .

```
> alpha[HF]:= H/(H + K[a]); alpha[F]:= K[a]/(H + K[a]);
```

$$\alpha_{HA} = 0.9697$$

$$\alpha_F = 0.0303$$

This implies that *this* solution of HF is only 3.03% dissociated and that 96.97% of the HF remains associated. By the standard given in Chapter 3 (page 38), HF is clearly a weak acid. However, if one were to rework this problem (back on page 74) with  $C_{\text{HF}} \leq 6.6 \cdot 10^{-7}$ , suddenly  $\alpha_{\text{A}^-}$  is greater than 0.999.<sup>65</sup> So is HF *sometimes* a strong acid? No. This is why the concentration of the acid is part of the definition of a strong electrolyte: it is an electrolyte (or in this case an acid) that dissociates  $\geq 99.9\%$  in a concentrated ( $\geq 1 \text{ M}$ ) solution. Said another way, for a strong monoprotic acid,  $\alpha_{\text{A}^-}$  will be at least 0.999, even when  $C_{\text{HA}} \geq 1 \text{ M}$ .

What is the relationship between  $K_a$  and  $C_{\text{HA}}$  for a *given*  $\alpha_{\text{A}^-}$ ? For this, we use the definition of  $\alpha_{\text{A}^-}$  (4-21) along with the polynomial expression for an acid solution (4-13). When  $\alpha_{\text{A}^-} = 0.999$  is substituted into 4-21,  $[\text{H}^+] = 0.001K_a$ . When  $[\text{H}^+]$  in 4-13 is replaced by  $0.001K_a$ , and  $K_w$  is set at  $10^{-14}$  a simple expression is produced, in terms only of  $C_{\text{HA}}$  and  $K_a$ . Solving this for  $C_{\text{HA}}$  gives  $C_{\text{reqd}}$  which is the maximum  $C_{\text{HA}}$  one can have in solution and achieve 99.9% dissociation for the given  $K_a$ .

```
> restart; Eqn := H^3 + K[a]*H^2 + (-K[w] - K[a]*C[HA])*H -  
K[w]*K[a] = 0: H:= 0.001*K[a]: K[w]:= 1e-14: Eqn; C[reqd]:=  
solve(Eqn, C[HA]);
```

$$0.0000 K_a^3 + 0.0010 \left( -1.0000 \cdot 10^{-14} - K_a C_{\text{HA}} \right) K_a - 1.0000 \cdot 10^{-14} K_a = 0$$

$$C_{\text{reqd}} := \frac{1.0010 \cdot 10^{-11} \left( 1.0000 \cdot 10^8 K_a^2 - 1.0000 \right)}{K_a}$$

This expression for  $C_{\text{reqd}}$  says a lot. If  $K_a$  is set equal to 999 (obviously a strong acid) in the expression above,  $C_{\text{reqd}}$  becomes 1.0 M. So we might simply define a strong acid as one with  $K_a \geq 999$ , and if  $K_a$ 's for the eight strong acids delineated in Chapter 3 were available, this would be reasonable. Returning to the expression for  $C_{\text{reqd}}$ , notice that when  $K_a$  is set to  $\leq 10^{-4}$ ,  $C_{\text{reqd}} \leq 0$ .

```
> K[a]:= 1E-4; C[reqd]; K[a]:= 9.999E-5; C[reqd];
```

$$\begin{aligned} K_a &:= 0.0001 \\ C_{\text{reqd}} &:= 0.0000 \\ K_a &:= 0.0001 \\ C_{\text{reqd}} &:= -2.0021 \cdot 10^{-11} \end{aligned}$$

Of course  $C_{\text{reqd}}$  cannot be less than zero. So we are shown that if  $K_a$  is less than  $10^{-4}$ , the acid, at *any* concentration, cannot dissociate more than 99.9%. We might then propose that an acid with  $K_a \leq 10^{-4}$  is a weak acid at *any* concentration. Example Problem 4 illustrates this point further.

Before closing the discussion on weak acid equilibration in water, one more point might be made regarding the 3° polynomial used to find  $[H^+]$ . Even without the benefit of a mathematics engine like Maple, the roots for this polynomial can be extracted with only moderate difficulty. In subsequent chapters it will become evident that for a polyprotic acid,  $H_nA$ , the polynomial used to extract  $[H^+]$  will be of the  $(n+2)$  degree. Reducing  $n$  by even 1, can be helpful. This is possible by making a very reasonable approximation. For the polynomial (4-13) used for HA, presume that

$$K_a K_w \approx 0. \quad 4-23$$

Given that  $K_w \approx 10^{-14}$  and if HA is indeed a weak acid so that  $K_a < 1$ ,  $K_a K_w$  is effectively negligible. Removing it from 4-13 allows  $[H^+]$  to be factored out producing a quadratic:

$$[H^+]^2 + K_a [H^+] - K_a C_{HA} - K_w = 0. \quad 4-24$$

And as with Equation 3-26 there are two roots and only one has real, physical meaning. It is

$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4(K_w + K_a C_{HA})}}{2} \quad 4-25$$

How does this compare with 3-27?

$$[H^+] = \frac{C_{HA} + \sqrt{C_{HA}^2 + 4K_w}}{2} \quad 3-27$$

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The most important similarity is that neither expression yields  $[H^+] = 0$  when  $C_{HA} = 0$ , but 4-25 is not *quite* right. The root at  $C_{HA} = 0$  is slightly greater than  $\sqrt{K_w}$  and it depends on  $K_a$ , but it is very close, and in that 4-25 is an *approximation*, it is quite good. Consider the use of 4-25 in the solution of the 1.0 M HF problem ( $K_a = 6.6 \times 10^{-4}$ ).

```
> restart; H:=(1/2)*(-K[a] + sqrt(K[a]^2 + 4*(K[w]+K[a]* C[HF])));  
C[HF]:= 1: K[a]:= 6.6e-4: K[w]:= 1.007e-14: H;
```

$$H := -\frac{1}{2} K_a + \frac{1}{2} \sqrt{K_a^2 + 4 K_w + 4 K_a C_{HF}}$$

$$0.0254$$

Using the cubic expression,  $[H^+]$  was found (page 76) to be 0.0254. Reformatting the output will show that these values match to ten significant figures!

Turning now to the equilibration of weak bases, how do the mass balance and charge balance constraints apply to aqueous solutions of a weak *base*? The



model will be left to the reader as an exercise (Example Problem 3), while the



model *will* be used to make the comparison to the mathematics of weak acid equilibria. For simplicity,  $n$  will be taken to be zero. This is a good example because M could be  $NH_3$  and so  $MH^+$  would be  $NH_4^+$ . With  $n = 0$ , the equilibration becomes:



While developing the expression for  $[H^+]$  for this weak base, it will be convenient to discuss the concept of the conjugate acid of a weak base and an important relationship between the  $K_b$  of a weak base and the  $K_a$  of its conjugate acid. Of course weak acids have conjugate bases, and this will be discussed in terms of the HA.

Consider first the mass balance requirement for the weak base M given that its analytical concentration is  $C_M$ . Inasmuch as it is either protonated  $MH^+$  or still de-protonated as M, the expression should be:

$$C_M = [M] + [MH^+].$$

4-26

The comparison of strong bases to weak bases is the same as it was in the discussion of strong and weak acids: If M were a strong base (like OH<sup>-</sup>) it would exist in solution ≥ 99.9% as MH<sup>+</sup> (H<sub>2</sub>O). The weaker M is as a base, the smaller the amount of MH<sup>+</sup> is formed. This is more clearly articulated by writing the K<sub>b</sub> for the protonation of M; it is a trivial modification of 4-4.

$$K_b = \frac{[MH^+][OH^-]}{[M]} \quad 4-27$$

A very weak base, M, is characterized by a very small K<sub>b</sub>, which, from 4-27 implies a small [MH<sup>+</sup>] and [OH<sup>-</sup>] with a concomitantly large [M].

It will be necessary to replace either [M] or [MH<sup>+</sup>] in 4-26 with its congener; that is to express [MH<sup>+</sup>] in terms of [M] or [M] in terms of [MH<sup>+</sup>]. Either operation can be managed by rearranging 4-27 to

$$[M] = \frac{[MH^+][OH^-]}{K_b} \quad 4-26$$

and also,

$$[MH^+] = \frac{K_b[M]}{[OH^-]} \quad 4-27$$

Either expression can be used to replace either component in 4-26, but such a substitution leaves an [OH<sup>-</sup>] in the mass balance expression, and this will create an inconvenience<sup>66</sup> in that ultimately, it is [H<sup>+</sup>] that is sought. The [OH<sup>-</sup>] in each expression can be replaced using 3-24:

$$[OH^-] = K_w / [H^+]. \quad 3-24$$

This transforms 4-28 into

$$[M] = \frac{[MH^+]K_w}{K_b[H^+]} \quad 4-30$$

and 4-29 into

$$[MH^+] = \frac{[M][H^+]K_b}{K_w} \quad 4-31$$

Now, either can be used in 4-26 for a substitution that will replace either congener and leave the result in terms of [H<sup>+</sup>]. We will make those substitutions soon in order to write a mass balance expression in terms of [H<sup>+</sup>], C<sub>M</sub> and equilibrium constants.

But first, notice that 4-31 also can be rearranged:

$$\frac{K_w}{K_b} = \frac{[H^+][M]}{[MH^+]} \quad 4-32$$

What reaction does this imply with  $[H^+]$  and  $[M]$  in the numerator and  $[MH^+]$  in the denominator?



This is the dissociation of the acid  $MH^+$ , and given that, its equilibrium constant would be  $K_a$ . So

$$\frac{K_w}{K_b} = K_a \quad 4-33$$

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$\text{MH}^+$  is the conjugate acid to M, and M is the conjugate base to  $\text{MH}^+$ . Equation 4-33 provides the relationship between the  $K_b$  for M and the  $K_a$  for  $\text{MH}^+$ . It mathematically illustrates what should be intuitive, chemically: if M is a relatively strong base, it will have a relatively large  $K_b$ , and from 4-33 that implies that  $K_a$  must be relatively small, and as  $K_a$  increases,  $K_b$  must decrease. In terms of acid / base chemistry, a relatively strong M would be more effective at abstracting and binding a proton, and so, its conjugate acid would be less inclined to releasing that proton. This rationale can be summarized into a simple, important principle in acid / base chemistry: The stronger the base, the weaker its conjugate acid, and the weaker the base, the stronger its conjugate acid. In terms of acids (HA), the stronger the acid, the weaker its conjugate base ( $\text{A}^-$ ) and *visa versa*. It will be shown in Chapter 5 that solutions of  $\text{MH}^+$  will be acidic and solutions of  $\text{A}^-$  will be alkaline.

Before resuming the derivation of the expression for  $[\text{H}^+]$ , one more comment regarding 4-33 is appropriate. To determine the pH of a solution of a weak base,  $K_b$  is required. However, thermodynamic tables, like Appendix IV, often do not include  $K_b$  (or more correctly  $K_b^\circ$ ) values. Instead, they take a more general approach and list values *only* for acids,  $K_a$ , and treat weak bases as their conjugate acids. So, for example, rather than provide the  $K_b$  for  $\text{NH}_3$ , the  $K_a$  for  $\text{NH}_4^+$  is provided. This does not add a step to the calculation of  $[\text{H}^+]$ . Indeed it saves a step as will be shown here.

We continue the derivation of a polynomial (in  $[\text{H}^+]$ ) for a weak base by reducing the number of variables in the mass balance expression (4-26). We can do this by using *either* 4-30 or 4-31 to remove *either*  $[\text{M}]$  or  $[\text{MH}^+]$ , respectively. We will use 4-30 to remove  $[\text{M}]$  because that term is for a neutral component and that makes it useless when we get to the charge balance requirement:

$$[\text{MH}^+] + [\text{H}^+] = [\text{OH}^-]. \quad 4-34$$

Combining 4-30 and 4-26 gives:

$$C_M = \frac{[\text{MH}^+]K_a}{[\text{H}^+]} + [\text{MH}^+] \quad 4-35$$

Which, on rearrangement, gives:

$$[\text{MH}^+] = \frac{[\text{H}^+]C_M}{K_a + [\text{H}^+]} \quad 4-36$$

Using 4-36 along with  $[\text{OH}^-] = K_w / [\text{H}^+]$  in 4-34 gives a charge balance expression in terms of constants  $K_a$  and  $K_w$ , parameter  $C_M$  and the variable of interest,  $[\text{H}^+]$ .

$$\frac{[\text{H}^+]C_M}{K_a + [\text{H}^+]} + [\text{H}^+] = \frac{K_w}{[\text{H}^+]} \quad 4-37$$

This can be rewritten as a 3° polynomial exactly as 4-12 was transformed to 4-13. That is by multiplying through by  $[H^+]$  and then by  $(K_a + [H^+])$ .

$$[H^+]^3 + (K_a + C_M)[H]^2 - K_w[H] - K_a K_w = 0. \quad 4-38$$

Just as the cubic 4-13 could be approximated as a quadratic by taking  $K_a K_w$  to be approximately 0, so too can 4-38. It becomes

$$[H^+]^2 + (K_a + C_M)[H] - K_w \approx 0. \quad 4-39$$

with one, “physically real,” root  $[H^+] =$

$$\frac{-(K_a + C_M) + \sqrt{\{(K_a + C_M)^2 + 4K_w\}}}{2} \quad 4-40$$

but be advised that because the solution is alkaline,  $[H^+] < 10^{-7}$  and so dropping the  $K_a K_w$  can be risky. See problem 1b in Chapter 5.

The similarities between cubic expressions 4-13 and 4-38 and the quadratic expressions 4-24 and 4-39 are subtle. The fact that  $K_a$  appears in the weak acid *and* in the weak base expressions can cause confusion. **Care must be taken to recognize the difference between  $C_{HA}$  and  $C_M$ .** HA is an acid and that is self evident, but M must be a base as described in Equation 4-3, and so  $K_a$  is for  $MH^+$ . Of course when the base is represented as MOH, it is clear that a base is involved, but the concept of a conjugate acid,  $M^+$  in this case, is unconventional, and so the polynomial expression is typically written in terms of  $K_b$  (see Example Problem 3).

The final point in weak base equilibration is that of  $\alpha_M$  and  $\alpha_{MH^+}$ . Development of expressions for these exactly follows the derivation of 4-21 and 4-22 for weak acids. Recall, these came from the mass balance expression where  $[HA]$  was written in terms of  $[A^-]$  (4-7), and then where  $[A^-]$  was written in terms of  $[HA]$ . The expression for  $\alpha_{MH^+}$  is already nearly complete. From the definition of  $\alpha$

$$\alpha_{MH^+} = \frac{[MH^+]}{C_M}$$

and a rearrangement of 4-36 we find

$$\alpha_{MH^+} = \frac{[H^+]}{K_a + [H^+]} \quad 4-41$$

It is no coincidence that 4-41 looks like 4-22. After all,  $MH^+$  and HA are both acids in solution with their conjugate bases, M and  $A^-$ , respectively. It is left to the reader to show that the expression for  $\alpha_M$  looks like 4-21.<sup>67</sup>

### Example Problems

1. Use the appropriate cubic polynomial (4-13 or 4-38) to calculate the pH of the following solutions. Use Debye-Hückel for activity coefficient calculations.
  - a) 0.25 M HCN
  - b) 0.066 M N(CH<sub>3</sub>)<sub>3</sub>
2. Consider a solution of a strong acid, HSa and a weak acid, HWa.
  - a) From charge balance and mass balance requirements, create a polynomial that is expressed in terms of [H<sup>+</sup>], C<sub>HSa</sub>, C<sub>HWa</sub>, K<sub>a</sub>, and K<sub>w</sub>.
  - b) Use this polynomial to find the pH of a solution that is 0.050 M in HSa and 0.060 M in HWa. Use the Davies Equation to calculate activity coefficients; take K<sup>°</sup><sub>a</sub> to be  $6.7 \times 10^{-3}$  and K<sup>°</sup><sub>w</sub> to be  $1.00 \times 10^{-14}$ .
3. For a solution of weak base, MOH, use charge balance and mass balance requirements to create a polynomial that is expressed in terms of [OH<sup>-</sup>], C<sub>MOH</sub>, K<sub>b</sub>, and K<sub>w</sub>. Also, write expressions for  $\alpha_{M+}$  and  $\alpha_{MOH}$  in terms of K<sub>b</sub> and [OH<sup>-</sup>].
4. Create a plot of K<sub>a</sub> vs. C<sub>HA</sub> showing how K<sub>a</sub> must increase with C<sub>HA</sub> to achieve  $\alpha_{A^-} = 0.999$ , and  $\alpha_{A^-} = 0.995$  between C<sub>HA</sub> = 0 and  $1 \times 10^{-6}$ .

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**Solutions to Example Problems**

1. a. This is a solution of a weak acid, and so **4-13** is the appropriate polynomial to be solved.

From Appendix II,  $a_{CN^-} = 3$ ,  $a_{OH^-} = 3.5$ ,  $a_H^+ = 9$ . From Appendix IV,  $K_a^\circ = 6.2 \cdot 10^{-10}$ .<sup>68</sup> Using  $K_w = 1.00 \cdot 10^{-14}$  will be sufficiently precise given the precision of  $C_{HCN}$  and  $K_a^\circ$ .

The procedure for finding the pH of this solution follows what was presented on page 74 *et seq.*, but to make activity coefficient corrections, Debye-Hückel will replace Davies. For this, some of the input for the solution to Problem #1 in Chapter 3 can be copied. Notice that some of the output is suppressed (colon in place of semicolon), that the = 0 part of the polynomial has been left out,<sup>6</sup> and that the output formatting has been changed to show more precision.

```
> restart; K[w[o]] := 1.00e-14; K[a[o]] := 6.2 e-10; H[HA]
:= H^3 + K[a]*H^2 - (K[a] *C[HCN] + K[w])*H - K[a]* K[w];
K[a] := K[a[o]]; K[w]:= K[w[o]]; C[HCN] := 0.25; H[HA]; H
:= fsolve(H [HA], H, 0..1); mu := 0.5*(H + (C[HCN]*K[a]/(H
+ K[a])) + (K[w]/H));
```

$$H_{HA} := H^3 + K_a H^2 - (K_a C_{HCN} + K_w) H - K_a K_w$$

$$H^3 + 6.200000 \cdot 10^{-10} H^2 - 6.200100 \cdot 10^{-10} H - 6.200000 \cdot 10^{-24}$$

$$H := 0.000012$$

$$\mu := 0.000012$$

$H[HA]$  output is requested to verify that all constants and parameters have been defined so that it is entirely in terms of  $H$ , and the  $H$  output is requested so that it can be compared to the output in the next iteration to see if a third iteration might be necessary. Arguably the  $\mu$  output is unnecessary.

Changing only the subscripts and values for Part **a**, the definitions for **Gamma ['H'] etc.** are taken from Chapter 3 and used in the next input paragraph. Recall that the single quotation marks around H are required because H has been defined in the previous input paragraph.

```
> Gamma ['H'] := 10^((-0.511*sqrt(mu)/(1 + 0.329*9*sqrt(mu)))); 
Gamma [OH] := 10^((-0.511*sqrt(mu)/(1 + 0.329*3.5*sqrt(mu)))); 
Gamma [CN] := 10 ^((-0.511*sqrt(mu)/(1 + 0.329*3*sqrt(mu))));
```

$$\Gamma_H := 0.995900$$

$$\Gamma_{OH} := 0.995874$$

$$\Gamma_{CN} := 0.995871^{69}$$

Adjustments are now made to  $K_a$  and  $K_w$  and the reiteration begins after H is undefined. All output is suppressed here.

```
> K[a]:= K[a[o]] / (Gamma['H']*Gamma[CN]): K[w]:= K[w[o]] /  
 (Gamma['H']*Gamma[OH]): H:= 'H':
```

This input and the following input could have been combined.

```
> H[HA]:= H^3+K[a]*H^2 - (K[a]*C[HCN] + K[w])*H -  
 K[a]*K[w] = 0: H:= fsolve(H[HA], H, 0..1); mu := 0.5*(H +  
 (C[HCN]*K[a]/(H + K[a])) + (K[w]/H)):
```

$$H := 0.000013$$

Good enough because H has not changed perceptively. (If the output is reformatted to more significant figures, it can be shown that this is within 0.5% of the previous  $[H^+]$ .) Still, it is prudent to refine  $\gamma_{H^+}$  also with a second iteration and then calculate the pH.

```
> Gamma['H'] := 10^((-0.511*sqrt(mu) / (1 + 0.329*9*sqrt(mu))));  
 pH := -log[10](Gamma['H'] * H);
```

$$\begin{aligned}\Gamma_H &:= 0.995891^{70} \\ pH &:= 4.904828\end{aligned}$$

$pH = 4.905$  would be the appropriate way to report this answer.

1. b. This is a solution of a weak base, and so **4-38** is the appropriate polynomial to be solved. From Appendix II,  $a_{HN(CH_3)_3^+} = 4$ , and again,  $a_{OH^-} = 3.5$ , and  $a_{H^+} = 9$ . From Appendix IV,  $K_a^\circ = 1.6 \cdot 10^{-10}$  (from  $10^{-9.8}$ ). As in Part a, using  $K_w = 1.00 \cdot 10^{-14}$  will be sufficiently precise given the precision of  $C_{HN(CH_3)_3}$  and  $K_a^\circ$ .

The solution begins very much as 1a did, but with **4-38** in place, and holding the output to four decimal places.

```
> restart; K[w[o]] := 1.00e-14: K[a[o]] := 1.6e-10: C['M']  
 := 0.066: K[a] := K[a[o]]: K[w] := K[w[o]]: H['M'] :=  
 H^3 + (K[a] + C['M'])*H^2 - K[w]*H - K[w]*K[a]; H :=  
 fsolve(H['M'], H, 0..1);
```

$$\begin{aligned}H_M &:= H^3 + 0.0660 H^2 - 1.0000 \cdot 10^{-14} H - 1.6000 \cdot 10^{-24} \\ H &:= 5.0000 \cdot 10^{-12}\end{aligned}$$

The output shows that all constants and parameters for the cubic have been defined. Notice that the  $K_w K_a$  term is indeed negligible ( $1.6 \cdot 10^{-24}$ ). So paring this cubic equation down to a quadratic would be legitimate.

The next step, calculation of  $\mu$ , requires some thought: it is not a simple replication  $\mu$  for the HA problem! Here,  $\mu = \frac{1}{2} \{ [H^+] + [MH^+] + [OH^-] \}$ . The difference is that  $[MH^+]$  has replaced  $[A^-]$ . These are  $\alpha_{MH} + C_M$  and  $\alpha_A - C_{HA}$ , respectively. A comparison of **4-21** to **4-41** shows that these alphas are not equivalent; they are complimentary; as one increases the other decreases. Using **4-41** to express  $[MH^+]$  in the calculation of  $\mu$  follows.

```
> mu := 0.5 * (H + (C['M']*H/(H + K[a])) + (K[w]/H));
```

$\mu := 0.0020$

Another difference between the weak acid problem and the weak base problem is revealed:  $\mu$  does *not* equal  $[H^+]$  here. Indeed, it can be shown, by the argument on pages 75 and 76, that  $\mu = [OH^-]$ .

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Continuing, now, with the corrections to  $K_a^\circ$  and  $K_w^\circ$  a difference between the  $K_a$  for HA and the  $K_a$  for  $MH^+$  becomes important. The relationship between  $K_a$  and  $K_a^\circ$  for HA was deduced from Equation 4-16 to get 4-17. But the dissociation of  $MH^+$  to M and  $H^+$  puts a neutral product, M, in the numerator and a charged reactant,  $MH^+$ , in the denominator. So it follows that:

$$K_a^\circ = \frac{\{H^+\}\{M\}}{\{MH^+\}}$$

and from 2-3

$$K_a^\circ = \frac{\gamma_{H^+}[H^+]\gamma_M[M]}{\gamma_{MH^+}[MH^+]}$$

and from 2-10

$$K_a^\circ = \frac{\gamma_{H^+}\gamma_M K_a}{\gamma_{MH^+}}$$

2-7 allows

$$K_a^\circ = \frac{\gamma_{H^+} K_a}{\gamma_{MH^+}}$$

Finally, with a rearrangement:

$$K_a = \frac{\gamma_{MH^+} K_a^\circ}{\gamma_{H^+}}$$

So correcting  $K_a^\circ$  to  $K_a$  is different for  $MH^+$  than it was for HA. After calculating the three requisite activity coefficients, the corrections to  $K_a^\circ$  and  $K_w^\circ$  are made.

```
> Gamma['H'] := 10^((-0.511*sqrt(mu)/(1 + 0.329*9*sqrt(mu)))):
Gamma[OH] := 10^((-0.511*sqrt(mu)/(1 + 0.329*3.5*sqrt(mu)))):
Gamma[Me3NH] := 10^((-0.511*sqrt(mu)/(1 + 0.329*4*
sqrt(mu)))); K[w] := K[w[o]]/(Gamma['H']*Gamma[OH]); K[a] := K[a[o]]*Gamma[Me3NH]/Gamma['H'];
```

$$\begin{aligned}K_w &:= 1.1013 \cdot 10^{-14} \\K_a &:= 1.5948 \cdot 10^{-10}\end{aligned}$$

These K's are shown to illustrate how the activity coefficients have affected each.  $K_w$  increased by 10%, but  $K_a$  is still very close to  $K_a^0$ . This is because to "correct" it we used two, approximately equal  $\gamma$ 's, and one in the numerator and one in the denominator, and so their effects cancel.

We continue to reiterate with a lot of the output suppressed.

```
> H := 'H': H['M'] := H^3 + (K[a] + C['M'])*H^2 - K[w]*H -
   K[w]*K[a] = 0: H := fsolve(H['M'], H, 0..1); mu := 0.5*(H
   + (C['M']*H / (H + K[a])) + (K[w]/H)): Gamma['H'] :=
   10^((-0.511*sqrt(mu) / (1 + 0.329*9*sqrt(mu)))): Gamma[OH] :=
   10^((-0.511*sqrt(mu) / (1 + 0.329*3.5*sqrt(mu)))):
   Gamma[Me3NH] := 10^((-0.511*sqrt(mu) / (1 + 0.329*4*sqrt(mu)))):
   K[w] := K[w[o]] / (Gamma['H']*Gamma[OH]): K[a] :=
   K[a[o]]*Gamma[Me3NH] / Gamma['H']:
```

$$\begin{aligned} H &:= 5.2429 \cdot 10^{-12} \\ \mu &:= .0021 \\ \Gamma_H &:= 0.9536 \end{aligned}$$

$[H^+]$  has increased by nearly 5% from ( $5.000 \cdot 10^{-12}$ ) in the first iteration. So another iteration is worth pursuing. This requires only a reentry of the previous input paragraph which will not be shown. It yields:

$$\begin{aligned} H &:= 5.2483 \cdot 10^{-12} \\ \mu &:= .0021 \\ \Gamma_H &:= 0.9536 \end{aligned}$$

This third calculation of  $[H^+]$  shows a negligible difference from its previous value, likewise for  $\mu$ . And so,  $\gamma_{H^+}$  is recalculated and used in

```
> pH := -log[10](Gamma['H'] * H);
pH := 11.3006
```

which would be reported as  $pH := 11.301$

2. a. The derivation of this expression will be done "by hand" but then developed on Maple in order to provide another example of how it can be used to carry out algebra.

Two mass balance expressions will be necessary, one for the strong acid,

$$C_{\text{Hsa}} = [\text{HSa}] + [\text{Sa}^-],$$

which can be simplified for a strong acid, because “no” HSa would remain associated; the other mass balance is for the weak acid,

$$C_{\text{HWa}} = [\text{HWa}] + [\text{Wa}^-],$$

which requires both concentration terms. From the weak acid mass balance and the equilibrium expression for  $K_a$  we can express  $[\text{HWa}]$  and  $[\text{Wa}^-]$ .

$$[\text{HWa}] = \frac{C_{\text{HWa}}[\text{H}^+]}{[\text{H}^+] + K_a}$$

$$[\text{Wa}^-] = \frac{C_{\text{HWa}}K_a}{[\text{H}^+] + K_a}$$

The charge balance requirement is

$$[\text{H}^+] = [\text{Sa}^-] + [\text{Wa}^-] + [\text{OH}^-].$$

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Using the three substitutions expressed in the previous paragraph along with the  $K_w/[H^+]$  substitution for  $[OH^-]$  gives

$$[H^+] = C_{HSa} + \frac{C_{HWa}K_a}{[H^+] + K_a} + \frac{K_w}{[H^+]}$$

Multiplying each side, first by  $[H^+]$  and then by  $[H^+] + K_a$  gives

$$[H^+]^3 + (K_a + C_{HSa})[H^+]^2 - (C_{HSa}K_a + C_{HWa}K_a + K_w)[H^+] - K_aK_w = 0.$$

This should be compared to 3-26 and 4-13. When  $C_{HWa} = 0$ , it is appropriate to make  $K_a = 0$ . With these substitutions:

$$[H^+]^3 + C_{HSa}[H^+]^2 - K_w[H^+] = 0.$$

Factoring out  $[H^+]$  leaves Equation 3-26, which is appropriate for an aqueous solution of strong acid only. When  $C_{HSa} = 0$ , the equation is identical to 4-13, as it should be for a solution of a weak acid only. So this is a reasonable (and correct) expression.

The derivation of this 3° polynomial on Maple might look something like:

```
> restart; ChBal:= H = Sa + Wa + OH; Sa:= C[HSa]; Wa:=
K[a]*C[HWa]/(H + K[a]); OH:= K[w]/H; ChBal;
```

$$ChBal := H = Sa + Wa + OH$$

$$Sa := C_{HSa}$$

$$Wa := \frac{K_a C_{HWa}}{H + K_a}$$

$$OH := \frac{K_w}{H}$$

$$H = C_{HSa} + \frac{K_a C_{HWa}}{H + K_a} + \frac{K_w}{H}$$

Several of the steps used in earlier derivations, like  $OH := solve(K[w] = H*OH, OH)$ , have been omitted because by this point they should be second-nature operations. The last output, above, is the 3° polynomial which can be manipulated into a conventional form by the following operations:

```
> ChBal := simplify(H*(H + K[a])*ChBal);
```

$$\text{ChBal} := H^2 (H + K_a) = \\ C_{HSa} H^2 + C_{HSa} H K_a + K_a C_{HWa} H + K_w H + K_w K_a$$

To create a polynomial in the  $ax^3 + bx^2\dots$  format, we will subtract the right hand side of the `ChBal` expression from its left side, and then we will collect all of the “H” terms, shown in two steps for clarity.

```
> ChBal:= lhs(ChBal) - rhs(ChBal)=0;
```

$$\text{ChBal} := H^2 (H + K_a) = \\ C_{HSa} H^2 + C_{HSa} H K_a + K_a C_{HWa} H + K_w H + K_w K_a$$

```
> ChBal:= collect(ChBal,H);
```

$$\text{ChBal} := H^3 + (K_a - C_{HSa}) H^2 + (-K_a C_{HWa} - K_w \\ - C_{HSa} K_a) H - K_w K_a = 0$$

2. b. After assigning values to  $C_{HSa}$ ,  $C_{HWa}$  and  $K_a$ , it becomes a simple matter to solve this polynomial for  $[H^+]$ , but it might have gone unnoticed in Chapter 3, Problem 1a (page 50) that it is not necessary to express a polynomial in its conventional form before it is solved. Purely to illustrate this point, the previous two inputs are ignored, and the problem is returned to:

$$H = C_{HSa} + \frac{K_a C_{HWa}}{H + K_a} + \frac{K_w}{H}$$

From here, it is sufficient to begin assigning values to coefficients.

```
> K[wo]:= 1.00e-14: K[ao]:= 6.7e-3: C[HSa]:= 0.050: \\ C[HWa]:= 0.060: K[a]:= K[wo]: K[w]:= K[wo]: ChBal; H:= \\ fsolve(ChBal);
```

$$H = 0.050 + \frac{6.000 \cdot 10^{-16}}{H + 1.000 \cdot 10^{-14}} + \frac{1.000 \cdot 10^{-14}}{H} \\ H := 0.050$$

Notice first that `fsolve` returns only one root for this 3° polynomial; it appears to have missed two of the roots.<sup>71</sup> Also, notice that `(ChBal)` was used and not `(ChBal, H)`. This is because H is the only unknown in ChBal expression. `solve`, by the way, does not miss roots! If `solve` is used, Maple returns:

$$H := 0.050, -9.408 \cdot 10^{-15}, -2.126 \cdot 10^{-13}$$

All three are *real* roots, although only the first one is physically possible.

Inasmuch as `fsolve` seems to blunder onto the desired root, the reiterations will be continued without regard to the missed solutions. This allows us to use `H := fsolve` and then use the newly found  $[H^+]$  to find  $[W_a^-]$  and  $[OH^-]$ . The calculation of  $\mu$  and  $\gamma$  follows and these are then applied to  $K_a$  and  $K_w$  as illustrated on page 74 *et seq.* We resume from:

$$H := 0.0500$$

```
> mu := 0.5 * (H + C[HSa] + (K[a]*C[HWa] / (H + K[a])) + (K[w]/H));
Gamma[ion] := 10^(-0.5 * ((sqrt(mu))) - 0.15*sqrt(mu)): K[a]
:= K[a[o]]/Gamma[ion]^2: K[w]:= K[w[o]] /Gamma[ion]^2: H :=
'H': H := fsolve(ChBal);
```

$$\mu := 0.0500$$

$$H := 0.0606$$


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- 2<sup>nd</sup> place: MSc Econometrics and Operations Research
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Sources: Keuzegids Master ranking 2013; Elsevier 'Beste Studies' ranking 2012; Financial Times Global Masters in Management ranking 2012

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A couple of comments might be useful here. First, notice how it is necessary to un-define H before recalculating it in the next command. Also “uninteresting” calculations like  $\Gamma_{\text{ion}}$  (which is the same for  $\text{H}^+$ ,  $\text{OH}^-$  and  $\text{Wa}^+$ ) is suppressed along with  $K_a$  and  $K_w$ . The next iteration is *purely* a cut and paste of the input shown immediately above.

$$\begin{aligned}\mu &:= 0.0606 \\ H &:= 0.0612\end{aligned}$$

Another cut and paste of that input produces:

$$\begin{aligned}\mu &:= 0.0612 \\ H &:= 0.0612\end{aligned}$$

which is clearly a “stable” result. We can then add

>  $\text{pH} := -\log[10] (\text{Gamma}[\text{ion}] * \text{H}) ;$

$$\text{pH} := 1.3740$$

The four places in the mantissa are excessive given the two significant figure data. One should report 1.374.

3. Between the derivation of 4-13 and solving Problem 2, there should be little need for exhaustive detail for developing this expression. The solution to this problem is nothing more than the derivation of 4-13 with  $[\text{H}^+]$  replaced by  $K_w/[\text{OH}^-]$  rather than  $[\text{OH}^-]$  being replaced with  $K_w/[\text{H}^+]$ . The charge balance is a little different too.

Equilibrium expression

$$K_b = \frac{[\text{M}^+][\text{OH}^-]}{[\text{MOH}]}$$

leads to

$$[\text{MOH}] = \frac{[\text{M}^+][\text{OH}^-]}{K_b}$$

and then from

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

we can create

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

for use in the charge balance expression to follow, but first the mass balance expression:

$$C_{MOH} = [MOH] + [M^+]$$

From the rearrangement of  $K_b$  above,  $[MOH]$  is replaced giving:

$$C_{MOH} = \frac{[M^+][OH^-]}{K_b} + [M^+]$$

The charge balance expression is:

$$[H^+] + [M^+] = [OH^-].$$

Using the new expression for  $[M^+]$  and the expression for  $[H^+]$  from  $K_w$ , yields

$$\frac{K_w}{[OH^-]} + \frac{K_b C_{MOH}}{K_b + [OH^-]} = [OH^-]$$

After multiplying through by

$$[OH^-] \times (K_b + [OH^-])$$

and isolating all terms on the left side:

$$[OH^-]^3 + K_b[OH^-]^2 - (K_b C_{MOH} + K_w)[OH^-] - K_b K_w = 0$$

This is another 3° polynomial in the image of 4-13, just as one might expect.

What follows is still another example of using Maple to perform (simple) algebra. But rather than duplicate what has been illustrated above, modifications are offered, not to confuse but rather to illustrate the variations on strategy.

```
> restart; H := solve(K[w] = H*OH, H); MOH := solve(K[b] =
M*OH/ MOH, MOH); M:= solve (C["MOH"]= M + MOH,M); ChBal :=
H + M = OH;
```

$$H := \frac{K_w}{OH}$$

$$MOH := \frac{M OH}{K_b}$$

$$M := \frac{C_{\text{"MOH"}} K_b}{K_b + OH}$$

$$ChBal := \frac{K_w}{OH} + \frac{C_{\text{"MOH"}} K_b}{K_b + OH} = OH$$

Notice that `C["MOH"]` was used in place of `C[MOH]`, this is because MOH is previously defined, and no, protecting MOH as '`MOH`' is not effective here,<sup>55</sup> and Maple will return an `Error, recursive assignment` message. So we are stuck with the unsightly quotation marks.

At this point we could solve for OH and see the three roots, each expressed in terms of  $K_w$ ,  $K_b$  and  $C_{\text{"MOH"}}$  by calling `OH := solve(ChBal, OH);`, but the output is dozens of lines long,<sup>72</sup> and not useful. Instead, we will rearrange the output into the  $ax^3 + bx^2 + cx + d = 0$  form of this cubic polynomial. The output will not be shown for each command (although ";" is shown). There are certainly a lot of ways to achieve the desired form. One such possibility is:

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```
> ChBal:= lhs(ChBal) - rhs(ChBal); ChBal:= simplify(ChBal);
ChBal := - OH*(K[b] + OH)*ChBal; ChBal:= collect(ChBal,OH);
```

$$\begin{aligned} ChBal &:= OH^3 + OH^2 K_b + (-K_w \\ &\quad - C_{MOH} K_b) OH - K_w K_b \end{aligned}$$

The expression for  $\alpha_M^+$  and  $\alpha_{MOH}$  come from the mass balance expressions given in the first part of this solution. Already, we have shown that:

$$[M^+] = \frac{K_b C_{MOH}}{K_b + [OH]}$$

Rearranging this to get  $[M^+]/C_{MOH}$  which is  $\alpha_M^+$  gives:

$$\alpha_{M^+} = \frac{[M^+]}{C_{MOH}} = \frac{K_b}{K_b + [OH]}$$

Probably the simplest way to derive  $\alpha_{MOH}$  would be from

$$\alpha_M^+ + \alpha_{MOH} = 1.$$

So,

$$\alpha_{MOH} = 1 - \alpha_M^+,$$

and therefore:

$$\alpha_{MOH} = 1 - \frac{K_b}{K_b + [OH]} = \frac{[OH]}{K_b + [OH]}$$

4. The strategy used on page 78 is used here, but expanded to produce two expressions, one for  $\alpha_{A^-} = 0.999$  and the other for  $\alpha_{A^-} = 0.995$ . With two conditions shown, the effect of allowing this smaller alpha will become evident.

Recall that setting  $\alpha_{A^-}$  equal to 0.999 in 4-21 gives

$$[H^+] = 0.001001 K_a \approx 0.001 K_a$$

Likewise, when  $\alpha_{A^-}$  is set equal to 0.995,

$$[H^+] \approx 0.005 K_a$$

These substitutions will be made for  $[H^+]$  in Equation 4-13 creating two “alpha-specific” expressions. One could cut and paste (with minor modifications) the input from Problem 1a. Then, for each condition, H is replaced with  $0.001*K[a]$  or  $0.005*K[a]$ , and the output is reformatted to six significant digits, the minimum necessary to get non-zero coefficients for  $K_a^3$ .

```
> restart; Exp := H^3+K[a]*H^2-(K[a]*C[HA] + K[w])*H
- K[a]*K[w]: K[w] := 1e-14: Exp999 := subs(H =
0.001*K[a],Exp); Exp995 := subs(H = 0.005*K[a],Exp); K999
:= solve(Exp999, {K[a]}); K995 := solve(Exp995, {K[a]});
```

$$\begin{aligned}Exp999 &:= 0.000001 K_a^3 - 0.001000 (K_a C_{HA} + 1.000000 \cdot 10^{-14}) K_a - 1.000000 \cdot 10^{-14} K_a \\Exp995 &:= 0.000025 K_a^3 - 0.005000 (K_a C_{HA} + 1.000000 \cdot 10^{-14}) K_a - 1.000000 \cdot 10^{-14} K_a\end{aligned}$$

$$\begin{aligned}K999 &:= \left\{ K_a = 0.000000 \right\}, \left\{ K_a = 499.500500 C_{HA} \right. \\&\quad \left. + 9.990010 \cdot 10^{-8} \sqrt{2.500000 \cdot 10^{19} C_{HA}^2 + 1.002001 \cdot 10^6} \right\}, \left\{ K_a = 499.500500 C_{HA} \right. \\&\quad \left. - 9.990010 \cdot 10^{-8} \sqrt{2.500000 \cdot 10^{19} C_{HA}^2 + 1.002001 \cdot 10^6} \right\}\end{aligned}$$

$$\begin{aligned}K995 &:= \left\{ K_a = 0.000000 \right\}, \left\{ K_a = 99.502488 C_{HA} \right. \\&\quad \left. + 9.950249 \cdot 10^{-8} \sqrt{1.000000 \cdot 10^{18} C_{HA}^2 + 40401.000000} \right\}, \left\{ K_a = 99.502488 C_{HA} \right. \\&\quad \left. - 9.950249 \cdot 10^{-8} \sqrt{1.000000 \cdot 10^{18} C_{HA}^2 + 40401.000000} \right\}\end{aligned}$$

These expressions for K are 3° polynomial (in  $K_a$ ), and so there are three roots. The first root for K999 and for K995 are  $K_a = 0$ ; these are useless because  $K_a = 0$  implies a “non-acid” and would exist at  $[H^+] = 0$ , which is impossible in water. Of the remaining two roots for each polynomial, the *third* produces  $K_a < 0$ , also useless. So, each expression will be restricted to  $K999[2]$  and  $K995[2]$ , that is the second roots that are returned. After reformatting the output (to two figures):

```
> K999 := subs(K999[2], K[a]); K995 := subs(K995[2], K[a]);
```

$$\begin{aligned}K999 &:= 499.500500 C_{HA} + 9.990010 \cdot 10^{-8} \sqrt{2.500000 \cdot 10^{19} C_{HA}^2 + 1.002001 \cdot 10^6} \\K995 &:= 99.502488 C_{HA} + 9.950249 \cdot 10^{-8} \sqrt{1.000000 \cdot 10^{18} C_{HA}^2 + 40401.000000}\end{aligned}$$

Finally, we request a plot of these expressions over the  $C_{HA} = 0$  to  $10^{-6}$  range. This plot corroborates the statements made on page 78: that is,  $K_a \geq 10^{-4}$  is required to achieve  $\alpha_{A^-} \geq 0.999$  even as  $C_{HA}$  approaches zero. After the plot is rendered, grid lines, a legend and numeric formatting are carried out as described on page 30 *et seq.*

```
> plot({K999,K995},C[HA] = 0..1e-6,axes = box), [red,blue];
```

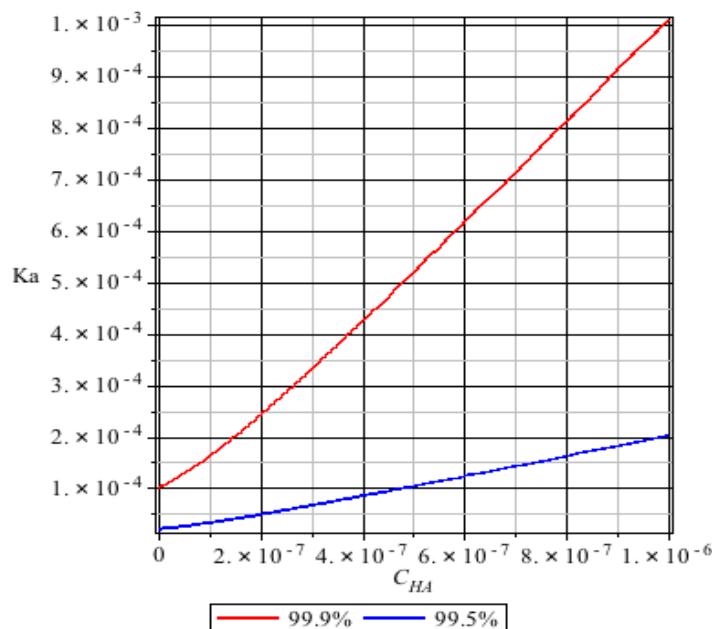


Figure 4-1

Notice that the slope of the K999 vs.  $C_{HA}$  line is  $\approx 1000$ . This implies that  $K_a$  must be about one thousand times larger than  $C_{HA}$  in order to assure 99.9% dissociation of HA. Moreover, appropriately, a smaller<sup>73</sup>  $K_a$  is required to achieve less dissociation, that is  $\alpha_{A^-} \geq 0.995$ .

# 5 The Salts of Weak Acids and Weak Bases

In Chapter 3 the concept of the acid and base was introduced but in narrow terms. There, it was in regard to the electrolyte MA: when  $M^{n+}$  is  $H^+$ , MA is an acid, and when  $A^{n-}$  is  $OH^-$ , MA is a base. Here we add that when  $M^{n+}$  is not  $H^+$ , **and**  $A^-$  is not  $OH^-$ , MA is referred to as a salt.

In Chapter 4, the definition of the base was expanded to treat M ( $n = 0$ ) as a proton acceptor ( $\longrightarrow .MH^+$ ). By adding this new kind of cation, the concept of the conjugate acid and conjugate base was introduced and this expanded the definition of the acid and base.  $MH^+$ , the conjugate acid of the base M, and  $A^-$ , the conjugate base of the acid HA now fit the definitions of acids and bases. It is not surprising that  $MH^+$  is an acid because, like HA, it contains a labile proton, but  $A^-$  looks nothing like the Chapter 3 definition of a base, MOH. However,  $A^-$  accepts protons (like  $OH^-$ ) and that is what makes it a base.

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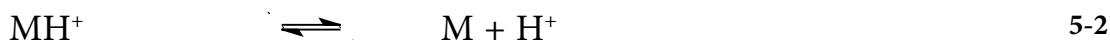


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The acid / base properties of conjugate acids and bases are explored in this chapter. First, MHA is considered where  $M^\circ$  is a base as defined in Chapter 4 and  $A^-$  is the anion of a strong acid. That is,  $A^-$  is any anion on Table 3-1, except the last two. Second, we consider the salt MA is where  $A^-$  is *not* one of the first eight anions in Table 3-1 (*i.e.* it is the anion of a weak acid), but  $M^{n+}$  is among the “+1” cations of that table. Finally, the salt MHA will be studied where  $M^\circ$  is a base (Chapter 4), and  $A^-$  is again, not among the first eight anions on Table 3-1; that is, again,  $A^-$  is the anion of a weak acid.

So we begin by considering the dissociation (in water) of the salt MHA described by 5-1.  $MH^+$  is the conjugate acid of the neutral (often an organic molecule) M, and  $A^-$  is the conjugate base of a strong acid HA. This dissociation is presumed to be complete.<sup>74</sup> It is necessary to examine other *possible* reactions.



After Equation 5-1, only 5-2 seems reasonable, while 5-3 would be unreasonable because if M has *any* affinity for  $OH^-$ , it would certainly not have formed  $MH^+$ . That is to say, 5-2 and 5-3 imply contradictory properties of M. Finally, 5-4 is forbidden because here,  $A^-$  has been expressly restricted to the anions of strong acids and that means they have no measurable affinity for  $H^+$ . In other words, 5-4 lies entirely to the left.

Inasmuch as the pH of an aqueous solution is affected by the balance between the activity of  $H^+$  and  $OH^-$ , it is clear that the extent to which 5-2 proceeds left or right will affect that balance. And of course, the extent of that dissociation is described by its equilibrium constant  $K_a$ . From Chapter 4 we recall that for 5-2:

$$K_a = \frac{K_w}{K_b} = \frac{[H^+][M]}{[MH^+]}$$

Since 5-1 and 5-2 are the only significant reactions for the dissolution of MHA (besides the dissociation of  $H_2O$  to  $H^+ + OH^-$ ), it seems that this solution should be acidic. After all,  $MH^+$  contributes  $H^+$  to the solution while  $A^-$  does nothing to affect the  $H^+/OH^-$  balance.

Calculating the pH of a solution of MHA is a lot<sup>75</sup> like calculating the pH of a solution of the weak acid, HA: it depends on  $C_{MHA}$  and  $K_a$  just as the pH of the HA solution depends on  $C_{HA}$  and  $K_a$ . For MHA, mass balance requires:

$$C_{MHA} = [MH^+] + [M],$$

and by substitution for the equilibrium expression above, [M] can be replaced to give:

$$C_{MHA} = [MH^+] + \frac{[MH^+]K_a}{[H^+]}$$

which leads to:

$$[MH^+] = \frac{[H^+]C_{MHA}}{[H^+] + K_a}$$

This will be required for the charge balance expression:

$$[H^+] + [MH^+] = [A^-] + [OH^-], \quad 5-5$$

so that  $[MH^+]$  can be replaced. The “total” dissociation of MHA in 5-1 allows that

$$[A^-] = C_{MHA}.$$

Using the well-worn  $[OH^-] = K_w/[H^+]$  produces a charge balance equation in terms of  $C_{MHA}$ ,  $K_a$ ,  $K_w$  and, of course  $[H^+]$ :

$$[H^+] + \frac{[H^+]C_{MHA}}{[H^+] + K_a} = C_{MHA} + \frac{K_w}{[H^+]} \quad 5-6$$

Notice the similarity between this charge balance expression and that of Equation 4-12. Here,  $C_{MHA}$  replaces  $C_{HA}$ , but more significantly, there is an additional contributor to the positive side of the charge balance equation. Nevertheless, 5-6 like 4-12 is converted to a 3° polynomial in the same way, giving:

$$[H^+]^3 + K_a[H^+]^2 + C_{MHA}[H^+]^2 = C_{MHA}[H^+]^2 + K_aC_{MHA}[H^+] + K_w[H^+] + K_aK_w.$$

This leads to

$$[H^+]^3 + K_a[H^+]^2 - (K_aC_{MHA} + K_w)[H^+] - K_aK_w = 0,$$

which is a trivial variation on 4-13, the expression for a solution of  $C_{HA}$ ! So although the derivation appeared to be headed in a new direction at the charge balance stage, it turns out that solving for the pH of an  $NH_4Cl$  solution given  $C_{NH_4Cl}$  and the  $K^o_a$  for  $NH_4^+$  is exactly like calculating the pH of an HF solution given  $C_{HF}$  and the  $K^o_a$  for HF. This also implies that solutions of MHA are acidic. And finally, the “quadratic approximation” of 4-13, that is 4-24 can be used just as easily for *these* solutions.

Suppose that instead of M being a weak base,  $M^+$  is the cation of a *strong* base, and instead of  $A^-$  being the anion of a strong acid, it is the anion of a *weak* acid. (So MA could be KF, but not KCl.) Suppose also that MA completely dissociates (to  $M^+ + A^-$ ). As we proceed to develop an expression for  $[H^+]$  for such an aqueous solution of MA, we will discover that it exactly duplicates the expression for a solution of  $M^0$ , that is **4-38**.

As in the MHA analysis, it is necessary to examine other *possible* reactions, either dissociations (**5-7**) or hydrolyses (**5-8**, **5-9**, and **5-10**).



**5-8** is disqualified on the grounds that MOH has been expressly characterized as a strong base and that requires that **5-8** lie completely to the left. **5-9** would imply that  $M^+$  is a base of sorts, and although  $M^0$  might be a base as in the preceding treatment of MHA,  $M^+$  would have *no* affinity for  $H^+$ . (A cation attracting a proton?) So **5-9** can safely be discarded. Finally, **5-10** is considered, and this is very plausible because HA is a weak acid and that implies some affinity between  $H^+$  and  $A^-$ . Recognize that **5-10** is a variation on **5-4**; just add an  $OH^-$  to both sides of **5-4** to get **5-10**.

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The equilibration of reaction **5-10** (or **5-4**) is expressed with  $K_b$  as described in the conjugate acid / base discussion in Chapter 4.<sup>76</sup>

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

With only **5-7** and **5-10** as the legitimate contributors to the condition of the solution, it can be seen that the solution should be alkaline:  $M^+$  does nothing to add or remove  $H^+$  while  $A^-$  removes at least some  $H^+$  from solution.

As we did for the solution of MHA, we begin with a mass balance expression and use equilibrium expressions to make the necessary substitutions.

$$C_{MA} = [HA] + [A^-].$$

$[MA]$  is never addressed because **5-7** is taken to be “complete” and that means  $[MA] = 0$ . From the equilibrium expression given above,  $[HA]$  can be expressed in terms of  $K_a$ .<sup>77</sup>

$$[HA] = \frac{K_w[A^-]}{K_a[OH^-]} = \frac{[H^+][A^-]}{K_a}$$

Replacing  $[HA]$  in the mass balance expression and rearranging terms gives

$$[A^-] = \frac{C_{MA}K_a}{[H^+] + K_a}$$

Notice the similarity to **4-11**.

The charge balance here is different than the charge balance of **4-10** because of the extra cation,  $M^+$ . Here charge balance is

$$[H^+] + [M^+] = [A^-] + [OH^-].$$

Is it clear that  $[M^+] = C_{MA}$ ?<sup>78</sup> With the replacement of  $[OH^-]$ , the charge balance is reduced to the appropriate parameters.

$$[H^+] + C_{MA} = C_{MA}K_a + [OH^-] \quad \text{5-11}$$

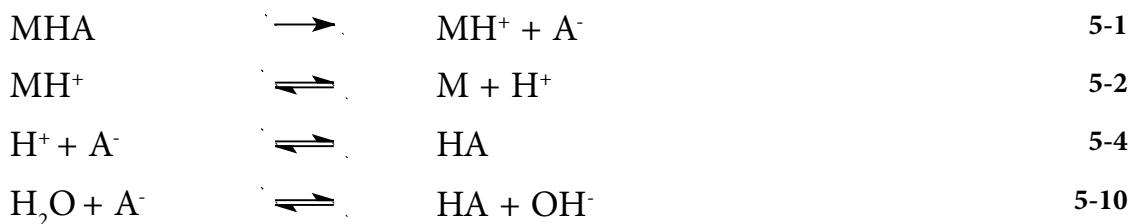
Notice the symmetry with **5-6** and the difference with **4-12** which is caused by the appearance of  $M^+$  which does not exist in the HA problem. (Left to the reader), **5-11** can be rearranged to

$$[H^+]^3 + (K_a + C_{MA})[H^+]^2 - K_w[H^+] - K_aK_w = 0.$$

Isn't this, indeed, remarkably similar to **4-38**, ( $[H^+]^3 + (K_a + C_M)[H]^2 - K_w[H] - K_a K_w = 0$ ) arguably, a trivial variation on it? The consequence of this identity is that calculating the pH of the salt of a weak acid like KF or NaCN given  $C_{MA}$  and the  $K^{\circ}_a$  for HF or HCN is a lot<sup>79</sup> like calculating the pH of a weak base like NH<sub>3</sub> given  $C_{NH_3}$  and the  $K^{\circ}_a$  for its conjugate acid NH<sub>4</sub><sup>+</sup>. Likewise, the "quadratic approximation" **4-39** can be adapted to calculate the pH of the salt of a weak acid, but with caution (cf. problem 1b).

So far, this chapter has offered nothing new from Chapter 4, at best a review with minor variations. However, the final treatment of a salt, MHA, where MH<sup>+</sup> is the conjugate acid of a *weak* base, M, and A<sup>-</sup> is the conjugate base of a *weak* acid, HA, produces an interesting, and important condition. This would be a salt like NH<sub>4</sub>F or pyridinium acetate (C<sub>5</sub>H<sub>6</sub><sup>+</sup>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup>), where ammonia and pyridine are weak bases and hydrofluoric acid and acetic acid are weak acids.

All the relevant reactions have already been explored.



Unlike in the first analysis of MHA, A<sup>-</sup> is the anion of a *weak* acid and so **5-4** (or **5-10**) becomes a legitimate contributor to the pH of the solution. Consequently, there exist two reactions each affecting the pH but in opposite ways: **5-2** increases H<sup>+</sup> activity while **5-4** diminishes it. The more dominate reaction (larger  $K_{eq}$ ) will determine if the solution is acidic or alkaline.

Analysis of this solution borrows only basic principles from the previous two analyses. Where "strong acid" MHA allowed a simple substitution for  $[A^-] = C_{HA}$  and the "strong base" MA allowed  $[M^+] = C_{MA}$  in the charge balance equation, *this* salt affords no such simplicity. Neither mass balance expression is simple, *but both mass balance expressions equal each other*.

Beginning with the charge balance expression, reconsider:

$$[H^+] + [MH^+] = [A^-] + [OH^-]. \quad \text{5-11}$$

The substitutions for [MH<sup>+</sup>] and [A<sup>-</sup>] will, as before, derive from the *two* mass balance expressions.

$$C_{MHA} = [MH^+] + [M] \quad \text{5-12}$$

and

$$C_{MHA} = [HA] + [A^-]<sup>80</sup> \quad \text{5-13}$$

From the many examples provided to this point, it should be evident that:

$$[\text{MH}^+] = \frac{[\text{H}^+]\text{C}_{\text{MHA}}}{[\text{H}^+] + \text{K}_{\text{aM}}}$$

and,

$$[\text{A}^-] = \frac{\text{K}_{\text{aM}}\text{C}_{\text{MHA}}}{[\text{H}^+] + \text{K}_{\text{aA}}}$$

The added notation to each  $\text{K}_a$  is critical because we require *two, unrelated* dissociation constants. The  $\text{K}_{\text{aM}}$  would be the dissociation constant for the acid  $\text{MH}^+$  while  $\text{K}_{\text{aA}}$  pertains to the dissociation of the weak acid HA.

Implementing these substitutions produces a charge balance expression in the appropriate terms.

$$[\text{H}^+] + \frac{[\text{H}^+]\text{C}_{\text{MHA}}}{[\text{H}^+] + \text{K}_{\text{aM}}} = \frac{\text{K}_{\text{aA}}\text{C}_{\text{MHA}}}{[\text{H}^+] + \text{K}_{\text{aA}}} + \frac{\text{K}_W}{[\text{H}^+]}$$

Multiplying the expression by each of the three denominators and moving all terms to one side produces the desired expression in conventional, polynomial form.

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$$[H^+]^4 + (K_{aA} + K_{aM} + C_{MHA})[H^+]^3 + (K_{aA}K_{aM} - K_w)[H^+]^2 - (K_{aA}K_{aM}C_{MHA} + K_{aA}K_w + K_{aM}K_w)[H^+] - K_{aA}K_{aM}K_w = 0$$

Now, with an expression decidedly different than what was derived in Chapter 4, indeed a 4° polynomial, we can return to Maple, first to revisit some of the operations that have been presented and second to explore the properties of this new polynomial. What follows is a derivation of the polynomial expression for *this* particular kind of MHA. Many of the substitutions should be sufficiently familiar to the reader that they are used with no explanation, and many of the outputs have been seen frequently enough that they can be suppressed without ambiguity. Of course the reader is welcome to reconstruct the inputs using the semicolon in order to express these missing elements.

```
> restart; ChBal:= H + MH = A + OH; OH:= K[w]/H; MH:= H* C[MHA] / (H + K[aM]): A:= K[aA]*C[MHA] / (H + K[aA]): ChBal;
```

$$H + \frac{H C_{MHA}}{H + K_{aM}} = \frac{K_{aA} C_{MHA}}{H + K_{aA}} + \frac{K_w}{H}$$

As we have done in the past, the following executions are broken into separate input lines so that the user can see how the polynomial is developing. The reader who is accomplished in Maple might string these operations together and suppress their output until the end, but that is not advised.

```
> ChBal:= lhs(ChBal) - rhs(ChBal);81
```

$$ChBal := H + \frac{H C_{MHA}}{H + K_{aM}} - \frac{K_{aA} C_{MHA}}{H + K_{aA}} - \frac{K_w}{H}$$

```
> ChBal:= H* (H + K[aM]) * (H + K[aA]) * ChBal;
```

$$ChBal := H(H + K_{aM})(H + K_{aA}) \left( H + \frac{H C_{MHA}}{H + K_{aM}} - \frac{K_{aA} C_{MHA}}{H + K_{aA}} - \frac{K_w}{H} \right)$$

```
> ChBal := simplify(ChBal);
```

$$ChBal := H(H + K_{aM})(H + K_{aA}) \left( H + \frac{H C_{MHA}}{H + K_{aM}} - \frac{K_{aA} C_{MHA}}{H + K_{aA}} - \frac{K_w}{H} \right)$$

```
> ChBal4°:= collect(ChBal, H);
```

$$\begin{aligned} ChBal4^\circ := & H^4 + (C_{MHA} + K_{aM} + K_{aA}) H^3 \\ & + (-K_w + K_{aM} K_{aA}) H^2 \\ & + (-K_w K_{aM} - K_w K_{aA} - K_{aA} C_{MHA} K_{aM}) H \\ & - K_w K_{aM} K_{aA} \end{aligned}$$

In this step the polynomial has been rendered into the familiar form and it has been tagged with 4° because we are going to experiment with it later. Recall how the 3° polynomial (4-13) was simplified to a quadratic (4-24) because its intercept,  $K_a K_w$  is so close to zero that it could be dropped from the cubic equation and  $[H^+]$  could be factored out. Now consider *ChBal4°*; it has an even smaller intercept ( $-K_w K_{aM} K_{aA}$ ) because it contains a second  $K_a$  which is most certainly much less than one. Suppose that this intercept,  $-K_w K_{aM} K_{aA}$  were removed from *ChBal4°* and *H* were factored out. This would create a 3° polynomial in  $[H^+]$ . That operation might look like the following. Notice how the cubic polynomial is created from the 4° polynomial by *adding*  $K[w] * K[aM] * K[aA]$  and simplifying the result all in one step. Then, the terms are collected to give it the common form.

```
> ChBal3° := simplify((ChBal4° + (K[w]*K[aM]*K[aA]))/H); ChBal3° :=  
collect(ChBal3°, H);
```

$$\begin{aligned} ChBal3° &:= H^3 + H^2 C_{MHA} + H^2 K_{aM} + H^2 K_{aA} - K_w H \\ &\quad + K_{aA} H K_{aM} - K_w K_{aM} - K_w K_{aA} - K_{aA} C_{MHA} K_{aM} \\ ChBal3° &:= H^3 + (C_{MHA} + K_{aM} + K_{aA}) H^2 \\ &\quad + (-K_w + K_{aM} K_{aA}) H - K_w K_{aM} - K_w K_{aA} \\ &\quad - K_{aA} C_{MHA} K_{aM} \end{aligned}$$

The intercept for *ChBal3°* has three terms, but the  $K_{aA} C_{MHA} K_{aM}$  term is *not* small enough to throw out.<sup>82</sup> Consequently this 3° polynomial cannot be further reduced to a 2° polynomial by taking its intercept to be  $\approx 0$  and factoring out another  $[H^+]$ . The reader is invited to explore that simplification, but long ago Butler<sup>83</sup> presented two, even simpler expressions for  $[H^+]$  for this weak acid / weak base MHA. First, he offers<sup>84</sup>

$$[H^+] = \sqrt{\frac{K_{aA}(K_w + K_{aM}C_{MHA})}{K_{aA} + C_{MHA}}} \quad 5-14$$

which requires that  $K_{aA}$  and  $K_{aM}$  are small compared to  $C_{MHA}$ . 5-14 can be further simplified by adding two restrictions: suppose that  $K_w \ll K_{aM}C_{MHA}$  and that  $K_{aA} \ll C_{MHA}$ . Under these modest restrictions, the numerator becomes  $K_{aA}K_{aM}C_{MHA}$ , the denominator becomes  $C_{MHA}$  and the expression simplifies to:

$$[H^+] = \sqrt{K_{aA}K_{aM}} \quad 5-15$$

which is remarkable and yet somewhat intuitive. It is remarkable in that the  $[H^+]$ , under these restrictions loses all dependence on  $C_{MHA}$ , but intuitive in that this dependence is a *geometric* average of the two acid dissociation constants. If  $K_{aA} \times K_{aM}$  is greater than  $10^{-14}$ ,  $[H^+]$  will exceed  $10^{-7}$  and the solution will be acidic,<sup>85</sup> and when  $K_{aA} \times K_{aM}$  is less than  $10^{-14}$ , the solution will be alkaline. Although 5-15 might, on occasion, yield an inaccurate answer, it is an excellent, quick check to see if the solution will be alkaline or acidic.

Knowing that *ChBal4°* was rigorously derived, *ChBal3°*, 5-14 and 5-15 can be evaluated by comparing their performance to that benchmark. For these comparisons, ionic strength, activity coefficients and ion activity will be ignored because these effects would come into play equally for all four models. We will look only at  $[H^+]$ . When the activity coefficients are needed, however, we will discover that a strategy *unlike* what was used in Chapter 4 is more effective; this will be discussed after the models have been compared.

Continuing with the worksheet already started, 5-14 and 5-15 are entered.

```
> H2° := sqrt((K[aA] * (K[w] + K[aM]*C[MHA])) / (K[aA] + C[MHA])); H0°  
:=sqrt(K[aA]*K[aM]);
```

$$H2^\circ := \sqrt{\frac{K_{aA} (K_w + K_{aM} C_{MHA})}{K_{aA} + C_{MHA}}}$$

$$H0^\circ := \sqrt{K_{aM} K_{aA}}$$

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Now we can begin to compare outputs. The  $3^\circ$  and  $4^\circ$  polynomials are implicit expressions of  $[H^+]$  but **5-14** and **5-15** are explicit expressions. So the two sets of expressions are labeled and will be handled differently. Consider the salt of a weak acid ( $K_{aA} = 0.01$ ) and a weak base ( $K_{aM} = 0.01$ ) where  $C_{MHA} = 0.01 \text{ M}$ . We will restrict the output to six decimal places here. Also for the  $4^\circ$  and  $3^\circ$  polynomials, we have restricted the solutions to  $[H^+] = 0$  to  $C_{MHA}$  because these polynomials will return four or three solutions, respectively, and only  $[H^+] > 0$  is legitimate. (See page 74.)

```
> C[MHA]:= 0.01: K[aM]:= 0.01: K[aA]:= 0.01: K[w] := 1.00e-
14: H4°:= fsolve(ChBal4°, H, 0..C[MHA]); H3°:= fsolve
(ChBal3°, H, 0..C[MHA]); 'H2°' = H2°; 'H0°' = H0°;

H4° := 0.004142
H3° := 0.004142
H2° = 0.007071
H0° = 0.010000
```

The cubic polynomial performs remarkably well, but this should not be surprising given the nature of the approximation needed to convert *ChBal4°* into *ChBal3°*. The quadratic gives a value that is much larger than the  $3^\circ$  and  $4^\circ$  solutions. Not good, but given that the quadratic is to be used only when  $K_{aA}$  and  $K_{aM}$  are small compared to  $C_{MHA}$ , it is obvious that in this test case they are not small enough. Changing *only*  $K_{aA}$  and  $K_{aM}$  to much smaller values will allow another assessment, but notice that we cannot simply use ' $H2°' = H2°; 'H0°' = H0°;$ ' because these are defined by the previous  $K_{aM}$  and  $K_{aA}$ . Also, we will show more decimal places to make our point.

```
> K[aA]:=1e-4:K[aM] := 1e-4: H4° := fsolve(ChBal4°, H,
0..C[MHA]); H3° := fsolve( ChBal3°, H, 0..C[MHA]); H2° :=
sqrt((K[aA]*(K[w]+ K[aM]*C[MHA]) / (K[aA]+ C[MHA])))); H0° :=
sqrt(K[aA] *K[aM]);

H4° := 0.000098058
H3° := 0.000098058
H2° = 0.000099504
H0° = 0.000100000
```

Much better! Even the simplest solution is within 2% of the most rigorous solution. This exercise can go on forever, but an extensive comparison of the four models will eventually lead to two conclusions:

- *ChBal3°* is an excellent approximation of *ChBal4°* unless  $C_{MHA}$  becomes very small (*i.e.* less than  $10^{-5} \text{ M}$ ).

- A  $K_{aA}$ ,  $K_{aM}$ , and  $C_{MHA}$  combination can be found that will make any of the three expressions the best approximation to  $ChBal4^\circ$ . Said another way, none of the three approximations of  $ChBal4^\circ$  is always the best, and there are cases for which any of the three is the worst.

These conclusions would imply that  $ChBal4^\circ$  is the only safe calculation of  $[H^+]$ , but  $ChBal3^\circ$  is reliable for all *analytically* interesting solutions of MHA (*i.e.*  $C_{MHA}$  greater than  $10^{-5} \text{ M}$ ).

Before putting any of the expressions to use for calculating the pH of a solution of MHA or MA, it would be appropriate to point out a prudent change in strategy from the calculations made in Chapter 4. There, calculations were begun with the approximation that  $\mu \approx 0$  and so  $K_w \approx K_w^\circ$  and  $K_a \approx K_a^\circ$ . After  $[H^+]$  was determined, based on those approximations,  $\mu$  was found and from it the appropriate  $\gamma$ 's were calculated and applied to  $K_w^\circ$  and  $K_a^\circ$  to improve the approximations on  $K_w$  and  $K_a$ , respectively. For salts, it is not necessary to begin with such a crude approximation of  $\mu$ .

First let us consider MHA where  $MH^+$  is the conjugate acid of the *weak* base M and  $A^-$  is the anion of the *strong* acid HA. (This is the first condition of MHA, addressed on page 102.) Recall that

$$\mu = \frac{1}{2}\{[MH^+] + [H^+] + [A^-] + [OH^-]\}.$$

From charge balance requirements of 5-5, it should be apparent that we need consider only the cations *or* only the anions. We can replace  $[MH^+] + [H^+]$  with  $[A^-] + [OH^-]$  or *visa versa*. So that,

$$\mu = \{[MH^+] + [H^+]\} = \{[A^-] + [OH^-]\}.$$

Attacking the anions is easier because  $A^-$  is from a strong acid; that means

$$[A^-] = C_{MHA}.$$

Also, in discussing *this* form of MHA, it was inferred that its solution must be acidic (page 102). This means that  $[OH^-]$  must be less than  $10^{-7}$  which makes it an insignificant contributor to  $\mu$ . And so with

$$[A^-] + [OH^-] \approx [A^-] = C_{MHA},$$

then

$$\mu = C_{MHA}.$$

The only limitation to this approximation is that  $C_{MHA} \gg [OH^-]$ , but with  $[OH^-] < 10^{-7}$ , this should be a non-factor because that would require  $\mu < 10^{-7}$  where ionic strength is not a factor.<sup>86</sup>

For the calculation of ionic strength for MA where  $M^+$  is the cation of a *strong* base and  $A^-$  is the anion of the *weak* acid HA, the approach is the mirror image of the approach described above, but a few symbols will change. Now,

$$\mu = \{[M^+] + [H^+]\} = \{[A^-] + [OH^-]\},$$

and we will attack the cations because

$$[M^+] = C_{MA},$$

and because the solution will be alkaline (page 105),  $[H^+] < 10^{-7}$ . And so when  $C_{MA} \gg 10^{-7}$ ,

$$[M^+] + [H^+] \approx [M^+] = C_{MA}$$

and then,

$$\mu = C_{MA}.$$

So  $\mu = C_{MHA}$  when  $A^-$  is from a strong acid, and  $\mu = C_{MA}$  when  $A^-$  is from a weak acid. What about  $\mu$  for MHA when  $A^-$  is from a weak acid? Again page 112 we have

$$\mu = \{[MH^+] + [H^+]\} = \{[A^-] + [OH^-]\},$$



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but here

$$[A^-] = \alpha_{A^-} \times C_{MHA}$$

and

$$[MH^+] = \alpha_{MH^+} \times C_{MHA}$$

This will not be simple, especially in that each alpha contains a *different*  $K_a$ . That is  $K_{aA}$  and  $K_{aM}$ , respectively. The good news is that only one of these is needed (along with *either*  $[H^+]$  or  $[OH^-]$ ). More good news is that  $[H^+] \approx \sqrt{K_{aM} K_{aA}}$ . This allows a good estimation of either alpha and so a good estimation of  $\mu$ , certainly a better first guess than  $\mu \approx 0$ .

At the risk of being too clever, one can replace  $[H^+]$  with  $\sqrt{K_{aM} K_{aA}}$ , and with a little algebra get:

$$\mu \approx \sqrt{K_{aM} K_{aA}} \left\{ \frac{C_{MHA} + \sqrt{(K_{aM} K_{aA}) + K_{aM}}}{\sqrt{(K_{aM} K_{aA}) + K_{aM}}} \right\}$$

### Example Problems

1. Using Debye-Hückel, calculate the pH of a 0.075 M solution of:
  - a)  $\text{NH}_4\text{NO}_3$
  - b) KF
  - c)  $\text{NH}_4\text{F}$  (using the 4° polynomial)
2. Ignoring ionic strength effects, illustrate the performance of 5-14 by plotting  $[H^+] \text{ vs. } C_{\text{NH}_4\text{F}}$  for  $C_{\text{NH}_4\text{F}} = 0$  to 0.01 M. Compare this to 5-15. At  $C_{\text{NH}_4\text{F}} = 0.002$  M, which is more accurate?
3. Calculate the pH of a solution that is 0.033 M  $\text{HN}(\text{CH}_3)_3\text{Cl}$  and 0.011 M in:
  - a) KCl
  - b) HCl
  - c) KOH

### Solutions to Example Problems

1. a)  $\text{NH}_4\text{NO}_3$  This is the salt of a weak base,  $\text{NH}_3$ .  $\text{NH}_4^+$  is the conjugate acid of that weak base.  $\text{NO}_3^-$  is the anion (or conjugate base) of the *strong* acid  $\text{HNO}_3$ ; it has no affinity for protons. So the net effect on the solution is an increase in  $[H^+]$ . This  $[H^+]$  can be determined by solving the cubic polynomial

$$[H^+]^3 + K_a [H^+]^2 - (K_a C_{MHA} + K_w) [H^+] - K_a K_w = 0,$$

which is a trivial variation on 4-13. The adjustments of each  $K^\circ$  to  $K$  can be made at the onset by taking  $\mu$  to equal  $C_{\text{NH}_4\text{NO}_3}$  (as per page 112). This will yield a relatively low ionic strength where activity coefficients from Debye-Hückel are similar to those of Daves (Problem 2, Chapter 2). For illustration, the cubic will be approximated as a quadratic (see page 79).

$$[\text{H}^+]^2 + K_a[\text{H}^+] - (K_a C_{\text{MHA}} + K_w) = 0.$$

Looking ahead to 1b and 1c, it is evident that we will need a different  $K_a$  in 1b, but then need *this*  $K_a$  for  $\text{NH}_4^+$  again. To avoid the need to define and then “undefine” each  $K_a$ , the  $K_{aM}$  nomenclature will be used here. Then in 1b,  $K_{aA}$  will be used so that each  $K_a$  is in place for 1c.

From Appendix II:  $a_{\text{H}^+} = 9$ ,  $a_{\text{NH}_4^+} = 2.5$ ,  $a_{\text{OH}^-} = 3.5$  From Appendix III:  $K_w^\circ = 1.00 \times 10^{-14}$  From Appendix IV:  $K_a^\circ (K_{aM})$  for  $\text{NH}_4^+ = 5.689 \times 10^{-10}$

```
> restart; Quad:=(H^2+K[aM]*H - (K[aM]*C[NH4NO3] +
K[w])); μ := 0.075: g['H'] := 10^(-0.511*sqrt(μ)) /
(1 + 0.329*9*sqrt(μ)); g[NH4]:= 10^(-0.511*sqrt(μ)) /
(1 + 0.329*2.5 *sqrt(μ)); g[OH]:= 10^(-0.511* sqrt(μ)) /
(1+0.329*3.5 *sqrt(μ)); K°[aM]:= 5.689e-10: K°[w]:= 1.00e-14: K[aM]:= g[NH4]*K°[aM]/g['H']; K[w]:= K°[w] / (g['H']*g[OH]); C[NH4NO3] := 0.075:
```

$$\begin{aligned} \text{Quad} &:= H^2 + K_{aM}H - K_{aM}C_{\text{NH}_4\text{NO}_3} - K_w \\ g_H &:= 0.8370 \\ g_{\text{NH}_4} &:= 0.7687 \\ g_{\text{OH}} &:= 0.7827 \\ K_{aM} &:= 5.22521 \cdot 10^{-10} \\ K_w &:= 1.5264 \cdot 10^{-14} \end{aligned}$$

Notice that  $K_{aM}$  is calculated from  $K_{aM}^\circ$ , not in the way it is for HA, but as it would be from  $\text{MH}^+$  (page 89). Notice also the single quotation marks around H in  $[\text{H}]$ . These are needed because when pH is ultimately calculated, H will have been assigned a numerical value, and if  $g[\text{H}]$  were called again, that numerical value would appear as a subscript to g. Now to calculate  $[\text{H}^+]$  with added output precision:

```
> H1a:= fsolve(Quad, H, 0.. C[NH4NO3]);
```

$$H1a := 0.00000626$$

We can proceed directly to the pH calculation because  $\mu$  was known at the onset, and so  $\gamma_{\text{H}^+}$ ,  $K_{\text{aM}}$  and  $K_w$  were known too. First, to show the correctness of  $\mu$ ,

```
> mu1a := (1/2) * (H1a + (H1a*C[NH4NO3] / (K[aM] + H1a)) + C[NH4NO3]  
+ K[w]/H1a);
```

$\mu_{\text{1a}} := 0.07500$

So

```
> pH := evalf(-log[10](g['H']*H1a));
```

$pH := 5.2806$

With two significant figures in  $K_a$  and  $C_{\text{NH}_4\text{NO}_3}$ , a mantissa of three places is appropriate.  $pH = 5.281$

The advertisement features a background of a runner's legs in motion on a trail at sunset. On the left, the Gaiteye logo is displayed with the tagline "Challenge the way we run". Below the logo, the text "EXPERIENCE THE POWER OF FULL ENGAGEMENT..." is written in large white letters. In the bottom right corner, there is a yellow call-to-action button with the text "READ MORE & PRE-ORDER TODAY" and the website "WWW.GAITEYE.COM". A hand cursor icon is positioned over the button. The overall theme is performance and innovation in running.

1. b. KF is the salt of a weak acid, HF. F<sup>-</sup> is the conjugate base of that acid, and by binding protons while K<sup>+</sup> has no effect on the H<sup>+</sup> or OH<sup>-</sup> concentration, the solution should be alkaline. Finding [H<sup>+</sup>] does not require the `restart` command; indeed, that would be inefficient because C<sub>KF</sub> = C<sub>NH4NO3</sub> and so  $\mu$ ,  $\gamma_{H^+}$ ,  $\gamma_{OH^-}$  and K<sub>w</sub> are unchanged and need not be recalculated. We will not even have to unassign H because we used `H1a` for the solution to the quadratic. K°<sub>aA</sub> and a<sub>F<sup>-</sup></sub> are assigned from the appendices 6.6 × 10<sup>-4</sup> and 3.5 respectively.<sup>87</sup>

```
> K°[aA] := 6.6e-4: g[F] := 10^(-0.511*sqrt(μ)/(1 + 0.329*3.5*sqrt(μ))); K[aA] := K°[aA]/(g['H']*g[F]);
```

$$g_F := 0.78273 \\ K_{aA} := 0.0010074$$

Here the quadratic approximation will be tested against the cubic expression. This should be a tougher test because here, K<sub>aA</sub> is six orders of magnitude smaller than K<sub>aM</sub> was in **1a**, and because this solution should be alkaline (page 105), it will be more difficult (mathematically) to discard the K<sub>a</sub>K<sub>w</sub> term from the cubic. One more point, for illustration, rather than replace the cubic and quadratic expressions in `fsolve` in **1a** with appropriate versions for the solution of KF, the `solve` operation is used and a *list* of solutions is requested (page 43).

```
> C[KF]:= 0.075: H1b[cubic]:= solve(H^3+(K[aA]+C[KF])*H^2 - K[w]*H - K[aA]*K[w], {H}); H1b[quad]:= solve(H^2 + (K[aA] + C[KF])*H - K[w], {H});
```

$$H1b_{cubic} := \{H = 1.4224 \cdot 10^{-8}\}, \{H = -1.4224 \cdot 10^{-8}\}, \{H = -0.0760\} \\ H1b_{quad} := \{H = 2.0082 \cdot 10^{-13}\}, \{H = -0.0760\}$$

Appropriately, each expression returned only one physically real ([H<sup>+</sup>] > 0) solution, but here the quadratic approximation has failed badly! The cautious reader might suspect that this failure is due to the change from `fsolve` in **1a** to `solve` here; it is not. Apparently discarding K<sub>a</sub>K<sub>w</sub> from the cubic was inappropriate. It is interesting, however, that the second root of the quadratic “exactly” matched the third root of the cubic.

Using a different approach than used in **1a**, that is by proceeding from the first root of  $H1b_{cubic}$  (`H1b[cubic][1]`) the ionic strength can be checked.

```
> H:= subs(H1b[cubic][1],H); μ := (1/2)*(H+C[KF] + (K[aA]*C[KF]/(K[aA] + H)) + K[w]/H);
```

$$H := 1.4224 \cdot 10^{-8}$$

$$\mu := .0750$$

As expected, the solution is alkaline ( $[H^+] < 10^{-7}$ ) and, indeed,  $\mu = C_{KF}$ . So the pH is:

$$> pH := evalf(-\log[10] (g['H']^*H));$$

$$pH := 7.9243$$

This is reported as **pH = 7.924**.

- c.  $\text{NH}_4\text{F}$  This is the salt of the weak base  $\text{NH}_3$  and weak acid, HF.  $\text{NH}_4^+$  will tend to make the solution acidic while  $\text{F}^-$  will tend to make it alkaline. Whichever prevails,  $K_{aM}$  or  $K_{aA}$  will determine whether the solution is acidic or alkaline. That becomes evident by using 5-15.  $K_{aM}$  was calculated for **1a** and  $K_{aA}$  was calculated for **1b**. But those calculations were based on a knowledge of  $\mu$ , which here, we do not have. Using  $[H^+] \approx \sqrt{K_{aM} K_{aA}}$  we can estimate  $\mu$  (cf. page 114).

$$> C[NH4F] := 0.075; H\_est := \sqrt{K[aM]*K[aA]}; \mu := 0.5*(H\_est + (H\_est*C[NH4F]/(H\_est + K[aM])) + (K[aA]*C[NH4F]/(H\_est + K[aA])) + (K[w]/H\_est));$$

$$H\_est := 6.12759 \cdot 10^{-7}$$

$$\mu = 0.07493$$

So it happens that for  $\text{NH}_4\text{F}$ ,  $\mu \approx C_{MHA} = 0.075$ . It would be pointless to adjust the gammas and K's from  $\mu = 0.075$  to  $\mu = 0.0749$ . Rather, one should proceed directly to the application of the 4° polynomial. This can be done by copying the expression from page 107, or more directly by cutting that expression as it was derived on page 108. Rather than endure three invalid and one valid solution to this polynomial, we can restrict the search to **0..1E-6**. The 1E-6 comes from slightly enlarging the **H\_est** found above. We will also compare the polynomial solution to  $[H^+] \approx \sqrt{K_{aM} K_{aA}}$ . Finally, recall that we assigned H a value in **1b**. So it must be unassigned if it is to be used in the polynomial expression below.

$$> H := 'H': H1c[0^\circ] := \sqrt{K[aA]*K[aM]}; H1c[4^\circ] := \text{fsolve}(H^4 + (C[NH4F] + K[aM] + K[aA])*H^3 + (-K[w] + K[aM]*K[aA])*H^2 + (-K[w]*K[aM] - K[w]*K[aA] - K[aA]*C[NH4F]*K[aM])*H - K[w]*K[aM]*K[aA], H, 0..1E-6);$$

$$H1c_0^\circ := 7.25531322 \cdot 10^{-7}$$

$$H1c_4^\circ := 7.20840727 \cdot 10^{-7}$$

This is an impressive performance by the simplistic, 0°, expression. It differs from the rigorous 4° expression by only 0.65%. With the results this close, it should be obvious that replacing  $H_{est}$  with  $H1c_{4^{\circ}}$  will give the same  $\mu = 0.07493$ . And with these values for  $[H^+]$  so close, the log operation to render the respective pH's will give effectively the same values.

```
> pH[0°]:= evalf(-log[10](g['H']*H1c[0°])); pH[4°]:= evalf(-  
log[10](g['H']*H1c[4°]));
```

$$\begin{aligned} pH_{0^{\circ}} &:= 6.21662 \\ pH_{4^{\circ}} &:= 6.21944 \end{aligned}$$

These would be reported as **pH = 6.217** and **6.219**.

2. To determine which expression produces the more accurate answer, we need the correct answer and that comes from the 4° polynomial. Again, `restart` is *not* used so that the previously assigned constants can be used, including  $H_{est}$ , but a few terms will require reassignment.

```
> K[aA] := K°[aA]: K[aM] := K°[aM]: K[w] := K°[w]: C[NH4F]  
:= 'C[NH4F]': H_515 := H_est: H_514 := sqrt((K[aA]*(K[w] +  
K[aM]*C[NH4F]))/(K[aA] + C[NH4F]));
```



$$H_{515} := 6.12759 \cdot 10^{-7}$$

$$H_{514} := \sqrt{\frac{6.6000 \cdot 10^{-18} + 3.7547 \cdot 10^{-13} C_{NH4F}}{0.0007 + C_{NH4F}}}$$

```
> NMplot([H_515,H_514],C[NH4F] = 0..0.01);
```

The correctness of these plots is determined by comparing them to calculations of  $[H^+]$  made from the rigorously derived 4° polynomial (page 108). We can cut and paste from **1c** after assigning  $C[NH4F]$  a value of 0.002 M.

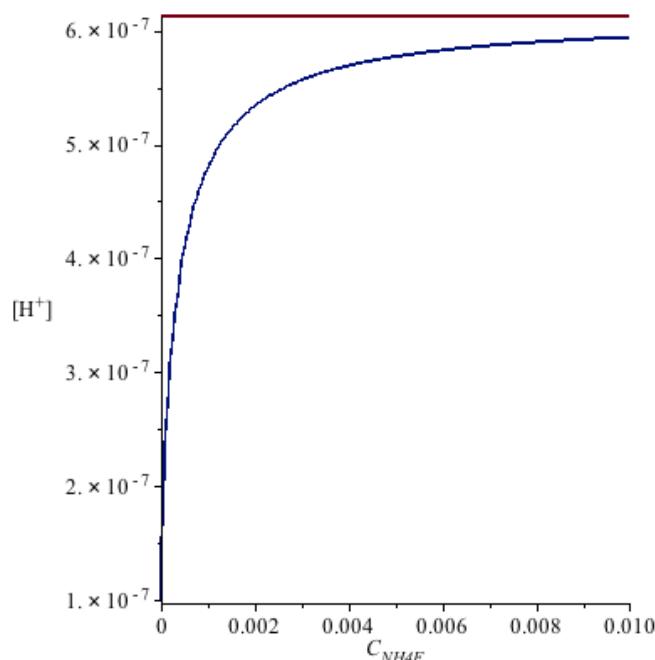


Figure 5-1

```
> C[NH4F] := 0.002: H4° := fsolve(H^4 + (C[MHA] + K[aM] + K[aA]) * H^3 + (-K[w] + K[aM] * K[aA]) * H^2 + (-K[w] * K[aM] - K[w] * K[aA] - K[aA] * C[MHA] * K[aM]) * H - K[w] * K[aM] * K[aA], H, 0..7E-7); H2° := sqrt(K[aA] * (K[w] + K[aM] * C[MHA]) / (K[aA] + C[MHA]));
```

$$H4^\circ := 5.3354 \cdot 10^{-7}$$

$$H_{514} := 5.3366 \cdot 10^{-7}$$

Again, we precluded the physically impossible values for  $[H^+]$  by inserting  $0..1E-7$  in the `fsolve` command. By inspection, it is the quadratic expression (blue line in 5-1) that is closer to the correct solution,  $5.3354 \cdot 10^{-7}$  at  $C_{NH4F} = 0.002$  M.

3. a. This problem, especially parts **b** and **c**, is intended as a segue to Chapter 6. It is also worthy of comparison to problem **2b** in Chapter 4. In Part **a**, KCl, being the salt of a strong acid / strong base provides only spectator ions. ( $K^+$  will not bind  $Cl^-$  or  $OH^-$ , and  $Cl^-$  will not bind  $K^+$  or  $H^+$ .) However this strong electrolyte will contribute to the ionic strength. The “inertness” of the KCl can be demonstrated mathematically by applying the discussion of page 47 *et seq.*

$$[K^+] = C_{KCl}$$

$[Cl^-]$  comes from both KCl and the  $HN(CH_3)_3Cl$ , hereafter referred to as MHCl. Combining these principles into a charge balance expression produces, first

$$[H^+] + [K^+] + [MH^+] = [Cl^-] + [OH^-]$$

and then,

$$[H^+] + \epsilon_{KCl} + \frac{[H^+]C_{MHCl}}{[H^+] + K_a} = \epsilon_{KCl} + C_{MHCl} + \frac{[H^+]}{K_a}$$

So the charge balance expression, and ultimately the cubic polynomial in  $[H^+]$ , is unaffected by the presence of KCl. The KCl will simply augment the ionic strength,

$$\mu \approx C_{MHCl} + C_{KCl}$$

which will be confirmed.

From Appendix II:  $a_{H^+} = 9$ ,  $a_{Me_3NH} = 4$ ,  $a_{OH^-} = 3.5$  From Appendix III:  $K_w^\circ = 1.00 \times 10^{-14}$   
From Appendix IV:  $K_a^\circ$  for  $(CH_3)_3NH^+ = 1.585 \times 10^{-10}$

```
[ = restart; C[KCl]:= 0.011; C[MHCl]:= 0.033; mu:=
C[KCl] + C[MHCl]; g['H']: = 10^(-0.511*sqrt(mu)/(1 +
0.329*9*sqrt(mu))): g[Me3NH]:= 10^(-0.511*sqrt(mu)/
(1 + 0.329*4*sqrt(mu))): g[OH]:= 10^(-0.511*sqrt(mu)/
(1 + 0.329*3.5*sqrt(mu))): K°[a]:= 1.585e-10; K°[w]:= 1.00e-14; K[a]:= g[Me3NH]*K°[a]/g['H']; K[w]:= K°[w]/
(g['H']*g[OH]);
```

$$\begin{aligned}\mu &:= 0.0440 \\ K_a &:= 1.5211 \cdot 10^{-10} \\ K_w &:= 1.4205 \cdot 10^{-14}\end{aligned}$$

Most of the output has been suppressed because so much of this solution is a trivial variation on problem #1 which provided confidence in the results. The calculation is nothing more than solving the cubic polynomial derived on page 103 where it was described as a trivial variation on **4-13**.

```
> H3a:= fsolve(H^3+K[a]*H^2 - (K[a]*C[MHCl] + K[w])*H
-K[a]*K[w],H,0..C[MHCl]);
```

$$H3a := 0.00000224$$

```
> H := H3a; μ := (1/2)*(H + C[KCl] + (H*C[MHCl]/(H + K[a])) +
C[KCl] + C[MHCl] + K[w]/H);
```

$$\mu := .04400$$

Indeed, this is very close to  $C_{\text{MHCl}} + C_{\text{KCl}}$ . So  $\gamma_{\text{H}^+}$  is close enough to proceed.

```
> pH := evalf(-log[10](g['H']*H));
```

$$pH := 5.7152$$

**pH 5.715** would be reported.

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3. b. Replacing KCl in **3a** with HCl significantly changes the nature of the problem. The changes are that now,

$$\mu \approx C_{\text{MHCl}} + C_{\text{HCl}}$$

and

$$[\text{Cl}^-] = C_{\text{MHCl}} + C_{\text{HCl}}$$

The significant change comes in the form of the charge balance:

$$[\text{H}^+] + \frac{[\text{H}^+]C_{\text{MHCl}}}{[\text{H}^+] + K_a} = C_{\text{HCl}} + C_{\text{MHCl}} + \frac{[\text{H}^+]}{K_a}$$

With  $C_{\text{HCl}}$  on *only* the right side of the equation,  $[\text{H}^+]$  must increase in order to maintain the charge balance. This supports the obvious: adding HCl to a solution will cause  $[\text{H}^+]$  to increase!

From here the problem can be solved with one line of input, only one line because a short cut will be used that will expose many of the derivations done to this point as superfluous. Recall from problem **2b** in Chapter 4 that when an expression like the charge balance given here is relatively simple, it is not necessary to render it into a conventional polynomial form. Rather, one can enter it directly into `solve` or `fsolve`.<sup>88</sup>

```
> H := 'H': C[HCl]:= 0.011: mu := C[MHCl] + C[HCl]: H3b:=
  solve(H + (H*C[MHCl]/(H + K[a])) = C[HCl] + C[MHCl] +
  K[w]/H, {H});
```

$$\begin{aligned} H3b := \{H = 0.0110\}, \{H = -3.2234 \cdot 10^{-13}\}, \\ \{H = -6.0940 \cdot 10^{-10}\} \end{aligned}$$

We will continue the calculation using the `subs` command introduced on page 44.

```
> H:= subs(H3b[1],H); mu:=(1/2) * (H + (H*C[MHCl]/(H +
  K[a])) + C[HCl] + C[MHCl] + K[w]/H); pH:= evalf(-log[10]
  (g['H']*H));
```

$$\begin{aligned} H &:= 0.0110 \\ \mu &:= 0.0440 \\ pH &:= 2.0247 \end{aligned}$$

The **pH = 2.025** is not particularly interesting, but  $[H^+]$  equals 0.011 which equals  $C_{HCl}$ . This says that the  $HN(CH_3)_3Cl$  had no measurable effect on the  $[H^+]$ . Is that reasonable? Given that the  $K_a^o$  for  $(CH_3)_3NH^+$  is not more than one billionth ( $10^{-9}$ ) as large as  $K_a^o$  for a strong acid like HCl, yes. Other than the contribution to  $\mu$  by  $HN(CH_3)_3Cl$ , this is just like problem 3d from Chapter 3.

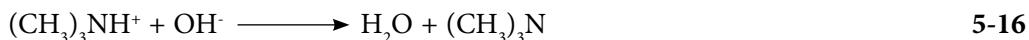
3. c. Replacing the HCl in **3b** with KOH affects the charge balance in the opposite way: it moves the contributor from the right (anion) side to the left (cation) side. There might be a temptation to use

$$[OH^-] = C_{KOH}.$$

This would be a serious mistake. It is incorrect, chemically, because the KOH is not the only source of  $[OH^-]$ , although it is very nearly the only source. The problem with inserting  $C_{KOH}$  for  $[OH^-]$  is that it would cancel out the  $C_{KOH}$  on the cation side because

$$[K^+] = C_{KOH}.$$

Finally, there might be an inclination, by chemists, to address the neutralization of the acid  $(CH_3)_3NH^+$  by the KOH (or OH<sup>-</sup>) as



Remarkably, this is not necessary! This neutralization process is ruled entirely by the mass balance and charge balance restrictions we have defined. Consider the expression for  $[(CH_3)_3NH^+]$ .

$$[(CH_3)_3NH^+] = \frac{[H^+]C_{(CH_3)_3HCl}}{[H^+] + K_a}$$

As  $[OH^-]$  increases,  $[H^+]$  will decrease and as  $[H^+]$  decreases so must  $[(CH_3)_3NH^+]$ . This will be the point of acid / base titrations addressed in Chapter 7.

The charge balance for a solution of KOH and MHCl is

$$[H^+] + C_{KOH} + \frac{[H^+]C_{MHCl}}{[H^+] + K_a} = C_{MHCl} + \frac{K_w}{[H^+]}$$

Analogous to **b**,  $C_{KOH}$  is added to only one side of the charge balance equation. Because  $[H^+]$  is the only variable on the left side of the charge balance equation,  $[H^+]$  must decrease as  $C_{KOH}$  i.e  $[K^+]$  increases, little surprise here. Using the route of **b**,

```
>H:='H': C[KOH]:= 0.011: μ:= C[MHCl] + C[KOH]: H3c:= solve  
(H + C[KOH] + (H*C[MHCl]/(H + K[a]))) = C[MHCl] + K[w]/  
H, {H});
```

$$H3c := \{H = 3.0615 \cdot 10^{-10}\}, \{H = -6.4163 \cdot 10^{-13}\}, \\ \{H = -0.0110\}$$

```
>H:= subs(H3c[1],H): μ:= (1/2)*(H + C[KOH] + (H*C[MHCl])/  
(H+K[a])) + C[MHCl] + K[w]/H);
```

$$\mu := 0.03305$$

It would appear that the approximation,  $\mu \approx C$ , or in this case  $C_{\text{MHCl}} + C_{\text{KOH}}$  ( $= 0.044$ ) has finally failed, but for good reason: Equation 5-16 above. As discussed earlier, the added  $\text{OH}^-$  will remove the ionic component  $(\text{CH}_3)_3\text{NH}^+$  from solution. It should not be surprising that adding an agent that removes an ionic solute without replacing it will diminish the ionic strength of the solution. A reiteration with this diminished ionic strength will be carried out before proceeding to the calculation for the pH.



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For the sake of illustration, after using the new ionic strength to reevaluate the activity coefficients and then,  $K_a$  and  $K_w$ , the `fsolve` command will be used instead of `solve` which was used earlier. Recall that `fsolve` can be manipulated to find only the desired ( $[H^+] > 0$ ) root, but notice the narrow range,  $0..1e-7$ , that is used to help Maple find that root. Knowing that this solution is alkaline ( $[H^+] < 10^{-7}$ ) allows this narrow range.

```
> H:= 'H': g['H']: = 10^(-0.511*sqrt(mu)/(1 +
0.329*9*sqrt(mu))): g[Me3NH]:= 10^(-0.511*sqrt(mu)/(1
+ 0.329*4*sqrt(mu))): g[OH]:= 10^(-0.511*sqrt(mu)/(1 +
0.329*3.5*sqrt(mu))): K[a]:= g[Me3NH]*K°[a]/g['H']; K[w]:= K°[w]/(g['H']*g[OH]): H3c:= fsolve(H + C[KOH] + (H*C[MHCl])/
(H + K[a])) = C[MHCl] + K[w]/H,H, 0..1e-7);
```

$$K_a := 1.5327 \cdot 10^{-10}$$

$$H3c := 3.0841 \cdot 10^{-10}$$

An output for  $K_a$  is sought for comparison to those values that were found for  $\mu = 0.044$  (page 121). The difference is less than 1%. Once again,  $\mu$  is verified, and anticipating a good match, pH is calculated.

```
>H:= H3c: mu:= (1/2)*(H + C[KOH] + (H*C[MHCl])/(H + K[a])) +
C[MHCl] + K[w]/H; pH:= evalf(-log[10](g['H']*H));
```

$$\mu := 0.033045$$

$$pH := 9.5713$$

**pH 9.571** is reported here. Despite the considerable error in presuming that  $\mu = C_{\text{MHCl}} + C_{\text{KOH}}$ , the corrected  $[H^+]$  was only 0.7% higher, and the pH was barely changed.

# 6 Buffer Solutions

A buffer solution, more precisely a pH buffer or acid / base buffer solution, is one that shows a meaningful resistance to change in its pH when either an acid or base is added to that solution. In Chapter 3 it was shown that adding a small amount of strong acid or strong base to a solution can profoundly change the pH of that solution.<sup>89</sup> Chapter 5, Problem 3, however, showed that some solutions are more resistant to changes in pH. For further illustration consider again that problem (first column below) and compare it to other solutions of analogous makeup.

	0.033 M HN(CH <sub>3</sub> ) <sub>3</sub> Cl	0.044 M KCl	0.033 M N(CH <sub>3</sub> ) <sub>3</sub>
<i>a</i>	add 0.011 M KCl $\mu = 0.044$ pH = 5.715	$\mu = 0.044$ pH = 6.990	add 0.011 M KCl $\mu = 0.012_6$ pH = 11.146
<i>b</i>	add 0.011 M HCl $\mu = 0.044$ pH = 2.025	0.033 M KCl 0.011 M HCl $\mu = 0.044$ pH = 2.025	add 0.011 M HCl $\mu = 0.011$ pH = 10.174
<i>c</i>	add 0.011 M KOH $\mu = 0.033$ pH = 9.571	0.033 M KCl 0.011 M KOH $\mu = 0.044$ pH = 11.955	add 0.011 M KOH $\mu = 0.011$ pH = 12.002

**Table 6-1**

The “benchmark” solution is the 0.044 M KCl solution: there  $[H^+] = [OH^-]$ .<sup>90</sup> This is an example of a solution that has effectively no buffer capacity, no meaningful ability to resist a change in its pH. The other two solutions, one of a weak base, trimethylamine (third column) and one of the conjugate acid of that weak base, *i.e.* trimethylammonium (first column) fare much better. The HN(CH<sub>3</sub>)<sub>3</sub>Cl solution, already slightly acidic, shows marginal resistance to a decrease in its pH when HCl is added, but the N(CH<sub>3</sub>)<sub>3</sub> solution, already strongly alkaline, shows resistance to the effects of adding either HCl or KOH. Arguably, these examples of buffer capacity are a consequence of Le Châtelier’s principle: it *should* be especially difficult to lower the pH of an acidic solution or to raise the pH of an alkaline solution. But there is more to the buffer properties of these solutions than Le Châtelier’s principle.

Each of these solutions, unlike the KCl solution, contains a residual acid (CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup> and base N(CH<sub>3</sub>)<sub>3</sub> which help to mitigate the effects of added OH<sup>-</sup> and H<sup>+</sup>, respectively. Recall, from Chapter 4<sup>91</sup> that [(CH<sub>3</sub>)<sub>3</sub>NH<sup>+</sup>] and [N(CH<sub>3</sub>)<sub>3</sub>] can be calculated once [H<sup>+</sup>] has been determined.

$$[(\text{CH}_3)_3\text{NH}^+] = \frac{[\text{H}^+]\text{C}_{(\text{CH}_3)_3\text{NHCl}}}{[\text{H}^+] + K_a}$$

and,

$$[(\text{CH}_3)_3\text{N}] = \frac{K_a \text{C}_{(\text{CH}_3)_3\text{NHCl}}}{[\text{H}^+] + K_a}$$

(These expressions pertain to the trimethylammonium chloride solution; for the trimethylamine solution,  $\text{C}_{(\text{CH}_3)_3\text{N}}$  should be used.) Applying these expressions to the  $(\text{CH}_3)_3\text{NHCl}$  and  $(\text{CH}_3)_3\text{N}$  solutions shows their make up to be:

	0.033 M $(\text{CH}_3)_3\text{NHCl}$ 0.011 M KCl	0.033 M $(\text{CH}_3)_3\text{N}$ 0.011 M KCl
$[\text{H}^+]$	$2.2_5 \cdot 10^{-6}$	$7.8_9 \cdot 10^{-12}$
$-\log_{10}[\text{H}^+]$	5.64	11.10
$[(\text{CH}_3)_3\text{NH}^+]$	$0.033_0$	$1.5_7 \cdot 10^{-3}$
$[(\text{CH}_3)_3\text{N}]$	$2.2_5 \cdot 10^{-6}$	$0.031_4$

Table 6-2

Table 6-1 shows that the strongly alkaline,  $(\text{CH}_3)_3\text{N}$  solution resists pH changes in both directions more effectively than the  $(\text{CH}_3)_3\text{NHCl}$  solution can. (Compare the  $\Delta\text{pH}$  between row *a* and row *b* and row *a* and row *c* for each column.) Table 6-2 shows that the  $(\text{CH}_3)_3\text{N}$  solution has a better (not necessarily a good) balance in its  $(\text{CH}_3)_3\text{NH}^+$  and  $(\text{CH}_3)_3\text{N}$  concentrations than the  $(\text{CH}_3)_3\text{NHCl}$  has. These properties are not a coincidence. Resistance to the addition of acid requires the presence of  $(\text{CH}_3)_3\text{N}$  and the resistance to the effects of base requires the presence of  $(\text{CH}_3)_3\text{NH}^+$ ; the more of each, the more effective the buffer.

If indeed it is the balance of weak acid and weak base in solution that provides buffer capacity, then there are four strategies for creating such solutions:

- A mixture of a weak acid and the salt of that weak acid.
- A mixture of a weak base and the salt of that weak base.
- The salt of a weak acid / weak base.
- A partially protonated polyprotic acid or base.

The first three strategies will be studied here and the fourth strategy will be deferred to Chapter 8 where polyprotic acids and bases are introduced.

Consider a solution made to contain a weak acid, HA, and the salt of that weak acid, MA. By definition, A<sup>-</sup> will be the anion of a weak acid and that means that it is not in Table 3-1. By necessity,<sup>92</sup> M<sup>+</sup> is monovalent member of Table 3-1, except of course H<sup>+</sup>. The solution can be described as having concentrations C<sub>HA</sub> and C<sub>MA</sub>. Such a solution, for example, could be acetic acid and sodium acetate or hydrofluoric acid and potassium fluoride. From here an abbreviated derivation of an expression for [H<sup>+</sup>] is provided.

Charge balance:

$$[H^+] + [M^+] = [A^-] + [OH^-].$$

Mass balance:

$$[M^+] = C_{MA}$$

and,

$$[A^-] = \frac{(C_{HA} + C_{MA})K_a}{[H^+] + K_a}$$

6-1

---

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The variation between Equations 4-11 and 6-1 is due to the fact that in this solution there are two sources of  $A^-$ , which are HA *and* MA. Using  $[OH^-] = K_w/[H^+]$  along with these mass balance substitutions yields an implicit expression for  $[H^+]$ .

$$[H^+] + C_{MA} = \frac{(C_{HA} + C_{MA})K_a}{[H^+] + K_a} + \frac{K_w}{[H^+]} \quad 6-2$$

which yields the polynomial:

$$[H^+]^3 + (K_a + C_{MA})[H^+]^2 - (K_a C_{HA} + K_w)[H^+] - K_a K_w = 0. \quad 6-3$$

This is a logical equation. If  $C_{MA}$  is set equal to zero, we have effectively a solution of a weak acid and we appropriately get 4-13, the expression for a solution of a weak acid. If  $C_{HA}$  is set equal to zero, we have effectively the salt of a weak acid and we appropriately get 4-38, the expression for the solution of the salt of a weak acid. Indeed, Equation 6-3 is the general expression to those two earlier expressions, and like those expressions it can be approximated as a quadratic:

$$[H^+]^2 + (K_a + C_{MA})[H^+] - (K_a C_{HA} + K_w) = 0. \quad 6-4$$

Extracting the physically legitimate ( $[H^+] > 0$ ) root gives:

$$[H^+] = \frac{-(K_a + C_{MA}) + \sqrt{(K_a + C_{MA})^2 + 4(K_a C_{HA} + K_w)}}{2} \quad 6-5$$

For a useful buffer solution,  $[H^+]$  will always be much, much greater than  $K_a K_w$ , and so 6-4 will *always* be an excellent replacement for 6-3. The effects of  $C_{HA}$ ,  $C_{MA}$ , and  $K_a$  on  $[H^+]$  are not obvious, even from 6-5. So these will be explored here.

For “legitimate” buffer solutions,  $C_{HA}$  and  $C_{MA}$  are somewhat constrained and rarely exceed 0.5 M or lie below  $10^{-3}$  M.<sup>93</sup>  $K_a$ , however, can range over many orders of magnitude. This makes it possible to create buffer solutions that stabilize the pH of a solution at any of a wide range of pHs. To address the variation of  $K_a$  over several orders of magnitude an alternate expression for  $K_a$  (or any  $K_{eq}$  for that matter) is provided here.

The activity of  $H^+$  has been seen to vary over many orders of magnitude and so it is commonly expressed as pH, defined in Equation 3-15 as *minus* the  $\log_{10}$  of the hydrogen ion *activity*. The practice of expressing values of considerable variability as  $-\log_{10}$  is widespread in solution chemistry; the negative sign compensates for the fact that nearly all of the variability occurs between zero and one.<sup>94</sup> Therefore,

$$pK_a = -\log K_a \quad 6-6$$

and so,

$$K_a = 10^{-pK_a}. \quad 6-7$$

The  $K_a$  in the expression for  $[H^+]$ , 6-5, can be modified using 6-7. Inasmuch as the evaluation of 6-5 will be done with Maple, this substitution will be done there as well. Here we will use a variation on the `subs` command we have used earlier. This is `algsubs`, a command that allows an algebraic substitution into an expression.

```
> restart; Expr[65]:= (1/2)*(-(K[a] + C[MA]) + sqrt((K[a] + C[MA])^2
+ 4*(K[a]*C[HA] + K[w]))); Expr:= algsubs(K[a] = 10^(-pKa),
Expr[65]);
```

$$Expr_{65} := -\frac{1}{2} K_a - \frac{1}{2} C_{MA} + \frac{1}{2} \sqrt{K_a^2 + 2 K_a C_{MA} + C_{MA}^2 + 4 K_a C_{HA} + 4 K_w}$$

$$Expr_{65} := -\frac{1}{2} 10^{-pKa} - \frac{1}{2} C_{MA} \\ + \frac{1}{2} \sqrt{C_{MA}^2 + (10^{-pKa})^2 + 4 K_w + 2 C_{MA} 10^{-pKa} + 4 C_{HA} 10^{-pKa}}$$

For the following illustrations it will be necessary to abuse the definition of pH by neglecting ionic strength effects.<sup>95</sup> This is a prudent omission because the point is to show the relationship among these parameters as they change over orders of magnitude, and inasmuch as  $\gamma_{H^+}$  etc. vary only between 0.3 and 1.0, these other terms produce *relatively* minor effects. Continuing the worksheet:



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```
> pH := -log[10](Expr[65]);
```

$$pH := -\frac{1}{\ln(10)} \left( \ln \left( -\frac{1}{2} 10^{-pK_a} - \frac{1}{2} C_{MA} + \frac{1}{2} \sqrt{C_{MA}^2 + (10^{-pK_a})^2 + 4 K_w + 2 C_{MA} 10^{-pK_a} + 4 C_{HA} 10^{-pK_a}} \right) \right)$$

We have three variables here:  $pK_a$ ,  $C_{MA}$  and  $C_{HA}$ . First, let us explore how  $C_{MA}$  and  $C_{HA}$  *individually* affect the pH at a given  $pK_a$ . For this, a powerful tool in Maple will be introduced, the three dimensional plot. For illustration, a moderate  $pK_a$  (= 7) will be selected, and  $C_{HA}$  and  $C_{MA}$  will be allowed to range widely. Continuing with the previous worksheet:

```
> C[Effects]:= subs(K[w] = 1E-14, pKa = 7, pH);
```

$$C_{Effects} := -\frac{1}{\ln(10)} \left( \ln \left( -\frac{1}{20000000} - \frac{1}{2} C_{MA} + \frac{1}{2} \sqrt{C_{MA}^2 + 5.0000 \cdot 10^{-14} + \frac{1}{5000000} C_{MA} + \frac{1}{2500000} C_{HA}} \right) \right)$$

```
> plot3d(C[Effects], C[MA] = 0..0.3, C[HA] = 0..0.3, axes = boxed,  
labels =[C[MA], C[HA], "pH"], orientation = [30, 45], grid =  
[50, 50]);
```

The Effects of  $C_{HA}$  and  $C_{MA}$  on pH

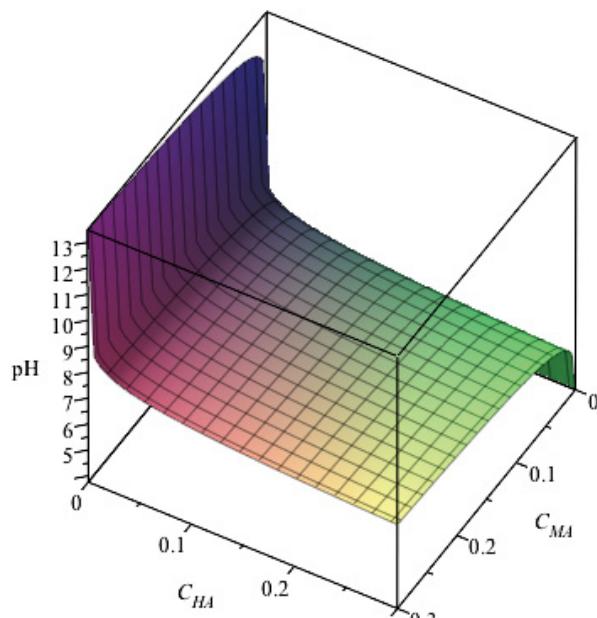


Figure 6-1

First, comments on the Maple input are in order; then the output will be addressed. `plot3d` requires two inputs, the function (or name of the function) to be plotted, and the range of each of the two variables in that function. All inputs, including optional inputs, are separated with commas. Following the required inputs, many options that control the look of the graph can be added, in any order. The boxed axes are called here; the default *i.e.* no axes specification, will render a plot without axes. The “labels” option is particularly important for the three dimensional plot because axis identity is ambiguous without it. Brackets are used around lists of inputs, here that would be MA, HA and “pH”. The quotations are needed because pH has been assigned and cannot be used without those quotation marks (which protect it as a string). The next option used here is especially useful. It establishes the angles,  $\theta$  and  $\phi$ , from which the plot is viewed. The default values are  $45^\circ$  (above the  $x$ - $y$  plane) and  $45^\circ$  (off the  $x$ - $z$  plane). The last option `grid = [50, 50]`. It sets the number of grids on the surface. The title for Figure 6-1 was added by clicking on the plot and going to the **Plot** tab in the menu bar, sliding down to **Title** and over to **Add Title**.

No explanation here can replace a few minutes of experimenting with values to watch the effects of changing  $\theta$  and  $\phi$  on the form (and usefulness) of the plot. One can change these values within the `plot3d` command, or better, click on the plot and go to the **Plot** menu and drag down to **Manipulator** and over to the options. One will find more options here than were seen for two dimensional plots.<sup>96</sup> Among the options is the Rotate manipulator (which happens to be the default function for `plot3d`). This can be used to “spin” the plot and quickly find the most effective angle for displaying a 3D plot.

The three prominent features of the output plot are the steep rise in pH where  $C_{HA}$  approaches zero, the precipitous fall in pH where  $C_{MA}$  approaches zero and the broad plateau at  $pH \approx 7$  for most non-zero values of  $C_{HA}$  and  $C_{MA}$ . The high pH at  $C_{HA}$  equals zero should not be surprising because such a solution is, therefore, nothing more than a solution of MA, and that has been shown to be an alkaline solution (page 105). Likewise the low pH where  $C_{MA}$  approaches zero should be expected because this constitutes a simple solution of HA, a weak acid. Furthermore,  $[H^+]$  is limited by  $K_a$ . Had a larger  $K_a$  been selected for this illustration, the solution would have achieved a pH less than 4. Most important, however, is that a larger  $K_a$  (smaller  $pK_a$ ) would have relocated the plateau to a lower pH, and that is the critical effect of  $pK_a$  on pH. The reader is invited to experiment with  $C_{HA}$ ,  $C_{MA}$ , and  $pK_a$  values and observe the effects on the output.

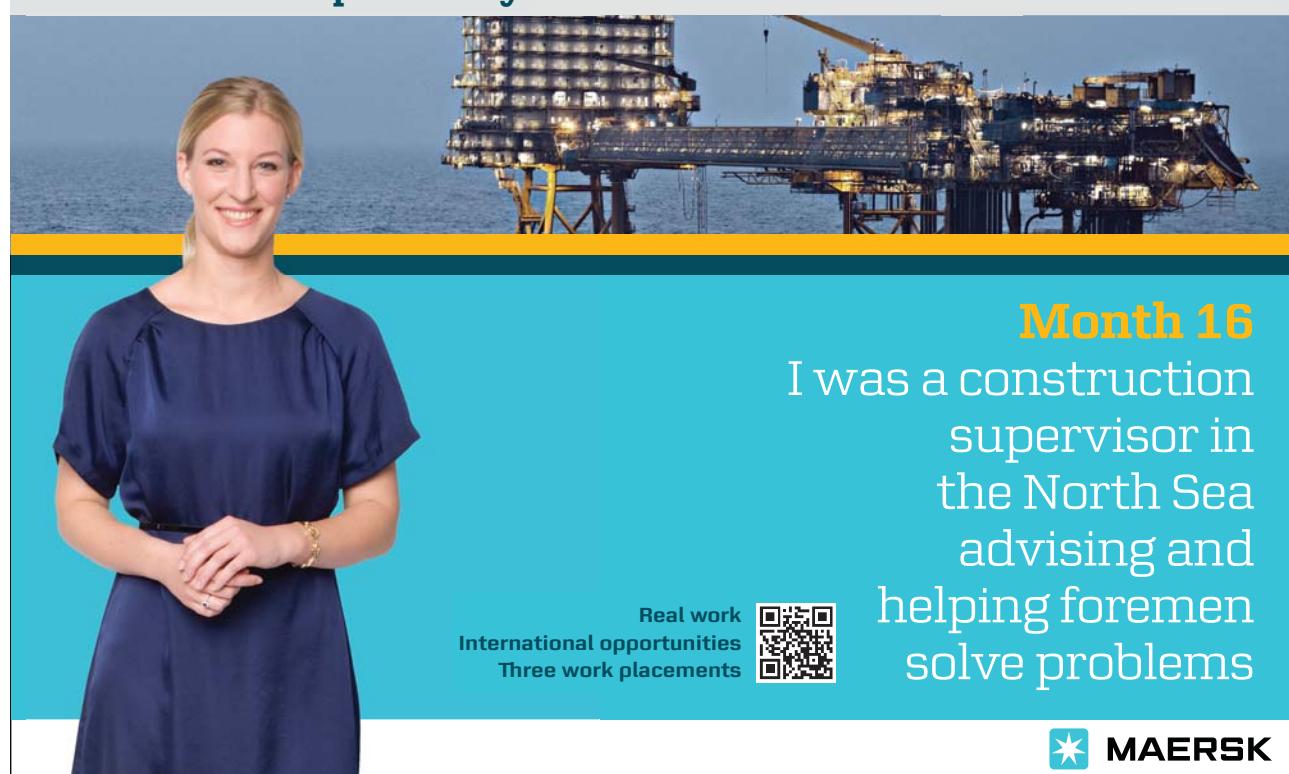
It is the large, nearly level plateau that is the heart of this chapter. It lies nominally at a pH equal to the  $pK_a$ . The modest change in pH despite the  $C_{HA}:C_{MA}$  ratio is the essence of the buffer solution. What does the  $C_{HA}:C_{MA}$  ratio have to do with adding  $H^+$  or  $OH^-$  to a buffer solution? Consider this: MA is added to a buffer solution to provide an abundance of  $A^-$  which is present to neutralize  $H^+$  that might be added, and likewise, HA is added to provide, yes, HA which is present to neutralize any  $OH^-$  that might be added. So adding  $H^+$  effectively converts MA into HA (+  $M^+$ ) which is like increasing the  $C_{HA}:C_{MA}$  ratio. Adding  $OH^-$  (as MOH) effectively converts HA into MA (+  $H_2O$ ) and that is like decreasing the  $C_{HA}:C_{MA}$  ratio.

It is evident from Figure 6-1 that the pH of the solution is only modestly affected by varying the  $C_{\text{HA}}:C_{\text{MA}}$  ratio. Here we will demonstrate the effects of changing  $C_{\text{HA}}:C_{\text{MA}}$  on the pH of the solution and on the ability of that solution to resist changes in pH when a strong acid or strong base is added. Again, for simplicity, it will be necessary to ignore ionic strength effects, and again, this will create only a minor error in the results, which are used only for demonstration. When procedures are described for preparing a buffer solution of  $C_{\text{HA}}$  and  $C_{\text{MA}}$  (page 146 *et seq.*) ionic strength will be considered and the pH will be accurately achieved. Finally, for *this* demonstration, the conventional method for preparing a buffer solution will be introduced. It is *not* to add enough HA and then enough MA to a solution to achieve a desired  $[\text{HA}]:[\text{A}^-]$ ; rather one of two processes is used: *a*. A solution of MA is prepared and then enough strong acid is added to achieve the desired  $[\text{HA}]:[\text{A}^-]$  or *b*. a solution of HA is prepared and then enough strong base is added to achieve that desired  $[\text{HA}]:[\text{A}^-]$ .

When either of these procedures is used to prepare an HA/ $\text{A}^-$  buffer, the concept of  $C_{\text{HA}}$  and  $C_{\text{MA}}$  takes on a very different meaning: it becomes abstract because, for example, treating a solution of MA with strong acid will certainly increase  $[\text{HA}]$  but there is no  $C_{\text{HA}}$ , *per se*, and likewise, treating a solution of HA with a strong base will certainly increase the  $[\text{A}^-]$ , but there will be no  $C_{\text{MA}}$ . Nevertheless, solutions will behave as though they had a given  $C_{\text{HA}}:C_{\text{MA}}$ .

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We will proceed to illustrate both of these buffer solutions, simultaneously. But in order to study solutions made by these procedures, Equation 6-3 must be modified to remove either  $C_{HA}$  (for the MA solution treated with strong acid) or  $C_{MA}$  (for the HA solution treated with strong base). Consider first the solution of MA, concentration  $C_{MA}$ , treated with a strong acid, HSa. Enough HSa will be added to achieve an *apparent*  $C_{HA}$ , at which point the strong acid will have a concentration  $C_{HSa}$ .<sup>97</sup> Here the charge balance is:

$$[H^+] + [M^+] = [A^-] + [Sa^-] + [OH^-].$$

$[M^+]$  becomes  $C_{MA}$  because MA is a strong electrolyte and it is the only source of  $M^+$ . Likewise, since HSa is a strong acid,  $[Sa^-]$  becomes  $C_{HSa}$ .  $[A^-]$  can be taken from 6-1, but without the  $C_{HA}$  term which is zero in *this* solution. Then, using  $[OH^-] = K_w/[H^+]$ , the charge balance is expressed exclusively in terms of  $[H^+]$ , equilibrium constants and solution concentrations. These substitutions lead us to the familiar cubic polynomial:

$$[H^+]^3 + (K_a + C_{MA} - C_{HSa})[H^+]^2 - (K_a C_{HSa} + K_w)[H^+] - K_a K_w = 0. \quad 6-8$$

which can be approximated as a quadratic<sup>98</sup> because  $K_a K_w \approx 0$ .

$$[H^+]^2 + (K_a + C_{MA} - C_{HSa})[H^+] - (K_a C_{HSa} + K_w) = 0. \quad 6-9$$

Likewise we can address the buffer solution that is made by treating a solution of HA with a strong base MOH.

Charge balance:

$$[H^+] + [M^+] = [A^-] + [OH^-].$$

With substitutions:

$$[H^+]^3 + (K_a + C_{MOH})[H^+]^2 + (K_a C_{MOH} - K_a C_{HA} - K_w)[H^+] - K_a K_w = 0, \quad 6-10$$

and with  $K_a K_w \approx 0$ .

$$[H^+]^2 + (K_a + C_{MOH})[H^+] + (K_a C_{MOH} - K_a C_{HA} - K_w) = 0 \quad 6-11$$

With Equations 6-9 and 6-11 we have two expressions<sup>99</sup> for  $[H^+]$  for buffer solutions made from mixing a strong acid with MA, or mixing a strong base with HA, respectively. Now we proceed to isolate the (appropriate) root of each to create a plot of pH vs. either  $C_{HSa}$  or  $C_{MOH}$  simultaneously. First, we will begin by directly entering these two equations into Maple, solving them (for  $[H^+]$ ) and choosing the root that gives only  $[H^+] > 0$ .

```
> restart; HSa_Exp:= solve(H^2 + (K[a] + C[MA] - C[HSa])*H -
(K[a]*C[HSa] + K[W]), {H}); MOH_Exp:= solve(H^2 + (K[a] + C[MOH])*H
+ (K[a]*C[MOH] - K[a]*C[HA] - K[W]), {H});
```

$$\begin{aligned} HSa\_Exp := & \left\{ H = -\frac{1}{2} K_a - \frac{1}{2} C_{MA} + \frac{1}{2} C_{HSa} \right. \\ & + \frac{1}{2} \sqrt{K_a^2 + 2 K_a C_{MA} + 2 K_a C_{HSa} + C_{MA}^2 - 2 C_{MA} C_{HSa} + C_{HSa}^2 + 4 K_W} \Bigg\}, \left\{ H = -\frac{1}{2} K_a \right. \\ & - \frac{1}{2} C_{MA} + \frac{1}{2} C_{HSa} - \frac{1}{2} \sqrt{K_a^2 + 2 K_a C_{MA} + 2 K_a C_{HSa} + C_{MA}^2 - 2 C_{MA} C_{HSa} + C_{HSa}^2 + 4 K_W} \Bigg\} \\ MOH\_Exp := & \left\{ H = -\frac{1}{2} K_a - \frac{1}{2} C_{MOH} + \frac{1}{2} \sqrt{K_a^2 - 2 K_a C_{MOH} + C_{MOH}^2 + 4 K_a C_{HA} + 4 K_W} \right\}, \left\{ H = \right. \\ & -\frac{1}{2} K_a - \frac{1}{2} C_{MOH} - \frac{1}{2} \sqrt{K_a^2 - 2 K_a C_{MOH} + C_{MOH}^2 + 4 K_a C_{HA} + 4 K_W} \Bigg\} \end{aligned}$$

Notice that only the first root of each expression contains a  $+ \sqrt{\cdot}$  term, making these the roots that yield  $[H^+] > 0$ . So they will be selected using the `subs` command.<sup>100</sup> But first, along with  $K_w$  values for  $C_{MA}$  and  $C_{HA}$  will be assigned; they will be made equal so that the symmetry (equivalence) of the two buffer preparation techniques can be illustrated.

```
> K[W]:= 1E-14; C[HA]:= 0.30; C[MA]:= 0.30; H_HSa:= subs(HSa_Exp
[1], H); H_MOH:= subs(MOH_Exp[1], H);
```

$$\begin{aligned} H\_HSa := & -\frac{1}{2} K_a - 0.1500 + \frac{1}{2} C_{HSa} \\ & + \frac{1}{2} \sqrt{K_a^2 + 0.6000 K_a + 2 K_a C_{HSa} + 0.0900 - 0.6000 C_{HSa} + C_{HSa}^2} \\ H\_MOH := & -\frac{1}{2} K_a - \frac{1}{2} C_{MOH} \\ & + \frac{1}{2} \sqrt{K_a^2 - 2 K_a C_{MOH} + C_{MOH}^2 + 1.2000 K_a + 4.0000 10^{-14}} \end{aligned}$$

So that these comparisons can be made at two, decidedly different values of  $K_a$ , e.g.  $10^{-4}$  and  $10^{-10}$ , again we use the subs command and create two expressions for each buffer solution. Only one of the four outputs will be shown below.

```
> H_HSa4:= subs(K[a]=1E-4, H_HSa); H_HSa10:= subs(K[a] =1E-10,H_
HSa); H_MOH4:= subs (K[a]=1E-4,H_MOH);H_MOH10:= subs(K[a]=1E-
10,H_MOH);
```

$$H_HSa4 := -0.1501 + \frac{1}{2} C_{HSa} + \frac{1}{2} \sqrt{0.0901 - 0.5998 C_{HSa} + C_{HSa}^2}$$

From previous plotting exercises, it should be a simple matter to create a plot of any of these four expressions,<sup>101</sup> but we will introduce a way to consolidate the plots of several functions that do not use the same variables. To do this we need to save the plot *structures*. We can group the HSa plots in to one structure and the MOH plots into a second structure because each pair has the same *x* axis,  $C_{HSa}$  and  $C_{MOH}$ , respectively.

```
[ =HSa_plot:= plot([-log[10](H_HSa4),-log[10](H_HSa10)], C[HSa] =
0..0.30, color = [red,blue], labels = ["Con. of HSa or MOH",
 "pH"], axes = boxed):MOH_plot:= plot([-log[10](H_MOH4),-log[10]
(H_MOH10)],C[MOH] = 0..0.30, color =[green,black], labels =
["Con. of HSa or MOH", "pH"], axes = boxed):
```

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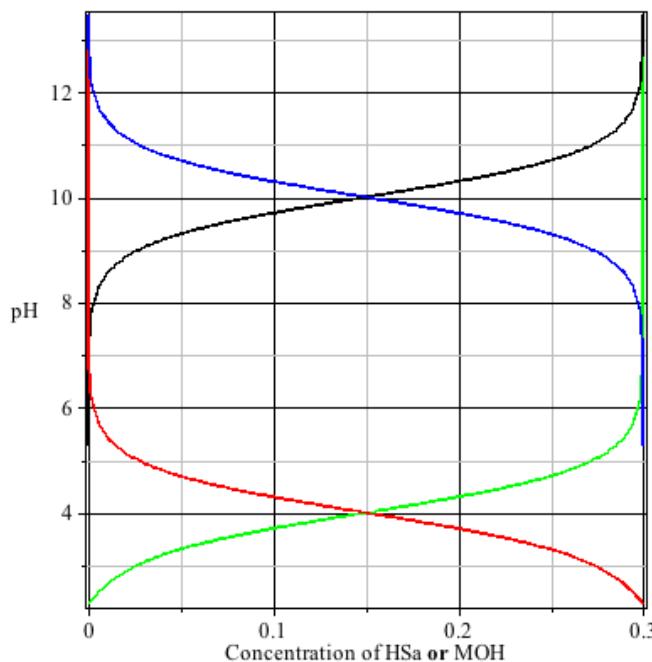
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This renders no output, and for good reason. When a name is assigned to a plot, the plot *structure* for that plot is stored. It is large (and uninteresting), and so ending the input assignment with a colon is strongly recommended.<sup>102</sup> The input above also includes measures to manage the appearance of each plot, for example axes labels and axis type (boxed, here). Not designating an axis label would leave the default C[HSa] label on the *x* axis, and that would be inappropriate for the H\_MOH plots. This will be apparent in the composite plot that follows:

```
> plots[display] ({HSa_plot,MOH_plot});
```

Figure 6-2 corroborates the comments on Figure 6-1. Here, when  $C_{\text{HSa}} = \frac{1}{2}C_{\text{MA}} = 0.15 \text{ M}$  or  $C_{\text{MOH}} = \frac{1}{2}C_{\text{HA}} = 0.15 \text{ M}$ ,  $\text{pH} = \text{pK}_a$ . This is the same as  $C_{\text{MA}} = C_{\text{HA}}$  in Figure 6-1. And again we see that the slope of each curve,  $\frac{d\text{pH}}{dc}$ , is minimal at these special mid points. The point here is that all four of these buffer solutions show a distinct resistance to changing pH where [HA] and [A<sup>-</sup>] are appreciable. Next we will demonstrate how this resistance to changing pH can be enhanced by increasing the concentration of MA or HA.



**Figure 6-2**

The resistance to change in pH can be illustrated symbolically in what is known as Buffer Index,  $\beta$ .<sup>103</sup> It is the *negative, inverse* of the slope of a pH plots like Figure 6-2. In the terminology used here, that would be,

$$\beta = -\frac{dC_{\text{HSa}}}{dpH} \quad 6-12$$

The negative sign is added to achieve a  $\beta > 0$ , because, as Figure 6-2 shows, the pH decreases with increasing  $C_{\text{HSA}}$ . A buffer solution is equally capable of resisting change to pH from the addition of a strong base, but in the opposite direction. So we remove the negative sign and write:

$$\beta = \frac{dC_{\text{MOH}}}{dpH} \quad 6-13$$

A larger  $\beta$  implies a more effective buffer.

The buffer index can be derived by solving 6-8 for  $C_{\text{HSA}}$  after a  $C_{\text{HA}}$  term is reintroduced. This is done by starting over with the charge balance expression for an HA, MA, HSA solution:



A few changes will be made here: rather than  $[\text{A}^-] = \alpha_{\text{A}} \times C_{\text{MA}}$  we will use  $\alpha_{\text{A}} \times (C_{\text{MA}} + C_{\text{HA}})$  as Equation 6-1. From the familiar substitutions and isolating  $C_{\text{HSA}}$ , this can be rearranged to

$$C_{\text{HSA}} = C_{\text{MA}} + [\text{H}^+] - \frac{(C_{\text{MA}} + C_{\text{HA}})K_a}{[\text{H}^+] + K_a} - \frac{K_w}{[\text{H}^+]}$$

Here, another Maple command is introduced, the derivative. We will use it to find  $dC/dH$  and  $dH/dpH$ .

```
> restart; C[HSA]:= C[MA] + H - ((C[MA] + C[HA])*K[a]/(H + K[a])) - (K[W]/H); pH:= -log[10](H); dCdH := diff(C[HSA],H); dpHdH:= diff(pH,H);
C_HSA:= C_MA + H - (C_MA + C_HA) K_a / (H + K_a) - K_W / H
pH:= -ln(H) / ln(10)
dCdH:= 1 + (C_MA + C_HA) K_a / (H + K_a)^2 + K_W / H^2
dpHdH:= -1 / H ln(10)
```

Like `solve(expr, ...)` or `plot(expr, ...)`, the command `diff(expr, ...)`<sup>104</sup> can be used either by entering the name ( $C_{\text{HSA}}$ ) of a previously assigned expression or by entering an expression itself (e.g.  $10^{\text{pH}}$ ). The next step requires a recollection of the chain rule.<sup>105</sup> So

$$\frac{-dC_{\text{HSA}}}{dpH} = \frac{-dC_{\text{HSA}}}{dH} \times \frac{dH}{dpH} = \frac{-dC_{\text{HSA}}}{dH} \div \frac{dpH}{dH}$$

This becomes:

```
> beta:=-dCdH/dpHdH;
```

$$\beta := \left( 1 + \frac{(C_{MA} + C_{HA}) K_a}{(H + K_a)^2} + \frac{K_w}{H^2} \right) H \ln(10)$$

The `simplify` command does not simplify this expression for  $\beta$ , at least not to the form commonly given in textbooks. We can achieve this common form by taking  $[H^+]$  inside the parentheses and converting `ln(10)` to 2.303. We can make one other, less general, substitution:  $C_{MA} + C_{HA}$  is the buffer solution, and so we could replace that term with  $C_{\text{Buffer}}$ .<sup>106</sup> These substitutions produce:

$$\beta = 2.303 \left( [H^+] + \frac{[H^+] K_a C_{\text{Buffer}}}{([H^+] + K_a)^2} + \frac{K_w}{[H^+]} \right) \quad 6-14$$

And from this, the variables that affect  $\beta$  can be identified. Obviously, 2.303 and  $K_w$  are constants and cannot alter  $\beta$ . Less obvious is that  $[H^+]$ , for a buffer solution, is not *always* legitimate variable. This is because a buffer is often prepared to a target pH, *i.e.*  $[H^+]$ , and so  $[H^+]$  might be thought of as a *quasi* constant. This leaves only  $K_a$  and  $C_{\text{Buffer}}$  as legitimate variables. Clearly increasing  $C_{\text{Buffer}}$  increases the middle term so  $\beta$  increases (linearly), but the effect of  $K_a$  is not so obvious. Notice that:

$$\frac{[H^+] K_a}{([H^+] + K_a)^2} = \frac{[H^+]}{[H^+] + K_a} \times \frac{K_a}{[H^+] + K_a} = \alpha_{HA} \times \alpha_{A^-}$$



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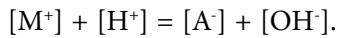
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and inasmuch as  $\alpha_{\text{HA}} + \alpha_{\text{A}^-} = 1$ , this can be rewritten as:

$$= \alpha_{\text{A}^-} \times (1 - \alpha_{\text{A}^-}) \text{ or } \alpha_{\text{HA}} \times (1 - \alpha_{\text{HA}}).$$

Trial and error will show that the product of these terms reaches a maximum at each  $\alpha = 0.5$ , and that requires that  $K_a$  equals  $[\text{H}^+]$ . And therefore,  $\beta$  reaches a maximum at  $K_a = [\text{H}^+]$ , a point made with Figures 6-1 and 6-2, and which will be made again in Figure 6-3.

Before making that point, one can derive the same expression for  $\beta$  for the condition of adding a strong base MOH as  $C_{\text{MOH}}$  to a solution of  $C_{\text{HA}} + C_{\text{MA}}$  starting from



On the “strong base side” of the buffer problem, there are two sources of  $[\text{M}^+]$ ,  $C_{\text{MOH}}$  and  $C_{\text{MA}}$ , but as with the strong acid problem, there are also two sources of  $[\text{A}^-]$ ,  $C_{\text{HA}}$  and  $C_{\text{MA}}$ . Making these substitutions, one can show that

$$C_{\text{MOH}} = \frac{(C_{\text{MA}} + C_{\text{HA}})K_a}{[\text{H}^+] + K_a} - C_{\text{MA}} - [\text{H}^+] + \frac{K_w}{[\text{H}^+]}$$

Proceeding with Maple as with the  $C_{\text{HSa}}$  situation, but using Equation 6-13 produces an identical expression for  $\beta$ , that is 6-14.

A plot of 6-14 can be used to make the point that  $\beta$  increases as  $C_{\text{Buffer}}$  increases and reaches a maximum at  $[\text{H}^+] = K_a$ . We will use a `restart` and begin again by entering  $\beta$  in the form of Equation 6-14. So that the point can be made over a wide range of  $K_a$  values, 6-14 can be written with  $K_a = 10^{-pK_a}$  using `algsubs`.

```
> restart; beta:= 2.303*(H+(H *K[a]*C[Buffer]/(H+K[a])^2)+K[w]/H):
beta:= algsubs(K[a] =10^(-pK[a]),beta);107
```

$$\beta := \frac{\frac{2.3030 H C_{\text{Buffer}} 10^{-pK_a}}{\left(H + 10^{-pK_a}\right)^2} + 2.3030 H + \frac{2.3030 K_w}{H}}{H}$$

$[\text{H}^+]$  will be set at an arbitrary value, say  $10^{-7}$  and  $K_w$  will be set at  $10^{-14}$ .

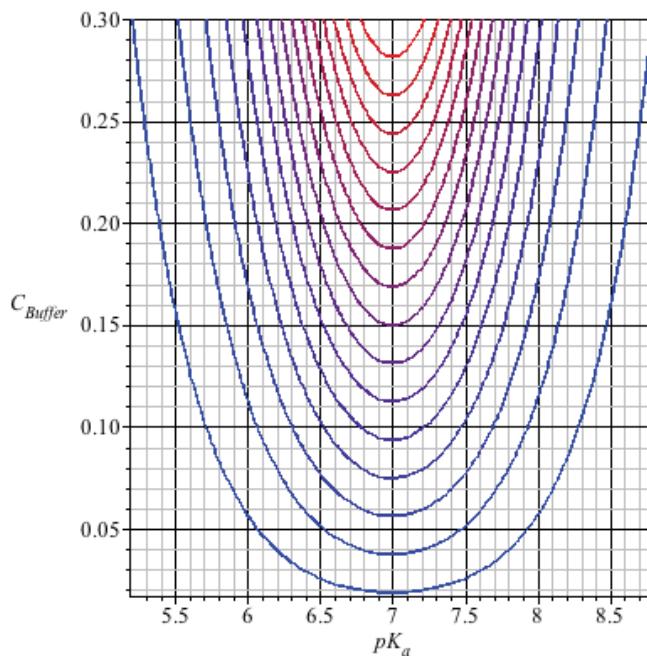
```
> K[w] := 1E-14 :H := 1E-7 : beta;
```

$$\frac{\frac{2.3030 10^{-7} C_{\text{Buffer}} 10^{-pK_a}}{\left(1.0000 10^{-7} + 10^{-pK_a}\right)^2} + 4.6060 10^{-7}}{H}$$

With  $[H^+]$  and  $K_w$  assigned, we can simultaneously examine the effects of  $C_{\text{Buffer}}$  and  $pK_a$  on  $\beta$ . The 3D plot would be a good choice (left to the reader), but instead we will introduce another tool, the contour plot.

The `contourplot` is first called from the plot package using `with(plots)` followed by a *colon* (lest every plot package available be listed in the output). Or, one can call `with(plots, contourplot);`.

```
> with(plots): contourplot( beta,pK[a]= 4..10,C[Buffer] =
0..0.3,contours = 15,grid = [100,100], coloring= [blue, red]);
```



**Figure 6-3**

We have called the expression for  $\beta$  and plotted it over the region  $pK_a = 4$  to  $10$  ( $K_a = 10^{-4}$  to  $10^{-10}$ ) and  $C_{\text{Buffer}} = 0$  to  $0.3$  M. Then we implemented several plotting options which were listed before the closing parenthesis. The `contours =` option established how many contour lines were drawn; the `grid` option instructed the program to create 10,000 calculation points (as a  $100 \times 100$  grid). The default here is considerably less and that yields “raggedy” plots. The advantage of calling the `coloring` option is that it made clear which contour lines represented the minimum  $\beta$  and which the maximum  $\beta$ ; the first color called is for the minimum. (We could have added a legend as well, but that would entail *a lot* of editing with fifteen curves.)

So Figure 6-3 shows what Figures 6-1 and 6-2 illustrated, and more. The “more” is that the largest  $\beta$  (red contour line) is found at the highest  $C_{\text{Buffer}}$ . Notice also the ridge running vertically at  $pK_a = 7$  which is equal to the pH of this buffer solution and that there is no red contour (highest  $\beta$ ) below pH 6.5 or above pH 7.5.

A simple variation on the HA/A<sup>-</sup> buffer is a mixture of M and MH<sup>+</sup>, where M represents a *weak* base. An example would be a solution of NH<sub>3</sub> and NH<sub>4</sub>Cl. Replacing HA with BH<sup>+</sup> and A<sup>-</sup> with B exactly replicates every element of our previous discussion on buffers. (This particular buffer is addressed in Problem 2b at the end of this chapter.) A third kind of buffer solution is the salt of a weak acid *and* weak base which introduced in Chapter 5 (page 106). It was shown that such a solution has a somewhat fixed pH, [H<sup>+</sup>]  $\approx \sqrt{K_{aM} \times K_{aA}}$  as given in Equation 5-15. Here it will be shown that these solutions show resistance to changing pH as a strong acid or strong base is added.

We begin by considering the addition of strong acid, HSa, to the MHA solution. Reference to the earlier discussion on buffer index (page 140) and the weak electrolyte discussion (page 106) might be useful for the following derivation. From charge balance:

$$[H^+] + [MH^+] = [Sa^-] + [A^-] + [OH^-]$$

along with familiar substitutions:<sup>108</sup>

$$[H^+] + \frac{[H^+]C_{MHA}}{[H^+] + K_{aM}} = C_{HSa} + \frac{K_{aA}C_{MHA}}{[H^+] + K_{aA}} + \frac{K_w}{[H^+]}$$

After isolating C<sub>HSa</sub> on the left hand side of the expression:

$$C_{HSa} = [H^+] + \frac{[H^+]C_{MHA}}{[H^+] + K_{aM}} - \frac{K_{aA}C_{MHA}}{[H^+] + K_{aA}} - \frac{K_w}{[H^+]}$$

We will allow Maple to finish from here:

```
> restart; C[HSa]:= H + H*C[MHA]/(H+K[aM]) - K[aA]*C[MHA]/(H+K[aA]) - K[w]/H;
```

$$C_{HSa} := H + \frac{H C_{MHA}}{H + K_{aM}} - \frac{K_{aA} C_{MHA}}{H + K_{aA}} - \frac{K_w}{H}$$

We will find  $\frac{dC_{HSa}}{dH}$  as we did earlier (page 139), but for variety, rather than finding and applying  $\frac{dpH}{dH}$ , we will find and use  $\frac{dH}{dpH}$ .

```
> dCdH:= diff(C[HSa],H); H_Ion := 10^(-pH); dHdpH:= diff(H_Ion,pH);
```

$$dCdH := 1 + \frac{C_{MHA}}{H + K_{aM}} - \frac{HC_{MHA}}{(H + K_{aM})^2} + \frac{K_{aA} C_{MHA}}{(H + K_{aA})^2} + \frac{K_w}{H^2}$$

$$dHdpH := -10^{-pH} \ln(10)$$

Applying the chain rule and then replacing the residual  $10^{-pH}$  with H gives :

```
> beta:= -dCdH*dHdpH: beta:= subs(10^(-pH)= H, beta);
```

$$\beta := \left( 1 + \frac{C_{MHA}}{H + K_{aM}} - \frac{HC_{MHA}}{(H + K_{aM})^2} + \frac{K_{aA} C_{MHA}}{(H + K_{aA})^2} + \frac{K_w}{H^2} \right) H \ln(10)$$

If we take  $H$  inside the parentheses and convert  $\ln(10)$  to 2.303 as we did to produce Equation 6-14 we produce an expression a lot like that equation, in which  $\beta$  increases directly with an increase in  $C_{\text{Buffer}}$  ( $C_{\text{MHA}}$  here), and one that shows a dependence on the acid dissociation constant. But the relationship between  $\beta$  and either  $K_{\text{aA}}$  or  $K_{\text{aM}}$  is not obvious. So we will illustrate this by choosing a  $[\text{H}^+]$ , arbitrarily at  $1 \times 10^{-7}$ ,  $C_{\text{MHA}} = 0.30 \text{ M}$ ,  $K_w = 1 \times 10^{-14}$  and then use a 3D plot to display these effects.

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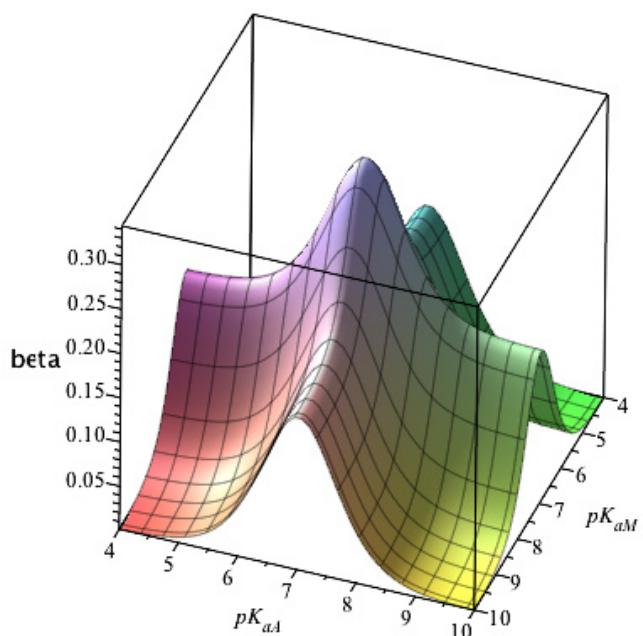
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```
> H:= 1E-7: C[MHA] := 0.30: K[w]:= 1E-14: beta:= subs({ K[aM] =
10^(-pK[aM]), K[aA] =10^(-pK[aA]) },beta);
```

$$\beta := 1.000 \cdot 10^{-7} \left( 2.000 + \frac{0.300}{1.000 \cdot 10^{-7} + 10^{-pK_{aM}}} - \frac{3.000 \cdot 10^{-8}}{\left( 1.000 \cdot 10^{-7} + 10^{-pK_{aM}} \right)^2} \right. \\ \left. + \frac{0.300 \cdot 10^{-pK_{aA}}}{\left( 1.000 \cdot 10^{-7} + 10^{-pK_{aA}} \right)^2} \right) \ln(10)$$

```
> plot3d(beta, pK[aM]= 4..10, pK[aA]=4..10, axes = boxed, labels
=[pK[aM], pK[aA], "beta"], orientation = [30,45], grid=[50,50]);
```



**Figure 6-4**

The result is interesting, but by no means surprising. Notice that the buffer capacity reaches a maximum where each  $K_a$  approaches  $[H^+]$  ( $pK_a = pH = 7$ ) and reaches an absolute maximum where both dissociation constants equal  $[H^+]$ .

The primary consideration for buffer preparation is target pH, and for that target to be achieved, the consequences of ionic strength and activity coefficients *must* be resurrected. From Equation 3-15 it is evident that the pH of a solution cannot be known with any confidence without knowing  $\gamma_{H^+}$ , and this cannot be known without an appropriate application of either the Debye-Hückel (2-6) or Davies (2-8) equations. These equations become suspect as the ionic strength of the solution increases, and the ionic strength increases as the concentration of electrolyte increases (3-13). So, the confidence in pH increases with decreasing electrolyte concentration. However, Equation 6-14 and the expression for  $\beta$  for MHA (page 144) imply that a buffer is most effective at the highest possible concentration.

In deciding whether to use a high or low concentration of buffer, the purpose of the buffer solution should be considered, and yes, there is more than one purpose to a buffer solution. First, the solution might be needed as a pH standard, one where pH must be known as well as possible but where the stability of that pH will not be challenged by *appreciable* additions of acid or base. In this case the concentration of the buffer should be sufficiently low that Debye-Hückel can be used with confidence. Of course, it cannot be so dilute that it offers negligible buffer capacity.

As a second purpose for a buffer solution, it might be required to hold a pH against more considerable additions of acids or bases, where pH stability is more important than precise knowledge of the solution's pH. Here, the concentration of solute should be maximized, but it should not be so concentrated that even the Davies Equation is questionable.

*In either case, the first choice to make after selecting a target pH is the ionic strength. From  $[H^+]$ , the necessary  $K_a$  or  $K_{aA}$  and  $K_{aM}$  can be selected, and with  $\mu$ , all other concentrations can be determined.* The advantage of establishing  $\mu$  early in the calculation is that all of the necessary activity coefficients can be determined before any other calculations. This precludes the need for the reiterations that were necessary in Chapter 4 and Chapter 5 calculations. One example calculation is provided here. Others will be found among the Example Problems.

Suppose that one is to create 1.00 L of a pH 5.000 buffer from either acetic acid,  $HC_2H_3O_2$ , ( $K_a^\circ = 4.47 \times 10^{-5}$ ) or from potassium acetate by adding the appropriate amount of 6.0 M KOH or 6.0 M HCl, respectively. Provide instructions.

Given the precision to which the target pH is stated, it would be wise to presume that this buffer is to be prepared with a high degree of confidence in its pH. So a relatively small  $\mu$  would be advised. Let us make  $\mu = 0.0500$ . It will be necessary to calculate  $[H^+]$  from the pH,  $K_a$  from  $K_a^\circ$  and  $K_w$  from  $K_w^\circ$ . For these calculations,  $\gamma_{H^+}$ ,  $\gamma_{OH^-}$ , and  $\gamma_{OAc^-}^{109}$ , will be needed. All of these calculations will be carried out with a single input line as follows. It might be necessary to recall Equations 4-17 and 3-15. Values for  $a_{H^+}$ ,  $a_{OH^-}$  and  $a_{OAc^-}$  are taken from Appendix II,  $K_w^\circ$  is taken from Appendix III and  $K_a^\circ$  from Appendix IV.

```
> restart;  $\mu := 0.050$ :  $a[H] := 9$ :  $a[OH] := 3.5$ :  $a[OAc] := 4.5$ :
 $\Gamma_H := 10^{-(-0.511 * \sqrt{\mu}) / (1 + 0.329 * a[H] * \sqrt{\mu})}$ ;
 $\Gamma_{OH} := 10^{-(-0.511 * \sqrt{\mu}) / (1 + 0.329 * a[OH] * \sqrt{\mu})}$ ;
 $\Gamma_{OAc} := 10^{-(-0.511 * \sqrt{\mu}) / (1 + 0.329 * a[OAc] * \sqrt{\mu})}$ ;
 $K^a := 4.75e-5$ :  $K^w := 1.009e-14$ :  $K_a := K^a / (\Gamma_H * \Gamma_{OAc})$ ;
 $K_w := K^w / (\Gamma_H * \Gamma_{OH})$ ;  $pH := 5.000$ ;  $H :=$ 
 $\text{solve}(\Gamma_H * H = 10^{-pH}, H)$ ;
```

$$\begin{aligned}\Gamma_H &:= 0.853599 \\ \Gamma_{OH} &:= 0.811210 \\ \Gamma_{OAc} &:= 0.820646 \\ K_a &:= .000068^{110} \\ K_w &:= 1.457149 \cdot 10^{-14} \\ pH &:= 5.000000 \\ H &:= 0.000012\end{aligned}$$

It is worth noting the order in which variables have been assigned. A useful strategy is to make an assignment and from there work *backwards* assigning every component of that assignment so that each is in place when a calculation is required. This is why the  $\mu$  was assigned before the activity coefficients were calculated, and the activity coefficients were calculated before  $K_a$  and  $K_w$  were calculated. The output is requested for each calculated value so that it can be checked to assure that results were reasonable.

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Next, the assigned value of  $\mu$  will be used, and to do this it is necessary to recall the discussion on calculating  $\mu$  (page 40, specifically Eqn 3-13). That is, inasmuch as the sum of the anion charges must equal the sum of the cation charges, then for the HOAc + KOH buffer,

$$\mu = \{[H^+] + [K^+]\} = \{[OAc^-] + [OH^-]\}$$

and for the KOAc + HCl buffer

$$\mu = \{[H^+] + [K^+]\} = \{[OAc^-] + [OH^-] + [Cl^-]\}.$$

First, the preparation of the HOAc + KOH buffer will be described, then the KOAc + HCl buffer. The following familiar, substitutions, will be required:

$$[OAc^-] = \frac{K_a C_{HOAc}}{[H^+] + K_a}$$

$$[K^+] = C_{KOH}$$

and of course,

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

```
> C[KOH]:= solve(mu = H + C[KOH], C[KOH]); OH:= K[w]/H; OAc:=
C[HOAc]*K[a]/(H + K[a]); C[HOAc]:= solve(mu = OAc + OH,C[HOAc]);
C_KOH := 0.049988
OAc := 0.852684 C_HOAc
C_HOAc := 0.058638
```

From this, we have the instructions for the HOAc + KOH buffer: make the solution 0.0500 M in KOH and 0.0586 M in acetic acid. More explicitly, for a 1.00 L solution, this means to add 0.0500 mole (2.80<sub>5</sub> g) of KOH and 0.0586 mole (3.51<sub>9</sub> g) of HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> to a 1 liter volumetric flask and dilute these contents to volume.

It was not necessary to display the results of the [OAc<sup>-</sup>] calculation, but it is interesting in that it indicates that 85.2% of the acetic acid added to this solution will be dissociated, and so 14.7% will remain in the protonated form. Finally, the buffer index for this solution can be calculated by defining  $\beta$  (6-14) with the nomenclature used previously.

```
> beta := evalf(ln(10) * ((K[w]/H) + H + (C[HOAc]*K[a]*H/(H+K[a]))^2));
```

$$\beta := 0.016987$$

This is not particularly impressive in comparison to earlier examples, but here  $C_{\text{HOAc}}$  is only 0.0586 M, and  $K_a$  is not equal to  $[\text{H}^+]$ .

For the KOAc + HCl buffer, we return to the expression for  $\mu$  that is appropriate for this system. Two changes are required

$$[\text{OAc}^-] = \frac{K_a C_{\text{KOAc}}}{[\text{H}^+] + K_a}$$

and,

$$[\text{K}^+] = C_{\text{KOAc}}$$

Also,

$$[\text{Cl}^-] = C_{\text{HCl}}$$

```
> C[KOAc]:= solve(H+C[KOAc]=μ, C[KOAc]); OAc:=K[a]*C[KOAc] / (H+K[a]); C[HCl]:= solve(μ = OAc+OH+C[HCl]);111
```

$$C_{\text{KOAc}} := 0.049988$$

$$OAc := 0.042624$$

$$C_{\text{HCl}} := 0.07376$$

So the recipe requires 0.0500 mole of  $\text{KC}_2\text{H}_3\text{O}_2$  (4.90<sub>8</sub> g) and 0.0738 mole (6.14<sub>7</sub> mL of 12 M HCl) diluted to 1.00 L. And for a little more information,<sup>112</sup>

```
> alpha["OAc"]:= OAc/C[KOAc]; beta:= evalf(ln(10)*((K[w]/H) + H + (C[KOAc]*K[a]*H/(H+K[a]))^2)); pH:= -log[10](0.853599*H);
```

$$\alpha_{\text{OAc}} := 0.852684$$

$$\beta := 0.014485$$

$$pH := 5.000000$$

These are the same values found for the KOH/ $\text{HC}_2\text{H}_3\text{O}_2$  solution, although the buffer capacity is lower. This is because here,  $C_{\text{Buffer}}$  is smaller. These observations corroborate Figures 6-2 and 6-3.

This chapter began by describing buffer solutions as mixtures of solutions of  $C_{MA}$  and  $C_{HA}$ . So we should be able to prepare a pH 5.000 buffer solution of 0.0500 ionic strength from a mixture of  $KC_2H_3O_2$  and  $HC_2H_3O_2$ . What we find is a composite of the previous two exercises.

$$\mu = \{[H^+] + [K^+]\} = \{[OAc^-] + [OH^-]\}$$

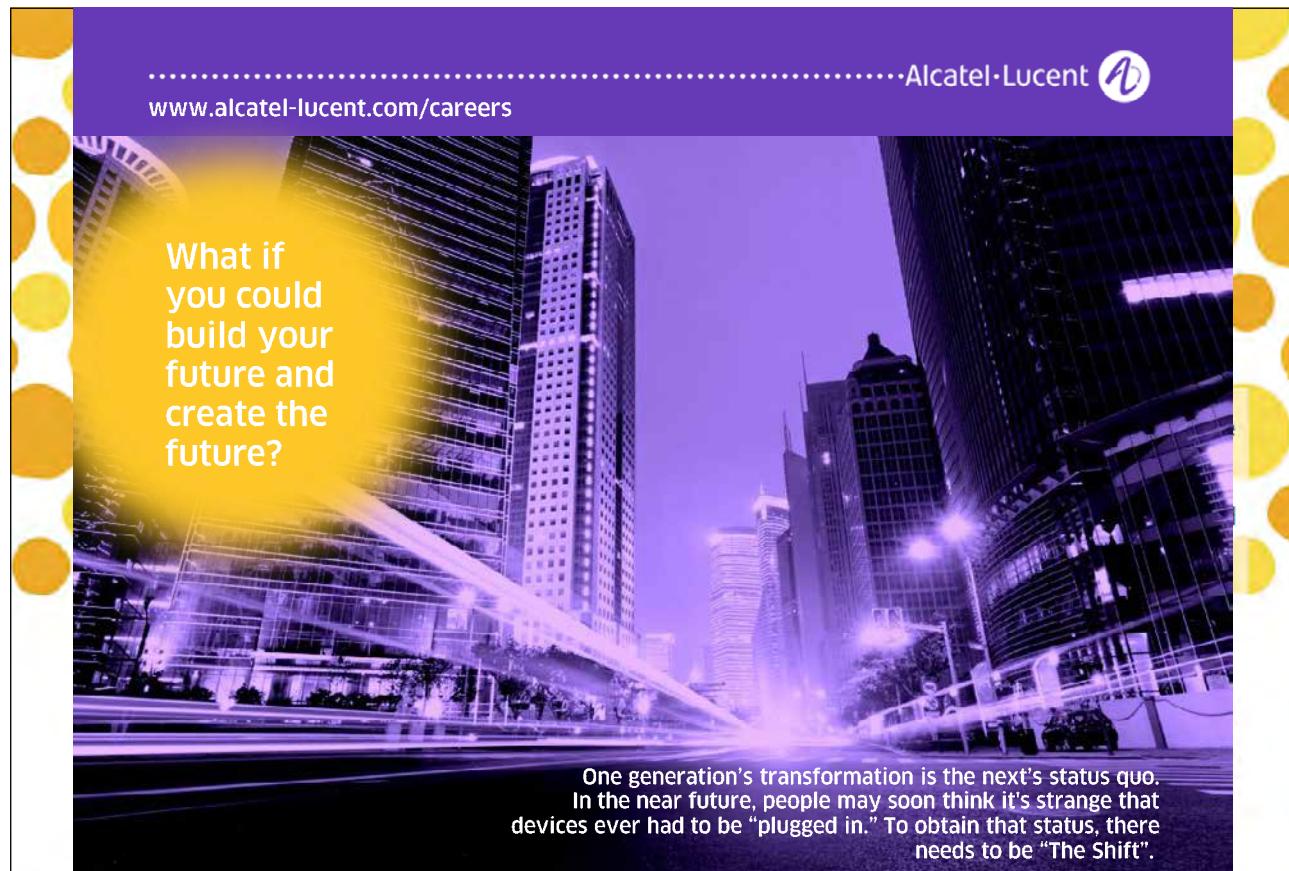
$$[OAc^-] = \frac{K_a(C_{KOAc} + C_{HOAc})}{[H^+] + K_a}$$

and,

$$[K^+] = C_{KOAc}.$$

$\mu$  has been set at 0.0500 and  $[H^+]$  is set from  $pH = 5.000$ , and therefore  $C_{KOAc} = [K^+]$  is also set as  $(\mu - 10^{-pH}/\gamma_{H^+}) = 0.049988$  just as it was in the  $HCl / KC_2H_3O_2$  problem above. So  $C_{KOAc}$  will not be reassigned.  $[OAc^-]$ , however, will be larger because of the contribution from  $C_{HOAc}$ , which we need to recalculate.

```
> C[HOAc]:= 'C[HOAc]': OAc:= K[a]*(C[KOAc] + C[HOAc])/(H + K[a]);
C[HOAc]:= solve(mu = OAc + OH);
```



.....

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$$\text{OAc} := 0.042624 + .852684 C_{\text{HOAc}}$$

$$C_{\text{HOAc}} := 0.008650$$

For our information:

> OAc;

$$0.050000$$

which is not surprising given that  $\mu = 0.050 = [\text{OAc}^-] + [\text{OH}^-]$  and  $[\text{OH}^-] \approx 0$  in this pH 5.000 solution. Also,

```
> C[Buffer]:= C[KOAc] + C[HOAc]; alpha["OAc"]:= OAc/(C[KOAc]
+ C[HOAc]); beta:= evalf(ln(10)*((K[w]/H) + H + ((C[KOAc]
+ C[HOAc])*K[a]*H/(H + K[a]))^2));
```

$$C_{\text{Buffer}} := 0.058638$$

$$\alpha_{\text{OAc}} := 0.852684$$

$$\beta := 0.016987$$

The  $C_{\text{Buffer}}$  value should explain why  $\beta$  here matches the  $\beta$  found for the KOH/ $\text{HC}_2\text{H}_3\text{O}_2$  buffer, and the fact that  $\alpha_{\text{OAc}}$  is identical for all three solutions derives from the fact that all three solutions, with the same  $\mu$ , have the same  $[\text{H}^+]$  and  $K_a$ , and Equation 4-21 requires that these be the same.

### Example Problems

1. The point was made (page 133 regarding Figure 6-1) that when  $C_{\text{HA}}$  is equal to  $C_{\text{MA}}$  for an HA/A<sup>-</sup> buffer,  $-\log[\text{H}^+]$  will equal the  $pK_a$  for the weak acid. This is not *always* true. Indeed as  $(C_{\text{HA}} + C_{\text{MA}})$  approaches zero,  $-\log[\text{H}^+]$  will exceed  $pK_a$ .
  - a) Illustrate this point with a plot of pH ( $-\log[\text{H}^+]$ ) vs.  $pK_a$  using  $(C_{\text{HA}} + C_{\text{MA}}) = 0.0025, 0.025$  and  $0.25$  with  $C_{\text{HA}} = C_{\text{MA}}$ . Ionic strength effects can be ignored to make this point.
  - b) Explain this deviation.
2. Provide instructions for the preparation of the following buffer solutions.
  - a) pH 10.00,  $\mu = 0.25$ , from 5.00 M HIO and 6.00 M NaOH.
  - b) pH 10.00,  $\mu = 0.025$ , from 14.3 M NH<sub>3</sub>(aq) and 12.0 M HCl. Work from  $pK_b^\circ$  for NH<sub>3</sub> = 4.752.
3. Describe the properties (pH,  $\alpha_{\text{MH}}$ ,  $\mu$ , and  $\beta$ ) for a buffer prepared from 0.050 M (CH<sub>3</sub>)<sub>3</sub>NHNO<sub>2</sub> (trimethylammonium nitrite).

4. Show that if a buffer of pH 6.00 is to be prepared from the salt of a weak acid and weak base, presuming that  $[H^+] \approx \sqrt{K_{aA} K_{aM}}$ , it is more effective when  $pK_{aA} = pK_{aM} = 6.00$  than it is when  $pK_{aA} = 3.00$  and  $pK_{aM} = 9.00$ .

### Solutions to Example Problems

1. a. First, the expression for  $[H^+]$  as a function of  $K_a$ ,  $C_{MA}$ , and  $C_{HA}$  (Equation 6-5) will be recalled, and this will be converted into an exponential expression (as on page 131, see *Expr<sub>65</sub>*).

```
> restart; Expr:= (1/2)*(-(K[a] + C[MA]) + sqrt((K[a]
+ C[MA])^2 + 4*(K[a]*C[HA] + K[w]))); Expr:=
algsubs(K[a]=10^(-pKa),Expr); pH:= -log[10](Expr);
```

The output, being predictable, is not provided here. It can be inferred from the next output. The next step is to customize the pH expression for the condition that  $C_{HA}$  is equal to  $C_{MA}$  by replacing both with one parameter  $C_{Buffer}$ . The `algsubs` command is used twice<sup>113</sup> for this.

```
> pH:= algsubs(C[MA] = C[Buffer],pH); pH:= algsubs (C[HA] =
C[Buffer],pH);
pH:= -1/ln(10) ln(-1/2 10^-pKa - 1/2 C_Buffer
+ 1/2 sqrt(6 10^-pKa C_Buffer + C_Buffer^2 + (10^-pKa)^2 + 4 K_w))
```

Three, special conditions for pH will be created, for  $C_{Buffer} = 0.0025 \text{ M}$ ,  $C_{Buffer} = 0.0250 \text{ M}$  and for  $C_{Buffer} = 0.2500 \text{ M}$ . Inserting the assignment for  $K_w$  at the beginning of this input line will embed its value in both, special pH expressions. Subscripting here can create problems with the assignment of these special expressions. So it is avoided here.

```
> K[w]:= 1e-14: pH_0025:= subs(C[Buffer]= 0.0025,pH):
pH_025:= subs(C[Buffer]= 0.025, pH); pH_25:=
subs(C[Buffer]= 0.25, pH):
```

And now these are plotted with the vertical axis label, legend and grid lines being added from the **Plot** menu after the plot is rendered. From the **Plot** menu, the vertical axis is modified to include  $-\log[H^+] = 0$ .

```
> plot([pH_0025,pH_025,pH_25], pKa = 0..10,color = [orange,
blue,green],axes = box);
```

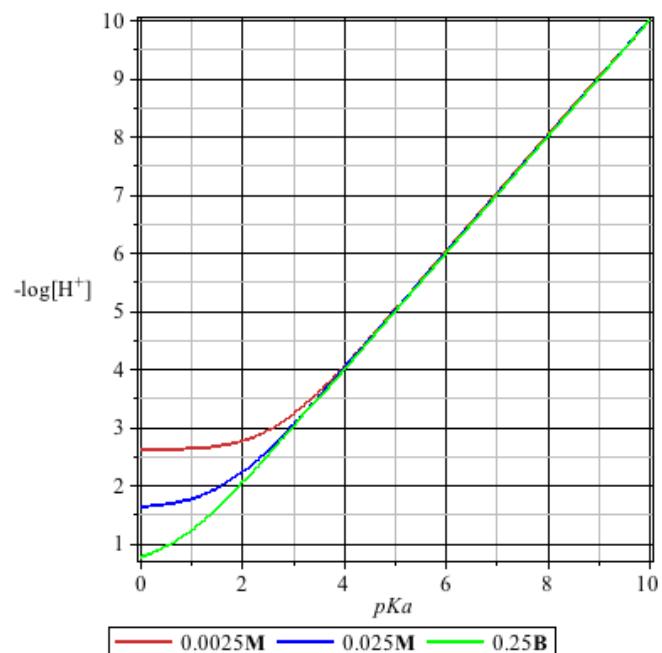


Figure 6-5

1. b. Recall from Chapter 1<sup>114</sup> (page 9) the discussion regarding the effect of dilution on equilibration. For a reaction like the dissociation of an acid, HA, *i.e.*  $\text{HA} \longrightarrow \text{H}^+ + \text{A}^-$  the extent of dissociation *increases* as  $C_{\text{HA}}$  (or  $C_{\text{HA}} + C_{\text{MA}}$ ) *decreases*. This dissociation is limited to 100%. So if 0.0025 M HA dissociates 100%, the  $[\text{H}^+]$  reaches its maximum value of 0.0025,<sup>115</sup> and that gives  $-\log_{10}(0.0025) = 2.6$ , precisely the limit observed here. For the 0.0250 M solution, this gives  $-\log_{10}(0.0250) = 1.6$ , and even for  $C_{\text{Buffer}} = 0.2500$ ,  $-\log_{10}C = 0.6$  which is greater than any  $pK_a < 0.6$ .

The lesson here is that buffers at low pH are difficult to achieve with low  $C_{\text{Buffer}}$ . For example, preparing a pH 2.00 buffer from a  $pK_a = 2.00$  acid is not simply a  $C_{\text{HA}} = C_{\text{MA}}$  system if the buffer concentration is small ( $\leq 0.010$  M).

2. a. This problem is a variation on the buffer solution preparation described on page 146 *et seq.*

From Appendix III:  $K_w^\circ = 1.01 \times 10^{-14}$  From Appendix IV:  $pK_a^\circ$  for  $\text{HIO} = 10.64$

Given the relatively large ionic strength (0.25) and that  $a_{\text{IO}^-}$  is not listed in Appendix II, the Davies Equation (2-8) will be used to find  $\gamma$ .

```
> restart; mu := 0.25: Gamma := 10^(-0.5*((sqrt(mu)/(1 + sqrt(mu))) + 0.15*mu)); K_w[w] := 1.01e-14: K[a] := 10^(-10.64): K[w] := K[w]/Gamma^2; K[a] := K[a]/Gamma^2; pH := 10.00; H := solve(Gamma*H = 10^(-pH));
```

$$\begin{aligned}\Gamma &:= 0.6525 \\ K_w &:= 2.3722 \cdot 10^{-14} \\ K_a &:= 5.3806 \cdot 10^{-11} \\ pH &:= 10.0000 \\ H &:= 1.5326 \cdot 10^{-10}\end{aligned}$$

Keeping in mind that:

$$\mu = \{[\text{H}^+] + [\text{Na}^+]\} = \{[\text{IO}^-] + [\text{OH}^-]\}$$

one might guess that  $\mu = 0.25 = C_{\text{NaOH}}$  because  $[\text{Na}^+] = C_{\text{NaOH}}$  and because  $[\text{H}^+] = 1.6 \cdot 10^{-10}$ , and this is correct. Rather than solve it by inspection, we will allow Maple to discover this. Then  $C_{\text{HIO}}$  will be calculated from the other side of the ionic strength expression. For information,  $a_{\text{IO}^-}$  and  $[\text{OH}^-]$  are requested.

```
> C[NaOH]:= solve(μ = C[NaOH] + H); C[HIO]:= solve(μ=(K[a]*C[HIO]/(H + K[a])) + (K[w]/H)); alpha[IO]:= K[a]/(H + K[a]);
OH:= K[w]/H;
```

$$C_{\text{NaOH}} := 0.2500$$

$$C_{\text{HIO}} := 0.9615$$

$$a_{\text{IO}} := 0.2598$$

$$\text{pH} := 10.0000$$

$$OH := 0.0002$$

Notice that at 25.9% dissociated, the  $C_{\text{HIO}}$  provides that  $[\text{IO}^-]$  will equal  $0.2498 \text{ M} = (0.2598 \times 0.9615)$ . Adding this to the  $[\text{OH}^-]$  which is  $1.5 \times 10^{-4} \text{ M}$  brings the total anion concentration up to 0.25 which is  $\mu$ . Notice also that with the  $\text{pK}_a^\circ$  for HIO known only to two decimal places, it is not possible to know the pH of one of its solutions to better than two decimal places. And so, the pH of this buffer is given as 10.00.

The explicit instructions for the preparation of this buffer solution are to use 0.250 mole of NaOH and 0.931 mole of HIO in a one liter volumetric flask. Using 6.00 M NaOH and 5.00 M HIO solutions requires:

$$0.250 \text{ mole NaOH} \times \frac{1000 \text{ mL}}{6.00 \text{ mole NaOH}} = 41.67 \text{ mL NaOH(aq)}$$

$$0.931 \text{ mole HIO} \times \frac{1000 \text{ mL}}{5.00 \text{ mole HIO}} = 186.2 \text{ mL HIO}$$

respectively. Or using Maple, converting the volumes to mL, and truncating the output:

```
> V[NaOH] := 1000*C[NaOH]/6; V[HIO] := 1000*C[HIO]/5;
```

$$V_{\text{NaOH}} := 41.67$$

$$V_{\text{HIO}} := 192.30$$

So 41.7 mL of 6.00 M NaOH and 192 mL of 5.00 M HIO are added to a one liter volumetric flask and diluted to volume.

2. b.  $K_a$  will be required, and working from  $\text{pK}_b^\circ$  will require some algebra that is best done prior to engaging Maple:

$$K_a = \frac{K_w}{K_b} = \frac{K_w^{\circ} \gamma_{\text{NH}_4^+} \gamma_{\text{OH}^-}}{\gamma_{\text{H}^+} \gamma_{\text{OH}^-} K_b^{\circ}} =$$

$$\frac{K_w^{\circ} \gamma_{\text{NH}_4^+}}{\gamma_{\text{H}^+} K_b^{\circ}} = \frac{K_w^{\circ} \gamma_{\text{NH}_4^+}}{\gamma_{\text{H}^+} 10^{-\text{pK}_b^{\circ}}}$$

For this buffer solution with its relatively low ionic strength, Debye-Hückel will be used to find each activity coefficient.

From Appendix II:  $a_{H^+} = 9$ ,  $a_{NH_4^+} = 2.5$ ,  $a_{OH^-} = 3.5$  From Appendix III:  $K_w^\circ = 1.01 \times 10^{-14}$

```
> restart; mu := 0.025: G[H] := 10^(-0.511*sqrt(mu)/(1 + 0.329*9*sqrt(mu))); G[NH4] := 10^(-0.511*sqrt(mu)/(1 + 0.329*2.5*sqrt(mu))); G[OH] := 10^(-0.511*sqrt(mu)/(1 + 0.329 * 3.5*sqrt(mu))); K[w] := 1.01e-14: pK[b] := 4.752: K[a] := K[w]*G[NH4]/(G[H]*10^(-pK[b])); K[w] := K[w]/(G[H]*G[OH]): pH := 10.00: H := solve(G[H] *H=10^(-pH));
```

$$\begin{aligned}G_H &:= 0.8810 \\G_{NH_4} &:= 0.8482 \\G_{OH} &:= 0.8544 \\K_a &:= 5.4392 \cdot 10^{-10} \\H &:= 1.1351 \cdot 10^{-10}\end{aligned}$$

For this solution:

$$\mu = \{[H^+] + [NH_4^+]\} = \{[Cl^-] + [OH^-]\}$$



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Sources: Keuzegids Master ranking 2013; Elsevier 'Beste Studies' ranking 2012; Financial Times Global Masters in Management ranking 2012

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And from mass balance:

$$[\text{NH}_4^+] = \frac{[\text{H}^+]\text{C}_{\text{NH}_3}}{[\text{H}^+] + \text{K}_a}$$

and,

$$[\text{Cl}^-] = \text{C}_{\text{HCl}}$$

Applying each of these to  $\mu$  gives:

```
> C[NH3]:= solve(mu= H + (H*C[NH3]/(H + K[a]))); C[HCl]:= solve(mu= C[HCl] + K[w]/H);
```

$$\begin{aligned}\text{C}_{\text{NH}_3} &:= 0.1460 \\ \text{C}_{\text{HCl}} &:= 0.0249\end{aligned}$$

Using 14.3 M NH<sub>3</sub>(aq) and 12.0 M HCl to create these concentrations requires:

```
> V[NH3]:= 1000*C[NH3]/14.3; V[HCl] := 1000*C[HCl]/12;
```

$$\begin{aligned}V_{\text{NH}_3} &:= 10.2094 \\ V_{\text{HCl}} &:= 2.0735\end{aligned}$$

So, this pH 10.00 buffer solution is prepared by adding 10.2<sub>1</sub> mL of concentrated (14.3 M) aqueous ammonia solution and 2.0<sub>7</sub> mL of concentrated (12.0 M) hydrochloric acid to a one liter volumetric flask and diluting to volume.

3. Notice that this problem does not ask for a target pH. That is because the pH is predetermined by the K<sub>aA</sub> and K<sub>aM</sub> for the salt. For comparison, the pH of the solution will be determined from the four expressions developed in Chapter 5<sup>116</sup> for the salt of a weak acid, weak base.

From Appendix II:

$$a_{\text{H}^+} = 9, a_{\text{Me}_3\text{NH}^+} = 4, a_{\text{OH}^-} = 3.5, a_{\text{NO}_2^-} = 3$$

From Appendix III:

$$K_w^\circ = 1.01 \times 10^{-14}$$

From Appendix IV:

$$pK_{aA}^{\circ} = 3.14 \text{ and } pK_{aM}^{\circ} = 9.80$$

For this solution,

$$\mu = \{[H^+] + [Me_3NH^+]\} = \{[NO_2^-] + [OH^-]\}$$

Recall from the discussion on page 112 that

$$\mu \approx C_{MHA}$$

and that Problem 1c of Chapter 5 showed this to be an excellent approximation. So, it is prudent to take  $\mu$  to be 0.050. Also, recall that the correction of  $K_{aM}^{\circ}$  to  $K_{aM}$  is not like the  $K_a^{\circ}$  to  $K_a$  correction.<sup>117</sup>

```
> restart; mu:= 0.050: G[H]:= 10^(-0.511*sqrt(mu)/(1 +
0.329*9*sqrt(mu))); G[Me3NH]:= 10^(-0.511*sqrt(mu)/(1 +
0.329*4*sqrt(mu))); G[OH]:= 10^(-0.511*sqrt(mu)/(1 +
0.329*3.5*sqrt(mu))); G[NO2]:= 10^(-0.511*sqrt(mu)/(1 +
0.329*3*sqrt(mu))); K°[w]:= 1.01e-14: pK°[aA]:= 3.14: pK°[aM]:= 9.80: K[aA]:= 10^(-pK°[aA])/(G[H]*G[NO2]); K[aM]:= G[Me3NH]*10^(-pK°[aM])/G[H]; C[MHA]:=0.05: K[w]:= K°[w]/(G[H]*G[OH]):
```

The output here is predictable and not shown in order to conserve space.  $C[MHA]$  is used to designate  $C_{(CH_3)_3NHO_2}$  for brevity and for continuity with the Chapter 5 worksheets that used that designation. Cutting and pasting from the appropriate worksheets from Chapter 5:

```
> ChBal4°:= H^4+(C[MHA] + K[aM]+ K[aA])*H^3 +
(-K[w]+K[aM]*K[aA])*H^2 + (-K[w]*K[aM] - K[w]*K[aA] -
K[aA]*C[MHA]*K[aM])*H -K[w]*K[aM]*K[aA]; ChBal3°:= H^3 +
(C[MHA] + K[aM] + K[aA])*H^2 + (-K[w] + K[aM]*K[aA])*H -
K[w]*K[aM] - K[w]*K[aA] - K[aA]*C[MHA]*K[aM]; H2°:=
sqrt((K[aA]*(K[w] + K[aM]*C[MHA])/ (K[aA] + C[MHA]))));
H0°:=sqrt( K[aA]*K[aM]);
```

$$ChBal4^\circ := H^4 + 0.0511 H^3 + 1.4493 \cdot 10^{-13} H^2 - 7.9913 \cdot 10^{-15} H - 2.3267 \cdot 10^{-27}$$

$$ChBal3^\circ := H^3 + 0.0511 H^2 + 1.4493 \cdot 10^{-13} H - 7.9913 \cdot 10^{-15}$$

$$H2^\circ := 3.9564 \cdot 10^{-7}$$

$$H0^\circ := 3.9940 \cdot 10^{-7}$$

The third and fourth degree polynomials require two more steps.

```
> H4° := fsolve(ChBal4°, H, 0.. 1e-6); H3° := fsolve(ChBal3°, H, 0..1e-6);
```

$$H4^\circ := 3.9564 \cdot 10^{-7}$$

$$H3^\circ := 3.9564 \cdot 10^{-7}$$

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One might have used the `solve` command here, and this would have yielded four (real) roots for  $H4^\circ$  and three for  $H3^\circ$ ; in each case only one would have been physically real ( $[H^+] > 0$ ). It would then have been necessary to select the appropriate root before proceeding, something like the input used on page 123. But inasmuch as we had an excellent estimate of the one, legitimate root from  $H2^\circ$  and  $H0^\circ$ , it was simple enough to use `fsolve` and restrict the search for the root as on page 111.

As shown in Chapter 5, the  $[H^+]$  for this type of solution can be calculated from one of four expressions, but only the  $4^\circ$  expression is always correct. Here, even the most simplistic expression ( $H0^\circ$ ), one that requires several approximations provides a solution that is within one percent of the  $H4^\circ$  solution. After taking the log of these activities, all four answers are indistinguishable, given the two decimal place limit on precision.

```
> pH[0°]:= -log[10] (G[H]*H0°); pH[2°]:= -log[10] (G[H]*H2°);
pH[3°]:= -log[10] (G[H]*H3°); pH[4°]:= -log[10] (G[H]* H4°);

pHo = 6.4673
pH2 = 6.4714
pH3 = 6.4715
pH4 = 6.4714
```

For  $\alpha_{MH^+}$ ,  $\mu$  and  $\beta$  the solution to the  $4^\circ$  polynomial,  $H4^\circ$ , is used for  $[H^+]$ .

```
> alpha[MH]:= H4° / (H4° + K[aM]); mu:= (1/2) * (H4° + (H4° * C[MHA] /
(H4° + K[aM])) + (K[aA] * C[MHA] / (H4° + K[aA])) + K[w] / H4°); beta:=
evalf(ln(10) * (H4° + (K[w] / H4°) + C[MHA] * H4° * ((1 / (H4° + K[aM])) -
(H4° / (H4° + K[aM]) ^ 2) + (K[aA] / (H4° + K[aA]) ^ 2))));
```

$$\alpha_{MH} := 0.99962$$

$$\mu := 0.04998$$

$$\beta := 0.00009$$

It was necessary to reformat the output precision to get a useful value for  $\beta$ . Notice that, indeed,  $\mu = C_{MHA}$ .

4. Either buffer solution should yield a buffer of  $\text{pH} \approx 6.0$  because  $[\text{H}^+] \approx \sqrt{K_{\text{aA}} K_{\text{aM}}}$ . No concentration,  $C_{\text{MHA}}$ , has been specified. So to be confident in the illustration, two distinctly different concentration will be assigned. For the larger  $C_{\text{Buffer}}$ , ionic strength will be a factor, but, nevertheless,  $[\text{H}^+]$  will be taken as  $10^{-\text{pH}}$  and the  $K_{\text{a}}$ 's will not be corrected. The expression for  $\beta$  can be cut and pasted into another input line *after* a **restart** command. Then  $[\text{H}^+]$  and  $K_w$  can be assigned (*albeit* approximately for  $C_{\text{MHA}} > 0.01$ ), and by using the **subs** command each set of conditions can be designated. It was necessary to increase output precision to eight decimal places.

```
> restart; H:= 1e-6: K[w]:=1e-14: beta:= evalf(ln(10)*(H +
(K[w]/H) + C[MHA]*H*((1/(H + K[aM])) - (H/(H + K[aM])^2) +
(K[aA]/(H + K[aA])^2))));
```

$$\beta := 0.0000023 + 0.0000023 C_{\text{MHA}} \left( \frac{1}{0.0000010 + K_{\text{aM}}} - \frac{0.0000010}{(0.0000010 + K_{\text{aM}})^2} + \frac{K_{\text{aA}}}{(0.0000010 + K_{\text{aA}})^2} \right)$$

This output is provided to ascertain that  $\beta$  is in the correct form. It is, and so,

```
> beta1 := subs({K[aA]=1e-6,K[aM]=1e-6,C[MHA]=0.5},beta);
beta2:= subs({K[aA] = 1e-6,K[aM]=1e-6,C[MHA]= 0.005},beta);
beta3 := subs({K[aA]=1e-3,K[aM]=1e-9, C[MHA]=0.5},beta);
beta4 := subs({K[aA]=1e-3,K[aM]= 1e-9,C[MHA] =
0.005},beta);
```

$$\begin{aligned}\beta_1 &:= 0.5756486 \\ \beta_2 &:= 0.0057588 \\ \beta_3 &:= 0.0023003 \\ \beta_4 &:= 0.0000253\end{aligned}$$

This can be put into a table for clarification

	$C_{\text{Buffer}} = 0.005$	$C_{\text{Buffer}} = 0.500$
$pK_{\text{aA}} = 6$		
$pK_{\text{aM}} = 6$	$\beta_2 = 5.76 \cdot 10^{-3}$	$\beta_1 = 5.76 \cdot 10^{-1}$
$pK_{\text{aA}} = 3$		
$pK_{\text{aM}} = 9$	$\beta_4 = 2.50 \cdot 10^{-5}$	$\beta_3 = 2.30 \cdot 10^{-3}$

This exercise quantitatively establishes what was shown in Figure 6-4 which is that it is not enough that  $\text{pH} = \sqrt{K_{\text{aA}} K_{\text{aM}}}$ , but that for the maximum buffer capacity  $K_{\text{aA}} \approx K_{\text{aM}}$ . Also this exercise reaffirms Figure 6-3 in that  $\beta$  increases with  $C_{\text{Buffer}}$ .

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# 7 Acid / Base Titrations and an Introduction to Maple Programming

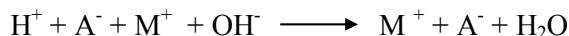
The acid / base titration is the first purely *analytical* application of ionic equilibrium we encounter. In Chapter 6, the relationship between the pH of a solution and its composition was finalized.<sup>118</sup> Indeed, the form of that relationship (e.g. Figure 6-2) is the essence of the acid / base titration curve. The mathematics required to create such a titration curve are essentially identical to what was used in Chapter 6. For clarity, the effects of ionic strength were ignored there, and initially they will be ignored here too. In this chapter, the pH curves of the previous chapter will be converted to titration curves by converting parameters like  $C_{\text{HA}}$  and  $C_{\text{MOH}}$  into expressions for their respective volumes,  $V_{\text{HA}}$  and  $V_{\text{MOH}}$ , etc. In the final pages of this chapter a more rigorous study of titration curves will be presented where ionic strength effects will be addressed.

The acid / base titration can be categorized in several ways. The most obvious is that either an acid is titrated with a base or that a base is titrated with an acid. Also the acid can be weak or strong just as the base can be weak or strong. This creates several acid / base titration possibilities, but in every case, the object is to achieve an equivalence point by adding exactly the right amount of titrant<sup>119</sup> to the titrand<sup>120</sup> to cause a neutralization.

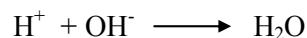
We begin with the simplest titration, the strong acid / strong base titration.



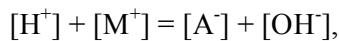
If HA<sup>121</sup> is a strong acid, and MOH is a strong base, then MA is a strong electrolyte salt as described in Chapter 3, and the process is:



with a net ionic equation:



Notice that it is not yet important to distinguish the titrand from the titrant. This is because the mathematics are identical whether the acid or the base is the titrand. What follows should appear to be similar to the presentation in Chapter 6. Consider the charge balance requirement:



and two mass balance requirements: for a *strong* acid,

$$C_{\text{HA}} = [\text{A}^-]$$

and a *strong* base,

$$C_{\text{MOH}} = [\text{M}^+].$$

Using  $K_w/[\text{H}^+] = [\text{OH}^-]$  allows the charge balance to be written in terms of  $[\text{H}^+]$ ,  $K_w$  and the concentration of the titrant and titrand.

$$[\text{H}^+] + C_{\text{MOH}} = C_{\text{HA}} + \frac{K_w}{[\text{H}^+]} \quad 7-1$$

Equation 7-1 might have been derived in Chapter 6 to describe the mixture of a strong acid and a strong base, but such a solution has “no” buffer capacity, and had no place there. Also, 7-1 is not in the form conducive to describing the acid / base titration because *titrations* are carried out monitoring the *volumes* of titrant and titrand, not their concentrations. These conversions are straightforward.

As a titrant is added to the fixed volume of titrand, there is a volume increase and concomitant dilution of each solution. Take  $C^{\circ}_{\text{titrand}}$  to be the concentration of the titrand dispensed into the receiving flask for titration, and let that volume be  $V^{\circ}_{\text{titrand}}$ . Likewise, take  $C^{\circ}_{\text{TITRANT}}$  to be the concentration of titrant loaded into the burette from which it will be incrementally *dispensed*, and the total volume dispensed at any point to be  $V_{\text{TITRANT}}$ . The  $\circ$  is omitted here because  $V_{\text{TITRANT}}$  is not a “hard” constant or parameter; rather, it is the defining variable throughout the titration. Using the presumption that the total volume of titrand at any point in the titration is  $V^{\circ}_{\text{trand}} + V_{\text{TITRANT}}$ , the concentration at any such point is:

$$C_{\text{titrand}} = \frac{V^{\circ}_{\text{titrand}} C^{\circ}_{\text{titrand}}}{V_{\text{TITRANT}} + V^{\circ}_{\text{titrand}}} \quad 7-2a$$

and

$$C_{\text{TITRANT}} = \frac{V_{\text{TITRANT}} C^{\circ}_{\text{TITRANT}}}{V_{\text{TITRANT}} + V^{\circ}_{\text{titrand}}} \quad 7-2b$$

Now it becomes necessary to decide which agent (acid or base) is the titrant and which is the titrand. Then making these substitutions into 7-1 leads to a charge balance expression for the titration of a strong acid with a strong base or a strong base with a strong acid. The former case (HA is the titrand) will be studied and this will be done on Maple.

```
> restart; OH := K[w]/H; M := C° [MOH] * V[MOH] / (V° [HA] + V[MOH]); A := C° [HA] * V° [HA] / (V° [HA] + V[MOH]); ChBal := H + M = A + OH;
```

$$OH := \frac{K_w}{H}$$

$$M := \frac{C^{\circ}_{MOH} V_{MOH}}{V^{\circ}_{HA} + V_{MOH}}$$

$$A := \frac{C^{\circ}_{HA} V^{\circ}_{HA}}{V^{\circ}_{HA} + V_{MOH}}$$

$$ChBal := H + \frac{C^{\circ}_{MOH} V_{MOH}}{V^{\circ}_{HA} + V_{MOH}} = \frac{C^{\circ}_{HA} V^{\circ}_{HA}}{V^{\circ}_{HA} + V_{MOH}} + \frac{K_w}{H}$$

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This last output can be rendered into a quadratic in its familiar form (e.g. Equation 3-26), but it is sufficiently simple as it is that it can be solved by Maple directly.

```
> H_Expr := solve(ChBal, {H});
```

$$\begin{aligned} H_{\text{Expr}} := & \left\{ H = \frac{1}{2} \frac{1}{V_{\text{HA}}^{\circ} + V_{\text{MOH}}} \left( -C_{\text{MOH}}^{\circ} V_{\text{MOH}} + C_{\text{HA}}^{\circ} V_{\text{HA}}^{\circ} \right. \right. \\ & + \left( C_{\text{MOH}}^{\circ 2} V_{\text{MOH}}^2 - 2 C_{\text{MOH}}^{\circ} V_{\text{MOH}} C_{\text{HA}}^{\circ} V_{\text{HA}}^{\circ} + C_{\text{HA}}^{\circ 2} V_{\text{HA}}^{\circ 2} + 4 K_w \right. \\ & \left. \left. V_{\text{HA}}^{\circ 2} + 8 V_{\text{HA}}^{\circ} K_w V_{\text{MOH}} + 4 K_w V_{\text{MOH}}^2 \right)^{1/2} \right\}, \left\{ H = \right. \\ & -\frac{1}{2} \frac{1}{V_{\text{HA}}^{\circ} + V_{\text{MOH}}} \left( C_{\text{MOH}}^{\circ} V_{\text{MOH}} - C_{\text{HA}}^{\circ} V_{\text{HA}}^{\circ} \right. \\ & + \left( C_{\text{MOH}}^{\circ 2} V_{\text{MOH}}^2 - 2 C_{\text{MOH}}^{\circ} V_{\text{MOH}} C_{\text{HA}}^{\circ} V_{\text{HA}}^{\circ} + C_{\text{HA}}^{\circ 2} V_{\text{HA}}^{\circ 2} + 4 K_w \right. \\ & \left. \left. V_{\text{HA}}^{\circ 2} + 8 V_{\text{HA}}^{\circ} K_w V_{\text{MOH}} + 4 K_w V_{\text{MOH}}^2 \right)^{1/2} \right\} \end{aligned}$$

Inspection of the two roots shows that it is the first root that will provide the physically legitimate solution, *i.e.*  $[\text{H}^+] > 0$ . So, using the `subs` command (as on page 44) gives:

```
> H:= subs(H_Expr[1], H);
```

$$\begin{aligned} H := & \frac{1}{2} \frac{1}{V_{\text{HA}}^{\circ} + V_{\text{MOH}}} \left( -C_{\text{MOH}}^{\circ} V_{\text{MOH}} + C_{\text{HA}}^{\circ} V_{\text{HA}}^{\circ} \right. \\ & + \left( C_{\text{MOH}}^{\circ 2} V_{\text{MOH}}^2 - 2 C_{\text{MOH}}^{\circ} V_{\text{MOH}} C_{\text{HA}}^{\circ} V_{\text{HA}}^{\circ} + \right. \\ & C_{\text{HA}}^{\circ 2} V_{\text{HA}}^{\circ 2} + 4 K_w V_{\text{HA}}^{\circ 2} + 8 V_{\text{HA}}^{\circ} K_w V_{\text{MOH}} + 4 K_w \\ & \left. \left. V_{\text{MOH}}^2 \right)^{1/2} \right) \end{aligned}$$

This is the explicit expression for  $[\text{H}^+]$  as a function of the  $K_w$  and the concentrations and volumes of a strong acid / strong base titration. Taking this directly to “pH” (actually  $-\log_{10}[\text{H}^+]$ ) requires:

```
> pH:=-log[10](H);
```

$$\begin{aligned}
 pH := -\frac{1}{\ln(10)} & \left( \ln \left( \frac{1}{2} \frac{1}{V^{\circ}_{HA} + V_{MOH}} \right) \left( -C^{\circ}_{MOH} V_{MOH} \right. \right. \\
 & + C^{\circ}_{HA} V^{\circ}_{HA} \\
 & + \left( C^{\circ}_{MOH}^2 V_{MOH}^2 \right. \\
 & - 2 C^{\circ}_{MOH} V_{MOH} C^{\circ}_{HA} V^{\circ}_{HA} + C^{\circ}_{HA}^2 V^{\circ}_{HA}^2 + 4 K_w \\
 & \left. \left. V^{\circ}_{HA}^2 + 8 V^{\circ}_{HA} K_w V_{MOH} + 4 K_w V_{MOH}^2 \right)^{1/2} \right) \right)
 \end{aligned}$$

Creating a titration plot requires setting only four parameters and choosing a range for the volume of titrant. The reader is invited to explore the effect of each parameter, but as an example here let:

- $V^{\circ}_{HA} = 25.00 \text{ mL}$
- $C^{\circ}_{HA} = 0.050 \text{ M}$
- $C^{\circ}_{MOH} = 0.050 \text{ M}$
- $K_w = 1.0 \cdot 10^{-14}$

The titrant volume routinely ranges from zero to some point well beyond the equivalence point, say 10%. Recall that the equivalence point for a monoprotic system requires that moles of HA exactly equal the moles of MOH. For review:

$$\text{moles}_{HA} = \text{moles}_{MOH}$$

so

$$C^{\circ}_{HA} x V^{\circ}_{HA} = C^{\circ}_{MOH} x V^{\#}_{MOH}.$$

where  $V^{\#}_{MOH}$  is the volume of MOH (titrant) *at the equivalence point*. So,

$$V^{\#}_{MOH} = \frac{C^{\circ}_{HA} V^{\circ}_{HA}}{C^{\circ}_{MOH}} = 25.00 \text{ mL.} \quad 7-3$$

We will use  $V_{stop} = 1.1V^{\#}_{MOH}$  so that the relationship between pH and  $V_{MOH}$  can be described 10% beyond the equivalence point.

```
> V^{\circ}[HA] := 25: C^{\circ}[HA] := 0.05: C^{\circ}[MOH] := 0.05: K[w] := 1.0e-14: pH;
V["stop"] := 1.1*C^{\circ}[HA]*V^{\circ}[HA]/C^{\circ}[MOH];
```

$$pH := - \frac{\ln\left(\frac{1}{2} \frac{-0.050 V_{MOH} + 1.250 + \sqrt{0.003 V_{MOH}^2 - 0.125 V_{MOH} + 1.563}}{25 + V_{MOH}}\right)}{\ln(10)}$$

$$- \frac{\ln\left(\frac{1}{2} \frac{-0.050 V_{MOH} + 1.250 + \sqrt{0.003 V_{MOH}^2 - 0.125 V_{MOH} + 1.563}}{25 + V_{MOH}}\right)}{\ln(10)}$$

$$V_{\text{"stop":}} := 27.500$$

The output for pH is requested so that it can be seen to contain only one variable,  $V_{MOH}$ . The quotation marks are required around `stop` because Maple reserves the words `quit`, `done` and `stop` for other operations. Notice that the output setting for significant digits is three decimal places at this point in the worksheet. Not evident is the need to set the Preferences to Round calculations to at least fifteen significant digits.<sup>122</sup> Using the default ten significant digits produces an erratic plot after  $V_{MOH} = 25$  mL. This is because at 25 mL, the calculations for  $[H^+]$  require the subtraction of two values that are so nearly equal that their difference can be computed as zero unless the “Round calculation to” is set to  $\geq 20$  digits.

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Finally, we create the titration plot for titrating 25.00 mL of 0.050 M strong acid with 0.050 M strong base. The range of  $V_{MOH}$  is 0 to  $V_{stop}$ . The grid lines are added and the vertical axis range is changed to 1 to 12 from the Plot menu after the **plot** is rendered.

```
> plot(pH, V[MOH] = 0..V["stop"], axes = box, color = green,
      labels= ["V[MOH]", "-log[H+]"]);
```

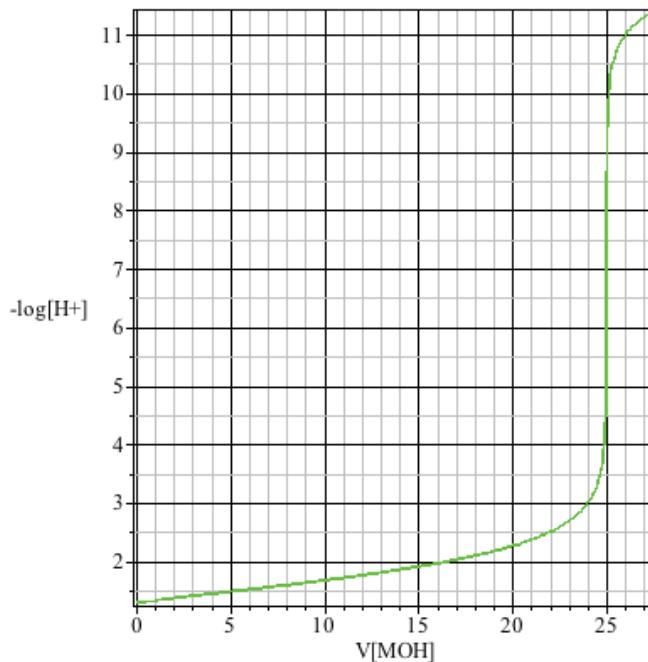


Figure 7-1

The shape of the titration curve should reveal its analytical utility: at  $V^*_{MOH}$ ,  $\frac{\Delta pH}{\Delta V_{MOH}}$  shows a spectacular increase. As long as a large change in pH can be detected, an equivalence point can be recognized and so the concentration of the titrand,  $C^*_{HA}$  can be ascertained from  $V^*_{HA}$ ,  $C^*_{MOH}$  and  $V^*_{MOH}$ .<sup>123</sup> Detecting a sudden change in pH is simple: it is done either potentiometrically with an electrode that responds to  $H^+$  activity, that is  $\{H^+\}$  or by using an acid / base indicator.

Before addressing the use of acid / base indicators it is necessary to explain how they work. These indicators are, themselves, weak acids, but they are indicators because their forms HA and A<sup>-</sup> are different colors. Consider:



7-4

From Le Châtelier's Principle (page 9), it would be expected that in an acidic solution, the dissociation of HIn is suppressed (7-4 driven to the left), and from the illustration, the indicator would produce a blue titrand. As OH<sup>-</sup> is added to the solution, H<sup>+</sup> is consumed, dissociation of HIn is enhanced and the solution appears red.

These acids are so special that their dissociation constants are given a special notation,  $K_{In}$  and  $pK_{In}$ . Modifying 4-21 and 4-22 gives:

$$\alpha_{In^-} = \frac{K_{In}}{[H^+] + K_{In}} \quad 7-5$$

and,

$$\alpha_{HIn} = \frac{[H^+]}{[H^+] + K_{In}} \quad 7-6$$

The rule of thumb<sup>124</sup> is that an indicator like this would be distinctly red when  $[In^-] \geq 10 \times [HIn]$ , and distinctly blue when  $[HIn] \geq 10 \times [In^-]$ . From 7-5 and 7-6 the solution will become distinctly red when  $[H^+]$  falls just below  $0.1K_{In}$ , as this would make  $\alpha_{In^-}$  equal to 0.909 which means that 90.9% of the indicator is in the  $In^-$  form, and therefore 9.09% is in the  $HIn$  form, the prescribed 10:1 ratio. When  $[H^+]$  just exceeds  $10K_{In}$ ,  $\alpha_{HIn}$  will reach 0.909 meaning that 90.9% of the indicator in the  $HIn$ , i.e. blue form with 9.09% in the  $In^-$  form. In terms of pH and  $pK_{In}$ , the solution achieves  $\alpha_{In^-}$  equal to 0.909 when pH (more correctly minus  $\log[H^+]$ ) equals minus  $\log(0.1K_{In})$  which is  $pK_{In} + 1$ .<sup>125</sup> Conversely,  $\alpha_{HIn}$  will reach 0.909 when  $-\log[H^+] = -\log(10K_{In})$  which is at  $pH = pK_{In} - 1$ .<sup>126</sup>

Where the pH of the titrand is within  $pK_{In} \pm 1$ , the titrand color is in transition. The  $pH_{EqPt}$  depends on the direction of the titration. If the titrant is the base, then as in Figure 7-1, the titrand would be an acid and would start out blue and be titrated to a red end point. That transition will not be distinct until  $[H^+]$  falls below  $0.1K_{In}$  or pH exceeds  $pK_{In} + 1$ . If the titrant is an acid, the titrand (a base) should start out with the indicator largely in the  $In^-$  form, and titrant should be added until the titrand is distinctly blue. This will occur when the pH falls below  $pK_{In} - 1$ . Given that the goal is to achieve  $pH_{End} = pH_{EqPt}$ , an indicator with the appropriate  $pK_{In}$  should be selected based on this principle. How close  $pK_{In}$  must lie to  $pH_{EqPt}$  will be illustrated here, by continuing with our HA / MOH titration.

First we might calculate the obvious, that  $pH_{EqPt} = 7.00$ .<sup>127</sup> This is done by using the equivalence point volume of MOH,  $V^*$ . Continuing with the current worksheet:

```
> V[MOH]:= C°[HA]*V°[HA]/C°[MOH]; pH[EqPt]:= evalf(pH);
```

$$V_{MOH} := 25.000$$

$$pH_{EqPt} := 7.000$$

Inasmuch as the titrant is a base, the endpoint should be reached just as  $\alpha_{In^-} = 0.909$ , and that should occur at pH 7.000. The most suitable indicator will have a  $K_{In}$  that makes that happen. Using  $10^{-7.000}$  for  $[H^+]$  in Equation 7-5 allows

```
> K[In]:= solve(0.909 = K[In]/(10^(-7.000) + K[In])); pK[In]:=  
-log[10](K[In]);
```

$$K_{In} := 9.989 \cdot 10^{-7}$$
$$pK_{In} := 6.000$$

And yes,  $K_{In}$  could have been found from  $\alpha_{HIn} = 0.0909$ , and no,  $K[In]$  did not have to be included in the `solve` command because it was the only variable in the expression.

We now have the ideal indicator, and Appendix V allows us to make the best selection. Chlorophenol Red with a  $pK_{In} = 6.1$  is closest to the ideal  $pK_{In}$ . The 10:1 rule would predict a change at  $pH \approx 7.1$ , but the Table more specifically predicts a transition<sup>128</sup> (from yellow to red) at  $pH 6.8 - 0.1 = 6.7$  which is early, but how early?

This can be calculated by unassigning  $V_{MOH}$  and assigning  $[H^+]$  its endpoint value of  $10^{-6.7}$ .

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```
> V[MOH]:='V[MOH]'; H:= 10^(-6.7); ChBal;
```

$$\begin{aligned} V_{MOH} &= V_{MOH} \\ H &= 1.9953 \cdot 10^{-7} \end{aligned}$$

$$1.995 \cdot 10^{-7} + \frac{0.050 V_{MOH}}{25 + V_{MOH}} = \frac{1.250}{25 + V_{MOH}} + 5.012 \cdot 10^{-8}$$

Notice that ChBal is not a quadratic in  $V_{MOH}$  and solving for  $V_{MOH}$  will yield the *endpoint* volume of titrant.

```
> V[EndPt]:=solve(ChBal);
```

$$V_{EndPt} := 24.9999$$

Indeed the endpoint is early, but imperceptibly so. A titration error is due to the difference between  $V^*$  ( $V_{EqPt}$ ) and  $V_{EndPt}$  where  $V_{EndPt}$  is the volume at which the analyst *believes* that the equivalence point has been reached. Using  $V^*$  for  $V_{EndPt}$ , that error becomes  $(V^* - V^*)$ ,<sup>129</sup> and the *relative* error, as a percentage is

$$\% \text{ R.E.} = \frac{100 \times |V^* - V^*|}{V^*}$$

7-7

```
> Error:= V[EndPt] - 25.00; RelError:= 100*abs(V[EndPt] - 25.00);
```

$$Error := -0.0001$$

$$RelError := 0.0149$$

A relative error of less than 0.1% constitutes excellent analytical work. Other indicators can easily meet this criterion.<sup>130</sup> The criterion is so easily met only because  $\Delta p\text{H}/\Delta V$  is large at the equivalence point, and this is true for strong acid / strong base titrations *as long as the equivalence point concentration,  $C^*$ , is reasonably large*. What is reasonable? We might first learn to calculate  $C^*$  directly.

$C^*$  is easy to calculate at the equivalence point for a 1:1 titration, because

$$C^*_{\text{titrand}} = \frac{V^*_{\text{titrand}} C^*_{\text{titrand}}}{V^*_{\text{TITRANT}} + V^*_{\text{titrand}}} \quad 7-8\text{a}$$

$$C^*_{\text{TITRANT}} = \frac{V^*_{\text{TITRANT}} C^*_{\text{TITRANT}}}{V^*_{\text{TITRANT}} + V^*_{\text{titrand}}} \quad 7-8\text{b}$$

Inasmuch as the denominator in each expression is identical, and we have shown, on page 167, that the numerators are equal, then  $C_{\text{titrand}}^{\#} = C_{\text{TITRANT}}^{\#}$  and we can use *either* expression. But also, if we use a minor variation of Equation 7-3

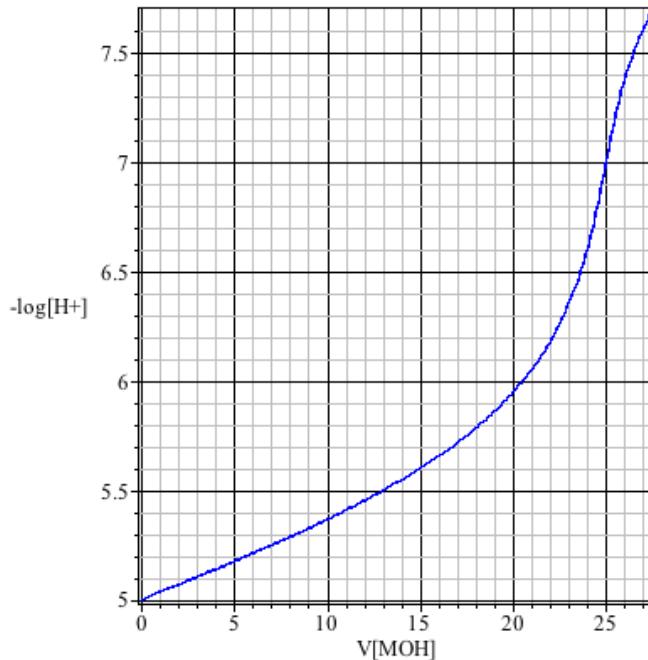
$$V_{\text{TITRANT}}^{\#} = \frac{C_{\text{titrand}}^{\circ} V_{\text{titrand}}^{\circ}}{C_{\text{TITRANT}}^{\circ}} \quad 7-9$$

and substitute this into Equation 7-8b we find

$$C^{\#} = \frac{C_{\text{titrand}}^{\circ} X C_{\text{TITRANT}}^{\circ}}{C_{\text{titrand}}^{\circ} + C_{\text{TITRANT}}^{\circ}} \quad 7-10$$

Interesting. The analytical concentration of both the titrand and titrant *at the equivalence point* can be found without either  $V^{\circ}$  or  $V^{\#}$ .

Now we might explore an unreasonable  $C^{\#}$ , for example  $5.0 \times 10^{-6} \text{ M}$ . This is the  $C^{\#}$  for titrating  $10^{-5} \text{ M}$  HA with  $10^{-5} \text{ M}$  MOH. It should be apparent that  $V_{\text{MOH}}^{\#}$  would equal  $V_{\text{HA}}^{\circ}$ , as in the previous example. Indeed, we can recreate that worksheet changing only this pair of  $C^{\circ}$ 's and inspect the titration plot.<sup>131</sup>



**Figure 7-2**

Notice that again the  $\text{pH}_{\text{EqPt}}$  is 7.00, but that it requires a considerable  $\Delta V_{\text{MOH}}$  to effect a large  $\Delta \text{pH}$ . From this plot we can estimate that if  $\text{pH}_{\text{EndPt}} = 6.7$ ,  $V^{\circ}$  would be about 24.0 mL,<sup>132</sup> a full 1.0 mL (4.0%) premature. But not only would the endpoint be early, the color transition would occur over a relatively large  $\Delta V$ , maybe several drops. A well designed titration will have a sharp, distinct color change.

This does not mean that the titration of  $1.0 \cdot 10^{-5} \text{ M}$  strong acid cannot be more precisely titrated. If the problem is a low  $C^*$ , increase it, and this can be done with a larger  $C^\circ_{\text{MOH}}$ . If  $C^\circ_{\text{MOH}}$  were increased to  $1.0 \cdot 10^{-4} \text{ M}$ ,  $C^*$  would become  $9.1 \cdot 10^{-6}$  and if  $V_{\text{HA}}$  is to remain at 25, then  $V\%$  becomes 2.50 mL. A 5 mL buret would be appropriate because  $V$  can be read to  $\pm 0.01 \text{ mL}$ .

While  $C^*$  is the only significant limitation to titrating strong acids with strong bases and *vice versa*, titrating a weak acid with a strong base or a weak base with a strong acid presents an additional problem:  $K_a$  (or  $K_b$ ) cannot be especially small. “Especially small” will become apparent in the following discussion.

If HA is a weak acid, then only one change to the charge balance expression, 7-1, is required:  $[A^-] = C_{\text{HA}}$  is replaced using 4-11 which takes into consideration the limited dissociation of HA to  $\text{H}^+$  and  $\text{A}^-$ .

$$[A^-] = \frac{C_{\text{HA}} K_a}{[\text{H}^+] + K_a} \quad 4-11$$

We can pursue this circumstance with Maple and look at the effects of  $K_a$  on the titration plot. Again, MOH will be a strong base and taken as the titrant and HA will be the titrand. The predictable and uninteresting outputs will be suppressed.

```
> restart; OH := K[w]/H; M := C°[MOH]*V[MOH]/(V°[HA] + V[MOH]):  
C[HA] := C°[HA]*V°[HA]/(V°[HA]+V[MOH]); A := K[a]*C[HA]/(H + K[a]);  
ChBal := H + M = A + OH;
```

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*ChBal :=*

$$H + \frac{C_{MOH}^{\circ} V_{MOH}}{V_{HA}^{\circ} + V_{MOH}} = \frac{K_a C_{HA}^{\circ} V_{HA}^{\circ}}{(V_{HA}^{\circ} + V_{MOH})(H + K_a)} + \frac{K_w}{H}$$

The implicit expression of  $[H^+]$  is a cubic polynomial, and it can be solved directly in this form using `solve (ChBal, {H});`, but the result is many, many unintelligible pages of the three roots. It would be discovered that using this cubic, even after converting it to the  $ax^3 + bx^2 + cx + d$  form cannot be used with the `plot3d` command.<sup>133</sup> In order to create a three dimensional plot, it is necessary to pare this polynomial to a quadratic. The use of the cubic polynomial will be resurrected immediately after the effect of  $pK_a$  on the titration plot is illustrated in the plot. (Not only will Figure 7-3 illustrate the effects of  $pK_a$ , it will reveal the perils of estimating the cubic polynomial with a quadratic.)

The process of estimating a cubic as a quadratic was discussed on page 79 and again on page 130. Review those discussions if what follows is not clear.

```
> ChBal := simplify((V^°[HA] + V[MOH]) * (H+K[a])*H*ChBal) :
> ChBal := lhs(ChBal) - rhs(ChBal) :
> ChBal := collect(ChBal,H);
```

$$\begin{aligned} ChBal := & (V_{HA}^{\circ} + V_{MOH}) H^3 + (C_{MOH}^{\circ} V_{MOH} + (V_{HA}^{\circ} \\ & + V_{MOH}) K_a) H^2 + (C_{MOH}^{\circ} V_{MOH} K_a - K_w V_{MOH} \\ & - K_w V_{HA}^{\circ} - K_a C_{HA}^{\circ} V_{HA}^{\circ}) H - K_w V_{HA}^{\circ} K_a - K_w V_{MOH} K_a \end{aligned}$$

The output has been suppressed to this point because it is familiar. The cubic polynomial is shown so that a new operation can be introduced here. It is a simple operation for extracting terms from an expression. The `op(n, expr)` command displays the  $n^{\text{th}}$  operand (component) of the expression, `expr`. Inasmuch as it is the constants, that is, the fourth and fifth components of `ChBal` that we wish to remove (by taking them to be approximately zero) we can subtract them out of `ChBal`. So we subtract the fourth and fifth components of `ChBal` to get the quadratic version of `ChBal`.

```
> ChBal := ChBal - op(4,ChBal) - op(5,ChBal);
```

$$\begin{aligned} ChBal := & (V_{HA}^{\circ} + V_{MOH}) H^3 + (C_{MOH}^{\circ} V_{MOH} + (V_{HA}^{\circ} \\ & + V_{MOH}) K_a) H^2 + (C_{MOH}^{\circ} V_{MOH} K_a - K_w V_{MOH} \\ & - K_w V_{HA}^{\circ} - K_a C_{HA}^{\circ} V_{HA}^{\circ}) H \end{aligned}$$

Next we combine three operations into a single command. First, we divide ChBal through by H to make it a quadratic; then we simplify the expression, and finally collect all the terms

```
> ChBal:= collect(simplify(ChBal/H),H);
```

$$\begin{aligned} ChBal := & \left( V_{HA}^o + V_{MOH} \right) H^2 + \left( C_{MOH}^o V_{MOH} + V_{HA}^o K_a \right. \\ & \left. + V_{MOH} K_a \right) H + C_{MOH}^o V_{MOH} K_a - K_w V_{MOH} \\ & - K_w V_{HA}^o - K_a C_{HA}^o V_{HA}^o \end{aligned}$$

The next two steps can be carried out in either order. Solving the quadratic first would produce a general, but more complicated output. So here, we will define all of the constants needed to address the question at hand, and *then* solve the resulting quadratic for its two roots. Either output is too complex (and long) to display here.

```
> V°[HA]:= 25: C°[HA]:= 0.05: C°[MOH]:= 0.05: K[w]:= 1.01e-14: H_
roots:= solve(ChBal,{H}):
```

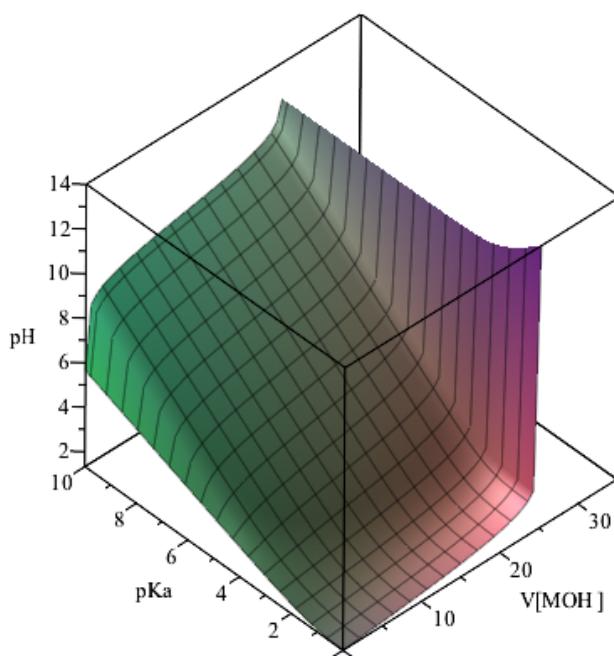
Inspection would show that it is the first of the two roots that yields  $[H^+] > 0$ . That root will be selected and displayed<sup>134</sup> after we replace  $K_a$  with  $10^{-pK_a}$  and then convert H to pH. This produces an expression for pH (actually  $-\log_{10}[H^+]$ ) as a function of  $C_{HA}^o$ ,  $C_{MOH}^o$ ,  $V_{HA}^o$ ,  $V_{MOH}$ ,  $K_w$  and  $pK_a$ .

```
> H_ion:= subs(H_roots[1],H); H:= algsubs(K[a]=10^(-pKa), H_ion);
pH:= -log[10](H);
```

$$\begin{aligned} pH := & -\frac{1}{\ln(10)} \left( \ln \left( \frac{1}{25.000 + V_{MOH}} \left( 1.000 \cdot 10^{-8} \left( -1.250 \cdot 10^9 \cdot 10^{-pK_a} \right. \right. \right. \right. \right. \\ & \left. \left. \left. \left. \left. \left. - 5.000 \cdot 10^7 \cdot V_{MOH} \cdot 10^{-pK_a} - 2.500 \cdot 10^6 \cdot V_{MOH} \right. \right. \right. \right. \right. \\ & \left. \left. \left. \left. \left. \left. + \left( 3.125 \cdot 10^{17} \cdot 10^{-pK_a} + 1.563 \cdot 10^{18} \cdot \left( 10^{-pK_a} \right)^2 \right. \right. \right. \right. \right. \\ & \left. \left. \left. \left. \left. \left. + 1.250 \cdot 10^{17} \cdot V_{MOH} \cdot \left( 10^{-pK_a} \right)^2 + 2.500 \cdot 10^{15} \cdot V_{MOH}^2 \cdot \left( 10^{-pK_a} \right)^2 \right. \right. \right. \right. \right. \\ & \left. \left. \left. \left. \left. \left. + 6.250 \cdot 10^{12} \cdot V_{MOH}^2 - 2.500 \cdot 10^{14} \cdot V_{MOH}^2 \cdot 10^{-pK_a} + 63125.000 \right. \right. \right. \right. \right. \\ & \left. \left. \left. \left. \left. \left. + 5050.000 \cdot V_{MOH} + 6.250 \cdot 10^{15} \cdot V_{MOH} \cdot 10^{-pK_a} \right)^{1/2} \right) \right) \right) \right) \end{aligned}$$

pH can now be plotted from  $V_{\text{MOH}} = 0$  to 35 mL (10 mL beyond the equivalence point) and  $\text{pK}_a = 0$  (a relatively strong acid at  $K_a = 1$ ) to 10 (a very weak acid  $K_a = 10^{-10}$ ). It will be necessary to prescribe<sup>135</sup>  $\geq 15$  significant digits to preempt floating point errors.

```
> plot3d(pH,V[MOH] = 0..35, pKa = 0..10, axes = boxed, labels =
["V[MOH ]","pKa","pH"],orientation = [225,45], grid = [50,50]);
```



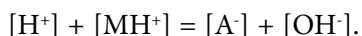
**Figure 7-3**

The plot shows that where HA is a relatively strong acid ( $\text{pK}_a \leq 2$ ), it looks like Figure 7-1 with its sharp rise in pH at the equivalence point and its low pH at  $V_{\text{MOH}} \approx 0$ . Where HA is very weak ( $\text{pK}_a > 8$ ), the starting point of the titration ( $V_{\text{MOH}} = 0$ ) has risen and the  $\Delta\text{pH}$  at the equivalence point ( $V_{\text{MOH}} = 25$ ) has decreased. And so, the equivalence point becomes less and less distinctive, something like the problem illustrated in Figure 7-2. There are two remedies: use a higher concentration of MOH (to increase  $C^*$ ) or use an *aprotic* solvent.<sup>136</sup>

The diminished  $\frac{\Delta\text{pH}}{\Delta V}$  at the equivalence point shown in Figure 7-3 where  $\text{pK}_a \geq 8$  and in Figure 7-2 are for different reasons. The small rise in pH in the weak acid example has occurred despite the relatively large  $C^*$  (0.025 M). This added issue for weak acid or weak base titrations produces other issues, and these will be explored by considering, this time, the titration of a weak *base* with a strong *acid*.

As we revisit the  $pK_a$  effect point we will make an important modification to the calculations: instead of relying on the plot command to evaluate the quadratic expression, the  $[H^+]$  and pH will be computed, point by point from the cubic expression. The inadequacy of the quadratic is apparent in Figure 7-3 where roots could *not* be found. This is why the surface abruptly stops at  $\approx 25$  mL MOH. The abrupt cutoff is not an artifact of the plot: it was caused by the way Maple computes points for a plot. The most rigorously correct solution is a computation of  $[H^+]$  at each  $V_{\text{TITRANT}}$ . This creates a set of points that can be plotted with the `plots[pointplot]` command.

First, we attend to the charge balance expression for a weak base being titrated with a strong acid. Recall, that weak bases are denoted as molecular species,  $M$ ,<sup>137</sup> not MOH. And when this weak base abstracts a proton, either from HA or  $H_2O$  it forms its conjugate acid  $MH^+$ . So the charge balance used on page 164 becomes:



$M$ , being a base, allows that  $[MH^+]$  is a function of  $K_a$ ,  $[H^+]$ , and  $C_M$  as described in Chapter 4.

$$[MH^+] = \frac{[H^+]C_M}{K_a + [H^+]} \quad 4-36$$

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What follows is a substitution of **4-36** into the charge balance expression above. Then taking M to be the titrand and HA, a strong acid ( $[A^-] = C_{HA}$ ), to be the titrant, the dilution factors (Equations **7-2a** and **7-2b**) are applied. Without showing intermediate output, the cubic expression for charge balance is given.

```
> restart; OH := K[w]/H; C[M] := C°[M]*V°[M] / (V[HA] + V°[M]); MH :=  
H*C[M] / (K[a] + H); A := C°[HA]*V[HA] / (V[HA] + V°[M]); ChBal := H +  
MH = A + OH;
```

*ChBal* :=

$$H + \frac{H C_M V_M}{(V_{HA} + V_M) (K_a + H)} = \frac{C_{HA} V_{HA}}{V_{HA} + V_M} + \frac{K_w}{H}$$

Notice the symmetry between this charge balance expression and that from the weak acid / strong base titration (page 175 output). Here,  $K_a$  pertains to the dissociation of the conjugate acid  $MH^+ \longrightarrow H^+ + M$ . This means that a large  $K_a$  implies a small  $K_b$  for M (Equation **4-33**), and so a small  $pK_a$  implies a large  $pK_b$  which represents a very weak base, M.

We will illustrate  $pK_a$  effects on the plot by examining four weak bases of distinctly different strength, namely  $pK_a = 2, 5, 8$  and  $11$ , and this can be done with four charge balance expressions, each with one of these  $pK_a$  values. First, we might assign all constants that are common to the four expressions.

```
> C°[M]:=0.25; C°[HA]:= 0.25; V°[M]:= 25.0; K[w]:= 1.01E-14:ChBal;
```

$$H + \frac{6.250 H}{(V_{HA} + 25.000) (K_a + H)} = \frac{0.250 V_{HA}}{V_{HA} + 25.000} + \frac{1.010 \cdot 10^{-14}}{H}$$

From here the four expressions are created; only the first is shown.

```
> ChBal2:= subs(K[a]= 1E-2, ChBal); ChBal5:= subs(K[a]= 1E-5,  
ChBal): ChBal8:= subs (K[a]= 1E-8, ChBal): ChBal11 := subs(K[a]=  
1E-11, ChBal):
```

$$\begin{aligned} ChBal2 &:= H + \frac{6.250 H}{(V_{HA} + 25.000) (0.010 + H)} \\ &= \frac{0.250 V_{HA}}{V_{HA} + 25.000} + \frac{1.010 \cdot 10^{-14}}{H} \end{aligned}$$

This shows that only  $V_{HA}$  and  $[H^+]$  remain. We can explore the effectiveness of `fsolve` and `solve`.

```
> V[HA]:= 0.00: H2Rts:= fsolve (ChBal2, {H}); H2Rts:= solve
(ChBal2, {H});
```

```
H2Rts := {H = -0.260}
H2Rts := {H = 1.971 10-8},
{H = -1.971 10-8}, {H = -0.260}
```

`fsolve` has failed to find all three roots, as it sometimes does. More important, it has failed to find the only physically useful root,  $1.971 \cdot 10^{-8}$ . Adding `, 0 .. 1E-3` to that command will steer it to the desired root, but we are about to compute hundreds of roots for the four cubic polynomials, and the range over which the real root is to be found will increase. It will be shown (in Problem 3) how this can be achieved, but here it is simpler to use the roots found from `solve`. We have shown that it is the first of the three roots that we wish to use. And so we will use the `subs` command to select that root.

The task at hand is evident: find the pH of a solution given one of four values of  $K_a$  for each  $V_{TITRANT}$  throughout a titration. With  $V_{TITRANT}$  increments of, say, 0.10 mL and an equivalence point of 25 mL, it would require 250 (0 to 25.0 mL) just to reach the equivalence point, 300 to exceed the equivalence point by 20% (30.0 mL). This can be done in under one minute by programming Maple to carry out the necessary procedures. These procedures will be embedded in a “for” or “do” loop. This begins by assigning a starting value for  $V_{HA}$  (which has already been done in the previous command line). An integer,  $i$  in this case, is chosen that will be incremented (upward from 1 by 1)<sup>138</sup> each time the loop is cycled until that integer reaches the defined limit which follows “to.” The end of the loop is identified by the `end`<sup>139</sup> command. The loop is begun with  $V[HA] = 0.0$  mL and at each cycle will increment it by 0.1 mL. With three hundred cycles, we will calculate the pH at 0.0, 0.1, 0.2,... 29.9 mL. All four charge balance expressions will be evaluated at all 300 points. They are expressed on separate command lines *only* for clarity.

```
> for i to 300 do140, 141
> H2Rts:= solve(ChBal2, {H}): H2[i]:= subs(H2Rts[1], H): pH2[i]:= 
-log[10](H2[i]):
> H5Rts:= solve(ChBal5, {H}): H5[i]:= subs(H5Rts[1], H): pH5[i]:= 
-log[10](H5[i]):
> H8Rts:= solve(ChBal8, {H}): H8[i]:= subs(H8Rts[1], H): pH8[i]:= 
-log[10](H8[i]):
> H11Rts:= solve(ChBal11, {H}): H11[i]:= subs(H11Rts[1], H):
pH11[i]:= -log[10](H11[i]):
> V[i]:= V[HA]: V[HA]:= V[HA] + 0.10: end:
```

The final line assigns the current  $V_{HA}$  to  $V_i$ , then increments  $V_{HA}$  by 0.1 mL and finally terminates the loop when  $i$  reaches 300. We now have a pH2, pH5, pH8 and pH11 for all three hundred values of  $V_{HA}$ . They are (mercifully) not shown because the loop was terminated with a colon, but *any* one of the values can be called. For example:

```
> V[251], H2[251], pH2[251];142
```

25.000, 0.031, 1.513

The next step is to create sequences of values (pairs of points) for point-by-point plotting. This requires the `seq` command. The colon is essential here to spare one pages of output.

```
> pH_2 := [seq([V[i], pH2[i]], i = 1..300)]; pH_5 := [seq([V[i],  
pH5[i]], i = 1..300)]; pH_8 := [seq([V[i], pH8[i]], i = 1..300)];  
pH_11 := [seq([V[i], pH11[i]], i = 1..300)];
```

This produces exactly the required data format for plotting points in Maple. To see *one* such plot one might enter:

```
> plots[pointplot](pH_2, style = line, color = "DarkRed", axes =  
boxed, labels = ["mL[HA]", "pH"]);
```



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The plot is not shown because it will be shown along with the other three titration plots. However, the reader is invited to replace `pH_2` with `pH_5 etc.`, hit the [return] key and inspect each of the four plots. When it is clear that each plot has the correct “look,” a plot *structure* is assigned to each plot. This is necessary because the `pointplot` allows the plotting of only one set of points! Notice that all four structures share some of the same attributes like `axes` and `labels`, and so these need not be included in all four structures. On the other hand plotting `style` (line as opposed to points) and `color`<sup>143</sup> must be provided for each. Again, there is no need to see the output.

```
> pH_A := plots[pointplot](pH_2, style = line, color = "DarkRed",
  axes = boxed, labels = ["mL[HA]", "pH"]); pH_B := plots
  [pointplot](pH_5, style = line, color = blue); pH_C:=
  plots[pointplot](pH_8, style = line, color = "DarkOrchid"); pH_D:=
  plots [pointplot](pH_11, style= line, color= "DarkGreen");
```

Finally, the composite of the four `pointplot` structures is rendered. The grid lines are subsequently added from the plot menu. And although the plot structures have been assigned, the ability to alter the scaling on either axis is still available.

```
> plots[display]({pH_A, pH_B, pH_C, pH_D});
```

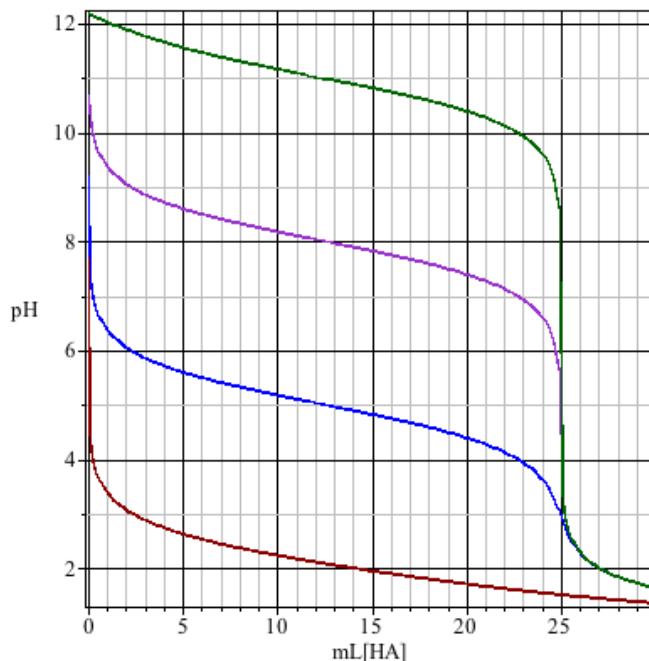


Figure 7-4

The plot (Figure 7-4) reveals “reversal of fortunes,” that *unlike* in Figure 7-3, a small  $pK_a$  produces the imperceptible  $\Delta pH/\Delta V$  at the equivalence point (25 mL) and that it is the base with the large  $pK_a$  that is so easily titrated. Recall that this is because a small  $pK_a$  represents an especially weak base. This base is *so* weak that the 0.25 M HA can barely protonate it. So the pH of the titration solution drops immediately, as though one were adding a strong acid to water! On the other extreme, when  $pK_a = 11$ , M is a moderately strong base. So, at  $V_{HA} = 0$ , the solution is  $C^{\circ}_M$  is and strongly alkaline ( $pH \approx 12$ ).

So, the small  $\Delta pH$  at the equivalence point in Figures 7-3 and 7-4 is caused not by the small  $C^{\circ}_{MOH}$  or small  $C^{\circ}_{HA}$ , respectively, but by a small  $K_a$  or  $K_b$ , respectively. That is, the pH beyond the equivalence point was not the issue as it was for Figure 7-2: it was the pH leading up to the equivalence point. This leads to that second problem with these titrations alluded to earlier.

What property of a weak acid or weak base solution makes its pH change so little when a strong base or strong acid is added to it? Buffer capacity,  $\beta$ ! And recall from page 141 that the  $\beta$  increases as the fractions ( $\alpha$ ) of protonated and unprotonated agents approach 0.5; indeed, notice that where  $V_{TITRANT} = 1/2 V^*$  in Figures 7-3 and 7-4,  $\Delta pH/\Delta V$  is minimal. This is because  $\beta$  is maximized there, and that is because the  $\alpha$ 's are  $\approx 0.5$ . This fact is particularly useful in estimating the  $K_a$  of HA or  $MH^+$  from a titration plot. Recall that  $\alpha$ 's are  $\approx 0.5$  at  $[H^+] = K_a$  (*i.e.*  $pH = pK_a$ ). So  $pK_a \approx pH$  at  $V_{TITRANT} = 1/2 V^*$ .

While a large  $\beta$  is the point of a buffer solution, it is to be wholly avoided in an acid /base titration where a large  $\Delta pH/\Delta V$  is needed for equivalence point detection. We might say that these poorly defined titration plots suffer from an excessive buffer capacity at the equivalence point. From the  $pH_{EqPt}$  we can find the  $\alpha$  at the equivalence point. First it is necessary to find each  $pH_{EqPt}$  and this is done by substituting  $V^*$  (= 25.00 mL) into each  $pH_2$ ,  $pH_5$  etc. And we already have these stored. Remember that at  $i = 251$ ,  $V_{HA} = 25.00$  mL (the equivalence point). and that gives  $pH_{Equivalence\ point}$  for all for bases.

```
> V[EqPt]:= V[251]; pH[EqPt2] := pH2[251]; pH[EqPt5]:= pH5 [251];
pH[EqPt8]:= pH8[251]; pH[EqPt11]:= pH11[251];
```

```
VEqPt := 25.000
pHEqPt2:= 1.513
pHEqPt5:= 2.953
pHEqPt8 := 4.452
pHEqPt11 := 5.950
```

When titrating a weak base, M, with a strong acid, it is expected that at the equivalence point, 99.9% (page 9) of M will be protonated.<sup>144</sup> We use Equation 4-41 to find the  $\alpha_{MH^+}$  for each  $pK_a$ .

```
> alpha[MH_2]:= 10^(-pH[EqPt2])/(10^(-2) + 10^(-pH[EqPt2]));  
alpha[MH_5]:= 10^(-pH[EqPt5])/(10^(-5) + 10^(-pH[EqPt5]));  
alpha[MH_8]:= 10^(-pH[EqPt8])/(10^(-8) + 10^(-pH[EqPt8]));  
alpha[MH_11]:= 10^(-pH[EqPt11])/(10^(-11) + 10^(-pH[EqPt11]));
```

$$\begin{aligned}\alpha_{MH\_2} &:= 0.754 \\ \alpha_{MH\_5} &:= 0.991 \\ \alpha_{MH\_8} &:= 1.000 \\ \alpha_{MH\_11} &:= 1.000\end{aligned}$$

These alphas tell all: with  $pK_a = 2$ , that is with  $K_b = 10^{-12}$ , only 75% of M is protonated at the equivalence point. This is logical in that M is a very weak base and so it is not easily protonated. This  $\alpha$  being  $< 0.999$  leaves the solution with considerable buffer capacity and that means a relatively small  $\Delta p\text{H}/\Delta V$ . The pH5 equivalence point gives us an idea of just how close  $\alpha_{MH^+}$  must come to 0.999 to get a sharp endpoint: apparently 0.991 is *not* quite close enough because Figure 7-4 does not show a sharp  $\Delta p\text{H}$  at the equivalence point.

This titration of the  $K_a = 10^{-5}$  weak base with a strong acid can be explored further. The ideal indicator would have  $\alpha_{HIn} = 0.909$  at  $pH = 2.953 = pH_{EqPt}$ . So after temporarily changing the output format to six digits:



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```
> K[In5]:= solve(0.909 = 10^(-pH[EqPt5]) / (10^(-pH[EqPt5]) + K));
pK[In5]:= -log[10](%);
```

$$\begin{aligned}K_{In5} &:= 0.000111 \\pK_{In5} &:= 3.953010\end{aligned}$$

Appendix V leads one to Bromophenol Blue with its  $pK_{In} = 3.9$ , nearly perfect! But look at the pH range over which the purple to yellow transition should occur: the titrand would just begin to turn yellow at about 18 mL (pH 4.6) and be completely purple at 25 mL (pH 3.0). One would expect a uselessly broad transition and imperceptible endpoint. The difference in color between 24.5 and 25.0 mL would be imperceptible. If we revisit the pH5 data

```
> V[246]; pH5[246]; alpha [HIn5]:= 10^(-pH5[246]) / (10^(-pH5[246])+0.000111);
```

$$\begin{aligned}24.500 \\3.378 \\\alpha_{HIn5} &:= 0.791\end{aligned}$$

One should not expect a solution with 79% of the indicator in its HIn form to have an *appreciably* different color than a solution with 91% of the indicator in its HIn form. This is a full 0.50 mL prior to the equivalence point.

The failure of this titration is *not* due to a choice of the indicator; indeed Bromophenol Blue is just about perfect. An indicator with a smaller  $pK_{In}$  would yield a measurably late endpoint.

The titration of M with  $K_a = 10^{-2}$  ( $K_b = 10^{-12}$ ) cannot be salvaged with an adjustment to  $C^\circ_{HA}$ . It requires a non-aqueous condition which removes  $H_2O$  as a base that competes with M for  $H^+$ . This too is deferred to the exercises at the end of this chapter (Problem 5).

Because of these issues with small  $K_a$ 's and small  $K_b$ 's the titration of a weak acid with a weak base has *no* analytical relevance. But it will be described qualitatively here because it is an interesting problem in ionic equilibrium. The charge balance will, again be:

$$[H^+] + [MH^+] = [A^-] + [OH^-].$$

The  $[MH^+]$  and  $[A^-]$  terms can be treated as they were on page 107, but because  $MH^+$  and  $A^-$  do not come from the same compound, the  $C_{MHA}$  mass balance cannot be used. Instead,  $C_M$  and  $C_{HA}$  are needed. When the charge balance is expressed as a polynomial, it will be discovered to be of the fourth degree. It can be pared down to a cubic, but no further. This will leave a messy next step, discovering the one root where  $[H^+] > 0$ . In the final analysis, it will be shown that the equivalence point (where, of course,  $C_M$  must equal  $C_{HA}$ ) Equation 5-14 and possibly 5-15 apply. That is

$$pH_{EqPt} \approx \frac{1}{2}(pK_{aA} + pK_{aM})$$

$pH_{EqPt}$  should then be used to calculate all four alphas in order to assess buffer capacity (more correctly, lack thereof). This will lead to a prediction regarding the sharpness of an endpoint.

For all the care that was taken in selecting an indicator and calculating titration error, it can be argued that the calculations were not sufficiently rigorous to allow such accuracy; ionic strength effects were ignored, and for the titration of weak acid and weak bases, the necessary cubic polynomial was approximated as a quadratic. How much accuracy was sacrificed?

The limitations of estimating the cubic polynomial with a quadratic was illustrated in Figure 7-3. We can quantify a comparison with a pair of data sets, one using the cubic, the other the quadratic, and for this we will return to the titration of a weak acid with a strong base. That will allow us to use the input from page 175 *et seq.* We will arbitrarily select  $K_a = 10^{-3}$  for HA,  $C^o_{HA} = C^o_{MOH} = 0.25 \text{ M}$  and  $V^o_{HA} = 10.00 \text{ mL}$ . Most, if not all, of the following input will look familiar. Output will be suppressed until it gets interesting.

```
> restart; OH := K[w]/H; M := C^o[MOH]*V[MOH] / (V^o[HA] + V[MOH]):  
C[HA] := C^o[HA]*V^o[HA] / (V^o[HA] + V[MOH]); A := K[a]*C[HA] / (H +  
K[a]); ChBal3° := H + M = A + OH;  
  
> ChBal3° := simplify((V^o[HA] + V[MOH])*(H + K[a])*H*ChBal3°):  
ChBal3° := lhs(ChBal3°) - rhs(ChBal3°); ChBal3° := collect  
(ChBal3°, H);  
  
ChBal3° := ( $V^o_{HA} + V_{MOH}$ )  $H^3 + (C^o_{MOH} V_{MOH} + (V^o_{HA}$   
 $+ V_{MOH}) K_a) H^2 + (C^o_{MOH} V_{MOH} K_a - K_w V_{MOH} - K_w V^o_{HA}$   
 $- K_a C^o_{HA} V^o_{HA}) H - K_w V^o_{HA} K_a - K_w V_{MOH} K_a$   
  
> ChBal_2 := ChBal3° - op(4, ChBal3°) - op(5, ChBal3°);  
  
> ChBal2° := collect(simplify(ChBal_2/H), H);
```

$$\begin{aligned} ChBal2^o := & \left( V_{HA}^o + V_{MOH} \right) H^2 + \left( C_{MOH}^o V_{MOH} + V_{HA}^o K_a \right. \\ & \left. + V_{MOH} K_a \right) H + C_{MOH}^o V_{MOH} K_a - K_w V_{MOH} - K_w V_{HA}^o \\ & - K_a C_{HA}^o V_{HA}^o \end{aligned}$$

All of the parameters will be assigned here along with  $V_{MOH} = 0$  so that we can see which of the roots from each *ChBal* will be the physically real root. (Other values for  $V_{MOH}$  might be tried, but if  $V_{MOH} \neq 0$ , be sure to reset it to zero for the computations that follow in the for loop below.) *solve*, not *fsolve* will be used; it can be shown that *fsolve* is unable to find the  $[H^+]$  root without *a priori* knowledge of its value. (This problem is addressed in Problem 3 at the end of this chapter.)

```
> V°[HA]:= 10.00: C°[HA]:= 0.25: C°[MOH]:= 0.25: K[w]:= 1.01e-14:  
K[a]:= 1E-3; V[MOH]:= 0.00: H_cubic:= fsolve (ChBal3°, {H}); H_  
quad:= fsolve (ChBal2°, {H});
```

```
H_cubic:= {H= -0.016}, {H= -4.040 10⁻¹⁴}, {H= 0.015}  
H_quad:= {H= -0.016}, {H= 0.015}
```

360°  
thinking.

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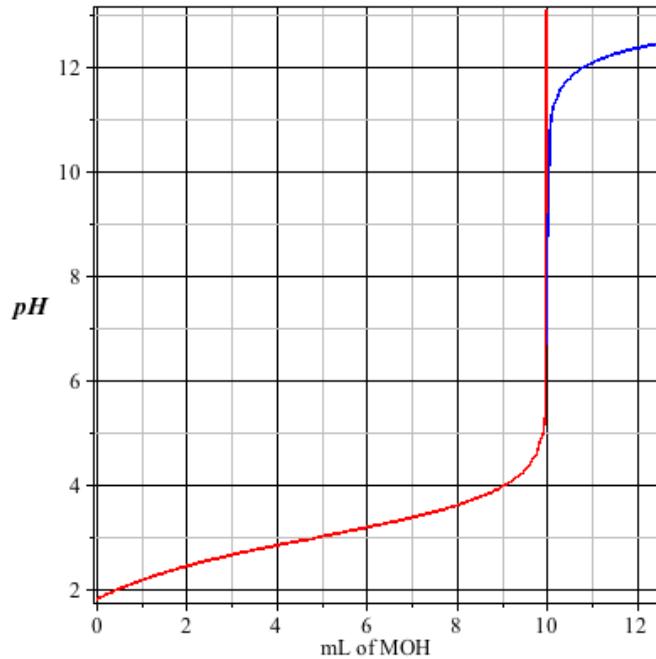
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Appropriately, there are three solutions for the cubic and two for the quadratic. It is the third root from the cubic and second root from the quadratic that we require.<sup>145</sup> We can now create a for loop which will compute the roots throughout the titration. With  $C_{\text{HA}}^{\circ} = C_{\text{MOH}}^{\circ}$ , then  $V_{\text{EqPt}} = V_{\text{HA}}^{\circ} = 10.0 \text{ mL}$ ; a titration to 125% of this, at 0.05 mL increments should be suitable to make the point.

```
> for i to 250 do
> H_cubic:= solve(ChBal3°,{H}): H3[i]:= subs(H_cubic[1],H):
pH3[i]:= -log[10](H3[i]): H_quad:= solve(ChBal2°,{H}): H2[i]:= 
subs(H_quad[1],H): pH2[i]:= -log[10](H2[i]):
> V[i]:= V[MOH]: V[MOH]:= V[MOH] + 0.050: Hmax3°:= H3[i]: Hmax2°:=
H2[i]: end:
> Cubic:= [seq([V[i],pH3[i]],i= 1..250)]: Quad:= [seq([V[i],
pH2[i]],i= 1..250)]:146
> plot([Cubic,Quad], color = [blue,red], axes = boxed);
```



**Figure 7-5**

The two plots are identical up to equivalence point, but thereafter, the quadratic cannot find a physically real root. This is illustrated by examining  $V_{\text{MOH}}$ ,  $[\text{H}^+]$  and pH near the equivalence point. The output is displayed as a table for clarity.<sup>147</sup>

```
>V[200], H3[200], H2[200]; v[201], H3[201], H2[201]; v[202], H3[202],
H2[202];
```

Also (using “right click”) the formatting for *this* output line was changed to scientific notation.

$V_{MOH}$	$[H^+]_{Cubic}$	$[H^+]_{Quad}$
9.95	$4.985 \cdot 10^{-6}$	$4.985 \cdot 10^{-6}$
10.00	$8.953 \cdot 10^{-9}$	$8.016 \cdot 10^{-14}$
10.05	$1.620 \cdot 10^{-11}$	$-4.936 \cdot 10^{-6}$

The inadequacy of the quadratic is evident, and predictable if one recalls that it is based on the presumption that  $-K_w \cdot V_{MOH} - K_w \cdot V^o_{HA} - K_a \cdot C^o_{HA} \cdot V^o_{HA} \ll [H^+]$ , and that at  $[H^+] < 10^{-8}$  this is not true.

Notice that the pH increases from 5.302 ([pH3 \[200\]](#)) at 9.95 mL to 8.048 ([pH3 \[201\]](#)) at the 10.00 mL equivalence point. So this equivalence point should be easily detected.

Finally, let us address the question regarding the importance of ionic strength in creating a titration plot. We saw in Figure 3-2 that pH is measurably affected by  $\mu$ . To answer this question we will create titration plots by solving the cubic polynomial charge balance expression for  $[H^+]$ , without and then with corrections for  $\mu$ . Using  $C^o_{HA}$ ,  $C^o_{MOH}$ , and  $K_a$  from our previous discussion, we will create one charge balance expression that uses  $K_a^o$  and  $K_w^o$  and another that uses  $K_a$  and  $K_w$ . Because we will not be paring these cubics to quadratics, it will not be necessary to convert them to the  $ax^3 + bx^2 + cx + d$  form. Despite their unconventional form, it is found that `fsolve` can find the  $[H^+] > 0$  roots throughout the titration. This will allow the opportunity to illustrate new programming techniques.

```
> restart: C[MOH]:= C°[MOH]*V[MOH]/(V[MOH] + V°[HA]): C[HA]:= C°[HA]*V°[HA]/(V[MOH] + V°[HA]): M:= C[MOH]: A:= K[a]*C[HA]/(H + K[a]): OH:= K[w]/H: ChBal:= H + M = A + OH;
```

$$ChBal := H + \frac{C^o_{MOH} V_{MOH}}{V_{MOH} + V^o_{HA}} = \frac{K_a C^o_{HA} V^o_{HA}}{(V_{MOH} + V^o_{HA})(H + K_a)} + \frac{K_w}{H}$$

```
> ChBal°:= subs(K[a]=1e-3, K[w] = 1.01e-14, ChBal);
```

$$ChBal° := H + \frac{C^o_{MOH} V_{MOH}}{V_{MOH} + V^o_{HA}} = \frac{0.001 C^o_{HA} V^o_{HA}}{(V_{MOH} + V^o_{HA})(H + 0.001)} + \frac{1.010 \cdot 10^{-14}}{H}$$

So *ChBal*<sup>o</sup> differs from *ChBal* in that it has  $K_a$  and  $K_w$  fixed, while *ChBal* will allow these values to be changed throughout the for loop as  $\mu$  changes. *fsolve* (*ChBal*...) and *fsolve* (*ChBal*<sup>o</sup>...) will provide  $[H^+]$  with and without corrections to the  $K_a^o$  and  $K_w^o$  for ionic strength. We can create a loop wherein  $V_{MOH}$  is incremented from 0 mL to 120% of the equivalence point; that should be 12 mL. But as  $V_{MOH}$  changes,  $\mu$  also changes, and so it is necessary to “nest” another loop within the volume-incrementing loop that calculates the new  $\mu$  at each  $V$ .

First let us review some ionic strength calculations. Recall that, because all ions are monovalent (page 112):

$$\mu = [H^+] + [M^+] = [A^-] + [OH^-]$$

The  $[H^+] + [M^+]$  is the easier side to use because we will be calculating  $[H^+]$  at every  $V_{MOH}$  and  $[M^+]$  is equal to  $C_{MOH}$  which is directly related to  $V_{MOH}$  as assigned in the opening line of this worksheet. So, the newly calculated  $[H^+]$  will be combined with the new  $V_{MOH}$  to compute each  $\mu$ . This will be used to calculate the  $\gamma$ 's with the Davies Equation (2–8).<sup>148</sup> The activity coefficients will then be used to adjust  $K_a$  and  $K_w$  to find a new and improved  $[H^+]$ . This process is *exactly* what was described on page 74 *et seq.*, but here the reiterations will be carried out automatically within a three cycle loop.<sup>149</sup>

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Before setting up the nested loops, all constants will be assigned as well as a starting point for  $\gamma_{\text{H}^+}$  which, because we are using the Davies Equation, will equal  $\gamma_{\text{A}^-}$  and  $\gamma_{\text{OH}^-}$ ; call these  $\text{g}[\text{Ion}]$ . Inasmuch as the Davies Equation allows for a larger ionic strength, we can continue with  $C_{\text{MOH}}^\circ$  and  $C_{\text{HA}}^\circ = 0.25 \text{ M}$  and this will enhance the ionic strength effects.

```
> C°[MOH]:= 0.25: C°[HA]:= 0.25: V°[HA]:= 10.00: V[MOH]:= 0.00:
g[Ion]:=1; Hamax:= 0.25: Hcmax:= 0.25:
```

We assign here a pair of maximum  $[\text{H}^+]$  values (`Hamax` and `Hcmax`) to be used to frame the `fsolve` search. 0.25 is easily larger than the largest root that will be found because it equals  $C_{\text{HA}}^\circ$  and HA is a weak acid. These maxima will be adjusted to the newly computed  $[\text{H}^+]$  at each cycle of the loop. We can do this because each successive  $[\text{H}^+]$  must be smaller because a base is added to the titrand.

Now for the *nested* loop (`for i`) where the ionic strength corrections for  $K_a$  and  $K_w$  are made. These might look peculiar because they do not contain specific  $\gamma$ 's.

```
> for j to 120 do
> for i to 3 do
> K[a]:= (1e-4)/(g[Ion]^2); K[w]:= 1.01e-14/(g[Ion]^2);
> H[i]:= fsolve(ChBal,H,0.. Hamax);
> μ:= H[i] + M; g[Ion]:= 10^(-0.5*((sqrt(μ)/(1 + sqrt(μ))) +
0.15*μ));
> end;
> Hc[j]:= fsolve(ChBal°,H,0.. Hcmax); Hcmax:= Hc[j]; pHc[j]:= -
-log[10](fsolve(ChBal°, H,0..Hcmax)); Hamax:= H[3]; pHa[j]:=-
log[10](g[Ion]*H[3]); V[j]:= V[MOH]; V[MOH]:= V[MOH] + 0.1;
> end:
```

The outer loop (for  $j$ ) is terminated with a colon to suppress the 120 values for the pH calculated with ( $\text{pHa}$ ) and without ( $\text{pHc}$ ) ionic strength effects. We can peek at a few points which are tabulated for clarity.

```
> V[100],pHa[100],pHc[100], V[102],pHa[102],pHc[102];
```

Volume	pH <sub>activity</sub>	pH <sub>concentration</sub>
9.900	5.857	4.999
10.000	8.407	8.048
10.100	10.950	11.090

This illustrates first that ionic strength considerations make a measurable difference, and second that  $\frac{\Delta \text{pH}}{\Delta V}$  at the equivalence point is considerable. So endpoint detection should be easy. To complete the discussion, we will plot the two pH calculations. We could proceed with a simple plot of the two sequences as we did in the previous discussion (the effect of using a quadratic in place of a cubic expression for charge balance), but these plots are best displayed as points, and so we will proceed as described on page 181 *et seq.* First, it is necessary to create a sequence of point pairs for each calculation. This is done with the `seq` command.

```
> pH_conc:= [seq([V[j],pHc[j]], j= 1..120)]; pH_act:= [seq([V[j], pHa[j]], j=1..120)];
```

Now `pointplot` can be called, and displayed (but not shown here) to assure correctness. Then, the plot structure can be assigned. To accentuate the differences, the line `style = lines` is not used.

```
> Concentration:= plots[pointplot](pH_conc, color = "DarkRed",
    axes = boxed, labels = ["mL[MOH]", "pH"]): Activity:= plots
    [pointplot](pH_act, color = "DarkBlue", axes = boxed, labels =
    ["mL[MOH]", "pH"]):
> plots[display]({Concentration, Activity});
```

The answer to the ionic strength effects question is clear: the effects are minimal! The two plots, despite an ionic strength of about 0.25, are nearly identical, and given that *location* of the equivalence point is the primary function of the titration plot, this precaution is unnecessary. In Chapter 8 we will begin dealing with divalent and trivalent anions, and there activity coefficients change dramatically with increasing ionic strength. (*Cf.* Figure 2-5.)

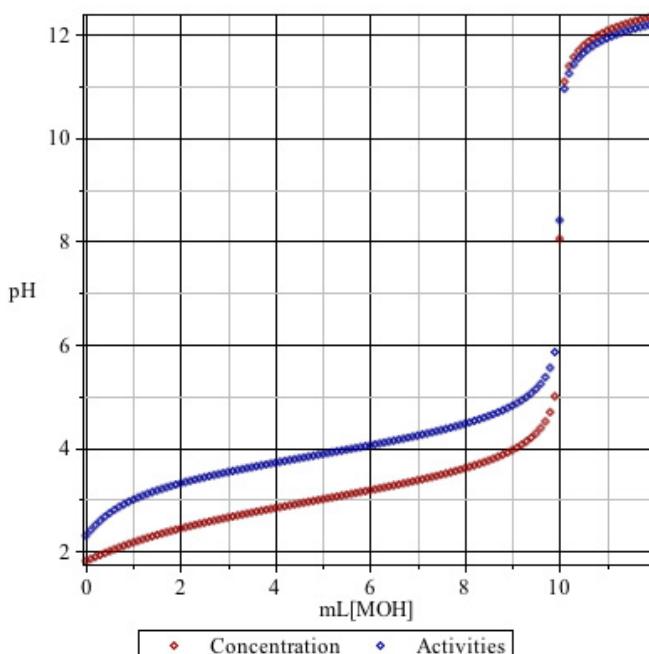


Figure 7-6

### Example Problems

1. Use the cubic polynomial to calculate the pH at, and 1% *before*, the equivalence point, and select a suitable indicator for the following titrations. Also, comment on the completeness of each titration at the equivalence point.
  - a) 10.00 mL of 0.110 M Formic Acid with 0.150 M NaOH.
  - b) 5.00 mL of 0.166 M NH<sub>3</sub>(aq) with 0.106 M HCl.
2. Calculate the titration error in Problem 1a presuming that the Bromothymol Blue endpoint is at pH 7.60.
3. Use the cubic polynomial to recreate the point that was made with Figure 7-3. That is, the perils of titrating a very weak acid with a strong base. Again, take C°<sub>MOH</sub> and C°<sub>HA</sub> to be 0.050 M; V°<sub>HA</sub> = 25.00 mL. Use K<sub>a</sub> = 10<sup>-4</sup>, 10<sup>-6</sup>, 10<sup>-8</sup> and 10<sup>-10</sup>.

Be aware that `pointplot` will be necessary to accumulate the roots of the cubic polynomial and that `plots[display]` will be necessary to consolidate the four plots.

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4. It was illustrated in this chapter that a small equivalence point concentration,  $C^*$ , leads to an ambiguous endpoint, especially for weak acid or weak base titrations. With these titrations, it becomes difficult to achieve  $\alpha_{A^-}$  or  $\alpha_{BH^+} \geq 0.999$ , respectively. Create a plot that illustrates the  $C^*$  necessary to achieve an  $\alpha = 0.999$  for a given  $K_a$ . (A log / log plot is most suitable here.)
5. Consider the titration of trimethylamine in acetonitrile using perchloric acid as a titrant. Perchloric acid is chosen because, even in acetonitrile, it completely dissociates ( $> 99.9\%$  to  $H^+ + ClO_4^-$ ). Trimethylamine is like one of the “excessively” weak bases depicted in Figure 7-4. Its  $pK_a$  in water is 9.8, but because acetonitrile suppresses ion formation, its  $pK_a = 17.6$  in acetonitrile.<sup>150</sup> Create a plot for the titration of 10.00 mL of 0.010 M  $(CH_3)_3N$  with 0.010 M  $HClO_4$ .

Because this problem is a considerable deviation from what has been presented so far, a few hints are offered here. In the absence of water,<sup>151</sup> there is no  $[OH^-]$  and  $K_w$  is irrelevant. Acetonitrile has an autoprotolysis<sup>152</sup> constant for:



equal to  $2.51 \cdot 10^{-29}$ . This is fourteen orders of magnitude smaller than that of water, and it means that the pH range for non aqueous solutions of acetonitrile, is 0 to about 29. (For aqueous solutions it is around 0 to 15.) The charge balance for this titration should be

$$[H^+] + [BH^+] = [A^-] + [CH_2CN^-].$$

And as we expressed  $[OH^-]$  as  $K_w/[H^+]$  in aqueous solutions, here we would express  $[CH_2CN^-]$  as  $K_{AN}/[H^+]$ . Because HA is a strong acid,  $[A^-] = C_{HA}$ , and it should be clear that  $BH^+$  (*i.e.*  $(CH_3)_3NH^+$ ) would be  $\alpha_{BH^+} \times C_B$ . These substitutions lead to a cubic polynomial similar to what has been derived (*e.g.* page 179 *et seq.*), but the  $K_{AN}/[H^+]$  term here is spectacularly small; so small that it is necessary *only* where  $V_{HA} < 2 \cdot 10^{-3}$  mL. At  $V_{HA} = 0$ ,  $C_{HA} = 0$  and so  $[H^+] + [BH^+] = 0$ , and because  $[BH^+] \geq 0$ ,  $[H^+]$  also must be  $\leq 0$  *if the  $K_{AN}/[H^+]$  term is omitted*. This cannot be correct.

There are several options to creating this titration plot. One might use the cubic polynomial and from it find the  $[H^+] > 0$  root for all  $V_{HA}$  through and beyond the equivalence point. Alternatively, one could drop the  $K_{AN}/[H^+]$  term and create the plot from the quadratic that this produces, and to avoid the  $V_{HA} = 0$  problem, the titration plot could be started at  $V_{HA} = 10^{-6}$ , or use the cubic polynomial to calculate the pH at  $V_{HA} = 0$ . The latter is the simpler approach.

6. As a precursor to Chapter 8, create a titration plot for the titration of 10.00 mL of 0.111 M HAa and 0.122 M HAb with 0.100 M strong base MOH. Take the  $pK_a$  for HAa to be 3.55, and the  $pK_a$  for HAb to be 5.85.

### Solutions to Example Problems

- We will create the familiar cubic polynomial using more specific notations for the various ions. Output is minimized for the first command.

```
> restart; Na:= C[NaOH]: For:= C[HFor]*K[a]/(H + K[a]): OH:=
  K[w]/H: ChBal:= H + Na = For + OH;
> C[NaOH]:= V[NaOH]*C°[NaOH]/(V[NaOH] + V°[HFor]):C[HFor]:= 
  V°[HFor]*C°[HFor]/(V[NaOH] + V°[HFor]): ChBal;
```

$$H + \frac{V_{NaOH} C^°_{NaOH}}{V_{NaOH} + V^°_{HFor}} = \frac{V^°_{HFor} C^°_{HFor} K_a}{(V_{NaOH} + V^°_{HFor})(H + K_a)} + \frac{K_w}{H}$$

The output is shown to confirm that the expression is in terms of only the parameters and  $V_{NaOH}$ . Now these parameters can be assigned values and a solution to the cubic polynomial at the equivalence point volume can be sought. The equivalence point volume is calculated from Equation 7-3.

```
> V°[HFor]:= 10.00: C°[HFor]:= 0.110: C°[NaOH]:= 0.150:
  V[NaOH]:= C°[HFor] * V°[HFor]/C°[NaOH];
```

$$V_{NaOH} := 7.333$$

$K_a$  for formic acid is found from Appendix IV, and  $K_w$  from Appendix III.

```
> K[a]:= 10^(-3.751): K[w]:= 1.01E-14: Heqpt:=
  fsolve(ChBal, {H}, 0..1E-5);
```

$$Heqpt := 5.306 \cdot 10^{-9}$$

```
> pHeqpt:= -log[10](Heqpt); alpha[Formate]:= K[a]/(Heqpt +
  K[a]);
```

$$\begin{aligned} pH_{eqpt} &:= 8.27519 \\ \alpha_{Formate} &:= 0.99997 \end{aligned}$$

$\alpha_{\text{Formate}} = 0.99997$  tells us that at the equivalence point the formic acid is sufficiently deprotonated. This also predicts minimal buffer capacity at this point; that is a significant  $\Delta \text{pH} / \Delta V$ , but more reliably, we can compute the pH at  $V_{\text{NaOH}} \approx V_{\text{eqpt}}$ . This is the point of the calculation of the pH, 1% before the equivalence point.

```
> V[NaOH] := 0.99*V[NaOH]; H99:= solve(ChBal, {H});
```

```
VNaOH := 7.260
H99 := 0.000
```

Reformatting the output from the menu shows that  $[\text{H}^+]$  at 7.260 mL of NaOH is  $1.79 \cdot 10^{-6}$ , but rather than carry out this reformatting, we might simply take the base ten log of the apparent 0.000 M

```
> pH99:= -log[10](H99);
```

```
pH99 := 5.748
```

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A  $\Delta\text{pH}$  of  $8.275 - 5.748 = 2.527$  within 1% of the equivalence implies a clear indication of the equivalence point, and there should be a significant color change with an indicator with the proper  $K_{\text{In}}$ . This indicator should be 90.9% deprotonated at the equivalence point. So:

```
> pK[In]:= evalf(-log[10](solve(0.909 =K[In] / (Heqpt +
K[In]))));
```

$$pK_{\text{In}} := 7.276$$

Appendix V provides that Bromothymol Blue is close to perfect although the prescribed pH = 7.6 for a complete change to blue would be premature. But given that at 1% premature the pH99 = 5.7, the endpoint would be much less than 1% early. (See Problem 2 below.)

b. Again a cubic polynomial will be derived to describe the charge balance, and again output is minimal until it becomes interesting.

```
> restart; NH4:= C[NH3]*K[a]/(H + K[a]): Cl:= C[HCl]: OH:=
K[w]/H: ChBal:= H + NH4 = Cl + OH;
```

```
> C[NH3]:= V°[NH3]*C°[NH3]/(V°[NH3] + V[HCl]): C[HCl]:= 
V[HCl]*C°[HCl]/(V°[NH3] + V[HCl]): ChBal;
```

$$\begin{aligned} H + \frac{V^{\circ}_{\text{NH3}} C^{\circ}_{\text{NH3}} K_a}{(V^{\circ}_{\text{NH3}} + V_{\text{HCl}})(H + K_a)} \\ = \frac{V_{\text{HCl}} C^{\circ}_{\text{HCl}}}{V^{\circ}_{\text{NH3}} + V_{\text{HCl}}} + \frac{K_w}{H} \end{aligned}$$

```
> V°[NH3]:= 5.00: C°[NH3]:= 0.166: C°[HCl]:= 0.106: V[HCl]:= 
C°[NH3]*V°[NH3]/C°[HCl];
```

$$V_{\text{HCl}} := 7.830$$

```
> K[a]:= 10^(-9.24): K[w]:= 1.01E-14: Heqpt:= fsolve(ChBal,
H, 0..1);
```

$$Heqpt := 0.065$$

Again,  $K_a$  is found from Appendix IV.

```
> pHEqpt := -log[10](HEqpt); alpha[Ammonium] := HEqpt / (HEqpt + K[a]);
```

$$\begin{aligned} pHeqpt &:= 1.189 \\ a_{\text{Ammonium}} &:= 1.000 \end{aligned}$$

Although this  $\alpha_{\text{Ammonium}}$  implies little buffer capacity and that would suggest a dramatic  $\Delta\text{pH}/\Delta V$  at the equivalence point, the pH at 99% of  $V_{\text{EqPt}}$  disproves that.

```
> V[HCl] := 0.99*V[HCl]; H99 := fsolve(ChBal, H)153; pH99 := -log[10](H99);
```

$$\begin{aligned} V_{\text{HCl}} &:= 7.752 \\ H99 &:= 0.064 \\ pH99 &:= 1.191 \end{aligned}$$

This is not a satisfactory  $\Delta\text{pH}$ : the issue is that the plateau approaching the equivalence point is so low, that there is not enough “room” to effect a large  $\Delta\text{pH}$ .<sup>154</sup> This was seen in Figure 7-4; this problem is a recreation of the  $K_b = 10^{-8}$  graph.

Despite this unsatisfactory  $\Delta\text{pH}$ , an indicator can be selected. Because the titrant is an acid, the endpoint will be evident when  $\alpha_{\text{HIn}} \geq 0.909$ .

```
> pK[In] := evalf(-log[10](solve(0.909 = HEqpt / (HEqpt + K[In]))));
```

$$pK_{\text{In}} := 2.189$$

Appendix V suggests Tropeoline OO, but still the  $\Delta\text{pH}/\Delta V$  suggests a poorly resolved endpoint!

- What follows might easily have been part of the worksheet for Problem 1a, but for clarity, we start fresh:

```
> restart; Na := C[NaOH]: For := C[HFor]*K[a]/(H + K[a]): OH := K[w]/H: C[NaOH] := V[NaOH]*C°[NaOH] / (V[NaOH] + V°[HFor]): C[HFor] := V°[HFor]*C°[HFor] / (V[NaOH] + V°[HFor]): ChBal := H + Na = For + OH;
```

$$\begin{aligned} ChBal &:= H + \frac{V_{NaOH} C^o_{NaOH}}{V_{NaOH} + V^o_{HFor}} \\ &= \frac{V^o_{HFor} C^o_{HFor} K_a}{(V_{NaOH} + V^o_{HFor})(H + K_a)} + \frac{K_w}{H} \end{aligned}$$

Several commands from Problem 1a are combined into one input line above. We now have only to assign values to all of the constants. But for this problem,  $V_{NaOH}$  is *unknown* and  $[H^+]$  is known ( $10^{-7.60}$ ).

```
> V°[HFor]:= 10.00: C°[HFor]:= 0.110: C°[NaOH]:= 0.150: H:=
10^
(-7.60); K[a]:= 10^(-3.751): K[w]:= 1.01E-14: ChBal;
```

$$\begin{aligned} &2.512 \cdot 10^{-8} + \frac{0.150 V_{NaOH}}{V_{NaOH} + 10.000} \\ &= \frac{1.100}{V_{NaOH} + 10.000} + 4.021 \cdot 10^{-7} \end{aligned}$$



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Appropriately, we have an expression with only  $V_{NaOH}$  as the unknown. This is the  $V_{NaOH}$  necessary to give the pH = 7.60 endpoint.

```
> V[EndPoint]:= solve(ChBal);
```

$$V_{EndPoint} := 7.332$$

Recall:

```
> V[EqPt]:= C°[HFor]*V°[HFor]/C°[NaOH];
```

$$V_{EqPt} := 7.333$$

and from page 172:

```
> Error:= V[EndPoint] - V[EqPt]; RelError:= 100*abs(Error) / V[EqPt];
```

$$Error := -0.001 \text{ (mL)}$$

$$RelError := 0.014 \text{ (%)}$$

3. The common output is not provided here even though the input uses a semicolon. Notice the similarity to Problem 1a at the onset, but then the cubic polynomial is formatted to its conventional  $aH^3 + bH^2 + cH + d$  form. This is because in its “native” form, `fsubsolve` is unable to extract a legitimate root for  $K_a = 10^{-10}$ . While `solve` might have been used followed by the selection of the appropriate root, as in Problem 1a, here, this alternate approach is used.

```
> restart: M:= C[MOH]: A:= C[HA]*K[a]/(H + K[a]): OH:=
K[w]/H: ChBal:= H + M = A + OH:
> C[MOH]:= V[MOH]*C°[MOH]/(V[MOH] + V°[HA]): C[HA]:= V°[HA]
*C°[HA]/(V[MOH] + V°[HA]); ChBal;
> ChBal:= simplify(H*(V[MOH] + V°[HA])*(H + K[a])*ChBal);
> ChBal:= collect((lhs(ChBal) - rhs(ChBal)), H);
```

$$\begin{aligned} ChBal &:= (V_{MOH} + V^°_{HA}) H^3 + (V_{MOH} C^°_{MOH} + (V_{MOH} + V^°_{HA}) K_a) H^2 \\ &\quad + (V_{MOH} C^°_{MOH} K_a - K_w V^°_{HA} - K_w V_{MOH} - V^°_{HA} C^°_{HA} K_a) H \\ &\quad - K_w V_{MOH} K_a - K_w V^°_{HA} K_a \end{aligned}$$

```
> C°[MOH]:= 0.050: C°[HA]:= 0.050: V°[HA]:= 25.00: K[w]:= 1.01E-14: ChBal_4:= subs(K[a]=1E-4,ChBal); ChBal_6:= subs(K[a]=1E-6,ChBal); ChBal_8:= subs(K[a]= 1E-8,ChBal); ChBal_10:= subs(K[a] = 1E-10,ChBal); Hmax := 0.05: V[MOH]:=0:
```

$$\begin{aligned} \text{ChBal\_4} &:= (V_{\text{MOH}} + 25.00000) H^3 + (0.05010 V_{\text{MOH}} \\ &\quad + 0.00250) H^2 + (0.00000 V_{\text{MOH}} - 0.00013) H \\ &\quad - 1.01000 10^{-18} V_{\text{MOH}} - 2.52500 10^{-17} \end{aligned}$$

After the parameters are assigned, only `ChBal_4` is shown. An `Hmax` is assigned ( $= C_{\text{HA}}$ ) which will narrow the search for the floating point calculation of the only physically real root, and then  $V_{\text{MOH}}$  is assigned 0 mL to begin the loop. It is prudent to insert `Test:= fsolve(ChBal_4, H, 0..Hmax);` to see if a root can be found. The other three charge balance expressions are trivial modifications of `ChBal_4`.

And now for the loop. Here we will use 275 cycles, incrementing  $V_{\text{MOH}}$  by 0.1 mL each time through the loop. Again, the pH will be directly calculated from the `fsolve` output. Here we add a new feature: the range over which `fsolve` searches is steadily narrowed as each increment of  $V_{\text{MOH}}$  produces a smaller and smaller  $[\text{H}^+]$  (higher and higher pH). Setting `Hmax` equal to the previous  $[\text{H}^+]$  accomplishes this.

```
> for i to 275 do
> pH4[i]:= -log[10](fsolve(ChBal_4,H, 0.. Hmax)); pH6[i]:= -log [10](fsolve(ChBal_6, H, 0..Hmax)): pH8[i]:= -log[10](fsolve(ChBal_8, H, 0..Hmax)): pH10[i]:= -log[10](fsolve(ChBal_10, H, 0..Hmax)): V[i]:= V[MOH]:
> V[MOH]:= V[MOH] + 0.10: Hmax:= 10^(-pH4[i]):
> end:
```

We might pause here to inspect some of the computations near the equivalence point. These are tabulated for clarity.

```
> V[249]; pH4[249]; pH6[249]; pH8[249]; pH10[249];
> V[250]; pH4[250]; pH6[250]; pH8[250]; pH10[250];
> V[251]; pH4[251]; pH6[251]; pH8[251]; pH10[251];
> V[252]; pH4[252]; pH6[252]; pH8[252]; pH10[252];
```

V <sub>MOH</sub>	pH4	pH6	pH8	pH10
24.80	6.095	8.091	9.935	11.155
24.90	6.398	8.386	10.060	11.169
25.00	8.198	9.197	10.195	11.183
25.10	9.995	10.005	10.330	11.197

Even without the titration plots, the quality of these titrations is clear: with  $pK_a \geq 8$ , the  $\Delta pH/\Delta V$  is not satisfactory. But we continue by creating sequences of the four sets of computations, avoiding the semicolon terminator.

```
> pH_4:= [seq([V[i], pH4[i]], i = 1..275)]:  
pH_6:= [seq([V[i], pH6[i]], i= 1..275)]: pH_8:=  
[seq([V[i],pH8[i]]], i= 1..275)]: pH_10:= [seq([V[i],  
pH10[i]], i= 1..275)]:
```

Here we might peek at what we are creating by plotting just one of the sequences.

```
> plots[pointplot](pH_4, style = line, color = "DarkRed",  
axes = boxed, labels = ["mL[MOH]", "pH"]);
```

"I studied English for 16 years but...  
...I finally learned to speak it in just six lessons"  
Jane, Chinese architect

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The plot is not shown here, but because it is precisely what was desired, all four sequences can be expressed as plot structures. Recall that it is *not* necessary to include all the options in all four structures. This is because the options of the first structure are carried into every structure in the composite plot. A few new colors are added, and because these are strings, quotation marks are required. The output is of little use, although one is shown.

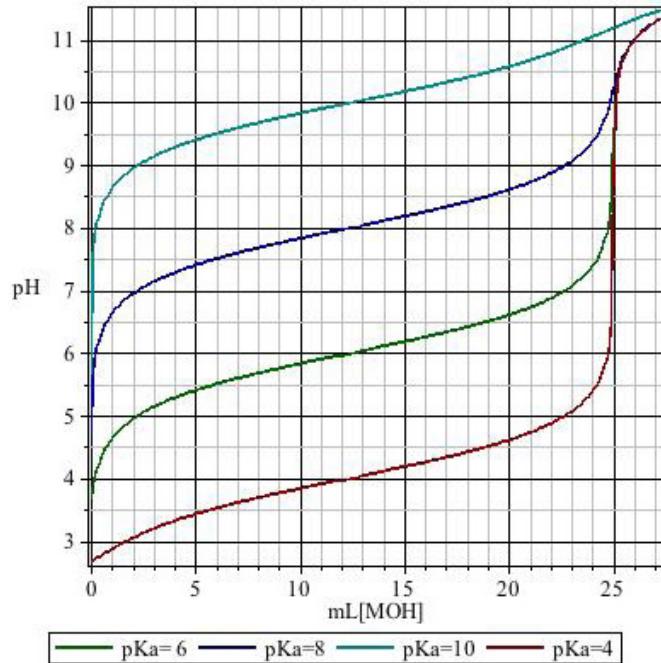
```
> pKa4:= plots[pointplot](pH_4, style = line, color =
  "DarkRed", axes = boxed, labels = ["mL[MOH]", "pH"]);
pKa6:= plots [pointplot]
(pH_6, style = line, color = "DarkGreen"): pKa8:=
plots[pointplot] (pH_8, style = line, color = "DarkBlue"):
pKa10:= plots [pointplot](pH_10, style = line, color =
"DarkCyan"):

pKa4:= PLOT(...)
```

*etc.*

Finally:

```
> plots[display]({pKa4, pKa6, pKa8, pKa10});
```



**Figure 7-7**

It should be clear that the titration of HA with  $pK_a = 8$  would be difficult and at  $pK_a = 10$ , impossible.

4. Recall that at the equivalence point,  $C_{\text{Acid}} = C_{\text{Base}}$ . We will arbitrarily choose to presume that MOH is a strong base and that HA is a weak acid. Our requirement is therefore that  $\alpha_{A^-} = 0.999$ . It was shown earlier that this puts  $[H^+]$  at  $0.001K_a$  (shown in the first line).

```
> restart; alpha[A]:= 0.999; H:= solve(alpha[A] = K[a]/(H + K[a]), H);
```

$$H := 0.001K_a$$

```
> K[a]:=10^(-pKa); C[MOH]:= C[EqPt]; C[HA]:= C[EqPt]; M:=
C[MOH]; A:= alpha[A]*C[HA]; K[w]:= 1.01E-14; OH:= K[w]/H;
ChBal:= H + M = A + K[w]/H;
```

$$\begin{aligned} ChBal &:= 0.001 \cdot 10^{-pKa} + C_{EqPt} = 0.999 C_{EqPt} \\ &\quad + \frac{1.009 \cdot 10^{-11}}{10^{-pKa}} \end{aligned}$$

```
> C[EqPt]:= solve(ChBal, C[EqPt]); log_C:= log[10](C[EqPt]);
```

$$\begin{aligned} C_{EqPt} &:= -\frac{1}{10.000^{-1.000 pKa}} \left( 7.000 \cdot 10^{-32} \left( -1.441 \cdot 10^{23} + 1.430 \cdot 10^{31} \left( 10.000^{-1.000 pKa} \right)^2 \right) \right) \\ log\_C &:= \frac{1}{\ln(10)} \left( \ln \left( -\frac{1}{10.000^{-1.000 pKa}} \left( 7.000 \cdot 10^{-32} \left( -1.441 \cdot 10^{23} + 1.430 \cdot 10^{31} \left( 10.000^{-1.000 pKa} \right)^2 \right) \right) \right) \right) \end{aligned}$$

This second step expresses  $C_{\text{EqPt}}$  on a logarithmic scale. And finally, for the plot of the expression. Notice a complete use of defaults (color, axes *etc.*) but the post rendering addition of gridlines.

```
> plot(log_C, pKa = 2..10,
labels = ["pK[a]", "log(C[EqPt])"]);
```

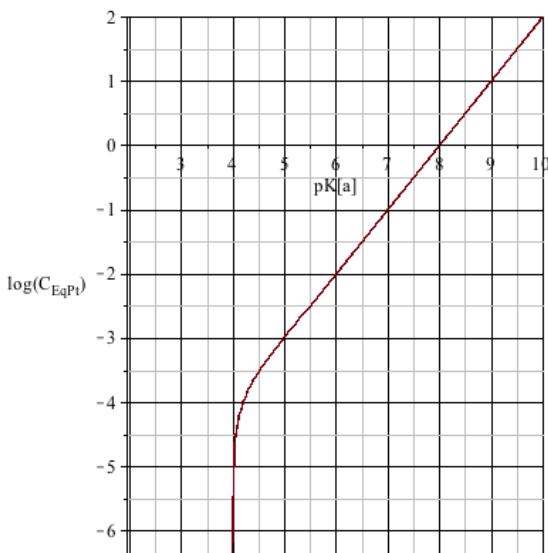


Figure 7-8

This plot shows that when  $pK_a$  is *less* than about 4, the acid is sufficiently strong that it can be deprotonated by any concentration of strong base. This is somewhat a compliment to the discussion on page 78 regarding the dissociation of weak acids as a function of  $C_{HA}$ . When an acid's  $pK_a$  exceeds about 8, the *required* equivalence point concentration of strong base is about  $10^0 = 1.0 \text{ M}$ . A little exploration of Equation 7-10 will reveal that  $C^\circ$  must be less than either  $C^\circ$ . So  $C^\circ_{HA}$  would have to exceed  $1.0 \text{ M}$ , and exceed it considerably unless  $C^\circ_{MOH}$  is  $\gg 1.0 \text{ M}$ .

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5. We will use only the cubic expression for charge balance.

```
> restart; C[B]:= C°[B]*V°[B] / (V°[B] + V[HA]): C[HA]:= C°[HA]* V[HA] / (V°[B] + V[HA]): BH:= C[B]*H/(K[a] + H): A:= C[HA]: CH2CN:= K[AN]/H: ChBal:= H + BH = A + CH2CN;
```

$$\begin{aligned} ChBal &:= H + \frac{C_B V_B H}{(V_B + V_{HA})(K_a + H)} \\ &= \frac{C_{HA} V_{HA}}{V_B + V_{HA}} + \frac{K_{AN}}{H} \end{aligned}$$

Now for the assignment of constants. It would be found that `fsolve` cannot find roots between about 9.8 and 10.0 mL. So we will use `solve` directly and choose the appropriate root.

```
> C°[B]:= 0.010: C°[HA]:= 0.010: V°[B]:= 10.00: V[HA]:= 0.00: K[a]:= 10^(-17.6): K[AN]:= 2.51E-29: Rts:= solve(ChBal, {H});
```

```
Rts := {H = 7.940 10⁻²³}, {H = -7.940 10⁻²³}, {H = -0.010}
```

The first root is what we will need. So

```
> for i to 300 do
> Rts:= solve(ChBal, {H}): H[i]:= subs(Rts[1], H):
pH[i]:= -log[10](H[i]);
> V[i]:= V[HA]: V[HA]:= V[HA] + 0.04:
> end:
```

We will name the sequence of data points for point plotting.

```
> Results:=[seq([V[i], pH[i]], i= 0..300)]:
```

Before plotting the results, we might inspect a few interesting points.

```
> V[1], pH[1]; V[251], pH[251];
```

```
0.000, 22.100
10.000, 9.951
```

```
> plot(Results, axes = boxed, labels = ["mL[HA]", "pH"]);
```

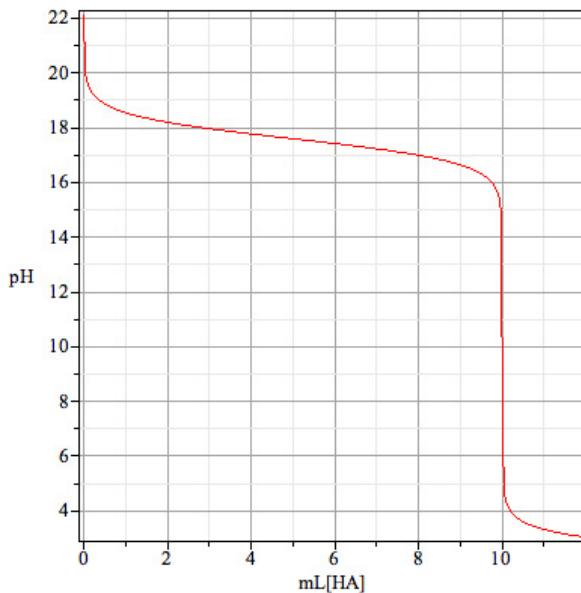


Figure 7-9

The  $\frac{\Delta \text{pH}}{\Delta V}$  at the equivalence point is spectacular. So recognizing the equivalence point with an acid / base indicator should be trivial, but the indicator selection cannot be made from Appendix V because not only do  $K_a$ 's change in acetonitrile, so do  $K_{in}$ 's. The  $pK_{in}$  for several indicator in acetonitrile have been tabulated by Koltoff *et al.* (*Anal. Chem.*, **39** (1967) 315–320).

6. We begin with the charge balance expression noting here that there are three anions,  $Aa^-$ ,  $Ab^-$ , and of course  $OH^-$ , and that the first two are tied to independent C's and  $K_a$ 's.

```
> restart; C[HAa]:= V° [HA]*C° [HAa] / (V° [HA] + V[MOH]):  
C[HAb]:= V° [HA]*C° [HAb] / (V° [HA] + V[MOH]): C[MOH]:=  
V[MOH]*C° [MOH] / (V° [HA] + V[MOH]): K[aa]:= 10^(-pKaa):  
K[ab]:= 10^(-pKab): Aa:= C[HAa]*K[aa] / (H + K[aa]): Ab:=  
C[HAb]*K[ab] / (H + K[ab]); OH:= K[w]/H: M:= C[MOH]: ChBal:=  
H + M = Aa + Ab + OH;
```

$$Ab := \frac{V_{HA}^{\circ} C_{HAb}^{\circ} 10^{-pKab}}{(V_{HA}^{\circ} + V_{MOH}) (H + 10^{-pKab})}$$

$$\begin{aligned} ChBal &:= H + \frac{V_{MOH} C_{MOH}^{\circ}}{V_{HA}^{\circ} + V_{MOH}} \\ &= \frac{V_{HA}^{\circ} C_{HAa}^{\circ} K_{aa}}{(V_{HA}^{\circ} + V_{MOH}) (H + K_{aa})} \\ &\quad + \frac{V_{HA}^{\circ} C_{HAb}^{\circ} K_{ab}}{(V_{HA}^{\circ} + V_{MOH}) (H + K_{ab})} + \frac{K_w}{H} \end{aligned}$$

Notice the order in which the assignments are made; with this order, each successive assignment is incorporated.  $[Ab^-]$  is shown to illustrate its difference from the way  $[A^-]$  has been expressed.  $V_{HA}^o$  represents the mixture of HAa and HAb.

```
> V°[HA]:= 10.00: C°[HAa]:= 0.111: C°[HAb]:= 0.122: K[aa] :=  
10^(-3.55): K[ab]:= 10^(-5.85): K[w]:= 1.01E-14: C°[MOH]:=  
0.100: V[MOH]:= 0.00: ChBal;
```

$$H = \frac{0.000}{H + 0.000} + \frac{1.723 \cdot 10^{-7}}{H + 0.000} + \frac{1.010 \cdot 10^{-14}}{H}$$

Appropriately, the charge balance expression contains only one unknown,  $[H^+]$ . After assigning values to the constants, and setting  $V_{MOH}$  to 0, we will see if Maple can extract an  $[H^+] > 0$  root from this quadric polynomial, if not with `fsolve`, then with `solve`.

```
> fsolve(ChBal, H, 0..0.1); solve(ChBal, {H});
```

```
0.005  
{H = 0.005}, {H = -4.335 10^-14}, {H = -0.000}, {H = -0.006}
```

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Apparently<sup>155</sup> `fsolve` will do; the `solve` output shows that this is indeed a 4° polynomial (with its four roots), and that only one of the roots has physical meaning. This test of `fsolve` is a false positive, however. When `fsolve` is applied at  $V_{MOH} = 10.9$  mL, a solution is *not* found! Indeed, `fsolve` is “lost” until 23.40 mL of MOH. This is discovered only by creating the sequence of points as described in problem 3 above and displaying it. And so, it will be necessary to use `solve` and select the first root. This output is far too complicated to be displayed.

We can now create a program to generate a pH at each increment of  $V_{MOH}$ . Titration 10.00 mL of 0.111 M HAa and 0.122 M HAb with 0.100 M MOH would require:

$$V^{\#}_{MOH} = \frac{(0.111M + 0.122M)X 10.00 \text{ mL}}{0.100M}$$

= 23.30 mL; 0.10 mL increments to 27 mL should produce a clear plot. `H_roots` represents the four roots found by the `solve` command. Inasmuch as the first root found appears to be the  $[H^+] > 0$  root, that root, `H_root[1]`, will be selected, and the `-log[10]` operation will be performed to give the pH directly.

```
> for i to 270 do
> H_roots:= solve(ChBal,{H}): pH[i]:= -log[10](subs(H_
roots[1], H)): V[i]:= V[MOH]:V[MOH]:= V[MOH] + 0.1: end:
```

The 270 ordered pairs are now sequenced for plotting on `pointplots`, and the plot is rendered.

```
> Results:=[seq([V[i],pH[i]],i= 1..270)]:
> plots[pointplot](Results,axes = boxed,labels = ["mL[MOH]",
"pH"]);
```

The line and color options are not included here. This will show the pH plot as black, open circle points, the default `pointplot`.

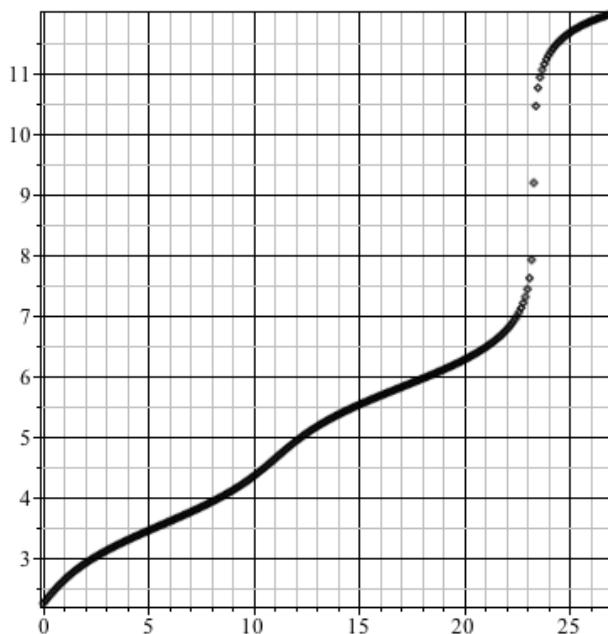


Figure 7-10

The ambiguous equivalence point for the titration of H<sub>AA</sub>, the stronger of the two acids is a result of the buffer capacity at the equivalence point pH. This buffer capacity is due to the appreciable fraction of H<sub>Ab</sub> and A<sup>-</sup>. Consider:

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```
> pHeqpt:= 4.5: alpha["Aa"]:= 10^(-pKaa)/(10^(-pHeqpt) +  
10^(-pKaa)); alpha["Ab"]:= 10^(-pKab)/(10^(-pHeqpt) + 10^(-  
pKab));
```

$$\alpha_{\text{Aa}} := 0.899$$

$$\alpha_{\text{Ab}} := 0.043$$

What has likely happened here is that the MOH has begun to remove protons from HAb before completely (or at least 99.9%) removing protons from HAa. Had pKab – pKaa been greater than 3, the first equivalence point would have been sharper. This issue will be addressed in the next chapter.

# Endnotes for Part I

1. Although Butler's book (Addison-Wesley, 1964) was preceded by and has been followed by many excellent texts on the subject, it is unlikely that a better book will ever be published.
2. For gas phase reactions the reaction quotient is often estimated by expressing reactants and products in terms of partial pressures. This aspect of chemical equilibrium will not be addressed because it has no relevance to ionic equilibrium.
3. It is not a constant like Faraday's constant or  $\pi$  because it changes with conditions such as temperature. Chapter 2 addresses the approximate nature of  $K_{eq}$  in detail.
4. An example would be the analysis of a solution of unknown  $\text{Cl}^-$  concentration. An excess of  $\text{Ag}^+$  is added, and the resulting  $\text{AgCl}$  precipitate is weighed. From the mass of  $\text{AgCl}$ , we know the number of moles of  $\text{AgCl}$  and so the number of moles (and mass) of  $\text{Cl}^-$  in the solution.
5. Because the charge must balance, at least two agents must carry a charge in order to constitute an ionic reaction. So, although  $z$  can be any integer including zero,  $z_A$  and  $z_B$  cannot both equal zero. We could have been more specific, for example, and written:  $\text{A}^{2+} + \text{B}^{3-} \rightleftharpoons \text{C}^{1-}$
6. Some of that work has been to correlate molality (moles of solute per kg of solvent) to activity, but the more relevant correlation for equilibrium calculations is between molarity and activity.
7. "log" implies a base ten logarithm. The original form of the Debye-Hückel equation is equation 2-4 without its denominator.
8. This might seem uselessly restrictive, but recognize that the purpose of the activity coefficient is to provide corrections to equilibrium constants; that equilibrium constants change with temperature and solvent; and that most published values for  $K_{eq}$  are for aqueous solutions at 25°C. So with  $K_{eq}$  limited to aqueous solutions at 25°C there is no disadvantage to limiting the equation to these same conditions! Values for A and B in aqueous solution at other temperatures are provided in Appendix I.
9. Davies, C.W., *Ion Association*, Butterworths, London, 1962, p. 41.
10.  $:=$  is the assignment operator and is not to be confused with  $=$ . Consider that  $x = 2*x$  is possible only when  $x = 0$ , but as long as  $x$  has been assigned a value,  $x := 2*x$  instructs Maple to double that previously defined value for  $x$ .
11. An aside here: typing "m" with the [alt] key depressed will directly display the Greek m which is  $\mu$ . But entering "mu" will also give  $\mu$  as an output! Maple, however, treats these entries as different inputs. So choose one method and stay with it.
12. The [ENTER] key can also be used.
13. From this point forward the [RETURN] key operation will not be indicated, but it is required at the end of each input paragraph. That is, after the last colon or semicolon following its input prompt >.

14. From this point on, the output line number will not be displayed. The line number is a useful attribute that will be used later. Equation labels can be disabled in the **Preferences** page as seen in Figure 2-3.
15. In the *document* mode,  $2x$  is taken as  $2*x$ , although  $x2$  is not.
16. Not to be confused with `mu := 'mu'` which would have *unassigned* the 0.07500000000 just determined for  $\mu$ .
17. Notice that Maple does not express  $\gamma$  as a power of 10: it uses  $e$  for exponential functions.
18. One can list expressions to be plotted in braces, {}, but cannot list colors in braces.
19. This is called the Point Probe. This “manipulator” can be changed to a tool that one can use to pan (Pan) or to re-scale (Scale) the plot, or to rotate 3D plots. From the menu at the top of the screen, pull down **Plot**, slide down to **Manipulator** and from there slide over to the available modes. Note that within the **Plot** menu, there are more than a dozen other adjustments that can be made to the plot.
20. This is not to be confused with the  $\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \text{AgCl}(s)$  precipitation reaction.
21. The  $^\circ$  in `K° [eq]` is achieved on some platforms (e.g. Macintosh) by using the [SHIFT] [OPTION][8] keys. In some examples we will use a subscript o such as  $K[o]$  to denote thermodynamic equilibrium constants.
22. The grid lines can be added after the plot is produced by activating the plot menu as described on the previous page and clicking on the grid-like icon.
23. Notice how the use of brackets within brackets, [[]], produces subscripts within subscripts in the output. These multiple brackets cannot be used throughout the subscript. For example  $[\text{Na}[2]\text{SO}[4]]$  will not work!
24. By cutting and pasting, if you will.
25. Notice the appearance of  $\mu$  in place of mu. When “mu” is entered, Maple returns  $\mu$ , but recall that  $\mu$  can be entered directly by using the [OPTION][m] keys.
26. This does not mean that a new worksheet must be created. Beginning the next input paragraph with `restart:` is sufficient. Moreover, this strategy does not preclude the use of the cut and paste commands from earlier inputs to save typing (and minimize errors).
27. `Factor` would have been the logical designation but it is protected by Maple because it is a command.
28. Be careful with this “post output numeric formatting”: it can cause Maple to suppress the text portion of the output. So, for example `x := 6` becomes `6`, and **this cannot be reversed** without opening a new worksheet altogether!
29. Unless specified otherwise, the solvent is water at 25°C. See Example Problem 5 in Chapter 7 for an example of non-aqueous equilibrium.
30. `Totally` is in quotes because dissociation is never quite total. See S.J. Hawkes, *J. Chem. Ed.*, **73**, 421–2 (1996).

31.  $\text{H}^+$  would certainly seem to violate this principal because the charge density of  $\text{H}^+$  (a bare proton) would be spectacularly large. However, in aqueous solutions,  $\text{H}^+$  is *entirely* hydrated and exists primarily as  $\text{H}_3\text{O}^+$  with some higher levels of hydration like  $\text{H}_5\text{O}_2^+$ .
32. Insoluble implies  $< 0.005 \text{ M}$  at  $\mu < 0.01$ ; slightly soluble implies  $> 0.005 \text{ M} < 0.05 \text{ M}$  at  $\mu < 0.01$ .
33. We will soon discover a subtle but important exception to these two mass balance expressions when  $\text{M}^{n+} = \text{H}^+$  or when  $\text{A}^{n-} = \text{OH}^-$ .
34. Known also as autoprotolysis.
35. It will be shown in Chapter 4 that even a *weak* electrolyte like HA can dissociate  $\geq 99.9\%$  in very dilute solutions. It is the ability to dissociate extensively in concentrated solutions that is the mark of a strong electrolyte.
36. pH is only crudely approximated as  $-\log[\text{H}^+]$ . See Hawkes, S.J., *J. Chem. Educ.*, **1994**, 71, 747–749 for details.
37. This is a reasonable presumption, but a presumption nevertheless: It is possible to add another electrolyte to a solution of HA to augment the ionic strength.
38. Values for  $K_w^\circ$  at various temperatures can be found in Appendix III.
39. When an *output* is pasted into an input line (*i.e.* following a  $>$ ), the format is automatically changed into the appropriate text. That is to say, one can drag the cursor over a region of output (*blue text*) cut and then paste that into an input line and get the reformatted input  $>$  *input text*.
40. The **Numeric Formatting** here has been adjusted as described on page 34.
41. The plot shown here was modified as described in Chapter 2 (page 30 *et seq.*) The y axis was labeled from the **Plot > Axes > Edit vertical** menu; the legend (which *not* a title) was added from **Plot > Edit Legend** or  $>$  **Position**; the pH numbering was formatted from **Format > Numeric Formatting...**
42. Of course adding *other* electrolytes that increase  $\mu$  will decrease  $\gamma_{\text{H}^+}$  and make the use of **3-17** or **3-18** inappropriate. Equation **3-16** is the rigorous route because it makes no presumption on the source of ionic strength. See the problems at the end of this chapter.
43. This creates an interesting situation: When the electrolyte concentration becomes substantial and so the ionic strength is substantial, the Davies Equation might be used to find  $\gamma_{\text{H}^+}$  and  $\gamma_{\text{OH}^-}$ . But because the Davies Equation produces  $\gamma_{\text{H}^+} = \gamma_{\text{OH}^-}$ , we are returned to **3-31**.
44. There are effectively four approaches to these problems. They are the combinations of considering or not considering ionic strength and autoprotolysis.
45. On making this cut and paste operation, the **5.678 10<sup>-7</sup>** will automatically transform to **5.6780\*10<sup>(-7)</sup>**.
46. Because  $[\text{OH}^-] = K_w^\circ / [\text{H}^+]$ , **(3-24)**.
47. This will appear to be a contradiction as we proceed to solve for  $[\text{H}^+]$  expressly *not* ignoring the autoprotolysis of water. But this step is to get the total ion concentration and the contribution of ions from the dissociation of water is *nothing* compared to  $C_{\text{HNO}_3}$  and  $C_{\text{KNO}_3}$ .
48. For variety, we have regressed from the **K° [w]** designation to a designation some might prefer.
49. **%%** tells Maple to use the output previous to the last (previous to the previous) output.

50. Maple does *not* allow a direct, floating point evaluation of pH if the argument includes an expression like  $C_{\text{HNO}_3} = 0.55$ . So `evalf(eval...)` is necessary.
51. This is by the Brønsted-Lowrey definition of acid. It defines an acid as an electrolyte that produces a net gain in  $\text{H}^+$ , or more exactly  $\{\text{H}^+\}$ .
52. We will continue to presume that the solvent is water, but HA itself could serve as the solvent for  $\text{H}^+$  and  $\text{A}^-$ . An example is 100%  $\text{H}_2\text{SO}_4$ .
53. One variation is the creation an acid solution with most metallic ions by  $\text{M}^{n+} + \text{H}_2\text{O} \rightleftharpoons \text{MOH}^{n-1} + \text{H}^+$  (where  $n \geq 2$ ). This has an equilibrium constant  $K_h$ ,  $h$  for hydrolysis. Another:  $\text{M}^{n+}$  can also bind to  $\text{OH}^-$  to lower the pH. Cf. Part II page 61.
54. When  $n < 0$ ,  $\text{M}^n$  is an anion, and this situation is effectively the same as treating  $\text{A}^{n-}$  as a base. This is addressed briefly on page 80 (as the conjugate base of HA) and extensively in Chapter 5.
55. The reader is asked to excuse the sudden use of WeakAcid in place of HA. If HA or even 'HA' is used here, it is evaluated in the `HA :=` command in the next input paragraph. That is, the single quotes do *not* protect *all* inputs from being evaluated. This sometimes happens (*cf.* page 64).
56. The `= 0` part of the input is *not* necessary; it is included here partly for clarity and partly out of habit. If this is left off, Maple will presume that the expression equals zero, and solve it accordingly when `solve` or `fsolve` is called.
57. See **Figure 3-1**.
58. One of the physically impossible solutions for  $C_{\text{WeakAcid}} = 0$  is  $-K_a$ . This is a fascinating solution because it contains  $K_a$  but, if there is *no* weak acid in the solution, for *what* weak acid do we find  $K_a$ ?
59. This is an aqueous solution because  $K_w$  is included in the expression. Were it not aqueous, we would include a K appropriate to the solvent's autoprotolysis. (See problem 5, page 194). If that K should be zero, then  $[\text{H}^+] = 0$  becomes possible.
60. That is, a constant,  $K^{\circ a}$ , at a *specific temperature and solvent*, presumably 25°C and presumably water.
61. See Example Problem 2b at the end of this chapter for an example of a "missed" solution.
62. If HF were a strong acid, the root would have been *slightly* larger than  $C_{\text{HF}}$  and the solution would not have been found!
63.  $K = K^{\circ}$  implies that every  $\gamma$  was taken to be exactly 1, but from the resulting  $[\text{H}^+]$  each  $\gamma$  was taken to be 0.8463 and this value was used to calculate the pH.
64. Notice that adding Equations 4-11 and 4-18 gives Equation 4-6.
65. Because  $C_{\text{HF}}$  is so small,  $\mu$  will be negligible and so it will not be necessary to reiterate the calculation of  $[\text{H}^+]$ . This means that  $K_w \approx K^{\circ w}$ , and  $K_a \approx K^{\circ a}$ .
66. An inconvenience is not an insurmountable obstacle: Indeed, one could use mass and charge balance to solve for  $[\text{OH}^-]$  and then convert the solution to  $[\text{H}^+]$  using  $[\text{H}^+] = K_w / [\text{OH}^-]$ .

67. This will entail the following: 1. Replace  $K_w/K_b$  in **4-32** with  $K_a$ . 2. Rearrange this modified **4-32** to express  $[MH^+]$  in terms of  $[M]$ . 3. Use this new expression for  $[MH^+]$  in **4-26** to create a mass balance expression that is exclusively in terms of  $[H^+]$ ,  $K_a$ ,  $C_M$ , and  $[M]$ . 4. Rearrange this mass balance expression to give  $[M]/C_M$  which is equal to  $\alpha_M$ .
68. Appendix IV gives a  $pK_a$  for HCN = 9.21. From Equation **6-7**  $K_a = 10^{-pK_a}$ .
69. This is a good example of the *relative unimportance* of the  $a$  term in Debye-Hückel. Here,  $a_{OH^-}$  is nearly twenty percent larger than  $a_{CN^-}$ , and yet the two  $\gamma$ s differ by only 3 parts in a million!
70. Apparently a second iteration of  $\gamma_{H^+}$  was not necessary since it changed by  $\approx 0.002\%$ , but this is due largely to the very small  $K_a$  for HCN. Because HCN is such a weak acid,  $\mu \approx 0$  even at large  $C_{HCN}$ . Always reiterate at least the activity coefficient for  $H^+$ .
71. If, however, the polynomial had been written in  $ax^3 + bx^2 + cx + d = 0$  form, with or without the  $= 0$ , all three roots would have been returned.
72. This kind of output is often referred to as wallpaper.
73. It is difficult to read this value from the plot, but when  $C_{HA} := 1 \times 10^{-6}$ , K995 returns  $2.04 \times 10^{-4}$ .
74. This is because almost all applications of MHA entail total dissociation to  $MH^+$  and  $A^-$ . It is possible to address this problem with only a *partial* dissociation of MHA by inserting a  $K_{eq}$  for that dissociation. While this is an interesting contingency, it is uncommon and of little, if any, *analytical* utility.
75. The only difference is in the way ionic strength is estimated in the first iteration for  $[H^+]$ . This point is addressed on page 112.
76. Page 80 *et seq.*
77. Not in terms of  $K_b$  because  $K_b$  is typically not provided. See page 82.
78.  $[M^+] = C_{MA}$  because **5-7** lies completely to the right. This is by far the most common situation with salts like MA, and an incompletely dissociated MA is of little analytical utility.
79. The difference lies in the way that ionic strength is calculated. This will be illustrated below.
80. Combining **5-12** and **5-13** shows that  $[MH^+] + [M] = [HA] + [A^-]$  which is interesting but not particularly useful.
81. Recall that the “= 0” is not needed because Maple presumes that an expression is equal to zero *unless otherwise specified*.
82. unless  $C_{MHA}$  is less than about  $10^{-4}$  M.
83. J.N. Butler, *Ionic Equilibrium, a Mathematical Approach*, 1964, Addison-Wesley Publishing Co, Reading, MA. pp 164–165.
84. **5-14** and **5-15** have been modified to comply with the terminology presented here.
85. Recall (page 47) that  $[H^+] = 10^{-7}$  is not a strict definition of neutrality, but it is generally useful (*i.e.* close enough).
86. See Chapter 2. And of course the addition of another strong electrolyte like KCl would further influence  $\mu$ . See problem 3a in this chapter.
87. Because  $a_F = a_{OH^-}$ , one could use  $g[F] := g[OH^-]$ .

88. Recall also that when either `solve` or `fsolve` will do, `solve` is the better choice because `fsolve` does have a proclivity for missing some of the roots to more complicated polynomials. (Again see page 93.)
89. For example, Problems 1d and 3d in Chapter 3.
90. The pH is less than 7.00 because  $\gamma_{H^+} > \gamma_{OH^-}$ .
91. Specifically Equations 4-18 and 4-11.
92. With this restriction on  $M^{n+}$ ,  $M^{n+}$  will not affect the pH by forming  $MOH^{n-1} + H^+$ .
93. See the discussion on page 146.
94. The log of a value between zero and one is negative.
95. Indeed, what is presented here, for study is not pH but rather it is simply  $-\log_{10}[H^+]$ .
96. See page 24 for the discussion on manipulating 2D plots.
97. This would be like adding  $HCl(aq)$  to a sodium fluoride solution to give an HF / NaF solution.
98. See Equation 4-24 and the discussion that follows.
99. Those uncomfortable with the abbreviated derivations given here can review the process described in Chapter 4, particularly Equation 4-13.
100. Recall page 44.
101. For example > `plot(-log[10](H_HSa4), C[HSa]=0..0.3);`
102. It is rare that one can write a plot command and have the plot look exactly as it was intended to look. In order to sneak a preview, one might, for example here, have called for one of the plots with “`plot({-log[10](H_HSa4), ...}`” and then after deciding that the plot is acceptable, prefix that input with “`HSa_plot :=`” and replace semicolons with colons.
103. Van Slyke, D.D., *J. Biol. Chem.*, **52**, 525 (1922).
104. This `diff` command can be skipped with a simple keystroke: If one “right clicks” or clicks on the output for the `C_HSa` output with the [Control] and [Command] keys held down, a menu appears. On that menu is Differentiate with a sub menu of every variable in the expression.
105. Rather than divide by  $\frac{dpH}{dH}$ , one can multiply by  $\frac{dH}{dpH}$ . This option is exercised on page 144.
106. This substitution does *not* preclude one from entering either  $C_{MA} = 0$  or  $C_{HA} = 0$ .
107. There is an interesting inadequacy in the `algsubs` command: `algsubs(H=10^(-pH), beta)` does not replace *all* H's with  $10^{-pH}$ . So one cannot achieve an exponential equivalent to 6-14 this way.
108. Recall (from page 106) that  $K_{aM}$  pertains to the dissociation of  $MH^+$  into  $H^+$  + M, and  $K_{aA}$  pertains to the dissociation of HA into  $H^+$  and  $A^-$ .
109. The common abbreviation for the acetate ion,  $OAc^-$  will be used here. This is A<sup>-</sup> in the general terms used in this chapter. From Appendix II,  $a_{OAc^-} = 4.5$ .
110. The output precision was reset to six decimal places in order to capture values for  $[H^+]$  and  $K_a$ .
111. Notice that ,`C[HCl]` has been omitted from the `solve` command. When there is only one variable to be solved for, this can be done.
112. We will not simply call `Gamma[H]` for the pH because H had been assigned and therefore Maple would have returned `G_0.000012`.

113. This command does *not* allow both substitutions, simultaneously, something like  
`algsubs({C[Buffer]=C[HA], C[Buffer]=C[MA]}, pH).`
114. See also the discussion on page 78 and Problem 4 in Chapter 4.
115. Actually, this does not consider the autoprotolysis of H<sub>2</sub>O (Chapter 3). Indeed, if (C<sub>HA</sub> + C<sub>MA</sub>) = 0, [H<sup>+</sup>] = 10<sup>-7</sup>, not zero because [H<sup>+</sup>] = √K<sub>w</sub>.
116. pages 107 *et seq.*
117. page 89.
118. That is, for monoprotic acids and bases. The polyprotic acids and bases are introduced in Chapter 8.
119. The titrant is the solution delivered (typically from a buret) *to* the solution being titrated.
120. The titrand is the solution being titrated. It is a fixed volume, typically delivered from a pipette.
121. We might have used HSa here as in Problem 2, Chapter 4.
122. See Figure 2-4 and the discussion on page 20 for more detail.
123. By rearranging 7-3 and solving for C°<sub>HA</sub>.
124. Some colors are easier to discern than others. So this is only a rule of thumb. Where specific pH for a given color change is provided, as in Appendix V, it should be used. Other indicator issues are addressed in that Appendix and at the end of Chapter 9.
125. -log(0.1K<sub>In</sub>) = -log(0.1) - logK<sub>In</sub> = pK<sub>In</sub> + 1.
126. No distinction between K°<sub>In</sub> and K<sub>In</sub> will be made here for two reasons. First, many values for K<sub>In</sub> are reported for  $\mu \approx 0.1$  which reasonably approximates most titrations. Second, the *exact* location of pH<sub>EndPt</sub> is not critical in determining the titration error. This *will* be demonstrated.
127. We use pH = -log[H<sup>+</sup>] rather than -log{H<sup>+</sup>}, that is ignoring ionic strength effects, until the end of this chapter.
128. See footnote #2 in Appendix V for an explanation of this correction.
129. The order of the volumes is important only in that if the end point is premature, that is V% is less than V# this shows a negative error.
130. It is left to the reader to show that using Cresol Red with an acid to base transition at pH 8.7 would require 25.005 mL of MOH. This is a 0.5% titration error.
131. This too is left to the reader with the note that this exercise is an *exact* recreation of the previous worksheet with only the C° for HA and MOH changed to 1.00 10<sup>-5</sup>.
132. If necessary, by using the Point Probe as described In Endnote 19.
133. Warning, unable to evaluate the function to numeric values in the region; see the plotting command's help page to ensure the calling sequence is correct
134. See page 42 for details.
135. Through **Preferences > Precision**.

136. More generally, a solvent with an autoprotolysis constant less than that of water's, *i.e.*  $< 10^{-14}$ . Why? Because if  $K_a$  is  $< 10^{-13}$  or so, water provides a measurable fraction of protons to the solution. So the aprotic solvent makes HA the predominant source of  $H^+$  even when  $K_a$  is "especially small." It is a simple enough exercise to replace  $K_w$  with a much smaller value and re-plot pH. (See Problem 5 at the end of this chapter.)
137. B and  $BH^+$  might also be used.
138. To start this loop at  $i \neq 1$ , begin the line with "for  $i$  from  $n$ " where  $n$  must be an integer, and for increments other than 1, precede the "to" with "by  $m$ " where  $m$  is also an integer.
139. Older releases of Maple used `od` (do backwards!) in place of `end`.
140. The reader should notice that on the Maple worksheet, the execution lines or groups (`>`) will become joined. This is evident from a square bracket (`[]`) at the extreme left edge of the worksheet. These brackets are *not* shown in this book. Execution groups can be joined or split by selecting **Split or Join** from the **Edit** menu.
141. Notice no colon or semicolon here; the line break is not required exactly here, but the break (with [return]) is suggested so that the reader can clearly recognize the beginning of the loop. Also, when creating this worksheet, the user will encounter a [Warning, premature end of input](#) message *until* the appropriate input has been supplied. This includes, but is not limited to the `end` statement.
142. A comma between requested outputs instead of a semicolon gives the outputs on one line.
143. Some "new" colors are provided here. Some require quotation marks because they are strings.
144. Titrating a weak acid with a strong base should lead to  $\alpha_{A^-} \geq 0.999$  at the equivalence point.
145. A warning here: when the program below is executed with `subs(H_cubic[3], H)` and `subs(H_quad[2], H)` and the resulting data are plotted, the plot is empty. Trial and error showed that indeed, it was the *first* root of each polynomial that produced real roots.
146. This step is required even though `plots[pointplot]` is not going to be used. This provides an argument (target) for the `plot` command.
147. Commas between requested outputs will put all three outputs on one line.
148. We do not use Debye-Hückel Equation because  $A^-$  is generic and so we do not know its ionic radius,  $a$ . Moreover,  $\mu > 0.1$  where Debye-Hückel begins to fail.
149. In Chapter 4, it was shown that three iterations are sufficient; that standard is applied here.
150. J.F. Coetzee and G.R. Padamanabhan, *J. Amer. Chem. Soc.*, **87**, 5005–10.
151. Concentrated perchloric acid is  $\approx 28\%$   $H_2O$ . This water is removed by making the perchloric acid solution with an acetic anhydride solvent.
152. This discussion entails several simplifications on the behavior of weak bases in acetonitrile. See the reference in Endnote 150 for a more rigorous description.
153. Notice that the range for searching  $H$  has been omitted, evidently without consequence.
154. That is, the pH of 0.106 M HCl is not a lot lower than the pH at the equivalence point, so a large  $\Delta pH$  cannot be achieved.
155. Recall that this one-point check on `fsolve` has failed before as in the previous problem where it failed in a region near the equivalence point.

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