

## Complex Equilibria: What to do when assumptions aren't okay

To this point in creating acid base equilibria we have made our lives simple by working with compounds and amounts that reduce calculations to 4 forms:

$$[H^+] = C_a \quad [H^+] = (K_a C_a)^{1/2} \quad [H^+] = K_a (C_a / C_b) \quad [H^+] = (K_{a1} K_{a2})^{1/2}$$

To do this we either used monoprotic acids and bases with K values between  $10^{-4}$  and  $10^{-10}$ , or we used polyprotic acids with well separated K values in that K range. And we always used high concentrations, like  $C = 0.1M$ . Armed with these two simple approximation ideas: high C and K far apart, we could do a lot of water chemistry problems very simply.

But these approximations don't always work. For example, we couldn't work problems like

- |  |  |
|--|--|
| • What is the pH of 0.1M sulfuric acid?                | Reason: ( $K_s$ too close)                     |
| • What is the pH of 0.1M $HClO_2$ ( $K_a=10^{-2}$ )?   | Reason: ( $K_a$ too close to strong acid case) |
| • What is the pH of 0.1M $CH_3OH$ ( $K_a=10^{-14}$ )?  | Reason: ( $K_a$ too close to $K_w$ )           |
| • What is the pH of $10^{-8}M$ HCl or $10^{-8}M$ NaOH? | Reason: (C too small so $K_w$ matters)         |

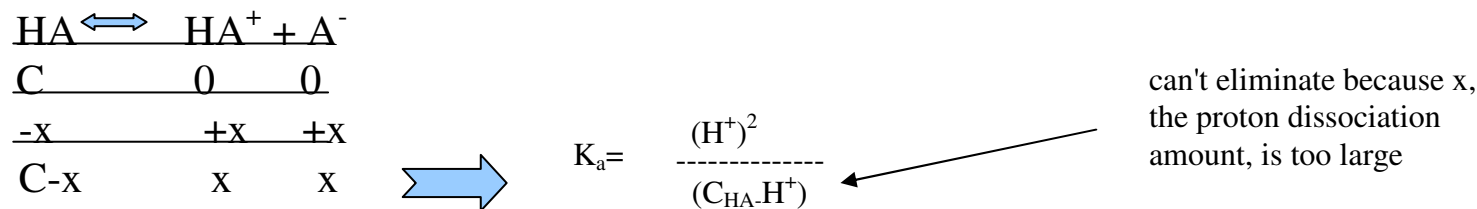
To illustrate, consider the problem if

- 0.1 M  $H_2SO_4$ : this should be a strong acid case but there are multiple sources of  $H^+$  from three dissociations

$$K_{a1} = \frac{(H^+)(HSO_4^-)}{(H_2SO_4)} = \text{infinity} \quad K_{a2} = \frac{(H^+)(SO_4^{2-})}{(HSO_4^-)} = 1.1 \times 10^{-2} \quad K_w = (H^+)(OH^-) = 1 \times 10^{-14}$$

and while we can ignore the  $H^+$  from  $K_w$ , we can't ignore the  $H^+$  from the  $K_{a2}$  and simply use  $H^+ = C_a$  if this was a simple strong acid case like 0.1M HBr.

- 0.1M  $\text{HClO}_2$ : this should be a weak acid case but while we can ignore  $K_w$  because it is far from  $K_a=10^{-2}$  we can't make the assumption that yields  $\text{H}^+=(KC)^{1/2}$  and instead must use the quadratic solution from the RICE expression



- 0.1M  $\text{CH}_3\text{OH}$ : this should be a weak acid case but the  $K_a$  and  $K_w$  are too close so we have to consider both the methanol as a weak acid and the water as a weak acid at the same time

$K_w = (\text{H}^+)(\text{OH}^-) = 10^{-14}$

in addition to

$K_a = (\text{H}^+)(\text{OH}^-) = 10^{-14}$

}

2 approximately equal sources of  $\text{H}^+$  means  
have to use equation with  $K_a + K_w$   
simultaneously

- $10^{-8}$  M  $\text{HCl}$  : this should be a strong acid case but the  $C$  is so small that the  $\text{H}^+$  from  $K_w$  is significant and we must consider the  $(\text{H}^+)(\text{OH}^-) = K_w$  equilibrium

**General treatment of all chemical equilibrium** (how to get exact solutions to equilibrium problems no matter how complicated the system if you can do a little math.)

The basic idea for finding solutions borrow from something you learned to do way back in middle school: solving a series of simultaneous equations. For example, if you know how to solve the following problem:

Find x and y for  $3x + 4y = 13$   
 $2x - 4/3y = -11$  (remember?? all that back substitution stuff??)

then you can do complex equilibrium problems in a remarkably straightforward manner.

**The recipe for complex equilibria problems:**

- identify the number unknowns in the system
- create a number of equations involving those unknowns (from mass balance, charge balance and equilibrium equations)
- solve the series of equations for the unknowns.

That's it, simple as pie.

But what are the equations we use?

They must contain only known constants (like known K values or starting concentrations (like  $C_{HA}$ ) and some subset of the unknowns equilibrium concentrations.

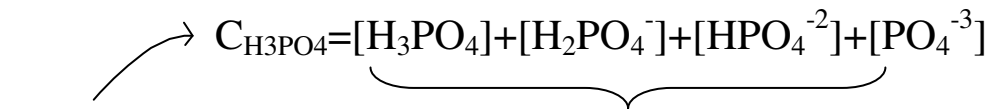
## There are 3 kinds of equations we can create:

- **equilibrium equations** like  $\frac{K_a(A^-)}{(HA)}$  or  $K_w = (H^+)(OH^-)$

(Note that in water equilibria, the  $K_w$  equation is always used. Also note that mono, di and triprotic acids have one, two and three equilibrium equations to use.)

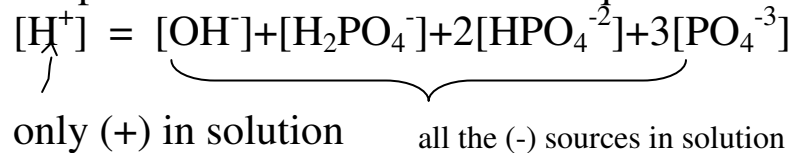
- **mass balance equations** in which some known starting amount of analytical material is equated to all the forms it can make at equilibrium in solution

for example, when as add  $H_3PO_4$  to solution, all the  $PO_4^{-3}$  can be found in one of four equilibrium forms



The amount of an atom in solution must equal the amount you start with. Here all the P in  $H_3PO_4$  has to become

- **charge balance equation** in which we assume the solution is electrically neutral and that all of the cation concentration are placed on one side and must equal all the anions placed on the other side--



**\*\*Note that we put coefficients in front of the multiply charged anions to weight the extra charge each provides**

**So now that we have a bunch of equations, what do we do? Find their simultaneous solutions:**

The engineers and those with a little linear algebra background know all about setting up giant matrices to crank out solutions for **n** unknowns and **n** equations. The rest of us will do a bunch of clunky substitutions to get our answers (or just approximate to death!!)

Example. 0.1M HCl in H<sub>2</sub>O has 3 unknown concentrations:  
H<sup>+</sup>, OH<sup>-</sup>, Cl<sup>-</sup>. so set up 3 simultaneous equations and solve.

Example. 0.1M H<sub>3</sub>PO<sub>4</sub> in H<sub>2</sub>O has 6 unknown concentrations:  
H<sub>3</sub>PO<sub>4</sub>, H<sub>2</sub>PO<sub>4</sub><sup>-</sup>, HPO<sub>4</sub><sup>-2</sup>, PO<sub>4</sub><sup>-3</sup>, H<sup>+</sup>, OH<sup>-</sup> so set up 6 simultaneous equations and solve

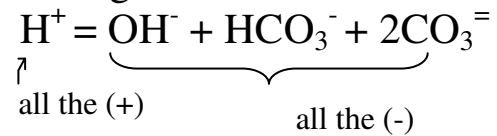
Example. What is the [H<sup>+</sup>], [OH<sup>-</sup>], [H<sub>2</sub>CO<sub>3</sub>], [HCO<sub>3</sub><sup>-</sup>], [CO<sub>3</sub><sup>-</sup>] when I toss 1 x 10<sup>-4</sup> moles H<sub>2</sub>CO<sub>3</sub> in 1L of solution?

I have 5 equations to solve for 5 unknown concentrations. Let's take this one all the way and write down all the equations:

Equation 1. Mass balance



Equation 2. Charge balance



Equation 3	} equilibrium equations	$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$
Equation 4		$K_{a1} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$
Equation 5		$K_{a2} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$

5 equations, 5 unknowns. We can solve!!!

Of course no general chemistry course will make you solve this set of equations. But the point is that you can!! All you need to know is how to find a source of equations.

## Applying the general equilibrium treatment to a couple of our favorite systems:

- **Strong acid case**—works at every concentration of strong acid including dilute cases

Example: What is the pH of  $8 \times 10^{-8} \text{ M HCl}$ ?

Answer: There are 3 unknowns:  $\text{H}^+$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$

So there are 3 equations

- (1)  $K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$  ← equilibrium equation
- (2)  $[\text{H}^+] = [\text{Cl}^-] + [\text{OH}^-]$  ← charge balance equation
- (3)  $C_{\text{HCl}} = [\text{Cl}^-]$  ← mass balance equation

Now let's do some back substitutions to get a simple equation with one unknown,  $[\text{H}^+]$ .

Substitute (3)  $\rightarrow$  (2)  $\text{H}^+ = C_{\text{HCl}} + \text{OH}^-$  ; substitute (2)  $\rightarrow$  (1)  $K_w = [\text{H}^+](\text{H}^+ - C_{\text{HCl}})$  and rearranging to a quadratic:

$$[\text{H}^+]^2 - [\text{H}^+]C_{\text{HCl}} - K_w = 0 \leftarrow \text{a quadratic to find } \text{H}^+ \text{ exactly.}$$

Wow!!, the exact solution for a strong acid (when you don't want to or can't use  $\text{H}^+ = C_a$

So for  $C_{\text{HCl}} = 8 \times 10^{-8} \text{ M}$  and  $K_w = 1 \times 10^{-14}$

$$[\text{H}^+]^2 - [\text{H}^+](8 \times 10^{-8}) - 1 \times 10^{-14} = 0$$

yields  $[\text{H}^+] = 1.5 \times 10^{-7}$

$$\text{pH} = 6.82$$

Recall we did this problem earlier using common sense.

What is the pH of  $8 \times 10^{-8}$  M HCl?

- a 7.09 <-- no, it is basic and HCl is acidic
- b 7.96 <-- no, it is basic and HCl is acidic
- c **6.82 <-- only possible answer since it must be slightly less than pH 7**
- d 7 <-- no, it is neutral and HCl is acidic
- e 1.56 <-- no,  $8 \times 10^{-8}$  M is very dilute, pH is near 7

- **Weak acid case**—works at every concentration or  $K_a$  for weak acid including dilute cases. Remember, the slacker equation for a weak acid is  $(KC)^{0.5}$  what is the true answer?

For a monoprotic weak acid in solution we have 4 unknowns

[H<sup>+</sup>]      [OH<sup>-</sup>]      [HA]      [A<sup>-</sup>]

so we need 4 equations

mass balance     $C_{HA} = HA + A^-$

charge balance     $H^+ = A^- + OH^-$

$K_a$                  $K_a = ([H^+][A^-])/[HA]$

$K_w$                  $K_w = [H^+][OH^-]$

Without sweating the details, we can back substitute to get a cubic solution in terms of [H<sup>+</sup>] (you lonely types should do this with me on Friday night.)

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



So that is the truth--note that in the cubic, if we ignore  $K_w$  we get our friend the quadratic and if  $C \gg H^+$  we get  $(KC)^{1/2} = H^+$  which is the approximation we have used to a weak acid when  $C$  is large and  $K$  is far away from others.

So now let's do a calculation.

What is the pH of  $1 \times 10^{-4}$  M phenol if  $K_a = 1.3 \times 10^{-10}$

Solving a cubic on your handy graphing calculator yields

$$\text{pH} = 6.8 \text{ for the } 10^{-4} \text{ M phenol solution}$$

That was quite a lot of work to find out that dilute weak acids have a pH of just under 7!

But at least we know it exactly!! And if we want, we can use a cubic to get the exact answer while everyone else is getting kind of a right answer using the  $(KC)^{0.5}$  equation. This is why engineers get to feel superior—they use higher order polynomials to solve their problems!!