

Monoprotic Acid-Base Equilibria (CH 10)

- Chapter 10 – monoprotic acids
 - A monoprotic acid can donate one proton.
 - This chapter includes buffers; a way to 'fix' the pH.
- Chapter 11 – polyprotic acids
 - A polyprotic acid can donate multiple protons.
 - This chapter is just an extension of chapter 10.
- Chapter 12 – acid base titrations.

Strong acids and bases

Accounting for activity, calculate the pH of 0.10 M HCl.

- HCl is a strong acid, so it totally dissociates.
 - Table 6-2
 - The concentration of H^+ will be 0.10 M.
- Solution:
 - The ionic strength of 0.10 M HCl is 0.10 M, at which the activity coefficient of H^+ is 0.83 (Table 8-1).
 - The pH is $-\log A_{H^+}$
 - $pH = -\log[H^+]\gamma_{H^+} = -\log(0.10)(0.83)=1.08$
- If you know $[H^+]$, you can always find $[OH^-]$ {or vice versa}.
 - Because $[H^+][OH^-] = K_w = 1.0 \times 10^{-14}$
 - AND $pH + pOH = 14.00$

Strong acids and bases

- We can neglect the concentration of H^+ and OH^- due to the auto-protolysis of water only if the 'extra' H^+ or OH^- is much greater than 10^{-7} .

What is the pH of 1.0×10^{-8} M M HCl?

- HCl is a strong acid, so it totally dissociates.
 - You memorized table 6-2 didn't you?
 - The concentration of H^+ will be 10^{-8} **PLUS** the H^+ from water autoprotolysis.
 - An activity correction can be neglected here because the ionic strength is very small.
- Solution:

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

Let x be our unknown OH^- concentration.

$$(10^{-8} + x)(x) = 1.0 \times 10^{-14}$$

Rearrange

$$x^2 + (10^{-8})x - (1.0 \times 10^{-14}) = 0$$

Use quadratic formula to solve for x :

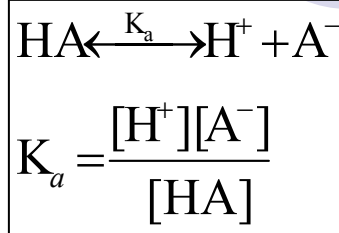
$$x = \frac{-10^{-8} \pm \sqrt{(10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$
$$= 9.6 \times 10^{-8} \text{ M or } -1.1 \times 10^{-7} \text{ M}$$

Reject the negative solution.

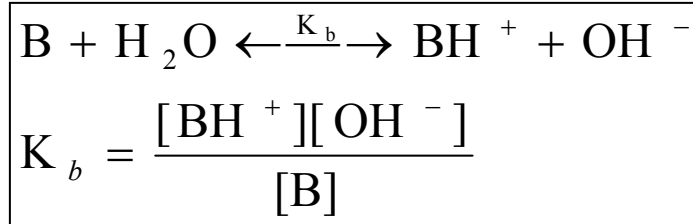
$$\text{pH} = -\log[H^+] = -\log\{10^{-8} + 9.6 \times 10^{-8}\} = 6.97.$$

Weak acids and bases {review}

- Weak acid dissociation:



- Weak base dissociation:



- Remember, a base is a proton acceptor. Just because you see OH^- doesn't imply base.

- **Always!**

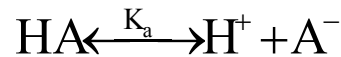
$$K_a \cdot K_b = K_w$$

- The conjugate base of a weak acid is a weak base.
- The conjugate acid of a weak base is a weak acid.

Implies →

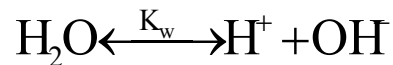
Weak-acid equilibria

- Consider a weak acid HA that has a given K_a . Find the pH of the solution:
- What are the pertinent reactions?



- What is the charge balance?

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



- What is the mass balance?

- Let's call the formal concentration F .

Formal concentration is the total number of moles of a compound dissolved in a liter.

The formal concentration of a weak acid is the total amount of HA placed in the solution.

- $F = [\text{A}^-] + [\text{HA}]$

- Equilibria:

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

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

Weak-acid equilibria

- Even though called ‘weak’, any respectable acid will give an $[H^+]$ concentration much greater than the $[H^+]$ concentration due to water autoprotolysis.
 - In other words, if the $[H^+]$ from the acid dissociation is much greater than the $[H^+]$ from the water dissociation then $[A^-]$ will be much greater than $[OH^-]$.
 - Because the ‘extra’ $[H^+]$ came from the HA dissociation.
 - The charge balance equation reduces to $[H^+] \approx [A^-]$.
 - This reduces a cubic equation to a quadratic equation.
 - “I have trouble solving cubic equations.”
- Let $[H^+] = x$, then:
 - Charge balance says that $[H^+] \approx [A^-] = x$.
 - AND mass balance says that $[HA] = F - [A^-] = F - x$.
- Plugging these results into the acid dissociation equilibria gives:

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

Weak-acid equilibria

- When dealing with a weak acid, you should immediately realize that $[H^+] \approx [A^-] \approx x$
 - Unless the acid is very dilute or too weak.

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

- This results in using the quadratic formula!
- In a solution of a weak acid, $[H^+]$ is derived almost entirely from the weak acid, not from the H_2O dissociation.
- Unless the acid is very dilute or too weak.

Weak-acid equilibria: A possible approximation.

- The quadratic formula can always be used to solve weak acid problems.
 - Unless the acid is very dilute or too weak.
- However, the problem is even easier if you can neglect x from the denominator.

$$K_a = \frac{x^2}{F-x} \approx \frac{x^2}{F}$$

- This can **ONLY** be done if x is **MUCH** smaller than $[HA]$.
 - How do I know if x is much smaller than $[HA]$?
 - Make the approximation and solve the problem.
 - If your answer supports your assumption then your answer is fine.
 - Suppose you are given that $[HA]$ is 0.1 M and you find $[A^-]$ to be 1×10^{-6} , then you are safe to say that $x = [A^-] \ll [HA]$.

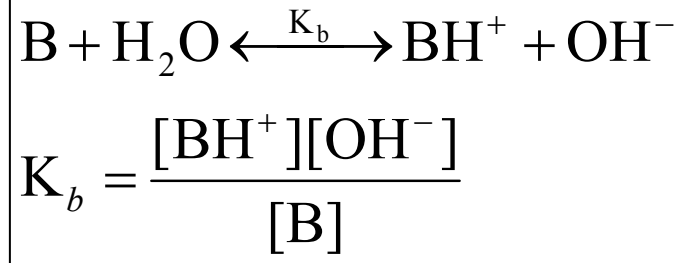
Fraction of dissociation

- The fraction of dissociation, α , is defined as the fraction of an acid HA in the form of A⁻.

$$\alpha = \frac{[A^-]}{[A^-] + [HA]} = \frac{x}{x + (F - x)} = \frac{x}{F}$$

Weak-base equilibria

- The treatment of weak bases is almost the same as that of weak acids.



- We suppose that nearly all of the OH^- comes from the reaction of $\text{B} + \text{H}_2\text{O}$ and little comes from the dissociation of water.
- The formal concentration of base will be:

$$[\text{B}] = F - [\text{BH}^+] = F - x$$

○ because $F = [\text{B}] + [\text{BH}^+]$

Weak-base equilibria example

Find the pH of 0.10 M ammonia. {It's not 13.}

- Pertinent reactions:



- Woops, we have no K_b tables in our text.
 - But, $K_a \times K_b = K_w$, and K_a for NH_4^+ is listed in our table at the back of the book.
 - $K_b = K_w / K_a$.
- To find the pH of 0.10 M NH_3 , we set up and solve the equation

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = K_b = \frac{K_w}{K_a} = \frac{10^{-14.00}}{5.70 \times 10^{-10}} = 1.75 \times 10^{-5}$$

- If we let $x = [\text{NH}_4^+]$, the x also = $[\text{OH}^-]$ through stoichiometry.
- Also, $[\text{NH}_3] = F - x$ where $F = 0.10$ M.

$$\frac{(x)(x)}{F - x} = \frac{x^2}{0.1 - x} = 1.75 \times 10^{-5}$$

Weak-base equilibria example continued

Find the pH of 0.10 M ammonia. {It's not 13.}

- Let's assume $x \ll 0.1$ to avoid a quadratic equation.

$$\frac{x^2}{0.1} = 1.75 \times 10^{-5}$$

$$x^2 = 1.75 \times 10^{-6}$$

$$[\text{OH}^-] = x = \sqrt{1.75 \times 10^{-6}} = 1.32 \times 10^{-3} \text{ M}$$

- 1.32×10^{-3} is not $\ll 1 \times 10^{-1}$, so we should probably not make that assumption.

- Using the quadratic formula.

$$\frac{x^2}{0.1 - x} = 1.75 \times 10^{-5}$$

$$x^2 = (1.75 \times 10^{-5})(0.1 - x)$$

$$x^2 = (1.75 \times 10^{-5})(0.1) - (x)(1.75 \times 10^{-5})$$

$$x^2 + (x)(1.75 \times 10^{-5}) - (1.75 \times 10^{-6}) = 0$$

$$x = \frac{-1.75 \times 10^{-5} \pm \sqrt{(1.75 \times 10^{-5})^2 - 4(1)(-1.75 \times 10^{-6})}}{2(1)}$$

$$= 1.31 \times 10^{-3} \text{ M or } -1.32 \text{ (throw out negative solution)}$$

We get a slightly different answer, but the difference is in our first uncertain digit.

We would have been fine making the assumption after all!

Weak-base equilibria example continued

Find the pH of 0.10 M ammonia. {It's not 13.}

- Find the pH now that we know $[\text{OH}^-] = x = 1.31 \times 10^{-3} \text{ M}$.

$$\text{pOH} = -\log(1.31 \times 10^{-3}) = 2.88$$

$$\text{pH} = 14.00 - \text{pOH} = 14.00 - 2.88 = 11.12$$

- The solution is less basic than if the ammonia was totally dissociated.