

# 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  $1.0 \times 10^{-8}$  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  $x$ :

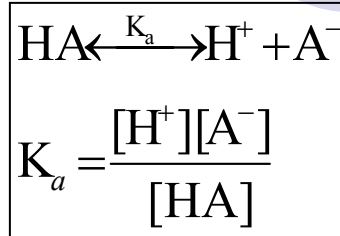
$$x = \frac{-10^{-8} \pm \sqrt{(10^{-8})^2 - 4(1)(-1.0 \times 10^{-14})}}{2(1)}$$
$$= 9.6 \times 10^{-8} \text{ M or } -1.1 \times 10^{-7} \text{ M}$$

Reject the negative solution.

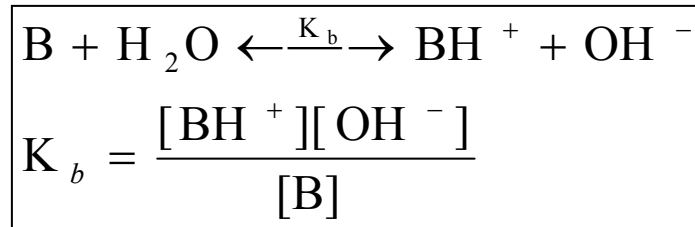
$$\text{pH} = -\log[H^+] = -\log\{10^{-8} + 9.6 \times 10^{-8}\} = 6.97.$$

# Weak acids and bases {review}

- Weak acid dissociation:



- Weak base dissociation:



- Remember, a base is a proton acceptor. Just because you see  $\text{OH}^-$  doesn't imply base.

- **Always!**

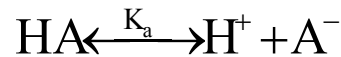
$$K_a \cdot K_b = K_w$$

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

Implies  $\longrightarrow$

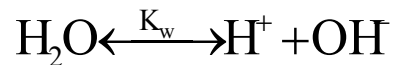
# Weak-acid equilibria

- 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  $1 \times 10^{-6}$ , then you are safe to say that  $x = [A^-] \ll [HA]$ .



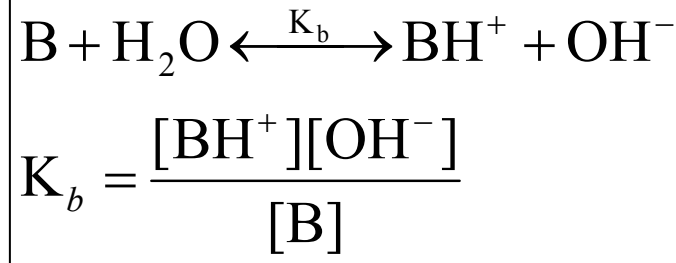
# Fraction of dissociation

- The fraction of dissociation,  $\alpha$ , is defined as the fraction of an acid HA in the form of A<sup>-</sup>.

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

# Weak-base equilibria

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



- We suppose that nearly all of the  $\text{OH}^-$  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  $\text{NH}_4^+$  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  $\text{NH}_3$ , 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.

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

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

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

- $1.32 \times 10^{-3}$  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.