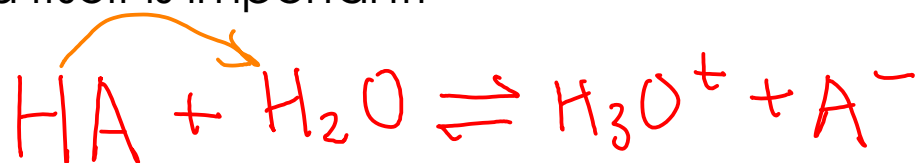


For a WEAK ACID, equilibrium does not lie far to the right. The ionization equilibrium of the acid itself is important!



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

acid ionization constant

Again, water's concentration will not change significantly, so it is folded into the ionization constant

(HA) = concentration of undissociated acid

For a WEAK BASE, equilibrium does not lie far to the right. The ionization equilibrium of the base itself is important!



$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$$

base ionization constant

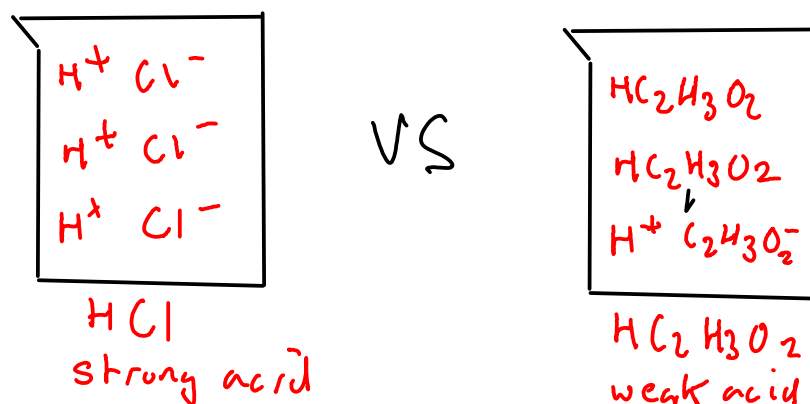
Values for K_a and K_b can often be found in data books / tables / or on the web.

In OpenStax, these constants are in Appendix H and Appendix I!

WEAK ELECTROLYTES

- In solutions of weak acids or bases, the UNDISSOCIATED form is present in significantly high concentration.

- The pH of a solution of weak acid will be HIGHER than the pH of a strong acid solution with the same nominal concentration!



Fewer molecules of the weak acid ionize, so the concentration of hydrogen/hydronium ion is lower, meaning a higher pH!

- The pH of a solution of weak base will be LOWER than the pH of a strong base solution with the same nominal concentration!

Consider a 0.100M solution of nitrous acid, a WEAK ACID (HNO_2)



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.6 \times 10^{-4}$$

See
Appendix H
in OpenStax
for K_a values

What is the pH of the solution?

We will assume that all hydronium ion in solution comes from the acid (nitrous acid). While nitrous acid is a weak acid, it's FAR stronger than water itself! Set up an equilibrium chart.

Species	[Initial]	Δ	[Equilibrium]
H_3O^+	0	+X	X
NO_2^-	0	+X	X
HNO_2	0.100	-X	0.100 - X

Let "x" equal the change in hydronium ion concentration.

Now, plug in to the equilibrium expression (K_a):

$$\frac{(x)(x)}{(0.100 - x)} = 4.6 \times 10^{-4}$$

$$\frac{x^2}{0.100 - x} = 4.6 \times 10^{-4}$$

$$\frac{x^2}{0.100 - x} = 4.6 \times 10^{-4}$$

Assume "x" is very small,
 $x \ll 0.100$

$$0.100 - x \approx 0.100$$

$$\frac{x^2}{0.100} = 4.6 \times 10^{-4}$$

$$x^2 = 4.6 \times 10^{-5}$$

$$x = 0.00678233$$

$$[\text{H}_3\text{O}^+] = 0.00678233 \text{ M}$$

$$\text{pH} = \boxed{2.17}$$

This is a quadratic, We can solve it with the quadratic equation:

$$ax^2 + bx + c = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

WHEN can we know that "x" is small enough to ignore in the subtraction:

- 1) Acid/base equilibria, a few solubility calculations
- 2) "x" is defined as representing products.
- 3) The K_a or K_b is 1000 times (or more ... more is better!) SMALLER than the initial concentration of acid or base!

Using this simplifying assumption, solving for "x" became really easy. But would we get the same thing using the quadratic equation?

Calculating the pH using the quadratic equation to solve for "x" gave a pH of 2.18, a difference of 1 in the last significant figure and below the margin of error for a typical routine pH measurement.

Compare:

- Weak acid HNO_2 : pH of 0.10 M solution = 2.17

Let's compare the pH of the weak nitrous acid with the pH of a strong acid like nitric acid:

0.10 M HNO_3 , what is pH?



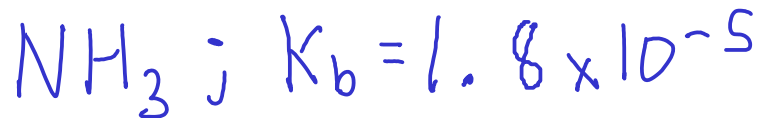
$$[\text{H}_3\text{O}^+] = [\text{HNO}_3]_{\text{nominal}} = 0.10 \text{ M}$$

$$\text{pH} = 1.00$$

The stronger the acid:

- the lower the pH of a solution of given concentration will be
- the higher the concentration of hydronium ion (when compared to the nominal acid concentration)

Consider an 0.100 M solution of the weak base ammonia:



See Appendix I in OpenStax for K_b values



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

What is the pH?

Set up an equilibrium chart to reduce the number of variables in the K_b expression!

Species	[Initial]	Δ	[Equilibrium]
OH^-	0	+x	x
NH_4^+	0	+x	x
NH_3	0.100	-x	0.100 - x

Let "x" equal the change in hydroxide ion concentration.

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{(x)(x)}{(0.100-x)} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.100-x} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

Assume $x \ll 0.100$,
 so $0.100 - x \approx 0.100$

$$\frac{x^2}{0.100} = 1.8 \times 10^{-5}$$

$$x^2 = 1.8 \times 10^{-6}$$

$$x = 0.0013416408 = [\text{OH}^-]$$

$$\text{So, } \underline{\underline{\text{pOH}}} = -\log_{10}(0.0013416408) = 2.87 \quad \text{pOH} = -\log_{10}[\text{OH}^-]$$

$$\text{pH} + \text{pOH} = 14.00$$

$$\text{pH} = 14 - 2.87 = \boxed{11.13}$$

If we solve the problem using the quadratic equation to determine "x", we'll get a pH of 11.13, no different than the answer from the simplification.

Compare pH to the pH of an 0.100 M solution of the strong base NaOH:

$$\text{pH}_{\text{NH}_3} \approx 11.13$$



$$[\text{OH}^-] = [\text{NaOH}]_{\text{nominal}} = 0.100 \text{ M}$$

$$\text{pOH} = 1.00$$

$$\text{pH} = 13.00$$

The stronger the base:

- the higher the pH will be for a solution of given concentration
- the higher the HYDROXIDE concentration (compared to the nominal base concentration)