

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



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{NO}_2^-]}{[\text{HNO}_2]} = 4.5 \times 10^{-4}$$

Found on page A-14 in Ebbing 10th edition. These K values are determined experimentally like other equilibrium constants.

What is the pH of the solution?

To find pH, we need to determine the concentration of HYDRONIUM ION at equilibrium, but (unlike the strong acid case) we can't assume all the acid ionizes. We need to solve the equilibrium expression of the acid.

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

$$\frac{(x)(x)}{(0.100 - x)} = 4.5 \times 10^{-4}$$

Look familiar? This is very similar to the equilibrium problems from Chapter 14!

$$\frac{(x)(x)}{(0.100 - x)} = 4.5 \times 10^{-4}$$

$$\frac{x^2}{0.100 - x} \approx 4.5 \times 10^{-4}$$

K_a is small, so there's only a small fraction of acid that ionizes. That means 'x' is small compared to the molarity of the acid. If 'x' is small relative to 0.1, then ...

$$0.100 - x \approx 0.100$$

$$\frac{x^2}{0.100} = 4.5 \times 10^{-4}$$

$$x^2 = 4.5 \times 10^{-5}$$

$$x = 0.0067082039 = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 2.17$$

(Solving the quadratic equation would have given a pH of 2.19)

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 is it safe to assume x is small enough to drop from the subtraction term? When the initial concentration is 1000x or more larger than the value of K_a or K_b !

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?



0.10 M HNO_3 , $[\text{H}_3\text{O}^+] = 0.10$

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:



What is the pH?



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

We need to solve this expression for HYDROXIDE concentration, since HYDROXIDE is the only term in this equilibrium that relates to HYDRONIUM ...

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

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

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

This is a quadratic equation, but we can simplify it IF x is small compared to 0.100 ...

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



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

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

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

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

$$\text{pOH} = 2.87$$

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

$$\boxed{\text{pH} = 11.13}$$

(If you'd solved this with the quadratic formula, you'd have gotten a pH of 11.13 ... same as we got with the assumption!)

Be careful! We have calculated pOH (the negative log of the HYDROXIDE concentration). We need to CONVERT it to pH!

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

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



So, 0.100 M NaOH has $[\text{OH}^-] = 0.100$

$$\text{pOH} = -\log_{10}(0.100) = 1.00$$

$$\text{pH} = 14.00 - 1.00 = \boxed{13.00}$$

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)