

Comp 11: Acid-Base Equilibria

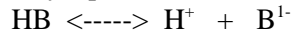
I. Equilibrium Constant for the Dissociation of a Weak Acid-- K_a

A. Weak Acid description:

1. it is an acid only partially dissociated in water
2. The equation for the partial dissociation of the weak acid HB _____.
3. The products of the dissociation are _____ and _____, the conjugate base.
4. How can one identify a weak acid in general?
 - a. it has an H at the start of the formula
 - b. it is not one of the strong acids (You should know these from memory: HCl, HBr, HI, HNO₃, H₂SO₄, HClO₄).

B. Expression for K_a

1. The equilibrium expression for the dissociation of a weak acid follows the general rules for any equilibrium reaction.



$$K_a = \frac{[\text{H}^+][\text{B}^-]}{[\text{HB}]}$$

Example: Acetic acid, HC₂H₃O₂, partially dissociates in water. Write the equation for its dissociation and the equilibrium expression for K_a .

NOTE: C₂H₃O₂¹⁻ (acetate ion) is often written as OAc¹⁻ when the interest is in the acetate ion as a whole. The formula for acetic acid, thus would be HOAc.

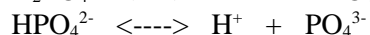
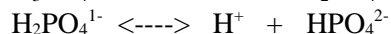


$$K_a = \frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]}$$

NOTE: K_a always means dissociation, so H⁺ is always in the numerator. The anion which results from the dissociation of the weak acid is known as the **conjugate base**. It accepts the proton (hydrogen ion) and reforms the undissociated molecule.

Example: Write the dissociation equation for the dissociation of nitrous acid in water. What is the conjugate base? Write the expression for the K_a .

2. Weak acids with more than one ionizable H⁺, H₃PO₄, for example, dissociate stepwise, one H⁺ at a time. Each step has a different K_a expression and a different K_a value. The K_a value decreases with each successive step. The steps for the dissociation of H₃PO₄ are: (all are in aqueous solution)



NOTE: the conjugate base for the first step becomes the weak acid of the second step. Now write the equations for the stepwise dissociation of carbonic acid.

3. The ions and molecules are enclosed in brackets, [], when they are written in the equilibrium expression, just as with other equilibrium reactions. This means that the concentrations are given in moles/liter, or molarity.

4. The equilibrium concentration of the undissociated weak acid is equal to the original concentration minus the amount of the weak acid that is dissociated.

$$[\text{HB}] = (\text{HB}) - [\text{H}^+]$$

C. What does K_a tell you?

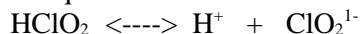
1. the smaller the value of K_a , the weaker the acid is
2. when two weak acids are compared, the one with the smaller K_a
 - a. is the weakest
 - b. has a smaller $[\text{H}^+]$
 - c. has a higher pH
 - d. has a larger $[\text{HB}]$

D. Determination of K_a

1. Given a known amount of weak acid in a given volume, as well as the pH of the resulting solution. (In other words, the original concentration of the weak acid and the $[\text{H}^+]$)

Example: A solution of HClO_2 is prepared by dissolving 1.369 g of HClO_2 in enough water to make 100.0 mL of solution. The pH of the resulting solution is 1.36.

First, write the dissociation equation:



Next, write the K_a expression:

$$K_a = \frac{[\text{H}^+][\text{ClO}_2^{1-}]}{[\text{HClO}_2]}$$

Then calculate K_a . Set up a chart as was done with other equilibrium problems.

Species	OC	Change	EC
HClO_2			
H^+			
ClO_2^{1-}			

The OC for the HClO_2 can be calculated by dividing the mass of the acid by the volume in liters and then by the molar mass, which for HClO_2 is 68.46 g/mol.

The change for the acid will have a negative sign and the changes for the H^+ and ClO_2^{1-} will be positive.

The pH is then used to calculate the $[\text{H}^+]$

$$[H^+] = \text{inverse log } -\text{pH} = \text{inverse log}(-1.36) = 0.0437 \text{ M}$$

Since the OC for the H^+ was zero, then the change in concentration for the H^+ is $+0.0437 \text{ M}$. This is also the change for the ClO_2^{1-} . The change for the $HClO_2$ is a negative 0.0437 M , so the EC would be $0.2000 \text{ M} - 0.0437 \text{ M} = 0.1563 \text{ M}$.

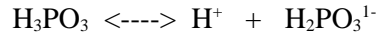
$$K_a = \frac{[H^+][ClO_2^{1-}]}{[HClO_2]} = \frac{[0.0437][0.0437]}{[0.1563]} = 0.1222$$

Example: A one-liter solution of nitrous acid contains 11.76 g of the weak acid. The solution has a pH of 1.955. Calculate K_a for HNO_2 .

Species	OC	Change	EC
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2. Given the original concentration and percent dissociation of the acid.

Example: A 0.300 M phosphorous acid solution is 33.3% dissociated in the first-step. The equation for the first-step dissociation is



The K_a expression is: $K_a = \frac{[H^+][H_2PO_3^{1-}]}{[H_3PO_3]}$

33.3% dissociation means that 33.3% of the phosphorous acid has dissociated or changed into H^+ and $H_2PO_3^{1-}$. The change in the H_3PO_3 is therefore, $(0.300)(0.333) = 0.0999 \text{ M}$. It has a negative sign, and the change for the two ions is a positive 0.0999 M each. The remainder of the problem is carried out as any other equilibrium problem.

Species	OC	Change	EC
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Example: The second-step dissociation of a 0.0100 M solution of oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$, is 7.35% of the $\text{HC}_2\text{O}_4^{1-}$ ion. Calculate K_a for the second-step dissociation of oxalic acid.

Species _____ OC _____ Change _____ EC _____

E. Applications of K_a :

1. Determination of the $[\text{H}^+]$ or pH of a solution of a weak acid when the OC is known.

Example: Phenol ($\text{C}_6\text{H}_5\text{OH}$) has a $K_a = 1.6 \times 10^{-10}$. Determine the $[\text{H}^+]$ in a solution prepared by dissolving 0.500 mol of phenol to form 5.00 L of solution.

Species _____ OC _____ Change _____ EC _____

We don't know any of the EC values, so we let the change for each be "x". The phenol change would be -x, giving the EC for phenol as 0.100 - x. The change for the two ions would be +x for each, with an EC of just x for each.

Substitution into the K_a expression gives:

$$K_a = \frac{[\text{H}^+][\text{C}_6\text{H}_5\text{O}^{1-}]}{[\text{C}_6\text{H}_5\text{OH}]} = \frac{[x][x]}{[0.100-x]} = 1.6 \times 10^{-10}$$

Most weak acids have such small dissociation constants that we may assume the amount dissociated is so much smaller than the original concentration that it is negligible when compared to the original concentration. In the preceding equation then we can assume $0.100 - x = 0.100$. You have to always write out the assumption and test later whether it is valid.

Assume that $x \ll 0.100$

$$\frac{[x][x]}{0.100} = 1.6 \times 10^{-10}$$

Species OC Change EC

HCN

H⁺

CN¹⁻

Since 1 mol of NaCN provides about 1 mol of CN¹⁻, we have 0.0500 mol of CN¹⁻ as an original concentration rather than just x as when it is the acid alone.

You may assume that $x \ll$ the concentrations of the HCN and CN¹⁻ and so ignore x in the two terms that contain it.

Example: Calculate [H⁺] for a solution that is 0.100 M in both H₂CO₃ and NaHCO₃. The K_a for the dissociation of H₂CO₃ to H⁺ and HCO₃¹⁻ is 4.2×10^{-7} .