Chemistry 2000 Slide Set 19b: Organic acids
Acid dissociation equilibria

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March 22, 2020

Acid dissociation equilibria

- If we know the K_a and concentration of an acid, we can calculate the pH.
- Reminder:

$$\mathrm{pH} = -\log_{10} a_{\mathrm{H}^+}$$

- We usually don't need to take the autoionization of water into account unless the concentration of protons liberated from the acid is similar to the concentration of protons generated by autoionization.
- We often can treat the acid as if it's mostly undissociated.
- Note that we'll assume 25°C in all of the following calculations.

Example: pH of a phenol solution

- Calculate the pH of a 0.32 M phenol solution.
  The pK_a of phenol is 9.95.

- The equilibrium is

$$C_6H_5OH_{(aq)} \rightleftharpoons C_6H_5O^-_{(aq)} + H^+_{(aq)}$$

  with equilibrium expression

$$K_a = \frac{(a_{C_6H_5O^-})(a_{H^+})}{a_{C_6H_5OH}}$$

- $K_a = 10^{-pK_a} = 10^{-9.95} = 1.1 \times 10^{-10}$

Example: pH of a phenol solution (continued)

$$C_6H_5OH_{(aq)} \rightleftharpoons C_6H_5O^-_{(aq)} + H^+_{(aq)} \qquad K_a = 1.1 \times 10^{-10}$$

- 0.32 M solution

Hypotheses:

1. Water autoionization is not a significant source of protons.
   Then we would have $a_{C_6H_5O^-} \approx a_{H^+}$.
2. Very little of the phenol dissociates.
   Then $a_{C_6H_5OH} \approx 0.32$.

Example: pH of a phenol solution (continued)

- We have

$$K_a = 1.1 \times 10^{-10} = \frac{(a_{C_6H_5O^-})(a_{H^+})}{a_{C_6H_5OH}}$$

with our hypotheses $a_{C_6H_5O^-} \approx a_{H^+}$ and $a_{C_6H_5OH} \approx 0.32$.

- Therefore

$$1.1 \times 10^{-10} = \frac{(a_{H^+})^2}{0.32}$$

- $\implies a_{H^+} = 6.0 \times 10^{-6}$
- $\mathrm{pH} = -\log_{10}(6.0 \times 10^{-6}) = 5.22$

Example: pH of an acetic acid solution

- Calculate the pH of a 4.2×10^{-5} M ethanoic (acetic) acid solution.
  The pK_a of ethanoic acid is 4.76.

- We always start with basics:

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

  with equilibrium expression

$$K_a = \frac{(a_{CH_3COO^-})(a_{H^+})}{a_{CH_3COOH}}$$

- $K_a = 10^{-pK_a} = 10^{-4.76} = 1.7 \times 10^{-5}$

Example: pH of an acetic acid solution (continued)

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)} \qquad K_a = 1.7 \times 10^{-5}$$

- 4.2×10^{-5} M solution
- Our usual hypotheses (water autoionization unimportant, very little of the acid dissociates) lead to

$$1.7 \times 10^{-5} = \frac{(a_{H^+})^2}{4.2 \times 10^{-5}}$$
$$\therefore a_{H^+} = 2.7 \times 10^{-5}$$

- This violates our assumption that very little of the acetic acid dissociates, since it implies that $[CH_3COO^-] = 2.7 \times 10^{-5}$ M out of a total of 4.2×10^{-5} M.

Example: pH of an acetic acid solution (continued)

$$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-_{(aq)} + H^+_{(aq)}$$

	$[CH_3COOH]$	$[CH_3COO^-]$	$[H^+]$
I	4.2×10^{-5}	0	0
C	$-x$	x	x
E	$4.2 \times 10^{-5} - x$	x	x

$$K_a = \frac{(a_{CH_3COO^-})(a_{H^+})}{a_{CH_3COOH}}$$

$$1.7 \times 10^{-5} = \frac{x^2}{4.2 \times 10^{-5} - x}$$

Example: pH of an acetic acid solution (continued)

$$1.7 \times 10^{-5} = \frac{x^2}{4.2 \times 10^{-5} - x}$$

- If you have a calculator with this feature, you can solve this equation directly.
- Otherwise, rearrange to the quadratic equation

$$x^2 + 1.7 \times 10^{-5} x - 7.1 \times 10^{-10} = 0$$

with solution

$$x = \frac{1}{2} \left\{ -1.7 \times 10^{-5} \pm \sqrt{(1.7 \times 10^{-5})^2 - 4(-7.1 \times 10^{-10})} \right\}$$

- The $+$ sign gives the correct solution:

$$x = 2.0 \times 10^{-5}$$

Example: pH of an acetic acid solution (continued)

- Since $a_{H^+} = x$,

$$\mathrm{pH} = -\log_{10}(2.0 \times 10^{-5}) = 4.71$$

General lessons

- It is surprisingly hard to give general rules that cover all possible cases that can arise in solving acid dissociation equilibria.
- Some cases come up more often than others.
- In the following, we're going to assume that a_{HA} is calculated from the *initial* amount of acid, i.e. not taking dissociation into account, i.e. the amount you would put in for HA the I row of an ICE table.
- The (slightly unusual) case where $a_{\mathrm{HA}} \sim \sqrt{K_w}$ requires some thought. We will leave this case aside as it comes up relatively rarely in real problems.

General lessons

Do we need to consider water autoionization?

For an acid-base equilibrium

$$HA \rightleftharpoons H^+ + A^- \qquad K_a = \frac{(a_{H^+})(a_{A^-})}{a_{HA}}$$

- $K_w = (a_{H^+})(a_{OH^-})$ and $K_a a_{HA} = (a_{H^+})(a_{A^-})$.
- Dividing one equation by the other, we have

$$\frac{K_w}{K_a a_{HA}} = \frac{a_{OH^-}}{a_{A^-}}.$$

- If $K_w \ll K_a a_{HA}$, then $a_{OH^-} \ll a_{A^-}$ or, to put it another way, autoionization of water will be negligible since the amount of H^+ from the dissociation of HA will be much greater than the amount of H^+ from the autoionization of water.

General lessons

Do we need a full ICE table?

- Define $q = K_a / a_{\mathrm{HA}}$, so that $K_a = q a_{\mathrm{HA}}$.
- The equilibrium relationship becomes

$$q(a_{\mathrm{HA}})^2 = (a_{\mathrm{H^+}})(a_{\mathrm{A^-}})$$

- If water autoionization is negligible, then $a_{\mathrm{H^+}} = a_{\mathrm{A^-}}$, so

$$q(a_{\mathrm{HA}})^2 = (a_{\mathrm{A^-}})^2$$

  or

$$a_{\mathrm{A^-}} = \sqrt{q}\, a_{\mathrm{HA}}$$

- We see that $a_{\mathrm{A^-}} \ll a_{\mathrm{HA}}$ provided $\sqrt{q} \ll 1$.
- Punchline: very little acid dissociates if $K_a \ll a_{\mathrm{HA}}$.

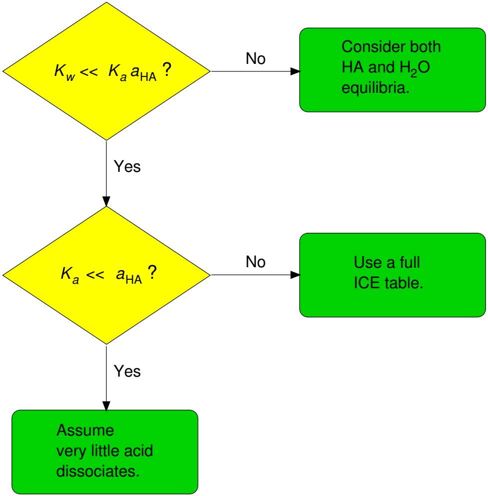
General lessons

But how small is "much smaller"?

- In practice, in acid-base problems, one thing is "much smaller" than another if it's less than 5% of the second quantity or, to put it another way, if the ratio of the large to the small thing is at least 20.

General lessons

A flowchart for the common cases



Balance of acid and conjugate base at given pH

- Sometimes, we put an acid into a solution of fixed pH (a buffer) and want to know how much is in the acid and how much in the conjugate base form.
- This is an easy problem because the pH fixes a_{H^+}, which immediately gives us the ratio of the conjugate base to the acid:

$$\frac{K_a}{a_{\mathrm{H}^+}} = \frac{a_{\mathrm{A}^-}}{a_{\mathrm{HA}}}$$

- This can easily be converted to percentages of the two forms if we add the equation

$$[\mathrm{HA}] + [\mathrm{A}^-] = 100\%$$

(with a slight abuse of notation).

Example: ethanoic acid at pH 4

Suppose that we want to calculate the proportions of ethanoic acid ($K_a = 1.74 \times 10^{-5}$) and of the ethanoate ion (conjugate base) at pH 4.

$$\frac{K_a}{a_{H^+}} = \frac{1.74 \times 10^{-5}}{10^{-4}} = 0.174 = \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$\therefore [CH_3COO^-] = 0.174[CH_3COOH] \quad (1)$$

$$\text{and} \quad [CH_3COOH] + [CH_3COO^-] = 100\% \quad (2)$$

Substituting equation (1) into (2), we get

$$\therefore [CH_3COOH] + 0.174[CH_3COOH] = 1.174[CH_3COOH] = 100\%$$

$$\therefore [CH_3COOH] = 85\%$$

$$\therefore [CH_3COO^-] = 15\%$$

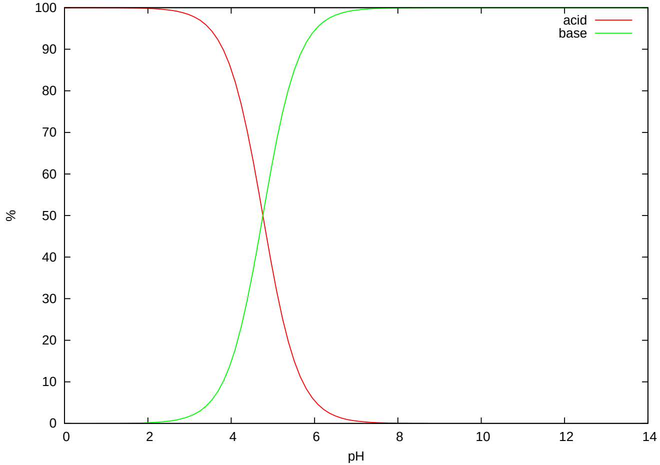
Distribution curves

- If we repeat the above calculation at a number of different pH values and plot the results, we obtain distribution curves for the acid and its conjugate base.
- Note: If pH $=$ pK_a, we have

$$\frac{a_{A^-}}{a_{HA}} = \frac{10^{-pK_a}}{10^{-pH}} = 1$$

In other words, 50% of the acid is undissociated, and 50% in the form of the conjugate base when pH $=$ pK_a.

Distribution curve of ethanoic acid

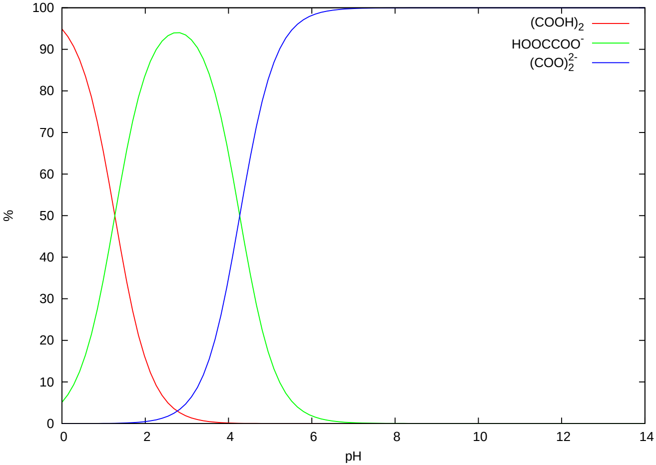


Distribution curves for polyprotic acids

- The calculation is analogous for polyprotic acids except that there are two (or more) equilibria and three (or more) forms of the acid to consider.
- When the pK_a's of a polyprotic acid differ by several units, the distribution curves look like a simple superposition of distribution curves for the monoprotic case.

Distribution curves of ethanedioic acid

$pK_{a1} = 1.27$, $pK_{a2} = 4.27$



Take a log, have an equation named after you...

- We are now familiar with the equation

$$K_a = \frac{(a_{A^-})(a_{H^+})}{a_{HA}}$$

- If we take the negative log of this equation, we get

$$-\log_{10} K_a = -\log_{10} a_{H^+} - \log_{10}\left(\frac{a_{A^-}}{a_{HA}}\right)$$
$$\therefore \mathrm{p}K_a = \mathrm{pH} - \log_{10}\left(\frac{a_{A^-}}{a_{HA}}\right)$$
$$\text{or} \quad \mathrm{pH} = \mathrm{p}K_a + \log_{10}\left(\frac{a_{A^-}}{a_{HA}}\right)$$

- This last equation is called the Henderson-Hasselbalch equation.