BOX 2.1.   Calculation of Acid Dissociation Constants (K_a) and Derivation of the Henderson–Hasselbalch Equation
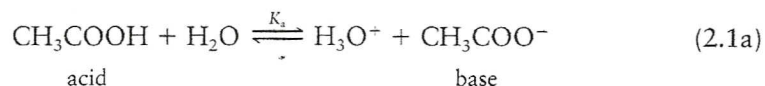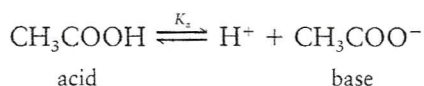
(I) Calculation of K_a and pK_a values.

Suppose that a 0.1 M CH_3COOH (acetic acid) solution is ionized 1.3% at 298K. What is the K_a for CH_3COOH?

$$CH_3COOH + H_2O \xrightleftharpoons{K_a} H_3O^+ + CH_3COO^- \qquad (2.1a)$$
$$\text{acid} \qquad\qquad\qquad\qquad \text{base}$$

or

$$CH_3COOH \xrightleftharpoons{K_a} H^+ + CH_3COO^-$$
$$\text{acid} \qquad\qquad \text{base}$$

Brönsted and Lowry defined an acid as a proton donor and a base as a proton acceptor. According to Lewis an acid is an electron-pair acceptor and a base is an electron-pair donor. The definitions of Lewis are general and also include species that do not have a reactive H^+ (Harris, 1987). In Eq. (2.1a) CH_3COOH is an acid and CH_3COO^- is a base because the latter can accept a proton to become CH_3COOH. Acetic acid and CH_3COO^- are a conjugate acid–base pair. The K_a for the second reaction in Eq. (2.1a) is

$$K_a = \frac{[H^+]\,[CH_3COO^-]}{[CH_3COOH]}, \qquad (2.1b)$$

where brackets indicate concentration in mol liter^{-1}, $[H^+]$ = 0.1 mol liter^{-1} × 0.013 = 0.0013 mol liter^{-1}, $[CH_3COO^-]$ = 0.1 mol liter^{-1} × 0.013 = 0.0013 mol liter^{-1}, and $[CH_3COOH]$ = (0.1000 mol liter^{-1})−(0.0013 mol liter^{-1}) = 0.0987 mol liter^{-1}. Substituting in these values in Eq. (2.1b),

$$K_a = \frac{[0.0013 \text{ mol liter}^{-1}][0.0013 \text{ mol liter}^{-1}]}{[0.0987 \text{ mol liter}^{-1}]}$$
$$= 1.071 \times 10^{-5} \text{ mol liter}^{-1} \qquad (2.1c)$$

The higher the K_a, the more dissociation of the acid into products and the stronger the acid. Acetic acid has a low K_a and thus is slightly dissociated. It is a weak acid. One can also calculate a pK_a for CH_3COOH where

$$pK_a = -\log K_a = -\log 1.071 \times 10^{-5} \text{ mol liter}^{-1} \qquad (2.1d)$$
$$pK_a = 4.77 \qquad (2.1e)$$

The lower the pK_a, the stronger the acid. For example, hydrochloric acid (HCl), a strong acid, has $pK_a = -3$.

(II) Derivation of Henderson–Hasselbalch Equation

One can derive a relationship, known as the Henderson–Hasselbalch equation, between pK_a and pH that is very useful in studying weak acids and in preparing buffers. A buffer is a solution whose pH is relatively constant when a small amount of acid or base is added. Since soils behave as weak acids, the Henderson–Hasselbalch equation is useful in understanding how, if pH and pK_a are known, the protonation and deprotonation of functional groups [formally defined in Chapter 5; an example would be the carboxyl ($R—C{=}O—OH$, where R is an aliphatic group) functional group of soil organic matter in soils] can be assessed.

We know for CH_3COOH that the K_a can be derived from Eq. (2.1b). Taking the $-\log$ of both sides of Eq. [2.1b] results in

$$-\log K_a = \frac{-\log [H^+] [CH_3COO^-]}{[CH_3COOH]}. \qquad (2.1f)$$

Rearranging,

$$-\log K_a = -\log [H^+] - \log \frac{[CH_3COO^-]}{[CH_3COOH]}. \qquad (2.1g)$$

Simplifying,

$$pK_a = pH - \log \frac{[CH_3COO^-]}{[CH_3COOH]}. \qquad (2.1h)$$

Rearrangement yields,

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]} \qquad (2.1i)$$

or

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}. \qquad (2.1j)$$

If $[CH_3COO^-] = [CH_3COOH]$, then

$$pH = pK_a + \log 1. \qquad (2.1k)$$

Since $\log 1 = 0$, Eq. (2.1k) becomes

$$pH = pK_a. \qquad (2.1l)$$

Therefore, when the $pH = pK_a$, 50% of the acid is dissociated (CH_3COO^-) and 50% is undissociated (CH_3COOH). If one is studying the dissociation of a carboxyl functional group associated with soil organic matter, and the pK_a is 5, at pH 5, 50% would be in the undissociated carboxyl ($R—C{=}O—OH$) form and 50% would be in the dissociated, carboxylate ($R—C{=}O—O^-$) form.

Solution pH > pka   deprotonated form dominant
Solution pH < pka   protonated form dominant