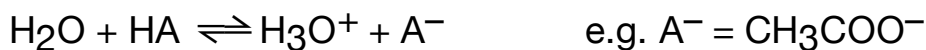


## Acid base dissociation constants

useful for partially dissociated (i.e. **weak**) acids/bases

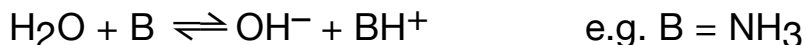
### dissociation of weak acids:



$$K = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}; \quad K[\text{H}_2\text{O}] = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = K_a$$

$K_a$  = acid dissociation constant

### dissociation of weak bases:



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

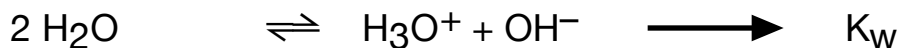
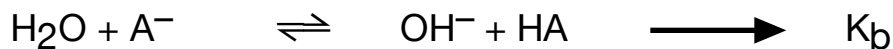
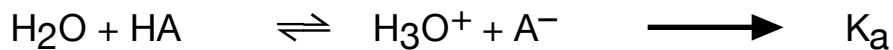
$K_b$  = base dissociation constant

generally:

all carboxylic acids are weak acids

all carboxylate anions are weak bases

## Relationship between $K_a$ and $K_b$



$$K_a \times K_b = K_w$$

We only need to know  $K_a$  or  $K_b$  to calculate the other

Example:

For a calculation, we need the  $K_b$  of mystic base. But we can only find the  $K_a$  of its conjugated acid, mystic acid:  $K_a = 3.4 \times 10^{-9}$

$$K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{3.4 \times 10^{-9}} = 2.9 \times 10^{-6}$$

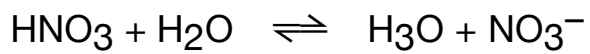
HA and  $\text{A}^-$  are **conjugated** acid-base pairs. Each acid has a conjugated base and vice versa,

e.g.:  $\text{NH}_3$  (base) and  $\text{NH}_4^+$  (conjugated acid of  $\text{NH}_3$ )

## pH- calculations (strong acids)

example: 0.03 M HNO<sub>3</sub>

remember: HNO<sub>3</sub> is fully (100%) dissociated



$$[\text{H}_3\text{O}^+] = 0.030 \text{ mol/L}$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log 0.03 = 1.52$$

## pH- calculations (weak acids)

example: 0.030 M acetic acid

acetic acid is a weak acid and only partially dissociated. The degree of dissociation depends on the concentration of acetic acid and decreases with increasing concentration. At infinite dilution, weak acids are fully (100%) dissociated.

Sources of  $\text{H}_3\text{O}^+$ :  $2 \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

$\text{H}_2\text{O} + \text{HA} \rightleftharpoons \text{H}_3\text{O}^+ + \text{A}^-$

However,  $[\text{H}_3\text{O}^+]$  from acid dissociation suppresses dissociation of  $\text{H}_2\text{O}$

—————> ignore  $K_w$

We know:

**$K_{\text{acetic acid}} = 1.75 \times 10^{-5}$**

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

each dissociating HA yields equal numbers of  $\text{H}_3\text{O}^+$  and  $\text{A}^-$ -ions:

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

analytical (formal) concentration of HA =  $\sum$  of constituent species:

$$[\text{HA}] + [\text{A}^-] = C_{\text{HA}} = 0.03 \text{ mol/L} \longrightarrow [\text{HA}] = C_{\text{HA}} - [\text{A}^-]$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}_3\text{O}^+]^2}{C_{\text{HA}} - [\text{H}_3\text{O}^+]}$$

$$[\text{H}_3\text{O}^+]^2 - K_a[\text{H}_3\text{O}^+] - K_a C_{\text{HA}} = 0$$

quadratic expression!

$$[\text{H}_3\text{O}^+] = \frac{-K_a + \sqrt{K_a^2 + 4K_a C_{\text{HA}}}}{2} = 7.16 \times 10^{-4}$$

$$\text{pH} = 3.15$$

However, quadratic expressions are awkward, so let's simplify:

$$C_{\text{HA}} \approx [\text{HA}] \quad \longrightarrow \quad K_a = \frac{[\text{H}_3\text{O}^+]^2}{C_{\text{HA}}}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a C_{\text{HA}}} = 7.25 \times 10^{-4}$$

$$\text{pH} = 3.14, \text{ a virtually identical result!}$$

error only large, when:

- moderately strong acid ( $K_a > 10^{-2}$ )
- acid concentration low ( $< 10^{-5}$  M)

## Titration curve calculations

titration of strong acid with strong base:

50.0 mL of 0.050 M HCl is titrated with 0.10 M NaOH

A) initially, only HCl present in solution

$$[\text{H}_3\text{O}^+] = 5.0 \times 10^{-2}$$

$$\text{pH} = 1.30$$

B) before the equivalence point

assume all  $[\text{H}_3\text{O}^+]$  is due to HCl dissociation;  $[\text{H}_3\text{O}^+]$  from autoprotolysis of water is suppressed

e.g. @ 20.0 mL NaOH added:

$$[\text{H}_3\text{O}^+] = \frac{\text{initial moles HCl} - \text{moles NaOH added}}{\text{Total volume}}$$

$$[\text{H}_3\text{O}^+] = \frac{50.0 \text{ mL} \times 0.050 \text{ M} - 20.0 \text{ mL} \times 0.10 \text{ M}}{70.0 \text{ mL}} = 7.14 \times 10^{-3}$$

$$\text{pH} = 2.15$$

C) at equivalence point

no excess of HCl or NaOH

all  $[\text{H}_3\text{O}^+]$  from autoprotolysis of water

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = \sqrt{K_w} = 10^{-7}$$

$$\text{pH} = 7.00$$

D) Beyond equivalence point

assume all  $\text{OH}^-$  is due to NaOH excess

e.g. @ 25.1 mL NaOH added:

$$[\text{OH}^-] = \frac{\text{moles of excess NaOH}}{\text{Total volume}}$$

$$[\text{OH}^-] = \frac{25.1 \text{ mL} \times 0.10 \text{ M} - 50.0 \text{ mL} \times 0.050 \text{ M}}{75.1 \text{ mL}} = 1.33 \times 10^{-4}$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = 7.52 \times 10^{-11}$$

$$\text{pH} = 10.12$$

or:

$$\text{pOH} = 3.88$$

$$\text{pH} = \text{p}K_w - \text{pOH} = 14 - 3.88 = 10.12$$

## A closer look at the equivalence point region:

What is the pH @24.99999 mL of NaOH added?

$$[\text{H}_3\text{O}^+] = \frac{50.0 \text{ mL} \times 0.050 \text{ M} - 24.99999 \text{ mL} \times 0.10 \text{ M}}{74.99999 \text{ mL}} = 1.33 \times 10^{-8}$$

$$\text{pH} = 7.88 \text{ ????}$$

How can an excess of HCl generate an alkaline solution???

—————→ Something is wrong with our equation.

: At extreme dilutions, we have to take the autoprotolysis of water into account!!! and we need to apply a **systematic treatment of equilibrium**:

Consider to calculate the pH of  $1.33 \times 10^{-8}$  M HCl:

1) write a charge balance equation:

species in solution are  $\text{H}_3\text{O}^+$ ,  $\text{OH}^-$  and  $\text{Cl}^-$ :

$$[\text{H}_3\text{O}^+] = [\text{Cl}^-] + [\text{OH}^-]$$

2) write a mass balance equation:

$$[\text{Cl}^-] = 1.33 \times 10^{-8}$$

3) equilibria to consider:

$$[\text{H}_3\text{O}^+] \times [\text{OH}^-] = K_w$$



We have three unknowns and three equations: problem can be solved!

We want to calculate the pH, so let's set

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

and

$$[\text{OH}^-] = [\text{H}_3\text{O}^+] - [\text{Cl}^-]$$

Now:

$$K_w = [\text{H}_3\text{O}^+] \times [\text{OH}^-]$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{K_w}{\{[\text{H}_3\text{O}^+] - [\text{Cl}^-]\}}$$

$$[\text{H}_3\text{O}^+]^2 - [\text{H}_3\text{O}^+][\text{Cl}^-] - K_w = 0 \quad \text{another quadratic equation!}$$

$$[\text{H}_3\text{O}^+] = \frac{[\text{Cl}^-] + \sqrt{[\text{Cl}^-]^2 + 4K_w}}{2} = \frac{1.33 \times 10^{-8} + \sqrt{(1.33 \times 10^{-8})^2 + 4(1 \times 10^{-14})}}{2} = 1.067 \times 10^{-7}$$

$$\text{pH} = 6.97$$

This makes much more sense!

**Effect of initial acid concentration on shape of titration curve**  
(each acid titrated with strong base)

