pH calculations

BBT3009 Biochemistry

Dr. Sanjiv Kumar Maheshwari,

Brønsted-Lowry concept of acids and bases

- Acid is a proton donor
- Base is a proton acceptor

$$\underset{\text{Acid}}{HCl(aq)} + \underset{\text{Base}}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+(aq)} + \underset{\text{Conjugate base}}{Cl^-(aq)}$$

$$\underset{\text{Acid}}{H_2O(l)} + \underset{\text{Base}}{NH_3(aq)} \rightleftharpoons \underset{\text{Conjugate acid}}{NH_4^+(aq)} + \underset{\text{Conjugate base}}{OH^-(aq)}$$

Which of the following are conjugate acid-base pairs?

A) HCl, NaOH

B) H_2O, OH^-

C) H_2SO_4, SO_4^{2-}

D) H_2SO_3, HSO_3^-

E) $HClO_4$, ClO_3^-

F) $H_3C\text{-}NH_2$, $H_3C\text{-}NH_3^+$

Autoionization of water

Water is amphoteric as it can behave both as acid and base

$$2\ H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

Ion-product constant for water:

$$K_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

In pure water at 25 ºC:

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}\ \text{mol/L}$$

$K_w = (1.0 \times 10^{-7}\ \text{mol/L}) \times (1.0 \times 10^{-7}\ \text{mol/L}) = \mathbf{1.0 \times 10^{-14}\ mol^2/L^2}$

Constant!

pH

pH= -log $_{10}$(activity of H^+)

pOH= -log$_{10}$(activity of OH^-)

Ion-product of water (constant!):

pH + pOH = 14

Activity = f . c
f is activity coefficient,
f<1,
c is molar concentration

E.g.:

pH=7 (neutral): $[H^+] = 10^{-7}$ M = 0.0000001 mol/l
pH=1 (acidic): $[H^+] = 10^{-1}$ M = 0.1 mol/l
pH=13 (alkaline): $[H^+] = 10^{-13}$ M = 0.0000000000001 mol/l

Strong acid

E.g. HCl, HNO_3, H_2SO_4
In aqueous solution fully dissociates to H^+ and A-

pH of strong acid can be calculated as

$$pH = -\log (f \times [H^+])$$

For HCl: $[H^+]= [HCl]$
For H_2SO_4: $[H^+]= 2 \times [H_2SO_4]$

Calculating the pH of strong acid solutions

Example: Calculate the pH of 0.06 mol/L HCl.

pH = − log0.06 = 1.22

Calculating the pH of strong acid solutions

Example 2: Calculate the pH of 0.02 mol/L H_2SO_4.

pH = − log0.04 = 1.3979 = ~ 1.4

Calculating the pH of strong acid solutions

Example 3: Calculate the pH of 1.0×10^{-10} M HCl.

$\text{pH} = -\log\cancel{(10^{-10}) = 9}$ …. alkaline?

Water contributes more protons than HCl in this case (10^{-7} M), pH will be the same as in pure water, i.e. 7

Strong base

E.g. NaOH, KOH, $Ba(OH)_2$
In aqueous solution fully dissociate to metal ion and OH-

pH of strong base can be calculated as

$$\text{pOH} = -\log (f \times [OH^-])$$
$$\text{pH} = 14 - \text{pOH} = 14 - (-\log (f \times [OH^-])$$

For NaOH: $[OH^-] = [NaOH]$
For $Ba(OH)_2$: $[OH^-] = 2 \times [Ba(OH)_2]$

Calculating the pH of strong base solutions

Example:

a) Calculate the pH of NaOH 0.5 mol/L. pH = 14−(−log0.5) = ~13.7

b) If this solution is diluted 10-fold, what will be the resulting pH?

pH = ~12.7

Weak acid

E.g. H_2CO_3, CH_3COOH

Only some small fraction of molecules in solution dissociates to anion and proton:

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+$$

$$K_d = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]}$$

$$\boxed{pH = \tfrac{1}{2} \times pK - \tfrac{1}{2} \times \log [AH]}$$

$$\boxed{pK = -\log K_d}$$

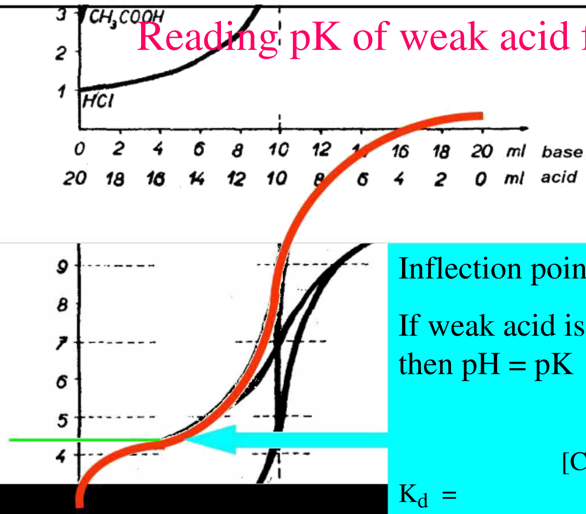
- If we know pK (K_d) and concentration of a weak acid solution, we can calculate (predict) pH of the solution:

$$\boxed{pH = \tfrac{1}{2} \times pK - \tfrac{1}{2} \times \log [AH]}$$

- If we measure pH of a weak acid solution of a known concentration, we can determine its pK (K_d):

$$\boxed{pK = 2 \times pH + \log [AH]}$$

Reading pK of weak acid from titration curve



Inflection point:

If weak acid is just half-titrated, then pH = pK

$$K_d = \frac{[\cancel{CH_3COO^-}] \,.\, [H^+]}{[\cancel{CH_3COOH}]}$$

Calculating the pH of weak acid solutions

Example: Calculate the pH of 0.01 mol/L acetic acid.
$K_a = 1.8 \times 10^{-5}$.

$$pH = \tfrac{1}{2} \times pK - \tfrac{1}{2} \times \log [AH]$$

$$pK = -\log(1.8 \times 10^{-5}) = 4.7447$$

$$pH = \tfrac{1}{2} \times 4.7447 - \tfrac{1}{2} \times \log 0.01 =$$
$$= 2.372 - (-1) = \underline{3.372}$$

Calculating the pH of weak acid solutions

Example 2: Calculate the pH of 0.1 mol/L hypochlorous acid.
$K_a = 3.5 \times 10^{-8}$.

$$pH = \tfrac{1}{2} \times pK - \tfrac{1}{2} \times \log [AH]$$

$$pK = -\log(3.5 \times 10^{-8}) = 7.456$$

$$pH = \tfrac{1}{2} \times 7.456 - \tfrac{1}{2} \times \log 0.1 =$$
$$= 3.728 - (-0.5) = 4\underline{.228}$$

Weak base

E.g. NH_3(aq), organic amines

A fraction of molecules in aqueous solution accepts proton from water:

$$NH_3(aq) + H_2O \leftrightarrow NH_4^+ + OH^-$$

$$K_d = \frac{[NH_4^+] \times [OH^-]}{[NH_3]}$$

$$\boxed{pOH = ½ \times pK - ½ \times \log [B]}$$

$$\boxed{pH = 14 - pOH = 14 - ½ \times pK + ½ \times \log [B]}$$

Calculating the pH of weak base solutions

Example: Calculate the pH of 5 mol/L aqueous ammonia. $K_b = 1.8 \times 10^{-5}$.

$$pH = 14 - ½ \times pK_b + ½ \times \log [B]$$

$$pK_b = -\log(1.8 \times 10^{-5}) = 4.745$$

$$pH = 14 - ½ \times 4.7447 + ½ \times \log 5 =$$
$$= 14 - 2.37236 + 0.349 = \underline{11.977}$$

Hydrolysis of salts

Reaction of dissolved salts with water, e.g.:

A) Anion from a strong acid, cation from a weak base, e.g. NH_4Cl:

$NH_4^+ + H_2O \leftrightarrow NH_3 + H_3O^+$ …pH is acidic

$Cl^- + H_2O \leftrightarrow$ no reaction

B) Anion from a weak acid, cation from a strong base, e.g. $NaHCO_3$:

$Na^+ + H_2O \rightarrow$ no reaction

…pH is alkaline

$HCO_3^- + H_2O \leftrightarrow H_2CO_3 + OH^-$

Calculate the pH of 0.5 mol/L sodium hydrogen carbonate, $NaHCO_3$. The K_{a1} of carbonic acid is 4.3×10^{-7}.

$$pH = 14 - ½ \times pK_b + ½ \times \log [B]$$

$$pK_a = -\log(4.3 \times 10^{-7}) = 5.3665$$

$$pK_b = 14 - 5.3665 = 8.6335$$

$$pH = 14 - ½ \times 8.6335 + ½ \times \log 0.5 =$$
$$= 14 - 4.31675 + (-0.30103) = \underline{9.382}$$