pH calculations
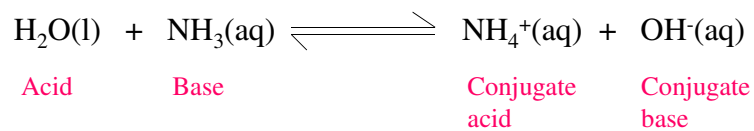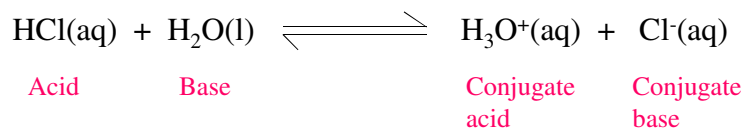
MUDr. Jan Pláteník, PhD

Brønsted-Lowry concept of acids and bases

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

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

Acid   Base   Conjugate   Conjugate
                                        acid   base

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

Acid   Base   Conjugate   Conjugate
                                        acid   base

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:

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

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

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$_2$SO$_4$
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$_2$SO$_4$: [H$^+$]= ~ [H$_2$SO$_4$]
(2nd H$^+$ does not fully dissociate, K$_d$= ~10^{-2})

Calculating the pH of strong acid solutions

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

$pH = - \log 0.06 = \underline{1.22}$

If activity coefficient is known/given:
e.g. f = 0.879, then $pH = - \log(0.879 \times 0.06) = \underline{1.28}$

Calculating the pH of strong acid solutions

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

$pH = - \log 0.02 = 1.3979 = \underline{\sim 1.4}$

Calculating the pH of strong acid solutions

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

$pH = -\log(10^{-10}) = 10$ …. 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

LiOH, NaOH, KOH, Ca(OH)$_2$, Ba(OH)$_2$
In aqueous solution fully dissociate to metal ion and OH$^-$

pH of strong base can be calculated as

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

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:

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

$$K_d = \frac{[CH_3COO^-] \times [H^+]}{[CH_3COOH]}$$
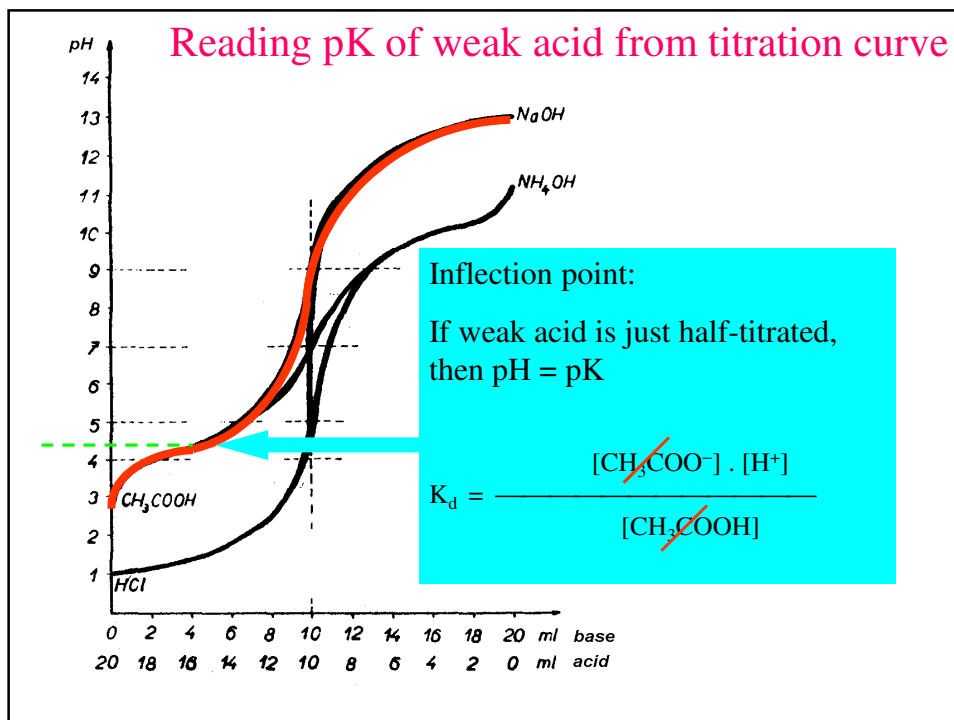
$$pH = ½ \times pK − ½ \times \log [AH]$$

$$pK = −\log K_d$$

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

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

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

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

Reading pK of weak acid from titration curve

Inflection point:

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

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

Calculating the pH of weak acid solutions

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

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

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

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

Calculating the pH of weak acid solutions

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

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

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

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

Titration

- Reaction: A + B → C
- **Substance A:** unknown concentration, amount (solution volume) known
- **Substance B:** known concentration, is used to determine concentration of A
    - added gradually to A until the reaction is just complete, and the consumed amount is recorded
    - an **indicator** is needed to show that the reaction has reached completion

Types of titration

- **Neutralisation reaction (acid-base titration)**

$$HCl + NaOH \rightarrow NaCl + H_2O$$
ionic: $H^+ + OH^- \rightarrow H_2O$

indicator e.g. phenolphthalein (in acid colourless, but violet in alkali

- **Precipitation reaction**
- **Redox reaction**

Titration calculations

Example: An unknown sample of sulfuric acid H_2SO_4 was titrated with the known KOH solution. It was found that 12 mL of the KOH c=0.1 mol/L was needed for just complete neutralisation of 10 mL H_2SO_4 unknown sample.

What is concentration of sulfuric acid in the sample?

Equation: H_2SO_4 + 2 KOH $\rightarrow$ K_2SO_4 + 2 H_2O

Calculation: H_2SO_4 KOH

$$c_1 \cdot v_1 \; = \; c_2 \cdot v_2$$

$$c_1 \; = \; c_2 \cdot v_2 / v_1$$

$$c_1 \; = \; 0.1 \cdot 12 / 10 = 0.12$$

Including stoichiometry : $c(H_2SO_4) = 0.12/2 = \underline{0.06 \text{ mol/L}}$

Weak base

E.g. NH_3(aq), organic amines

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

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

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

$$pOH = \tfrac{1}{2} \times pK - \tfrac{1}{2} \times \log [B]$$

$$pH = 14 - pOH = 14 - \tfrac{1}{2} \times pK + \tfrac{1}{2} \times \log [B]$$

Calculating the pH of weak base solutions

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

$$pH = 14 \ - \ \tfrac{1}{2} \times pK_b \ + \ \tfrac{1}{2} \times log \ [B]$$
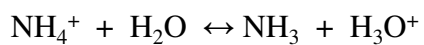
$$pK_b = -log(1.8 \times 10^{-5}) = 4.745$$

$$pH = 14 - \tfrac{1}{2} \times 4.7447 + \tfrac{1}{2} \times log5 =$$
$$= 14 - \ 2.37236 + 0.349 = \underline{11.977}$$

Hydrolysis of salts

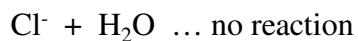Reaction of dissolved salts with water, e.g.:

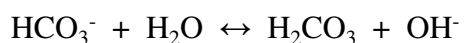A) Anion from a strong acid, cation from a weak base, e.g.
   NH_4Cl:

   $NH_4^+ \ + \ H_2O \ \leftrightarrow NH_3 \ + \ H_3O^+$

   $Cl^- \ + \ H_2O \ \dots$ no reaction

   …pH is acidic

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

   $Na^+ \ + \ H_2O \ \dots$ no reaction

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

   …pH is alkaline

pH of salt will be:

Anion is from…

	strong acid e.g. HCl	**weak acid** e.g. H_2CO_3
strong base e.g. NaOH	**NEUTRAL** e.g. NaCl	**BASIC** e.g. $NaHCO_3$
weak base e.g. NH_4OH	**ACIDIC** e.g. NH_4Cl	**ACIDIC/BASIC (depends on pK…)** e.g. NH_4HCO_3

Cation is from…

Calculate the pH of 0.5 mol/L sodium hydrogen carbonate, $NaHCO_3$. The K_{a1} of carbonic acid is 4.3×10^{-7}.
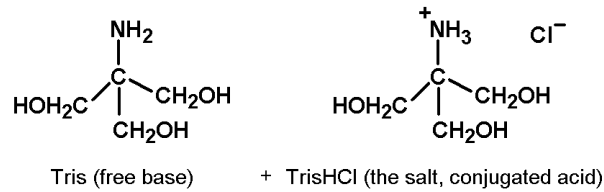
$$pH = 14 - \tfrac{1}{2} \times pK_b + \tfrac{1}{2} \times \log [B]$$

$$pK_a = -\log(4.3 \times 10^{-7}) = 6.3665$$

$$pK_b = 14 - 6.3665 = 7.6335$$

$$pH = 14 - \tfrac{1}{2} \times 7.6335 + \tfrac{1}{2} \times \log 0.5 =$$
$$= 14 - 3.81675 + (-0.1505) = \underline{10.033}$$

Buffers

- Mixture of weak acid and its conjugate base (salt), e.g.:
  - $CH_3COOH + CH_3COONa$
  - $NaH_2PO_4 + Na_2HPO_4$
- Mixture of weak base and its conjugate acid (salt), e.g.:
  - Tris + TrisHCl

Tris (free base)   +   TrisHCl (the salt, conjugated acid)
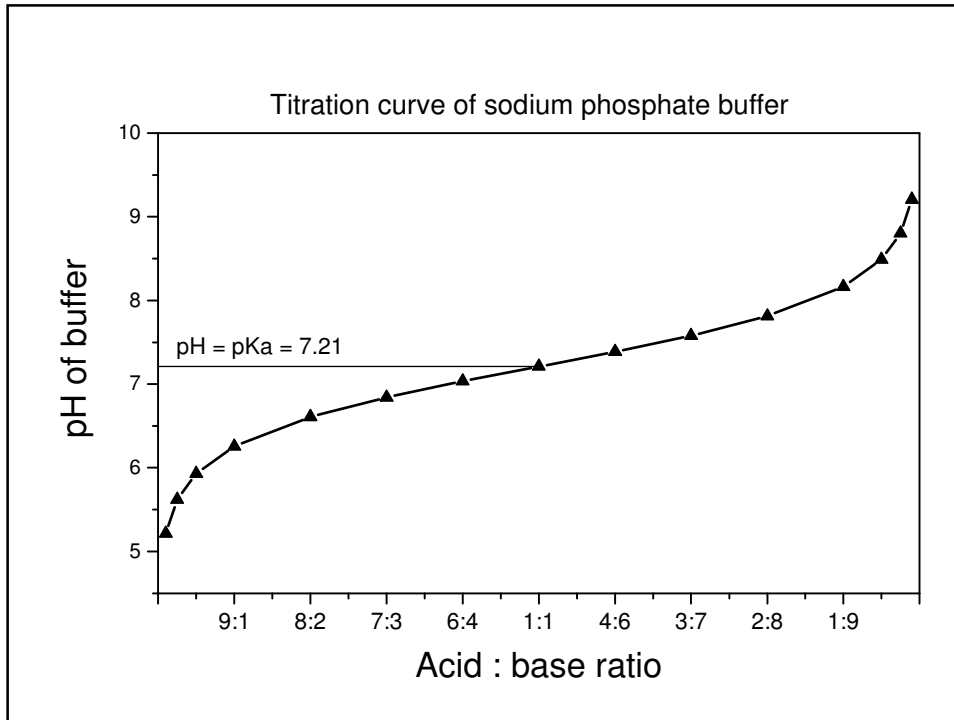
Tris stands for: **Tris(hydroxymethyl)aminomethane**

Henderson-Hassebalch equation

$$pH = pK_a + \log \frac{[A^-]}{[AH]}$$

pK_a …negative log of dissociation constant of the weak acid

$[A^-]$ …substance concentration of the salt/conjugate base

$[AH]$ …substance concentration of the weak acid

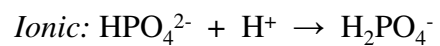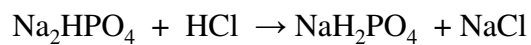## Titration curve of sodium phosphate buffer

pH = pKa = 7.21

pH of buffer (y-axis)

Acid : base ratio (x-axis: 9:1, 8:2, 7:3, 6:4, 1:1, 4:6, 3:7, 2:8, 1:9)

How buffer works

E.g. phosphate buffer: NaH_2PO_4 + Na_2HPO_4

$$pH = pK_a + \log \frac{\blacksquare \blacksquare}{\blacksquare \blacksquare}$$

Addition of strong acid:

Na_2HPO_4 + HCl $\rightarrow$ NaH_2PO_4 + NaCl

Ionic: HPO_4^{2-} + H^+ $\rightarrow$ $H_2PO_4^-$

$$pH = pK_a + \log \frac{\blacksquare}{\blacksquare \blacksquare \blacksquare}$$

How buffer works

E.g. phosphate buffer: NaH_2PO_4 + Na_2HPO_4

$$pH = pK_a + \log \frac{\blacksquare\ \blacksquare}{\blacksquare\ \blacksquare}$$

Addition of strong base:

NaH_2PO_4 + $NaOH$ → Na_2HPO_4 + H_2O

Ionic: $H_2PO_4^{2-}$ + OH^- → HPO_4^{2-} + H_2O
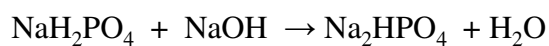
$$pH = pK_a + \log \frac{\blacksquare\ \blacksquare\ \blacksquare}{\blacksquare}$$

Calculating the pH of buffer

Example 1: Calculate the pH of acetate buffer 0.1 mol/L, in which the acid:salt ratio is 2:3.

$K_a = 1.8 \times 10^{-5}$.

pH = pK_a + log [A⁻]/[AH]

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

pH = 4.7447 + log 3/2 =
= 4.7447 + 0.17609 =
= <u>4.92</u>

Calculating the pH of buffer

Example 2: Calculate the pH of sodium phosphate buffer that originated from mixing 150 mL of 0.1 M NaH_2PO_4 and 250 mL of 0.05 M Na_2HPO_4. $pK_a = 7.21$.

$pH = pK_a + \log [A^-]/[AH]$

NaH_2PO_4: 0.1 mol/L $\times$ 0.15 $= 0.015$ mol

Na_2HPO_4: 0.05 mol/L $\times$ 0.25 $= 0.0125$ mol

$pH = 7.21 + \log 0.0125/0.015 =$
$= 7.21 + (-0.07918) =$
$= \underline{{\sim}7.13}$

Calculating the pH of buffer

Example 3: 500 mL of Tris free base 0.1 M was combined with 20 mL of 1 M HCl. What is predicted pH of the resulting Tris/HCl buffer? Tris $pK_b = 5.98$.

$pH = pK_a + \log [A^-]/[AH]$

$pK_a = 14 - pK_b$

Tris free base: 0.05 mol
HCl: 0.02 mol
Tris + HCl $\rightarrow$ TrisHCl

$pH = (14 - 5.98) + \log (0.05-0.02)/0.02 =$
$= 8.02 + 0.176 =$
$= 8.196 = \underline{{\sim}8.2}$