

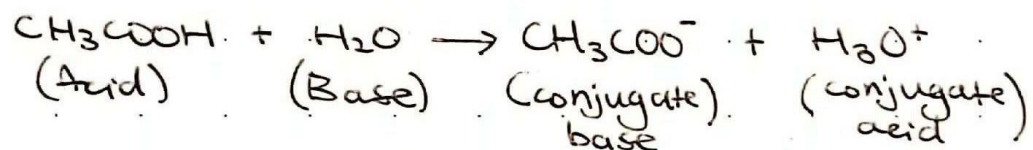
Acid Base Equilibrium

Lin Mingwan (2020)

Theories of Acid and Bases.

- 1) Arrhenius Theory - Acid produce H^+ , Base produce OH^-
- 2) Bronsted - Lowry Theory - Acid donates proton. Base accepts proton
- 3) Lewis Theory - Acid is an electron pair acceptor. Base is an electron pair donator

Conjugate Acid and Conjugate Base



Strength of Acid/Base depends on their degree of dissociation

$$\alpha = \frac{\text{Amt of acid dissociated}}{\text{Initial amount}}$$

Acid dissociation constant (K_a)

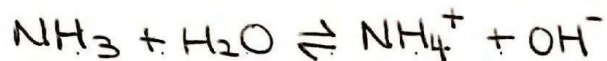


$$pK_a = -\lg K_a$$

$$K_a = \frac{[A^-][H_3O^+]}{[HA]} \text{ mol dm}^{-3}$$

The higher the K_a (the stronger the acid), the smaller the pK_a .

Base dissociation constant (K_b)



$$pK_b = -\lg K_b$$

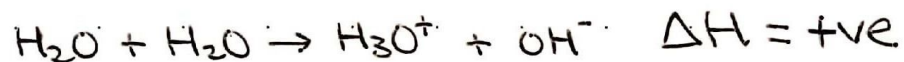
$$K_b = \frac{[OH^-][NH_4^+]}{[NH_3]} \text{ mol dm}^{-3}$$

The higher the K_b (the stronger the base), and the smaller the pK_b .

$$pH = -\lg[H^+] \quad pOH = -\lg[OH^-] \quad pH + pOH = 14 \quad (\text{Round off to 2dp})$$

Ionic Product of Water

$pH + pOH = 14$ only at $25^\circ C$.



$$K_c = \frac{[H_3O^+][OH^-]}{[H_2O]} \rightarrow \text{Constant}$$

Useful Results

$$K_w = K_a \times K_b$$

$$pK_w = pK_a + pK_b$$

$$K_w = [H_3O^+][OH^-] = 1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} \text{ at } 25^\circ C$$

$$pK_w = -\lg K_w = 14$$

* Water is Neutral at all temperature.

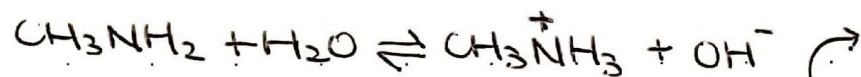
Neutral is when $[H^+] = [OH^-]$.

As temperature increase, the value of K_w will increase because by Le-Chatelier's principle a higher temperature would favour the endothermic reaction, to partially offset the increase in temperature. Autoionisation of water is endothermic.

Finding pH of weak ^{base} acid using ICE Table.

Q1) Calculate the pH of 0.1 mol/dm^3 CH_3NH_2 , given $K_b = 4.54 \times 10^{-4}$, at $25^\circ C$

	B		CA	OH^-
I	0.1		0	0
C	-x		+x	+x
E	0.1-x		x	x



$$K_b = \frac{[OH^-][CH_3NH_3^+]}{[CH_3NH_2]}$$

Let $[OH^-]$ be x

$$\frac{x^2}{[CH_3NH_2 - x]} = 4.54 \times 10^{-4}$$

Since $x \ll 0.1$ as CH_3NH_2 is a weak acid

$$\frac{x^2}{0.1} = 4.54 \times 10^{-4}$$

$$x = 0.00674$$

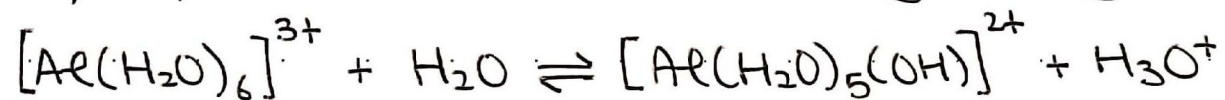
$$-\lg [0.00674] = 2.17 \quad (pOH)$$

$$pH = 11.83 \text{ (2dp)}$$

Important! K_a, K_b, K_c, K_w are all constant unless temperature is changed

Salt Hydrolysis.

1) Hydrolysis of metal cation with high charge/size ratio

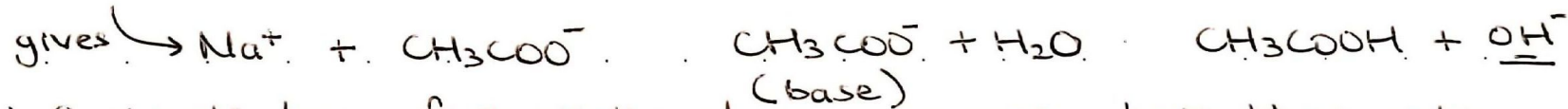


Reasoning: High $\frac{\text{charge}}{\text{size}}$ ratio, attracts H_2O electron density, increase polarity of OH bond, easier to break.

2) Anionic Hydrolysis

Salt form from strong base but weak acid.

E.g. CH_3COONa



Reasoning: Conjugate base of a weak acid is a stronger base than water

3) Cationic Hydrolysis

Salt from strong acid but weak base.

e.g. NH_4Cl .



Example

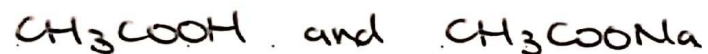
Calculate the pH of 0.05 mol/dm^3 CH_3COONa ($K_a = 1.75 \times 10^{-5}$)



Buffer solutions - solutions that resist pH changes when small amount of acid or base are added, or when solution is diluted.

Because there is a large reservoir of conjugate acid-base pair to remove small amount of acid / base

Acidic Buffer - weak acid and its conjugate base.



Basic Buffer - weak base and its conjugate acid.



pH of acid buffer.

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{salt}]}{[\text{acid}]}$$

pOH of basic buffer

$$\text{pOH} = \text{pK}_b + \lg \frac{[\text{salt}]}{[\text{base}]}$$

Buffer can work effectively as long as $\frac{[\text{salt}]}{[\text{acid}]} / \frac{[\text{salt}]}{[\text{base}]} \approx 1$



Calculating pH (Summary)

1) pH of strong acid/base.

E.g. 0.1 mol of HCl in 1 dm³

$$\text{pH} = -\lg(0.1) = 1$$

0.2 mol of NaOH in 1 dm³

$$\text{pOH} = -\lg[0.2] = 0.699$$

$$\text{pH} = 14 - 0.699 = 13.3$$

2) pH of weak acid/base

E.g. 0.1 mol of CH₃COOH in 1 dm³ $K_a = 1.8 \times 10^{-5}$

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

Find $[\text{H}_3\text{O}^+]$ and do $-\lg[\text{H}^+]$

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

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

$$\frac{x^2}{[0.1 - x]} = 1.8 \times 10^{-5}$$

Since CH₃COOH is a weak acid, $x \ll 0.1$

$$x^2 = 1.8 \times 10^{-5} \times (0.1)$$

$$x = \sqrt{\quad}$$

$$-\lg x = 2.87 \quad \text{pH}$$

Find pH of 0.1 mol/dm³ ethylamine

$$K_b = 6.4 \times 10^{-4}$$

Method 1.

$$\frac{[\text{AH}^+][\text{OH}^-]}{[\text{A}]} = 6.4 \times 10^{-4}$$

$$\frac{x^2}{[0.1 - x]} = 6.4 \times 10^{-4}$$

Since weak, $x \ll 0.1$

$$x = \sqrt{6.4 \times 10^{-4} \times 0.1}$$

$$-\lg[x] = 2.096$$

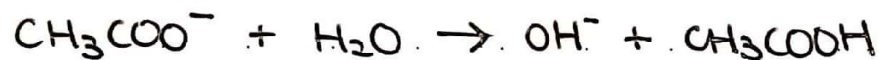
$$\text{pH} = 14 - 2.096 \approx 11.90$$

3) pH of Salt Solution (SAWB / WASB)

0.1 mol/dm³

E.g. $\wedge$ CH_3COONa , K_a of $\text{CH}_3\text{COOH} = 1.75 \times 10^{-5}$

↳ Alkaline salt.



$$K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-]}$$

$$K_b = \frac{K_w}{K_a} = 5.71 \times 10^{-10}$$

Since CH_3COO^- is a weak base, $x \ll 0.1$

$$\frac{x^2}{0.1} = K_b$$

$$5.71 \times 10^{-11} = x^2$$

$$x = \sqrt{5.71 \times 10^{-11}}$$

$$-\lg x = \text{pOH} = 5.12$$

$$\text{pH} = 14 - 5.12$$

$$= 8.88$$

① Find K_b

② Find OH^-

③ Find pH.

4) Finding pH from Buffer Solution.

E.g. Find the pH of Buffer prepared by mixing 20cm^3 of NH_3 (0.1mol/dm^3) and 30cm^3 of NH_4Cl (0.1mol/dm^3) K_b of $\text{NH}_3 = 1.8 \times 10^{-5}\text{mol/dm}^3$

Step ① Determine whether buffer is acidic/basic

Step ② Find concentration of respective species.

$$n_{\text{NH}_3} = \frac{0.1}{1000} \times 20 = 0.002$$

$$[\text{NH}_3] = \frac{0.002}{50} \times 1000 = 0.04\text{mol/dm}^3$$

$$n_{\text{NH}_4^+} = \frac{0.1}{1000} \times 30 = 0.003$$

$$[\text{NH}_4^+] = \frac{0.003}{50} \times 1000 = 0.06\text{mol/dm}^3$$

Step ③ Use formula

For acidic buffer

For Basic buffer

$$\text{pH} = \text{pK}_a + \lg \frac{[\text{salt}]}{[\text{acid}]} \quad \text{pOH} = \text{pK}_b + \lg \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{pOH} = -\lg(1.8 \times 10^{-5}) + \lg \frac{0.06}{0.04}$$

$$= 4.92$$

$$\text{pH} = 14 - 4.92 = 9.079 = 9.08$$

Look at pK_a value of acidic species

OR

pK_b value of basic species.

If $\text{pK}_a < 7$, acidic buffer
vice versa

Indicators for Acid/Base Titration.

Methyl Orange (Red to Yellow)	Orange	pH Range: 3-5	} Strong Acid Weak Base
Phenolphthalein (Colourless to Pink)	Pale Pink	pH Range: 8-10	
Thymolphthalein (Colourless to Blue)	Pale Blue	pH Range: 8-10	} Strong Base Weak Acid

How to choose Indicators for Titration

- 1) Working Range of Indicator falls within the steep slope of titration curve.
- 2) Colour change is sharp.

