Acid Base Equilibrium

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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 donater

Conjugate Acid and Conjugate Base

$$\underset{\text{(Acid)}}{CH_3COOH} + \underset{\text{(Base)}}{H_2O} \rightarrow \underset{\text{(conjugate base)}}{CH_3COO^-} + \underset{\text{(conjugate acid)}}{H_3O^+}$$

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)

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

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

$pK_a = -\lg K_a$

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

Base dissociation constant (K_b)

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

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

$pK_b = -\lg K_b$

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

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

Ionic Product of Water

$pH + pOH = 14$ only at 25°C.

$H_2O + H_2O \rightarrow H_3O^+ + OH^-$ $\Delta H = +ve$

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

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

$pK_w = -lg K_w = 14$

Useful Results

$K_w = K_a \times K_b$

$pK_w = pK_a + pK_b$

*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/dm³ CH_3NH_2, given $K_b = 4.54 \times 10^{-4}$, at 25°C

	B (Base)	CA (conjugate acid)	OH^-
I	0.1	0	0
C	$-x$	$+x$	$+x$
E	$0.1-x$	x	x

$CH_3NH_2 + H_2O \rightleftharpoons CH_3\overset{+}{N}H_3 + OH^-$

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

Let $[OH^-]$ be x

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

Since $x << 0.1$ as CH_3NH_2 is a weak acid

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

$x = 0.00674$

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

$pH = 11.83$ (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

$$[Al(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_3O^+$$

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

gives → $Na^+ + CH_3COO^-$ $\quad$ $\underset{\text{(base)}}{CH_3COO^-} + H_2O$ $\quad$ $CH_3COOH + \underline{OH^-}$

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.

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

Example

Calculate the pH of 0.05 mol/dm³ CH_3COONa ($K_a = 1.75 \times 10^{-5}$)

$$CH_3COO^- + H_2O \rightarrow CH_3COOH + H_3O^+$$

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.

CH_3COOH and CH_3COONa

Basic Buffer - weak base and its conjugate acid.

NH_3 and NH_4Cl

pH of acid buffer.

$$pH = pK_a + \lg\frac{[salt]}{acid}$$

pOH of basic buffer

$$pOH = pK_b + \lg\frac{[salt]}{[base]}$$

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

Calculating pH (Summary)

1) pH of strong acid/base.

E.g. 0.1 mol of HCl in $1dm^3$

$pH = -lg(0.1) = 1$

0.2mol of NaOH in $1dm^3$

$pOH = -lg[0.2] = 0.699$

$pH = 14 - 0.699$

$= 13.3$

2) pH of weak acid / base

E.g. 0.1 mol of CH_3COOH in $1dm^3$. $Ka = 1.8\times10^{-5}$

$$Ka = \frac{[H_3O^+][A^-]}{[HA]}$$

Find $[H_3O^+]$ and do $-lg[H^+]$

$Ka = 1.8\times10^{-5}$

Let $[H_3O^+]$ be x

$$\frac{x^2}{[HA - x]} = 1.8\times10^{-5}$$

Since CH_3COOH is a weak acid, $x << HA$

$x^2 = 1.8\times10^{-5} \times (0.1)$

$x = \sqrt{}$

pH

$-lg\,x = 2.87$

Find pH of 0.1mol/dm^3 ethylamine

$k_b = 6.4\times10^{-4}$.

Method 1.

$$\frac{[AH^+][OH^-]}{[A]} = 6.4\times10^{-4}$$

$$\frac{x^2}{[0.1 - x]} = 6.4\times10^{-4}$$

Since WB, $x << 0.1$

$x = \sqrt{6.4\times10^{-4}\times0.1}$

$-lg[x] = 2.096$

$pH = 14 - 2.096$

≈ 11.90

3) pH of Salt Solution (SAWB / WASB)

$0.1\ mol/dm^3$

E.g. CH_3COONa , Ka of $CH_3COOH = 1.75 \times 10^{-5}$

↳ Alkaline salt.

① Find K_b

② Find OH^-

③ Find pH.

$$CH_3COO^- + H_2O \rightarrow OH^- + CH_3COOH$$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

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

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

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

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

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

$$-\lg x = pOH = 5.12$$

$$pH = 14 - 5.12$$

$$= 8.88$$

4) Finding pH from Buffer Solution.

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

step ① Determine whether buffer is acidic/basic

Look at pKa value of acidic species
OR
pKb value of basic species.
If pKa < 7, acidic buffer
vice versa

step ② Find concentration of respective species.

$n_{NH_3} = \frac{0.1}{1000} \times 20 = 0.002$

$[NH_3] = \frac{0.002}{50} \times 1000 = 0.04 mol/dm^3$

$n_{NH_4^+} = \frac{0.1}{1000} \times 30 = 0.003$

$[NH_4^+] = \frac{0.003}{50} \times 1000 = 0.06 mol/dm^3$

Step ③ Use formula

For acidic buffer

$$pH = pKa + lg\frac{[salt]}{[acid]}$$

For Basic buffer

$$pOH = pK_b + lg\frac{[salt]}{[base]}$$

$$pOH = -lg(1.8\times10^{-5}) + lg\frac{0.06}{0.04}$$

$$= 4.92$$

$$pH = 14 - 4.92 = 9.079 = 9.08$$

Indicators for Acid/Base Titration.

Methyl Orange (Red to Orange Yellow) pH Range : 3-5 } Strong Acid Weak Base

Phenolphthalein (Colourless to Pale Pink Pink) pH Range : 8-10

Thymolphthalein (Colourless to Pale Blue Bule) 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.