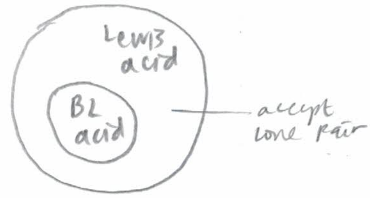


acids and bases.

PROPERTIES OF ACIDS & BASES (REVISION NOTES)

reactions

- acid + base → salt + water
  - $NaOH + HCl \rightarrow NaCl + H_2O$ ∴ $Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^+ + H_2O$

ionic eqn = $H^+ + OH^- \rightarrow H_2O$ = same enthalpyΔ ∴ $H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O(l)$

- acid + metal → salt + hydrogen
  - $Mg_{(s)} + 2H^+ \rightarrow Mg^{2+} + H_2$

{ neutralisation = exothermic! }

- acid + carbonate → salt + CO_2 + water
  - if a carbonate is insoluble ⇒ will NOT have ION breakdown (e.g $CaCO_3$)
- acid + metal oxide → salt + water
- ammonia + acid → ammonium salt
  - $NH_3 + HCl \rightarrow NH_4Cl$

properties of acids (theory)

bronsted lowry — acids are H^+ donors $HCl_{(aq)} \rightarrow H^+_{(aq)} + Cl^-_{(aq)}$
— bases are H^+ acceptors $OH^-_{(aq)} + H^+_{(aq)} \rightarrow H_2O(l)$

!! must have non-bonding e⁻ (pair) bc H^+ has 0 e⁻.

lewis theory — acids are lone pair acceptors (electrophile)
— bases are lone pair donators ⇒ form COORDINATE BOND. (nucleophile)

conjugate acids/bases

AFTER acid donates H^+ → conjugate base (as it can later accept H^+)
AFTER base accepts H^+ → conjugate acid (later donate H^+)

e.g. $\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\text{c. acid}}{NH_4^+} + \underset{\text{c. base}}{OH^-}$ ↳ differ by ONE proton.

the stronger the acid, the weaker its conjugate base

amphiprotic/ amphoteric

water can be a donor/ acceptor of H^+:

$\underset{\text{acts as acid}}{OH^-} \longleftarrow H_2O \longrightarrow \underset{\text{acts as base}}{H_3O^+}$ ∴ AMPHIPROTIC e.g. HCO_3^-

amphoteric is a more general term; can act as "acid" & "base"
BUT not all acids/bases gain/lose H^+ ions.

strengths of acids/bases

- strength = nothing to do with pH → a "STRONG" acid completely dissociates in water to donate a proton — BINARY term.

e.g $HCl \longrightarrow H^+ + Cl^-$

weak = $CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$

? dissociation depends on Δ electronegativity! = more polar = more dissociation
BUT... H-F so strong, water can't break bond

- strong acids / bases have higher conductivity than weak acids / bases
  ↳ also have faster reactions (measure through conductivity probe)

The pH scale

- a measure of H^+ concentration

  pH = $-\log[H^+(aq)]$ $[H^+] = 10^{-pH}$

  $[1\times10^{-0}]$ = pH = 0
  $[1\times10^{-1}]$ = pH 1
  $[1\times10^{-2}]$ = pH 2
  10 fold change

  what is pH of water?

  $H_2O \rightleftharpoons H^+ + OH^-$ reversible ∴ we need the kc value!!

  $k_c = [H^+][OH^-]$ because denominator = 1

  $K_w = [H^+][OH^-] = 10^{-14}$ at 298K (ionic product constant!)

  pK_w is the log of K_w (and $\log a \times \log b = \log a + \log b$)

  ∴ $pK_w = pH + pOH = 14$

  ∴ pH = 7, pOH = 7 in water.

  since $[H^+] = [OH^-]$ ∴ $K_w = [H^+]^2$ or $[OH^-]^2$!

  ∴ pK_w = 2pH or 2pOH

  pH values ... < 7 = acid =7, neutral > 7 = alkali / base

  pH = 14 − pOH

Acid deposition

- acid leaves the atmosphere & falls to the surface of the earth → wet (rain/snow) → dry (smoke)
  → rain is naturally acidic as $H_2O + CO_2 \rightarrow H_2CO_3$ (carbonic acid)
  has pH of 5.6 ∴ < 5.6 = acid rain
- $SO_2 + H_2O \rightarrow H_2SO_3$ (sulphur dioxide), $SO_3 + H_2O \rightarrow H_2SO_4$ (coal)
- $2NO + O_2 \rightarrow 2NO_2$, $2NO_2 + H_2O \rightarrow HNO_3 + HNO_2$ (nitrogen dioxide) (cars)
  - $S + O_2 \rightarrow SO_2$ // $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$
  - $N_2 + O_2 \rightarrow 2NO$ // $4NO_2 + O_2 + 2H_2O \rightarrow 4HNO_3$
- effects of acid deposition
  - $CaCO_3 + H_2SO_3 \rightarrow CaSO_3 + H_2O + CO_2$ // $CaCO_3 + 2HNO_3 \rightarrow Ca(NO_3)_2 + H_2O + CO_2$
    ↳ eroded by acid rain
  - lakes / fish / very sensitive to pH
  - reduced nutrients in the soil e.g. Mg^{2+}, chlorophyll.
- reducing acid rain

  pre-combustion: ONLY ONE; remove sulphur from coal

  catalytic converters: $2NO + CO \rightarrow N_2 + CO_2$ (post)

  treat SO_2 with CaO (scrubbing)

calculations with acids & bases

$pOH = -\log_{10}[OH^-]$ $\quad pK_w = -\log_{10} K_w$ $\quad pK_w = 14$ @ 298K

$\therefore \quad pH + pOH = 14$

K_w & temperature

$H_2O \rightleftharpoons OH^- + H^+$ is endothermic $\uparrow$ temp $\uparrow$ conc of H^+

$\uparrow$ conc of $[H^+]$ = higher pH!! = more acidic?? NO

$[H^+]$ and $[OH^-]$ increase $\therefore$ pH change BUT remains neutral!

weak acids

whenever there is $\rightleftharpoons$ = weak acid, must use K_c value

$\frac{[KA][H^+]}{[HA]}$ = IF K_a (K_c of acid) is large, more H^+ produced $\therefore$ stronger acid

smaller, weaker acid.

$pK_a = -\log_{10} K_a \quad \therefore$ pK_a = larger = weaker acid. (-ve sign!

weak bases

- $B + H_2O \rightleftharpoons BH^+ + OH^- \quad \therefore K_c = \frac{[BH^+][OH^-]}{[B]}$
- stronger weak bases, pK_b of 1 or 2 ... etc.

CALCULATIONS

$HA \rightleftharpoons H^+ + A^- \quad \therefore \quad K_a = \frac{[H^+][A^-]}{[Ha]}$

since $[H^+] = [A^-]$, top = $[H^+]^2$

	HA	H^+	A^-
I	i	–	–
C	$-x$	$+x$	$+x$
E	$i-x$	x	x

$\therefore = \frac{[x]^2}{[i-x]}$ and since x is vvv sma (⇌ = hardly any)

$\therefore i - x \simeq x$

THIS ASSUMES initial concentration DOES NOT CHANGE.

e.g. pH = ? if $pK_a = 4.2$, $[0.1]$ ...

$10^{-4.2} = \frac{[H^+]^2}{0.1} \quad \therefore \quad \sqrt{0.1 \times 10^{-4.2}} = [H^+]$

$\therefore -\log_{10}$ Ans = pH

e.g. K_a = ? if $[0.01]$ pH = 3.1 $\quad \therefore [H^+] = 10^{-3.1}$

$(10^{-3.1})^2 \div [0.01] = K_a = 6.31 \times 10^{-5}$

in bases ... $K_b = \frac{[OH^-]^2}{[B]}$ SINCE ... pOH + pH = 14

logic... with a CA+CB pair $K_w = K_a \times K_b = 1 \times 10^{-14} \quad \therefore pK_w = pK_a + pK_b$

e.g. $\overset{B}{NH_3} + H_2O \rightleftharpoons \overset{CA}{NH_4^+} + OH^-$

$K_b = \frac{[OH^-]\cancel{[NH_4^+]}}{\cancel{[NH_3]}} \quad K_a = \frac{\cancel{[NH_3]}[H^+]}{\cancel{[NH_4^+]}} \quad K_a \times K_b = [OH^-][H^+]$

$\therefore pK_w = 14!$

pH curves

buffer solutions: resist changes in pH when small amounts of acids / bases are added

- ACIDIC BUFFERS

· pH remains constant and acidic (< 7)

· you need a mix of weak acid and its salt (ie conjugate base)

e.g. weak acid, CH_3CO_2H (ethanoic acid) and CH_3CO_2Na (sodium ethanoate)

METHOD ONE (to make buffer)

1. weak acid partially dissociates

$CH_3CO_2H \rightleftharpoons CH_3CO_2^- + H^+$

weak acid forms strong conjugate base

2. salt fully dissociates

$CH_3CO_2Na \rightarrow CH_3CO_2^- + Na^+$

increased conc of conjugate base

∴ $\uparrow H^+$ will be insignificant compared to high conc of acid and its conj. base.

METHOD TWO (to make buffer)

Neutralising excess weak acid & strong base (limiting)

· acid needs to be weak for partial dissociation

$CH_3CO_2H + NaOH \rightarrow CH_3CO_2Na + CH_3CO_2H + H_2O$

initial moles 0.2 | 0.1 moles | 0.0 moles | 0.1 moles (leftover acid)

left over 0.1 | 0.0 | 0.1

↳ leftover $CH_3CO_2H \overset{AND}{=} CH_3CO_2Na \longrightarrow \boxed{CH_3COO^-} + Na^+$

conjugate base

$\boxed{CH_3CO_2H \rightleftharpoons H^+ + CH_3CO_2^-}$

same as method 1.

→ addition of CB ⇒ shifts equilibrium

should be equal conc of leftover acid and its salt!

- BASIC BUFFERS (same idea)

· pH remains constant with pH > 7

· weak base + its salt (conjugate acid)

① e.g. NH_3 and NH_4Cl

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

and $NH_4Cl \rightarrow NH_4^+$ and Cl^-

∴ if H^+ added, OH^- reacts with H^+

∴ if OH^- added, shift to the left

SHOULD BE equal conc of NH_3 & NH_4

② · neutralisation of acid (limit, strong) and weak base (excess)

$NH_3 + HCl \rightarrow NH_4Cl$ (+ leftover NH_3)

0.2 mol | 0.1 mol | ~~0.1 mol~~ | 0.

0.1 mol | | 0.1 mol | (~~0.1 mol~~)

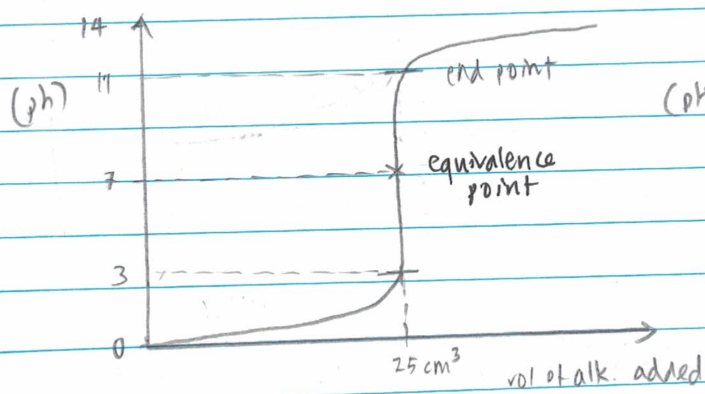
∴ $NH_4Cl \rightarrow \boxed{NH_4^+} + Cl^-$ supply

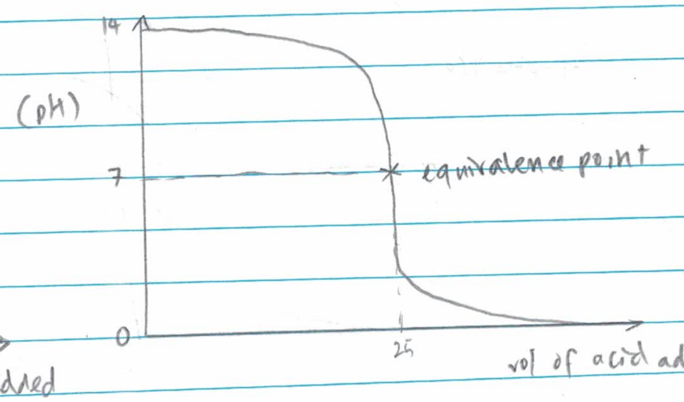
$NH_3 + H^+ \rightleftharpoons NH_4^+$

v low conc

acid and base titrations & pH curves

strong acid, strong base (no buffer, no dissociation / full)



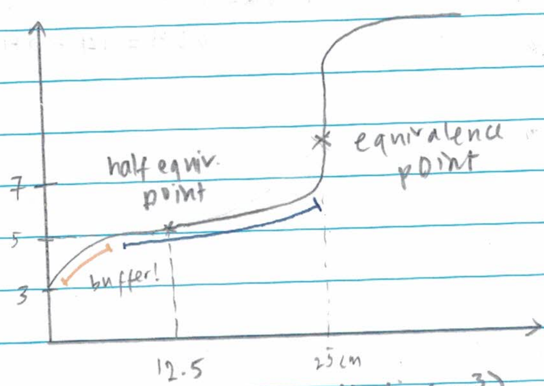


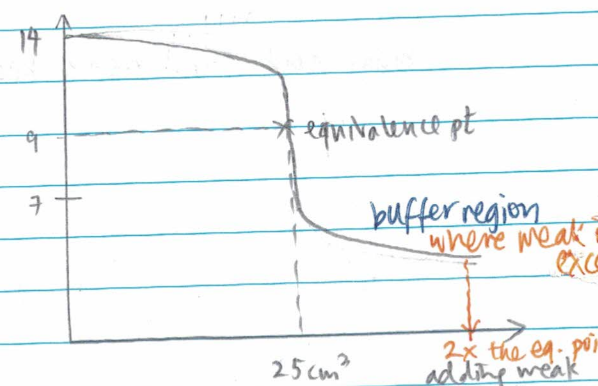
equivalence pt : where ONLY salt & water are present

end pt : volume of alkali (added substance) required for complete reaction ↔ 8 pH units (3-

↳ where indicator changes colour

weak acid, strong base





where end pt changes colour

equivalence point is HIGHER (pH 9) (9.3)

(∴ same conc)

end point is STILL 25 cm^3 as equimolar reaction @ neutralisation

⟼ rapid increase ⟼ buffer region (excess weak acid) ↔ 4 pH units (7-

whatever is weak + in excess!

→ buffer is flattest at half-equivalence point! ↳ the weak acid will partially dissoci

($\frac{1}{2}$ as much base as you have acid) $HA \rightleftharpoons H^+ + A^-$

[base] = [acid] (and the salt is also produced from neutralisation (e.g. $NaCH_3CO_2$) ↓ dissociat

initial	0		20
change	+10		-10
final	10	=	10

∴ using eqn $pH = pKa + \log\left(\frac{base}{acid}\right)$

∴ $pH = pKa$

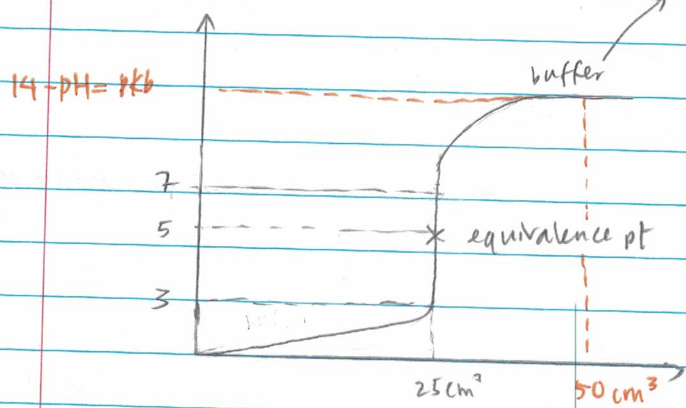
$Ka = \frac{[H^+][A^-]}{[HA]}$ $[A^-]=[HA]$ ∴ $Ka = [H^+]$

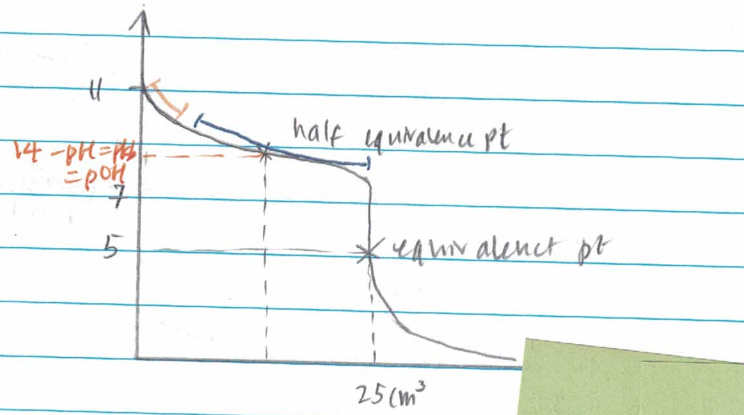
think: at eq. point, NO BASE OR ACID

at half, BASE = ACID

strong acid, weak base

BUFFER = weak substance in excess!





- equivalence pt is LOWER than pH 7 (and pH 5) → [pH 3.7]
- end point is 25 cm³ (pH ⟷ 4, from 3 → 7)
  - ⟼ rapidly ⟼ buffer solution

? half equivalence point pkb = pOH = 14 - pH
when reaction is HALF complete, $[NH_3] = [NH_4]$.
∴ $ka = [H_3O^+]$

(strong A) (weak base)

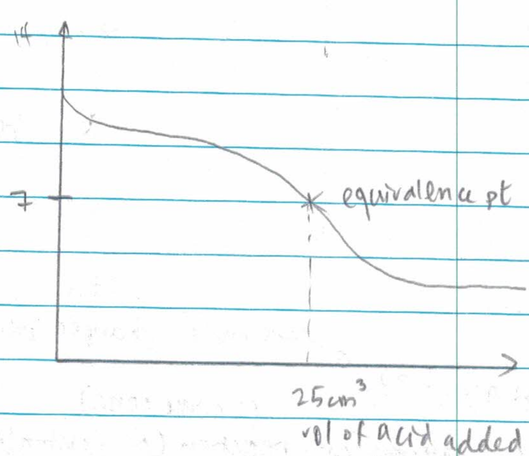
$HCl + NH_3 \rightleftharpoons NH_4Cl$ (kb ?)

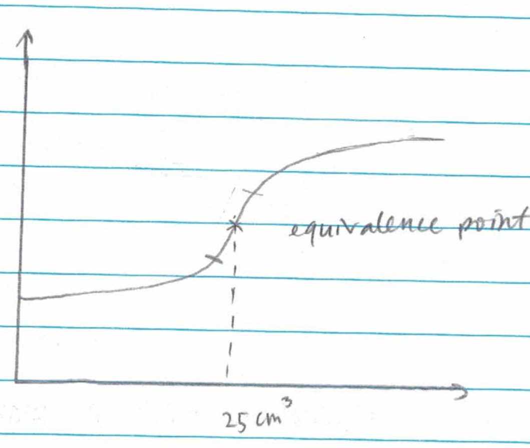
$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$\frac{[NH_3][H_3O^+]}{[NH_4^+]}$

$pOH = 14 - pH$

weak acid and weak base





e.g. CH_3COOH (weak acid) and adding NH_3 (weak base)

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

If you add NH_3

$CH_3COOH + NH_3 \rightleftharpoons NH_4^+ + CH_3COO^-$

at which point ... $[NH_3] = [NH_4^+]$

∴ have a buffer!

$\frac{1 \times 3}{3}$

SALT HYDROLYSIS

1. salt is produced in a neutralization (acid and alkali)
2. pH of salt depends on whether it makes water OH^- or H^+ (hydrolyse)

pattern

strong acid, weak base ← strong acid = no hydrolysis

check anki if confused!

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$NH_4^+ + H_2O \rightleftharpoons \boxed{NH_3} + H_3O^+ \ (H^+)$ pH < 7 (acidic)

strong base, weak acid

$CH_3CO_2Na \rightarrow CH_3CO_2^- + Na^+$

produce something w/o charge!

$CH_3CO_2^- + H_2O \rightleftharpoons \boxed{CH_3CO_2H} + OH^-$ pH > 7 (alkaline)

weak acid, weak base

depends on ka and kb values ($K_a > K_b$ = more acidic)
($pK_a < pK_b$ = more acidic)

! wate
oa

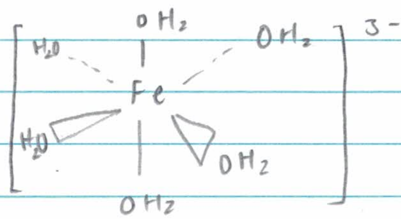
strong acid, strong base

always neutral as ions do not react / hydrolyse water e.g. Na^+ or Cl^-

acidity also depends on CHARGE

- 1+ tends to be neutral
- 2+ acidic
- 3+ more acidic

e.g



Fe^{3+} is lewis acid (empty d-orbitals)

H_2O is lewis base (donate LP)

Fe^{3+} has high charge density → causes attraction with OH^-

∴ H^+ ions are made ⇒ acidic solution.

list of strong acids

H_2SO_4	sulphuric acid
HNO_3	nitric acid
HCl	hydrochloric acid
HBr	

strong bases + $Ba(OH)_2$

NaOH	sodium hydroxide	GRP ONE
KOH	potassium hydroxide	
LiOH	lithium hydroxide	

$Mg(OH)_2$ → strong base

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

$[Fe(H_2O)_5]^{2+} \rightleftharpoons [Fe(H_2O)_4(OH^-)_2]^{1+} + H^+$

$[Fe(H_2O)_4]^{1+} \rightleftharpoons [Fe(H_2O)_3(OH^-)_3] + H^+$

ACID BASE INDICATORS

- all indicators are weak acids and bases.

one colour as weak acid — one colour as weak base

e.g. methyl orange, weak base indicator

acid ← $HIn \rightleftharpoons H^+ + In^-$ → base

(colour A) (colour B)

$\uparrow [H^+]$ shift LHS

∴ A is seen

- due to pka value — only change colour @ pH 3.46

when $[HIn] = [In^-]$ ∴ $ka = [H^+]$, $pka = pH$!

good for strong acid, weak base

e.g. phenolphthalein, weak acid indicator

$InOH \rightleftharpoons In^+ + OH^-$

colour A colour B

- pka value, phenolphthalein $pKa = 9.5$ // $pH = 9.5$

TIPPING POINT // endpoint → $[HIn] = [In]$ is the point where there is colour change.

↳ in mixture of both colours