Acid-Base titration

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Concepts :

- Titration Curve: a graph that shows how the concentration of a reactant varies as titrant is added.
- Equivalence point: point at which stoichiometric amounts of reactants (titrant and analyte) have been mixed. (Idea)
- End point: point near the equivalence point at which a sudden change in a physical property. (we measure actually)
- Titration Error: The difference between the end point and the equivalence point.

- V_e - volume of titrant at equivalence point.
  V_a - volume of titrant were added acid.
  V_b - volume of titrant were added base.

Acid - Base Titration

Strong Acid with Strong Base

1. Before equivalence point: $0 < V_a < V_e$

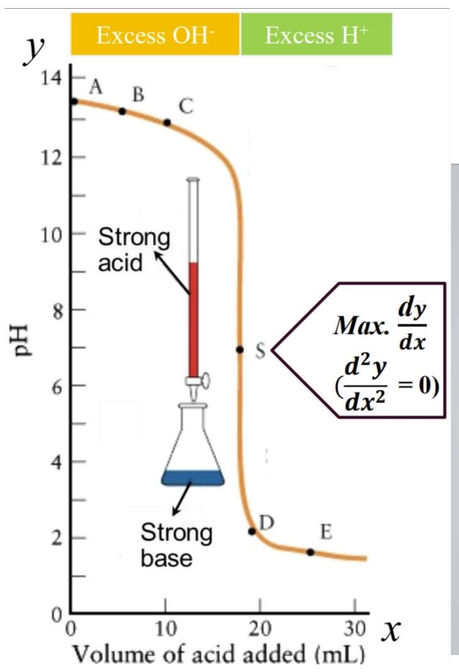
$$[OH^-] = \frac{c(OH^-)\cdot V(OH^-) - c(H^+)\cdot V(H^+)}{V(H^+) + V(OH^-)}$$

2. At equivalence point: $V_a = V_e$

$$[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7.00}$$

3. After equivalence point: $V_a > V_e$

$$[H^+] = \frac{c(H^+)\cdot V(H^+) - c(OH^-)\cdot V(OH^-)}{V(H^+) + V(OH^-)}$$



Titration of 20.00mL 0.1000 mol·L^{-1} HCl with 0.1000 mol·L^{-1} NaOH

NaOH mL	T%	Excess HCl/mL	Excess NaOH/mL	pH	[H⁺] calculation
0.00	0	20.00		1.00	Before titration [H⁺] = c(HCl)
18.00	90.0	2.00		2.28	$[H^+] = \frac{c(H^+)\cdot V(H^+) - c(OH^-)\cdot V(OH^-)}{V(H^+) + V(OH^-)}$
19.80	99.0	0.20		3.30	
19.98	99.9	0.02		4.30	End point: $[H^+] = [OH^-] = 10^{-7.00}$
20.00	100.0	0.00	0.00	7.00	
20.02	100.1		0.02	9.70	
20.20	101.0		0.20	10.70	$[OH^-] = \frac{c(OH^-)\cdot V(OH^-) - c(H^+)\cdot V(H^+)}{V(H^+) + V(OH^-)}$
22.00	110.0		2.00	11.68	
40.00	200.0		20.00	12.52	

Weak Acid with Strong base *

1. Before any base added:

$HA \overset{K_a}{\rightleftharpoons} H^+ + A^-$

$$[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4fK_a}}{2} \quad \left| \quad f \geq 100K_a \Rightarrow [H^+] = \sqrt{fK_a} \right.$$

2. Before equivalence point, $0 < V_b < V_e$

$pH = pK_b + \log\frac{[\text{Salt base}]}{[\text{Salt}]}$ ($[A^-]$ / $[HA]$)

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

$pH = pK_a$ when $V_b = \frac{1}{2}V_e$ ← Max buffer capacity β

3. At equivalence point, $V_b = V_e$

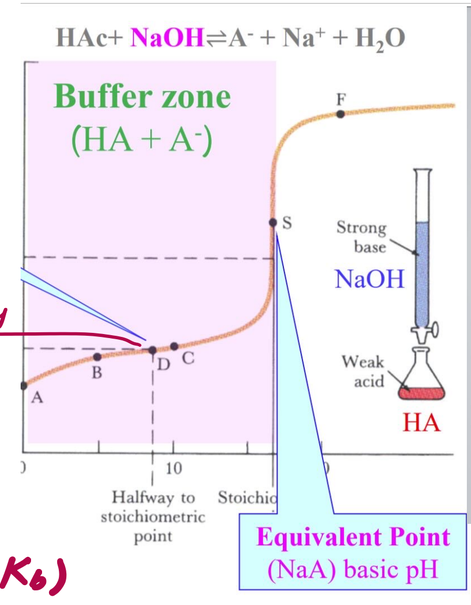
$A^- + H_2O \overset{K_b}{\rightleftharpoons} HA + OH^-$

$K_b = \frac{K_w}{K_a}$. $[OH^-] = \sqrt{K_b \cdot c(A^-)}$ $(c(A^-) \geq 100K_b)$

4. After equivalence point, $V_b > V_e$

$[OH^-] = c(NaOH) + [A^-]$ (Hydrolysis 水解)

$[OH^-] = c(NaOH)$



Titration of 20.00mL 0.10 mol·L^{-1} HA/HAc with 0.10 mol·L^{-1} NaOH

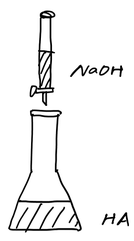
$K_a(HAc) = 10^{-4.76}$, $K_a(HA) = 10^{-7.00}$

NaOH mL	T%	compo-sition	pH (HAc)	pH (HA)	[H⁺] calculation
0	0	HA	2.88	4.00	$[H^+] = \sqrt{K_a \cdot c_a}$ when $f \geq 100\ K_a$, if not?
10.00	50.0	HA+A⁻	4.76	7.00	$[H^+] = \frac{[HA]}{[A^-]} K_a$ (buffer) Henderson–Hasselbalch equ.
18.00	90.0	HA+A⁻	5.71	7.95	
19.80	99.0	HA+A⁻	6.67	9.00	
19.96	99.8	HA+A⁻	7.46	9.56	
19.98	99.9	HA+A⁻	7.76	9.70	
20.00	100.0	A⁻	8.73	9.85	$[OH^-] = \sqrt{K_b \cdot c(A^-)}$ when $c(A^-) \geq 100\ K_b$
20.02	100.1	A⁻+OH⁻	9.70	10.00	
20.04	100.2	A⁻+OH⁻	10.00	10.13	
20.20	101.0	A⁻+OH⁻	10.70	10.70	$[OH^-] = c(NaOH) + [A^-]$ (Hydrolysis) Same with titration of strong base
22.00	110.0	A⁻+OH⁻	11.68	11.68	

Titration Error

$$\frac{C + C_0}{CC_0}\left[\frac{K_w}{[H^+]_{eq}} - [H^+]_{eq}\right]$$ strong acid

C_0 : [HA] C : [NaOH]
V_0 : [HA] v : titrated volume

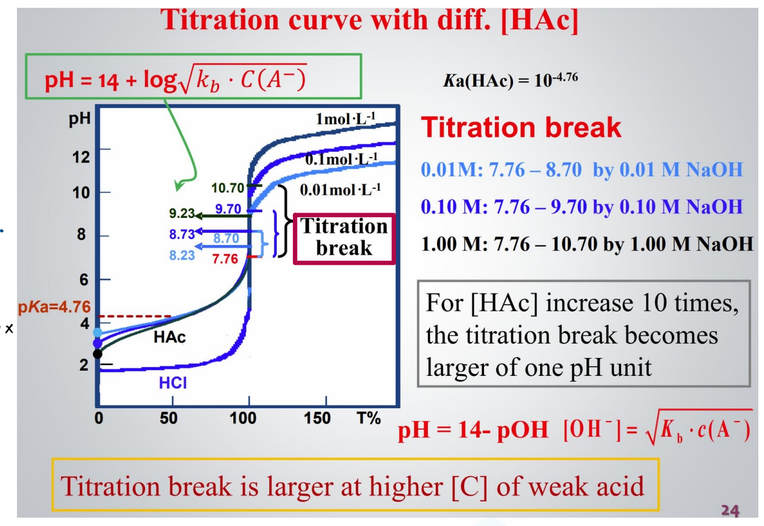


Conclusion: a.) One can calculate its titration error from the pH at end point.
b.) Titration error increase upon reagent dilution.

Given C, C_0 : $\frac{C + C_0}{CC_0} = x$ Dilution by a factor of 2: $\frac{\frac{1}{2}C + \frac{1}{2}C_0}{\frac{1}{2}C \cdot \frac{1}{2}C_0} = 2x$

Resulting From ↑ K_a and ↑ [C]
Titration break ↑ error ↓

Titration Break 滴定转折点

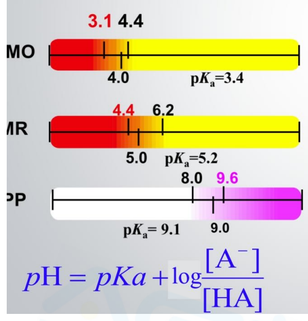


Find End point

① By indicator ② By mathematics → First Derivative *

Common Indicator for acid-base titration

Indicator	Color of acidic form	pKa	pH range of color change	Color of basic form
Methyl orange (MO)	red	3.4	3.2 to 4.4	yellow
Methyl red (MR)	red	5.0	4.8 to 6.0	yellow
Phenolphthalein (PP)	colorless	9.4	8.2 to 10.0	pink



How Indicator works?

$HIn \rightleftharpoons H^+ + In^-$

Color 1 Color 2

$$K_a = \frac{[H^+][In^-]}{[HIn]} \qquad \frac{[In^-]}{[HIn]} = \frac{K_a}{[H^+]}$$

[In-]/[HIn] > 10, pH > pK*a* + 1 → Basic Color

[In-]/[HIn] < 0.1, pH < pK*a* – 1→ Acidic color

Color change range: pH = p*Ka* ± 1

$$pH = pKa + \log\frac{[A^-]}{[HA]}$$

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T7-2. 50 mL of the base methylamine (CH_3NH_2) with a concentration of 0.042M was titrated with HCl and this are the results:

V(HCl)	pH	V(HCl)	pH	V(HCl)	pH
0	11.959	10	10.686	20	9.344
1	11.946	11	10.604	21	6.087
2	11.623	12	10.52	22	2.556
3	11.423	13	10.434	23	2.386
4	11.273	14	10.344	24	2.267
5	11.15	15	10.247	25	2.176
6	11.043	16	10.14	26	2.103
7	10.946	17	10.017	27	2.041
8	10.856	18	9.867	28	1.989
9	10.77	19	9.667	29	1.943

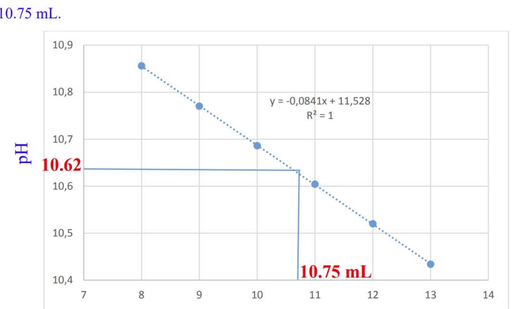
Given that the reaction is: $CH_3NH_2 + HCl \longrightarrow CH_3NH_3^+ + Cl^-$

a. What is the K_a of $CH_3NH_3^+$ (What is the K_b for the methylamine CH_3NH_2)?

To Find **pKa**

pKa = pH ($V_a = \frac{1}{2}V_e$)

volume of HCl. The pK_a is the pH at half volume of the titrant. That is to say, when $V_a = \frac{1}{2}V_e$ = 21.50 mL/2 = 10.75 mL. The pH after adding 10 mL is 10.686, after adding 11 mL the pH is 10.604. We can use the external standard (interpolation) to get the unknown pH at V_a = 10.75 mL.



So, the $CH_3NH_3^+$ pK_a is the pH at the HCl volume of 10.75 mL, which is 10.62.

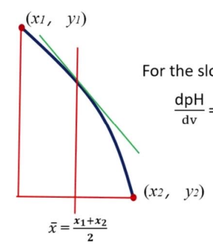
You also can use this formula to get pK_a

pKa = 10.686 + 0.75* (10.604-10.686) = 10.6245

pK_b for methylamine CH_3NH_2 is pK_b = 14 – pKa = 3.38

The sudden change of the pH locates at the range of 20 ~ 22 mL.

V(HCl)	pH
19	9.667
20	9.344
21	6.087
22	2.556
23	2.386

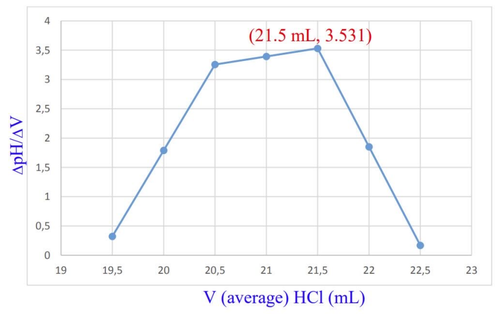


We can obtain the different slopes with the difference of HCl volume,

V̄	Slope (ΔpH/ΔV)
19.5	0.323
20.0	1.79
20.5	3.257
21.0	3.394
21.5	3.531
22.0	1.850
22.5	0.170

= 9.667 - 9.344 / 1

= 9.344 - 2.556 / 2



Prefixes with SI Units

Mega (M)	10^6	deci (d)	10^{-1}
Kilo (K)	10^3	centi (c)	10^{-2}
		milli (m)	10^{-3}
		micro (μ)	10^{-6}
		nano (n)	10^{-9}

Concentrations

Molarity (M: mol/L)

Molality (m: mol/kg)

Percent composition (w/w, v/v or w/v), % (v/v: volume percent; w/w: weight percent)

Parts per million, ppm:	$\frac{\text{mass of substance}}{\text{mass of sample}} \times 10^6$
Parts per billion, ppb	$\frac{\text{mass of substance}}{\text{mass of sample}} \times 10^9$

For aqueous solution: ppm = mg/L = μg/ml (0.001‰, 千分号)

ppb = ng/L = ng/ml

due to $\rho(H_2O) = 1.0\ g/ml$

Dilution formula

$(M_{conc})(V_{conc}) = (M_{dilu})(V_{dilu})$

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Stoichiometry 化學計量學

化学反应中化学物质的量关系的一门学科，它涉及到化学反应中反应物和生成物之间的摩尔关系，质量关系和体积比例等方面.

Limiting reagent: who is inadequate

Experimental error

Random error	+	Systematic error	=	Total Error
⇑		⇑		
Precision	+	Trueness	=	Accuracy
⇑		⇑		
Standard deviation	+	Bias	=	Measurement uncertainty

Example: · impure solvent

too narrow burette

incorrect inspection angle

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Propagation of errors

Addition: $y = x_1 + x_2$ $\quad e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$ → Absolute uncertainty

Multiplication: $y = x_1 x_2$ $\quad e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$ → Relative uncertainty

Significant Figures 有效数字

Addition / Subtraction: determined by fewest decimal places

$$\begin{array}{r} 1.362 \times 10^{-4} \\ +\ \boxed{3.1} \quad \times 10^{-4} \\ \hline 4.5 \quad \times 10^{-4} \end{array}$$

Multiplication / Division: limited by smallest number of S.F

$$\begin{array}{r} \boxed{34.60} \\ \div 2.46287 \\ \hline 14.50 \end{array}$$

Logarithm: $\log(\underbrace{x = 5.403 \times 10^{-8}}_{4\,S.F}) = \underbrace{-7.2674}_{4\ digits}$

Antilogarithm / Exponent: $\text{antilog}(\underbrace{-3.42}_{2\ digits}) = \underbrace{3.8 \times 10^{-4}}_{2\,S.F}$

Rounding: ① Round up: when more than halfway to the next higher digit.

② Round down: when more than halfway to the next higher digit.

③ Round to nearest even digit: exactly halfway (eg. 43.45→43.4)

S.F with uncertainty

The first digit (NOT ZERO) in absolute uncertainty is the last significant figure in magnitude.

eg. $0.09456\ (\pm 0.000153) = 0.09456\ (\pm 0.0002) = 0.0946\ (\pm 0.0002)$ ↗ 根据 error 来调整前面的 S.F

Deviation in random error

Deviation: the difference between the value (x_i) in one set and some fixed value, usually the mean ($\bar{x}$)

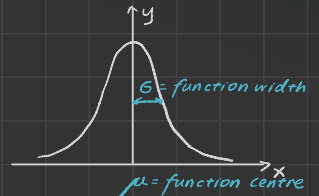
Individual deviation: $d_i = x_i - \bar{x}$

Average deviation: $\bar{d} = \frac{1}{n}\sum_{i=1}^{n} |x_i - \bar{x}|$

Standard Deviation (SD, s)

$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$, measure for precision

Normal (Gaussian) distribution



$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$$

$\mu \pm 1\sigma$	68.3%
$\mu \pm 2\sigma$	95.5%
$\mu \pm 3\sigma$	99.7%

$\lim_{N\to\infty} s = \sigma$

The population SD is σ

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Relative Standard Deviation (RSD)

$$RSD = \frac{s}{\bar{x}} \times 100\%$$

Standard deviation of the Mean (S_m)

Many sets of measurements are performed and the mean is calculated for each set. The SD of these means is calculated for estimating the width of the distribution of the means.

set 1	$\bar{x}_1 = 96$
set 2	$\bar{x}_2 = 97$
⋮	⋮
set m	$\bar{x}_m = 95$

$$S_m = \sqrt{\frac{\sum_i (\bar{x}_i - (\bar{\bar{x}})^2}{m-1}}$$

($\bar{\bar{x}}$: Means of the mean; m: No. of the set.)

Calculation of S_m directly from the N ($N > 1$) measurements:

$S_m = \frac{s}{\sqrt{N}}$, $S_m < S$, S_m decreases by a factor $\frac{1}{\sqrt{N}}$ through making N repeated measurements.

Presentation of the results

Experimental result:

- Mean
- SD of the mean
- NO. of the measurement

$\bar{x} = 0.15M$

$S_m = \frac{0.02}{\sqrt{6}} M$

$N = 6$

Instrument or method:

- SD of measurement
- No. of the measurements

$S = 0.02M$

$N = 6$

Calibration methods

A method to measure the unknown quantity from the known quantity from the known quantities of analyte (standards)

① Externel standard.

② Standard addition

③ Internal standard

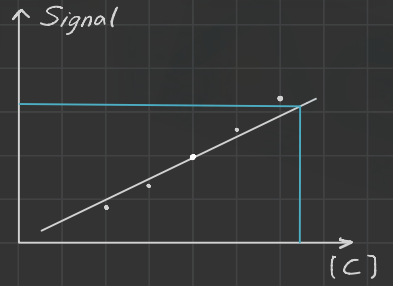
External Standard

① prepare multiple solutions containing different [C]s of analyte with known quantities.

② Measure signals for each [C].

③ Make the calibration curve.

④ Find the unknown [C] through the curve.



Matrix Effect: the change in the analytical signal caused by anything in the sample other than analyte

Standard Addition (Added standard the same substance as analyte)

Based on addition known quantities of analyte to the unknown.

(Samples are made in almost the same matrix.)

Signal intensity - I :

$I_x = k[X]_i$ ($[X]_i$: initial conc. of unknown)

$I_{(x+s)} = k([X]_f + [S]_f)$ ($[X]_f$: final conc. of unknown; $[S]_f$: final conc. of standard.)

$$\frac{I_x}{I_{x+s}} = \frac{[X]_i}{[X]_f + [S]_f}$$

$$[X]_f = [X]_i \frac{V_0}{V}$$

$$[S]_f = [S]_i \frac{V_s}{V}$$

eg. Na^+ in serum gave a signal of 4.27 mV

5 mL of 2.08 M NaCl Added to 95.0 mL serum sample.

The spiked serum gave a signal of 7.98 mV.

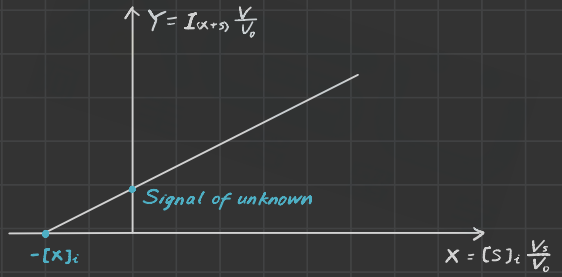
Find the conc. of Na^+ in serum.

$$\frac{I_x}{I_{x+s}} = \frac{[Na^+]_i}{0.95[Na^+]_i + \frac{2.08 \times 5}{100}} = \frac{4.27\,mV}{7.98\,mV} \Rightarrow [Na^+]_i = 0.113\,M$$

A solution with successive additions

Conc. of standard sample 非常大, V_s 非常小以尽可能不破坏 Matrix

$$\underbrace{I_{(x+s)}\left(\frac{V}{V_0}\right)}_{Y} = I_x + \frac{I_x}{[X]_i}\underbrace{[S]_i\left(\frac{V_s}{V_0}\right)}_{X}$$



Multiple solutions with constant V

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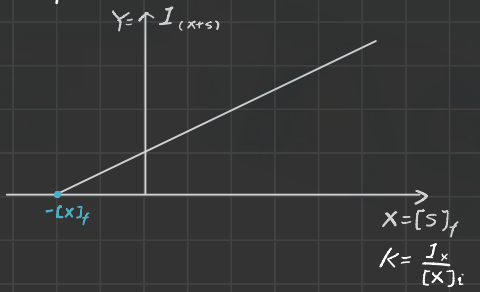


Add $V_0 = 5$ mL of unknown

Add standard of analyte [C] with increase V_s

Fill all to $V = 50$ mL

$$\underbrace{I_{(x+s)}}_{Y} = \frac{I_x}{[X]_i}[X]_f + \frac{I_x}{[X]_i}\underbrace{[S]_f}_{X}$$



Internal Standard

The added standard is the same substance as analyte to address matrix effect.

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Principles of chemical equilibrium

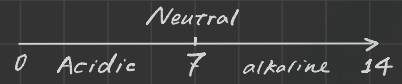
Reaction: $aA + bB \rightleftharpoons cC + dD$

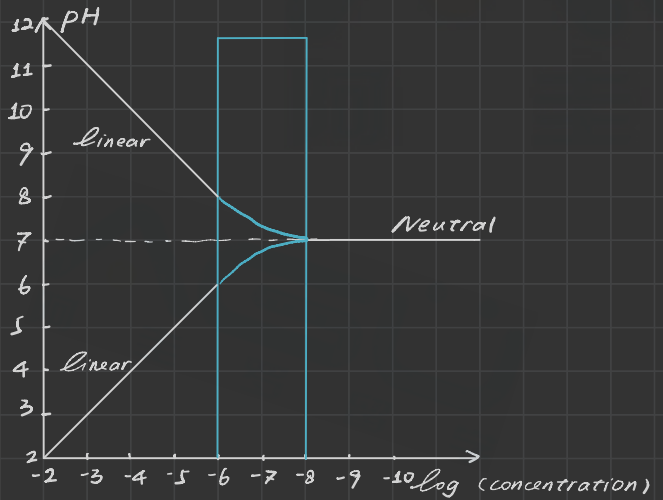
$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}, \quad \underbrace{K'}_{\text{reserved}} = \frac{1}{K}, \quad \underbrace{K_3}_{\text{Added}} = K_1 \cdot K_2$$

The PH Scale

$pH \approx -\log[H^+]$ $\quad$ $pOH = -\log[OH^-]$

The pH range generally:





Strong Acid / Base

HA	$\xrightarrow{K_a}$	$H^+ + A^-$	
f		$0 \quad 0$	$K_a = \frac{(f+y)x}{f-x}$
0		$f \quad f$	
H_2O	$\xrightarrow{K_w}$	$H^+ + OH^-$	$K_w = (f+y)y$
		$y \quad y$	

Strong Acid: $[H^+] = \frac{f + \sqrt{f^2 + 4K_w}}{2}$

Strong Base: $[H^+] = \frac{-f + \sqrt{f^2 + 4K_w}}{2}$

Weak Acid

HA	$\xrightarrow{K_a}$	$H^+ + A^-$	
f		$0 \quad 0$	$K_a = \frac{(x+y)x}{f-x}$
$f-x$		$x \quad x$	
H_2O	$\xrightarrow{K_w}$	$H^+ + OH^-$	$K_w = (x+y)y$
		$y \quad y$	

Weak Acid: $[H^+] = \frac{-K_a + \sqrt{K_a^2 + 4fK_a}}{2}$

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Simplify the formula:

$f \geq 10^{-6} M$: $[H^+] = f$

$f \geq 100 K_a$: $[H^+] = \sqrt{f K_a}$

Buffer solutions

weak acid + its conjugated base
weak base + its conjugated acid
} a solution that slightly changes its pH upon addition of acid, base or dilution.

$$HA \underset{}{\overset{K_a}{\rightleftharpoons}} H^+ + A^-$$

$$\log K_a = \log[H^+] + \log\frac{[A^-]}{[HA]} \Rightarrow pK_a = pH + \log\frac{[A^-]}{[HA]}$$

when $[A^-] = [HA]$, $pH = pK_a$

Buffer Capacity, β:

A quantity that represents the resistance of pH upon addition of strong acid/base.

$$\beta = \frac{dC_b}{dpH} = \frac{-dC_a}{dpH}$$, where C_a and C_b are the moles of strong acid/base per 1L to produce a unit change in pH.

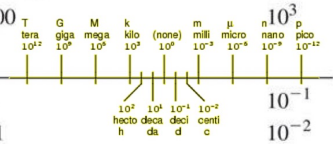
$$\beta = 2.3C \times \alpha(HA) \times \alpha(A^-)$$, $\beta_{max} = 0.575c$

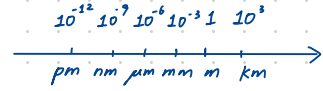
$$\alpha(A^-) = \frac{[A^-]}{[A^-]+[HA]} = \frac{K_a}{K_a + [H^+]}$$

$$\alpha(HA) = \frac{[HA]}{[HA]+[A^-]} = \frac{[H^+]}{K_a + [H^+]}$$

Common Prefixes with SI Units

Prefix[a]	Symbol	Meaning	Numerical Value	Scientific Notation
Prefixes That Increase the Size of the Unit				
tera	T	trillion	1 000 000 000 000	10^{12}
giga	G	billion	1 000 000 000	10^{9}
mega	M	million	1 000 000	10^{6}
kilo	k	thousand	1 000	10^{3}
Prefixes That Decrease the Size of the Unit				
deci	d	tenth	0.1	10^{-1}
centi	c	hundredth	0.01	10^{-2}
milli	m	thousandth	0.001	10^{-3}
micro	μ	millionth	0.000 001	10^{-6}
nano	n	billionth	0.000 000 001	10^{-9}
pico	p	trillionth	0.000 000 000 001	10^{-12}
femto	f	quadrillionth	0.000 000 000 000 001	10^{-15}





SI Unit

- meter (m) → Length
- kilogram (kg) → Mass
- second (s) → Time
- ampere (A) → Electric current
- kelvin (K) → Temperature
- mole (mol) → Amount of substance

Derived SI Units →

- force (newton, N), kg·m / s²
- pressure (pascal, Pa), N / m²
- energy (joule, J), N·m

Concentrations

Molarity, M (mol/L)

Molality, m (mol/kg)

- **Formal concentration** (formula units per liter), F
- **Percent composition** (w/w, v/v or w/v), %
- **Parts per million,** ppm
- **Parts per billion,** ppb

Weight percent $\frac{w}{w}$

Volume percent $\frac{v}{v}$

eg. 95% (w/w) ethanol contains 95 g of ethanol of every 100 g of solution.

$$ppm = \frac{\text{mass of substance}}{\text{mass of sample}} \times 10^{6} = mg/L = \mu g/mL$$

(if the density of solution is 1 g/ml)

$$ppb = \frac{\text{mass of substance}}{\text{mass of sample}} \times 10^{9} = \mu g/L = ng/mL$$

Making solutions

Dilution formula: $(M_{conc})(V_{conc}) = (M_{dil})(V_{dil})$

Stoichiometry

Dissolve -> Oxidize -> Precipitate -> Sinter -> Weigh

Limiting reagent

a. Find the number of moles of each available reactant;

b. Compare the number of moles present to the number of moles required for a complete reaction;

c. Determine the limiting one (who is inadequate).

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