Aqueous Solution Equilibria:

Acid-base:

\[ \text{CH}_3\text{COOH} + \text{CH}_3\text{NH}_2 \rightarrow \text{CH}_3\text{COO}^- \text{(aq)} + \text{CH}_3\text{NH}_3^+ \text{(aq)} \]

Conjugate acid-base pairs.

Almost entirely proton xfer rxs, so Bronsted-Lowry def'n of acid-base is usu. enough.

In general:

\[ aA + bB \rightleftharpoons cC + dD, \text{ write } K = K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} \]

\((c, d \text{ all in M units})\)

\((\text{Std. state is } 1 \text{ M})\)

If any solids, leave out \(A\) \text{ solid} = 1

If any pure liquids, use pressure in units of bar.

\((\text{Std state is } 1 \text{ bar})\)

In general, \(\Delta G_r^0 = -RT\ln K\) or \(K = e^{-\Delta G_r^0/RT}\)

Other types:

Can see that \(K\) depends on \(T\).

Solubility equil:

\[ \text{Hg}_2\text{Cl}_2 (s) \rightleftharpoons \text{Hg}_2^{2+} \text{(aq)} + 2\text{Cl}^- \text{(aq)} \]

\(K = K_{sp} = [\text{Hg}_2^{2+}][\text{Cl}^-]^2\) (leave out solid).

\(= 1.2 \times 10^{-18} \text{ (M}^3\) at 25°C.

Strictly speaking, \(K\) has no units, but often see people include units to remind themselves to use M, bar.
Complexation Rxs

\[ \text{Cu}^{2+} (aq) + 4 \text{NH}_3 \ (aq) \rightleftharpoons \text{Cu} (\text{NH}_3)_4^{2+} \]

\[ K = K_f = \frac{[\text{Cu} (\text{NH}_3)_4^{2+}]}{[\text{Cu}^{2+}][\text{NH}_3]^4} = 1.2 \times 10^{13} \]

formation const.

Redox rxns: e- xfer, coming in w/1 week.

In acid-base reactions, often need to deal with multiple equilibria: All eq. expressions must be satisfied simultaneously.

• Water "autoionization" (self-ionization)

\[ \text{H}_2\text{O}(l) + \text{H}_2\text{O}(l) \rightleftharpoons \text{H}_3\text{O}^+ (aq) + \text{OH}^- (aq) \]

hydronium hydronyl

Here water is both acid and base!

(amphiprotic; H+ donor or acceptor)

\[ K = K_w = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C} \]

\[ \Delta G^\circ = +79.89 \text{ kJ/mol at } 298 \text{ K} \]

Water is weak acid and weak base!

\[ K_w \] is numerically small because

\[ \Delta G^\circ \text{ is very positive. } (\Delta G^\circ = -RT \ln K) \]
\[ \text{pH, pOH} \]

Strictly, \[ \text{pH} = -\log a_{H^+} \approx -\log [H^+] \]
\[ \text{pOH} = -\log a_{OH^-} \approx -\log [OH^-] \]

Since \[ K_w = 1.0 \times 10^{-14} = [H^+] [OH^-] \]
\[ -14.00 = \log [H^+] + \log [OH^-] \]
\[ 14.00 = -\log [H^+] - \log [OH^-] \]
\[ \text{pH} + \text{pOH} = 14.00 \text{ at equilibrium.} \]

Pure, neutral water:

\[ 2H_2O \rightleftharpoons H_3O^+ + OH^- \]

Let \( x = \text{equil.} \) \[[H^+] = [OH^-] \]
\[ K_w = 1.0 \times 10^{-14} = x^2 \]
\[ x = 1.0 \times 10^{-7} = [H^+] = [OH^-] \]
\[ \text{pH} = \text{pOH} = 7.00 \]

Acidic: \( \text{pH} < 7, \text{pOH} > 7 \)
Basic: \( \text{pH} > 7, \text{pOH} < 7 \).
Weak acid: (acetic, formic, ...) HF

\[ \text{HA}(\text{aq}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{A}^- (\text{aq}) \]

or

\[ \text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{A}^- (\text{aq}) \]

Acid dissociation constant:

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

See Table 10.1.

Weak acids numerous. Strong acids less common

\((\text{HCl, HNO}_3, \text{H}_2\text{SO}_4)\).

\(x = (1.0 - x) \times x \times x\)

Ex. \(\text{CH}_3\text{COOH}(\text{aq}) \rightleftharpoons \text{H}^+ (\text{aq}) + \text{CH}_3\text{COO}^- (\text{aq})\)

\[ K_a = 1.8 \times 10^{-5} = \frac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \]

What is pH of 1.0 M acetic acid?

Let \( x = \text{eq. conc. of CH}_3\text{COO}^- \).

Approx: \( x = [\text{H}^+] \) also. (Neglect \( \text{H}^+ \) from water auto-protonesis).

\[ \frac{x^2}{1.0 - x} = 1.8 \times 10^{-5} \]
To be accurate:

\[ x^2 + 1.8 \times 10^{-5}x - 1.8 \times 10^{-5} = 0 \]

\[ x = -1.8 \times 10^{-5} \pm \sqrt{(1.8 \times 10^{-5})^2 + 4(1.8 \times 10^{-5})} \]

\[ (H^+) = 4.23 \times 10^{-3} \text{ M} \]

\[ pH = -\log (H^+) = 2.4 \]

\[ [OH^-] = \frac{1.0 \times 10^{-14}}{4.23 \times 10^{-3}} = 2.4 \times 10^{-11} \text{ M} \]

\[ pOH = 11.6 \]

Aside:

Many larger than \( 10^{-7} \text{ M} \) in neutral \( \text{H}_2\text{O} \), so neglect of \( \text{Kw} \) is ok.

But look at original eqs:

\[ \frac{x^2}{1.0-x} = 1.8 \times 10^{-5} \]

New approx: assume \( x \ll 1.0 \) (Check later)

\[ x^2 \approx 1.8 \times 10^{-5} \]

\[ x = \sqrt{1.8 \times 10^{-5}} = 4.23 \times 10^{-3} \text{ M} \ll 1.0 \]

Works fine!

Can see this in quadratic eq.
Weak base \((NH_3, \text{ other amines, } NH_2OH, \ldots)\)

Strong base:
\(KOH, NaOH\)

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

\[K = K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5} \quad (25^\circ C)\]

What is pH of 1.0 M \(NH_3(aq)\)?

Same eq! \(\frac{x^2}{1.0-x} = 1.8 \times 10^{-5}\)

\[B + H_2O \rightleftharpoons BH^+ + OH^-\]

\[K_b = \frac{[BH^+][OH^-]}{[B]} \quad x = [OH^-] = 4.2 \times 10^{-3} \text{ M}\]

\[pOH = 2.4 \quad pH = 11.6 \quad \left(\frac{[H^+]}{[OH^-]} = \frac{1.0 \times 10^{-14}}{[OH^-]}\right)\]

Table 10.2: weak base \(K_b\) 's.

Conjugate acid or base of weak acid or base is usu. weak itself!
Ex. What is pH of 1.0 M NaCH₃COO solution?

Na⁺ is spectator. But CH₃COO⁻ (aq) is weak base.

(conj. base of weak acid CH₃COOH).

* You won't find CH₃COO⁻ in Table 10.2.

What is chemistry? Start with what you have lots of!

\[
\text{CH}_3\text{COO}^- (aq) + \text{H}_2\text{O} (l) \rightleftharpoons \text{CH}_3\text{COOH} (aq) + \text{OH}^- (aq)
\]

\[
K = K_b = \frac{[\text{CH}_3\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{COO}^-][\text{H}^+]} = \frac{K_w}{K_a}
\]

For CH₃COO⁻: \(K_b = \frac{K_w}{K_a}\) for CH₃COOH

\[
K_b K_a = K_w
\]

for conj. acid-base pair.

Important:

Since \(K_w\) is so small, there is "lots of room" for both \(K_b\) and \(K_a\) to be small.

Often see \(pK_a = -\log K_a\) and \(pK_b = -\log K_b\)

\[
\log K_b + \log K_a = \log K_w = -14.00
\]

\[
pK_a + pK_b = 14.00 \quad \text{(conj. acid-base pair)}
\]
So for $\text{CH}_3\text{COO}^-$, $K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}}$

$$K_b = 5.6 \times 10^{-10} \quad \text{(quite weak)}$$

$$(1.0 - x) \quad x \quad x$$

$\text{H}_2\text{O} + \text{CH}_3\text{COO}^- \rightleftharpoons \text{CH}_3\text{COO}H + \text{OH}^-$

Neglecting $\text{H}_2\text{O}$ eq. here — might not work!

$$\frac{x^2}{1.0 - x} = 5.6 \times 10^{-10}$$

Assume $x \ll 1.0$

$$x = \sqrt{5.6 \times 10^{-10}} = 2.4 \times 10^{-5} \text{ M} = [\text{OH}^-]$$

$$240 \times \text{original } 10^{-3} \text{ M, so okay}$$

$pO_H = 4.6$

$pH = 9.4 \quad \text{(basic)}$
Mixtures (Buffers, Titrations)

1. Strong acid + strong base → salt solution.

Ex. Make sol'n that is 0.1 M NaOH and 0.2 M HCl. What happens?

Both NaOH and HCl ionize completely (strong base, acid)

So you have $[\text{Na}^+]_{\text{ini}} = [\text{OH}^-]_{\text{ini}} = 0.1 \text{ M}$

$[\text{H}^+]_{\text{ini}} = [\text{Cl}^-]_{\text{ini}} = 0.2 \text{ M}$.

NaCl is completely soluble, so no Na$^+$ + Cl$^-$ can.

But: $\text{H}^+ (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O} (l)$

$K = \frac{1}{[\text{H}^+] [\text{OH}^-]} = \frac{1}{K_w} = 1.0 \times 10^{-14}$ (1)

Goes to completion. When smoke clears, you have

$[\text{Na}^+] = 0.1 \text{ M}$, $[\text{Cl}^-] = 0.2 \text{ M}$, $[\text{OH}^-] = 0 \text{ M}$,

and $[\text{H}^+] = 0.1 \text{ M}$.

Better: $[\text{OH}^-] = \frac{1.0 \times 10^{-14}}{[\text{H}^+]} = 1.0 \times 10^{-13} \text{ M}$

($p\text{H} = 1$, $p\text{OH} = 13$.)

This is what happens as you titrate strong acid with strong base (or vice versa).
Weak acid + strong base (or vice versa)

Ex. soln is 0.1 M NaOH and 0.3 M CH₃COOH.

\text{strong base} \quad \text{weak acid}

Initial species: \(0.1 \text{ M Na}^+\), \(0.1 \text{ M OH}^-\), \(0.3 \text{ M CH}_3\text{COOH}\) (since weak acid)

Plausible rxn: put predominant species on left, xfer a proton

\[ \text{OH}^- (aq) + \text{CH}_3\text{COOH} (aq) \rightarrow \text{H}_2\text{O} (l) + \text{CH}_3\text{COO}^- (aq) \]

\[ K = \frac{[\text{CH}_3\text{COO}^-]}{[\text{OH}^-][\text{CH}_3\text{COOH}]} \times [\text{H}^+] = \frac{K_a}{K_w} \]

\[ K = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.8 \times 10^9 \quad \text{Huge!} \]

So again, rxn goes to completion to exc. approx.

First guess: \([\text{Na}^+] = 0.1 \text{ M}, [\text{OH}^-] \approx 0, [\text{CH}_3\text{COOH}] = 0.2 \text{ M}\]
\([\text{CH}_3\text{COO}^-] = 0.1 \text{ M}\)

What next? This is called buffer solution — contains large conc. of weak acid and its conjugate base.

Need to get the tiny concentrations correct. (We have the big ones)
Look at $K_a = \frac{[H^+][A^-]}{[HA]}$ in weak acid.

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

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

$$pK_a = pH - \log \left( \frac{[A^-]}{[HA]} \right)$$

Henderson-Hasselbalch Eq. given ratio controls pH!

In our problem, $K_a = 1.8 \times 10^{-5}$ so $pK_a = 4.74$

After rxn, we had $[\text{CH}_3\text{COOH}] = 0.2 \text{ M}$

$[\text{CH}_3\text{COO}^-] = 0.1 \text{ M}$

So $\log \left( \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right) = \log \left( \frac{1}{2} \right) = -0.30$

$$pH = 4.74 - 0.30 = 4.44$$

$$[H^+] = 3.6 \times 10^{-5}$$

$$[OH^-] = 2.8 \times 10^{-10}$$

Important: This is same solution you'd get by making 0.1M NaCH$_3$COO and 0.2 M CH$_3$COOH.

Slightly acidic because $K_a(\text{CH}_3\text{COOH}) = 1.8 \times 10^{-5}$

while $K_b(\text{CH}_3\text{COO}^-) = 5.6 \times 10^{-10} = K_a/K_w$
Weak base + strong acid much the same.

0.1 M NH₃(aq) and 0.3 M HCl

\[ H^+ (aq) + NH_3 (aq) \rightleftharpoons NH_4^+ (aq) \]

\[ K = \frac{[NH_4^+]}{[H^+][NH_3]} = \frac{1}{K_c(NH_4^+)} = \frac{K_b(NH_3)}{K_w} \]

\[ = \frac{1.8 \times 10^{-5}}{1 \times 10^{-14}} = 1.8 \times 10^9 \] (again!)

So really have 0.1 M NH₄⁺, 0.3 M Cl⁻, 0.2 M H⁺, very little NH₃ or OH⁻.

(Different from before, when we had excess weak acid. Here we have excess strong acid.)

\[ \text{Get } [OH^-] = \frac{1.0 \times 10^{-14}}{[H^+]} = 5.0 \times 10^{-14} \]

\[ \text{Get } [NH_3] \text{ from } K \text{ expression (have } NH_4^+, H^+) \]

\[ [NH_3] = \frac{[NH_4^+]}{[H^+]} (1.8 \times 10^9) = 2.8 \times 10^{-10} \text{ M.} \]

Check by plugging back into K.
Acid-base indicator (skip)

These are dye molecules that change in color depending on whether they are protonated or not.

\[ HIn(aq) \rightleftharpoons H^+(aq) + In^-(aq) \]

phenolphthalein: colorless \[ \rightarrow \] pink

Just another weak acid: has a pKa like others. Book calls it pKIn. It is \[ \underline{9.4} \] for phenolphthalein.

\[ \text{HIn } \rightarrow \text{ pK} = \text{pKa} + \log \left( \frac{[In^-]}{[HIn]} \right) \]

Put very small cone. of HIn into titration mixture so that it does not affect pH, which is dominated by other, majority chemicals.

When pH sweeps through the value pKa, ratio \[ \frac{[In^-]}{[HIn]} \] varies quickly.

\[ \text{pH} = \text{pKa} - 1, \log(\_\_) = -1, \text{ so } [In^-] = 0.1[HIn] \] (clear)

\[ \text{pH} = \text{pKa}, \log(\_\_) = 0, \text{ so } [In^-] = [HIn] \] (pink)

\[ \text{pH} = \text{pKa} + 1, \log(\_\_) = +1, \text{ so } [In^-] = 10[HIn] \] (red)

Trick is to choose pKIn close to the pH that occurs near the stoichiometric point (equivalence pt.), when acid added = acid base.
Not necessarily $a + pH = 7$!

Ex: Titrate weak acid with strong base

25.00 mL of 0.100 M CH₃COOH with 0.100M NaOH.

Calc. pH at A, B, S, C.

CH₃COOH $\rightleftharpoons$ H⁺ + CH₃COO⁻

A

0.100 M CH₃COOH

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

$$[H^+] = x = 4.2 \times 10^{-3}, \quad pH = 2.37$$

B

Half of CH₃COOH $\rightarrow$ CH₃COO⁻

$$\frac{[CH₃COO^-]}{[CH₃COOH]} = 1; \quad so \quad pH = pK_a = 4.79$$

C

At S, we have essentially all of CH₃COOH $\rightarrow$ CH₃COO⁻

Same as 0.050 M Na CH₃COO solution (note dilution)

$$CH₃COO^- + H₂O \leq CH₃COOH + OH^-$$

$K = \frac{K_w}{K_a} = 5.6 \times 10^{-10}$
\[ \frac{x^2}{0.050-x} = 5.6 \times 10^{-10} \]

\[ x = \sqrt{0.05 (5.6 \times 10^{-10})} = 5.3 \times 10^{-6} \text{ M} = [\text{OH}^-] \]

\[ [\text{H}^+] = 1.9 \times 10^{-9} \text{ M} \]

\[ \text{pH} = 8.7 \quad \text{(basic because } \text{CH}_3\text{COO}^- \text{ is base.)} \]

\( \text{C paste stoich. pt. Total volume now } 25.00 + 37.50 = 62.50 \text{ mL} \)

Original \( 0.1 \text{ M CH}_3\text{COOH} \rightarrow 0.1 \left( \frac{25.00}{62.50} \right) = 0.0400 \text{ M} \)

\( 0.1 \text{ M NaOH} \rightarrow 0.100 \left( \frac{37.50}{62.50} \right) = 0.0600 \text{ M} \)

\[ 0.0400 \text{ M} + 0.0600 \text{ M} \rightarrow 0.0400 \text{ M} \]

\( \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \)

\[ [\text{H}^+] = 1.0 \times 10^{-14} / [\text{OH}^-] = 5.00 \times 10^{-13} \text{ M} \]

\[ \text{pH} = 12.3 \]

Careful analysis shows that stoich. pt. is inflection pt. (where curvature changes +\rightarrow-).

For unknown, can measure Vol. at 5,

find pH at \( \frac{1}{2} \) that volume, get pK_a of unknown weak acid.
For strong acid + strong base, still get inflection point at stoich. pt, but now it occurs at neutral pH = 7.00.

Want to choose indicator with pK\text{in} \approx pH at \(\text{eq}\). Then \(\frac{[\text{In}]}{[\text{HIn}]}\) varies rapidly as titration goes through stoich. pt, color change is accurate signal.

(Need to know identity of weak acid to make good choice.)
Return to H H \[\text{e.g.}\]

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

Buffering action: If both \([A^-]\) and \([HA]\) are quite large, then pH is quite insensitive to:

a) dilution of solution (add water, ratio unchanged).

b) addition of small amounts of strong acid or strong base!

Example: human blood. \(pH = 7.35 - 7.45\)


Corbic acid \((\text{CO}_2^-)\) bicarbonate \((\text{CO}_2\text{H})\) anion.

Can't have pH go wild when you eat a lemon!

Suppose we want a buffer solution at \(pH = 4.0\).

Go to Table 10.1, find a weak acid with \(pK_a = 4.0\).

Benzoic acid: \(C_6H_5COOH\) has \(pK_a = 4.19\)

\(K_a = 6.5 \times 10^{-5}\)

\[
4.00 = 4.19 + \log \frac{[\text{B}^-]}{[\text{HB}^-]}
\]

\[
\log \left( \frac{[\text{B}^-]}{[\text{HB}^-]} \right) = -0.19
\]

\[
\frac{[\text{B}^-]}{[\text{HB}^-]} = 10^{-0.19} = 0.646
\]
\[ [B_2^-] = 0.646 \, [HB_2] \]

Many possible solutions, but one example is:

\[ [HB_2] = 0.100 \, M \]

\[ [B_2^-] = 0.0646 \, M \]

As first approx., mix up 0.100 M HBz plus 0.0646 M NaBz.

Buffering action:

Suppose we add 0.01 M strong base to this, (NaOH)

Net rxn: \( OH^- + HB_2 \rightarrow H_2O + B_2^- \)

Initial: 0.01 M 0.100 M 0.0646 M

Final: 0.090 M 0.0746 M

Ratio becomes \[ \frac{[B_2^-]}{[HB_2]} = \frac{0.0746}{0.090} = 0.829 \]

\[ \log \left( \frac{0.0746}{0.090} \right) = -0.0815 \]

\[ pH = 4.19 - 0.0815 = 4.11 \] (changed +0.11 towards more basic).

\[ \Delta pH = +0.11 \]

Comparison:

- add 0.01 M NaOH to pure water, pH jumps 7.0 \( \rightarrow \) 12.0.

\[ \Delta pH = +5.0 \]

- add 0.01 M NaOH to 0.100 M HBz,

pH jumps from 2.6 \( \rightarrow \) 3.2

\[ \Delta pH = +0.6 \]
- Add 0.01 M NaOH to 0.001 M Ba²⁻

  pH quite stable: 8.6 → 8.8

  \[ \Delta pK = 0.2 \]

  This is like ended titration: pH

Other way around?

- But, add 0.01 M HCl to our buffer:

  not react: \( \text{Ba}^2+ + \text{H}^+ \rightarrow \text{H} \text{Ba} \)

  initial: 0.0646  0.100

  After acid: 0.0546  ~0  0.11

  \[ \text{Ex: } \quad \text{pH} = 4.19 + \log \left( \frac{0.0546}{0.110} \right) \]

  \[ = 4.19 - 0.30 \]

  \[ = 3.89 \quad \text{(pretty good)} \]

  \[ \Delta pK = -0.11 \]

\( \text{Ba}^2+ \) solution alone doesn’t protect against acid.

Summary: To make buffer at certain pH, pick \( pK_r = \text{pH} \) so that \( \frac{[A^-]}{[H_A]} \approx 1.0 \).

Third way both acid and base are present in large quantity, ratio \( \frac{[A^-]}{[H_A]} \) is somewhat resistant to add in of either \( \text{OH}^− \) or \( \text{H}^+ \).