08
ACIDS & BASES

MONOPROTIC ACID-BASE TITRATIONS & BUFFERS

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ACIDS

General ideas

Acids: proton donors

Generally,

If $K_a > 1$, the acid is strong — examples: HCl, HNO_3

If $K_a < 1$, the acid is weak

If $K_a \ll 1$, the acid is very weak — examples: CH_3COOH, HCOOH

BASES

General ideas

Bases: proton acceptors

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+\,(aq) + OH^-\,(aq)$$

Generally,

If $K_b > 1$, the base is strong — examples: NaOH, KOH, $Ca(OH)_2$

If $K_b < 1$, the base is weak

If $K_b \ll 1$, the base is very weak — examples: CH_3COO^-, conjugate base of acid

AUTOIONIZATION OF WATER

Always present in aqueous media

When an ACID or a BASE or BOTH are both added to water,

three simultaneous equilibria are established.

$$HA\,(aq) + H_2O\,(aq) \rightleftharpoons H_3O^+\,(aq) + A^-\,(aq)$$

$$A^-\,(aq) + H_2O\,(l) \rightleftharpoons HA\,(aq) + OH^-\,(aq)$$

$$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$$

In many situations, one equilibrium will dominate over the other two.

CONJUGATE ACID-BASE PAIR

General ideas

For any conjugate acid-base pair,

$$K_a \times K_b = K_w = 1.0 \times 10^{-14}$$

Therefore,

If HA is a strong acid, then A^- is a very weak conjugate base.

If HA is a (medium) weak acid, then A^- is a (medium) weak conjugate base.

If HA is a very weak acid, then A^- is a strong conjugate base.

TITRATIONS

Acids & Bases

We will use NaOH as the strong base today.

$\mathrm{pH} = -\log[\mathrm{H}^+]$ vs. volume NaOH added

Generally,

Steep rise around the equivalence point – the point where the moles of NaOH added equals the initial moles of a (monoprotic) acid.

Indicator chosen must change color within this steep rise!

End point is the point where there is a distinct, *visual* change in color.

INDICATORS

How they work?

Indicator chosen must change color within this steep rise!

Equilibrium for the indicator in solution is:

$$\mathbf{HIn}\ (\boldsymbol{aq}) \rightleftharpoons \mathbf{H^+}\ (\boldsymbol{aq}) + \mathbf{In^-}\ (\boldsymbol{aq})$$

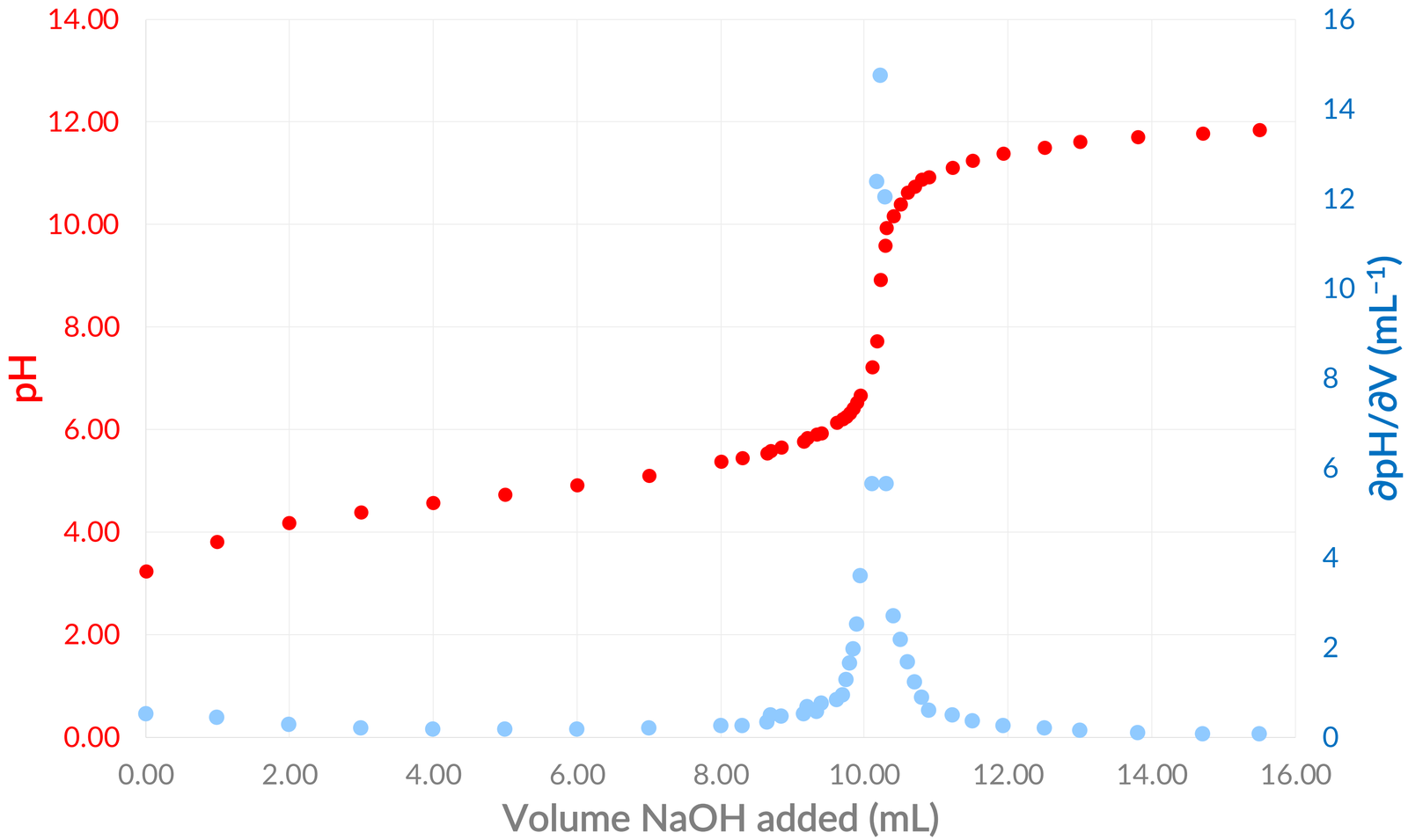
$$K_{a,\mathrm{In}} = \frac{[H^+][In^-]}{[HIn]}$$

Therefore,

$$\frac{[In^-]}{[HIn]} = \frac{K_{a,\mathrm{In}}}{[H^+]}$$

EXPECTED RESULTS

Volume NaOH added (mL)	pH	∂pH/∂V (mL^{-1})
0.00	3.25	0.526
1.00	3.82	0.434
2.00	4.18	0.292
3.00	4.40	0.205
4.00	4.58	0.172
5.00	4.75	0.172
6.00	4.92	0.172
7.00	5.11	0.205
8.00	5.37	0.260
8.30	5.45	0.260
8.65	5.55	0.325
8.70	5.59	0.497
8.85	5.65	0.456
9.15	5.77	0.515
9.20	5.84	0.671
9.33	5.91	0.584
9.40	5.94	0.751
9.62	6.13	0.835
9.70	6.21	0.945
9.75	6.26	1.286
9.80	6.33	1.657
9.85	6.42	1.963
9.90	6.53	2.531
9.95	6.66	3.590
10.10	7.22	5.643
10.18	7.74	12.371
10.22	8.94	14.762
10.29	9.58	12.032
10.30	9.94	5.654
10.40	10.17	2.695
10.50	10.40	2.182



TITRATIONS: EQUIVALENCE POINTS

Independent of initial concentrations

What would be pH at the *equivalence point* in a <u>strong</u> acid-strong base titration?

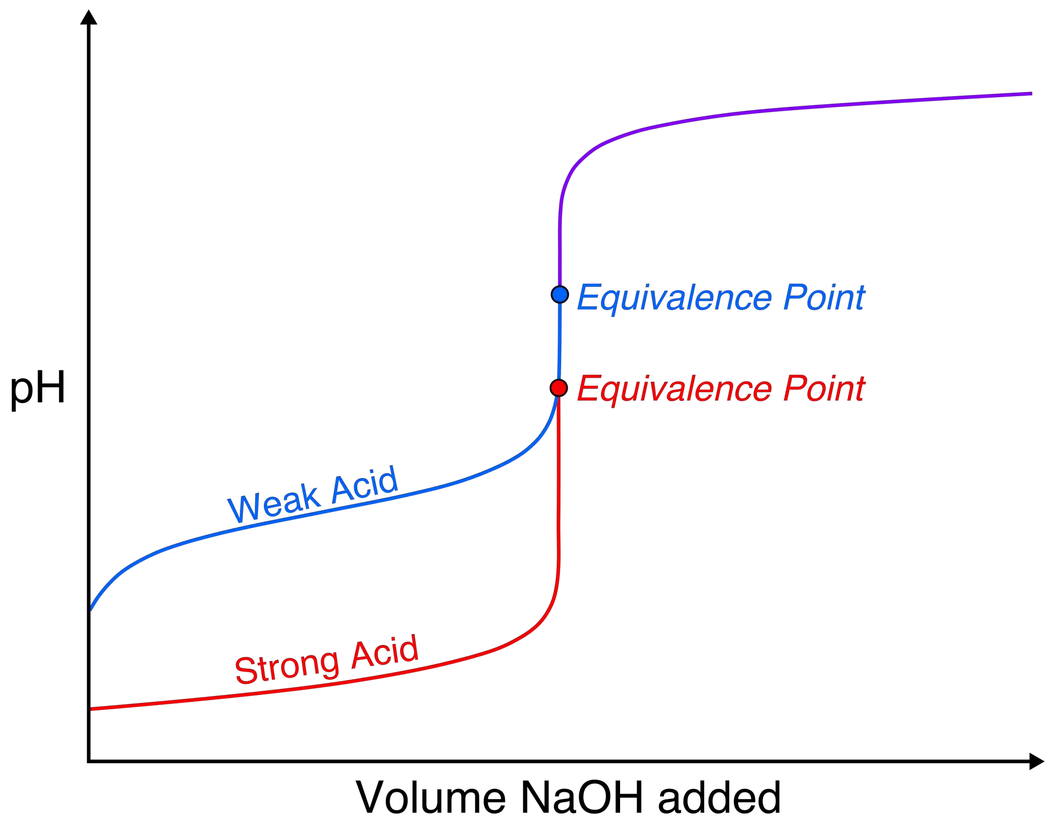
pH = 7

$$H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$$

What would be pH at the *equivalence point* in a <u>weak</u> acid-strong base titration?

pH > 7

$$HA (aq) + OH^- (aq) \rightarrow H_2O (l) + A^- (aq)$$
$$A^- (aq) + H_2O (l) \rightleftharpoons HA (aq) + OH^- (aq)$$



BUFFERS

Acids & Bases

Consists of a weak acid-conjugate base pair.

Essential in many biochemical processes.

Buffers have the ability to resist changes in pH when small amounts of strong acid (or strong base) are added.

Calculating the pH of a buffer

$$[H^+]_{buffer} = K_a \times \frac{[HA]_{eq}}{[A^-]_{eq}} \approx K_a \times \frac{[HA]_{initial}}{[A^-]_{initial}}$$

Notes

The pH electrode is delicate, so handle with care.

To work well, it needs to be well-immersed in the solution.

Plot both pH and its first derivative $\left({}^{\partial \mathrm{pH}}/_{\partial \mathrm{V}}\right)$.

Use ${}^{\partial \mathrm{pH}}/_{\partial \mathrm{V}}$ to choose NaOH increments during titration.

Near equivalence point, you must use very small increments of NaOH (i.e., one drop at a time).

If not, you will NOT be able to determine the equivalence point.