Chemistry 203

Spectrophotometric Determination of the pKa of Bromothymol Blue

Purpose

- To review the concepts of pH calculations and measurements.
- To learn about indicators and buffers.
- To learn how to use a pH-meter.
- To determine the pKa of Bromothymol Blue using the spectophotometer and the pH-meter.

pH of a Strong Acid

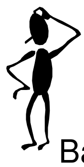
What is the pH of a 2×10^{-3} *M* HNO_3 solution?

HNO_3 is a strong acid – 100% dissociation.

HNO_3 (*aq*) + H_2O (*l*) $\longrightarrow$	H_3O^+ (*aq*) +	NO_3^- (*aq*)
0.002 *M*	0.0 *M*	0.0 *M*
0.0 *M*	0.002 *M*	0.002 *M*

pH = -log [H^+] = -log [H_3O^+] = -log(0.002) pH= 2.7

pH of a Strong Base



What is the pH of a 1.8×10^{-2} *M* $Ba(OH)_2$ solution?

$Ba(OH)_2$ is a strong base – 100% dissociation.

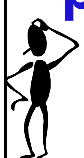
$$Ba(OH)_2\ (s) \longrightarrow Ba^{2+}\ (aq) + 2OH^-\ (aq)$$

0.018 *M*	0.0 *M*	0.0 *M*
0.0 *M*	0.018 *M*	0.036 *M*

pH + pOH = 14.00

pH = 14.00 – pOH = 14.00 + log(0.036)   pH= 12.56

pH of a Weak Acid



What is the pH of a 0.5 *M* HF solution (at 25^0C)?

$$HF\ (aq) \rightleftharpoons H^+\ (aq) + F^-\ (aq) \qquad K_a = \frac{[H^+][F^-]}{[HF]} = 7.1 \times 10^{-4}$$

	$HF\ (aq)$ $\rightleftharpoons$	$H^+\ (aq)$ +	$F^-\ (aq)$
Initial (*M*)	0.50	0.00	0.00
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.50 - x$	x	x

$$K_a = \frac{x^2}{0.50 - x} = 7.1 \times 10^{-4} \qquad K_a << 1 \qquad 0.50 - x \approx 0.50$$

$$K_a \approx \frac{x^2}{0.50} = 7.1 \times 10^{-4} \qquad x^2 = 3.55 \times 10^{-4} \qquad x = 0.019\ M$$

$[H^+] = [F^-] = 0.019\ M$ pH = -log $[H^+]$ = 1.72

$[HF] = 0.50 - x = 0.48\ M$

Ref. Chang, Sect. 15.5

When can I use the approximation?

$K_a << 1 \quad 0.50 - x \approx 0.50$

When x is less than 5% of the value from which it is subtracted.

$x = 0.019 \quad \frac{0.019\ M}{0.50\ M} \times 100\% = 3.8\%$

Less than 5%

Approximation ok.

What is the pH of a 0.05 M HF solution (at 25^{0}C)?

$K_a \approx \frac{x^2}{0.05} = 7.1 \times 10^{-4} \quad x = 0.006\ M$

$\frac{0.006\ M}{0.05\ M} \times 100\% = 12\%$

More than 5%

Approximation **not** ok.

Must solve for x exactly using quadratic equation or method of successive approximation.

Ref. Chang, Sect. 15.5

pH of Weak Bases

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

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

K_b is the ***base ionization constant***

$K_b \uparrow$ weak base strength $\uparrow$

Solve weak base problems like weak acids ***except*** solve for [OH^-] instead of [H^+].

Ref. Chang, Sect. 15.6

Ionization Constants of Conjugate Acid-Base Pairs

$$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq) \qquad K_a$$

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

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

$$K_aK_b = K_w$$

Weak Acid and Its Conjugate Base

$$K_a = \frac{K_w}{K_b} \qquad K_b = \frac{K_w}{K_a}$$

Ref. Chang, Sect. 15.7

Buffer Solutions

- Definition:

A ***buffer solution*** is a solution of:

1. A weak acid or a weak base

and 2. The salt of the weak acid or weak base

Both must be present!

A buffer solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base, and upon dilution.

- Examples:

HAc/NaAc

NH_3/NH_4Cl

- Importance:

Most chemical reactions take place at constant pH
Proper functioning of Enzymes
Metabolic processes
Calibration of pH-meters

pH of Buffers

Consider mixture of weak acid HA and its salt NaA

$NaA\ (s) \longrightarrow Na^+\ (aq) + A^-\ (aq)$

$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$

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

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

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

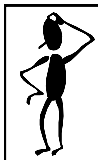
$$-\log [H^+] = -\log K_a + \log \frac{[A^-]}{[HA]}$$

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

Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Ref. Chang, Sect. 16.2



What is the pH of a solution containing 0.500 M CH_3COOH and 0.500 M CH_3COONa?

Mixture of weak acid and conjugate base!

An equal molar mixture of CH_3COOH and CH_3COONa

	$CH_3COOH(aq) \rightleftharpoons$	$H^+\ (aq)$ +	$CH_3COO^-\ (aq)$
Initial (M)	0.500	0.00	0.500
Change (M)	$-x$	$+x$	$+x$
Equilibrium (M)	$0.500 - x$	x	$0.500 + x$

Neglect x

$0.500 - x \approx 0.500$

$0.500 + x \approx 0.500$

CH_3COOH $pK_a = 4.76$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}$$

$$pH = 4.76 + \log \frac{[0.500]}{[0.500]}$$

pH = 4.76

Buffer Action: Addition of Base

Add 0.010mol of solid NaOH to 1.00L of the acetate buffer solution. Calculate the pH

Add strong base, the stoichiometric reaction:

	OH^- (*aq*) +	CH_3COOH (*aq*)	⟶	CH_3COO^- (*aq*) + H_2O (*l*)
Before	0.010	0.500		0.500
After	0.0	0.490		0.510

Then, the equilibrium reaction is treated with new initial concentrations, $[CH_3COOH]_0$=0.490M

$[CH_3COO^-]_0$ =0.510M

Plug into Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

pH=4.76+log(0.510)/(0.490)

pH=4.78

Only 0.02 pH unit change (increase)

Add this to 1.00L of pure water: pH rises from 7.00 to 12.00! 5 pH units.

Buffer Action: Addition of Acid

Add 0.010mol of gaseous HCl to 1.00L of the buffer solution

Add strong acid, the stoichiometric reaction:

	H+ (*aq*) +	CH_3COO^- (*aq*)	⟶	CH_3COOH (*aq*)
Before	0.010	0.500		0.500
After	0.0	0.490		0.510

Then, the equilibrium reaction is treated with new initial concentrations, $[CH_3COOH]_0$=0.510M

$[CH_3COO^-]_0$ =0.490M

Plug into Henderson-Hasselbalch equation

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

pH=4.76+log(0.490)/(0.510)

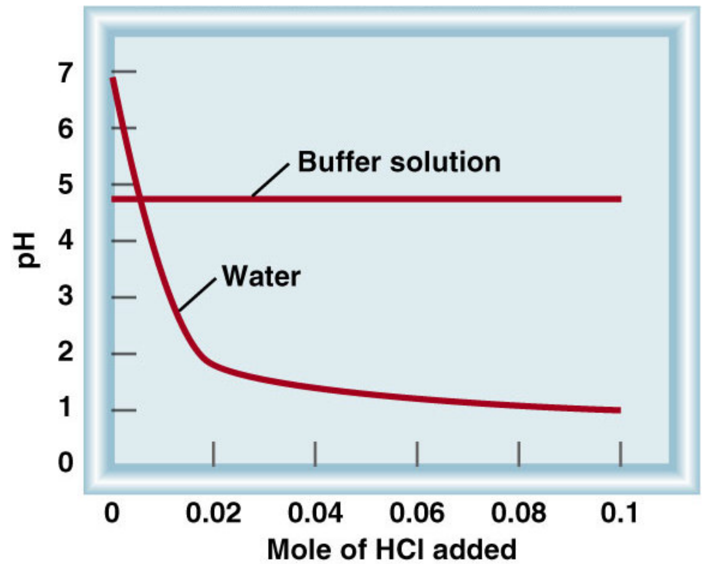
pH=4.74

Only 0.02 pH unit change (decrease)

Add this to 1.00L of pure water: pH drops from 7.00 to 2.00! 5 pH units.

$HCl \longrightarrow H^+ + Cl^-$

$HCl + CH_3COO^- \longrightarrow CH_3COOH + Cl^-$



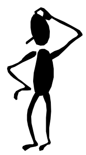
Ref. Chang, Sect. 16.3

Strength of a Buffer

- Buffer capacity represents the amount of protons or hydroxide ions the buffer can absorb without a significant change in pH.
- The higher the initial concentrations of acid and salt, the stronger the buffer action (the higher the buffer capacity).
- The pH of a buffer is determined by the ratio of $[A^-]/[HA]$, while the capacity of the buffer is determined by the magnitudes of $[HA]$ and $[A^-]$.
- The optimal buffer solution is the equimolar mixture of acid and its salt.
- When choosing a buffer with a desired pH, the pK_a of the acid should be as close as possible to the desired pH; For example, if the needed pH is 4.00 then the best choice will be an equimolar mixture of the acid HA whose pK_a is 4.00 and its salt. (K_a=1.0x10^{-4})

  $pH=pK_a + \log(1)$ $\qquad$ $pH=pK_a$

Buffer of Weak Base and its Salt



Calculate the pH of the 0.30 *M* NH_3/0.36 *M* NH_4Cl buffer system. What is the pH after the addition of 20.0 mL of 0.050 *M* NaOH to 80.0 mL of the buffer solution?

$$NH_4^+\ (aq) \rightleftharpoons H^+\ (aq) + NH_3\ (aq)$$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} \quad pK_a = 9.25 \quad pH = 9.25 + \log\frac{[0.30]}{[0.36]} = 9.17$$

	$NH_4^+\ (aq)$ +	$OH^-\ (aq)$ ⟶	$H_2O\ (l)$ +	$NH_3\ (aq)$
start (moles)	0.029	0.001		0.024
end (moles)	0.028	0.0		0.025

final volume = 80.0 mL + 20.0 mL = 100 mL

$$[NH_4^+] = \frac{0.028}{0.10} \quad [NH_3] = \frac{0.025}{0.10} \quad pH = 9.25 + \log\frac{[0.25]}{[0.28]} = 9.20$$

Ref. Chang, Sect. 16.3

Indicators

An **acid-base indicator** is a substance that displays different colors at different pH.

Such indicators are **weak acids or weak bases** depending on whether they are present in solution as their acidic form (HIn) or as their basic form (In-).

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^-$$

(***acidic***) (***basic***)

$$K_a = \frac{[H_3O^+][In^-]}{[HIn]}$$

K_a= Acid dissociation constant

As the pH of a solution changes, the equilibrium shown above will be driven either towards reactants (HIn) or products (In-).

At low pH values most of the indicator will be present in its acidic form, causing the solution color to correspond to that of HIn. At high pH values, most of the indicator will be in the In- form, causing the solution color to correspond to that of In-.

- Rearranging the above equation
- $$[H_3O^+] = Ka \frac{[HIn]}{[In^-]}$$
- Taking the -log of both sides

$$- \log [H_3O^+] = - \log Ka - \log \frac{[HIn]}{[In^-]}$$

$$\mathbf{pH = pKa + \log\frac{[In^-]}{[HIn]}}$$

when the concentrations of HIn and In^- in solution are equivalent, pH will be equal to the pKa of the indicator.

Spectrophotometrically, this corresponds to the pH where the absorbance of each form is half of its maximum absorbance.

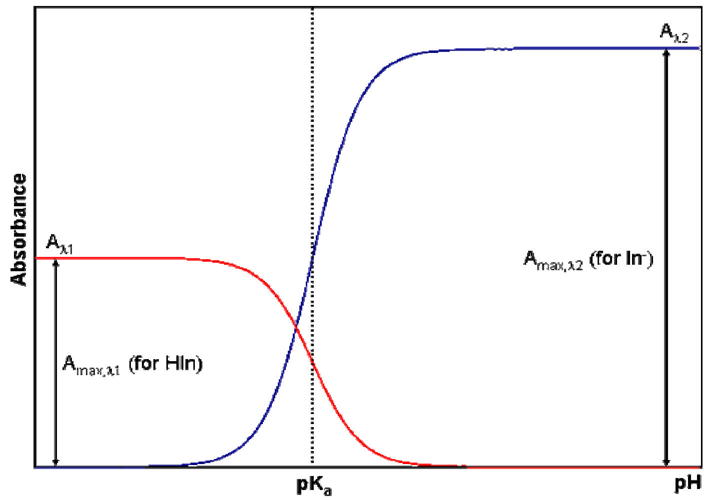
The indicator used in this experiment is **Bromothymol Blue**, BTB, also called **3,3'-dibromothymolsulfone-phthalein** (pH range: 6.0-7.8). It is **YELLOW** in acidic solutions and **BLUE** in basic solutions. The intermediate color is the green.

Determination of pKa of BTB

Determine the wavelength (λ1) where the acidic (HIn) but not the basic form (In-) of the indicator strongly absorbs radiation and the wavelength (λ2) where th basic but not the acid form strongly absorbs radiation.

Method 1:

- Prepare a set of **BTB** solutions at different pH (Refer to the manual).
- Measure the absorbance of each solution at the two wavelengths.
- Plot Absorbance versus pH at each wavelength.
- Determine pKa: It corresponds to the pH where the **absorbance of each form is half of its maximum absorbance.**



A plot of absorbance as a function of pH for an indicator.

Determination of pKa of BTB (continued)

Method 2:

$$pH = pK_a + \log \frac{[In-]}{[HIn]}$$

The ratio **[In-]/[HIn]** can be obtained from spectrophotometric measurements which are made at two wavelengths (λ1) and (λ2).

If **Beer's law** is obeyed, the absorbance at λ1 and λ2 are

$$A_{(\lambda 1)} = \varepsilon_{(HIn, \lambda 1)} \; b \; [HIn]$$
$$A_{(\lambda 2)} = \varepsilon_{(In-, \lambda 2)} \; b \; [In-]$$

where A is absorbance, ε is molar absorptivity and b is cell pathlength.

At any pH, the total concentration (C_T) of both forms of the indicator is constant and is the sum of the individual concentrations of each species: C_T = [HIn] + [In-]

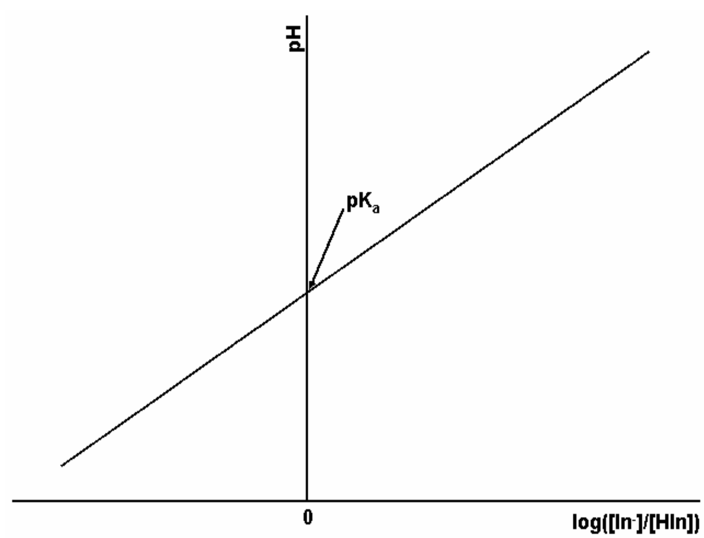
In highly acid solutions (lowest pH), C_T = [HIn]

In highly basic solutions (highest pH) C_T= [In^-]

By substitution, taking ratios and rearrangements, we can write

$$\frac{[In^-]}{[HIn]} = \frac{A_{\lambda 2} \cdot A_{\lambda 1}(lowest\ pH)}{A_{\lambda 1} \cdot A_{\lambda 2}(highest\ pH)}$$

The plot of pH versus log [In^-]/[HIn] yields a straight line of an intercept equal to pKa



A plot of pH as a function of log([In-]/[HIn]).