

Problem 22: Buffer solutions

1. The equilibrium, which governs the concentration of H^+ within the solution is $HCOOH \rightleftharpoons HCOO^- + H^+$

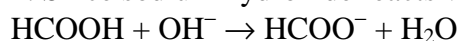
$$\text{Hence } K_a = \frac{[H^+][HCOO^-]}{[HCOOH]} = 2.1 \times 10^{-4}$$

and since $[HCOOH] \approx 0.200 \text{ M}$ and $[HCOO^-] \approx 0.150 \text{ M}$

$$[H^+] = 2.1 \times 10^{-4} \times \frac{0.200}{0.150} = 2.8 \times 10^{-4} \text{ M}$$

and **pH = 3.55**.

2. Since sodium hydroxide reacts with formic acid:



the concentration of formic acid in the solution is reduced to

$$[HCOOH] = 0.200 \text{ M} - 0.0100 \text{ M} = 0.190 \text{ M}$$

and the concentration of formate is increased to

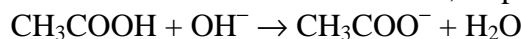
$$[HCOO^-] = 0.150 \text{ M} + 0.0100 \text{ M} = 0.160 \text{ M}$$

$$\text{Therefore: } [H^+] = 2.1 \times 10^{-4} \times \frac{0.190}{0.160} = 2.5 \times 10^{-4} \text{ M}$$

and **pH = 3.60**

Note that the addition of sodium hydroxide, which is a strong base, causes a very small increase of the pH of the solution.

3. Let V the volume of the solution of sodium hydroxide. Therefore, the final volume of the solution will be $(100.0 + V)$ mL and the number of mmol of CH_3COOH and OH^- which are mixed are $100.0 \text{ mL} \times 0.150 \text{ mmol/mL} = 15.00 \text{ mmol}$ and $V \text{ mL} \times 0.200 \text{ mmol/mL} = 0.200 \times V \text{ mmol}$, respectively. From the reaction:



it is obvious that the amount of acetate produced is $0.200 \times V$ mmol and the amount of acetic acid which remains unreacted is $(15.00 - 0.200 \times V)$ mmol. Hence, the concentration of each constituent in the buffer solution is:

$$[CH_3COOH] = \frac{(15.00 - 0.200 \times V)}{100.0 + V} \text{ M}$$

$$\text{and } [CH_3COO^-] = \frac{0.200 \times V}{100.0 + V} \text{ M}$$

From the acid dissociation constant expression of acetic acid

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

$$\text{it can be derived } \frac{[CH_3COO^-]}{[CH_3COOH]} = \frac{K_a}{[H^+]}$$

$$\text{and } \frac{\frac{0.200 \times V}{100.0 + V} \text{ M}}{\frac{(15.00 - 0.200 \times V)}{100.0 + V} \text{ M}} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-5}}$$

from which **$V = 48.21 \text{ cm}^3$** .

4. a

5. (i) c, (ii) b

6. (i) b, (ii) d

7. (i) c, (ii) c

8. (i) b, (ii) c

Problem 23: Titrations of weak acids

The titration reaction is



a) Initial pH

The pH of the solution before the titration begins, is calculated by the acid dissociation constant and the initial concentration of CH_3COOH :



From the acid dissociation constant expression:

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

the concentration of H^+ can be calculated:

$$[\text{H}^+] = \sqrt{1.8 \times 10^{-5} \times 0.1000} = 1.34 \times 10^{-3} \text{ M} \text{ and } \text{pH} = 2.87$$

b) pH after the addition of 10.00 cm^3 of titrant

The solution contains acetic acid and sodium acetate. Therefore it is a buffer solution. The concentration of each constituent is calculated:

$$[\text{CH}_3\text{COOH}] = \frac{(50.00 \text{ cm}^3 \times 0.1000 \text{ M}) - (10.00 \text{ cm}^3 \times 0.1000 \text{ M})}{60.00 \text{ cm}^3} = 0.0667 \text{ M}$$

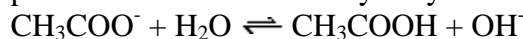
$$[\text{CH}_3\text{COO}^-] = \frac{10.00 \text{ cm}^3 \times 0.1000 \text{ M}}{60.00 \text{ cm}^3} = 0.01667 \text{ M}$$

These concentrations are then substituted into the dissociation constant expression of acetic acid for calculating the concentration of $[\text{H}^+]$:

$$[\text{H}^+] = 1.8 \times 10^{-5} \times \frac{0.0667}{0.01667} = 7.20 \times 10^{-5} \text{ M} \text{ and } \text{pH} = 4.14$$

c) pH at the equivalence point

At the equivalence point, all acetic acid has been converted to sodium acetate and the pH is calculated from the hydrolysis of acetate ions:



The volume of titrant required for the equivalence point (V_{ep}) is calculated:

$$V_{\text{ep}} = \frac{50.00 \text{ cm}^3 \times 0.1000 \text{ M}}{0.1000 \text{ M}} = 50.00 \text{ cm}^3$$

and the total volume of solution is 100.0 cm^3 . Therefore, at this point of the titration $[\text{CH}_3\text{COOH}] = [\text{OH}^-]$ and

$$[\text{CH}_3\text{COO}^-] = \frac{50.00 \text{ cm}^3 \times 0.1000 \text{ M}}{100.0 \text{ cm}^3} - [\text{OH}^-] \approx 0.0500 \text{ M}$$

$$\frac{[\text{OH}^-]^2}{0.0500 \text{ M}} = \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

$$[\text{OH}^-] = \sqrt{0.0500 \times 5.56 \times 10^{-10}} = 5.27 \times 10^{-6} \text{ M}$$

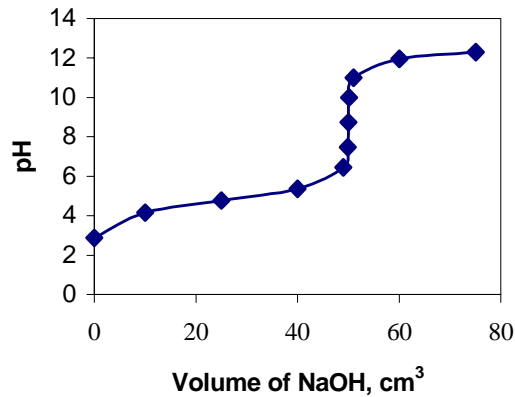
$\text{pOH} = 5.28$ and thus $\text{pH} = 14 - 5.28 = 8.72$

d) pH after the addition of 50.10 cm^3 of titrant

At this stage, all acetic acid has been converted to sodium acetate and the pH of the solution is calculated by the excess of sodium hydroxide, which has been added:

$$[\text{OH}^-] = \frac{(50.10 \text{ cm}^3 \times 0.1000 \text{ M}) - (50.00 \text{ cm}^3 \times 0.1000 \text{ M})}{100.1 \text{ cm}^3} = 1.0 \times 10^{-4} \text{ M}$$

Therefore $\text{pOH} = 4.00$ and $\text{pH} = 10.00$



Titration curve of 0.1000 M acetic acid with 0.1000 M NaOH

e) Selection of indicator

Since the pH at the equivalence point is 8.72, the appropriate acid base indicator is phenolphthalein.

2. (i) b, (ii) c, (iii) a, (iv) b, (v) c, (vi) d

Problem 24: Separation by extraction

1 Starting with an amount W_0 of S in phase 1, after the extraction this amount is distributed between the two phases as follows:

$$W_0 = (C_S)_1 V_1 + (C_S)_2 V_2$$

Since $D = (C_S)_2 / (C_S)_1$, we have

$$W_0 = (C_S)_1 V_1 + D(C_S)_1 V_2 = (DV_2 + V_1)(C_S)_1$$

Therefore, after removing phase 2, the remaining amount of S in phase 1 is:

$$W_1 = (C_S)_1 V_1 = W_0 \frac{V_1}{DV_2 + V_1}$$

By repeating extraction with a fresh portion of volume V_2 of phase 2, the amount W_1 of S is similarly distributed. After removing phase 2, the remaining amount of S in phase 1 is:

$$W_2 = (C_S)_1 V_1 = W_1 \frac{V_1}{DV_2 + V_1} = W_0 \left(\frac{V_1}{DV_2 + V_1} \right)^2$$

and so on. Therefore after n extractions with a fresh portion of volume V_2 of phase 2, the remaining amount of S in phase 1 will be:

$$W_n = W_0 \left(\frac{V_1}{DV_2 + V_1} \right)^n$$

2. (a) The remaining fraction of S after 1 extraction with 100 mL of chloroform is calculated using Equation 1.4:

$$f_1 = \frac{W_1}{W_0} = \left(\frac{50}{3.2 \times 100 + 50} \right)^1 = 0.135,$$

therefore the percentage of S extracted is $100 - 13.5 = \mathbf{86.5\%}$

(b) The remaining fraction of S after 4 extractions with 25 mL of chloroform each time is similarly calculated:

$$f_4 = \frac{W_4}{W_0} = \left(\frac{50}{3.2 \times 25 + 50} \right)^4 = 0.022,$$

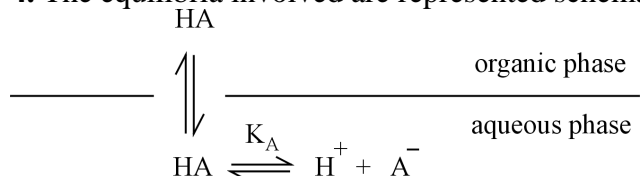
therefore the percentage of S extracted is $100 - 2.2 = 97.8\%$. The result is indicative of the fact that successive extractions with smaller individual volumes of extractant are more efficient than a single extraction with all the volume of the extractant.

3. Using Equation 1-4 we have:

$$0.01 = \left(\frac{100.0}{9.5 \times 25.0 + 100.0} \right)^n \quad \text{or} \quad 0.01 = 0.2963^n \quad \text{hence } n = \log(0.01)/\log(0.2963) =$$

3.78, therefore at least **4** extractions are required.

4. The equilibria involved are represented schematically as follows:



We have (subscripts w and o denote concentrations in aqueous and organic phase, respectively)

$$D = \frac{(C_{\text{HA}})_o}{(C_{\text{HA}})_w} = \frac{[\text{HA}]_o}{[\text{HA}]_w + [\text{A}^-]_w}$$

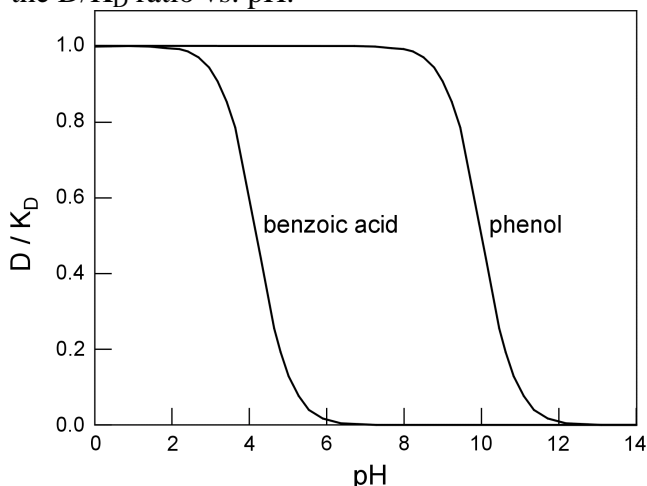
$$K_D = [\text{HA}]_o / [\text{HA}]_w \quad \text{and} \quad K_a = [\text{H}^+]_w [\text{A}^-]_w / [\text{HA}]_w$$

Combining all three equations we finally obtain:

$$D = \frac{K_D [\text{H}^+]_w}{[\text{H}^+]_w + K_a} \quad (1.5)$$

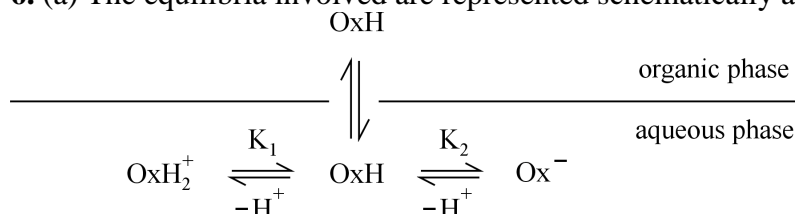
Last equation predicts that if $[\text{H}^+]_w \gg K_a$ (strongly acidic aqueous phase), then $D \approx K_D$ (i.e. D acquires the maximum possible value) and the acid is extracted (or prefers to stay) in the organic phase. On the other hand, if $[\text{H}^+]_w \ll K_a$ (strongly alkaline aqueous phase), we have $D \approx K_D [\text{H}^+]_w / K_a$, and because of the small value of D the acid is then extracted (or prefers to stay) in the aqueous phase. In this way, by regulating the pH of the aqueous phase, the course of extraction is shifted towards the desired direction.

5. (a) By using the previously derived Equation 1.5, we obtain the following plots of the D/K_D ratio vs. pH.



(b) From these plots it is clear that at the pH region 7-8 the distribution ratio for benzoic acid will be practically 0, whereas that of phenol will acquire the maximum possible value. Therefore, phenol can be efficiently separated from an aqueous solution of both compounds by extraction with diethylether, provided that the pH of this solution has been adjusted in the range 7 to 8 (e.g. by the presence of excess of NaHCO_3).

6. (a) The equilibria involved are represented schematically as follows:



We have the expressions

$$D = \frac{(C_{\text{OxH}})_o}{(C_{\text{OxH}})_w} = \frac{[\text{OxH}]_o}{[\text{OxH}_2^+]_w + [\text{OxH}]_w + [\text{Ox}^-]_w}$$

$$K_D = [\text{OxH}]_o / [\text{OxH}]_w = 720$$

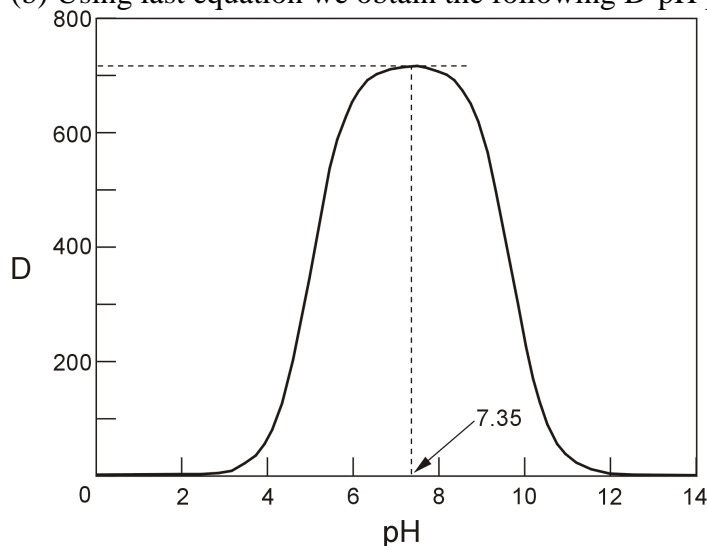
$$K_1 = \frac{[\text{OxH}]_w [\text{H}^+]_w}{[\text{OxH}_2^+]_w} = 1 \times 10^{-5}$$

$$K_2 = \frac{[\text{Ox}^-]_w [\text{H}^+]_w}{[\text{OxH}]_w} = 2 \times 10^{-10}$$

Combining all four equations, we have the sought-for expression

$$\begin{aligned}
 D &= \frac{[\text{OxH}]_o}{\frac{[\text{OxH}_2^+]_w [\text{H}^+]_w}{K_1} + [\text{OxH}]_w + \frac{K_2 [\text{OxH}]_w}{[\text{H}^+]_w}} \\
 &= \frac{[\text{OxH}]_o}{[\text{OxH}]_w} \cdot \frac{1}{\frac{[\text{H}^+]_w}{K_1} + 1 + \frac{K_2}{[\text{H}^+]_w}} = \frac{K_D}{\frac{[\text{H}^+]_w}{K_1} + 1 + \frac{K_2}{[\text{H}^+]_w}}
 \end{aligned}$$

(b) Using last equation we obtain the following D-pH plot:



(c) We calculate the 1st and 2nd derivative of the denominator, i.e.,

$$F([\text{H}^+]_w) = \frac{[\text{H}^+]_w}{K_1} + 1 + \frac{K_2}{[\text{H}^+]_w}$$

$$\text{whereupon we have the 1st derivative } F'([\text{H}^+]_w) = \frac{1}{K_1} - \frac{K_2}{[\text{H}^+]_w^2}$$

$$\text{and for the 2nd derivative } F''([\text{H}^+]_w) = \frac{2K_2}{[\text{H}^+]_w^3}$$

Since always $F''([H^+]_w) > 0$, then when $F'([H^+]_w) = 0$, $F([H^+]_w)$ is minimum under these conditions. Consequently, the distribution ratio is maximum when

$$\frac{1}{K_1} - \frac{K_2}{[H^+]^2} = 0 \text{ or } [H^+]_w = \sqrt{K_1 K_2} = \sqrt{(1 \times 10^{-5})(2 \times 10^{-10})} = 4.5 \times 10^{-8} \text{ M}$$

or pH = 7.35

Problem 25: Mass spectroscopy

1 The ionic fragment SiCl_2^+ will be represented by the following peaks:

M = 98	$^{28}\text{Si}^{35}\text{Cl}_2^+$
M+1 = 99	$^{29}\text{Si}^{35}\text{Cl}_2^+$
M+2 = 100	$^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}^+ + ^{30}\text{Si}^{35}\text{Cl}_2^+$
M+3 = 101	$^{29}\text{Si}^{35}\text{Cl}^{37}\text{Cl}^+$
M+4 = 102	$^{30}\text{Si}^{35}\text{Cl}_2^+ + ^{28}\text{Si}^{35}\text{Cl}^{37}\text{Cl}^+$
M+5 = 103	$^{29}\text{Si}^{37}\text{Cl}_2^+$
M+6 = 104	$^{30}\text{Si}^{37}\text{Cl}_2^+$

Therefore, the correct answer is 7.

2 The expected peaks and the corresponding probabilities are:

m/z = 45	$^{10}\text{B}^{35}\text{Cl}$	$0.199 \times 0.7577 = 0.151$
m/z = 46	$^{11}\text{B}^{35}\text{Cl}$	$0.801 \times 0.7577 = 0.607$
m/z = 47	$^{10}\text{B}^{37}\text{Cl}$	$0.199 \times 0.2423 = 0.048$
m/z = 48	$^{11}\text{B}^{37}\text{Cl}$	$0.801 \times 0.2423 = 0.194$

Hence, the base peak has nominal mass M = 46 and the relative intensities are:

M-1 = 45	$(0.151/0.607) \times 100 = 24.9\%$
M = 46	$= 100\%$
M+1 = 47	$(0.048/0.607) \times 100 = 7.9\%$
M+2 = 48	$(0.194/0.607) \times 100 = 32.0\%$

Therefore, the correct answer is C.

3 For the ion N_2^+ we have:

$$\begin{aligned} \text{M: } & ^{14}\text{N}^{14}\text{N} = (0.99634)^2 = 0.9927 \\ \text{M+1: } & ^{14}\text{N}^{15}\text{N} + ^{15}\text{N}^{14}\text{N} = 2 \times (0.99634 \times 0.00366) = 0.007293 \end{aligned}$$

hence, $(\text{M}+1)/\text{M} = 0.007293/0.9927 = 0.00735$ or 0.735%

For the ion CO^+ we have:

$$\begin{aligned} \text{M: } & ^{12}\text{C}^{16}\text{O} = 0.989 \times 0.99762 = 0.9866 \\ \text{M+1: } & ^{12}\text{C}^{17}\text{O} + ^{13}\text{C}^{16}\text{O} = (0.989 \times 0.00038) + (0.011 \times 0.99762) = 0.01135 \end{aligned}$$

hence, $(\text{M}+1)/\text{M} = 0.01135/0.9866 = 0.0115$ or 1.15%

For the ion CH_2N^+ we have:

$$\begin{aligned} \text{M: } & ^{12}\text{C}^1\text{H}_2^{14}\text{N} = 0.989 \times (0.99985)^2 \times 0.99634 = 0.9851 \\ \text{M+1: } & ^{13}\text{C}^1\text{H}_2^{14}\text{N} + ^{12}\text{C}^1\text{H}^2\text{H}^{14}\text{N} + ^{12}\text{C}^2\text{H}^1\text{H}^{14}\text{N} + ^{12}\text{C}^1\text{H}_2^{15}\text{N} = \\ & 0.011 \times (0.99985)^2 \times 0.99634 + 2 \times 0.989 \times 0.99985 \times 0.00015 \times 0.99634 + \\ & + 0.989 \times (0.99985)^2 \times 0.00366 = 0.01487 \end{aligned}$$

hence, $(\text{M}+1)/\text{M} = 0.01487/0.9851 = 0.0151$ or 1.51%

For the ion C_2H_4^+ we have:

$$\begin{aligned} \text{M: } & ^{12}\text{C}_2^1\text{H}_4 = (0.989)^2 \times (0.99985)^4 = 0.9775 \\ \text{M+1: } & ^{13}\text{C}^{12}\text{C}^1\text{H}_4 + ^{12}\text{C}^{13}\text{C}^1\text{H}_4 + ^{12}\text{C}_2^2\text{H}^1\text{H}_3 + ^{12}\text{C}_2^1\text{H}^2\text{H}^1\text{H}_2 + \\ & + ^{12}\text{C}_2^1\text{H}_2^2\text{H}^1\text{H} + ^{12}\text{C}_2^1\text{H}_3^2\text{H} = 2 \times 0.011 \times 0.989 \times (0.99985)^4 + \\ & + 4 \times 0.989 \times 0.00015 \times (0.99985)^3 = 0.02234 \end{aligned}$$

hence, $(\text{M}+1)/\text{M} = 0.02234/0.9775 = 0.0229$ or 2.29%

Therefore the correct answer is (b) CO^+