Problem 22: Buffer solutions

Buffer solutions are solutions which resist to changes in pH. Usually, buffer solutions consist of a weak acid and its conjugate base (for example CH_3COOH/CH_3COO^-) or a weak base and its conjugate acid (for example NH_3/NH_4^+). A buffer solution is formed by partial neutralization of a weak acid with a strong base or of a weak base with a strong acid. Alternatively, buffer solutions can be prepared by mixing the precalculated concentrations of each of the constituents.

The pH of a buffer solution, which is composed of a weak acid HA and its conjugate base A^- is calculated by the Henderson-Hasselbalch equation:

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

where K_a is the acid dissociation constant of the weak acid HA and [HA] and $[A^-]$ are the concentrations of HA and A^- in the buffer solution, respectively.

Questions

1. Calculate the pH of a buffer solution, which contains 0.200 M formic acid ($K_a = 2.1\times10^{-4}$) and 0.150 M sodium formate.

2. Calculate the change in pH of the buffer solution in Question 1 when 0.01000 M of sodium hydroxide is added to the solution.

3. Calculate the volume of 0.200 M of sodium hydroxide which must be added to 100.0 cm^3 of 0.150 M of acetic acid (CH_3COOH, $K_a = 1.8\times10^{-5}$) in order to prepare a buffer solution with pH = 5.00.

4. The pH of a buffer solution containing 0.0100 M benzoic acid (C_6H_5COOH, $K_a = 6.6\times10^{-5}$) and 0.0100 M sodium benzoate is: a. 5.00, b. 4.18, c. 9.82, d. 9.00

In the problems below equal volumes of the following solutions A and B are mixed:

5. A: 0.100 M CH_3COOH ($K_a = 1.8\times10^{-5}$), B: 0.0500 M NaOH

(i) The final solution: a. contains a weak acid, b. contains a strong base, c. is a buffer solution, d. none of the above

(ii) The pH of the final solution is: a. 3.02, b. 4.44, c. 3.17, d. 7.00

6 A: 0.100 M CH_3COOH ($K_a = 1.8\times10^{-5}$), B: 0.150 M NaOH

(i) The final solution: a. contains a weak acid, b. contains a strong base, c. is a buffer solution, d. none of the above

(ii) The pH of the final solution is: a. 12.00, b. 12.70, c. 13.18, d. 12.40

7. A: 0.150 M CH_3COOH, B: 0.100 M NaOH

(i) The final solution: a. contains a weak acid, b. contains a strong base, c. is a buffer solution, d. none of the above

(ii) The pH of the final solution is: a. 3.17, b. 3.02, c. 2.78, d. 3.22

8. A: 0.100 M CH_3COOH, B: 0.100 M NaOH

(i) The final solution: a. contains a weak acid, b. contains a strong base, c. is a buffer solution, d. none of the above

(ii) The pH of the final solution is:

a. 7.00, b. 13.00, c. 2.87, d. 3.02

Problem 23: Titration of weak acids

Weak acids are titrated with solutions of strong bases of known concentration (standard solutions). The solution of weak acid (**analyte**) is transferred into a 250-cm^3 conical flask and the solution of strong base (**titrant**) is delivered from a burette. The equivalence point of the titration is reached when the amount of added titrant is chemically equivalent to the amount of analyte titrated. The graph, which shows the change of pH as a function of volume of titrant added, is called **titration curve**.

The **equivalence point** of a titration is the theoretical point, which cannot be determined experimentally. It can only be estimated by observing some physical change associated with the process of the titration. In acid-base titrations, the **end point** is detected by using acid/base indicators.

Questions

1. Construct the titration curve by calculating a few characteristic points and select indicator for the titration of 50.00 cm^3 of 0.1000 M of acetic acid (CH_3COOH, $K_a = 1.8\times10^{-5}$) with 0.1000 M of sodium hydroxide; you may consult Table 1.

Table 1: Some common acid/base indicators

Common name	**Transition range, pH**	**Color change**
Methyl orange	3.2 - 4.4	red-orange
Methyl red	4.2 - 6.2	red-yellow
Bromothymol blue	6.0 - 7.6	yellow-blue
Phenol red	6.8 - 8.2	yellow-red
Phenolphthalein	8.0 - 9.8	colorless-red
Thymolphthalein	9.3 - 10.5	colorless-blue

2. Ascorbic acid (vitamin C, $C_6H_8O_6$) is a weak acid and undergoes the following dissociation steps:

$C_6H_8O_6 \rightleftharpoons C_6H_7O_6^- + H^+$ $\qquad K_{a1} = 6.8\times10^{-5}$

$C_6H_7O_6^- \rightleftharpoons C_6H_6O_6^{2-} + H^+$ $\qquad K_{a2} = 2.7\times10^{-12}$

Hence, ascorbic acid can be titrated with sodium hydroxide according to the first acid dissociation constant.

50.00 cm^3 of 0.1000 M of ascorbic acid are titrated with 0.2000 M of sodium hydroxide.

(i) The initial pH of the solution is:

a. 7.00, b. 2.58, c. 4.17, d. 1.00

(ii) The volume of titrant required for the equivalence point is:

a. 50.00 cm^3, b. 35.00 cm^3, c. 25.00 cm^3, d. 20.00 cm^3

(iii) The pH of the solution after the addition of 12.5 cm^3 of titrant is equal to:

a. 4.17, b. 2.58, c. 7.00, d. 4.58

(iv). The pH at the equivalence point is:

a. 7.00, b. 8.50, c. 8.43, d. 8.58

(v) The indicator, which must be chosen for the titration is: The appropriate indicator for the titration is (refer to Table 1):

a. bromothymol blue, b. phenol red, c. phenolphthalein, d. thymolphthalein

(vi) The pH of the solution after the addition of 26.00 cm^3 of titrant is:

a. 13.30, b. 11.30, c. 11.00, d. 11.42

Problem 24: Separation by Extraction

Extraction is one the most common separation methods and it is based on the distribution equilibria of a substance between two immiscible liquids whose densities differ appreciably so that they are separated easily after mixing.

The more usual case is the extraction of an aqueous solution with an organic solvent, whereupon the inorganic ions and the polar organic compounds are found mainly in the aqueous phase and the polar organic compounds distribute in the organic phase. Inorganic ions may be reacted with an appropriate reagent to yield a non-polar compound that distributes in the organic phase

When a species S (solute) is distributed between two solvents 1 and, then we have the following equilibrium

$$(S)_1 \overset{K_D}{\rightleftharpoons} (S)_2$$

where K_D is the ***distribution coefficient*** given by

$$K_D = \frac{(a_s)_2}{(a_s)_1} \tag{1}$$

where $(a_S)_1$ and $(a_S)_2$ are the activities of S in phases 1 and 2. For a given system of solvents and species S, K_D depends practically solely on temperature.

Separations by extraction are commonly performed with a ***separatory funnel*** (Fig. 1), a common and easy to use glass apparatus found in any chemical laboratory.

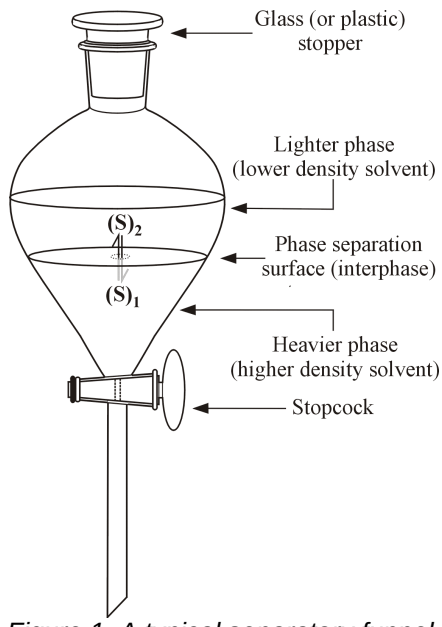


Figure 1. A typical separatory funnel.

Equation 1.1 is valid only if the solute S is present in both phases in the same form. Otherwise, if any dissociation, dimerization, complexation of the solute takes place, the ***distribution ratio***, D, is used instead, which is given by

$$D = (C_S)_2 / (C_S)_1 \tag{1.2}$$

where $(C_S)_1$ and $(C_S)_2$ are the analytical concentrations of S in phases 1 and 2 (rather than equilibrium concentrations of given species).

By convention, when one of the two solvents is water, Equation 1.2 is written with the aqueous concentration in the denominator and the organic solvent concentration in the numerator. D is a conditional constant dependent on a variety of experimental parameters like the concentration of S and of any other species involved in any equilibria with S in either phase and most likely on the pH of the aqueous phase (e.g. if S participates in any acid-base type equilibrium).

If W_0 g of S is initially present in V_1 mL of solvent 1 and S is extracted successively with equal fractions of V_2 mL of solvent 2, the quantity W_n of S that remains in phase 1 after n such extractions is given by

$$W_n = \left(\frac{V_1}{DV_2 + V_1}\right)^n W_0 \tag{3}$$

or

$$f_n = \frac{W_n}{W_0} = \left(\frac{V_1}{DV_2 + V_1}\right)^n \tag{4}$$

where f_n is the fraction of S that remains in solvent 1 after n extractions.

One can derive from Equations 1.3 and 1.4 that for a given volume of extractant, successive extractions with smaller individual volumes of extractant are more efficient than with all the volume of the extractant.

1 Prove Equation (3).

2 Substance S is distributed between chloroform and water with a distribution ratio D = 3.2. If 50 cm^3 of an aqueous solution of S is extracted with (a) one 100-cm^3, and (b) four 25-cm^3 portions of chloroform, calculated the percentage of S which is finally extracted in each case.

3 What is the minimum number of extractions required for the removal of at least 99% of substance X from 100 cm^3 of an aqueous solution containing

0.500 g of X, if each extraction is carried out with 25.0 cm^3 of hexane and the distribution coefficient is 9.5?

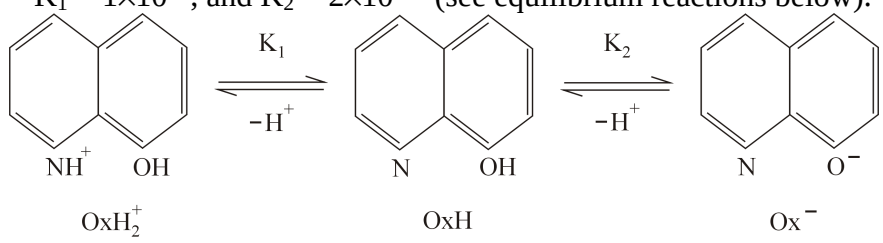
4 The weak organic acid HA with dissociation constant K_a (in water) is distributed between an organic solvent and water. If the only extractable species is the undissociated species HA with a distribution coefficient K_D and this is the only existing form of the acid in the organic phase, derive an expression showing the dependence of the distribution ratio D on $[H^+]$ of the aqueous phase and draw conclusions from the expression.

5 Benzoic acid and phenol are weak monoprotic organic acids with dissociation consntants 6.6×10^{-5} and 1×10^{-10}, respectively. Only the undissociated form of both compounds can be extracted from an aqueous solution with diethylether. (a) Draw a plot showing how the ratio D/K_D depends on pH for each compound, and (b) based on these plots propose a method for the separation of a mixture of these two compounds.

6 8-Hydroxyquinoline, $C_9H_6(OH)N$ (symbolized as: OxH), known also as "oxine", forms in acidic solutions the cation $C_9H_6(OH)NH^+$ (OxH_2^+) and in alkaline solutions the anion $C_9H_6(O^-)N$ (Ox^-). If chloroform extracts only the neutral molecule of oxine with a distribution coefficient $K_D = 720$,

(a) derive an expression showing the dependence of the distribution ratio, D, of 8-hydroxyquinoline on $[H^+]$ of the aqueous phase,
(b) draw a plot showing the dependence of D on pH of the aqueous phase, and
(c) calculate the pH at which D is maximized.

The consecutive dissociation constants of the cationic acid $C_9H_6(OH)NH^+$ are: $K_1 = 1\times10^{-5}$, and $K_2 = 2\times10^{-10}$ (see equilibrium reactions below).



Problem 25: Mass Spectroscopy

Mass spectrometry is based on the formation of a beam of ionic fragments by bombardment of test molecules usually with energetic electrons. The generated fragments are then separated by application of electrostatic or magnetic fields or by a combination of both. This separation depends on the *mass-to-charge ratio* (m/z) of each ionic fragment. In most cases fragments are singly charged (z=1), therefore the separation depends on the mass of each ion.

The capability of a mass spectrometer to differentiate between masses is usually expressed in terms of its *resolution*, which is defined as $R = m/\Delta m$, where Δm is the mass difference between two adjacent peaks that are just resolved and m is the nominal mass of the first peak. For example, in order to discriminate the ionic species $C_2H_4^+$ and CH_2N^+, which have the same *nominal mass* (m = 28), but different *exact masses* (28.0313 and 28.0187, respectively), an instrument with a resolution of at least $R = 28/(28.0313-28.0187) \approx 2200$ is required. Less expensive low resolution mass spectrometers ($R \approx 300$-1000) can readily differentiate simple ions (of relatively low relative mass) of different nominal masses.

Isotope peaks in Mass Spectrometry

Even with the low resolution mass spectrometers, the same ionic fragment can generate multiple adjacent peaks of different nominal mass attributable to ions having the same chemical formula but different isotopic compositions. For example, the ion

CH_3^+ consists of fragments of nominal mass ranging from 15 (fragment $^{12}C^1H_3^+$) up to 19 (fragment $^{13}C^2H_3^+$).
The relative intensity of isotope peaks depends on the natural isotopic composition of each element. For C the per cent natural *isotopic abundance* is 98.90% ^{12}C and 1.10% ^{13}C, and for H 99.985% ^1H and 0.015% ^2H. Therefore, the more intense peak (M=15) is attributed to the more abundant $^{12}C^1H_3^+$, the next in intensity but much smaller than peak M (M+1=16) is attributed to both $^{13}C^1H_3^+$ and $^{12}C^1H_2{}^2H^+$, whereas peak M+4, attributed to $^{13}C^2H_3^+$, has practically zero intensity due to the extremely low probability of occurrence.
Below is shown how the relative intensities of mass peaks for the ionic fragment CH_2Cl^+ can be exactly (without approximations) calculated, taking into consideration the isotopic abundance for C, H and Cl (75.77% ^{35}Cl and 24.23% ^{37}Cl).

Fragment M = 49	$^{12}C\,^1H_2\,^{35}Cl$:	$0.989\times(0.99985)^2\times0.7577 =$	0.7491
Fragments M+1 = 50	$^{13}C\,^1H_2\,^{35}Cl$:	$0.011\times(0.99985)^2\times0.7577 =$	0.00833
	$^{12}C\,^2H\,^1H\,^{35}Cl$:	$0.989\times0.00015\times0.99985\times0.7577 =$	0.00011
	$^{12}C\,^1H\,^2H\,^{35}Cl$:	$0.989\times0.99985\times0.00015\times0.7577 =$	0.00011
			0.00855
Fragments M+2 = 51	$^{13}C\,^2H\,^1H\,^{35}Cl$:	$0.011\times0.00015\times0.99985\times0.7577 =$	1.25×10^{-6}
	$^{13}C\,^1H\,^2H\,^{35}Cl$:	$0.011\times0.99985\times0.00015\times0.7577 =$	1.25×10^{-6}
	$^{12}C\,^1H_2\,^{37}Cl$:	$0.989\times(0.99985)^2\times0.2423 =$	0.240
			0.240
Fragments M+3 = 52	$^{13}C\,^2H_2\,^{35}Cl$:	$0.011\times(0.00015)^2\times0.7577 =$	1.9×10^{-10}
	$^{13}C\,^1H_2\,^{37}Cl$:	$0.011\times(0.99985)^2\times0.2423 =$	0.00266
	$^{12}C\,^1H\,^2H\,^{37}Cl$:	$0.989\times0.99985\times0.00015\times0.2423 =$	3.59×10^{-5}
	$^{12}C\,^2H\,^1H\,^{37}Cl$:	$0.989\times0.00015\times0.99985\times0.2423 =$	3.59×10^{-5}
			0.0027
Fragments M+4 = 53	$^{13}C\,^2H\,^1H\,^{37}Cl$:	$0.011\times0.00015\times0.99985\times0.2423 =$	4.0×10^{-7}
	$^{13}C\,^1H\,^2H\,^{37}Cl$:	$0.011\times0.99985\times0.00015\times0.2423 =$	4.0×10^{-7}
	$^{12}C\,^2H_2\,^{37}Cl$:	$0.989\times(0.00015)^2\times0.2423 =$	5.4×10^{-9}
			8.1×10^{-7}
Fragment M+5 = 54	$^{13}C\,^2H_2\,^{37}Cl$:	$0.011\times(0.00015)^2\times0.2423 =$	6×10^{-11}

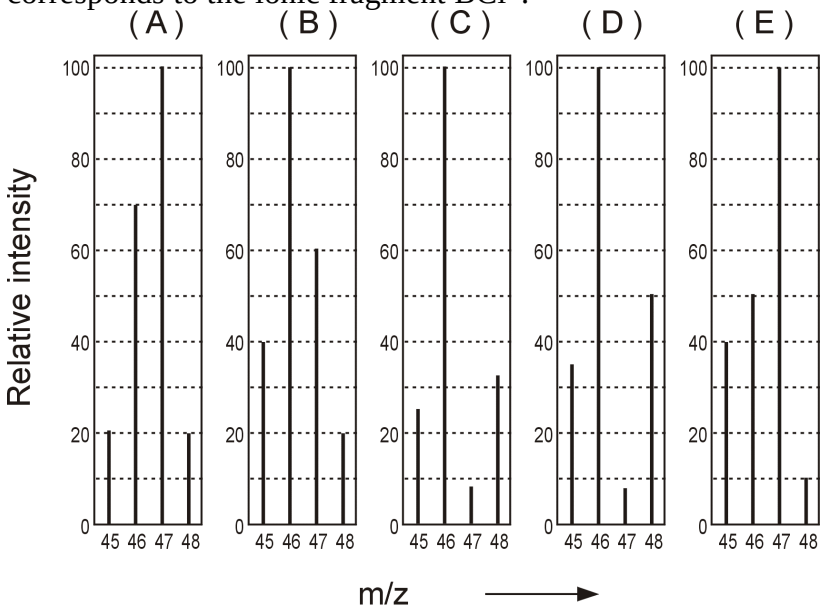
The intensity of each peak (from M to M+5) is proportional to the relative population of each fragment and the calculation of the probability is based on the summation of the probabilities of occurrence of all combinations resulting into the same nominal mass. The most intense peak is called *base peak* and the *relative intensities* of the other peaks are commonly reported as % of base peak.
Obviously, for the example above (ionic fragment CH_2Cl^+), the fragment M = 49 constitutes the base peak (relative intensity 100%). The relative intensities of the other fragments can be easily calculated, and we have:

Relative intensity for M	= 49:			100%
Relative intensity for M+1	= 50:	$(0.00855/0.7491)\times100$	=	1.14%
Relative intensity for M+2	= 51:	$(0.240/0.7491)\times100$	=	31.98%
Relative intensity for M+3	= 52:	$(0.0027/0.7491)\times100$	=	0.36%
Relative intensity for M+4	= 53:	$(8.1\times10^{-7}/0.7491)\times100$	=	1×10^{-4}%
Relative intensity for M+5	= 54:	$(6\times10^{-11}/0.7491)\times100$	=	8×10^{-9}%

[A Java applet demonstrating the isotopic peaks encountered in mass spectrometry principles can be found at the Internet site http://www.chem.uoa.gr/applets/appletMS/appl_MS2.html.]

1. Natural silicon consists of the following 3 stable isotopes: ^{28}Si, ^{29}Si, ^{30}Si, whereas natural chlorine consists of the following 2 stable isotopes: ^{35}Cl, ^{37}Cl. How many isotopic lines are expected for the ionic fragment $SiCl_2^+$?

2. The isotopic abundance for boron is: ^{10}B 19.9%, ^{11}B 80.1%, and for chlorine is: ^{35}Cl 75.77%, ^{37}Cl 24.23%. Which one of the following mass spectra patterns (A-E) corresponds to the ionic fragment BCl^+?



3. All the following ionic fragments: (a) N_2^+, (b) CO^+, (c) CH_2N^+, (d) $C_2H_4^+$ have nominal mass M = 28 and they cannot be resolved with a low resolution mass spectrometer. However, based on the relative intensity of the M+1 peak, identification still can be achieved. Identify the ionic fragment whose the relative intensity of the M+1 peak is 1.15. The following isotopic abundances are given:

H:	^{1}H: 99.985%	^{2}H: 0.015%	
C:	^{12}C: 98.9%	^{13}C: 1.1%	
N:	^{14}N: 99.634%	^{15}N: 0.366%	
O:	^{16}O: 99.762%	^{17}O: 0.038%	^{18}O: 0.20%