Buffer solutions

BUFFER SOLUTIONS CONTENTS 1. Introductions. 2. Principles of buffering. 3. Applications a. Simple buffering agents. b. " Universal" buffer mixtures. c. Common buffer compounds used in biology. 4. Buffer capacity. 5. Calculating buffer pH a. Monoprotic acids. b. Polyprotic acids. 6. Biblography. INTRODUCTION A buffer is an aqueous solution consisting of a mixture of a weak acid and its conjugate base or a weak baseand its conjugate acid. Its pH changes very little when a small amount of strong acid or base is added to it and thus it is used to prevent any change in the pH of a solution. Buffer solutions are used as a means of keeping pH at a nearly constant value in a wide variety of chemical applications. Many life forms thrive only in a relatively small pH range so they utilize a buffer solution to maintain a constant pH. One example of a buffer solution found in nature is blood. So far in discussing pH we have dealt only with solutions obtained by adding a single acid, such as acetic acid, or a single base, such as the acetate ion, to water. We must now turn to a consideration of solutions to which both an acid and a base have been added. The simplest case of such a solution occurs when the acid and base are conjugate to each other and also present in comparable amounts. Solutions of this special kind are called buffer solutionsbecause, as we shall shortly see, it is difficult to change their pH even when an appreciable amount of strong acid orstrong base is added. As a typical example of a buffer solution, let us consider the solution obtained when 3. 00 mol acetic acid ($HC_2H_3O_2$) and 2. 00 mol sodium acetate ($NaC_2H_3O_2$) are added to sufficient water to produce a solution of total volume 1 dm^3. The stoichiometric concentration of acetic acid, namely, c_a, is then 3. 00 mol dm—3, while the stoichiometric concentration of sodium acetate, c_b, is 2. 00 mol dm—3. As a result of mixing the two components, some of the

acetic acid, say x mol dm—3, is converted to acetate ion and hydronium ion. Principles of buffering [pic] [pic] Solution of a weak acid (pKa = 4. 7) with Simulated titration of an acidified alkali. [pic] Addition of hydroxide to a mixture of a weak acid and its conjugate base Buffer solutions achieve their resistance to pH change because of the presence of an equilibrium between the acid HA and its conjugate base A-. HA [pic] H+ + A- When some strong acid is added to an equilibrium mixture of the weak acid and its conjugate base, the equilibrium is shifted to the left, in accordance with Le Chatelier's principle. Because of this, the hydrogen ion concentration increases by less than the amount expected for the quantity of strong acid added. Similarly, if strong alkali is added to the mixture the hydrogen ion concentration decreases by less than the amount expected for the quantity of alkali added. The effect is illustrated by the simulated titration of a weak acid with pKa = 4. 7. The relative concentration of undissociated acid is shown in blue and of its conjugate base in red. The pH changes relatively slowly in the buffer region, pH = pKa ± 1, centered at pH = 4. 7 where [HA] = [A-]. The hydrogen ion concentration decreases by less than the amount expected because most of the added hydroxide ion is consumed in the reaction. OH- + HA â†' H2O + A- and only a little is consumed in the neutralization reaction which results in an increase in pH. OH- + H+ â†' H2O Once the acid is more than 95% deprotonated the pH rises rapidly because most of the added alkali is consumed in the neutralization reaction. Applications Buffer solutions are necessary to keep the correct pH for enzymes in many organisms to work. Many enzymes work only under very precise conditions; if the pH moves outside of a narrow range, the enzymes slow or stop working and can denature. In many cases denaturation can permanently disable their

catalytic activity. [1] A buffer of carbonic acid (H_2CO_3) and bicarbonate (HCO_3^-) is present in blood plasma, to maintain a pH between 7. 35 and 7. 45. Industrially, buffer solutions are used in fermentation processes and in setting the correct conditions for dyes used in colouring fabrics. They are also used in chemical analysis[2] and calibration of pH meters. The majority of biological samples that are used in research are made in buffers, especially phosphate buffered saline (PBS) at pH 7. 4. Simple buffering agents

Buffering agent	pKa	useful pH range
Citric acid	3. 13, 4. 76, 6. 40	2. 1 - 7. 4
Acetic acid	4. 8	3. 8 - 5. 8
K2HPO4,	7. 2	6. 2 - 8. 2
CHES	9. 3	8. 3—10. 3
Borate	9. 24	8. 25 - 10. 25

For buffers in acid regions, the pH may be adjusted to a desired value by adding a strong acid such ashydrochloric acid to the buffering agent. For alkaline buffers, a strong base such as sodium hydroxide may be added. Alternatively, a buffer mixture can be made from a mixure of an acid and its conjugate base. For example, an acetate buffer can be made from a mixture of acetic acid and sodium acetate. Similarly an alkaline buffer can be made from a mixture of the base and its conjugate acid. " Universal" buffer mixtures By combining substances with pKa values differing by only two or less and adjusting the pH, a wide-range of buffers can be obtained. Citric acid is a useful component of a buffer mixture because it has three pKa values, separated by less than two. The buffer range can be extended by adding other buffering agents. The following two-component mixtures (McIlvaine's buffer solutions) have a buffer range of pH 3 to 8.

0. 2M Na2HPO4 /mL	0. 1M Citric Acid /mL	pH…
20. 55	79. 45	3. 0
38. 55	61. 45	4. 0
51. 50	48. 50	5. 0
63. 15	36. 85	6. 0
82. 35	17. 65	7. 0
97. 25	2. 75	8. 0

A mixture containing citric acid,

potassium dihydrogen phosphate, boric acid, and diethyl barbituric acid can be made to cover the pH range 2. 6 to 12.[4] Other universal buffers are Carmody buffer[5] and Britton-Robinson buffer, developed in 1931. Compounds used in biology Common buffer | Common Name | | |[HA] |[A-] | [H+] | | I | C0 | 0 | Y | | C |-x | x | X | | E | C0-x | x | x+y | The first row, labelled I, lists the initial conditions: the concentration of acid is C0, initially undissociated, so the concentrations of A- and H+ would be zero; y is the initial concentration of added strong acid, such as hydrochloric acid. If strong alkali, such as sodium hydroxide, is added y will have a negative sign because alkali removes hydrogen ions from the solution. The second row, labelled C for change, specifies the changes that occur when the acid dissociates. The acid concentration decreases by an amount -x and the concentrations of A- and H+ both increase by an amount +x. This follows from the equilibrium expression. The third row, labelled E for equilibrium concentrations, adds together the first two rows and shows the concentrations at equilibrium. To find x, use the formula for the equilibrium constant in terms of concentrations: [pic] Substitute the concentrations with the values found in the last row of the ICE table: [pic] Simplify to: [pic] With specific values for C0, Ka and y this equation can be solved for x. Assuming that pH = -log10[H+] the pH can be calculated as pH = -log10x. Polyprotic acids % Percent of species formation calculated for a 10 mill molar solution of citric acid. Polyprotic acids are acids that can lose more than one proton. The constant for dissociation of the first proton may be denoted as Ka1 and the constants for dissociation of successive protons as Ka2, etc. Citric acid, H3A, is an example of a polyprotic acid as it can lose three protons. | Equilibrium | pKa value | | H3A [pic] H2A$^-$ + H+ | pKa1 = 3. 13 | |

H2Aâˆ' [pic] HA2âˆ' + H+ | pKa2 = 4. 76 | | HA2âˆ' [pic] A3âˆ' + H+ | pKa3 = 6. 40 | When the difference between successive pK values is less than about three there is overlap between the pH range of existence of the species in equilibrium. The smaller the difference, the more the overlap. In the case of citric acid, the overlap is extensive and solutions of citric acid are buffered over the whole range of pH 2. 5 to 7. 5. Calculation of the pH with a polyprotic acid requires a speciation calculation to be performed. In the case of citric acid, this entails the solution of the two equations of mass balance [pic] [pic] CA is the analytical concentration of the acid, CH is the analytical concentration of added hydrogen ions, Î²q are the cumulative association constants [pic] Kw is the constant for Self-ionization of water. There are two non-linear simultaneous equations in two unknown quantities [A3-] and [H+]. Many computer programs are available to do this calculation. The speciation diagram for citric acid was produced with the program HySS.[7] In general the two mass-balance equations can be written as [pic] In this general expression [A] stands for the concentration of the fully deprotonated acid and the electrical charge on this species is not specified. BIBLIOGRAPHY

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