CHEM 191

Chemical Reactions in Aqueous Solution

Module 1 Lecture 7

Buffers

Brown (15th) Chapter 17.2

1

Module 1 Lecture 7

Learning objectives

- Understand what is a Buffer solution
- Calculate the pH of a buffer solution
- Understand how to prepare a buffer of a specific pH
- Understand the concept of buffering capacity

2

Buffer solutions

- The pH of blood is about 7.4. If it changed to either 7 or 8 we would die. The pH is maintained by a buffer solution
- A ***buffer solution*** is a solution of a weak acid and its conjugate base (or a weak base and its conjugate acid), **both at reasonable concentration**, which will maintain a reasonably constant pH on addition of significant amounts of H_3O^+ or OH^- ions.
- The pH of a buffer solution is also unaffected by reasonable dilution of the solution.

  (A full definition of a buffer solution requires *both* of the above statements.)

3

A simple buffer

- A buffer solution containing acetic acid and sodium acetate in roughly equal concentrations will contain

  CH_3COOH + H_3O^+ (from acid)

  CH_3COO^- (from sodium acetate)

  Na^+ (from sodium acetate)

- If we add strong acid – H_3O^+ consumed by conjugate base

  $$\mathbf{CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)}$$

- If we add strong base – OH^- consumed by acid from the buffer

  $$\mathbf{CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)}$$

4

A simple buffer

NOTE that these are different sorts of acid-base equations to what we have seen so far.

Here a weak base is reacting with a **strong acid**, not with water

$$CH_3COO^-(aq) + H_3O^+(aq) \longrightarrow CH_3COOH(aq) + H_2O(l)$$

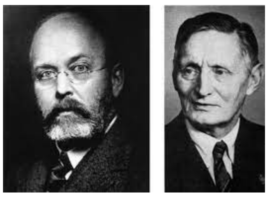
and a weak acid is reacting with a **strong base**, not with water

$$CH_3COOH(aq) + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$$

Reactions go to completion

5

Henderson-Hasselbalch Equation



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

- The **Henderson-Hasselbalch** equation can be used to calculate the pH of any **buffer solution**.
- It says that the pH of a buffer solution is controlled by the ratio $[A^-] / [HA]$
- It also shows that, when the ratio $[A^-] / [HA] = 1$ in the buffer solution, then $pH = pK_a$. (because $\log(1) = 0$)
- At this pH value, the concentrations of A^- and HA in solution are equal, and the buffer will be equally effective towards the addition of either acid or base.

6

Henderson-Hasselbalch Equation

- The equation can also be expressed in terms of numbers of moles, rather than concentrations.
  Remembering that $c = \frac{n}{V}$ the equation can be rewritten as

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$= \mathrm{p}K_\mathrm{a} + \log\frac{\frac{n_{\mathrm{A}^-}}{V}}{\frac{n_{\mathrm{HA}}}{\mathrm{V}}}$$

- Therefore,

$$\boxed{\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{n_{\mathrm{A}^-}}{n_{\mathrm{HA}}}} \quad ✓✓✓$$

7

Calculation of buffer pH

- What is the pH of a buffer solution made up of acetic acid (0.100 mol L^{-1}) and sodium acetate (0.100 mol L^{-1})?
- The sodium acetate will dissociate completely (it is a strong electrolyte, “all Na compounds are soluble”), to give Na^+(aq) and CH_3COO^-(aq) ions - a weak base)

$$\mathbf{CH_3COONa(s) \rightarrow Na^+(aq) + CH_3COO^-(aq)}$$

- The $[CH_3COO^-]$ will therefore be 0.100 mol L^{-1}

Note: The dissociation of acetic acid will be suppressed due to the presence of CH_3COO^-(aq) as a common ion.

$$CH_3COOH + H_2O \rightleftharpoons H_3O^+(aq) + CH_3COO^-(aq)$$

8

Calculation of buffer pH

If we know the concentrations of the weak acid and the conjugate base, we can put these directly into the Henderson Hasslebach equation

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

$$pH = pK_a + \log\frac{[\text{acetate}]}{[\text{acetic acid}]}$$

$$pH = 4.74 + \log\frac{(0.100)}{(0.100)} = 4.74$$

9

Problem

- One of the definitions of a buffer is that it maintains a relatively constant pH when strong acid or base is added. How much will the pH of our CH_3COOH/CH_3COO^- buffer change if 100 mL of 0.100 mol L^{-1} HCl is added to 1.00 L of the buffer solution?

- Before addition of the HCl, the ratio $[A^-] / [HA] = 1$. The added **strong** acid will react stoichiometrically with CH_3COO^- ion in solution to form CH_3COOH

$$CH_3COO^-(aq) + H_3O^+(aq) \rightarrow CH_3COOH(aq) + H_2O(l)$$

- This will then change the $[A^-] / [HA]$ ratio. Need to calculate the individual concentrations of A^- and HA

10

Solution

Use a concentration table

	$CH_3COO^-(aq)$ +	$H_3O^+(aq)$ →	$CH_3COOH(aq)$ + $H_2O(l)$
Before mixing the strong acid with the buffer	0.100 mol L^{-1} x 1 L = 0.100 mol	0.100 mol L^{-1} x 0.10 L = 0.010 mol	0.100 mol L^{-1} x 1 L = 0.100 mol
After mixing the strong acid with the buffer	0.100 mol – 0.010 mol = **0.090 mol** Amount decreases because it is being used up	**0 mol** (this is the limiting reactant)	0.100 mol + 0.010 mol = **0.110 mol** Amount increases because it is being produced

11

Solution

Now we can put these amounts into the Henderson Hasslebach equation

$$pH = pK_a + \log \frac{n(A^-)}{n(HA)}$$

$$pH = pK_a + \log \frac{n(\text{acetate})}{n(\text{acetic acid})}$$

$$pH = 4.74 + \log \frac{(0.090)}{(0.110)} = 4.65$$

So the pH decreases (as you might expect since you added acid) **but not by very much**.

12

Solution (cont)

Compare this with the pH change when 0.100 L of 0.100 mol L^{-1} HCl is added to 1.00 L of pure water.

n(HCl) = 0.100 L $\times$ 0.100 mol L^{-1} = 0.0100 mol

Final $[H_3O^+]$ = 0.0100 mol / 1.10 L = 0.00909 mol L^{-1}

Thus final pH = -log(0.00909) = 2.04

Initial $[H_3O^+]$ = 1 $\times$ 10^{-7} mol L^{-1}, thus initial pH = 7.00

Therefore change in pH = 2.04 – 7.00 = **- 4.96 !**

13

Buffer preparation

- Don't have to mix a weak acid with a salt of its conjugate base to make a buffer. We can, for example, add NaOH(aq) to a solution of CH_3COOH(aq)

$CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO^-(aq) + Na^+(aq) + H_2O$

- Addition of less than 1 mole equivalent of NaOH(aq) will give a buffer solution containing both CH_3COOH(aq) and CH_3COO^-(aq) in amounts determined by the amount of NaOH(aq) added.

- The same applies for a weak base – e.g. a buffer solution can be prepared by adding HCl(aq) to a solution of NH_3(aq)

$NH_3(aq) + HCl(aq) \rightarrow NH_4^+(aq) + Cl^-(aq)$

14

Example

- Calculate the pH of the buffer solution prepared by adding 300 mL of 0.500 mol L^{-1} NH_3 to 100 mL of 0.500 mol L^{-1} HCl. pK_a (NH_4^+) = 9.26

$$\mathbf{NH_3 + HCl \rightarrow NH_4^+ + Cl^-}$$

Note: weak base + strong acid give a reaction which goes to completion.

Before mixing the solutions

n(HCl) $= cV = 0.500 \text{ mol L}^{-1} \times 0.100 \text{ L} = 0.050 \text{ mol}$

$n(NH_3)$ $= cV = 0.500 \text{ mol L}^{-1} \times 0.300 \text{ L} = 0.150 \text{ mol}$

15

Solution

	NH_3	+	HCl	$\rightarrow$	NH_4^+	+ Cl^-
Before mixing	0.15 mol		0.05 mol		0	
After mixing	0.15 – 0.050 = **0.10 mol** Amount decreases because it is being used up		**0** (this is the limiting reactant)		0 + 0.05 = **0.05 mol** Amount increases because it is being produced	

$$\text{pH} = \text{p}K_a + \log\frac{n(NH_3)}{n(NH_4^+)} = 9.26 + \log\frac{0.100}{0.0500} = 9.56$$

16

Buffer capacity

- Can't endlessly add acid or base to a buffer without significant change in the pH. Will eventually get to the point when either the weak acid or the conjugate base is all used up and then the pH will change significantly. At this point, we say the ***buffer capacity*** has been exhausted.

- e.g. consider adding 0.100 mol L^{-1} NaOH to 50.0 mL of 0.100 mol L^{-1} CH_3COOH (5.00×10^{-3} mol CH_3COOH)

$$\mathbf{CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O}$$

As soon as we start adding OH^-, will have both CH_3COOH and CH_3COO^- in solution – i.e. a buffer solution. However, after addition of 50.0 mL of NaOH solution, will only have CH_3COO^-. Will no longer have a buffer solution.

17

Our buffers

- How does nature maintain pH?
- The pH of blood is kept constant at 7.4 *via* the following equilibria
- carbonate

$$\mathbf{H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-}$$

- haemoglobin and oxyhaemoglobin

$$\mathbf{HHb + H_2O \rightleftharpoons H_3O^+ + Hb^-}$$

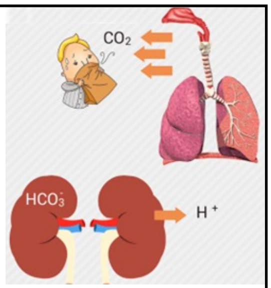
$$\mathbf{HHbO_2 + H_2O \rightleftharpoons H_3O^+ + HbO_2^-}$$

- phosphate

$$\mathbf{H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+}$$

18

Hyperventilation



- Rapid breathing/hyperventilation causes the expulsion of too much CO_2 causing light headedness.
- This process raises the pH of the blood (alkalosis) by increasing the ratio $[HCO_3^-]$ /$[H_2CO_3]$. (H_2CO_3 is formed by dissolving CO_2 in H_2O)
- This can supposedly be cured by breathing into a paper bag. This means that the expelled CO_2 is 'rebreathed', thereby increasing the $[H_2CO_3]$. This means that the $[HCO_3^-]$ / $[H_2CO_3]$ ratio decreases, and hence, from the Henderson-Hasselbalch equation, we would expect the pH to decrease to its normal value.

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[HCO_3^-]}{[H_2CO_3]}$$

19

✱ Homework ✱

Brown (15th)

Problems 17.62, 17.63, 17.65, 17.95, 17.98

some problems require K_a from Appendix D, Page 1515

Answers on Blackboard

20