Guided Inquiry – The theory of acid and bases

Objectives: In this guided inquiry worksheet, you will
- understand how to quantify the strength of an acid and base
- understand how to calculate the pH of an acid or base dissolved in water
- understand how a buffer works
- understand how to calculate the pH of a buffer

You are required to be familiar with the following concepts
- a conjugate acid and base pair
- the derivation of the equilibrium constant, K_c, and its significance
- the calculation of pH

Although not required in H2 Chemistry, you will be requested to solve quadratic equations.

Section 1: the pH of artificial vinegar

Vinegar contains ethanoic acid, CH_3CO_2H. Artificial vinegar found in supermarkets has a CH_3CO_2H concentration of 3.95 grams per 100 ml. The sour taste of vinegar can be attributed to the presence of H_3O^+ ions. We can measure this "sourness" through finding out the concentration of H_3O^+ ions in artificial vinegar.

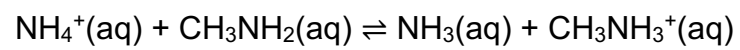|	
1	In water, CH_3CO_2H partially ionises to form H_3O^+ and $CH_3CO_2^-$ ions. The equilibrium is represented by $$CH_3CO_2H(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CH_3CO_2^-(aq)$$ State an expression for K_c of this equilibrium.
2	The K_c of this equilibrium is known as the K_a (acid dissociation constant) of ethanoic acid. The unit of K_a is hence mol dm^{-3}.
3	You are given that at 25 degrees Celsius, $K_a(CH_3CO_2H) = 1.74 \times 10^{-5}$ mol dm^{-3}. First, assume that CH_3CO_2H is **not** ionised at all when added to water. This is before the acid-base equilibria occurs. Calculate the concentration of CH_3CO_2H in vinegar, in mol dm^{-3}. Artificial vinegar found in supermarkets has a concentration of 3.95 grams per 100 ml. Refer to A_r values in your Data Booklet.
4	Let $[H_3O^+] = x$ mol dm^{-3}. By using a I-C-E table, or otherwise, express $[CH_3CO_2^-]$ and $[CH_3CO_2H]$ in terms of x and mol dm^{-3}.

5	Hence, give an expression for $K_a(CH_3CO_2H)$ in terms of x.
6	The expression (your answer to **5**) can be rearranged to form a quadratic equation in terms of x. Solve for x. You may use a graphing or scientific calculator.

Find the pH of artificial vinegar to 2 decimal places. |
| 7 | Consider the concentration of $[H_3O^+]$ and the initial concentration of ethanoic acid (before dissociation took place).

What is the percentage of ethanoic acid that has ionised in water? |
| 8 | The percentage you have found in **7** is small. Many weak acids dissociate sparingly in water. We are able to simplify our method to calculate x through an approximation.

The denominator of the expression you have found in **5** can be approximated to your answer in **3**—that is:

$$\frac{x^2}{0.656} = K_a$$

where the term $0.656 - x$ is rewritten as 0.656.

You do not need to solve a quadratic equation in x with this approximation. Use this new expression to solve for x again. |
| 9 | Compare your answer in **8** to your answer in **6**.

What is the percentage discrepancy of your answer in **8** as compared to your answer in **6**? In your opinion, is this percentage discrepancy acceptable? |
| 10 | In H2 Chemistry, you do not need to solve a quadratic equation. The approximation suggested in **8** will help you to avoid solving a quadratic equation. Why can the term $0.656 - x$ be approximated to 0.656? You should consider your answer to **7**. |

Section 2: the pH of ammonia

We are able to find the pH of a solution of ammonia with concentration 0.500 mol dm^{-3} with a similar method introduced in Section 1.

1	In water, ammonia partially ionises to form OH$^-$ and NH$_4^+$ ions. The equilibrium is represented by $$NH_3(aq) + H_2O(l) \rightleftharpoons OH^-(aq) + NH_4^+(aq)$$ The expression for K_c of this equilibrium is known as the K_b (base dissociation constant) of ammonia. The unit of K_b is hence mol dm^{-3}.
2	You are given that at 25 degrees Celsius, $K_b(NH_3) = 1.80 \times 10^{-5}$ mol dm^{-3}. Let [OH$^-$] = x mol dm^{-3}. By using a I-C-E table, or otherwise, express [NH$_4^+$] and [NH$_3$] in terms of x and mol dm^{-3}.
3	Find [OH$^-$] by using a similar approximation shown in Section 1, question **8**.
4	We will now find the pH of the solution of ammonia. We can relate [OH$^-$] and [H$_3$O$^+$] through an equation. Water ionises partially—the equilibrium is $$H_2O(l) \rightleftharpoons OH^-(aq) + H^+(aq)$$ $$K_c = [H^+][OH^-]$$ At 25 degrees Celsius, $K_c = 10^{-14}$ mol^2 dm^{-6}. This data can be found in your Data Booket and the equilibrium constant is known as K_w. Calculate the pH of 0.500 mol dm^{-3} of ammonia.
5	State the expression of $K_a(NH_4^+)$ and using information from **4**, calculate $K_a(NH_4^+)$.
6	The expressions pK_a, pK_b and pK_w can be calculated in the same way as pH. For example, pK_a = -log$_{10}$(K_a / mol dm^{-3}). Using the conjugate acid-base pair NH$_4^+$/NH$_3$ as an example, show that $K_aK_b = K_w$ and pK_a + pK_b = pK_w.

7	For any equilibrium, a larger value of K, the equilibrium constant, signifies that the position of equilibrium lies further to the <u>left / right</u>.
8	We will compare the strength of a few bases and acids using K_a values. Complete the table below.

Base	Conjugate acid	K_a of conjugate acid / mol dm^{-3}	pKₐ
NH_3		5.60×10^{-10}	
CH_3NH_2			10.6
$CH_3CO_2^-$		1.74×10^{-5}	
CO_3^{2-}		4.80×10^{-11}	
Cl^-			-7

Consider the acid HCO_3^- and CH_3CO_2H. Which of them is a stronger acid? Explain your answer using K_a values. A stronger acid is one that ionises to a larger extent.

9	A <u>higher / lower</u> K_a value would mean that the acid is stronger. A <u>higher / lower</u> pKₐ value would mean that the acid is stronger.
10	Now, we will compare the strengths of the bases CO_3^{2-} and $CH_3CO_2^-$. Calculate $K_b(CO_3^{2-})$ and $K_b(CH_3CO_2^-)$. From your calculations, <u>CO_3^{2-} / $CH_3CO_2^-$</u> is a stronger base.
11	Use your conclusion from **10** to answer the following questions. An acid **X** has a pKₐ value higher than that of another acid **Y**. **X** is a <u>stronger / weaker</u> acid than **Y**. **X** has a <u>higher / lower</u> K_a value than **Y**. The conjugate base of **X** is a <u>stronger / weaker</u> base than the conjugate base of **Y**.
12	Calculate the equilibrium constant, K_c, of the equilibrium below.

$$NH_4^+(aq) + CH_3NH_2(aq) \rightleftharpoons NH_3(aq) + CH_3NH_3^+(aq)$$

Hence, determine if CH_3NH_2 or NH_3 is the stronger base from the value of K_c.

Section 3: Buffering action

Antigen-based Rapid Test Kits contain a buffer solution. Some of the buffer solution contains *tris*. *tris* has the chemical formula $(HOCH_2)_3CNH_2$ and its conjugate acid is $(HOCH_2)_3CNH_3^+$. The pK_a of its conjugate acid is 8.07 at 25 degrees Celusius.

| 1	A buffer solution is a solution that maintains its pH when a small amount of acid or base is added to it. If the pH is maintained, then $[H_3O^+]$ is maintained too.
2	A buffer solution is found to have a pH of 7.5000 at 25 degrees Celsius. By considering the equilibrium $$(HOCH_2)_3CNH_3^+(aq) + H_2O(l) \rightleftharpoons (HOCH_2)_3CNH_2(aq) + H_3O^+(aq)$$ and the expression for K_a, calculate the ratio $$\frac{[(HOCH_2)_3CNH_2]}{[(HOCH_2)_3CNH_3^+]}$$ If you know the Henderson-Hasselbalch equation, do **not** use it.
3	Assume that in the buffer $[(HOCH_2)_3CNH_3^+] = 0.05$ mol dm^{-3}. 10^{-7} mol of H_3O^+ is added into 5.00 cm^3 solution of the buffer after a swab. The volume of the buffer remains the same. H_3O^+ is a strong acid, so any $(HOCH_2)_3CNH_2$ will react fully with H_3O^+ to form $(HOCH_2)_3CNH_3^+$. This equation is represented by $(HOCH_2)_3CNH_2 + H_3O^+ \rightarrow (HOCH_2)_3CNH_3^+ + H_2O$. Now, calculate the pH of the buffer to 4 decimal places.
4	What is the ratio $$\frac{[(HOCH_2)_3CNH_2]}{[(HOCH_2)_3CNH_3^+]}$$ when 10^{-7} mol of H_3O^+ is added into the buffer? Compare this value to your answer in **2**.

5	Hence, if the pH of the buffer were to be maintained, must the ratio $$\frac{[(HOCH_2)_3CNH_2]}{[(HOCH_2)_3CNH_3^+]}$$ be maintained?
6	To a fresh sample of 5.00 cm^3 solution of the buffer, 0.100 cm^3 of concentrated hydrochloric acid ($[H_3O^+]$ = 6.00 mol dm^{-3}) is added into the buffer. Will all $(HOCH_2)_3CNH_2$ be reacted? What will $[H_3O^+]$ be in the end? Hence, explain why only a **small amount** of acid or base should be added into the buffer solution.
7	If *more* acid or base is expected to be added into the buffer solution, what do you think can be done to make the buffer solution more effective? Consider what reacts with the acid or base in the buffer solution.
8	A 20.0 cm^3 of 0.100 mol dm^{-3} of *tris* solution is titrated against 0.100 mol dm^{-3} of hydrochloric acid. Calculate the pH of the solution when • 0 cm^3 • 10 cm^3 • 20 cm^3 of hydrochloric acid is added into it.

| 9 | When 10.0 cm^3 of hydrochloric acid is added into the *tris* solution, this results in a buffer solution being formed as both $(HOCH_2)_3CNH_2$ and $(HOCH_2)_3CNH_3^+$ are present in the solution.

However, when no hydrochloric acid is added into the *tris* solution, the *tris* contains almost exclusively $(HOCH_2)_3CNH_2$.

The graph of the pH of the solution against volume of hydrochloric acid added is shown below.

pH

volume of HC*l* added / cm^3
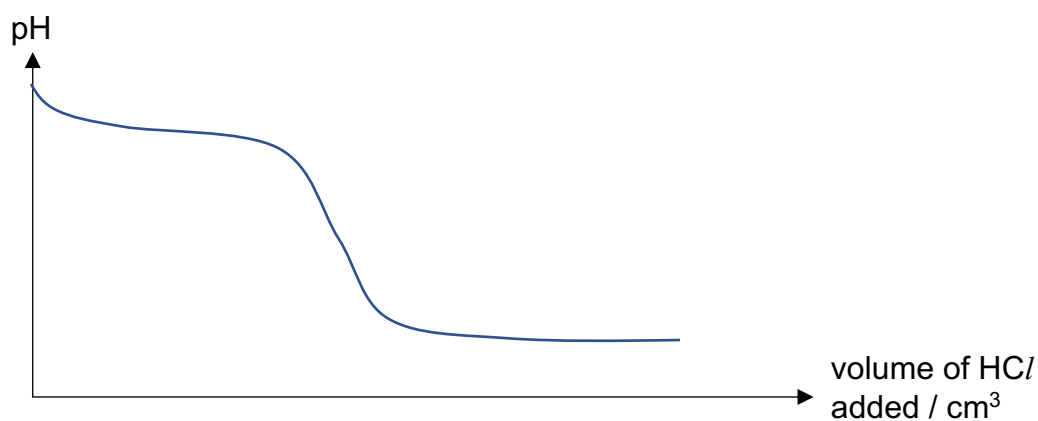
Construct an explain as to why there is a rather significant drop in pH at first, before the pH becomes relatively constant in the middle. You should take into account of the buffering action of the solution as hydrochloric acid is progressively added. |