

St. Andrew's Junior College H1 Chemistry 2022 Physical Chemistry Tutorial Theories of Acids and Bases

- 1. Identify the conjugate acid-base pair in the following reaction. HCl + NaHCO<sub>3</sub>  $\rightarrow$  H<sub>2</sub>CO<sub>3</sub> + NaCl
- 2. Calculate the pH of solutions with the following  $H_3O^+$  concentrations in mol dm<sup>-3</sup> (a) 6.80 x 10<sup>-3</sup> (b) 3.20 x 10<sup>-5</sup>
- **3.** Calculate the pH of solutions with the following OH<sup>-</sup> concentrations in mol dm<sup>-3</sup> (a)  $3.70 \times 10^{-10}$  (b)  $6.40 \times 10^{-5}$
- Calculate the H<sub>3</sub>O<sup>+</sup> and OH<sup>-</sup> concentrations in solutions with the following pH values:
   (a) 9.21
   (b) 13.7
- **5.** Calculate the pH and pOH of the following solutions:
  - (a)  $25 \text{ cm}^3 \text{ of } 0.200 \text{ mol } \text{dm}^{-3} \text{ of hydrochloric acid made up to } 500 \text{ cm}^3 \text{ of solution.}$
  - (b) 1.00 g of calcium hydroxide dissolved in water and made up to 250 cm<sup>3</sup> of solution
- 6. Explain the following terms: (i) pH (ii)  $K_a$  (iii)  $K_b$  (iv)  $K_w$
- 7. Calculate the *degree of dissociation* of the weak monobasic acids listed below:
  - (a) a solution of 0.0100 mol dm<sup>-3</sup> CH<sub>3</sub>COOH has a pH of 3.38.
  - (b) a solution of 0.200 mol  $dm^{-3}$  HCN has a pH of 5.05
- 8. Calculate the *percentage dissociation* of the weak monoacidic bases listed below:
  - (a) a solution of 0.0100 mol dm<sup>-3</sup> CH<sub>3</sub>NH<sub>2</sub> has [OH<sup>-</sup>] of 4.78 x  $10^{-7}$  mol dm<sup>-3</sup>.
  - (b) a solution of 0.0500 mol  $dm^{-3} C_6 H_5 N H_2$  has [OH<sup>-</sup>] of 9.65 x 10<sup>-5</sup> mol  $dm^{-3}$

**9.** (a) State if each of the following salts is acidic, basic or neutral.

	Salt	A, B or N
(i)	KBr	
(ii)	C <sub>6</sub> H₅ONa	
(iii)	NaCN	

	Salt	A, B or N
(iv)	$(C_6H_5NH_3)_2SO_4$	
(v)	(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> Br	
(vi)	CH₃COOK	

A – acidic salt ; B – basic salt ; N – neutral salt

(b) (i) For  $C_6H_5O^-Na^+$ , write an equation to illustrate its acidity/basicity.

(ii) For CH<sub>3</sub>NH<sub>3</sub>C*l*, write an equation to illustrate its acidity/basicity.

**10.** Indicate if the solution containing the specified species is a buffer solution. If it is, state if it is acidic or basic buffer.

	Solution	X or A or B
(a)	CH <sub>3</sub> COOH / CH <sub>3</sub> COONa	
(b)	CH₃COOH / NaCl	
(c)	HCl / NaCl	
(d)	HNO <sub>3</sub> / NaNO <sub>3</sub>	
(e)	HCN / KCN	
(f)	NH <sub>3</sub> / NH <sub>4</sub> NO <sub>3</sub>	
(g)	NaOH / Na <sub>2</sub> SO <sub>4</sub>	

X: not buffer A: acidic buffer B: basic buffer

#### ANSWERS

- **2** (a) 2.17 (b) 4.49
- **3** (a) 4.57 (b) 9.81
- 4 (a)  $[H_3O^+] = 6.17 \times 10^{-10} \text{ mol } \text{dm}^{-3}; [OH^-] = 1.62 \times 10^{-5} \text{ mol } \text{dm}^{-3}$ (b)  $[H_3O^+] = 2.00 \times 10^{-14} \text{ mol } \text{dm}^{-3}; [OH^-] = 0.500 \text{ mol } \text{dm}^{-3}$
- 5 (a) pH = 2; pOH = 12. (b) pOH = 0.967; pH = 13.0
- 7 (a)  $\alpha = 0.04$ (b)  $\alpha = 4.46 \times 10^{-5}$
- 8  $\alpha = 4.78 \times 10^{-3} \%$  $\alpha = 0.193 \%$
- **9** (a) (i) N (ii) B (iii) B (iv) A (v) A (vi) B
- **10** (a) A (b) X (c) X (d) X (e) A (f) B (g) X

#### Self – Check Answers:

**1.** Identify the Bronsted acid and its conjugate base and the Bronsted base and its conjugate acid in the following:

cid conjugate base

- 2 Applying pH =  $-\log [H^+]$  or pH =  $-\log [H_3O^+]$ (a) 2.17 (b) 4.49
- Applying pOH = log [OH<sup>-</sup>]
   Followed by pH = 14 pH
   (a) 4.57 (b) 9.81
- 4 (a)  $[H_3O^+] = 10^{-9.21} = 6.17 \times 10^{-10} \text{ mol } \text{dm}^{-3}$   $[OH^-] = 10^{-14} / [H_3O^+] = 1.62 \times 10^{-5} \text{ mol } \text{dm}^{-3}$ (b)  $[H_3O^+] = 10^{-13.7} = 2.00 \times 10^{-14} \text{ mol } \text{dm}^{-3}$  $[OH^-] = 10^{-14} / [H_3O^+] = 0.500 \text{ mol } \text{dm}^{-3}$
- (a) [HCI] = [H<sup>+</sup>] = [(25 / 1000) x 0.2] / (500/1000) = 0.01 mol dm<sup>-3</sup> pH = - log [H<sup>+</sup>] = 2 pOH = 14 − 2 = 12.

(b) mole of calcium hydroxide = 1.00 / [40.1 + 2(17)] = 0.0135 mol Mol of OH<sup>-</sup> ions = 0.0270[OH<sup>-</sup>] =  $0.0270 / 250 \times 1000 = 0.108$  mol dm<sup>-3</sup> pOH =  $- \log [OH^{-}] = 0.967$ pH = 14 - 0.967 = 13.0

6 (i) pH = -lg [H<sup>+</sup>]

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(ii) For a weak acid HA,  $HA(aq) + H_2O(I) \longrightarrow A^-(aq) + H_3O^+(aq)$  $\underbrace{[H^+(aq)][A^-(aq)]}_{K_a} = \underbrace{[HA(aq)]}_{mol dm^{-3}}.$ 

(iii) For a weak base B,  

$$B(aq) + H_2O(I) \implies BH^+(aq) + OH^-(aq)$$

$$\underbrace{[OH^-(aq)][BH^+(aq)]]}_{K_b} = \underbrace{[B(aq)]}_{mol dm^{-3}}.$$
(iv)  $H_2O(I) \implies H^+(aq) + OH^-(aq)$ 

 $K_{w}^{-} = [H^{+}][OH^{-}] mol^{2} dm^{-6}.$ 

degree of dissociation,  $\alpha = \frac{[H^+]}{[HA]}$ 

(c)  $\alpha = 10^{-3.38} / 0.01 = 0.04$ (d)  $\alpha = 10^{-5.05} / 0.2 = 4.46 \times 10^{-5}$ 

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$$\alpha = \frac{[OH^{-}]}{[B]} \times 100 \%$$
(a)  $\alpha = 4.78 \times 10^{-7} / 0.01 \times 100\% = 4.78 \times 10^{-3} \%$   
 $\alpha = 9.65 \times 10^{-5} / 0.05 \times 100\% = 0.193 \%$ 

**9** (a) (i) N (ii) B (iii) B (iv) A (v) A (vi) B

- (b) (i)  $C_6H_5O^- + H_2O \implies C_6H_5OH + OH^-$ (ii)  $CH_3N^+H_3 + H_2O \implies CH_3NH_2 + H_3O^+$
- **10** (a) A (b) X (c) X (d) X (e) A (f) B (g) X

## Theories of acids and bases

#### 1. [2013/P3/Q2]

(a) Explain what is meant by the terms *Brønsted-Lowry* base and *conjugate* acid-base pair.

Brønsted-Lowry base is a proton acceptor.

In an acid-base reaction, a H<sup>+</sup> is transferred from an acid to a base. For example:

 $HA = H^+ + A^-$ 

HA and A<sup>-</sup> is a conjugate acid-base pair, which differs by one H<sup> $\pm$ </sup>.

Examiner's comments:

Most candidates gave a correct definition of a Bronsted-Lowry base as a proton acceptor. Some defined a Lewis base (electron-pair donor) and a minority defined a Lewis acid. Far fewer were able to offer an adequate description of a conjugate acid-base pair. Several wrote about strong acids being associated with weak bases, or vice versa, without focussing on the fact that the pair differ by the presence or absence of a proton.

(b) The ammonia molecule can react in various ways: as an acid, base, oxidising agent or reducing agent.

Study the following reactions and decide in which way ammonia is reacting in each case. Explain your answers fully.

- (i)  $NH_3 + H_2O$  room temperature  $NH_4OH$
- (ii)  $NH_3 + HNO_2 \longrightarrow N_2 + 2H_2O$
- (iii)  $NH_3 + NaH \longrightarrow NaNH_2 + H_2$
- (iv)  $2NH_3 + NaOCl$  room temperature  $N_2H_2 + NaCl + H_2O$
- (i) Ammonia is reacting as a base.  $NH_3$  accepts a H<sup>+</sup> from H<sub>2</sub>O to form  $NH_4^+$ .
- (ii) Ammonia is reacting as a reducing agent.  $NH_3$  decreases the oxidation number of N from +3 in HNO<sub>2</sub> to 0 in N<sub>2</sub>.
- (iii) Ammonia is reacting as an acid.  $NH_3$  loses a H<sup>+</sup> to H<sup>-</sup> to form  $NH_2^-$ .
- (iv) Ammonia is reacting as a reducing agent.  $NH_3$  decreases the oxidation number of Cl from +1 in  $OCl^-$  to -1 in  $Cl^-$ .

Examiner's comments:

Some candidates correctly assigned the various roles of ammonia. Some candidates did not explain their reasons sufficiently. A number of candidates seemed to have confused oxidation with reduction, or acid with base.

# <u>K</u><u>w</u>

## 2. N2013/I/11

The dissociation constant,  $K_w$ , for the ionisation of water,  $H_2O \iff H^+ + OH^-$ , at different temperatures is given below.

Temperature / °C	<i>K</i> <sub>w</sub> / mol <sup>2</sup> dm <sup>-6</sup>
0	1.15 x 10 <sup>-15</sup>
25	1.00 x 10 <sup>-14</sup>
50	5.50 x 10 <sup>-14</sup>

What can be deduced from this information?

- **A** Only at 25°C are  $[H^+]$  and  $[OH^-]$  equal.
- **B** The equilibrium lies furthest to the right at 0°C.
- **C** The forward reaction is exothermic.
- **D** The pH of water decreases as temperature increases.

#### Ans: D

A: Incorrect.

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

 $[H^+] = [OH^-]$  for pure water at any temperature

**B:** Incorrect.  $K = \frac{Kf}{Kb} \frac{Kf}{Kb}$ . Comparing  $K_w$  at 0°C and 50°C,  $K_w$  at 0°C is smaller. This implies that at lower temperature, the backward reaction is favoured. Hence, the equilibrium position lies to the left at 0°C

Kf Kf

- **C:** Incorrect.  $K = \overline{Kb} \overline{Kb}$ . Comparing  $K_w$  at 0°C and 50°C,  $K_w$  at 50°C is larger. This implies that at higher temperature, the forward reaction is favoured. Hence, the forward reaction is endothermic.
- **D:** Correct.  $K_w = [H^+][OH^-]$  As temperature increases,  $K_w$  increases, implying [H<sup>+</sup>] increases. Thus, pH decreases.

## Calculations of [H<sup>±</sup>] and pH for strong acids and strong bases

## 3. [2012 P1 Q10]

Stomach juices have a pH of 1.0.

Aspirin is a monobasic (monoprotic) acid represented by HA ( $K_a = 1 \times 10^{-4} \text{ mol dm}^{-3}$ ) which dissociates into ions H<sup>+</sup> and A<sup>-</sup>.

What are the relative concentrations of  $H^+$ ,  $A^-$  and HA when aspirin from a tablet enters the stomach?

**A**  $[HA] > [H^+] = [A^-]$ 

 $\mathbf{B} \quad [\mathsf{H}^+] = [\mathsf{A}^-] > [\mathsf{H}\mathsf{A}]$ 

**C**  $[H^+] > [A^-] > [HA]$ 

**D**  $[H^+] > [HA] > [A^-]$ 

## Ans: D

Stomach juice, pH =1

 $[H^+] = 0.1 \text{ mol } dm^{-3}$ 

Since HA is a weak acid, it dissociates partially.

 $HA \implies H^+ + A^-$ 

high  $[H^+]$  will suppress the dissociation of aspirin thus  $[HA] > [A^-]$ 

## 4 2018/P2 Q7

Hydrogen chloride dissolves in water to give hydrochloric acid, which is a strong acid. Hydrogen fluoride dissolves in water to give hydrofluoric acid, which is a weak acid.

- (i) Explain the meaning of the terms acid, strong acid and weak acid, in terms of the Bronsted-Lowry theoy of acids.
   A strong acid <u>dissociates fully / completely in water</u> and is a proton donor.
   A weak acid <u>dissociates partially in water</u> and is a proton donor.
  - (ii) Suggest a reason why hydrochloric acid is a stronger acid than hydrofluoric acid. Chlorine has a larger atomic size than fluorine. There is <u>less effective orbital</u> <u>overlap</u> between hydrogen and chlorine. The <u>bond strength in HC/ is weaker</u> and hence the HC/ bond is more easily broken to release H<sup>+</sup>.
- (b) (i) Define the term pH.  $pH = -lg [H^+]$ 
  - (ii) Calculate the pH of a  $1.5 \times 10^{-4}$  mol dm<sup>-3</sup> solution of hydrochloric acid. [ANS: 3.82] pH = -lg ( $1.5 \times 10^{-4}$ ) = 3.82
  - (iii) Barium hydroxide is a strong base. Calculate the pH of a 0.075 mol dm<sup>-3</sup> solution of barium hydroxide. [ANS: 13.2]  $[OH^{-}] = 2 \times 0.075 = 0.15$ pOH = -lg 0.15 = 0.824pH = 14 - 0.824 = 13.2

## 5. J90/P2/2

Apple juice has a pH of 3.5.

- (a) (i) Define pH. pH = - log [H<sup>+</sup>]
  - (ii) Calculate the molar concentration of hydrogen ions in apple juice. [ANS: 3.16 x  $10^{-4}$  mol dm<sup>-3</sup>] [H<sup>+</sup>] =  $10^{-3.5}$  = 3.16 x  $10^{-4}$  mol dm<sup>-3</sup>

Apple juice can be titrated with standard alkali.

A 25.0 cm<sup>3</sup> sample of apple juice was exactly neutralised by 27.5 cm<sup>3</sup> of 0.10 mol dm<sup>-3</sup> sodium hydroxide using phenolphthalein as indicator.

(b) Assuming that apple juice contains a single acid which is monobasic, calculate the molar concentration of the acid in the juice.

## [ANS: 0.110 mol dm<sup>-3</sup>]

Amt of acid = amt of NaOH =  $0.0275 \times 0.01 = 0.00275$  mol [acid] = 0.00275 / 0.025 = 0.110 mol dm<sup>-3</sup>

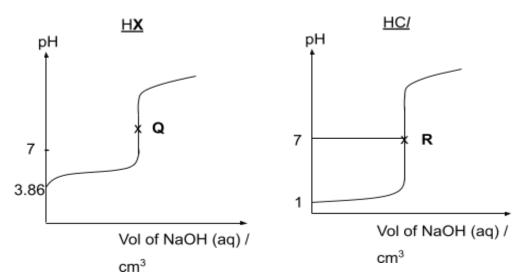
(c) (i) What do you understand by the terms strong and weak when applied to acids?

A strong acid fully dissociates in water whilst a weak acid partially dissociates in water.

- (ii) What can you deduce about the strength of the acid in apple juice using the two results you have obtained in (a)(ii) and (b)?
   [H<sup>+</sup>] << [HA]. Hence, apple juice is a weak acid.</li>
- (iii) Calculate the degree of dissociation of the acid in apple juice. [ANS: 2.87 x  $10^{-3}$ ] 3.16 x  $10^{-4}$  / 0.11 = 2.87 x  $10^{-3}$
- (d) Suggest why phenolphthalein is a suitable indicator for this titration. Titration of <u>weak acid with strong base</u> will result in basic salt formed. Equivalence point > 7 and its vertical section of the titration curve will lie between pH 7 - 10. Hence, the <u>working range of the indicator coincides with the</u> <u>equivalence point/rapid pH change in the titration curve</u>.

#### **Titration Curve**

6 A way to determine the acid strength of HX and HCl is to titrate with aqueous NaOH. 25.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HX and 25.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HCl was pipetted into two different conical flasks. They were titrated separately with 25.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> aqueous NaOH in the burette. A pH meter was used to measure the pH change in the conical flask when aqueous NaOH was added. The titration curves of pH against volume of aqueous NaOH added was plotted below for HX and HCl.



(a) Given that the initial pH of HX and HCl is 3.86 and 1 respectively, calculate the initial concentration of H<sup>+</sup> ions in HX and HCl.

[ANS: 1.38 x 10<sup>-4</sup>; ANS: 0.1.00 mol dm<sup>-3</sup>] Initial [H<sup>+</sup>] in HX =  $10^{-3.86} = 1.38 \times 10^{-4}$  mol dm<sup>-3</sup>

Initial [H<sup>+</sup>] in HC*l* =  $10^{-1}$  = 0.100 mol dm<sup>-3</sup>

- (b) Hence, deduce the acid strength of HX and HC*l*.
  [HX] = [HC*l*] = 0.100 mol dm<sup>-3</sup>
  [H<sup>+</sup>] in HX << [HX]</li>
  HX partially dissociates and hence it is a weak acid.
  [H<sup>+</sup>] in HC*l* = [HC*l*]
  HC*l* dissociates fully hence it is a strong acid.
- (c) State a suitable indicator for the titration between HX and NaOH. Phenolphthalein

## <u>Buffer</u>

7. N 95/1/4

"Acidity regulators" are food additives that have a buffering action on the pH of foodstuffs. Mixtures of citric acid and its sodium salt are often used for this purpose.  $C_5H_7O_4CO_2H \longrightarrow C_5H_7O_4CO_2^- + H^+ \qquad K_a = 7.4 \times 10^{-4} \text{ mol dm}^{-3}$ 

(a) With the aid of equations, explain how the citric acid / sodium citrate buffer system regulates the acidity on the addition of

(i)  $H^+$  ions, (ii)  $OH^-$  ions

 $\mathbf{C}_{5}\mathbf{H}_{7}\mathbf{O}_{4}\mathbf{C}\mathbf{O}_{2}\mathbf{H}+\mathbf{O}\mathbf{H}^{-}\Box\ \mathbf{C}_{5}\mathbf{H}_{7}\mathbf{O}_{4}\mathbf{C}\mathbf{O}_{2}^{-}+\mathbf{H}_{2}\mathbf{O}$ 

The **small amount of OH**<sup>-</sup> ions are removed by the **large amount of**  $C_5H_7O_4CO_2H$  in the buffer. Therefore pH remains almost unchanged.

 $H^+ + C_5 H_7 O_4 CO_2^- \longrightarrow C_5 H_7 O_4 CO_2 H$ 

The **small amount of H<sup>+</sup> ions** are removed by the <u>large amount</u> of  $C_5H_7O_4CO_2^-$  in the buffer. Therefore pH <u>remains almost unchanged</u>.

(b) Write an expression for the acid dissociation constant, K<sub>a</sub>, of citric acid. State the units.

 $K_a = [C_5H_7O_4CO_2^-][H^+] / [C_5H_7O_4CO_2H]$ Units: mol dm<sup>-3</sup>

(c) Define the term  $K_w$  and explain why, at 25°C, water has a pH of 7.

 $K_{w} = [H^{+}] [OH^{-}]$   $[H^{+}] [OH^{-}] = 1.00 \times 10^{-14}$ Since  $[H^{+}] = [OH^{-}],$   $[H^{+}]^{2} = 1.00 \times 10^{-14}$   $[H^{+}] = \sqrt{1.00 \times 10^{-14}} = 1.00 \times 10^{-7} \text{ mol dm}^{-3}$   $pH = - lg \quad (1.00 \times 10^{-7}) = 7$ 

8. J91/P3/4(a) & (b)

The water of Lake Nakuru in the Kenyan rift valley contains dissolved sodium carbonate and sodium hydrogencarbonate. The following equilibrium exists:

 $HCO_{3}^{-}(aq)$  -  $H^{+}(aq)$  +  $CO_{3}^{2-}(aq)$ 

(a) Explain how this solution acts as a buffer on the addition of either acid or alkali. Where there is a small amount of acid H<sup>+</sup> added, the large reservoir of CO<sub>3</sub><sup>2-</sup> will react with the addition H<sup>+</sup>. Hence, pH is maintained.

 $CO_3^{2-}$  + H<sup>+</sup>  $\longrightarrow$  HCO<sub>3</sub><sup>-</sup>

When there is small amount of alkali  $OH^-$  added, the large reservoir of  $HCO_3^-$  will react with the additional  $OH^-$ . Hence, pH is maintained.

 $HCO_3^- + OH^- \longrightarrow CO_3^{2-} + H_2O$ 

(b) (i) Write an expression for the acid dissociation constant, K<sub>a</sub>, of sodium hydrogen carbonate.

(ii)

$$[CO_3^{2-}(aq)]$$

The pH of Lake Nakuru is 10.3 and the ratio  $[HCO_3^-(aq)]$  is 0.958. Calculate the equilibrium constant for the above reaction using your answer to **(b)(i)**.

[ANS: 4.8 x 10<sup>-11</sup> mol dm<sup>-3</sup>]

$$HCO_{3}(aq) = H^{+}(aq) + CO_{3}^{2}(aq)$$

$$K_{a} = \underbrace{[CO_{3}^{2}][H^{\pm}]}_{[HCO_{3}^{-}]} = \underbrace{[CO_{3}^{2}]}_{[HCO_{3}^{-}]} \times [H^{+}]$$

$$= 0.958 \times 10^{-10.3} = 4.8 \times 10^{-11} \text{ mol dm}^{-3}$$