

## CHEM1102 Worksheet 9 – Answers to Critical Thinking Questions

The worksheets are available in the tutorials and form an integral part of the learning outcomes and experience for this unit.

### Model 1: A Solution Containing a Weak Acid

1.  $[\text{CH}_3\text{COOH}(\text{aq})]_{\text{initial}} = 2.0 \text{ M}$  and  $[\text{CH}_3\text{COOH}(\text{aq})]_{\text{equilibrium}} = 2.0 - x$ .

The small  $x$  approximation corresponds to the approximation:

$$[\text{CH}_3\text{COOH}(\text{aq})]_{\text{equilibrium}} = [\text{CH}_3\text{COOH}(\text{aq})]_{\text{initial}}$$

2.  $x = \sqrt{K_a \times [\text{HA}]_{\text{initial}}}$  or  $\text{pH} = -\log_{10}(\sqrt{K_a \times [\text{HA}]_{\text{initial}}})$

3. (a)  $\text{pH} = 2.229$ , % dissociation = 0.295 (c)  $\text{pH} = 2.531$ , % dissociation = 0.590

(b)  $\text{pH} = 2.380$ , % dissociation = 0.417 (d)  $\text{pH} = 2.681$ , % dissociation = 0.834

### Model 2: Addition of a Strong Base to a Weak Acid

1.  $\text{pH} = 4.158$ .

2. See below.

Amount of NaOH(s) added (mol)	0.000	0.100	0.200	0.300	0.400	0.500
$[\text{CH}_3\text{COOH}(\text{aq})]$ (M)	0.500	0.400	0.300	0.200	0.100	0.000
$[\text{CH}_3\text{COO}^-(\text{aq})]$ (M)	0.000	0.100	0.200	0.300	0.400	0.500
pH	2.531	4.158	4.584	4.936	5.362	9.229*

\* This value is calculated using Model 3.

3.  $\text{pH} = 4.76$

4. By measuring the pH when half the quantity of base needed for equivalence has been added.

### Model 3: Neutralizing a Weak Acid

1.  $[\text{CH}_3\text{COO}^-(\text{aq})] = 0.500 \text{ M}$ .

2.  $\text{pH} = 9.229$

3. See above.

4. The solution will be neutral and the pH will be 7.

5. At equivalence, the solution contains a weak base and is basic with  $\text{pH} > 7$ .

- Solution A consists of a 0.25 M aqueous solution of hydrazoic acid,  $\text{HN}_3$ , at 25 °C. Calculate the pH of Solution A. The  $\text{p}K_a$  of  $\text{HN}_3$  is 4.63.

As  $\text{p}K_a = -\log(K_a) = 4.63$ ,  $K_a = 10^{-4.63} = 2.34 \times 10^{-5}$ . The reaction table is:

	$\text{HN}_3(\text{aq})$	$\rightleftharpoons$	$\text{H}^+(\text{aq})$	$\text{N}_3^-(\text{aq})$
<b>t = 0</b>	<b>0.25</b>		<b>0</b>	<b>0</b>
<b>change</b>	<b>-x</b>		<b>+x</b>	<b>+x</b>
<b>equilibrium</b>	<b>0.25 - x</b>		<b>x</b>	<b>x</b>

$$\text{Hence, } K_a = \frac{[\text{H}^+(\text{aq})][\text{N}_3^-(\text{aq})]}{[\text{HN}_3]} = \frac{(x)(x)}{(0.25-x)} = \frac{x^2}{(0.25-x)} = 2.34 \times 10^{-5}$$

As  $K_a$  is very small, very little  $\text{HN}_3$  dissociates and  $x$  is tiny so  $(0.25 - x) \sim 0.25$

$$\text{Hence, } \frac{x^2}{(0.25)} = 2.34 \times 10^{-5} \quad \text{or } x = [\text{H}^+(\text{aq})] = 2.42 \times 10^{-3} \text{ M}$$

As  $\text{pH} = -\log[\text{H}^+(\text{aq})]$ :

$$\text{pH} = -\log(2.42 \times 10^{-3}) = 2.62$$

Answer: **2.62**

(ANSWER CONTINUES ON THE NEXT PAGE)

At 25 °C, 1.00 L of Solution B consists of 13.0 g of sodium azide ( $\text{NaN}_3$ ) dissolved in water. Calculate the pH of Solution B.

The relevant reaction is now:  $\text{N}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HN}_3(\text{aq}) + \text{OH}^-(\text{aq})$

As  $\text{N}_3^-$  is the conjugate base of  $\text{HN}_3$ , the equilibrium constant for this reaction is  $K_b$ , where  $\text{p}K_a + \text{p}K_b = 14.00$ .

Hence, using  $\text{p}K_a$  from above:

$$\text{p}K_b = 14.00 - 4.63 = 9.37 \text{ or } K_b = 10^{-9.37} = 4.27 \times 10^{-10}.$$

The molar mass of  $\text{NaN}_3$  is  $(22.99 (\text{Na})) + (3 \times 14.01 (\text{N})) = 65.02$ . The number of moles in 13.0 g is therefore:

$$\text{number of moles} = \frac{\text{mass}}{\text{molar mass}} = \frac{13.0}{65.02} = 0.200 \text{ mol}$$

As this is dissolved in 1.00 L,  $[\text{N}_3^-(\text{aq})] = \frac{\text{number of moles}}{\text{volume}} = \frac{0.200}{1.00} = 0.200 \text{ M}$

The relevant reaction table is now:

	$\text{N}_3^-(\text{aq})$	$\text{H}_2\text{O}(\text{l})$	$\rightleftharpoons$	$\text{HN}_3(\text{aq})$	$\text{OH}^-(\text{aq})$
<b>t = 0</b>	<b>0.200</b>			<b>0</b>	<b>0</b>
<b>change</b>	<b>-x</b>			<b>+x</b>	<b>+x</b>
<b>equilibrium</b>	<b>0.200 - x</b>			<b>x</b>	<b>x</b>

$$\text{The equilibrium constant } K_b = \frac{[\text{HN}_3(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{N}_3^-(\text{aq})]} = \frac{(x)(x)}{(0.200-x)} = \frac{x^2}{(0.200-x)}$$

$K_b$  is small so the amount of  $\text{N}_3^-(\text{aq})$  which is protonated is tiny and hence  $0.200 - x \sim 0.200$ .

$$\text{Hence, } \frac{x^2}{(0.200)} = 4.27 \times 10^{-10} \text{ or } x = [\text{OH}^-(\text{aq})] = 9.24 \times 10^{-10} \text{ M}$$

$$\text{As } \text{pOH} = -\log[\text{OH}(\text{aq})] = -\log(9.24 \times 10^{-10}) = 5.03$$

As  $\text{pH} + \text{pOH} = 14$ :

$$\text{pH} = 14 - 5.03 = 8.97$$

Answer: 8.97

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

**Solution C is a buffer system as it contains both a weak acid (HN<sub>3</sub>) and its conjugate base (N<sub>3</sub><sup>-</sup>(aq)). The pH can be obtained from the Henderson-Hasselbalch equation:**

$$\text{pH} = \text{pK}_a + \log \frac{[\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

Using  $\text{pK}_a = 4.63$ ,  $[\text{HA}(\text{aq})] = [\text{HN}_3(\text{aq})] = 0.25 \text{ M}$  and  $[\text{A}^-(\text{aq})] = [\text{N}_3^-(\text{aq})] = 0.200 \text{ M}$ :

$$\text{pH} = (4.63) + \log \frac{(0.200)}{(0.25)} = 4.53$$

Answer: **4.53**

If you wanted to adjust the pH of Solution C to be exactly equal to 4.00, which component in the mixture would you need to increase in concentration?

**To lower the pH, the acid concentration (HN<sub>3</sub>) is increased**