

- Solution A consists of a 0.25 M aqueous solution of hydrazoic acid, HN_3 , at 25 °C. Calculate the pH of Solution A. The $\text{p}K_a$ of HN_3 is 4.63.

Marks
8

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	$\text{H}^+(\text{aq})$	$\text{N}_3^-(\text{aq})$
t = 0	0.25		0	0
change	-x		+x	+x
equilibrium	0.25 - x		x	x

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

As K_a is very small, very little 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 (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 N_3^- is the conjugate base of 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 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	$\text{HN}_3(\text{aq})$	$\text{OH}^-(\text{aq})$
t = 0	0.200			0	0
change	-x			+x	+x
equilibrium	0.200 - x			x	x

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

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

$$\text{Hence, } \frac{x^2}{(0.200)} = 4.27 \times 10^{-10} \text{ or } x = [\text{OH}^-(\text{aq})] = 9.24 \times 10^{-6} \text{ M}$$

$$\text{As } \text{pOH} = -\log[\text{OH}(\text{aq})] = -\log(9.24 \times 10^{-6}) = 5.03$$

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 (HN₃) and its conjugate base (N₃⁻(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 pK_a = 4.63, [HA(aq)] = [HN₃(aq)] = 0.25 M and [A⁻(aq)] = [N₃⁻(aq)] = 0.200 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 (HN₃) is increased