Marks

• Boric acid, $B(OH)_3$, is a weak acid ($pK_a = 9.24$) that is used as a mild antiseptic and eye wash. Unusually, the Lewis acidity of the compound accounts for its Brønsted acidity. By using an appropriate chemical equation, show how this compound acts as a Brønsted acid in aqueous solution.

The boron atom in B(OH)₃ is electron deficient: it has 6 rather than 8 electrons in its valence shell. It acts as a Lewis acid by readily accepting the lone pair from the oxygen in a water molecule to go from sp^2 to sp^3 hybridisation.

$$\begin{array}{c} OH \\ I \\ HO \end{array} + H_2O \end{array} \xrightarrow{H} \begin{array}{c} OH \\ \oplus O \\ HO \end{array} \xrightarrow{H_2O} B(OH)_4^{\ominus} + H_3O^{\oplus} \\ H \\ H \\ OH \end{array}$$

Solution A consists of a 0.60 M aqueous solution of boric acid at 25 °C. Calculate the pH of Solution A.

As boric is a weak acid, $[H_3O^+]$ must be calculated using a reaction table (acid = B(OH)₃ and base = B(OH)₂⁻)

	acid	H ₂ O	 H_3O^+	base
initial	0.60	large	0	0
change	- <i>x</i>	negligible	+x	+x
final	0.60 - x	large	x	x

The equilibrium constant K_a is given by: $K_a = \frac{[H_3O^+][base]}{[acid]} = \frac{x^2}{0.60-x}$

As $pK_a = -\log_{10}K_a$, $K_a = 10^{-9.24}$ and is very small, $0.60 - x \sim 0.60$ and hence:

$$x^2 = 0.60 \times 10^{-9.24}$$
 or $x = 1.86 \times 10^{-5} \text{ M} = [\text{H}_3\text{O}^+]$

Hence, the pH is given by:

$$pH = -log_{10}[H_3O^+] = -log_{10}(1.86 \times 10^{-5}) = 4.73$$

pH = **4.73**

At 25 °C, 1.00 L of Solution B consists of 112 g of $NaB(OH)_4$ dissolved in water. Calculate the pH of Solution B.

The molar mass of NaB(OH)₃ is:

molar mass = [22.99 (Na) + 10.81 (B) + 4 (16.00 (O) + 1.008 (H))] g mol⁻¹ = 101.83 g mol⁻¹

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A mass of 112 g therefore corresponds to:

number of moles = mass / molar mass = $112 \text{ g} / (101.83 \text{ g mol}^{-1}) = 1.10 \text{ mol}$

A 1.00 L solution contains this amount has a concentration of 1.10 M.

As it is a weak base, [OH⁻] must be calculated by considering the equilibrium:

	base	H ₂ O	+	acid	OH-
initial	1.10	large		0	0
change	- <i>y</i>	negligible		+ <i>y</i>	+ <i>y</i>
final	1.10 - y	large		у	у

The equilibrium constant K_b is given by:

$$K_{\rm b} = \frac{[\rm{acid}][\rm{OH}^-]}{[\rm{base}]} = \frac{y^2}{(1.10 - y)}$$

For an acid and its conjugate base:

$$pK_a + pK_b = 14.00$$

 $pK_b = 14.00 - 9.24 = 4.76$

As $pK_b = 4.76$, $K_b = 10^{-4.76}$. K_b is very small so $1.00 - y \sim 1.00$ and hence: $y^2 = 1.10 \times 10^{-4.76}$ or y = 0.00437 M = [OH⁻]

Hence, the pOH is given by:

 $pOH = -log_{10}[OH^{-}] = log_{10}[0.00437] = 2.36$

Finally, pH + pOH = 14.00 so

pH = 14.00 - 2.36 = 11.64

pH = **11.64**

Using both Solutions A and B, calculate the volumes (mL) required to prepare a 1.0 L solution with a pH = 9.24.

The ratio of acid to conjugate base in the final needed can be calculated using the Henderson-Hasselbalch equation, $pH = pK_a + log \frac{[base]}{[acid]}$:

 $9.24 = 9.24 + \log \frac{[base]}{[acid]}$ so $\frac{[base]}{[acid]} = 1.00$ or [base] = [acid]

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A volume $V_{\rm a}$ of the acid and $V_{\rm b}$ of base are added together to give a solution with a total volume of 1.00 L so:

 $V_{\rm a} + V_{\rm b} = 1.00 \, {\rm L}$

Using $c_1V_1 = c_2V_2$, this mixing reduces the concentration of both:

acid: $(0.60 \text{ M}) \times V_a = c_{acid} \times (1.0 \text{ L})$ so $V_a = 1.67 \times c_{acid}$ base: $(1.10 \text{ M}) \times V_b = c_{base} \times (1.0 \text{ L})$ so $V_b = 0.909 \times c_{base}$

Using the concentration ratio from the Henderson-Hasselbalch equation above, the ratio of the volumes needed is therefore:

 $V_{\rm b}$ / $V_{\rm a}$ = (0.909 / 1.67) × $c_{\rm base}$ / $c_{\rm acid}$ = (0.909 / 1.67) × 1.00 = 0.545

or

 $V_{\rm b} = 0.545 \times V_{\rm a}$

From above, $V_a + V_b = 1.00$ L so:

 $V_{\rm a} + (0.545 \times V_{\rm a}) = 1.00 \text{ L}$ 1.545 $V_{\rm a} = 1.00 \text{ L}$ $V_{\rm a} = 0.647 \text{ L}$

Hence, $V_{\rm b} = (1.00 - 0.647)$ L = 0.35 L.

Answer: 650 mL of solution A and 350 mL of solution B