**Marks**
8

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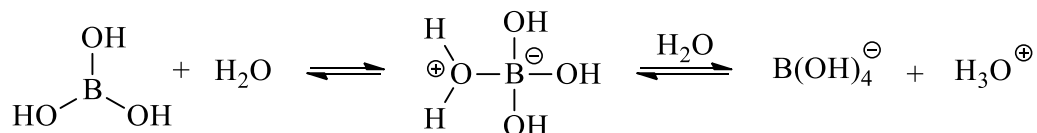
Solution A consists of a 0.60 M aqueous solution of boric acid at 25 °C. Calculate the pH of Solution A.

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_2O	$\rightleftharpoons$	H_3O^+	base
initial	0.60	large		0	0
change	-x	negligible		+x	+x
final	0.60 – x	large		x	x

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

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 $x = 1.86 \times 10^{-5}$ M = $[H_3O^+]$

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}

ANSWER CONTINUES ON THE NEXT PAGE

A mass of 112 g therefore corresponds to:

number of moles = mass / molar mass = 112 g / (101.83 g mol^{-1}) = 1.10 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	$\rightleftharpoons$	acid	OH$^-$
initial	1.10	large		0	0
change	-y	negligible		+y	+y
final	1.10 – y	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(1.10-y)}$$

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 ~ 1.00 and hence:

y^2 = 1.10 × 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$\frac{[\text{base}]}{[\text{acid}]}$:

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

A volume V_a of the acid and V_b of base are added together to give a solution with a total volume of 1.00 L so:

$V_a + V_b = 1.00$ **L**

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

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

$V_b / V_a =$ **(0.909 / 1.67) $\times c_{base} / c_{acid} =$ (0.909 / 1.67) $\times$ 1.00 = 0.545**

or

$V_b = 0.545 \times V_a$

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

$V_a + (0.545 \times V_a) = 1.00$ **L**
1.545 $V_a = 1.00$ L
$V_a = 0.647$ **L**

Hence, $V_b = (1.00 - 0.647)$ L $= 0.35$ L.

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

**Marks
9**

- 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.
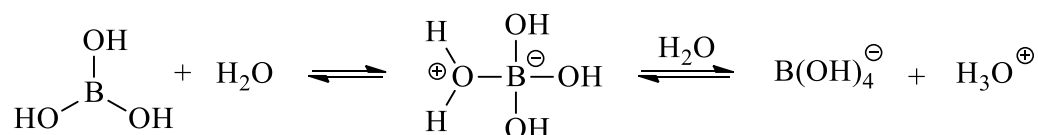
Solution A consists of a 0.40 M aqueous solution of boric acid at 25 °C. Calculate the pH of Solution A.

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_2O	$\rightleftharpoons$	H_3O^+	base
initial	0.40	large		0	0
change	-x	negligible		+x	+x
final	0.40 – x	large		x	x

The equilibrium constant K_a is given by: $K_a = \dfrac{[H_3O^+][base]}{[acid]} = \dfrac{x^2}{0.40-x}$

As $pK_a = -\log_{10}K_a$, $K_a = 10^{-9.24}$ and is very small, $0.40 - x \sim 0.40$ and hence:

$x^2 = 0.40 \times 10^{-9.24}$ or $x = 1.52 \times 10^{-5}$ M $= [H_3O^+]$

Hence, the pH is given by:

$pH = -\log_{10}[H_3O^+] = -\log_{10}(1.52 \times 10^{-5}) = 4.82$

pH = **4.82**

At 25 °C, 1.00 L of Solution B consists of 101.8 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}**

ANSWER CONTINUES ON THE PAGE

A mass of 101.8 g therefore corresponds to:

  number of moles = mass / molar mass = 101.8 g / (101.83 g mol^{-1}) = 1.000 mol

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

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

	base	H$_2$O	$\rightleftharpoons$	acid	OH$^-$
initial	1.00	large		0	0
change	-y	negligible		+y	+y
final	1.00 – y	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(1.00-y)}$$

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 ~ 1.00 and hence:

  y^2 = 1.00 × 10$^{-4.76}$ or y = 0.00417 M = [OH$^-$]

Hence, the pOH is given by:

  pOH = -log$_{10}$[OH$^-$] = log$_{10}$[0.00417] = 2.38

Finally, pH + pOH = 14.00 so

  pH = 14.00 – 2.38 = 11.62

pH = **11.62**

Using both Solutions A and B, calculate the volumes (mL) required to prepare a 1.0 L solution with a pH = 8.00.

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

$$8.00 = 9.24 + \log\frac{[\text{base}]}{[\text{acid}]} \quad \text{so} \quad \frac{[\text{base}]}{[\text{acid}]} = 10^{-1.24} = 0.0575$$

A volume V_a of the acid and V_b of base are added together to give a solution with a total volume of 1.0 L so:

$$V_a + V_b = 1.0 \text{ L}$$

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

acid: $(0.40 \text{ M}) \times V_a = c_{\text{acid}} \times (1.0 \text{ L})$ so $V_a = 2.5 \times c_{\text{acid}}$
base: $(1.00 \text{ M}) \times V_b = c_{\text{base}} \times (1.0 \text{ L})$ so $V_b = 1.0 \times c_{\text{base}}$

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

$$V_b / V_a = (1.0 / 2.5) \times c_{\text{base}} / c_{\text{acid}} = (1.0 / 2.5) \times 0.0575 = 0.023$$

or

$$V_b = 0.023 \times V_a$$

From above, $V_a + V_b = 1.0$ L so:

$$V_a + (0.023 \times V_a) = 1.0 \text{ L}$$
$$1.023 \, V_a = 1.0 \text{ L}$$
$$V_a = 0.980 \text{ L}$$

Hence, $V_b = 0.020$ L.

Marks
9

- 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 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.
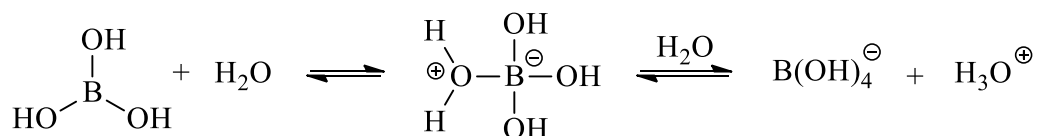
Solution A consists of a 0.050 M aqueous solution of boric acid at 25 °C. Calculate the pH of Solution A.

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_2O	$\rightleftharpoons$	H_3O^+	base
initial	0.050	large		0	0
change	-x	negligible		+x	+x
final	0.050 – x	large		x	x

The equilibrium constant K_a is given by: $K_a = \dfrac{[H_3O^+][\text{base}]}{[\text{acid}]} = \dfrac{x^2}{0.050-x}$

As $pK_a = -\log_{10}K_a$, $K_a = 10^{-9.24}$ and is very small, $0.050 - x \sim 0.050$ and hence:

$$x^2 = 0.050 \times 10^{-9.24} \qquad \text{or} \qquad x = 5.36 \times 10^{-6}\ M = [H_3O^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+] = -\log_{10}(5.36 \times 10^{-6}) = 5.27$$

pH = **5.27**

At 25 °C, 1.00 L of Solution B consists of 10.18 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}

ANSWER CONTINUES ON THE NEXT PAGE

A mass of 10.18 g therefore corresponds to:

number of moles = mass / molar mass = 10.18 g / (101.83 g mol^{-1}) = 0.100 mol

A 1.00 L solution contains this amount has a concentration of 0.100 M.

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

	base	H$_2$O	⇌	acid	OH$^-$
initial	0.100	large		0	0
change	-y	negligible		+y	+y
final	0.10 – y	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(0.100 - y)}$$

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 $0.100 - y \sim 0.100$ and hence:

$$y^2 = 0.100 \times 10^{-4.76} \text{ or } y = 0.00132 \text{ M} = [\text{OH}^-]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[\text{OH}^-] = \log_{10}[0.00132] = 2.88$$

Finally, pH + pOH = 14.00 so

$$pH = 14.00 - 2.88 = 11.12$$

pH = **11.12**

Using both Solutions A and B, calculate the volumes (mL) required to prepare a 1.0 L solution with a pH = 8.50.

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

$$8.50 = 9.24 + \log\frac{[\text{base}]}{[\text{acid}]} \quad \text{so} \quad \frac{[\text{base}]}{[\text{acid}]} = 10^{-0.74} = 0.182$$

ANSWER CONTINUES ON THE NEXT PAGE

A volume V_a of the acid and V_b of base are added together to give a solution with a total volume of 1.0 L so:

$V_a + V_b = 1.0$ L

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

acid: $(0.050 \text{ M}) \times V_a = c_{acid} \times (1.0 \text{ L})$ **so** $V_a = 20. \times c_{acid}$
base: $(0.100 \text{ M}) \times V_b = c_{base} \times (1.0 \text{ L})$ **so** $V_b = 10.0 \times c_{base}$

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

$V_b / V_a = (10.0 / 20.) \times c_{base} / c_{acid} = (10. / 20.) \times 0.182 = 0.0910$

or

$V_b = 0.0910 \times V_a$

From above, $V_a + V_b = 1.0$ L so:

$V_a + (0.0910 \times V_a) = 1.0$ L
$1.0091 \ V_a = 1.0$ L
$V_a = 0.917$ L

Hence, $V_b = 0.083$ L.

- Aqua ligands in coordination complexes are generally acidic. Briefly explain this phenomenon using $[Co(NH_3)_5(OH_2)]^{3+}$ as an example.

Co^{3+} has a high charge and is relatively small: it has a high charge density. When attached to water, it polarises the O–H bond in the aqua ligand.

This weakens the O–H bond causing the complex to be acidic in aqueous solution.

Solution A consists of a 0.10 M aqueous solution of $[Co(NH_3)_5(OH_2)](NO_3)_3$ at 25 °C. Calculate the pH of Solution A. The pK_a of $[Co(NH_3)_5(OH_2)]^{3+} = 5.69$.

As $[Co(NH_3)_5(OH_2)]^{3+}$ is a weak acid, $[H_3O^+]$ must be calculated using a reaction table (acid = $[Co(NH_3)_5(OH_2)]^{3+}$ and base = $[Co(NH_3)_5(OH)]^{2+}$

	acid	H₂O	⇌	H₃O⁺	base
initial	**0.10**	**large**		**0**	**0**
change	**-x**	**negligible**		**+x**	**+x**
final	**0.10 – x**	**large**		**x**	**x**

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][\text{base}]}{[\text{acid}]} = \frac{x^2}{0.10-x}$$

As pK_a = -$\log_{10}K_a$, $K_a = 10^{-5.69}$ and is very small, $0.10 - x \sim 0.10$ and hence:

$$x^2 = 0.10 \times 10^{-5.69} \qquad \text{or} \qquad x = 4.5 \times 10^{-4}\ M = [H_3O^+]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+] = -\log_{10}(4.5 \times 10^{-4}) = 3.35$$

pH = **3.35**

At 25 °C, 1.00 L of Solution B consists of 28.5 g of $[Co(NH_3)_5(OH)](NO_3)_2$ dissolved in water. Calculate the pH of Solution B.

The molar mass of $[Co(NH_3)_5(OH)](NO_3)_2$ is:

molar mass = (58.93 (Co) + 7 × 14.01 (N) + 7 × 16.00 (O) + 16 × 1.008 (H)) g mol⁻¹
= 285.128 g mol⁻¹

The number of moles present in 28.5 g is therefore:

number of moles = mass / molar mass = (28.5 g) / (285.128 g mol⁻¹) = 0.100 mol

ANSWER CONTINUES ON THE NEXT PAGE

If this is present in 1.00 L, then [base] = 0.100 M.

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

	base	H₂O	⇌	acid	OH⁻
initial	0.100	large		0	0
change	-y	negligible		+y	+y
final	0.100 – y	large		y	y

The equilibrium constant K_b is given by:

$$K_b = \frac{[\text{acid}][\text{OH}^-]}{[\text{base}]} = \frac{y^2}{(0.100-y)}$$

For an acid and its conjugate base:

$pK_a + pK_b = 14.00$

$pK_b = 14.00 – 5.69 = 8.31$

As $pK_b = 8.31$, $K_b = 10^{-8.31}$. K_b is very small so $0.100 – y \sim 0.100$ and hence:

$y^2 = 0.100 \times 10^{-8.31}$ or $y = 2.21 \times 10^{-5}$ M = [OH⁻]

Hence, the pOH is given by:

$pOH = -\log_{10}[\text{OH}^-] = \log_{10}[2.21 \times 10^{-5}] = 4.65$

Finally, pH + pOH = 14.00 so

pH = 14.00 – 4.65 = 9.35

| pH = **9.35** |

Using both Solutions A and B, calculate the volumes (in mL) required to prepare a 1.0 L solution with a pH = 7.00.

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

$$7.00 = 5.69 + \log\frac{[\text{base}]}{[\text{acid}]} \quad \text{so} \quad \frac{[\text{base}]}{[\text{acid}]} = 10^{1.31} = 20.4$$

As the base and acid have the same concentration, this is also the ratio of the volumes needed. As $V_{\text{acid}} + V_{\text{base}} = 1.0$ L and $V_{\text{base}} / V_{\text{acid}} = 20.4$:

$V_{\text{acid}} = 0.047$ L and $V_{\text{base}} = 0.953$ L

- A dilute solution of ammonia has a pH of 10.54. Calculate what amount of HCl(g) must be added to 1.0 L of this solution to give a final pH of 8.46. The pK_a of NH_4^+ is 9.24.

4

In the initial solution, pH = 10.54 so pOH = 14.00 – 10.54 = 3.46 and:

$$[OH^-(aq)] = 10^{-3.46} = 0.000347 \text{ M}$$

This is formed by the reaction below.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Hence, $[NH_4^+(aq)] = [OH^-(aq)] = 0.000347$ M. This reaction corresponds to K_b for NH_3. As K_a for $NH_4^+ = 9.24$, $K_b = 14.00 – 9.24 = 4.76$ and

$$K_b = \frac{[NH_4^+(aq)][OH^-(aq)]}{[NH_3(aq)]} = \frac{(10^{-3.46})(10^{-3.46})}{[NH_3(aq)]} = 10^{-4.76}$$

Hence, $[NH_3(aq)] = 10^{-2.16} = 0.00692$ M

This reacts with the added HCl(g):

	$H^+(aq)$	$NH_3(aq)$	$\rightleftharpoons$	$NH_4^+(aq)$
initial	x	0.00692		0.000347
final	0	0.00692 – x		0.000347 + x

At the final pH of 8.46, the Henderson-Hasselbalch equation can be used:

$$pH = pK_a + \log\frac{[NH_3(aq)]}{[NH_4^+(aq)]}$$

$$8.46 = 9.24 + \log\left(\frac{0.00692-x}{0.000347 + x}\right)$$

Solving this gives $x = 0.0059$ mol.

Answer: **0.0059 mol**

- A 300.0 mL solution of HCl has a pH of 1.22. Given that the pK_a of iodic acid, HIO_3, is 0.79, how many moles of sodium iodate, $NaIO_3$, would need to be added to this solution to raise its pH to 2.00?

3

Using pH = $-\log_{10}[H^+(aq)]$,

$$[H^+(aq)]_{initial} = 10^{-1.22} = 0.060 \text{ M}$$

$$[H^+(aq)]_{final} = 10^{-2.00} = 0.010 \text{ M}$$

Using pH = $-\log_{10}[H^+(aq)]$,

$$[H^+(aq)]_{initial} = 10^{-1.22} = 0.060 \text{ M}$$

$$[H^+(aq)]_{final} = 10^{-2.00} = 0.010 \text{ M}$$

The change of (0.060 – 0.010 M) = 0.050 M occurs due to the reaction with IO_3^-(aq) to produce HIO_3(aq). If $[IO_3^-(aq)] = x$, the reaction table is:

	$H^+(aq)$ +	$IO_3^-(aq)$	$\rightleftharpoons$	$HIO_3(aq)$
initial	0.060	*x*		0
change	-0.050	-0.050		+0.050
final	0.010	*x* – 0.050		0.050

As $pK_a = 0.79 = -\log_{10}K_a$:

$$K_a = \frac{[H^+(aq)][IO_3^-(aq)]}{[HIO_3(aq)]} = \frac{(0.010) \times (x - 0.050)}{0.050} = 10^{-0.79}$$

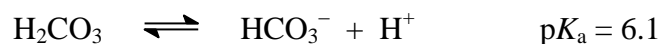**Thus, $x = 0.86$ M = $[IO_3^-(aq)]_{initial}$. This concentration corresponds to a 300.0 mL solution so the number of moles that have been added is:**

number of moles = concentration × volume
= (0.86 M) × (0.3000 L) = 0.26 mol

Answer: **0.26 mol**

**Marks
5**

- The primary buffering system in blood plasma is represented by the following equation:

$$H_2CO_3 \rightleftharpoons HCO_3^- + H^+ \qquad pK_a = 6.1$$

What is the ratio HCO_3^- : H_2CO_3 at the normal plasma pH of 7.4?

The Henderson-Hasselbalch equation with [acid] = [H₂CO₃] and [base] = [HCO₃⁻] can be used for this buffer system,

$$pH = pK_a + \log_{10}\left(\frac{[base]}{[acid]}\right)$$

$$= 6.1 + \log_{10}\left(\frac{[base]}{[acid]}\right) = 7.4$$

$$\frac{[base]}{[acid]} = 10^{(7.4-6.1)} = 10^{1.3} = 20$$

Answer: **[base] : [acid] = 20 : 1**

A typical person has 2 L of blood plasma. If such a person were to drink 1 L of soft drink with a pH of 2.5, what would the plasma pH be if it were not buffered? (Assume all of the H^+ from the soft drink is absorbed by the plasma, but the volume of plasma does not increase.)

As pH = -log₁₀[H⁺], the [H⁺] in the soft drink is,

$$[H^+]_{soft\ drink} = 10^{-2.5}\ M$$

1 L of soft drink therefore contains

number of moles = concentration × volume = $(10^{-2.5}\ mol\ L^{-1} \times 1\ L) = 10^{-2.5}\ mol$

If this amount is present in 2 L of plasma,

$$[H^+]_{plasma} = \frac{number\ of\ moles}{volume} = \frac{10^{-2.5}}{2}\ M$$

Hence the pH of the unbuffered plasma is

$$pH = -\log_{10}[H^+] = -\log_{10}\left(\frac{10^{-2.5}}{2}\right) = 2.8$$

Answer: **2.8**

ANSWER CONTINUES ON THE NEXT PAGE

What is the pH in this typical person with a normal HCO_3^- concentration of 0.020 M? Ignore any other contributions to the buffering.

Before the addition of the soft drink, $[HCO_3^-] = 0.020$ M and, at pH 7.4, $[H_2CO_3] = [HCO_3^-] / 20 = 0.0010$ M.

As the soft drink has $10^{-2.5}$ mol of H^+, its concentration when added to the plasma will again be $[H^+] = \dfrac{10^{-2.5}}{2}$ M before buffering. Adding it will decrease the base concentration and increase the acid concentration so that,

$$[HCO_3^-] = (0.020 - \frac{10^{-2.5}}{2}) \text{ M} = 0.018 \text{ M}$$

$$[H_2CO_3] = (0.0010 + \frac{10^{-2.5}}{2}) \text{ M} = 0.0026 \text{ M}$$

Hence,

$$pH = (6.1) + \log_{10}\left(\frac{0.018}{0.0026}\right) = 7.0$$

Answer: **7.0**

**Marks
2**

- Calculate the pH of a solution that is prepared by mixing 750 mL of 1.0 M potassium dihydrogenphosphate with 250 mL of 1.0 M potassium hydrogenphosphate.

  For H_3PO_4, $pK_{a1} = 2.15$, $pK_{a2} = 7.20$, $pK_{a3} = 12.38$

The hydrogenphosphate anion is the conjugate base of dihydrogenphosphate, corresponding to the second ionization of phosphoric acid (K_{a2}). K_{a1} is much larger than K_{a2} so the equilibrium will not be greatly affected by protonation of dihydrogenphosphate. K_{a3} is much smaller than K_{a2} so the equilibrium will also not be greatly affected by deprotonation of hydrogenphosphate. The solution is a buffer and the pH can be calculated using the Henderson-Hasselbalch equation:

$$\textbf{pH} = \textbf{pK}_a + \textbf{log}_{10}\left(\frac{\textbf{[base]}}{\textbf{[acid]}}\right) = \textbf{pK}_{a2} + \textbf{log}_{10}\left(\frac{\textbf{[hydrogenphosphate]}}{\textbf{[dihydrogenphosphate]}}\right)$$

After mixing, a 1.00 L solution is formed that contains 0.750 mol of dihydrogenphosphate and 0.250 mol of hydrogenphosphate. Thus:

$$\textbf{pH} = \textbf{7.20} + \textbf{log}_{10}\left(\frac{\textbf{0.250}}{\textbf{0.750}}\right) = \textbf{6.72}$$

Answer: **pH = 6.72**

- Solution A consists of a 0.15 M aqueous solution of nitrous acid (HNO_2) at 25 °C. Calculate the pH of Solution A. The pK_a of HNO_2 is 3.15.

Nitrous acid is a weak acid so [H_3O^+] must again be calculated:

	HNO$_2$(aq)	H$_2$O(l)	$\rightleftharpoons$	H$_3$O$^+$(aq)	NO$_2^-$(aq)
initial	0.15	large		0	0
change	-x	negligible		+x	+x
final	0.15 – x	large		x	x

The equilibrium constant K_a is given by:

$$K_a = \frac{[H_3O^+][NO_2^-]}{[HNO_2]} = \frac{x^2}{0.15 - x}$$

As $K_a = 10^{-3.15}$ is very small, $0.15 - x \sim 0.15$ and hence:

$$x^2 = 0.15 \times 10^{-3.15} \quad \text{or} \quad x = 0.0103 \text{ M} = [H_3O^+(aq)]$$

Hence, the pH is given by:

$$pH = -\log_{10}[H_3O^+(aq)] = -\log_{10}[0.0103] = 1.99$$

ANSWER: **pH = 1.99**

ANSWER CONTINUES ON THE NEXT PAGE

At 25 °C, 1.00 L of Solution B consists of 13.8 g of sodium nitrite ($NaNO_2$) dissolved in water. Calculate the pH of Solution B.

The formula mass of $NaNO_2$ is (22.99 (Na) + 14.01 (N) + 2×16.00 (O)) g mol^{-1} = 69 g mol^1. 13.8 g therefore corresponds to:

$$\text{amount of } NaNO_2 = \frac{\text{mass}}{\text{formula mass}} = \frac{13.8\,g}{69.0\,g\,mol^{-1}} = 0.200\,mol$$

A 1.00 L solution containing this amount has a molarity of 0.200 M. The nitrite ion acts as a base and [OH⁻(aq)] must be calculated from the equilibrium:

	NO_2^-(aq)	H_2O(l)	⇌	OH⁻(aq)	HNO_2(aq)
initial	0.200	large		0	0
change	-y	negligible		+y	+y
final	0.200 – y	large		y	y

The equilibrium constant K_b is given by:

$$K_a = \frac{[OH^-][HNO_2]}{[NO_2^-]} = \frac{y^2}{0.200 - y}$$

In aqueous solution, $pK_a + pK_b = 14.00$. Hence $pK_b = (14.00 - 3.15) = 10.85$ and as $K_b = 10^{-10.85}$ is very small, $0.200 - y \sim 0.200$ and hence:

$$y^2 = 0.200 \times 10^{-10.85} \quad \text{or} \quad y = 1.68 \times 10^{-6}\,M = [OH^-(aq)]$$

Hence, the pOH is given by:

$$pOH = -\log_{10}[OH^-(aq)] = -\log_{10}[1.68 \times 10^{-6}] = 5.77$$

As pH + pOH = 14, pH = 8.23

ANSWER: **pH = 8.23**

ANSWER CONTINUES ON THE NEXT PAGE

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

This solution contains an acid and its conjugate base so the Henderson-Hasselbalch equation can be used. As [acid] = [HNO$_2$] = 0.15 M and [base] = [NO$_2^-$] = 0.200 M:

$$\textbf{pH} = \textbf{p}K_\textbf{a} + \textbf{log}_{10}\left(\frac{\textbf{[base]}}{\textbf{[acid]}}\right) = \textbf{3.15} + \textbf{log}_{10}\left(\frac{\textbf{0.200}}{\textbf{0.15}}\right) = \textbf{3.27}$$

ANSWER: **pH = 3.27**

If you wanted to adjust the pH of the mixture of Solution A and Solution B to be exactly equal to 3.00, which component in the mixture would you need to increase in concentration?

The acid, HNO$_2$