

Answers to 90700 (3.7) NCEA 2004

1 After mixing volume = 100 mL

$$\begin{aligned}[\text{Ag}^+] &= \frac{50.0 \text{ mL}}{100.0 \text{ mL}} \times 0.020 \text{ mol L}^{-1} \\ &= 0.010 \text{ mol L}^{-1}\end{aligned}$$

$$\begin{aligned}[\text{Cl}^-] &= \frac{50.0 \text{ mL}}{100.0 \text{ mL}} \times 0.100 \text{ mol L}^{-1} \\ &= 0.050 \text{ mol L}^{-1}\end{aligned}$$

$$\begin{aligned}\text{IP} &= [\text{Ag}^+][\text{Cl}^-] \\ &= 0.010 \text{ mol L}^{-1} \times 0.050 \text{ mol L}^{-1} \\ &= 5.0 \times 10^{-4}\end{aligned}$$

$\text{IP} > K_s$ so a precipitate will form.

A = Correct calculation of IP or correct comparison of IP and K_s based on incorrect but relevant calculation, M = Correct calculation and correct comparison of IP and K_s

2 a i $\text{PbBr}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq})$

A = Equilibrium equation in either direction (accept \rightarrow). States not required

ii $K_s = [\text{Pb}^{2+}][\text{Br}^-]^2$

A = K_s expression correct

b

$$\begin{aligned}n(\text{PbBr}_2) &= \frac{0.422 \text{ g}}{367 \text{ g mol}^{-1}} \\ &= 1.15 \times 10^{-3} \text{ mol}\end{aligned}$$

$$\begin{aligned}c(\text{PbBr}_2) &= \frac{n}{V} \\ &= \frac{1.15 \times 10^{-3} \text{ mol}}{50.0 \times 10^{-3} \text{ L}} \\ &= 2.30 \times 10^{-2} \text{ mol L}^{-1}\end{aligned}$$

$$[\text{Pb}^{2+}] = 2.30 \times 10^{-2} \text{ mol L}^{-1}$$

$$\begin{aligned}[\text{Br}^-] &= 2 \times 2.30 \times 10^{-2} \text{ mol L}^{-1} \\ &= 4.60 \times 10^{-2} \text{ mol L}^{-1}\end{aligned}$$

$$\begin{aligned}K_s &= [\text{Pb}^{2+}][\text{Br}^-]^2 \\ &= 2.30 \times 10^{-2} \text{ mol L}^{-1} \times (4.60 \times 10^{-2} \text{ mol L}^{-1})^2 \\ &= 4.87 \times 10^{-5} \text{ L}\end{aligned}$$

A = Correct calculation of number of moles

OR one other correct process step completed eg correct calculation of $[\text{Pb}^{2+}]$ and $[\text{Br}^-]$ from incorrect n

OR correct calculation of K_s from incorrect ion conc,

M = Calculation process for K_s correct (allow 1 process error eg ratio $[\text{Pb}^{2+}]: [\text{Br}^-]$ is 1:1 or no. of moles in 50 mL used instead of conc.), E = K_s is correct and is in the range $4.86 - 4.88 \times 10^{-5}$

2
3

	Type	Reason
NaCl	neutral	NaCl is completely soluble, giving Na ⁺ and Cl ⁻ , neither of which react with water — neutral solution.
NH ₄ Cl	acidic	NH ₄ Cl is completely soluble to give NH ₄ ⁺ and Cl ⁻ . NH ₄ ⁺ reacts with water: $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_3 + \text{H}_3\text{O}^+$ so solution is acidic due to increase in concentration of H ₃ O ⁺ .
NaOCl	basic	NaOCl is completely soluble to give Na ⁺ and OCl ⁻ . OCl ⁻ reacts with water: $\text{OCl}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOCl} + \text{OH}^-$ so solution is alkaline due to the increase in concentration of OH ⁻ .

A = Type of solution (acidic etc) correctly stated for two solutions,

M = For all solutions the type of solution (acidic etc) is correctly stated

AND for two solutions type is linked to relevant species (OH⁻ or H₃O⁺ or H₂O),

E = Appropriate discussion for all three examples with correct chemical or word equations for the formation of OH⁻ and H₃O⁺

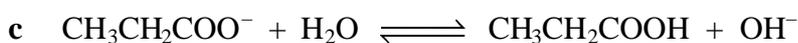
4 a

$$\begin{aligned} n(\text{NaOH}) &= cV \\ &= 0.125 \text{ mol L}^{-1} \times 15.0 \times 10^{-3} \text{ L} \\ &= 1.875 \times 10^{-3} \text{ mol} \\ n(\text{CH}_3\text{CH}_2\text{COOH}) &= n(\text{NaOH}) \\ &= 1.875 \times 10^{-3} \text{ mol} \\ c(\text{CH}_3\text{CH}_2\text{COOH}) &= \frac{n}{V} \\ &= \frac{1.875 \times 10^{-3} \text{ mol}}{25.0 \times 10^{-3} \text{ L}} \\ &= 0.0750 \text{ mol L}^{-1} \end{aligned}$$

A = Correct concentration including units

b $\text{p}K_a = 4.9 (\pm 0.1)$

A = Correct value



$$K_b = \frac{[\text{CH}_3\text{CH}_2\text{COOH}][\text{OH}^-]}{[\text{CH}_3\text{CH}_2\text{COO}^-]}$$

At the equivalence point $n(\text{CH}_3\text{COO}^-) = 1.875 \times 10^{-3} \text{ mol}$ in $25.0 + 15.0 = 40.0 \text{ mL}$ of solution.

$$\begin{aligned} c(\text{CH}_3\text{CH}_2\text{COO}^-) &= \frac{n}{V} \\ &= \frac{1.875 \times 10^{-3} \text{ mol}}{40.0 \times 10^{-3} \text{ L}} \\ &= 0.0469 \text{ mol L}^{-1} \end{aligned}$$

$$\begin{aligned}
 pK_b &= 14 - pK_a \\
 &= 14 - 4.9 \\
 &= 9.1 \\
 K_b &= 10^{-pK_b} \\
 &= 10^{-9.1} \\
 &= 7.94 \times 10^{-10}
 \end{aligned}$$

Assume (1) $[\text{CH}_3\text{CH}_2\text{COOH}] = [\text{OH}^-]$

(2) $[\text{CH}_3\text{CH}_2\text{COO}^-] = 0.0469 \text{ mol L}^{-1}$

$$7.94 \times 10^{-10} = \frac{[\text{OH}^-]^2}{0.0469 \text{ mol L}^{-1}}$$

$$\sqrt{7.94 \times 10^{-10} \times 0.0469 \text{ mol L}^{-1}} = [\text{OH}^-]$$

$$6.10 \times 10^{-6} \text{ mol L}^{-1} = [\text{OH}^-]$$

$$\text{pOH} = 5.21$$

$$\text{pH} = 8.79$$

A = Describes solution as alkaline either by writing the balanced equation

OR Writing a correct K_b expression

OR by writing a correct formula / correctly substituted formula to use in the calculation,

M = Method for calculation of pH generally correct with only one error eg no dilution factor in calculation of $[\text{CH}_3\text{CH}_2\text{COO}^-]$,

E = pH correctly calculated as 8.79 \pm 0.01 Or pH correctly calculated from student's incorrect answers to 4(a) and 4(b)

d Species present:

$[\text{Na}^+] > (= \text{ or } \approx) [\text{CH}_3\text{CH}_2\text{COOH}] = [\text{CH}_3\text{CH}_2\text{COO}^-] > [\text{H}_3\text{O}^+] \gg ([\text{OH}^-])$

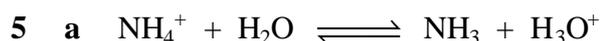
A = Identifies $[\text{CH}_3\text{CH}_2\text{COOH}] = [\text{CH}_3\text{CH}_2\text{COO}^-]$ or $[\text{CH}_3\text{CH}_2\text{COOH}] = [\text{CH}_3\text{CH}_2\text{COONa}]$,

M = Concentration of all species correctly compared. (May omit OH^- but must include Na^+)

e **Cresol red and Thymolphthalein** could be chosen because the pH ranges for the colour changes of these two indicators (and their pK_a values) lie within the range of the equivalence point i.e. the vertical portion of the graph/ the portion where there is a dramatic change in pH. Since vertical portion starts at pH = 7.4 and the equivalence point is at pH 8.79 (8.8) then an indicator that changes colour in the range 8.8 ± 1.4 ie 7.4 — 10.2 would be suitable. (The pK_a of the indicator will also lie within this range but need not be "at" or "close" to the exact equivalence point pH.)

A = Chooses both suitable indicators (explanation may be missing/ incorrect / irrelevant)

OR Chooses only one of the two suitable indicators with a valid reason (ie a reason that could also be applied to the second indicator that has not been selected), M = Recognises that two indicators are suitable and links their suitability to the presence in the vertical portion of the graph of either the pH range for the colour change or the pK_a value



$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$[\text{NH}_4^+] = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{K_a}$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}}$$

$$= 10^{-8.80}$$

$$= 1.58 \times 10^{-9} \text{ mol L}^{-1}$$

$$[\text{NH}_4^+] = \frac{(0.05 \text{ mol L}^{-1})(1.58 \times 10^{-9} \text{ mol L}^{-1})}{5.75 \times 10^{-10}}$$

$$= 0.138 \text{ mol L}^{-1}$$

Since we have one litre of solution, $n(\text{NH}_4^+) = 0.138 \text{ mol}$.

$$m(\text{NH}_4\text{Cl}) = nM$$

$$= 0.138 \text{ mol} \times 53.5 \text{ g mol}^{-1}$$

$$= 7.37 \text{ g}$$

A = Correctly substituted expression chosen that could lead to a correct concentration of NH_4^+ ie must correctly identify that NH_3 is the “base” with concentration 0.05 and that $[\text{NH}_3] = [\text{H}_3\text{O}^+]$,

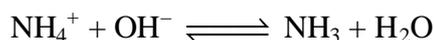
M = Correct expression is used to calculate mass of NH_4Cl (allow 1 arithmetic error)

OR correct value for $[\text{NH}_4^+]$ but does not calculate mass/ or calculates incorrect mass,

E = Completes all steps in calculation of correct mass and includes unit (g)

b For **this buffer** with $\text{pH} = 8.80$ the $[\text{NH}_3]$ is less than $[\text{NH}_4^+]$
 $\text{pH} < \text{p}K_a$ (since $[\text{NH}_3]/[\text{NH}_4^+]$ is < 1)

- the solution is a more effective buffer against added base than it is against added acid. This is because there is a larger proportion of acid to react with / neutralise the added base:



When $[\text{NH}_3]$ is greater than $[\text{NH}_4^+]$ pH is greater than 9.24 since $[\text{NH}_3]/[\text{NH}_4^+] > 1$ the solution buffers well against added acid, but less well against added OH^- . This is because there is a larger concentration of base to react with and neutralize the added acid.

- $\text{NH}_3 + \text{H}_3\text{O}^+ \rightleftharpoons \text{NH}_4^+ + \text{H}_2\text{O}$

When $[\text{NH}_3]$ is equal to $[\text{NH}_4^+]$

- pH is 9.24 (because $[\text{NH}_3]/[\text{NH}_4^+] = 1$)
- the solution is an equally effective buffer against the addition of either acid or base as either of the two previous reactions can occur

A non-specific description at Achieve level may include:

If $[\text{base}] > [\text{acid}]$ pH is more alkaline/more basic/increases.

If $[\text{base}] < [\text{acid}]$ pH is more acidic / decreases.

When small amounts of either acid or base are added to a buffer the pH changes very little because the acid species reacts with the added base (or OH^-) and the base reacts with added acid (H_3O^+).

A = Description of this buffer solution / a general buffer solution includes ONE of the following:

- Variation in pH of the buffer with different $[\text{acid}]$ or $[\text{base}]$ present

- The effectiveness of the buffer if $[\text{acid}] > [\text{base}]$ or $[\text{acid}] < [\text{base}]$
- The effect of adding small amounts of acid and base to a buffer,

M = Uses the relative [species] present in this buffer i.e. $[\text{NH}_4^+]$ and $[\text{NH}_3]$ to explain TWO of the following:

- Variation in pH of this buffer with $[\text{NH}_3] > [\text{NH}_4^+]$ and $[\text{NH}_3] < [\text{NH}_4^+]$
- The effectiveness of the buffer if $[\text{NH}_3] > [\text{NH}_4^+]$ and if $[\text{NH}_3] < [\text{NH}_4^+]$
- The effect of adding small amounts of H_3O^+ and OH^- to this specific buffer
(Correct chemical equations may be used),

E = Detailed discussion clearly identifies how variations in the relative concentrations of NH_3 and NH_4^+ ie $>$ and $<$ and $=$ affect both the pH and the effective working of this buffer with reference to either pK_a (=9.24) or the pH of the buffer in 5(a) (=8.80). (Correct chemical equations may be used)

Judgement Statement

Achievement:	Total of 7 opportunities answered at Achievement (or higher)
Merit:	Total of 8 opportunities answered with 4 at Merit level and 4 at Achievement level
Excellence:	Total of 9 opportunities answered with 3 at Excellence level, 2 at Merit level and 4 at Achievement level