Chapter 21 – Answers to questions (for in-chapter questions)

1. a) \( K_{s.p.} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})] \)
   b) \( K_{s.p.} = [\text{Pb}^{2+}(\text{aq})][\text{I}^-(\text{aq})]^2 \)
   c) \( K_{s.p.} = [\text{Bi}^{3+}(\text{aq})]^2[\text{S}^{2-}(\text{aq})]^3 \)

2. Because the value in Table 21.2 is measured at 25 °C when the solubility (and hence the solubility product) will be greater.

3. Because solubilities and therefore solubility products increase as temperature increases.

4. Because the solubility product for lead(II) chloride involves the multiplication of three concentration terms whereas that of lead sulfide involves only two.

5. \( \text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(\text{aq}) + \text{CO}_3^{2-}(\text{aq}) \)
   If the solubility of \( \text{CaCO}_3 \) is \( s \) mol dm\(^{-3}\)
   \[ [\text{Ca}^{2+}(\text{aq})] = [\text{CO}_3^{2-}(\text{aq})] = s \]
   \[ \therefore K_{s.p.}(\text{CaCO}_3) = [\text{Ca}^{2+}(\text{aq})][\text{CO}_3^{2-}(\text{aq})] = s \times s = \left(7 \times 10^{-5}\right)^2(\text{mol dm}^{-3})^2 \]
   \[ = 4.9 \times 10^{-9} \text{ mol}^2\text{dm}^{-6} \]

6. \( \text{Bi}_2\text{S}_3(s) \rightleftharpoons 2\text{Bi}^{3+}(\text{aq}) + 3\text{S}^{2-}(\text{aq}) \)
   \[ s \quad 2s \quad 3s \]
   \[ K_{s.p.} = (2s)^2(3s)^3 = 108 s^5 \]
   Correct answer is d.

7. a) \( \text{AgCl(s) } \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \)
   If the solubility is \( s \), then \([\text{Ag}^+(\text{aq})] = [\text{Cl}^-(\text{aq})] = s \)
   \[ \therefore K_{s.p.} = [\text{Ag}^+(\text{aq})][\text{Cl}^-(\text{aq})] = s \times s \]
   \[ = s^2 = 2.0 \times 10^{-10} \]
   \[ \therefore \text{Solubility, } s = 1.4 \times 10^{-5} \text{ mol dm}^{-3} \]
   b) \( \text{AgCl(s) } \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \)
\[ \text{NaCl(s) } \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \]
Let solubility of AgCl in 0.1 mol dm\(^{-3}\) NaCl = \( s^1 \)
Then, \([\text{Ag}^+(\text{aq})] = s^1 \) and \([\text{Cl}^-(\text{aq})] = s^1 + 0.1 \)
But \( s^1 \) is much less than 0.1, so \([\text{Cl}^-(\text{aq})] \approx 0.1 \)
\[ \therefore s^1 \times 0.1 = 2 \times 10^{-10} \]
\[ \therefore \text{Solubility of AgCl in 0.1 mol dm}^{-3}\text{NaCl} = 2 \times 10^{-9} \text{ mol dm}^{-3} \]
8. \( \text{AgBr(s)} \rightleftharpoons \text{Ag}^+(aq) + \text{Br}^-(aq) \)

If the solubility of AgBr(s) = \( s \),

Then \([\text{Ag}^+(aq)] = [\text{Br}^-(aq)] = s = 7 \times 10^{-7} \text{ mol dm}^{-3}\)

\[ \therefore K_{s.p.} = [\text{Ag}^+(aq)][\text{Br}^-(aq)] \]
\[ = 7 \times 10^{-7} \times 7 \times 10^{-7} = 4.9 \times 10^{-13} \text{ mol}^2 \text{dm}^{-6} \]

9. a. \( K_{s.p.} = [\text{Ag}^+(aq)]^2[\text{C}_2\text{O}_4^{2-}(aq)] \)

b. If the solubility of \( \text{Ag}_2\text{C}_2\text{O}_4 \) = \( s \),

then \([\text{Ag}^+(aq)] = 2s\) and \([\text{C}_2\text{O}_4^{2-}(aq)] = s\)

\[ \therefore K_{s.p.} = (2s)^2 \times s = 4s^3 = 5 \times 10^{-9} \]

\[ \Rightarrow s^3 = 1.25 \times 10^{-9}, \text{ and } s = 1.08 \times 10^{-3} \text{ mol dm}^{-3} \]

Concentration of silver ethanedioate = \( 1.08 \times 10^{-3} \text{ mol dm}^{-3} \)

c. The solubility product will increase as temperature increases because the solubility of silver ethanedioate will increase with temperature.

10. \( \text{HX(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{X}^-(aq) \)

a. Extent of dissociation increases as \([\text{H}_2\text{O}(l)]\) increases.

b. Extent of dissociation decreases as \([\text{H}_3\text{O}^+(aq)]\) increases.

c. Extent of dissociation decreases as \([\text{X}^-(aq)]\) increases.

11. a. \( \text{pH} = -\log [\text{H}^+(aq)] = -\log 10^{-3} = +3 \)

b. \( \text{pH} = -\log [\text{H}^+(aq)] = -\log 1 = 0 \)

c. \( \text{pH} = -\log [\text{H}^+(aq)] = -\log \left(3 \times \frac{50}{100}\right) = -\log 1.5 = +0.18 \)

12. a. Because, on dissociating, each water molecule produces one \( \text{H}^+ \) ion and one \( \text{OH}^- \) ion.

b. \( K_c = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \)

At \( 25^\circ \text{C} \), \([\text{H}^+][\text{OH}^-] = 10^{-14} \text{ mol}^2 \text{dm}^{-6} \)

and \([\text{H}_2\text{O}] = \frac{1000 \text{ g dm}^{-3}}{18 \text{ g mol}^{-1}} = 55.6 \text{ mol dm}^{-3} \)

\[ \therefore K_c = \frac{10^{-14}}{55.6} \text{ mol dm}^{-3} = 1.8 \times 10^{-16} \text{ mol dm}^{-3} \]

c. It increases.

d. \( \text{H}_2\text{O}(l) \rightleftharpoons \text{H}^+(aq) + \text{OH}^-(aq) \quad \Delta H = +58 \text{ kJ mol}^{-1} \)
If temp. increases, Le Chatelier’s principle suggests that the equilibrium in the above system will move to the right, thus increasing $[\text{H}^+]$, $[\text{OH}^-]$ and hence $K_w$ which equals $[\text{H}^+][\text{OH}^-]$.

13  a  $\text{pH} = -\log [\text{H}^+] = -\log 1 = 0$
   b  $\text{pH} = -\log [\text{H}^+] = -\log (2 \times 0.10) = -0.70$
   c  $\text{pH} = -\log [\text{H}^+]$ and $[\text{H}^+][\text{OH}^-] = 10^{-14}$
   $[\text{OH}^-] = 1.0 \text{ mol dm}^{-3}$, $\therefore [\text{H}^+] \times 1.0 = 10^{-14}$
   $\Rightarrow \text{pH} = -\log (10^{-14}) = +14.0$
   d  $[\text{OH}^-] = 0.10 \text{ mol dm}^{-3}$, $\therefore [\text{H}^+] \times 0.10 = 10^{-14}$
   $\Rightarrow \text{pH} = -\log (10^{-13}) = +13.0$
   e  $[\text{OH}^-] = 2.0 \text{ mol dm}^{-3}$, $\therefore [\text{H}^+] \times 2.0 = 10^{-14}$
   $\Rightarrow \text{pH} = -\log (\frac{1}{2} \times 10^{-14}) = -\log (0.5 \times 10^{-14}) = +13.70$

14  a  $C_6\text{H}_5\text{COOH}(\text{aq}) \rightleftharpoons C_6\text{H}_5\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$
   b  $K_a = \frac{[C_6\text{H}_5\text{COO}^-][\text{H}^+]}{[C_6\text{H}_5\text{COOH}]}$
   c  $\therefore K_a = \frac{[\text{H}^+]^2}{1.0}$, so $[\text{H}^+]^2 = 1.0 \times 6.4 \times 10^{-5} = 64 \times 10^{-6}$
   and $[\text{H}^+] = 8.0 \times 10^{-3} \text{ mol dm}^{-3}$
   d  $\text{pH} = -\log (8.0 \times 10^{-3}) = +2.1$

15  Because the pH changes as acid concentration changes.

16  Because the amount of $\text{H}^+$ ions with which the sodium hydroxide reacts will be the same in 1 mol of both nitric acid and ethanoic acid.

17  $K_a = \frac{[\text{HCOO}^-][\text{H}^+]}{[\text{HCOOH}]}$
   $\text{pH} = 2.4 = -\log [\text{H}^+] = (-3.0 + 0.6)$
   $\therefore [\text{H}^+] = 4.0 \times 10^{-3} \text{ mol dm}^{-3}$
   But $[\text{H}^+] = [\text{HCOO}^-] = 4 \times 10^{-3} \text{ mol dm}^{-3}$
   and $[\text{HCOOH}] \gg [\text{H}^+]$, so $[\text{HCOOH}] \approx 0.10 \text{ mol dm}^{-3}$
   $\therefore K_a = \frac{4 \times 10^{-3} \times 4 \times 10^{-3}}{0.10} = 1.6 \times 10^{-4} \text{ mol dm}^{-3}$

18  a  $pK_a = -\log K_a = -\log (1.3 \times 10^{-3}) = +2.89$
   b  $pK_a = -\log K_a = -\log (6.4 \times 10^{-5}) = +4.19$
19  a colourless,  b pink

20  a 7.0
   b  i yellow,  ii colourless,  iii green
   c Because phenolphthalein is not very soluble in water and some of the
      phenolphthalein remains insoluble as a cloudy suspension.

21  a between 8.2 and 10.2,  b between 5.5 and 7.5

22  a 7.0,  b 1.0,  c i approx 3 to 5,  ii 50 cm$^3$

23  a Because the initial solution being tested is 50 cm$^3$ of 0.1 mol dm$^{-3}$ HCl(aq) in each
      titration before any alkali is added.
   b Because the final solution in Figure 21.12 contains excess 0.1 mol dm$^{-3}$ NaOH(aq)
      which is a strong, fully dissociated alkali whereas that in Figure 21.13 is excess
      0.1 mol dm$^{-3}$ NH$_3$(aq) which is a weak, only partially dissociated alkali.

24  a Mol of NaOH = $\frac{0.1}{1000}$ dm$^3 \times 1.0$ mol dm$^{-3} = 10^{-4}$ mol
   b $10^{-4}$ mol dm$^{-3}$
   c pH = $-\log[H^+]$
      As $K_w = [H^+][OH^-] = 10^{-14}$ mol$^2$ dm$^{-6}$ and $[OH^-] = 10^{-4}$ mol dm$^{-3}$
      $\therefore [H^+] \times 10^{-4} = 10^{-14}$
      So $[H^+] = 10^{-10}$ and pH = $-\log(10^{-10}) = 10$
   d pH changes from 7 to 10
      So, change in pH = 3 units.

25  Because the mixture of ethanoic acid and sodium ethanoate acts as a buffer. When the
      small amount of NaOH is added, H$^+$ ions in the solution react with OH$^-$ ions from the
      NaOH forming water. Then, more ethanoic acid, CH$_3$COOH, dissociates into
      CH$_3$COO$^-$ and H$^+$ ions to restore the pH.

26  a $K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]} = 6.4 \times 10^{-5}$ mol dm$^{-3}$
   but $[C_6H_5COO^-] = [H^+]$ and $[C_6H_5COOH] \gg [H^+]$
   So $[C_6H_5COOH] \approx 0.01$ mol dm$^{-3}$
      $\therefore \frac{[H^+]^2}{0.01} = 6.4 \times 10^{-5}$, i.e. $[H^+]^2 = 6.4 \times 10^{-7} = 64 \times 10^{-8}$
      $\Rightarrow [H^+] = 8 \times 10^{-4}$ mol dm$^{-3}$
\[ \text{b} \quad \text{pH} = - \log (8 \times 10^{-4}) = -(0.90 - 4.0) = 3.1 \]

\[ \text{c} \quad \text{Assuming the benzoic acid is a very weak acid} \]
\[ [C_6H_5COOH] = 0.01 \text{ mol dm}^{-3} \]
\[ \text{and } [C_6H_5COO^-] = 0.02 \text{ mol dm}^{-3} \]
\[ \therefore \quad K_a = 6.4 \times 10^{-5} = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]} = \frac{0.02 \times [H^+]}{0.01} \]
\[ \text{So, } [H^+] = \frac{6.4 \times 10^{-5}}{2} = 3.2 \times 10^{-5} \text{ mol dm}^{-3} \]
\[ \text{So, } \text{pH} = - \log (3.2 \times 10^{-5}) = -(0.51 - 5.00) \]
\[ \therefore \quad \text{pH} = 4.49 \]

\[ \text{d} \quad \text{Mol NaOH in 1 cm}^3 \text{ of 1.0 mol dm}^{-3} \text{ NaOH} = \frac{1}{1000} \text{ dm}^3 \times 1 \text{ mol dm}^{-3} = 0.001 \text{ mol} \]

When this is added to 1 dm\(^3\) of the buffer,
\[ C_6H_5COOH(aq) + \text{NaOH(aq)} \rightarrow C_6H_5COONa(aq) + H_2O(l) \]
i.e. 0.001 mol of C\(_6\)H\(_5\)COOH is removed and 0.001 mol of C\(_6\)H\(_5\)COO\(^-\) is produced.
\[ \text{So, the resulting } [C_6H_5COOH] = 0.010 - 0.001 = 0.009 \text{ mol dm}^{-3} \]
\[ \text{and the resulting } [C_6H_5COO^-] = 0.020 + 0.001 = 0.021 \text{ mol dm}^{-3} \]
\[ \therefore \quad \text{Substituting in } K_a = \frac{[C_6H_5COO^-][H^+]}{[C_6H_5COOH]} = 6.4 \times 10^{-5} \]
we get, \[ \frac{0.021 \times [H^+]}{0.009} = 6.4 \times 10^{-5} \]
\[ \text{So, } [H^+(aq)] = 6.4 \times 10^{-5} \times \frac{9}{21} = 2.74 \times 10^{-5} \text{ mol dm}^{-3} \]
\[ \therefore \quad \text{pH} = - \log (2.74 \times 10^{-5}) = -(0.44 - 5.00) \]
\[ = 4.56 \]

\[ \text{e} \quad \text{pH changes from 4.49 to 4.56} \]
\[ \text{pH change} = 0.07 \text{ units} \]
27  a  \( \text{H}_2\text{CO}_3(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{HCO}_3^-(\text{aq}) \)

\[ K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.5 \times 10^{-7} \text{ mol dm}^{-3} \]

In the blood sample, [\( \text{H}_2\text{CO}_3 \)] = 1.8 \times 10^{-3} \text{ mol dm}^{-3} and [\( \text{HCO}_3^- \)] = 2.0 \times 10^{-2} \text{ mol dm}^{-3}, so substituting in the above equation,

\[ \frac{[\text{H}^+]\times 2.0\times 10^{-2}}{1.8\times 10^{-3}} = 4.5 \times 10^{-7} \text{ mol dm}^{-3} \]

\[ [\text{H}^+] = 4.5 \times 10^{-7} \times \frac{1.8\times 10^{-3}}{2.0\times 10^{-2}} = 4.05 \times 10^{-8} \]

So, \( \text{pH} = -\log(4.05 \times 10^{-8}) = -(0.61 - 8.00) = 7.39 \)

b  Mol HCl in 0.1 cm\(^3\) of 1.0 mol dm\(^{-3}\) HCl = \( \frac{0.1}{1000} \) dm\(^3\) \times 1.0 mol dm\(^{-3}\) = 0.0001 mol

When this is added to 1 dm\(^3\) of blood, \( \text{HCO}_3^- \)(aq) + HCl(aq) → \( \text{H}_2\text{CO}_3 \)(aq) + Cl\(^-\) (aq)

i.e. 0.0001 mol of \( \text{H}_2\text{CO}_3 \) is produced and 0.0001 mol of \( \text{HCO}_3^- \) is removed.

So, the resulting [\( \text{H}_2\text{CO}_3 \)] = 0.0018 + 0.0001 = 0.0019 \text{ mol dm}^{-3}

and the resulting [\( \text{HCO}_3^- \)] = 0.0200 - 0.0001 = 0.0199 \text{ mol dm}^{-3}

\[ \therefore \text{Substituting in } K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = 4.5 \times 10^{-7} \]

we get, \[ \frac{[\text{H}^+]\times 0.0199}{0.0019} = 4.5 \times 10^{-7} \]

So, [\( \text{H}^+ \)] = 4.5 \times 10^{-7} \times \frac{19}{199} = 4.30 \times 10^{-8} \text{ mol dm}^{-3}

and \( \text{pH} = -\log(4.30 \times 10^{-8}) = -(0.63 - 8.00) = 7.37 \)

c  pH changes from 7.39 to 7.37

\[ \therefore \text{pH change} = 0.02 \text{ units} \]