Chemistry in Context
Seventh edition

Chapter 21 – Answers to end of chapter questions

1  a  \( K_w = [H^+][OH^-] \)
    
    b  i  \([SO_4^{2-}] = 0.01 \text{ mol dm}^{-3} \)
    
    ii  \([H^+] = 2 \times 0.01 \text{ mol dm}^{-3} \)
        = 0.02 \text{ mol dm}^{-3} 

    \( K_w = [H^+][OH^-] \)

    Rearranging \([OH^-] = \frac{K_w}{[H^+]} \)
    
    = \frac{1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{0.02 \text{ mol dm}^{-3}} 
    
    = 5 \times 10^{-13} \text{ mol dm}^{-3} 

2  a  \( K_w = [H^+][OH^-] \)

    \([H^+] = \frac{K_w}{[OH^-]} \)
    
    = \frac{1 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}}{2.0 \text{ mol dm}^{-3}} 
    
    = 5 \times 10^{-15} \text{ mol dm}^{-3} 

    b  pH = -\log_{10}[H^+] 

    c  pH = -\log_{10}[5 \times 10^{-15}] 
    
    pH = 14.3 

3  a  i  Suppose the solubility of PbSO₄ in water = \( s \) \text{ mol dm}^{-3}, 

    PbSO₄(s) \rightleftharpoons Pb^{2+}(aq) + SO₄^{2-}(aq) 

    \( K_{s.p.}(\text{PbSO}_4) = [\text{Pb}^{2+}][\text{SO}_4^{2-}] \)

    \Rightarrow 1.6 \times 10^{-8} = s \times s 

    \therefore \text{ solubility PbSO}_4 \text{ in water} = s = 1.26 \times 10^{-4} \text{ mol dm}^{-3} 

    ii  Suppose the solubility of PbSO₄ in 0.1 \text{ mol dm}^{-3} Pb(NO₃)₂ = \( s' \)

    In this case \([\text{Pb}^{2+}] = (s' + 0.1) \text{ mol dm}^{-3}, [\text{SO}_4^{2-}] = s' \text{ mol dm}^{-3} \)

    \therefore K_{s.p.}(\text{PbSO}_4) = (s' + 0.1) \times s' = 1.6 \times 10^{-8} 

    Now, as \( s' \ll 0.1, \ 0.1 \times s' = 1.6 \times 10^{-8} \)

    \therefore \text{ solubility of PbSO}_4 \text{ in 0.1 mol dm}^{-3} \text{ Pb(NO}_3)_2 = 1.6 \times 10^{-7} \text{ mol dm}^{-3} 

    iii  Suppose the solubility of PbSO₄ in 0.01 \text{ mol dm}^{-3} Na₂SO₄ = \( s'' \)

    In this case, \([\text{Pb}^{2+}] = s'' \text{ mol dm}^{-3}, [\text{SO}_4^{2-}] = (0.01 + s'') \text{ mol dm}^{-3} \)

    \therefore K_{s.p.}(\text{PbSO}_4) = s'' \times (0.01 + s'') = 1.6 \times 10^{-8} 

    Now, as \( s'' \ll 0.01, \ s'' \times 0.01 = 1.6 \times 10^{-8} \)

    \therefore \text{ Solubility of PbSO}_4 \text{ in 0.01 mol dm}^{-3} \text{ Na}_2\text{SO}_4 = 1.6 \times 10^{-6} \text{ mol dm}^{-3}
b If a solution contains Pb$^{2+}$ or SO$_4^{2-}$ ions, they will add to the concentration of either Pb$^{2+}$ or SO$_4^{2-}$ and suppress the amount of PbSO$_4$ which can dissolve.

c The generalisation known as the common ion effect says that the solubility of a salt A$^+\, B^-$ is reduced by the presence of either A$^+$ or B$^-$ ions from a second source.

This is very well illustrated by the calculations in parts ii and iii of section a in this question; i.e. the solubility of PbSO$_4$ has been reduced by the presence of Pb$^{2+}$ ions from Pb(NO$_3$)$_2$ in part ii and by the presence of SO$_4^{2-}$ ions from Na$_2$SO$_4$ in part iii.

4 a $K_a$ gives a quantitative measure of the strength of an acid and the extent of its dissociation.

b Silicic, chloric(I), ethanoic, phosphoric(V) acid, nitric acid

c i $pK_a = -\log_{10}K_a$

ii $pK_a = -\log_{10}(7.9 \times 10^{-3}) = 2.10$

d i $K_a = \frac{[H^+][ClO^-]}{[HClO]}$

ii $K_a$ [HClO] = [H$^+$]$^2$ (since [H$^+$] = [ClO$^-$])

$\sqrt{(K_a[HClO])} = [H^+]$

$\sqrt{(3.7 \times 10^{-8} \text{ mol dm}^{-3} \times 1 \text{ mol dm}^{-3})} = [H^+]$

$1.9 \times 10^{-4} \text{ mol dm}^{-3} = [H^+]$

iii $\text{pH} = -\log_{10}[H^+]$

$= -\log_{10}1.9 \times 10^{-4}$

$= 3.7$

5 a HClO $\rightleftharpoons$ H$^+$ + ClO$^-$ $K_a = \frac{[H^+][ClO^-]}{[HClO]} = 3.2 \times 10^{-8}$

$[H^+] \approx [ClO^-]$

and $[HClO] = 1.25 \times 10^{-2} - [H^+] = 1.25 \times 10^{-2}$ as [H$^+$] is very small.

$\Rightarrow 3.2 \times 10^{-8} = \frac{[H^+]^2}{1.25 \times 10^{-2}}$

$\therefore [H^+] = 2 \times 10^{-5} \text{ mol dm}^{-3}$

Now, as [H$^+$][OH$^-$] = 10$^{-14}$ at 298 K

[OH$^-$] = 5 $\times$ 10$^{-10}$ mol dm$^{-3}$

b $\text{pH} = -\log[H^+]$

$= -\log(2 \times 10^{-5}) = -(0.30 - 5.0) = 4.7$

6 a Assuming the 1.0 mol dm$^{-3}$ HCl is fully dissociated, [H$^+$] = 1.0, so the pH = $-\log[H^+] = 0$. As water is added, its concentration will fall to say 10$^{-3}$ mol dm$^{-3}$ (pH = 1.0), then
10^{-2} \text{ mol dm}^{-3} (pH = 2.0), etc. Eventually, the HCl will be so dilute that the pH will be virtually the same as that of water; i.e. pH = 7 (at 298 K) and the pH will not change on further dilution.

b When nitric acid is titrated with ammonia, the pH changes rapidly from about 3 to 7 at the equivalence point. This requires an indicator which changes colour in this range. Methyl orange changes colour between pH 3 and 4.5, but phenolphthalein changes colour between 8 and 10 which is useless.

c The $[H^+]$ from pure water is $10^{-7}$. If the solution also contains $10^{-8} \text{ mol dm}^{-3}$ HCl, then the pH will be slightly less than 7.

7 \[ \text{H}_3\text{PO}_4 \rightleftharpoons \text{H}^+ + \text{HPO}_4^{2-} \]

\[ K_a = \frac{[\text{H}^+][\text{HPO}_4^{2-}]}{[\text{H}_3\text{PO}_4]} \]

\[ \text{pH} = -\log[H^+], \text{ if } \text{pH} = 7.4, [H^+] = 3.98 \times 10^{-8} \]

So, \[ 6.4 \times 10^{-8} = 3.98 \times 10^{-8} \cdot \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4]} \]

\[ \therefore [\text{H}_2\text{PO}_4] = 0.62 \]

8 a \[ 10^{-4} \text{ mol dm}^{-3} \text{ HCl}; [H^+] = 10^{-4} \Rightarrow \text{pH} = 4.0 \]

b \[ 10^{-4} \text{ mol dm}^{-3} \text{ Ba} (\text{OH})_2; [\text{OH}^-] = 2 \times 10^{-4} \]

Now, [H$^+$][OH$^-$] \(=\) 10$^{-14}$ at 298 K, \[ [H^+] = 5 \times 10^{-11}, \Rightarrow \text{pH} = 10.3 \]

c \[ 1.0 \text{ mol dm}^{-3} \text{ H}_2\text{X}; [H^-] \text{ would be } 2.0 \text{ mol dm}^{-3} \text{ if } 100\% \text{ dissociated. In } 50\% \text{ dissociated solution, } [H^-] = 1.0 \text{ mol dm}^{-3}. \]

\[ \therefore \text{pH} = -\log[H^+] = -\log[1.0] = 0 \]

d \[ \text{CH}_3\text{CH}_2\text{COOH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{COO}^- + \text{H}^+ \]

\[ K_a = \frac{[\text{CH}_3\text{CH}_2\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{CH}_2\text{COOH}]} \]

Now, \[ [H^+] \approx [\text{CH}_3\text{CH}_2\text{COO}^-] \]

and \[ [\text{CH}_3\text{CH}_2\text{COOH}] = 0.01 - [H^-] \approx 0.01 \text{ as } [H^-] \text{ is very small.} \]

\[ \therefore K_a = 1.45 \times 10^{-5} = \frac{[H^+]^2}{0.01}, \text{ so } [H^+] = 3.81 \times 10^{-4} \]

\[ \Rightarrow \text{pH} = -\log[H^+] = -\log(3.81 \times 10^{-4}) = -(0.58 - 4.00) = 3.42 \]

e \[ \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(l) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq}) \]

\[ K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} \]

$[\text{NH}_4^+] \approx [\text{OH}^-]$ and \[ [\text{NH}_4\text{OH}] = 1.0 - [\text{OH}^-] \approx 1.0 \text{ as } [\text{OH}^-] \text{ is very small} \]

\[ \therefore K_b = 1.7 \times 10^{-5} = \frac{[\text{OH}^-]^2}{1.0}, \text{ so } [\text{OH}^-] = 4.12 \times 10^{-3} \text{ mol dm}^{-3} \]
Now, \([H^+][OH^-] = 10^{-14}\) at 298 K

∴ \([H^+] \times 4.12 \times 10^{-3} = 10^{-14}\)

So, \([H^+] = 2.43 \times 10^{-12}\), pH = 11.61

9  
**a**  HCl(aq) is fully dissociated. So, in 0.1 mol dm\(^{-3}\) HCl, 
\([H^+] = 10^{-1}\) mol dm\(^{-3}\), so pH = 1.0.

CH\(_3\)COOH is only partially dissociated, and in 0.1 mol dm\(^{-3}\) CH\(_3\)COOH, \([H^+]\) is approx. 10\(^{-3}\), so pH ≈ 3.

**b**  No. The pH changes rapidly from about 7.0 to 10.5 during the titration. Methyl orange does not change colour in this pH range, but between 3.0 and 4.5.

**c**  Yes. Phenolphthalein changes colour between pH 8 and 10 which corresponds with the rapid pH change in the titration.

**d**  There is no sharp pH change at any point, so no indicator will change colour with the addition of a small excess of acid or alkali.

**e**  Using a pH meter.

10  
**a**  
\(HIn \rightleftharpoons H^+ + In^-\)

\(\text{ii} \quad K_a (HIn) = \frac{[H^+][In^-]}{[HIn]}\)

**b**  Yellow. Added OH\(^-\) ions react with, and so remove, H\(^+\) ions. This makes the equilibrium shift to the right, so [In\(^-\)] is greater than [H\(^+\)] and the solution is yellow.

**c**  
\(\text{i} \quad \text{pH at end point} = \text{p}K_a (HIn)\)

\(\text{pH} = 5.1\)

\(\text{pH} = -\log_{10}[H^+]\)

\([H^+] = 7.943 \times 10^{-5}\) mol dm\(^{-3}\)

\(\text{ii} \quad \text{pH} = 5.1\)

**d**  
\(\text{i} \quad 4.7\)

\(\text{ii} \quad 7.9\)

\(\text{iii} \quad 9.3\)

**e**  
\(\text{i} \quad \text{Any of the indicators in the table would be suitable}\)

\(\text{ii} \quad \text{Phenolphthalein}\)

\(\text{iii} \quad \text{Bromocresol blue or methyl red}\)

11  
**a**  Buffers are solutions that resist changes in pH on addition of acid or alkali, and on dilution.

**b**  
\(\text{i} \quad \text{HA} \rightleftharpoons H^+ + A^-\)

\(\text{MA} \rightarrow M^+ + A^-\)
ii On adding an acid, its $\textit{H}^+$ ions react with $\textit{A}^-$. This means that $[\textit{H}^+]$ changes very little, so pH changes little.

iii On adding an alkali, the $\textit{OH}^-$ ions react with $\textit{H}^+$. More HA dissociates, meaning that $[\textit{H}^+]$ changes very little, so pH changes little.

c
i Molar mass = 72 g
Mass of 0.02 mol = $0.02 \text{ mol} \times 72 \text{ g mol}^{-1} = 1.44 \text{ g}$

ii Let HA represent butanoic acid. Assume that $[\textit{HA}] = 0.02 \text{ mol dm}^{-3}$.

$K_a = \frac{[\textit{H}^+][\textit{A}^-]}{[\textit{HA}]}$

Rearranging and assuming that $[\textit{H}^+] = [\textit{A}^-]$

$[\textit{H}^+]^2 = [\textit{HA}] \times K_a$

$[\textit{H}^+] = \sqrt{0.02} \times 6.3 \times 10^{-5}$

$= 1.12 \times 10^{-3} \text{ mol dm}^{-3}$

iii pH = $-\log_{10}[\textit{H}^+]$

$pH = 4.65$

iv $[\textit{H}^+] = K_a \frac{[\textit{HA}]}{[\textit{A}^-]}$

$= 6.3 \times 10^{-5} \times 0.02/0.04$

$= 3.15 \times 10^{-5} \text{ mol dm}^{-3}$

So pH = $-\log_{10}[3.15 \times 10^{-5}]$

$= 4.50$