1. Answer is D. $H^+ = 10^{-14}/0.01 = 10^{-12}$. So pH = 12.

2. Answer is C. The dilution of HCl with pH 2 needs to be 10 fold. This is achieved by taking 100 cm$^3$ of the acid and adding 900 cm$^3$ of water.

3. Answer is D. The end point of the titration of a weak acid and a strong base needs an indicator which has a pH range above about 7.5.

4. Answer is C. For both indicators to be yellow, the pH must lie between 4.0 and 5.2 and the pH of 0.0001 mol dm$^{-3}$ HCl is 4.

5. Answer is C. $K_a = [H^+(aq)][ClO_2^{-}(aq)]/[HClO_2(aq)] = [H^+(aq)]^2/[HClO_2(aq)] = [H^+(aq)]^2/1$

   So $K_a = 2 = [H^+(aq)]^2$ and $[H^+(aq)] = \sqrt{2}$

6. Answer is D. The acid is weak and, after the sodium hydroxide has been added, a buffer solution is formed with the concentration of the anion being equal to the concentration of the acid that now remains. This means $K_a = [H^+(aq)]$ and $pK_a = \text{pH}$.

7. Answer is B. $[NH_4^+][NH_2^-] = 10^{-33}$ so when the concentration of the amide ion is $0.001 \text{ mol dm}^{-3}$ $[NH_4^+] = 10^{-33}/0.001 = 10^{-30} \text{ mol dm}^{-3}$.

8. Answer is B. Methanoic acid is the stronger acid and so donates protons to the weaker acid. This means $\text{CH}_3\text{CH}_2\text{COOH}_2^+$ will form. Methanoic acid loses a proton to form $\text{HCOO}^-$.  

9. Answer is B. A base is the substance in an acid–base reaction which receives a proton. In 1 this has been obtained from HF. In 2 it is more disguised but it is clear that the sulfuric acid has donated a proton. In 3 nitric acid is acting as an acid.

10. Answer is A. All metal salts are highly ionised. In a buffer, the ethanoate ion from the sodium ethanoate causes the ionisation of ethanoic acid to be suppressed and, in doing so, raises the pH of the mixture. So all three statements are correct.

11. In each of the following, the acid–base pairs are identified beneath the equations.

   e.g. $H_2O$ and $OH^-$ are a conjugate acid–base pair in a).

   a) $\text{HCO}_3^- + H_2O \rightleftharpoons \text{H}_2\text{CO}_3 + \text{OH}^-$

   Base 2 Acid 1 Acid 2 Base 1

   b) $\text{HCO}_3^- + \text{OH}^- \rightleftharpoons H_2O + \text{CO}_3^{2-}$

   Acid 1 Base 2 Acid 2 Base 1

   c) $\text{HCO}_3^- + \text{HCOOH} \rightleftharpoons \text{HCOO}^- + H_2O + \text{CO}_2$

   Base 2 Acid 1 Base 1

   The mixture of $\text{CO}_2$ and $H_2O$ can be regarded as Acid 2.

12. a) $pH = -\log(0.15) = 0.82$

    b) $K_a = \frac{[H^+(aq)][\text{CN}^- (aq)]}{[\text{HCN}(aq)]]}$
3 Acids, bases and buffers

\[
[H^+(aq)] = [CN^-(aq)]
\]

\[
\frac{[H^+(aq)]^2}{[HCN(aq)]} = [1]
\]

So \(4.8 \times 10^{-10} = [H^+(aq)]^2/0.15\)

Therefore, \([H^+(aq)] = \sqrt{0.627 \times 10^{-10}} = 7.9 \times 10^{-6}\) mol dm\(^{-3}\)

And \(pH = -\log(7.9 \times 10^{-6}) = 5.1\)

c) \([H^+(aq)][OH^-(aq)] = 10^{-14}\)

\([H^+(aq)][0.15] = 10^{-14}\)

\([H^+(aq)] = 6.67 \times 10^{-14}\) mol dm\(^{-3}\)

\(pH = -\log(6.67 \times 10^{-14}) = 13.2\)

(This can also be done using \(pH + pOH = 14\)

So \(pH - \log(0.15) = 14\)

\(pH - 0.82 = 14\)

\(pH 13.2\)

d) \(Na_2SO_4(aq)\) is a salt and is neutral. Therefore, the \(pH = 7\).

13 When 20 cm\(^3\) of 1.00 mol dm\(^{-3}\) HCl is added to 10 cm\(^3\) of 1.00 mol dm\(^{-3}\) NaOH a reaction will occur and the NaOH will be neutralised to produce neutral NaCl.

10 cm\(^3\) of the 1.00 mol dm\(^{-3}\) HCl will remain unneutralised [1], but this has now been diluted to the total volume of the mixture which is 30 cm\(^3\). This means the concentration of the HCl is now \((10/30) \times 1.00 = 0.333\) mol dm\(^{-3}\).

Therefore the \(pH = -\log(0.333) = 0.48\)

14 a) \([H^+(aq)][OH^-(aq)] = 10^{-14}\)

\([H^+(aq)][0.5] = 10^{-14}\)

\([H^+(aq)] = 2 \times 10^{-14}\) mol dm\(^{-3}\)

b) \(pH = 4\) so \([H^+(aq)] = 1 \times 10^{-4}\) mol dm\(^{-3}\) (0.0001 mol dm\(^{-3}\))

c) \(pH = 2.7\) so \([H^+(aq)] = 1 \times 10^{-2.7} = 2.0 \times 10^{-3}\) mol dm\(^{-3}\).

d) \(pH = 11.2\) so \([H^+(aq)] = 1 \times 10^{-11.2} = 6.3 \times 10^{-12}\) mol dm\(^{-3}\).

15 If the milk has a pH of 6.3 then \([H^+(aq)] = 1 \times 10^{-6.3} = 5.0 \times 10^{-7}\) mol dm\(^{-3}\).

16 If the solution of magnesium hydroxide has a pH of 10.5 then

\([H^+(aq)] = 1 \times 10^{-10.5} = 3.16 \times 10^{-11}\) mol dm\(^{-3}\)

So \([OH^- (aq)] = 3.16 \times 10^{-11}\) mol dm\(^{-3}\)

When magnesium hydroxide dissolves it breaks into its ions:

\[\text{Mg(OH)}_2 \rightarrow \text{Mg}^{2+} (aq) + 2\text{OH}^- (aq)\]

Therefore, there is one Mg\(^{2+}\) (aq) produced for every two OH\(^-\) (aq).

So \([\text{Mg}^{2+}] = 1.58 \times 10^{-4}\) mol dm\(^{-3}\)
17 a) \([\text{H}^+(\text{aq})] = 1 \times 10^{-2.45} = 3.55 \times 10^{-3} \text{ mol dm}^{-3}\)  

b) When citric acid ionises,
\[\text{H}_3\text{X} \rightarrow 3\text{H}^+(\text{aq}) + \text{X}^3-(\text{aq})\]
Therefore, the concentration of citrate ions will be \((3.55 \times 10^{-3})/3 = 1.18 \times 10^{-3} \text{ mol dm}^{-3}\)

18 a) Since the acid in apple juice is monobasic, 1 mol of it will be neutralised by 1 mol of the sodium hydroxide.

22.90 cm\(^3\) of the 0.120 mol dm\(^{-3}\) sodium hydroxide contains  
\[(22.90/1000) \times 0.12 = 0.0027(48) \text{ mol}.\]
This neutralises 25.0 cm\(^3\) of the apple juice, so the concentration of the acid in the apple juice is \((1000/25.0) \times 0.0027(48) = 0.110 \text{ mol dm}^{-3}\)

b) In the apple juice, \([\text{H}^+(\text{aq})] = 1 \times 10^{-3.5} = 3.16 \times 10^{-4} \text{ mol dm}^{-3}\)

c) If the anion of the acid in the apple juice is \(\text{A}^-\)
\[K_a = \frac{[\text{H}^+(\text{aq})][\text{A}^- (\text{aq})]}{[\text{HA}(\text{aq})]}\]
\([\text{H}^+(\text{aq})] = [\text{A}^- (\text{aq})]\]
\[= \frac{[\text{H}^+(\text{aq})]^2}{[\text{HA}(\text{aq})]}\]
\[= (3.16 \times 10^{-4})^2/0.11 = 9.09 \times 10^{-7} \text{ mol dm}^{-3}\]

19 a) When potassium ethanoate is dissolved into water it will be fully ionised.
\[\text{CH}_3\text{COO}^-\text{K}^+ \rightarrow \text{CH}_3\text{COO}^- + \text{K}^+\]
The water in which it is dissolved will be slightly ionised.
\[\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-\]
However the presence of the hydrogen ions from the water will be sufficient to create the equilibrium:
\[\text{CH}_3\text{COO}^- + \text{H}^+ \rightleftharpoons \text{CH}_3\text{COOH}\]
The effect is small, but the removal of hydrogen ions to form molecular \(\text{CH}_3\text{COOH}\) is sufficient to mean that a solution of potassium ethanoate is very slightly alkaline and has a pH above 7.
The interaction of equilibria in aqueous solution often causes small effects such as that described above. An alternative way of considering this is simply to say that water is a stronger acid than the ethanoate ion and, therefore, the equilibrium:
\[\text{H}_2\text{O} + \text{CH}_3\text{COO}^- \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-\]
is set up and will lie slightly to the right-hand side.
The two arguments are essentially similar.
b) The extent of the removal of hydrogen ions discussed in part a) depends on the strength of the acid. The weaker the acid, the greater is the formation of the molecular form. 

For HCN, the equilibrium $CN^- + H^+ \rightleftharpoons HCN$ lies further to the right-hand side than does the equilibrium $CH_3COO^- + H^+ \rightleftharpoons CH_3COOH$ so that a greater number of hydrogen ions will be removed from the water equilibrium. 

So, the fact that $K'CN^-$ produces a solution with a higher pH than $CH_3COO^-K^+$ indicates that HCN must be a weaker acid.

c) $NH_4^+Cl^-$ will be fully ionised when dissolved in water.

$NH_4^+Cl^- \rightarrow NH_4^+ + Cl^-$

The water in which it is dissolved will be slightly ionised.

$H_2O \rightleftharpoons H^+ + OH^-$

However the presence of the hydroxide ions from the water will be sufficient to create the equilibrium

$NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$

This results in the removal of some OH$^-$ ions from the water, leaving an excess of hydrogen ions, making the solution slightly acidic with a pH of between about 5–6.5.

An alternative way of considering this is simply to say that the $NH_4^+$ ion is a stronger acid than the water and therefore the equilibrium:

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H^+$

is set up and will lie slightly to the right-hand side.

20 a) $K_a = \frac{[H^+(aq)][CH_3CH_2COO^-(aq)]}{[CH_3CH_2COOH(aq)]}$

In the buffer solution it is considered that the concentration of $CH_3CH_2COO^-(aq)$ and the concentration of $CH_3CH_2COOH(aq)$ can be approximated to their initial concentrations. As the two solutions were mixed together, they will have diluted each other.

So the concentrations now are:

$[CH_3CH_2COO^-(aq)] = 0.05 \text{ mol dm}^{-3}$

$[CH_3CH_2COOH(aq)] = 0.05 \text{ mol dm}^{-3}$

Using the equilibrium constant above gives:

$1.3 \times 10^{-5} = \frac{[H^+(aq)][0.05]}{[0.05]}$

Therefore $[H^+(aq)] = 1.3 \times 10^{-5}$

And pH = 4.9

b) The addition of potassium propanoate would cause some of the $CH_3CH_2COO^-(aq)$ ions to react with $H^+(aq)$ ions in the buffer solution to form more $CH_3CH_2COOH(aq)$.

As a result, the value of the pH will rise.
21 a) If the pH of the acid is 2.7, $[H^+] = 10^{-2.7} = 2 \times 10^{-3}$ mol dm$^{-3}$

In the solution of ethanoic acid $[H^+(aq)] = [\text{CH}_3\text{COO}^-(aq)]$

So, $K_a = \frac{[H^+(aq)]^2}{[\text{CH}_3\text{COOH}(aq)\]}$

Therefore, $1.7 \times 10^{-5} = \frac{(2 \times 10^{-3})^2}{[\text{CH}_3\text{COOH}(aq)\]}$

So, $[\text{CH}_3\text{COOH}(aq)\] = (4 \times 10^{-6})/1.7 \times 10^{-5} = 0.23(5) = 0.24$ mol dm$^{-3}$

b) For a buffer of pH = 4 the concentration of $[H^+(aq)]$ must be $10^{-4}$ mol dm$^{-3}$

The concentration of the ethanoic acid stays the same so:

$[\text{CH}_3\text{COO}^-(aq)] = (0.235 \times 1.7 \times 10^{-5})/10^{-4} = 0.04$ mol dm$^{-3}$

The molar mass of sodium ethanoate = 82 g mol$^{-1}$

Therefore, the mass required is 82 \times 0.04 = 3.3 g (3.28 g)

22 When the solutions are mixed the 25.0 cm$^3$ of 0.500 mol NaOH reacts with 25.0 cm$^3$ of the 0.500 mol dm$^{-3}$ CH$_3$COOH to make CH$_3$COO$^-$ ions. 25.0 cm$^3$ of the 0.500 mol dm$^{-3}$ CH$_3$COOH remains unreacted.

The total volume of the solution is 75.0 cm$^3$. Each component has been diluted so that the concentrations of the ions are:

$[\text{CH}_3\text{COO}^-] = (25/75) \times 0.500 = 0.167$ mol dm$^{-3}$

and also

$[\text{CH}_3\text{COOH}] = (25/75) \times 0.500 = 0.167$ mol dm$^{-3}$

$[H^+(aq)] = K_a \times \frac{[\text{CH}_3\text{COOH}]/[\text{CH}_3\text{COO}^-]} = 1.7 \times 10^{-5} \times 0.167/0.167 = 1.70 \times 10^{-5}$ mol dm$^{-3}$

$pH = -\log(1.7 \times 10^{-5}) = 4.77$

23 a) The ‘neutral’ colour of the indicator occurs when $H\text{In} = \text{In}^-$

So this is at pH =4.1

b) Since the indicator changes colour at a relatively low pH value, the indicator would be suitable for the titration of a strong acid with either a strong base or a weak base.

24 a) At the mid-point of the reaction pH = $pK_{In}$

So $pH = -\log(6.31 \times 10^{-7}) = 6.2$

b) Writing the indicator as $H\text{In}$. The indicator equilibrium is:

$H\text{In} \rightleftharpoons H^+ + \text{In}^-$

Yellow Red
In acid solutions, the added $H^+$ pushes this equilibrium to the left and, therefore, the indicator appears as yellow. [1] In alkaline solutions, the added $OH^-$ reacts with the $H^+$ from the indicator and creates water. [1] This causes the indicator to adjust by creating more $In^-$ and, therefore, it appears as red. [1]

c) i) $0.0001 \text{ mol dm}^{-3}$ has a pH of 4 and so the indicator will be yellow. [1]

ii) Pure water has a pH of 7, so the indicator will be turning to its red colour, but to the eye it would probably appear orange as the conversion to the $HIn$ form will not be sufficiently completed. [1]

25 a) The equation for the neutralisation reaction is:

$$\text{CH}_3\text{CH}_2\text{COOH}(aq) + \text{NaOH}(aq) \rightarrow \text{CH}_3\text{CH}_2\text{COO}^-\text{Na}^+(aq) + \text{H}_2\text{O}(l)$$

The amount of propanoic acid used in the titration is $(25.0/1000) \times 0.020 = 5 \times 10^{-4} \text{ mol}$ [1]

The concentration of the sodium hydroxide is $0.025 \text{ mol dm}^{-3}$

Therefore, the volume required will be $5 \times 10^{-4}/0.025 \text{ dm}^3 = 0.02 \text{ dm}^3$ or $20.0 \text{ cm}^3$ [1]

(A little thought might, in fact, allow you to see that it must be $20 \text{ cm}^3$ without the need for a formal calculation.)

b) $K_a = \frac{[H^+(aq)][\text{CH}_3\text{CH}_2\text{COO}^-\text{(aq)}]}{[\text{CH}_3\text{CH}_2\text{COOH}(aq)]}$

and since $[H^+(aq)] = [\text{CH}_3\text{CH}_2\text{COO}^-\text{(aq)}]$

$$K_a = \frac{[H^+(aq)]^2}{[\text{CH}_3\text{CH}_2\text{COOH}(aq)]}$$

So $1.3 \times 10^{-5} = [H^+(aq)]^2/0.02$ [1]

Therefore, $[H^+(aq)] = \sqrt{2.6 \times 10^{-7}} = 5.1 \times 10^{-4} \text{ mol dm}^{-3}$ [1]

And $\text{pH} = -\log(5.1 \times 10^{-4}) = 3.3$ [1]

c) $[H^+(aq)][OH^-(aq)] = 10^{-14}$

$[H^+(aq)][0.025] = 10^{-14}$ [1]

$[H^+(aq)] = 4.0 \times 10^{-13} \text{ mol dm}^{-3}$ [1]

$\text{pH} = 12.4$ [1]
3 Acids, bases and buffers


(A rough sketch is fine in an answer to a question of this sort. However, the marking points would insist on the starting pH of 2.8, the end point at pH close to 7, when 20.0 cm³ of sodium hydroxide had been added and a final pH close to 12.4. Since the solution is diluted at this stage, it will be slightly less than this figure.)

e) There are many suitable indicators for a weak acid and strong base. An example is phenolphthalein. The requirement is that the indicator changes in a pH range of between 8–10.

26 a) The equation for the reaction is:

\[ 2\text{NaOH(aq)} + \text{H}_2\text{SO}_4(aq) \rightarrow \text{Na}_2\text{SO}_4(aq) + \text{H}_2\text{O(l)} \]

The amount of sulphuric acid used is \((50.0/1000) \times 1.00 = 0.0500 \text{ mol} \)

The amount of sodium hydroxide used is also 0.0500 mol.

However, as the equation indicates that twice the amount in moles of sodium hydroxide is required, the sulfuric acid must be in excess.

b) The heat produced by the reaction, \(q\), is:

\[ \text{total mass of the solution} \times \text{specific heat capacity} \times \text{the temperature rise} \]

Therefore \(q = 100.0 \times 4.18 \times (23.6 - 19.0) = 1922.8 \text{ J} \)

This heat is produced by the reaction of 0.05 mol of sodium hydroxide.

Therefore, the enthalpy change of neutralisation is,

\[ \Delta H = 1922.8/0.05 = 38.5 \text{ kJ mol}^{-1} \]

27 \( \text{HBr(aq)} + \text{NaOH(aq)} \rightarrow \text{NaBr(aq)} + \text{H}_2\text{O(l)} \) \( \Delta H^\circ = -57.6 \text{ kJ mol}^{-1} \)

\( \text{HCl(aq)} + \text{NH}_3(aq) \rightarrow \text{NH}_4\text{Cl(aq)} + \text{H}_2\text{O(l)} \)

\( \Delta H^\circ = -53.4 \text{ kJ mol}^{-1} \)

\( \text{H}_2\text{COOH(aq)} + \text{NH}_3(aq) \rightarrow \text{CH}_3\text{CO}_2\text{NH}_4(aq) \)

\( \Delta H^\circ = -50.4 \text{ kJ mol}^{-1} \)

The first reaction is between a strong acid and a strong base and will have the largest enthalpy change.

The second reaction is between a strong acid and a weak base and will, therefore, have the next largest enthalpy change.

The third reaction is between a weak acid and a weak base and will have the smallest enthalpy change.

28 a) At pH 12, \([\text{OH}^-(aq)] = 0.01 \text{ mol dm}^{-3} \)

At pH 11.5, \([\text{H}^+(aq)] = 10^{-11.5} = 3.16 \times 10^{-12} \text{ mol dm}^{-3} \)

So, at pH 11.5, \([\text{OH}^-(aq)] = 10^{-14}/3.16 \times 10^{-12} = 0.00316 \text{ mol dm}^{-3} \)

Therefore, the change in the concentration is 0.00684 \text{ mol dm}^{-3}
b) The neutral point of the indicator can be taken as 11.5. 
   If the indicator equilibrium is written as \( \text{NPBH} \rightleftharpoons \text{H}^+ + \text{NPB}^- \), the neutral point will be 
   when \( \text{NPBH} = \text{NPB}^- \) 
   and \( K_{\text{in}} = [\text{H}^+] \) 
   Therefore, \( K_{\text{in}} = 10^{-11.5} = 3.16 \times 10^{-12} \text{ mol dm}^{-3} \)

c) \( 3.16 \times 10^{-12} = [10^{-10.8}][\text{NPB}^-]/[\text{NPBH}] \)
   \( [\text{NPB}^-]/[\text{NPBH}] = 3.16 \times 10^{-12}/1.58 \times 10^{-11} = 0.20 \)

Challenge

29 a) If the acid equilibrium for aspirin is written as:
   \( \text{HA(aq)} \rightleftharpoons \text{H}^+(aq) + \text{A}^-(aq) \)
   \( \frac{[\text{H}^+ (aq)]}{[\text{HA(aq)}]} = 3.0 \times 10^{-4} \)
   If \( \text{pH} = 1 \), \([\text{H}^+(aq)] = 0.1 \text{ mol dm}^{-3} \)
   \( \frac{[\text{A}^- (aq)]}{[\text{HA(aq)}]} = 3.0 \times 10^{-4} \)
   This means the aspirin is very largely in its molecular form HA. This would be likely to 
   dissolve in the lipids on the stomach lining and, hence, bleeding might be a problem.

b) A pH of 7.4 means that \([\text{H}^+(aq)] = 4.0 \times 10^{-8} \text{ mol dm}^{-3} \)
   So, \( \frac{[\text{A}^-]}{[\text{HA}]} = \frac{3.0 \times 10^{-3}}{4.0 \times 10^{-8}} = 7.5 \times 10^4 \)
   The aspirin is now largely ionised and will be mostly present as the anion.

c) The relative formula mass of \( \text{Ca(OH)}_2 \) is 74.1.
   Therefore, the concentration of \( \text{Ca(OH)}_2 \) is 0.0100 mol dm\(^{-3}\).
   As calcium hydroxide is a strong base it will be fully ionised and the concentration of 
   hydroxide ions present will be 0.0200 mol dm\(^{-3}\).
   If \([\text{OH}^-(aq)] = 0.0200\), then \([\text{H}^+(aq)] = 10^{-14}/0.0200 \text{ mol dm}^{-3} \)
   This is a pH of 12.30.
   At this pH, hydrolysis of the aspirin would be very substantial.

d) i) \( \text{C}_6\text{H}_4(\text{OCOCH}_3)\text{CO}_2\text{H} + \text{H}_2\text{O} \rightleftharpoons \text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{H} + \text{CH}_3\text{COOH} \)
   Since the equilibrium constant has no units, the calculation can be done in moles 
   rather than mol dm\(^{-3}\).
   The molar masses of the components are:
   \( \text{C}_6\text{H}_4(\text{OH})\text{CO}_2\text{H} = 138 \text{ g mol}^{-1} \)
CH₃COOH = 60 g mol⁻¹
C₆H₅(OCOCH₃)CO₂H = 180 g mol⁻¹
H₂O = 18 g mol⁻¹

[1] for all four molar masses

Initially the amount of C₆H₅(OCOCH₃)CO₂H = 0.900/180 = 5.00 × 10⁻³ mol
and for H₂O = 0.100/18 = 5.55 × 10⁻³ mol.

At equilibrium 0.117 g of CH₃COOH is present or 0.117/60 = 1.95 × 10⁻³ mol
Therefore, the amounts, in moles, of the other components at equilibrium are:

C₆H₄(OH)CO₂H = 1.95 × 10⁻³ mol
C₆H₅(OCOCH₃)CO₂H = (5.00 – 1.95) × 10⁻³ = 3.05 × 10⁻³ mol
H₂O = (5.55 – 1.95) × 10⁻³ = 3.60 × 10⁻³ mol

\[ K_a = \frac{C_6H_4(OH)CO_2H \cdot CH_3COOH}{C_6H_5(OCOCH_3)CO_2H \cdot H_2O} = \frac{1.95 \times 10^{-3}}{3.05 \times 10^{-3}} \times \frac{1.95 \times 10^{-3}}{3.60 \times 10^{-3}} = 0.346 \]

ii) The percentage of aspirin that is hydrolysed is \( \frac{1.95 \times 10^{-3}}{5.00 \times 10^{-3}} \times 100 = 39.0\% \)