Full answers to self-check questions

This section contains answers for those self-check questions whose answers are found by carrying out a multi-step calculation. We show every step in these calculations, so you can check your working.

Chapter 2

2.7

Atomic mass of chlorine $= (35 \times 0.7578) + (37 \times 0.2422)$
$= 26.523 + 8.9614$
$= 35.4844$
$=$ **35.5** (to 3 significant figures)

Chapter 5

5.3

(a) Molar mass of potassium $= 39.1\ \text{g mol}^{-1}$

Amount in 25 g $= \dfrac{25\ \text{g}}{39.1\ \text{g mol}^{-1}}$

= **0.64 mol**

(b) Molar mass of sodium $= 23\ \text{g mol}^{-1}$

Amount in 25 g $= \dfrac{25\ \text{g}}{23\ \text{g mol}^{-1}}$

= **1.1 mol**

(c) Molar mass of nitrogen $= 14\ \text{g mol}^{-1}$

Amount in 50 g $= \dfrac{50\ \text{g}}{14\ \text{g mol}^{-1}}$

= 3.6 **mol**

5.4

(a) Molar mass of NaCl = (Molar mass of Na) + (Molar mass of Cl)
= 23 g mol^{-1} + 35.5 g mol^{-1}
= 58.5 g mol^{-1}

Number of moles in 40 g NaCl $= \dfrac{\text{mass of sample}}{\text{molar mass}}$

$= \dfrac{40 \text{ g}}{58.5 \text{ g mol}^{-1}}$

= **0.68 mol**

(b) Molar mass of $CaCO_3$ = (Molar mass of Ca) + (Molar mass of C) + (3 × molar mass of O)

= 40 g mol^{-1} + 12 g mol^{-1} + (3 × 16 g mol^{-1})
= 100 g mol^{-1}

Number of moles in 50 g $CaCO_3$ $= \dfrac{\text{mass of sample}}{\text{molar mass}}$

$= \dfrac{50 \text{ g}}{100 \text{ g mol}^{-1}}$

= **0.5 mol**

(c) Molar mass of $C_6H_{12}O_6$ = (6 × molar mass of C) + (12 × molar mass of H) + (6 × molar mass of O)

= (6 × 12 g mol^{-1}) + (12 × 1 g mol^{-1}) + (6 × 16 g mol^{-1})
= 180 g mol^{-1}

Number of moles in 100 g $C_6H_{12}O_6$ $= \dfrac{\text{mass of sample}}{\text{molar mass}}$

$= \dfrac{100 \text{ g}}{180 \text{ g mol}^{-1}}$

= **0.56 mol**

5.5

(a) Amount (in mol) = Volume of solution × concentration of solution
= $0.05\ \text{L} \times 0.5\ \text{mol L}^{-1}$
= **0.025 mol**

(b) Amount (in mol) = Volume of solution × concentration of solution
= $0.1\ \text{L} \times 1\ \text{mol L}^{-1}$
= **0.1 mol**

(c) Amount (in mol) = Volume of solution × concentration of solution
= $2\ \text{L} \times 0.1\ \text{mol L}^{-1}$
= **0.2 mol**

5.6

(a) Amount (in mol) = Volume of solution × concentration of solution
= $2\ \text{L} \times 0.5\ \text{mol L}^{-1}$
= **1 mol**

(b) Amount (in mol) = Volume of solution × concentration of solution
= $1\ \text{L} \times 2\ \text{mol L}^{-1}$
= **2 mol**

(c) Amount (in mol) = Volume of solution × concentration of solution
= $0.5\ \text{L} \times 1\ \text{mol L}^{-1}$
= **0.5 mol**

5.7

(a) Number of moles of glucose = Volume × concentration
= $0.25\ \text{L} \times 2\ \text{mol L}^{-1}$
= 0.5 mol

Mass of glucose required = Molar mass × number of moles present
= $180\ \text{g mol}^{-1} \times 0.5\ \text{mol}$
= **90 g**

(b) Number of moles of NaCl = Volume × concentration
= $1\ \text{L} \times 0.2\ \text{mol L}^{-1}$
= 0.2 mol

Mass of NaCl required = Molar mass × number of moles present
= $58.5\ \text{g mol}^{-1} \times 0.2\ \text{mol}$

= **11.7 g**

(c) Number of moles of KCl = Volume × concentration
= $0.1\ \text{L} \times 0.05\ \text{mol L}^{-1}$
= 0.005 mol

Mass of KCl required = Molar mass × number of moles present
= $74.6\ \text{g mol}^{-1} \times 0.005\ \text{mol}$
= **0.373 g**

5.8 0.5% of 200 mL = $\left(\frac{0.5}{100}\right) \times 200 = 1$

So we need 1g of peptone to produce a 200 mL solution containing 0.5% peptone w/v.

5.9 If we divide both sides of the equation by volume, we get:

$$\frac{\text{Amount of substance (mol)}}{\text{volume (L)}} = \frac{\text{concentration (mol L}^{-1}) \times \text{volume (L)}}{\text{volume (L)}}$$

The volume terms on the right-hand side cancel out:

$$\frac{\text{Amount of substance (mol)}}{\text{volume (L)}} = \frac{\text{concentration (mol L}^{-1}) \times \cancel{\text{volume (L)}}}{\cancel{\text{volume (L)}}}$$

To leave:

$$\frac{\text{Amount of substance (mol)}}{\text{volume (L)}} = \text{concentration (mol L}^{-1})$$

5.10

(a) Concentration $= \frac{\text{number of moles (mol)}}{\text{volume (L)}}$

$= \frac{0.5\ \text{mol}}{0.25\ \text{L}}$

= 2 mol L^{-1}

(b) Concentration $= \frac{\text{number of moles (mol)}}{\text{volume (L)}}$

$= \frac{3\ \text{mol}}{1\ \text{L}}$

= **3 mol L^{-1}**

(c) Concentration $= \dfrac{\text{number of moles (mol)}}{\text{volume (L)}}$

$= \dfrac{0.2\text{ mol}}{0.5\text{ L}}$

= **0.4 mol L^{-1}**

(d) If we rearrange $\text{concentration} = \dfrac{\text{amount (in mol)}}{\text{volume}}$ to isolate our unknown term, we get

$$\text{volume} = \frac{\text{amount (in mol)}}{\text{concentration}}$$

We know that the concentration = 0.2 M, and the number of moles = 0.5 mol. Therefore we calculate the volume as follows:

$$\text{volume} = \frac{0.5\text{ mol}}{0.2\text{ mol L}^{-1}}$$

= **2.5 L**

5.11

(a) Step 1: Number of moles of HCl in 20 mL of a 1 M solution

= concentration of solution × volume of solution

= 1 mol L^{-1} × 0.02 L

= 0.02 mol

Step 2: Concentration of diluted solution

$= \dfrac{\text{number of moles of HCl}}{\text{volume of diluted solution}}$

Volume of diluted solution = Volume of original solution + volume of water added

= 0.02 L + 0.08 L

= 0.1 L

Concentration of diluted solution $= \dfrac{0.02\text{ mol}}{0.1\text{ L}}$

= **0.2 mol L^{-1}**

(b) Step 1: Number of moles of glucose in 50 mL of a 0.5 M solution

= concentration of solution × volume of solution

= $0.5 \text{ mol L}^{-1} \times 0.05 \text{ L}$

= 0.025 mol

Step 2: Concentration of diluted solution

$$= \frac{\text{number of moles of glucose}}{\text{volume of diluted solution}}$$

Volume of diluted solution = Volume of original solution + volume of water added

= 0.05 L + 0.15 L

= 0.2 L

$$\text{Concentration of diluted solution} = \frac{0.025 \text{ mol}}{0.2 \text{ L}}$$

= **0.13 mol L^{-1}**

(c) Step 1: Number of moles of HNO_3 in 100 mL of a 2 M solution

= concentration of solution × volume of solution

= $2 \text{ mol L}^{-1} \times 0.1 \text{ L}$

= 0.2 mol

Step 2: Concentration of diluted solution

$$= \frac{\text{number of moles of HNO}_3}{\text{volume of diluted solution}}$$

Volume of diluted solution = Volume of original solution + volume of water added

= 0.1 L + 1.9 L

= 2 L

$$\text{Concentration of diluted solution} = \frac{0.2 \text{ mol}}{2 \text{ L}}$$

= **0.1 mol L^{-1}**

5.12

(a) Step 1: Number of moles of HCl in 200 mL of a 1 M solution

= concentration of solution × volume of solution

= $1 \text{ mol L}^{-1} \times 0.2 \text{ L}$

= 0.2 mol

Step 2:

$$\text{Volume of diluted solution} = \frac{\text{number of moles of HCl}}{\text{concentration of diluted solution}}$$

$$= \frac{0.2\ \text{mol}}{0.2\ \text{mol L}^{-1}}$$

$$= 1\ \text{L}$$

We *start* with 0.2 L (200 mL) of solution, and need to *end* with 1 L of solution. So we need to add (1 L – 0.2 L) = **0.8 L** (800 mL) to bring the volume of the diluted solution to 1 L.

(b) Step 1: Number of moles of glucose in 400 mL of a 0.9 M solution
= concentration of solution × volume of solution
= 0.9 mol L^{-1} × 0.4 L
= 0.36 mol

Step 2:

$$\text{Volume of diluted solution} = \frac{\text{number of moles of glucose}}{\text{concentration of diluted solution}}$$

$$= \frac{0.36\ \text{mol}}{0.5\ \text{mol L}^{-1}}$$

$$= 0.72\ \text{L}$$

We *start* with 0.4 L (400 mL) of solution, and need to *end* with 0.72 L of solution. So we need to add (0.72L – 0.4 L) = **0.32 L** to bring the volume of the diluted solution to 0.72 L.

(c) Step 1: Number of moles of protein in our required final solution
= concentration of final solution × volume of final solution
= 50 μM × 500 mL
= 5×10^{-5} mol L^{-1} × 0.5 L
= 0.000025 mol
= 2.5×10^{-5} mol

Step 2:

Volume of stock solution containing required number of moles

$$= \frac{\text{number of moles in final solution}}{\text{concentration of stock solution}}$$

$$= \frac{2.5\times10^{-5}\text{ mol}}{4\text{ mM}}$$

$$= \frac{2.5\times10^{-5}\text{ mol}}{4\times10^{-3}\text{mol L}^{-1}}$$

= 0.00625 L = **6.25 mL**

5.13

In the first 1 mL aliquot there will be 15000 bacteria. During the first dilution step we dilute these 15000 bacteria to a total volume of 5 mL. The concentration of this sample, given that concentration = number of bacteria/volume, is 15000/5 mL or 3000 bacteria/mL.

During the second dilution step we take a 1 mL aliquot of our current dilution, which must contain 3000 bacteria. During the second dilution step we dilute these 3000 bacteria to a total volume of 5 mL. The concentration of this sample, given that concentration = number of bacteria/volume, is 3000/5 mL or 600 bacteria/mL.

During the final dilution step we take a 1 mL aliquot of our current dilution, which must contain 600 bacteria. During the final dilution step we dilute these 600 bacteria to a total volume of 5 mL. The concentration of this sample, given that concentration = number of bacteria/volume, is 600/5 mL or 120 bacteria/mL.

So our final concentration is **120 bacteria/mL**.

5.15

Step 1 We calculate the number of moles of HNO_3 that have reacted:

Number of moles = concentration of HNO_3 × volume of HNO_3 added
= 0.7 M × 18.4 mL
= 0.7 mol L^{-1} × 0.0184 L
= 0.01288 mol (or 1.288×10^{-3} mol)

By inspecting the reaction scheme, $HNO_3 + KOH \rightarrow KNO_3 + H_2O$, we see that HNO_3 and KOH react with a 1:1 stoichiometry. So, 1.288 × 10-3 mol of KOH must have reacted during the titration.

Step 2 We calculate the concentration of KOH:

$$\text{Concentration} = \frac{\text{number of moles of KOH}}{\text{volume of KOH}}$$

We know that 30 mL (or 0.03 L) of KOH was present. So,

$$\text{Concentration} = \frac{1.228\times10^{-3}\,\text{mol}}{0.03\ \text{L}}$$

$$= 0.43\ \text{mol L}^{-1}$$

Therefore, the concentration of KOH present in our sample of KOH is **0.43 mol L^{-1}**

5.15

$$c = \frac{A}{\varepsilon} \quad \Rightarrow \quad \text{concentration} = \frac{\text{Absorbance}}{\text{Molar absorptivity}}$$

$$c = \frac{1.88}{15400}$$

$$= \mathbf{1.22 \times 10^{-4}\ mol\ L^{-1}}$$

Chapter 8

8.3

The central carbon atom participates in four covalent bonds:

1 single bond	1 triple bond
↓	↓
1 × sigma bond	1 × sigma bond 2 × pi bond

⇒ a total of **4** valence electron pairs.

- We can ignore the valence pairs that participate in the two pi bonds
- We are left with a total of **2** valence electron pairs

⇒ a central atom with two valence electron pairs adopts a **linear geometry**

Chapter 12

12.2

The stoichiometry of the reaction scheme tells us that propane and water are present in the ratio 1:4 – that is, for every one mole of propane that reacts, 4 mols of water are yielded.

We are told that 63 g of water is generated. The molar mass of water is 18 g mol^{-1}. So, 63 g of water is equivalent to 3.5 mol:

$$\frac{63\ \text{g}}{18\ \text{g mol}^{-1}} = 3.5\ \text{mol}$$

We know that 3.5 mol of water is produced, and we know that the ratio of propane to water is 1:4. Our unknown quantity is the amount of propane, in mol.

So we can write that $\frac{1}{4} = \frac{x\ \text{mol}}{3.5\ \text{mol}}$

If we multiply through by 3.5 mol to isolate our unknown quantity, we find:

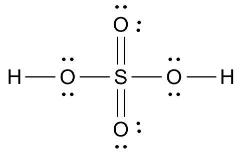
$$3.5\ \text{mol} \times \frac{1}{4} = x\ \text{mol}$$
$$0.875\ \text{mol} = x\ \text{mol}$$

So 0.875 mol of propane yields 3.5 mol of water. The molar mass of propane is 44 g mol^{-1}. 0.875 mol is equivalent to (0.875 mol × 44 g mol^{-1}) = **38.5 g of propane.**

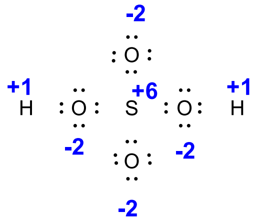
12.8

H_2SO_4

First we must draw a valid Lewis structure for sulfuric acid, showing all bonds and non-bonding electrons:



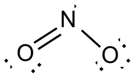
Next we give all the bonding electrons to the most electronegative atom in the bond. We compare this number to the number each atom would have if the electrons in each bond were to be shared equally:



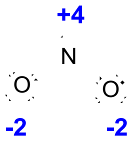
Hydrogen would have one electron if they were shared equally and now has no electrons; it has an oxidation number of +1. Each oxygen has 8 electrons instead of 6 if shared equally so has an oxidation number of -2. Sulfur would have 6 electrons if they were shared equally and now has zero so it has an oxidation number of +6. As a check the molecule should have an oxidation number of zero: (+1+1-2-2-2-2) also equals +6.

NO_2

Draw a Lewis structure that shows all bonding and non-bonding electrons:



Place all bonding electrons on the most electronegative atom and compare to the number each atom would have if the electrons were to be shared equally:



Each oxygen has 8 electrons, but would have 6 if electrons were to be shared equally so has an oxidation number of **-2**.

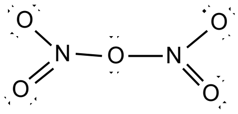
Nitrogen has one electron and would have five if they were shared equally so has an oxidation number of **+4**.

Nitrogen, N_2

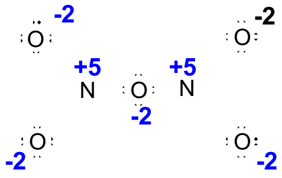
One of the rules for assigning oxidation numbers is that the oxidation state of any element such as Cu, O_2 Cl_2 and N_2, in its uncombined state is **zero**.

Dinitrogen pentoxide, N_2O_5

Draw a Lewis structure showing all bonding and non-bonding electrons:

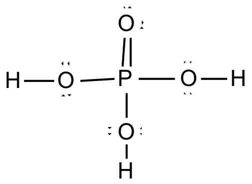


Assign all bonding electrons to the most electronegative atom and compare the electron count with the electrons on each atom if the bonding electrons were to be shared equally; assign the oxidation number accordingly:

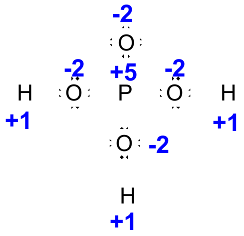


Phosphoric acid, H_3PO_4

Draw a Lewis structure

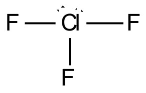


Assign and count electrons:

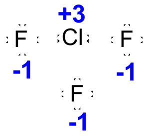


Chlorine trifluoride ClF_3

Draw a Lewis structure. If it helps, show all the non-bonding electrons on the fluorine as well. Halagens have 7 electrons in their outer shell.

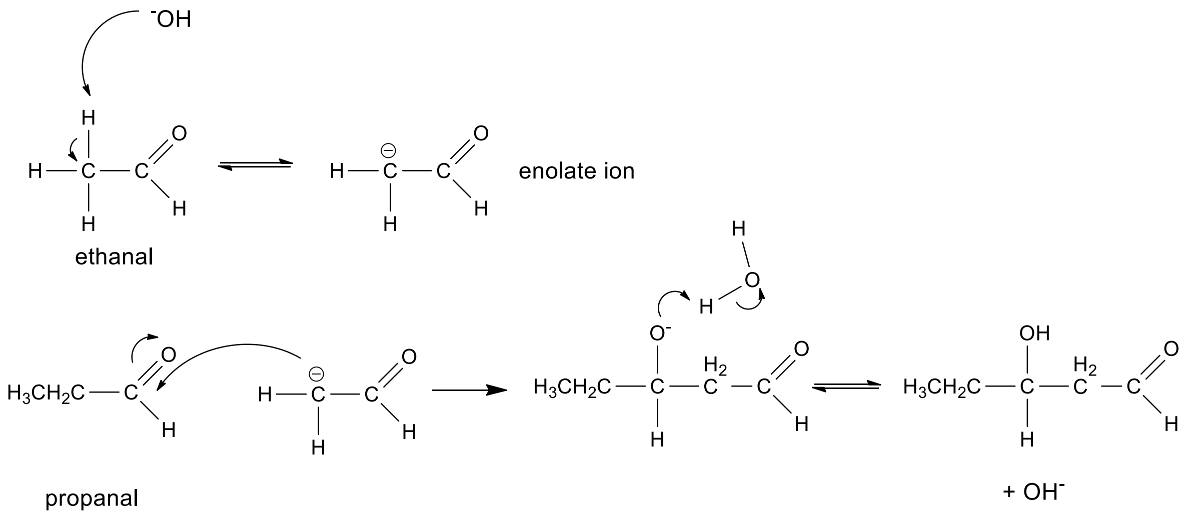


Assign all bonding electrons to the most electronegative atom – in this case fluorine. Compare the number of electrons in the structure you have drawn with the number of electrons on each atom if the electrons had been shared equally and assign the oxidation number accordingly.



Chapter 13

13.5



Chapter 14

14.1

(a) First, we need to convert the speed into units of metres per second. First, we convert km into m. There are 1000 m in 1 km, so the elephant walks at a speed of (7.2 x 1000) m – that is, 7200 m – per hour.

Next, we convert ‘per hour’ into ‘per second’. There are 3600 seconds in 1 hour. If the elephant walks 7200m in one hour (3600 sec) this is a rate of (7200/3600) m or 2 m in just one second (that is, ‘per second’).

So, the elephant walks at a speed of 2 m s^{-1}.

If the elephant has a mass of 5000 kg, then its kinetic energy when running at 2 m s^{-1} is given by:

$E = ½ m v^2$
$= ½ \times 5000\ kg \times (2\ m\ s^{-1})^2$
$= ½ \times 5000\ kg \times 4\ m^2\ s^{-2}$
$= 10000\ kg\ m^2\ s^{-2}$

Now, 1 kg m^2 s^{-2} is equivalent to 1 J (joule). Therefore, the kinetic energy of the elephant is **10000 J** (or 10 kJ).

(b) First, we need to rearrange E = ½ m v^2 to isolate the term we want to evaluate.

If E = ½ m v^2 then $v^2 = \frac{E}{0.5 \times m}$ so $v = \sqrt{\frac{E}{0.5 \times m}}$

We know that E, the kinetic energy of the dog, is 5.5 kJ; we must express this in joules. (5.5 kJ = 5500 J.) We also need to remember that 1 J is equivalent to 1 kg m^2 s^{-2}. Finally, we know that the mass of the dog is 30 kg. So we enter these values into our rearranged expression:

The units of kg on the top and bottom of the fraction cancel each other out

The square root of m^2 s^{-2} is m s^{-1}

$$v = \sqrt{\frac{E}{0.5 \times m}} = \sqrt{\frac{5500\ \text{kg m}^2\text{s}^{-2}}{0.5 \times 30\ \text{kg}}} = \sqrt{\frac{5500\ \text{m}^2\text{s}^{-2}}{15}} = 19\ \text{m s}^{-1}$$

So, the Labrador dog is running at a speed of 19 m s^{-1}.

(c) We begin by converting the speeds into metres per second. We do this in two stages: we convert from miles per hour into metres per hour, and then to metres per second.

First, we convert from miles per hour into kilometres per hour:
1 mile per hour = 1.61 km per hour. So, 40 miles per hour = 64.4 km per hour; 70 miles per hour = 112.7 km per hour.

We then multiply by 1000 to obtain the same value in *metres* per hour:
64400 metres per hour, and 112700 metres per hour.

Then, we divide by 3600 to obtain metres per second (given that there are 3600 seconds in an hour):
64400 metres per hour = 17.9 metres per second
112700 metres per hour = 31.3 metres per second

We're told that the car has a mass of 1250 kg. So we can now enter our values into the expression E = ½ m v^2:

<u>40 miles per hour</u>
E = ½ m v^2
= ½ × 1250 kg × (17.9 m s^{-1})^2
= 200256 kg m^2 s^{-2}
= 200256 J = **200.3 kJ**

<u>70 miles per hour</u>
E = ½ m v^2
= ½ × 1250 kg × (31.3 m s^{-1})^2
= 612306.3 kg m^2 s^{-2}
= 612306.3 J = **612.3 kJ**

14.4

$W = F \times d$

First, we calculate the force:

$F = \text{mass} \times \text{gravitational constant}$

$= 16\ \text{kg} \times 10\ \text{ms}^{-2}$

$= 160\ \text{kg m s}^{-2}$

$$\begin{aligned} W &= F \times d \\ &= 160\ \text{kg m s}^{-2} \times 8\ \text{m} \\ &= 1280\ \text{kg m}^2\ \text{s}^{-2} \end{aligned}$$

$1\ \text{kg m}^2\ \text{s}^{-2} = 1\ \text{J}$, so $1280\ \text{kg m}^2\ \text{s}^{-2}$ = **1280 J**

14.6

(a) $\Delta H = \sum E_{(\text{reactants})} - \sum E_{(\text{products})}$

$\boldsymbol{\sum E_{(\text{reactants})}}$:

$$\begin{aligned} CH_3CH_2OH &= 1(\text{C-C}) + 1(\text{C-O}) + 1(\text{O-H}) + 5(\text{C-H}) \\ &= 348\ \text{kJ mol}^{-1} + 358\ \text{kJ mol}^{-1} + 463\ \text{kJ mol}^{-1} + (5 \times 412\ \text{kJ mol}^{-1}) \\ &= 3229\ \text{kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} 3O_2 &= 3(497\ \text{kJ mol}^{-1}) \\ &= 1491\ \text{kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \boldsymbol{\sum E_{(\text{reactants})}} &= 3229\ \text{kJ mol}^{-1} + 1491\ \text{kJ mol}^{-1} \\ &= 4720\ \text{kJ mol}^{-1} \end{aligned}$$

$\boldsymbol{\sum E_{(\text{products})}}$:

$$\begin{aligned} 2CO_2 &= 2 \times (2 \times \text{C=O}) \\ &= 2 \times (2 \times 740\ \text{kJ mol}^{-1}) \\ &= 2 \times 1480\ \text{kJ mol}^{-1} \\ &= 2960\ \text{kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} 3H_2O &= 3 \times (2 \times \text{O-H}) \\ &= 3\ (2 \times 463\ \text{kJ mol}^{-1}) \\ &= 3 \times 926\ \text{kJ mol}^{-1} \\ &= 2778\ \text{kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \boldsymbol{\sum E_{(\text{products})}} &= 2960\ \text{kJ mol}^{-1} + 2778\ \text{kJ mol}^{-1} \\ &= \mathbf{5738}\ \text{kJ mol}^{-1} \end{aligned}$$

$\Delta H = \sum E_{(\text{reactants})} - \sum E_{(\text{products})}$
$= 4720\ \text{kJ mol}^{-1} - 5738\ \text{kJ mol}^{-1}$

$\mathbf{= -1018\ kJ\ mol^{-1}}$

(b) $\Delta H = \sum E_{(\text{reactants})} - \sum E_{(\text{products})}$

$\boldsymbol{\sum E_{(\text{reactants})}}$**:**

$6CO_2 = 6 \times (2 \times C{=}O)$
$= 6\ (2 \times 740\ \text{kJ mol}^{-1})$
$= 6 \times 1480\ \text{kJ mol}^{-1}$
$= 8880\ \text{kJ mol}^{-1}$

$6H_2O = 6 \times (2 \times O\text{–}H)$
$= 6\ (2 \times 463\ \text{kJ mol}^{-1})$
$= 6 \times 926\ \text{kJ mol}^{-1}$
$= 5556\ \text{kJ mol}^{-1}$

$\sum E_{(\text{reactants})} = 8880\ \text{kJ mol}^{-1} + 5556\ \text{kJ mol}^{-1}$
$= \mathbf{14436\ kJ\ mol^{-1}}$

$\boldsymbol{\sum E_{(\text{products})}}$**:**

$C_6H_{12}O_6 = 7(C\text{–}H) + 1(C{=}O) + 5(C\text{–}C) + 5(C\text{–}O) + 5(O\text{–}H)$

$= (7 \times 412\ \text{kJ mol}^{-1}) + (740\ \text{kJ mol}^{-1}) + (5 \times 348\ \text{kJ mol}^{-1}) +$
$(5 \times 358\ \text{kJ mol}^{-1}) + (5 \times 463\ \text{kJ mol}^{-1})$
$= 2884\ \text{kJ mol}^{-1} + 740\ \text{kJ mol}^{-1} + 1740\ \text{kJ mol}^{-1} + 1790\ \text{kJ mol}^{-1} +$
$2315\ \text{kJ mol}^{-1}$
$= 9469\ \text{kJ mol}^{-1}$

$6O_2 = 6 \times O{=}O$
$= 6 \times 497\ \text{kJ mol}^{-1}$
$= 2982\ \text{kJ mol}^{-1}$

$\sum E_{(\text{products})} = 9469\ \text{kJ mol}^{-1} + 2982\ \text{kJ mol}^{-1}$

$= \mathbf{12451\ kJ\ mol^{-1}}$

$\Delta H = \sum E_{(\text{reactants})} - \sum E_{(\text{products})}$

$= 14436\ \text{kJ mol}^{-1} - 12451\ \text{kJ mol}^{-1}$

$= \mathbf{+1985\ kJ\ mol^{-1}}$

14.8

(a) First, we evaluate $\Delta H^{\circ}_{f(products)}$:

$\Delta H^{\circ}_{\text{f (products)}} = \Delta H^{\circ}_{\text{f}}(2CH_3CO_2H(l)) + \Delta H^{\circ}_{\text{f}}(2CO_2(g)) + \Delta H^{\circ}_{\text{f}}(2H_2O(l))$

$=(2\times(-248.1\ \text{kJ mol}^{-1}) + (2\times(-393.5\ \text{kJ mol}^{-1}) + (2\times(-285.8\ \text{kJ mol}^{-1}))$

$= -1854.8\ \text{kJ mol}^{-1}$

We then evaluate $\Delta H^{\circ}_{f(reactants)}$:

$\Delta H^{\circ}_{\text{f (reactants)}} = \Delta H^{\circ}_{\text{f}}(2O_2(g)) + \Delta H^{\circ}_{\text{f}}(C_6H_{12}O_6(s))$

$=0 + (-1274.4\ \text{kJ mol}^{-1})$

$= -1274.4\ \text{kJ mol}^{-1}$

So, $\Delta H^{\circ}_{reaction}$ = (-1854.8 kJ mol^{-1}) – (-1274.4 kJ mol^{-1}) = **-580.4 kJ mol^{-1}**

14.11

$$\Delta S = \frac{\Delta q}{T}$$

Δq = 4.932 kJ or 4932 J

T = 30°C = (30+273) K = 303 K

$$\Delta S = \frac{4932\text{J}}{303\text{K}} = \mathbf{16.28\ J\ K^{-1}}$$

14.12

(a)

$$\Delta S = \frac{\Delta q}{T}$$

Δq = 50 kJ or 50000 J

T = 0°C = (0+273) K = 273 K

$$\Delta S = \frac{50000\text{J}}{273\text{K}} = 183.15\ \text{J K}^{-1}$$

(b) T now equals (100 + 273)K = 373 K

$\Delta S = \frac{50000\text{J}}{373\text{K}}$ = 134.05 J K^{-1}

14.13

First, we calculate ΔH° for the reaction by using the relationship

$$\Delta H^\circ_{reaction} = \Delta H^\circ_{f(products)} - \Delta H^\circ_{f(reactants)}$$
$$= ((-166.36 \text{ kJ mol}^{-1}) + (-393.51 \text{ kJ mol}^{-1})) - (-584.5 \text{ kJ mol}^{-1})$$
$$= -559.87 \text{ kJ mol}^{-1} + 584.5 \text{ kJ mol}^{-1}$$
$$= +24.63 \text{ kJ mol}^{-1}$$

We then feed our known variables into the equation

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
$$-53.33 \text{ kJ mol}^{-1} = +24.63 \text{ kJ mol}^{-1} - (298\text{K} \times \Delta S^\circ)$$
$$-77.96 \text{ kJ mol}^{-1} = -(298\text{K} \times \Delta S^\circ)$$
$$-\Delta S^\circ = \frac{-77.96 \text{ kJ mol}^{-1}}{298\text{K}}$$
$$= -0.2616 \text{ kJ K}^{-1} \text{ mol}^{-1}$$
$$\text{So } \Delta S^\circ = \mathbf{261.6 \text{ J K}^{-1} \text{ mol}^{-1}}$$

14.14

(a) $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$
ΔH° = -63 kJ mol^{-1}
T = 310 K
ΔS° = 220 J K^{-1} mol^{-1}

Convert ΔS° into kJ

ΔG° = -63 kJ mol^{-1} – ((310 K) × $\frac{220}{1000}$kJ K^{-1} mol^{-1})
= -63 kJ mol^{-1} – (310 K × 0.22 kJ K^{-1} mol^{-1})
= -63 kJ mol^{-1} – 68.2 kJ mol^{-1}

= -131.2 kJ mol^{-1}

Chapter 15

15.1

(b) $$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{[0.34]^2}{[0.185][0.098]^3}$$

$$= \frac{0.1156}{(0.185)\times(0.0009412)}$$

$$= \frac{0.1156}{0.0001741}$$

K_c = 664

15.2

$$p_{O_2} = x_{O_2} \times p$$
$$= 0.21 \times 33.7 \text{ kPa}$$
$$= 7.08 \text{ kPa}$$

15.3

$$K_p = \frac{(p_{CO})\times(p_{O_2})^{1/2}}{(p_{CO_2})} = \frac{(5.066\times10^{-47})\times(20.27)^{1/2}}{(30.40)} = \frac{2.2808\times10^{-46}}{30.4}$$
$$= 7.50\times10^{-48}$$

15.7

$$Q = \frac{[ADP][Pi]}{[ATP]}$$

$$= \frac{(0.003)\times(0.001)}{0.01}$$

$$= 0.0003$$

15.8

$$Q = \frac{[HI]^2}{[H_2][I_2]}$$

$$Q = \frac{[0.3]^2}{[1.3][0.7]}$$

$$Q = \frac{0.09}{0.91}$$

Q = 0.099

The value of K for the reaction is 51. $Q < K$ so the reaction proceeds from left to right (in the direction of the forward reaction) to reach equilibrium.

15.12

(a)

(i) ΔG $= -RT\ln K$
$= -(8.31 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (\ln 4.2 \times 10^{-7})$
$= -(2476.38 \text{ J mol}^{-1}) \times (-14.68)$
$= 36353.26 \text{ J mol}^{-1}$
= **36.4 kJ mol^{-1}**

(ii) ΔG $= -RT\ln K$
$= -(8.31 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (\ln 2.25 \times 10^{12})$
$= -(2476.38 \text{ J mol}^{-1}) \times (28.44)$
$= -70428.25 \text{ J mol}^{-1}$
= **–70.4 kJ mol^{-1}**

(iii) ΔG $= -RT\ln K$
$= -(8.31 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (\ln 9.4 \times 10^{-1})$
$= -(2476.38 \text{ J mol}^{-1}) \times (-0.062)$
$= 153.54 \text{ J mol}^{-1}$
= **0.153 kJ mol^{-1}**

(iv) ΔG $= -RT\ln K$
$= -(8.31 \text{ J K}^{-1} \text{ mol}^{-1}) \times (298 \text{ K}) \times (\ln 3.3 \times 10^{81})$
$= -(2476.38 \text{ J mol}^{-1}) \times (187.70)$
$= -464816.5 \text{ J mol}^{-1}$
= **–465 kJ mol^{-1}**

15.13

$$
\begin{aligned}
K &= \exp\left(\frac{-\Delta G^{\circ'}}{RT}\right) \\
&= \exp\left(\frac{-(-44\text{kJ mol}^{-1})}{8.31\text{JK}^{-1}\text{mol}^{-1}\times 298\text{K}}\right) \\
&= \exp\frac{+44\text{kJ mol}^{-1}}{2476.4\text{Jmol}^{-1}} \\
&= \exp\frac{44\times10^{3}\,\text{J mol}^{-1}}{2476.4\text{J mol}^{-1}} \\
&= \exp(17.77) \\
K &= 5.22\times10^{7}
\end{aligned}
$$

Chapter 16

16.4

Imagine that we start off with a drug at a concentration of 1M. The concentration will halve after each successive half-life as follows:

After half-life 1: 0.5 M
After half-life 2: 0.25 M
After half-life 3: 0.125 M
After half-life 4: 0.0625 M
After half-life 5: 0.0313 M
After half-life 6: 0.0157 M
After half-life 7: 0.0078 M

So, after seven half-lives, the concentration of the drug will be just 0.78% of its starting concentration – meaning that 99.22% will have been eliminated.

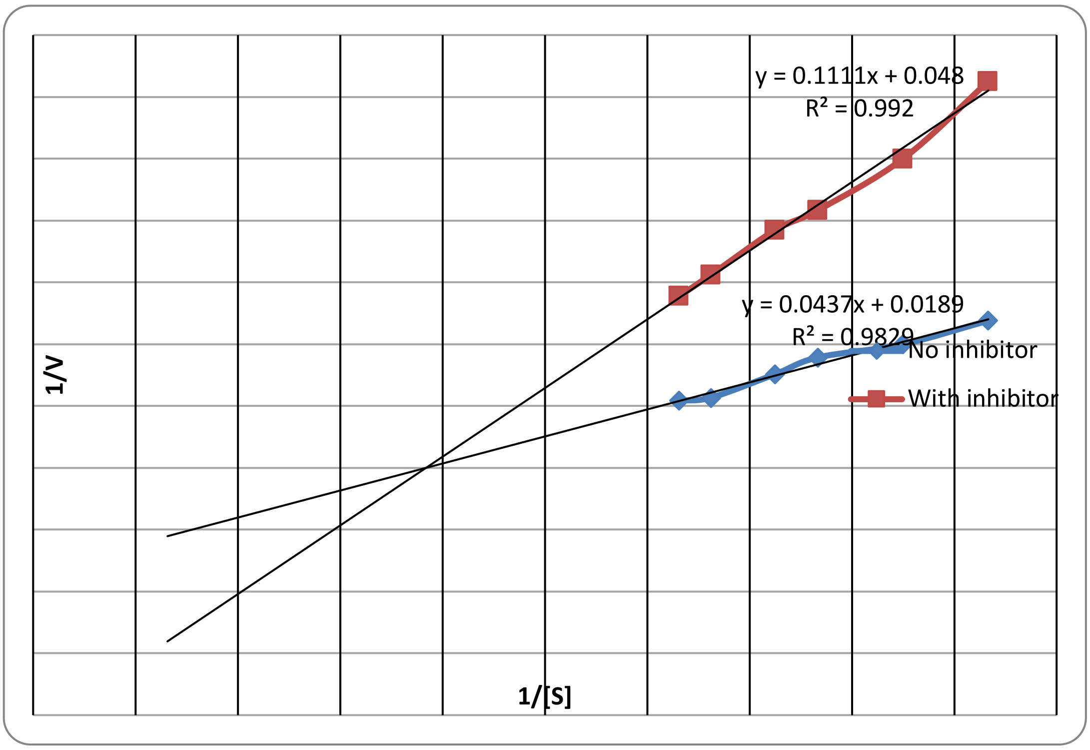
16.6

$$
v = \frac{\text{V}_{\text{max}}[\text{S}]}{K_{\text{M}}+[\text{S}]}
$$

$$
\begin{aligned}
\text{v} &= \frac{(15.2\text{ mmol mg}^{-1}\text{min}^{-1})\times 60\text{mM}}{105\text{mM}+60\text{mM}} \\
&= \frac{(15.2\text{ mmol mg}^{-1}\text{min}^{-1})\times 60\text{mM}}{165\text{mM}} \\
&= \frac{912\text{ mmol mg}^{-1}\text{min}^{-1}}{165} \\
&= 5.53\text{ mmol mg}^{-1}\text{min}^{-1}
\end{aligned}
$$

16.8

Your plot should look something like this:



Note that the two plots show that V_{max} is different in the presence and absence of inhibitor (the lines cross the y-axis at different points) but K_M is unchanged (the lines meet at the same point on the x-axis), which tells us that we are seeing noncompetitive inhibition.

Chapter 17

17.4

(a) pK_a = –log (2 × 10^{-5})
= **–(–4.70)**
= 4.70

(b) pK_b = –log (5.6 × 10^{-10})
= **–(–9.25)**
= 9.25

17.5

$[H^+][OH^-] = 10^{-14}$
$[OH^-] = 10^{-7}$

So $[H^+][10^{-7}] = 10^{-14}$

$[H^+] = \frac{10^{-14}}{10^{-7}}$

$[H^+]$ **$= 10^{-7}$ M**

17.6

(a) $K_a \times K_b = 1 \times 10^{-14}$

$K_b = 2.4 \times 10^{-8}$ M

$K_a \times (2.4 \times 10^{-8}) = 1 \times 10^{-14}$

$K_a = \frac{(1 \times 10^{-14})}{(2.4 \times 10^{-8})}$

$K_a = 4.2 \times 10^{-7}$ M

(b) $K_a \times K_b = 1 \times 10^{-14}$

$K_a = 2 \times 10^{-4}$ M

$K_b \times (2 \times 10^{-4}) = 1 \times 10^{-14}$

$K_b = \frac{(1 \times 10^{-14})}{(2 \times 10^{-4})}$

$K_b = 5 \times 10^{-11}$ M

17.7

Acid dissociation constant: $\mathrm{HA + H_2O \rightleftharpoons H_3O^+ + A^-}$

$$K_a = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}][\mathrm{H_2O}]}$$

And base dissociation constant $\mathrm{A^- + H_2O \rightleftharpoons HA + OH^-}$

$$K_b = \frac{[\mathrm{HA}][\mathrm{HO^-}]}{[\mathrm{A^-}][\mathrm{H_2O}]}$$

$$K_a \times K_b = \frac{[\mathrm{H_3O^+}][\mathrm{A^-}]}{[\mathrm{HA}][\mathrm{H_2O}]} \times \frac{[\mathrm{HA}][\mathrm{HO^-}]}{[\mathrm{A^-}][\mathrm{H_2O}]}$$

$$K_a \times K_b = [\mathrm{H_3O^+}][\mathrm{HO^-}] = K_w$$

If $K_w = K_a + K_b$

Then if we take logs of both sides $pK_w = pK_a + pK_b$

17.8

(a) pH $= –\log [H^+]$
$= –(\log (4.5 \times 10^{–5}))$
$= –(–4.35)$
= **4.35**

(b) pH $= –\log [H^+]$
$= –(\log (3.2 \times 10^{–7}))$
$= –(–6.49)$
= **6.49**

(c) pH $= –\log [H^+]$
So $3.0 = –\log [H^+]$
$-3.0 = \log [H^+]$

To isolate $[H^+]$ we use the rule that if y = log x, x = 10^y
So $[H^+] = 10^{-3}$
= **0.001 mol L^{-1}**

17.9

(a) pH $= –\log [H^+]$
$= –(\log (3.2 \times 10^{–3}))$
$= –(–2.49)$
= **2.49**

(b)
$[H_2SO_4] = 1.4 \times 10^{-2}$ mol L^{-1}. Therefore $[H^+] = 2 \times (1.4 \times 10^{-2}$ mol L$^{-1}) = 2.8 \times 10^{-2}$ mol L^{-1}

pH $= -\log [H^+]$.
So pH $= -\log [2.8 \times 10^{-2}$ mol L$^{-1}]$
$= - (-1.55)$
= **1.55**

17.10:

First, we can write down that:

$$K_a = 1.4 \times 10^{-4} = \frac{[H_3O^+][\text{lactate}]}{[\text{lactic acid}]}$$

If we set *x* to be the amount of lactic acid that has dissociated, and note that we started with 0.2 M (or 200 mM), we can write:

$$1.4 \times 10^{-4} = \frac{[x][x]}{[0.2 - x]}$$

We use the assumption that *x* is small, and so set 0.2 – *x* = 0.2

$1.4 \times 10^{-4} = \frac{[x]^2}{0.2}$

We then rearrange the equation to give:

$1.4 \times 10^{-4} \times 0.2 = [x]^2$

So

$x^2 = 2.8 \times 10^{-5}$

$x = \sqrt{2.8 \times 10^{-5}} = 0.0053$

So, for every 0.2 mol of lactic acid present at the start of the reaction, 0.0053 mol dissociated into hydrogen ions and lactate.

We can now calculate the pH:

pH = -log $[H^+]$
= -log 0.0053
= 2.3

17.11

(a) Substitute the values into the Henderson Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_\mathrm{a} + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\mathrm{pH} = 3.86 + \log\frac{0.045}{0.028}$$

$$\mathrm{pH} = 3.86 + \log 1.64$$

$$\mathrm{pH} = 3.86 + 0.216$$

$$\mathrm{pH} = 4.08$$

(b) In order to calculate a pH we need to know the concentration of H^+ in solution. However, citric acid is a weak acid, so only a small amount of it dissociates into citrate and H^+ at equilibrium.

$$\mathrm{CitCOOH} \rightleftharpoons \mathrm{CitCOO^-} + \mathrm{H^+}$$

If the pK_a of citric acid is 3.14, K_a is 7.2 x 10^{-4} (antilog -3.14)

$$K_a = \frac{[\mathrm{CitCOO^-}][\mathrm{H^+}]}{[\mathrm{CitCOOH}]} = 7.2 \times 10^{-4}$$

If we call the amount of citric acid which dissociates *x* then we can draw up the following table showing the concentration of all species at the beginning of the reaction and when equilibrium is reached:

$$\begin{array}{cccc} \text{CitCOOH} & \rightleftharpoons & \text{CitCOO}^- & + \text{H}^+ \\ 0.15 & & 0 & 0 \\ 0.15- x & & x & x \end{array}$$

	Substance		
	CitCOOH	CitCOO^-	H^+
Initial concentration (mol L^{-1})	0.15	0	0
Change in concentration	$-x$	x	x
Equilibrium concentration (mol L^{-1})	$0.15-x$	x	x

We can substitute these values into the equilibrium equation:

$$K_a = \frac{[\text{CitCOO}^-][\text{H}^+]}{[\text{CitCOOH}]} = \frac{x^2}{0.15-x} = 7.2\times10^{-4}$$

We can either solve the quadratic equation or use the approximation that *x* is so small that we can ignore it on the denominator.

Therefore:

$$K_a = \frac{[\text{CitCOO}^-][\text{H}^+]}{[\text{CitCOOH}]} = \frac{x^2}{0.15-x} = 7.2\times10^{-4}$$

$$x^2 = 0.15\times(7.2\times10^{-4}) = 1.08\times10^{-4}$$

$$x = 0.0104 = 1.04\times10^{2}$$

Since *x* is indeed small, our approximation was valid. Moreover, recall that we called *x* the amount of citric acid that is dissociated at equilibrium so *x* is also the concentration of H^+. So we can now calculate the pH of the solution:

$$\text{pH} = -\log[\text{H}^+] = -\log(0.0104)$$

$$\text{pH} = 1.98$$

17.12

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

First, we recall that pK_a = –log K_a = –log (1.77×10^{-5}), and we know that the pH = 2.88. So:

$$2.88 = -\log(1.77 \times 10^{-5}) + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

$$2.88 = 4.75 + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

$$-1.87 = \log\frac{[\text{A}^-]}{[\text{HA}]}$$

We then use the relationship that if y = log x, x = 10^y

$$\log\frac{[\text{A}^-]}{[\text{HA}]} = 10^{-1.87} = 0.013$$

So the ratio of base (A^-) to undissociated acid (HA) at equilibrium is 0.013.

We can equate 'base' with 'dissociated acid' so can say that the ratio of dissociated acid to undissociated acid is 0.013.

If we take the percentage of undissociated acid to be *x*, and the percentage of dissociated acid to be (100-*x*)%, we can write that

$$\frac{(100-x)}{x} = 0.013$$

We can then solve this equation:

$$\frac{(100-x)}{x} = 0.013$$

$$100 - x = 0.013x$$

$$1.013x = 100$$

$$x = 98.7$$

So, 98.7% of the ethanoic acid is undissociated, meaning that 1.3% has dissociated. This is what we'd expect for a weak acid (which, by definition, only dissociates to a limited extent).

17.16

Ratio of dissociated to undissociated acid = $10^{(\text{pH}-\text{p}K_a)}$
= $10^{(7.0-8.4)}$ = $10^{-1.4}$ = 0.04

If we let % of undissociated acid = *x*, then $x = \frac{100}{(0.04+1)} = 96.2\%$

So, 3.8% is dissociated.

17.18

$$\begin{aligned}\text{pH} &= \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}\\ &= 3.85 + \log\frac{(0.034)}{(0.03)}\\ &= 3.85 + \log(1.133)\\ &= 3.85 + 0.054\\ &= 3.90\end{aligned}$$

17.19
(a)

$$\text{pH} = \text{p}K_a + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

We are trying to achieve a pH of 9.1, and the pK_a of the ammonium ion is 9.25. Therefore

$$9.1 = 9.25 + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

Subtracting 9.25 from both sides to isolate the logarithmic term, we get:

$$-0.15 = \log\frac{[\text{A}^-]}{[\text{HA}]}$$

If $\log\frac{[\text{A}^-]}{[\text{HA}]} = -0.15$, $\frac{[\text{A-}]}{[\text{HA}]} = 10^{-0.15} = 0.71$. The conjugate base, A-, is ammonia, and the weak acid, HA, is the ammonium ion. Therefore, the ratio of conjugate base to weak acid that is needed in the buffer solution is **0.71:1**.

(b) Percentage of ammonia $= \left(\frac{0.71}{1.71}\right)\times 100 = 41.5\%$

Percentage of ammonium ion $= \left(\frac{1}{1.71}\right)\times 100 = 58.5\%$

We need a final volume of 200 mL 41.5% of 200 mL = (0.415 × 200) = 83 mL. 58.5% of 200 mL = (0.585 × 200) = **117 mL.**

So the required volume of ammonia is 83 mL, and the required volume of ammonium ion is 117 mL.

17.20
The first thing to remember is that the equation for a weak base dissolved in water lies almost completely to the right hand side of the equation:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^- \qquad (1)$$

The second thing to remember is that a weak acid reacts almost completely with a strong acid so equation (2) lies almost completely to the right hand side.

$$HA + HO^- \rightleftharpoons H_2O + A^- \qquad (2)$$

Let v L of NaOH be added.

The amount of NaOH added is (0.30 × v) mol and this is the amount of A- present in the new solution according to equation (2).

Hence the amount of HA is $(((50 \times 10^{-3}) \times 0.28) - 0.30v))$

We can now substitute these values into the Henderson Hasselbalch equation:

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$4.20 = 4.262 + \log\left(\frac{0.30\mathrm{v}}{((50\times10^{-3})\times0.28) - 0.30\mathrm{v}}\right)$$

Hence

$$\frac{0.30\mathrm{v}}{((50\times10^{-3})\times0.28) - 0.30\mathrm{v}} = 10^{4.20-4.262} = 0.867$$

$$\frac{0.30\mathrm{v}}{0.014 - 0.30\mathrm{v}} = 0.867$$

$0.30v = 0.867(0.014-0.30v)$
$0.30v = 0.012 - 0.260v$
$0.56v = 0.012$
v = 0.0214

Therefore 21.4 mL of NaOH is required.

Maths tools

MT 4.1

(a)

Let's break this down into two components:

Using the rule log ab = log a + log b we can write that log 2a = log 2 + log a

Using the rule $\log\frac{a}{b} = \log a - \log b$ we can write that $\log\frac{a}{2} = \log a - \log 2$

So, we can write:

$y = \log 2a + \log\frac{a}{2}$ as $y = \log 2 + \log a + \log a - \log 2$, which simplifies to $y = 2\log a$

(b)

(i) We start with $c = 2a + \log\frac{1}{b}$

Using the rule $\log\frac{1}{b} = -\log b$ we can write that $c = 2a - \log b$

We need to isolate b, so we first rearrange the equation to give $\log b = 2a - c$

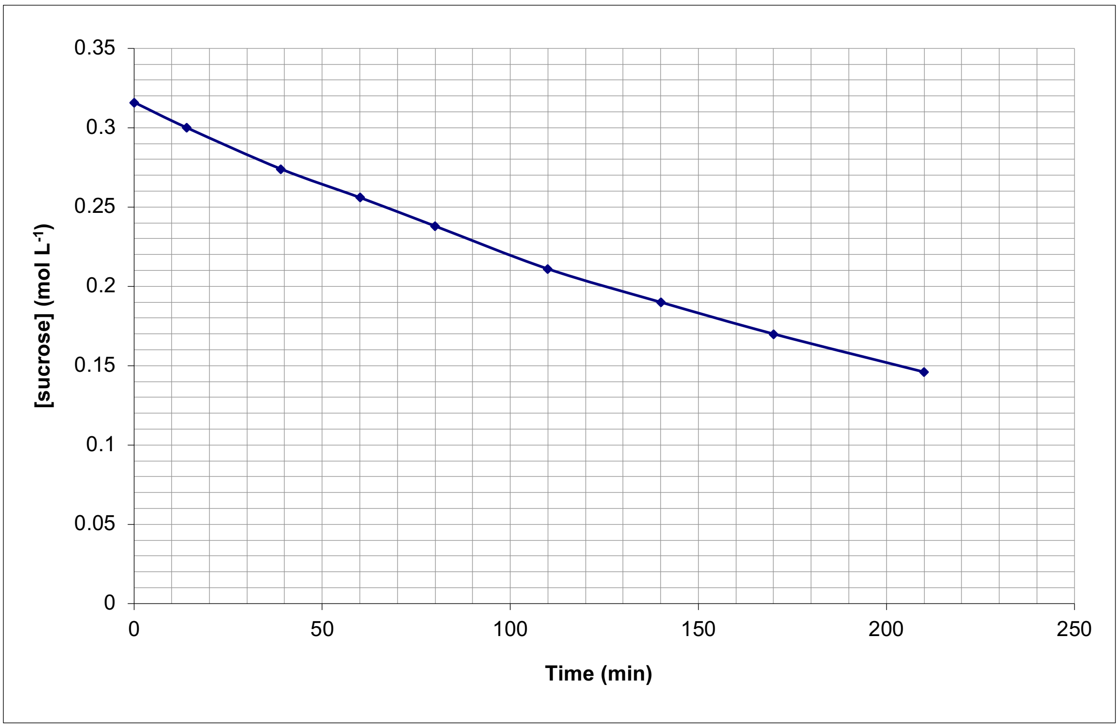
We then use the rule that if log y = x, y = 10^x.

So we can write that $b = 10^{(2a-c)}$

(ii) If a = 0.5 and c = 2, then b = $10^{(1-2)} = 10^{-1} = 0.1$

MT 5.1

The data should generate a plot similar to this:



The gradient of the tangent to the curve at 80 mins will give a negative value (as the curve is sloping downwards). However, when we express the rate, we simply state the value without worrying about the sign (whether it is positive or negative).

MT 6.1

We start with $1.4\times10^{-4}=\dfrac{(x^2)}{(0.15-x)}$, which we can rearrange to give $1.4\times10^{-4}(0.15-x)=x^2$.

If we multiply out the expression on the left hand side of the equation, we get

$2.1\times10^{-5}-1.4\times10^{-4}x=x^2$, which we can write as
$x^2+1.4\times10^{-4}x-2.1\times10^{-5}=0$

Considering the general form of the quadratic equation, $ax^2 + bx + c$, our values are:
a = 1; b = 1.4×10^{-4}; c = -2.1×10^{-5}

We then use $x=\dfrac{-b\pm\sqrt{b^2-4ac}}{2a}$:

$$x = \frac{-(1.4\times10^{-4}) \pm \sqrt{(1.4\times10^{-4})^2 - (4\times1\times(-2.1\times10^{-5}))}}{(2\times1)}$$

$$= \frac{(-1.4\times10^{-4}) \pm \sqrt{(1.96\times10^{-8}) + (8.4\times10^{-5})}}{2}$$

$$= \frac{(-1.8\times10^{-5}) \pm \sqrt{8.40196\times10^{-5}}}{2}$$

$$= \frac{(-1.8\times10^{-5}) \pm 9.166\times10^{-3}}{2}$$

So, $x = 4.574 \times 10^{-3}$ or -9.18×10^{-3}

As some of the acid has dissociated, the correct value of x is the positive one: 4.574×10^{-3} mol of lactic acid has dissociated.