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# Fundamentals

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## Answers to worked examples

### WE 1.1 Derived units

Work out the SI derived unit for molar mass (the mass of one mole of a substance).

#### Strategy

Write an equation for the molar mass and substitute the SI units for the various quantities.

#### Solution

Molar mass is the mass of substance per mole

$$M = m/n$$

where  $m$  is the mass of substance, which in the SI system has the unit **kg**, and  $n$  the amount of substance, which has the unit **mol**. The units of molar mass are therefore

$$\frac{\text{kg}}{\text{mol}} = \text{kg mol}^{-1}$$

Molar masses are often quoted in units of **g mol<sup>-1</sup>** and it is important to be careful to remember to convert them to **kg mol<sup>-1</sup>** before substituting into an equation or calculation.

### WE 1.3 Relative atomic mass of magnesium

Naturally occurring bromine contains <sup>79</sup>Br (abundance 50.69%) and <sup>81</sup>Br (abundance 49.31%). Calculate the relative atomic mass of naturally occurring bromine.

### **Strategy**

Use the relative abundances to calculate a weighted average relative atomic mass.

### **Solution**

The average relative atomic mass is given by the weighted average of the masses of the individual isotopes

$$\bar{A}_r = \sum_i x_i A_{r,i}$$

where  $x_i$  indicates the relative abundance of isotope  $i$ , and  $A_{r,i}$  is the relative atomic mass of isotope  $i$ . A percentage of 50.69 indicates a relative abundance of

$$50.69\% = 50.69/100 = 0.5069$$

so, using the precise relative atomic masses for the isotopes in Table 1.5, then

$$\bar{A}_r = 0.5069 \times 78.9183 + 0.4931 \times 80.9163 = 79.90$$

where the solution has been quoted to four significant figures because this is the same level of precision as for the relative abundances.

## **WE 1.5 Empirical formulae and molecular formulae**

A compound was found to contain 1.18% hydrogen, 42.00% chlorine, and 56.82% oxygen by mass. What is its empirical formula?

### **Strategy**

Determine the relative amounts, i.e. number of moles, of each element in 100 g of the compound from the relative composition by mass, using Equation 1.2. Find the simplest ratio, and hence the empirical formula, by dividing by the smallest relative amount.

### **Solution**

The compound contains 56.82% oxygen by mass. Thus, 100 g of the compound must contain 56.82 g of oxygen. According to Equation 1.2, this is equivalent to a relative amount of

$$n_{\text{O}} = m_{\text{O}}/M_{\text{O}} = 56.82 \text{ g}/16.00 \text{ g mol}^{-1} = 3.551 \text{ mol}$$

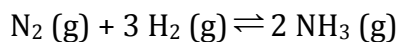
Setting the calculations for the other elements as a table,

	<b>H</b>	<b>Cl</b>	<b>O</b>
% mass	1.18%	42.00%	56.82%
mass, $m$	1.18 g	42.00 g	56.82 g
amount, $n$	$\frac{1.18 \text{ g}}{1.01 \text{ g mol}^{-1}}$ = 1.17 mol	$\frac{42.00 \text{ g}}{35.45 \text{ g mol}^{-1}}$ = 1.18 mol	$\frac{56.82 \text{ g}}{16.00 \text{ g mol}^{-1}}$ = 3.55 mol
ratio	$\frac{1.17 \text{ mol}}{1.17 \text{ mol}} = 1.00$	$\frac{1.17 \text{ mol}}{1.17 \text{ mol}} = 1.01$	$\frac{3.55 \text{ mol}}{1.17 \text{ mol}} = 3.00$

The simplest ratio of the amounts of the elements is thus H:Cl:O = 1:1:3, so that the empirical formula is HClO<sub>3</sub>.

### WE 1.7 Percentage yield of a reaction

In the Haber process, nitrogen reacts with hydrogen to form ammonia:



The reaction does not go to completion and an equilibrium mixture of reactants and products is formed. To investigate the equilibrium, 1.00 mol of nitrogen and 3.00 mol of hydrogen are sealed in a container at 100 atm pressure and 400°C. The equilibrium mixture contains 8.57 g of ammonia. What is the percentage yield of the reaction?

#### **Strategy**

Determine the maximum theoretical yield of ammonia from the stoichiometry of the reaction and the amounts of starting materials. Calculate the percentage yield from the ratio of the actual to the theoretical yield.

#### **Solution**

The stoichiometry of the reaction shows that when 1.00 mol of nitrogen is mixed with 3.00 mol of hydrogen, the maximum theoretical yield of ammonia is 2.00 mol. The molar mass of ammonia is

$$M = [14.00 + (3 \times 1.01)] \text{ g mol}^{-1} = 17.03 \text{ g mol}^{-1}$$

Thus, the maximum theoretical yield is

$$m = n \times M = 2.00 \text{ mol} \times 17.03 \text{ g mol}^{-1} = 34.06 \text{ g}$$

Then, using Equation 1.4,

$$\text{percentage yield} = \frac{\text{actual yield}}{\text{theoretical yield}} \times 100 = \frac{8.57 \text{ g}}{34.06 \text{ g}} \times 100 = 25.2\%$$

### WE 1.9 Naming inorganic compounds

What are the systematic names for (a) SeF<sub>4</sub> and (b) Fe(ClO<sub>4</sub>)<sub>3</sub>?

#### Strategy

Follow the rules for naming inorganic compounds on P.30–31.

#### Solution

(a) Selenium and fluorine can combine in more than one way, so the numbers of atoms in the formula need to be identified. Fluorine is more electronegative, so the compound is selenium tetrafluoride.

(b) Iron forms more than one type of ion, so the oxidation state needs to be indicated. The anion is perchlorate, ClO<sub>4</sub><sup>−</sup>, so the compound is iron(III) perchlorate or iron(III) chlorate(VII). Using IUPAC nomenclature, it is iron(III) tetraoxidochlorate(1−).

### WE 1.11 Constructing and balancing a redox equation from half equations

Fe<sup>2+</sup> ions are oxidized to Fe<sup>3+</sup> by MnO<sub>4</sub><sup>−</sup> ions in acidic solution. The MnO<sub>4</sub><sup>−</sup> ions are reduced to Mn<sup>2+</sup> ions. Construct half equations and a balanced overall equation for the reaction.

#### Strategy

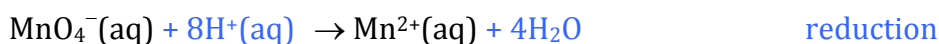
Write unbalanced half equations. Then balance the primary elements and then balance the secondary elements such as H and O. Balance the charge by adding electrons where appropriate. Finally, combine the two half equations, multiplying the equations as appropriate in order to ensure that the number of electrons balances. Cancel any components that appear on both sides of the equation.

### Solution

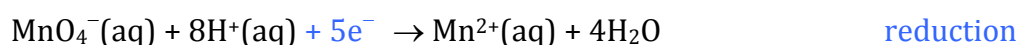
**Steps 1 and 2:** Writing the unbalanced half equations



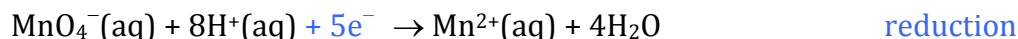
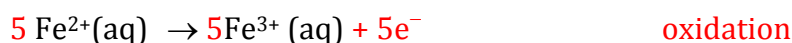
**Step 3:** Balance O and H by adding H<sub>2</sub>O and H<sup>+</sup> ions (in acidic solution)



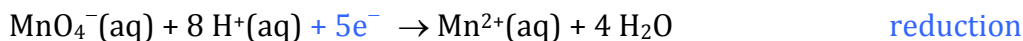
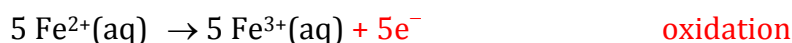
**Step 4:** Balance electric charge by adding electrons



**Step 5:** Multiply oxidation half equation  $\times 5$ , so number of electrons transferred is same in both half equations.



**Step 6:** Add the two half equations and cancel out the electrons



**Steps 7 and 8** No further simplification is necessary as atoms and charges balance.

### **WE 1.13 Finding out how much solute is in a given volume of solution**

A solution of sodium carbonate has a concentration of 0.157 mol dm<sup>-3</sup>. What volume of solution contains exactly 1.00 g of sodium carbonate?

#### Strategy

Determine the amount of sodium carbonate that corresponds to 1.00 g by calculating the molar mass and applying Equation 1.2. Use the definition of concentration to determine the volume of solution.

#### Solution

The molar mass of sodium carbonate, Na<sub>2</sub>CO<sub>3</sub>, is

$$M_{\text{Na}_2\text{CO}_3} = [(2 \times 22.99) + 12.00 + (3 \times 16.00)] \text{ g mol}^{-1} = 105.98 \text{ g mol}^{-1}$$

Using Equation 1.2, the amount of sodium carbonate in 1.00 g is

$$n_{\text{Na}_2\text{CO}_3} = m_{\text{Na}_2\text{CO}_3}/M_{\text{Na}_2\text{CO}_3} = 1.00 \text{ g}/105.98 \text{ g mol}^{-1} = 9.43 \times 10^{-3} \text{ mol}$$

Working out the volume from first principles, and the definition of concentration as the ratio of the amount of substance to the volume,

$$[\text{Na}_2\text{CO}_3] = n_{\text{Na}_2\text{CO}_3}/V$$

so that

$$V = n_{\text{Na}_2\text{CO}_3}/[\text{Na}_2\text{CO}_3] = 9.43 \times 10^{-3} \text{ mol}/0.157 \text{ mol dm}^{-3} = 60.1 \times 10^{-3} \text{ dm}^3$$

which is equivalent to a volume of 60.1 cm<sup>3</sup> because 1 cm<sup>3</sup> = 10<sup>-3</sup> dm<sup>3</sup>.

### WE 1.15 Gravimetric analysis

A 4.500 g sample of an oil containing the pesticide DDT (C<sub>14</sub>H<sub>9</sub>Cl<sub>5</sub>) was heated with sodium in alcohol to liberate all the chlorine present as Cl<sup>-</sup> ions. The mixture was treated with silver nitrate solution and 1.509 g of AgCl were recovered. Calculate the percentage (by mass) of DDT in the sample.

#### Strategy

Calculate the molar mass of silver chloride, AgCl, and hence the amount of chloride, Cl<sup>-</sup>, ions. Use the stoichiometry of DDT to determine the amount of that compound. Calculate the molar mass of DDT and thus the total mass of DDT present in the sample of oil. Finally, find the percentage by mass as the ratio of the total mass of DDT to the mass of the oil sample.

#### Solution

The molar mass of silver chloride is

$$M_{\text{AgCl}} = (107.87 + 35.45) \text{ g mol}^{-1} = 143.32 \text{ g mol}^{-1}$$

Thus, 1.509 g of silver chloride corresponds to

$$n_{\text{AgCl}} = m_{\text{AgCl}}/M_{\text{AgCl}} = 1.509 \text{ g}/143.32 \text{ g mol}^{-1} = 0.01053 \text{ mol}$$

Each DDT molecule contains five chlorine atoms, so that

$$n_{\text{DDT}} = n_{\text{AgCl}}/5 = 0.01053 \text{ mol}/5 = 2.106 \times 10^{-3} \text{ mol}$$

The molar mass of DDT is

$$M_{\text{DDT}} = [(14 \times 12.00) + (9 \times 1.01) + (5 \times 35.45)] \text{ g mol}^{-1} = 354.34 \text{ g mol}^{-1}$$

so that the mass of DDT in the sample of oil is

$$m_{\text{DDT}} = n_{\text{DDT}} \times M_{\text{DDT}} = 2.106 \times 10^{-3} \text{ mol} \times 354.34 \text{ g mol}^{-1} = 0.7462 \text{ g}$$

The percentage, by mass of DDT in the sample of oil is thus

$$\frac{m_{\text{DDT}}}{m_{\text{oil}}} \times 100 = \frac{0.7462 \text{ g}}{4.500 \text{ g}} \times 100 = 16.58\%$$

### WE 1.17 Equilibrium constants in terms of concentrations

An equimolar mixture of ethanoic acid and ethanol was heated at 373 K. At equilibrium, the concentration of ethanoic acid was found to be 0.820 mol dm<sup>-3</sup>.

Calculate the concentration of ethyl ethanoate in the equilibrium mixture.

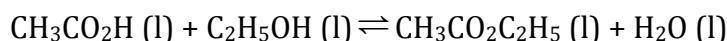
(*Hint.* Use the stoichiometric equation for the reaction to determine the concentration of ethanol in the equilibrium mixture.)

#### Strategy

Write a balanced chemical equation for the reaction and use it to produce an expression for the equilibrium constant in terms of the concentrations of the products and reactants. Rearrange the expression, using the value for the equilibrium constant in the Worked Example to determine the concentration of ethyl ethanoate.

#### Solution

The balanced equation for the reaction between ethanoic acid and ethanol is



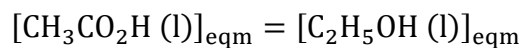
so that the equilibrium constant is

$$K = \frac{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 \text{ (l)}]_{\text{eqm}}[\text{H}_2\text{O (l)}]_{\text{eqm}}}{[\text{CH}_3\text{CO}_2\text{H (l)}]_{\text{eqm}}[\text{C}_2\text{H}_5\text{OH (l)}]_{\text{eqm}}} = 4.00$$

If equal amounts of ethanoic acid and ethanol are mixed initially, then



and



so that

$$K = \frac{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 (\text{l})]_{\text{eqm}}^2}{(0.820 \text{ mol dm}^{-3})^2} = 4.00$$

Rearranging,

$$[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 (\text{l})]_{\text{eqm}}^2 = 4.00 \times (0.820 \text{ mol dm}^{-3})^2$$

so that

$$[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 (\text{l})]_{\text{eqm}} = 2.00 \times 0.820 \text{ mol dm}^{-3} = 1.64 \text{ mol dm}^{-3}$$

## Answers to boxes

### Box 1.3 The Amesbury Archer

How do the three isotopes of oxygen vary in the number of protons, neutrons, and electrons present?

#### Strategy

Deduce the atomic number and mass numbers for the three isotopes of oxygen and hence the number of protons and neutrons.

#### Solution

The atomic number of oxygen is 8, so that all isotopes have 8 protons. However, for the three isotopes of oxygen, the number of neutrons in the nucleus does vary. The number of neutrons is given by the difference between the mass number and the atomic number, so that for  $^{16}_8\text{O}$ , the atomic number is 8, and therefore there are eight neutrons. In the same way, there are nine neutrons in  $^{17}_8\text{O}$ , and ten neutrons in  $^{18}_8\text{O}$ .

### Box 1.5 Measuring low concentrations

The label on a bottle of mineral water says it contains '27 mg calcium per litre'.

(a) What is the concentration of  $\text{Ca}^{2+}$  ions in ppm (by mass) and the percentage by mass of  $\text{Ca}^{2+}$  ions?

(b) What is the concentration of  $\text{Ca}^{2+}$  ions in mol dm<sup>-3</sup>?

#### Strategy

Assuming that the density of water is 1.0 g dm<sup>-3</sup>, calculate the mass of one litre of solution. Calculate the proportion of  $\text{Ca}^{2+}$  ions by mass as a fraction of the total mass.

#### Solution

Assuming that the density of mineral water is 1.0 g cm<sup>-3</sup>, then one litre of water, which is equivalent to a volume of 10<sup>3</sup> cm<sup>3</sup>, has, from Worked Example 1.1, a mass of

$$m = \rho \times V = 1.0 \text{ g cm}^{-3} \times 10^3 \text{ cm}^3 = 1.0 \times 10^3 \text{ g} = 1.0 \text{ kg}$$

Then, from Equation 1.6, the concentration by mass of  $\text{Ca}^{2+}$  ions is

$$\begin{aligned}\frac{m_{\text{Ca}^{2+}}}{m_{\text{total}}} &\approx \frac{m_{\text{Ca}^{2+}}}{m_{\text{H}_2\text{O}}} \\ &= \frac{0.027 \text{ g}}{1000 \text{ g}} \times 10^6 \text{ ppm} = 27 \text{ ppm} \\ &= \frac{0.027 \text{ g}}{1000 \text{ g}} \times 100\% = 0.027\%\end{aligned}$$

(b) The atomic mass of calcium is  $A = 40.1 \text{ g mol}^{-1}$  so that, from Equation 1.8,

$$\begin{aligned}[\text{Ca}^{2+}] &= \frac{n}{V} = \frac{m/A}{V} = \frac{m}{V} / A \\ &= 27 \times 10^{-3} \text{ g dm}^{-3} / 40.1 \text{ g mol}^{-1} \\ &= 6.7 \times 10^{-4} \text{ mol dm}^{-3}\end{aligned}$$

### Box 1.7 Potential energy and kinetic energy

(a) Calculate the energy needed for a bungee jumper weighing  $65.0 \text{ kg}$  to climb from the ground to a platform  $35.0 \text{ m}$  high.

(b) Calculate the kinetic energy of a nitrogen molecule travelling at  $500 \text{ m s}^{-1}$ .

#### Strategy

Use Equation 1.16, which defines how the potential energy of an object varies with its height above the surface of the Earth, and Equation 1.17, which defines an object's kinetic energy.

#### Solution

(a) The gravitational potential energy of the person standing on the platform is equal to the energy needed for the person to climb from the ground to the platform.

Thus, from Equation 1.16,

$$E_{\text{PE}} = mgh = 65.0 \text{ kg} \times 9.81 \text{ m s}^{-2} \times 35.0 \text{ m} = 22300 \text{ kg m}^2 \text{ s}^{-2} = 22.3 \text{ kJ}$$

(b) The molar mass of nitrogen is

$$M = (2 \times 14.00 \text{ g mol}^{-1}) = 28.00 \text{ g mol}^{-1}$$

so that, the mass of an individual nitrogen molecule must be

$$\begin{aligned}m &= M/N_{\text{A}} = 28.00 \text{ g mol}^{-1} / 6.022 \times 10^{23} \text{ mol}^{-1} \\ &= 4.651 \times 10^{-23} \text{ g} = 4.651 \times 10^{-26} \text{ kg}\end{aligned}$$

from Equation 1.17,

$$E_{\text{KE}} = \frac{1}{2}mv^2 = 4.651 \times 10^{-26} \text{ kg} \times (500 \text{ m s}^{-1})^2 = 5.81 \times 10^{-21} \text{ J}$$

### Box 1.9 Butane hair stylers

The label on a 'butane' refill for a hair styler states that it contains 14 g of 'isobutane'.

The formula of 'isobutane' is C<sub>4</sub>H<sub>10</sub>.

(a) Assuming the fuel burns completely, according to the thermochemical equation above, calculate the heat energy supplied from 14 g of 'isobutane'.

(b) Suggest a structural formula (see Section 1.3, p.12) for 'isobutane' and give its systematic IUPAC name.

(You can read about structural isomers and naming hydrocarbons in Section 9.5, p.415. You will be able to calculate enthalpy changes under more realistic conditions, not just 25°C, after studying Section 14.4, p.681.)

#### **Strategy**

Calculate the amount of isobutane that is equivalent to 14 g and hence work out the fraction of the molar enthalpy change.

#### **Solution**

(a) From the thermochemical equation, 2878 kJ of energy are supplied when 1 mol of butane reacts with oxygen at 298 K. The molar mass of isobutane is

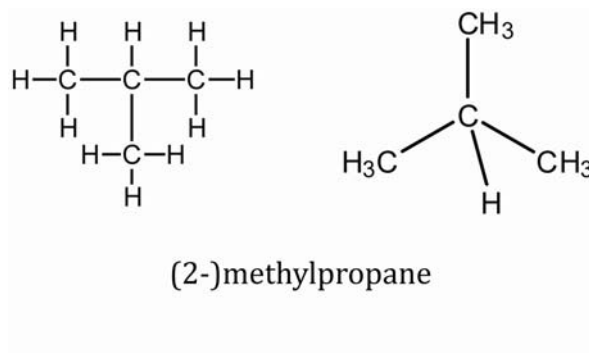
$$M = [(4 \times 12.00) + (10 \times 1.01)] \text{ g mol}^{-1} = 58.10 \text{ g mol}^{-1}$$

so that 14.0 g must correspond to an amount

$$n = m/M = 14.0 \text{ g}/58.10 \text{ g mol}^{-1} = 0.241 \text{ mol}$$

$$\Delta H = n \times \Delta_r H^\ominus = 0.241 \text{ mol} \times 2878 \text{ kJ mol}^{-1} = 690 \text{ kJ}$$

(b) Drawing the structure of isobutane in either a two- or three-dimensional form shows that the systematic IUPAC name is 2-methylpropane.



### Box 1.11 Why is Kevlar so strong?

In terms of intermolecular attractions, suggest why it is possible to make strong ropes out of KEVLAR<sup>®</sup> or nylon, but not from polythene (poly(ethene)).

#### Strategy

Consider the nature of the interactions between the chains.

#### Solution

Hydrogen bonding between adjacent chains in Kevlar and nylon leads to ordered structures in which the aligned chains cannot move past one another very easily. In poly(ethene), the only intermolecular attractions between the chains are the weaker London dispersion interactions. So, fibres made from nylon or Kevlar are stronger than fibres made from poly(ethene).

## Answers to end of chapter questions

1. The C–C bond length in a crystal of diamond is 0.154 nm. What is this distance in (a) metres, (b) picometres, (c) ångströms?

### Strategy

Use the SI prefixes in Table 1.2 to convert the bond length. Remember that 1 Å is equivalent to  $1 \times 10^{-10}$  m.

### Solution

(a)  $1.54 \times 10^{-10}$  m

(b) 154 pm

(c) 1.54 Å

3. A sealed flask holds 10 dm<sup>3</sup> of gas. What is this volume in (a) cm<sup>3</sup>, (b) m<sup>3</sup>, (c) litres?

### Strategy

Use the SI prefixes in Table 1.2.

### Solution

A volume of 10 dm<sup>3</sup>, which is equivalent to 1 L, may be written as

$$10 \text{ dm}^3 = 10 (\text{dm})^3 = 10 \times (10^{-1}\text{m})^3 = 10 \times 10^{-3}\text{m}^3 = 10^{-2}\text{m}^3 = 0.01 \text{ m}^3$$

But,  $1 \text{ m}^3 = 10^6 \text{ cm}^3$ , because

$$1 \text{ m}^3 = 1 \times (10^2\text{cm})^3 = 10^6 \text{ cm}^3$$

so that

$$10 \text{ dm}^3 = 10^{-2}\text{m}^3 = 10^{-2} \times 10^6 \text{ cm}^3 = 10^4 \text{ cm}^3$$

5. How many moles of atoms are contained in the following masses: (a) 22.0 g of magnesium; (b) 43.2 g of chlorine; (c) 126 mg of gold; (d) 1.00 kg of mercury?

### Strategy

Use Equation 1.2 to determine the amount of each element, using the SI prefixes in Table 1.2 to ensure that the units are consistent.

### **Solution**

The amount of each element is given by the ratio of the mass to the molar mass

$$n = m/M$$

(a) Thus, for magnesium, which has a molar mass of  $24.31 \text{ g mol}^{-1}$ , then

$$n_{\text{Mg}} = m_{\text{Mg}}/M_{\text{Mg}} = 22.0 \text{ g}/24.31 \text{ g mol}^{-1} = 0.905 \text{ mol}$$

(b) For chlorine,

$$n_{\text{Cl}} = m_{\text{Cl}}/M_{\text{Cl}} = 43.2 \text{ g}/35.45 \text{ g mol}^{-1} = 1.22 \text{ mol}$$

(c) For gold,

$$n_{\text{Au}} = m_{\text{Au}}/M_{\text{Au}} = 126 \times 10^{-3} \text{ g}/196.97 \text{ g mol}^{-1} = 6.40 \times 10^{-4} \text{ mol}$$

(d) For mercury,

$$n_{\text{Hg}} = m_{\text{Hg}}/M_{\text{Hg}} = 1 \times 10^3 \text{ g}/200.59 \text{ g mol}^{-1} = 4.99 \text{ mol}$$

7. The structure of succinic acid is shown below

- Write down the molecular formula of succinic acid and work out its molar mass.
- What is the empirical formula of succinic acid?
- What is the percentage of carbon in succinic acid?
- Calculate the amount of succinic acid in a  $0.125 \text{ g}$  sample of the pure acid.
- How many molecules of succinic acid are present in the  $0.125 \text{ g}$  sample?
- How many carbon atoms are present in the  $0.125 \text{ g}$  sample?

### **Strategy**

Consider the molecular formula of succinic acid. Use Equation 1.2 to determine the amount of succinic acid.

### **Solution**

(a) The molecular formula of succinic acid is  $\text{C}_4\text{H}_6\text{O}_4$ , so that the molar mass is

$$M = [(4 \times 12.01) + (6 \times 1.01) + (4 \times 16.00)] \text{ g mol}^{-1} = 118.1 \text{ g mol}^{-1}$$

(b) The empirical formula, which is the ratio of the elements, is  $\text{C}_2\text{H}_3\text{O}_2$ .

(c) There are four carbon atoms in each molecule of succinic acid. Thus, the proportion of the mass of the molecule that is carbon is

$$\%C = (4 \times 12.01 \text{ g mol}^{-1})/118.1 \text{ g mol}^{-1} \times 100\% = 40.7\%$$

(d) The amount of succinic acid is

$$n = m/M = 0.125 \text{ g}/118.1 \text{ g mol}^{-1} = 1.06 \times 10^{-3} \text{ mol}$$

(e) The number of molecules in 0.125 g succinic acid is

$$n \times N_A = 1.06 \times 10^{-3} \times 6.022 \times 10^{23} \text{ mol}^{-1} = 6.38 \times 10^{20}$$

(f) Every molecule of succinic acid contains four carbon atoms, so the total number in 0.125 g succinic acid

$$= 4 \times 6.38 \times 10^{20} = 2.55 \times 10^{21}$$

9. A stream running out from a copper mine contains a dilute solution of copper sulfate. As it passes over an iron grid, copper metal deposits on the grid.

(a) Write a balanced equation, with state symbols, for the reaction taking place.

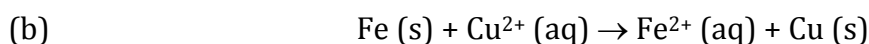
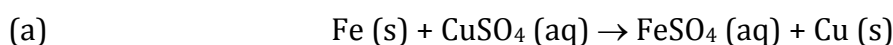
(b) Write an ionic equation for the reaction.

(c) Assign oxidation states to the elements in each of the reactants and products in the equation in (b). Use these values to decide what has been oxidized and what reduced.

### **Strategy**

Follow the approach used in Worked Example 1.10.

### **Solution**



(c) The oxidation state of iron changes from 0 to +2, as the Fe (s) reacts to form Fe<sup>2+</sup> (aq). The oxidation state of copper changes from +2 to 0 as the Cu<sup>2+</sup> (aq) reacts to form Cu(s). The iron is thus oxidised and the copper reduced.

11. Sodium chromate (Na<sub>2</sub>CrO<sub>4</sub>) can be prepared by oxidizing a chromium(III) salt with sodium peroxide (Na<sub>2</sub>O<sub>2</sub>) in alkaline solution. The Cr<sup>3+</sup> ions are oxidized to CrO<sub>4</sub><sup>2-</sup>

ions. The  $\text{O}_2^{2-}$  ions are reduced to  $\text{OH}^-$  ions. Construct half equations and a balanced overall equation for the reaction.

### **Strategy**

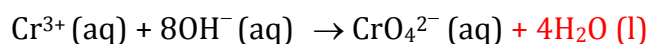
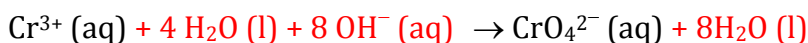
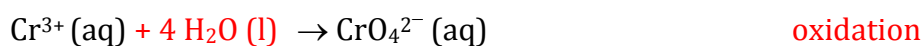
Follow the steps on P.34.

### **Solution**

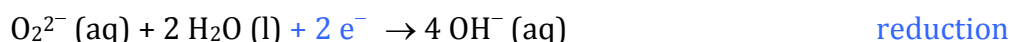
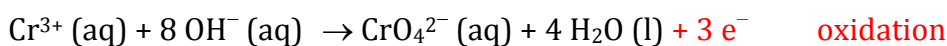
**Steps 1 and 2:** Writing unbalanced half equations, with elements other than O and H balanced



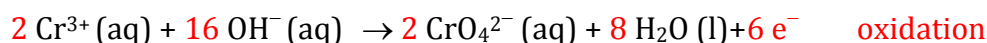
**Step 3:** The reaction takes place in alkaline solution. Balancing O and H by first adding  $\text{H}_2\text{O}$  to balance the O, then balancing the H by adding  $\text{H}_2\text{O}$  to the side of the half equation that needs H, whilst adding  $\text{OH}^-$  to the other side. Cancelling out any surplus water.



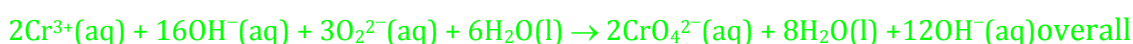
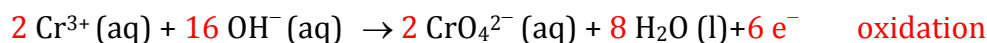
**Step 4:** Balancing electric charges by adding electrons



**Step 5:** Multiplying the oxidation equation  $\times 2$ , and the reduction equation  $\times 3$ , so that the number of electrons transferred is the same in both half equations.



**Step 6:** Adding the two half equations and cancelling out the electrons



**Steps 7 and 8:** Simplifying the equation by cancelling out  $\text{OH}^-(\text{aq})$  ions and  $\text{H}_2\text{O}(\text{l})$  molecules. The atoms and charges on each side of the equation balance.



13. The most common type of kidney stone is formed from calcium ethanedioate ( $\text{CaC}_2\text{O}_4$ ) which precipitates out in the urinary tract when concentrations of  $\text{Ca}^{2+}$  ions and  $\text{C}_2\text{O}_4^{2-}$  ions become too high. Magnesium ions are known to inhibit the formation of kidney stones. To analyse the concentrations of  $\text{Ca}^{2+}$  (aq) and  $\text{Mg}^{2+}$  (aq) in a sample of urine, the ions were precipitated as ethanedioates and the mixed precipitate of  $\text{CaC}_2\text{O}_4$  and  $\text{MgC}_2\text{O}_4$  analysed by gravimetric analysis.

The solid ethanedioates were first heated to form a mixture of  $\text{CaCO}_3$  and  $\text{MgO}$ . The mass of this mixture was 0.0433 g. This solid was then heated more strongly to give a mixture of  $\text{CaO}$  and  $\text{MgO}$ . The mass of the solid residue from this process was 0.0285 g. What was the mass of the  $\text{Ca}^{2+}$  ions in the original sample of urine?

### **Strategy**

Calculate the mass, and therefore the amount, of  $\text{CO}_2$  released when the  $\text{CaCO}_3$  is heated. Use the stoichiometry of the decomposition reaction to determine the amount of  $\text{CaCO}_3$ , and thus the mass of  $\text{Ca}^{2+}$  ions present in the original sample.

### **Solution**

The mass of  $\text{CaCO}_3$  and  $\text{MgO}$  is 0.0433 g, but decreases on heating strongly through the reaction



to 0.0285 g. The mass of  $\text{CO}_2$  must therefore be

$$m_{\text{CO}_2} = 0.0433 \text{ g} - 0.0285 \text{ g} = 0.0148 \text{ g}$$

The molar mass of  $\text{CO}_2$  is

$$M_{\text{CO}_2} = [12.01 + (2 \times 16.00)] \text{ g mol}^{-1} = 44.01 \text{ g mol}^{-1}$$

so that the amount of  $\text{CO}_2$  liberated is, from Equation 1.2

$$n_{\text{CO}_2} = m_{\text{CO}_2} / M_{\text{CO}_2} = 0.0148 \text{ g} / 44.01 \text{ g mol}^{-1} = 3.36 \times 10^{-4} \text{ mol}$$

The stoichiometry of the reaction is such that the amount of  $\text{CO}_2$  produced is equivalent to the amount of calcium carbonate that decomposes, so that

$$n_{\text{CaCO}_3} = n_{\text{CO}_2} = 3.36 \times 10^{-4} \text{ mol}$$

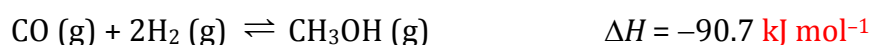
The molar mass of calcium is

$$M_{\text{Ca}} = 40.08 \text{ g mol}^{-1}$$

so that the mass of  $\text{Ca}^{2+}$  ions in the original sample of urine must have been

$$m_{\text{Ca}} = n_{\text{Ca}} \times M_{\text{Ca}} = 3.36 \times 10^{-4} \text{ mol} \times 40.08 \text{ g mol}^{-1} = 0.0135 \text{ g}$$

15. One stage in the manufacture of methanol from methane involves the conversion of synthesis gas (a mixture of CO and  $\text{H}_2$ ) to methanol. The conversion is carried out over a catalyst at a temperature of around 500 K and a pressure of 100 atm.



- (a) Write an expression for  $K_p$  for the reaction.  
 (b) At 500 K and 100 atm pressure, an equilibrium mixture contains 42%  $\text{CH}_3\text{OH}$  and 48% CO. Calculate a value for  $K_p$  at this temperature.  
 (c) Use Le Chatelier's principle to predict what would happen to the percentage of methanol in the mixture if: (i) the temperature increases; (ii) the pressure increases; (iii) hydrogen is added at constant temperature and pressure.

### Strategy

Calculate the partial pressures of each of the components from the proportions and the total pressure. Remember that the  $\text{H}_2$  makes up the remainder of the mixture.

### Solution

- (a) Following the method on P.64,

$$K_p = \frac{p_{\text{CH}_3\text{OH(g)}}}{p_{\text{CO(g)}} p_{\text{H}_2\text{(g)}}^2}$$

- (b) The partial pressure of the components depends upon the fraction,  $x$ , and total pressure  $p$  so that

$$p_{\text{CH}_3\text{OH(g)}} = x_{\text{CH}_3\text{OH(g)}} p = 0.42 \times 100 \text{ atm} = 42 \text{ atm}$$

$$p_{\text{CO(g)}} = x_{\text{CO(g)}} p = 0.48 \times 100 \text{ atm} = 48 \text{ atm}$$

The partial pressure of the remaining component,  $\text{H}_2$ , must therefore be

$$p_{\text{H}_2\text{(g)}} = p - p_{\text{CH}_3\text{OH(g)}} - p_{\text{CO(g)}} = 100 \text{ atm} - 42 \text{ atm} - 48 \text{ atm} = 10 \text{ atm}$$

So that

$$K_p = \frac{p_{\text{CH}_3\text{OH}(\text{g})}}{p_{\text{CO}(\text{g})}p_{\text{H}_2(\text{g})}^2} = \frac{42 \text{ atm}}{48 \text{ atm} \times (10 \text{ atm})^2} = 8.8 \times 10^{-3} \text{ atm}^{-2}$$

(c) (i) The forward reaction is exothermic, so, if the temperature increases, the position of equilibrium moves to the left. The percentage of methanol in the mixture therefore decreases.

(ii) The amount of gas increases when methanol reacts to form carbon monoxide and hydrogen. Thus, an increase in pressure causes the position of equilibrium to move to the right. The percentage of methanol in the mixture increases.

(iii) An increase in the partial pressure of hydrogen will cause the position of equilibrium to move to the left. The percentage of methanol in the mixture will therefore increase.