

## Cambridge Chemistry Challenge Lower 6th

June 2018

Some of the material in this booklet might be familiar to you, but other parts may be completely new. The questions are designed to be more challenging than those on typical AS papers, but you should still be able to attempt them. Use your scientific skills to work through the problems logically.

If you do become stuck on one part of a question, other parts might still be accessible, so do not give up. Good luck!

- The time allowed is 90 mins.
- Attempt all the questions.
- Write your answers in the answer booklet provided, giving only the essential steps in any calculations.
- Specify your answers to the appropriate number of significant figures and give the correct units.
- Please do not write in the right-hand margin.
- A periodic table and necessary constants are included on the next page.

1		2		3		4		5		6		7		8		9		10		11		12		13		14		15		16		17		18	
H		He		Li		Be		B		C		N		O		F		Ne		Na		Mg		Al		Si		P		S		Cl		Ar	
1	1.008	2	4.003	3	6.94	4	9.01	5	10.81	6	12.01	7	14.01	8	16.00	9	19.00	10	20.18	11	22.99	12	24.31	13	26.98	14	28.09	15	30.97	16	32.06	17	35.45	18	39.95
K		Ca		Sc		Ti		V		Cr		Mn		Fe		Co		Ni		Cu		Zn		Ga		Ge		As		Se		Br		Kr	
19	39.102	20	40.08	21	44.96	22	47.90	23	50.94	24	52.00	25	54.94	26	55.85	27	58.93	28	58.71	29	63.55	30	65.37	31	69.72	32	72.59	33	74.92	34	78.96	35	79.904	36	83.80
Rb		Sr		Y		Zr		Nb		Mo		Tc		Ru		Rh		Pd		Ag		Cd		In		Sn		Sb		Te		I		Xe	
37	85.47	38	87.62	39	88.91	40	91.22	41	92.91	42	95.94	43	101.07	44	102.91	45	106.4	46	107.87	47	112.40	48	114.82	49	118.69	50	121.75	51	127.60	52	126.90	53	131.30		
Cs		Ba		La*		Hf		Ta		W		Re		Os		Ir		Pt		Au		Hg		Tl		Pb		Bi		Po		At		Rn	
55	132.91	56	137.34	57	138.91	72	178.49	73	180.95	74	183.85	75	186.2	76	190.2	77	192.2	78	195.09	79	200.59	80	204.37	81	207.2	82	208.98	83	84	84	85	85	86		
Fr		Ra		Ac+																															
87		88		89																															

symbol
atomic number
mean atomic mass

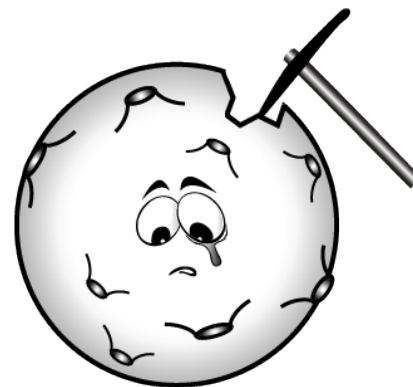
*Lanthanides		Ce		Pr		Nd		Pm		Sm		Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu	
58	140.12	59	140.91	60	144.24	61		62	150.4	63	151.96	64	157.25	65	158.93	66	162.50	67	164.93	68	167.26	69	168.93	70	173.04	71	174.97		
+Actinides		Th		Pa		U		Np		Pu		Am		Cm		Bk		Cf		Es		Fm		Md		No		Lr	
90	232.01	91		92	238.03	93		94		95		96		97		98		99		100		101		102		103			

The Avogadro constant  $N_A = 6.022 \times 10^{23} \text{ mol}^{-1}$

## 1. This question is about mining the moon.

If ever people are to live on the moon, it will be essential to make the most of the natural resources there. One idea that has been extensively looked into, is the extraction of oxygen gas from the minerals present. This could then be used for colonists to breathe, but also for rocket propulsion when mixed with fuels.

Most moon rock is composed of complex metal silicates which, for our purposes, may be thought of as composed of metal oxides and silicon dioxide.



One of the main silicate minerals on the moon is calcium-based anorthosite with the formula  $\text{CaAl}_2\text{Si}_2\text{O}_8$ .

- (a) By treating the mineral as if it were made up of simple oxides, calculate the percentage by mass of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  that it contains.

### Section I – Oxygen from ilmenite

Certain regions contain significant proportions of the mineral ilmenite,  $\text{FeTiO}_3$ , which provides the simplest route to producing oxygen. The rocks are classified as 'high-Ti' if they contain more than about 2.5% by mass of titanium. To extract oxygen from ilmenite, one suggested method is to reduce the ore with hydrogen (brought from Earth) to produce iron, titanium oxide and water. During the reaction, the titanium remains in its maximum oxidation state throughout. The water formed may then be electrolysed to re-form the hydrogen and liberate oxygen.

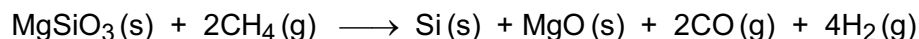
- (b) (i) By considering its position in the periodic table, what is the maximum oxidation state of titanium?
- (ii) Give the formulae of the two oxides that may be thought of as making up the mineral ilmenite.
- (iii) Give the equation for the reaction between ilmenite and hydrogen.
- (iv) Assuming the average Ti content of the rock used in the process is 2.50% by mass, how many tonnes of moon rock would be needed to produce a tonne of oxygen gas using this process?

Another variation is a multistep process which starts with the reduction of the iron species present in ilmenite using methane. In the first step, one mole of methane reacts with one mole of ilmenite to form five moles of products – three moles of which are gaseous under normal conditions.

- (c) Suggest an equation for this step.

## Section II – Oxygen from silicates

Although it needs higher temperatures, the methane process is more useful than the reduction with hydrogen since some silicates may also be reduced. The equation for the reduction of magnesium silicate is given below, together with some thermodynamic data at 298 K and standard conditions:



Substance	$\Delta_f H^\circ / \text{kJ mol}^{-1}$	$S^\circ / \text{J K}^{-1} \text{mol}^{-1}$
MgSiO <sub>3</sub> (s)	– 1549	67.76
CH <sub>4</sub> (g)	– 74.87	188.7
Si(s)		18.81
MgO(s)	– 601.6	26.95
CO(g)	– 110.5	197.7
H <sub>2</sub> (g)		130.7

- (d) (i) On heating the gaseous products of this reaction (although not necessarily in the ratio as formed) with a nickel catalyst, the methane is regenerated and water is also formed (which can later be electrolysed). Give the equation for this reaction to regenerate the methane.
- (ii) The standard entropy change for a reaction,  $\Delta_r S^\circ$ , gives a measure of the change in the amount of disorder that takes place during the reaction (i.e. [amount of disorder in the products] – [the amount of disorder in the reactants]). Would you expect  $\Delta_r S^\circ$  for the reaction from (d)(i) to be positive or negative? Briefly justify your answer.
- (iii) Calculate the standard **enthalpy** change at 298 K for the reaction between magnesium silicate and methane.
- (iv) Calculate the standard **entropy** change at 298 K for the reaction between magnesium silicate and methane.

A further thermodynamic quantity, the standard Gibbs energy of the reaction,  $\Delta_r G^\circ$ , may also be calculated using the equation:

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$$

This thermodynamic quantity is useful since it tells us whether the reactants or products are favoured at equilibrium:

- if the value of  $\Delta_r G^\circ$  is **positive**, it means the **reactants** are favoured at equilibrium;
- if the value of  $\Delta_r G^\circ$  is **negative**, it means the **products** are favoured at equilibrium.

- (e) (i) Calculate the value of  $\Delta_r G^\circ$  at 298 K for the reaction between magnesium silicate and methane. Are the products or reactants favoured at this temperature?
- (ii) Assuming that the values of  $\Delta_r H^\circ$  and  $\Delta_r S^\circ$  do not vary with temperature, calculate the minimum temperature at which the products will be favoured.

### Section III – Ion Plasma Separation

A further method to extract oxygen requires even higher temperatures. In this method the moon rock is heated to very high temperatures, typically over 8000 °C, by concentrating the Sun's rays onto the sample. At these temperatures, all the bonds in the sample are broken (the sample atomises) and some of the atoms are ionised into positively charged ions. Those that are ionised and those that are not may then be separated using magnetic or electric fields.

- (f) Suppose a rock is composed of the elements O, Na, Mg, Al, and Si (arranged in order of increasing atomic number). Arrange these elements in order of their **first ionization energies**, starting with the easiest to ionise.

For a monoatomic, gaseous element at one atmosphere and at a temperature  $T$  (in K), the fraction,  $\alpha$ , of the atoms that are ionized may be approximated by the equation:

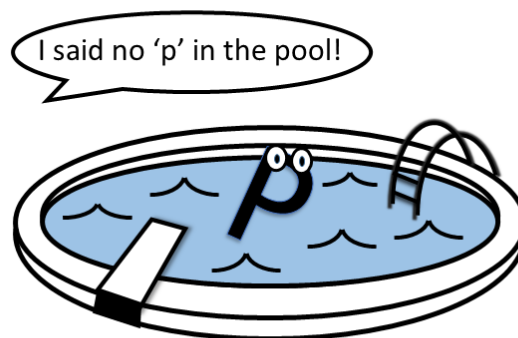
$$\alpha = \sqrt{\frac{C e^{-E_i/RT}}{T^{-5/2} + C e^{-E_i/RT}}}$$

where  $E_i$  is the first ionization energy of the element  
 $R$  is the gas constant = 8.314 J K<sup>-1</sup> mol<sup>-1</sup>  
and  $C$  is a constant whose numerical value is 6.58 x 10<sup>-7</sup> [some units]

- (g) (i) Deduce what units the constant  $C$  must have.
- (ii) A given sample of rock contains the elements Ti, Al, Mg, Si, and O. At a temperature of 10000 K, the Ti, Al, Mg and Si are all more than 50% ionized. Given the first ionization energy of oxygen is 1314 kJ mol<sup>-1</sup>, use the equation given to calculate the percentage of oxygen atoms that would be ionized at this temperature.

## 2. This question is about sweeteners and swimming pools.

From the earliest times, substances other than naturally occurring sugars have been used to sweeten food. The use of such compounds has greatly increased in recent years due to the awareness of metabolic disease caused by overconsumption of sugar. The effects of various sweeteners on human health are still debated, and there are also environmental issues to consider. For example, excretion of sweeteners in urine can potentially lead to water pollution. Recently, however, the excretion of sweeteners has been exploited in a novel method for determining the quality of water in swimming pools.



### Section I

Some of the first substances used to sweeten food were metal salts of carboxylic acids. A carboxylic acid contains the functional group  $\text{-COOH}$ . Carboxylic acids are named according to the total number of carbons in the molecule.

- (a) In your answer booklet draw the structural formulae of:
- (i) propanoic acid.
  - (ii) 2-methyl butanoic acid
- (b) Give the general formula for a saturated, aliphatic carboxylic acid (i.e. one where the  $\text{-COOH}$  functional group is attached to a straight- or branched-chain alkane).

One such sweetener was **salt A**, which forms a simple, hydrated, crystalline salt. Analysis of the percentage by mass of carbon, hydrogen and oxygen present in **salt A** gives 12.66% C, 3.16% H and 29.54% O. The empirical formula contains a single metal ion, **M**.

- (c) (i) Calculate the percentage by mass of metal ion **M** in **salt A**.  
(ii) Give the empirical formula of **salt A** using **M** for the metal ion.  
(iii) Identify the metal that reacts with the carboxylic acid to form metal ion **M**.

Gentle heating of hydrated **salt A** gives a solid (**salt B**) containing:

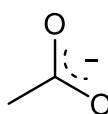
14.76% C, 1.85% H and 19.68% O.

- (d) (i) Give the empirical formula for **salt B** (using the symbol 'M' if necessary).  
(ii) Write a balanced chemical equation for the formation of **salt B** from **salt A** (again using the symbol 'M' if necessary).  
(iii) What is the oxidation state of metal ion **M** in salt A?  
(iv) Name the carboxylic acid whose anion is present in **salt B**.

**Salt B** can be synthesised by heating the metal with the carboxylic acid and aqueous hydrogen peroxide solution.

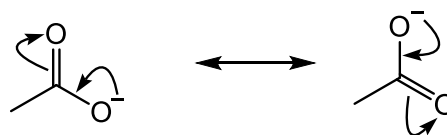
- (e) Write a balanced chemical equation for the formation of **salt B** in this reaction.

In aqueous solution a carboxylic acid can react with a base to form a carboxylate anion. In the carboxylate anion the charge is delocalised over two oxygen atoms and the central carbon atom. Delocalisation of negative charge stabilises an anion making it more likely to form. As a general rule, the more atoms over which charge is delocalised the more stable the anion.

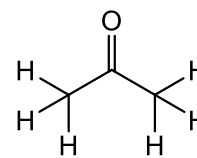


In this illustration the dotted line indicates that the C-O bonds are stronger than single bonds but weaker than double bonds

An alternative way of showing the delocalisation is to use curly arrows to show how the charge is shared. It is important to note that the two structures on the right do not represent different chemical species, they are just two representations of the same chemical species.



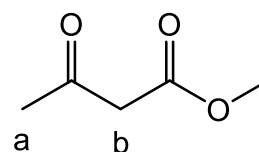
In some cases the protons attached to a carbon atom can be acidic. For example, the presence of carbonyl groups makes the protons attached to the adjacent carbon much more acidic than in an alkane.



**ketone C**

- (f) (i) Draw the structure of the anion formed when a base removes one proton from **ketone C**.  
 (ii) By analogy with the carboxylate anion use curly arrows to illustrate in your answer book how the charge on the anion formed from **ketone C** can be delocalised.

Protons on a carbon atom that is adjacent to two carbonyl groups are particularly acidic. For example in **methyl 3-oxobutanoate** the protons at position **b** are more acidic than those at position **a**. This is because a negative charge at position **b** can be delocalised over more atoms than one at position **a**.



**methyl 3-oxobutanoate**

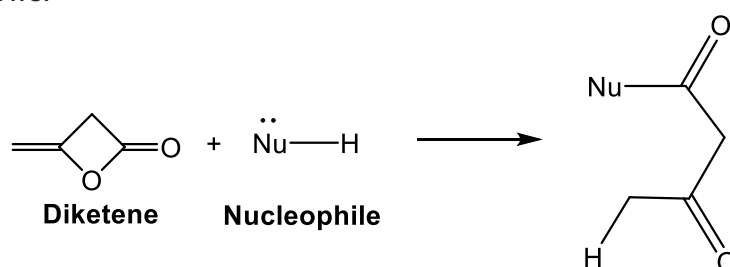
Addition of base to a solution of **methyl 3-oxobutanoate** results in loss of a proton from position **b**.

- (g) Draw **two** representations of the resulting anion in which the negative charge is on an oxygen atom.

## Section II

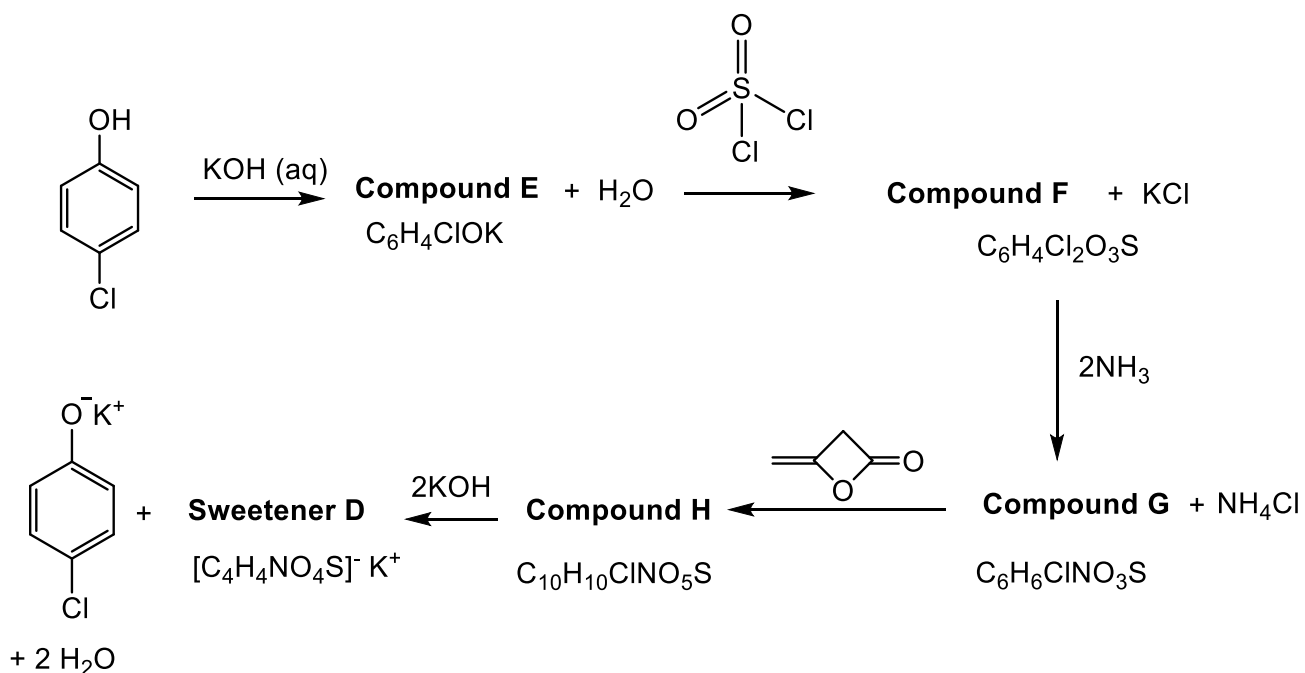
In 1968, Karl Clauss was working at the German chemical company Hoechst AG. Having contaminated his hands with some of the chemicals he was working with, he licked his fingers to turn over the page of a book. He noticed that his fingers tasted sweet and this led to the discovery of a well-used, artificial sweetener (**Sweetener D**).

The synthesis of **Sweetener D** involves a reagent called **diketene**, which will not be familiar to you. **Diketene** is a useful reagent in organic synthesis. The general reaction of **diketene** with a nucleophile is as follows:



- (h) On the structure of **diketene** in your answer booklet circle the atom in **diketene** that is attacked by the nucleophile.

The scheme for the total synthesis of **Sweetener D** is given below:



- (i) What does **Compound E** act as in this synthesis? Circle the correct answer in your answer booklet.
- electrophile                  radical initiator                  base                  nucleophile
- (j) Suggest structures for **Compounds E – G**.

The first step in the reaction forming **Sweetener D** from **Compound H** is deprotonation.

- (k) (i) Suggest a structure for **Compound H**
- (ii) Circle the most acidic proton on your structure for **Compound H** in the answer booklet.
- (iii) The final product, **Sweetener D**, contains a 6-membered ring. Suggest a structure for **Sweetener D**.

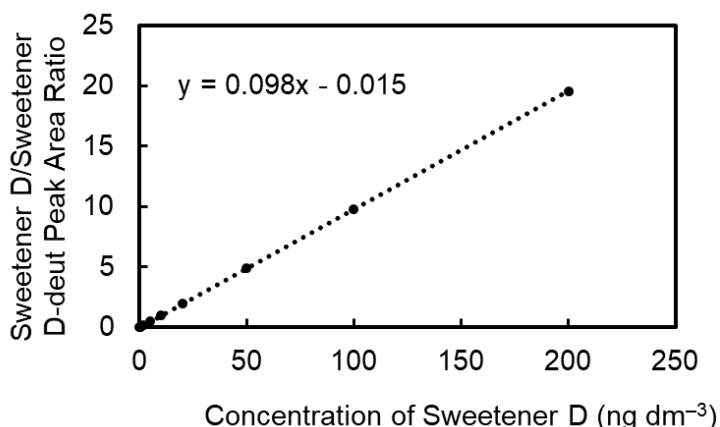


### Section III

Nitrogen-containing organic compounds in urine can react with chlorine in swimming pools to form compounds that are volatile and irritating to the eyes and respiratory system. A marker for the quantity of urine in the pool is therefore desirable. Consumption of **Sweetener D** is widespread in North America and, as it is excreted in the urine, it is ideal for use as a urinary marker in this region of the world.

The concentration of **Sweetener D** in a water sample can be determined using mass spectrometry. In this experiment the water sample is spiked with a known amount of deuterated **Sweetener D** (**Sweetener D-deut**) and the intensities of equivalent peaks from **Sweetener D** and **Sweetener D-deut** compared.

A calibration curve for calculating the concentration of **Sweetener D** from the **Sweetener D/Sweetener D-deut** peak intensity ratio is shown to the right:



The researchers from the University of Alberta who developed this methodology investigated the **Sweetener D** concentration in the public swimming pool of a major Canadian city.

Samples were taken from the city water supply in order to determine the baseline concentration of **Sweetener D** in city water. The mean concentration of **Sweetener D** was found to be  $0.0426 \text{ nmol dm}^{-3}$

(l) Convert the concentration of **Sweetener D** in the city water supply to units of  $\text{ng dm}^{-3}$ .

A water sample taken from the city swimming pool was diluted 20-fold with distilled water, spiked with **Sweetener D-deut** and analysed as described above. The **Sweetener D/Sweetener D-deut** peak area ratio found to be 0.750.

(m) Calculate the concentration of **Sweetener D** in the pool water in  $\text{ng dm}^{-3}$ .

Human urine samples (equal volume from 20 volunteers) were combined, diluted 100000-fold with distilled water, spiked with **Sweetener D-deut** and analysed as described above. The **Sweetener D/Sweetener D-deut** peak area ratio was 2.41.

(n) Calculate the concentration of **Sweetener D** in the urine sample in  $\text{ng dm}^{-3}$ .

The volume of the swimming pool from which the water sample was taken is  $840 \text{ m}^3$ .

(o) Calculate the volume of urine in the swimming pool in  $\text{dm}^3$ .

## **Acknowledgements**

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