C 3 L 6

Cambridge Chemistry Challenge Lower 6th

International Year of the Periodic Table

June 2019

> 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 A-level 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.

Group Number

Symbol
atomic number
mean atomic mass

Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	s-block		d-block										p-block					
1	**H** 1 1.008	**He** 2 4.003																**He** 2 4.003
2	**Li** 3 6.94	**Be** 4 9.01											**B** 5 10.81	**C** 6 12.01	**N** 7 14.01	**O** 8 16.00	**F** 9 19.00	**Ne** 10 20.18
3	**Na** 11 22.99	**Mg** 12 24.31											**Al** 13 26.98	**Si** 14 28.09	**P** 15 30.97	**S** 16 32.06	**Cl** 17 35.45	**Ar** 18 39.95
4	**K** 19 39.10	**Ca** 20 40.08	**Sc** 21 44.96	**Ti** 22 47.87	**V** 23 50.94	**Cr** 24 52.00	**Mn** 25 54.94	**Fe** 26 55.85	**Co** 27 58.93	**Ni** 28 58.69	**Cu** 29 63.55	**Zn** 30 65.38	**Ga** 31 69.72	**Ge** 32 72.63	**As** 33 74.92	**Se** 34 78.97	**Br** 35 79.90	**Kr** 36 83.80
5	**Rb** 37 85.47	**Sr** 38 87.62	**Y** 39 88.91	**Zr** 40 91.22	**Nb** 41 92.91	**Mo** 42 95.95	**Tc** 43	**Ru** 44 101.07	**Rh** 45 102.91	**Pd** 46 106.42	**Ag** 47 107.87	**Cd** 48 112.41	**In** 49 114.82	**Sn** 50 118.71	**Sb** 51 121.76	**Te** 52 127.60	**I** 53 126.90	**Xe** 54 131.29
6	**Cs** 55 132.91	**Ba** 56 137.34	* **Lu** 71 174.97	**Hf** 72 178.49	**Ta** 73 180.95	**W** 74 183.84	**Re** 75 186.21	**Os** 76 190.23	**Ir** 77 192.22	**Pt** 78 195.08	**Au** 79 196.97	**Hg** 80 200.59	**Tl** 81 204.38	**Pb** 82 207.2	**Bi** 83 208.98	**Po** 84	**At** 85	**Rn** 86
7	**Fr** 87	**Ra** 88	+ **Lr** 103	**Rf** 104	**Db** 105	**Sg** 106	**Bh** 107	**Hs** 108	**Mt** 109	**Ds** 110	**Rg** 111	**Cn** 112	**Nh** 113	**Fl** 114	**Mc** 115	**Lv** 116	**Ts** 117	**Og** 118

f-block

Lanthanoids: *	**La** 57 138.91	**Ce** 58 140.12	**Pr** 59 140.91	**Nd** 60 144.24	**Pm** 61	**Sm** 62 150.36	**Eu** 63 151.96	**Gd** 64 157.25	**Tb** 65 158.93	**Dy** 66 162.50	**Ho** 67 164.93	**Er** 68 167.26	**Tm** 69 168.93	**Yb** 70 173.05
Actinoids: +	**Ac** 89	**Th** 90 232.04	**Pa** 91 231.04	**U** 92 238.03	**Np** 93	**Pu** 94	**Am** 95	**Cm** 96	**Bk** 97	**Cf** 98	**Es** 99	**Fm** 100	**Md** 101	**No** 102

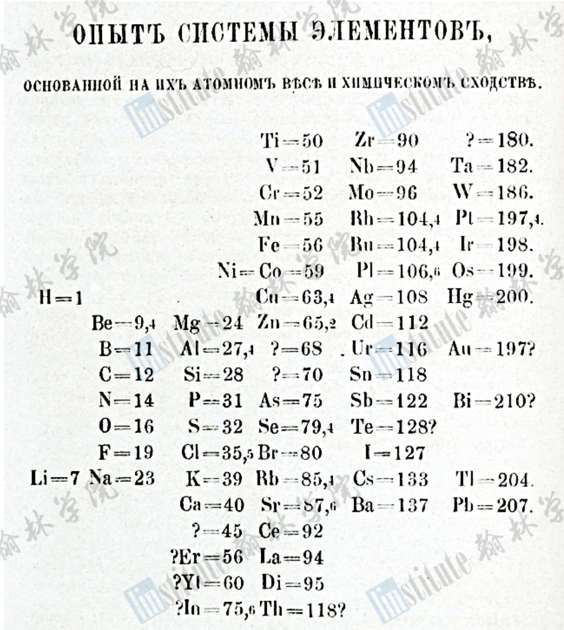
The Avogadro constant $N_A = 6.022\times10^{23}\ mol^{-1}$

1. This question is about the Periodic Table.

2019 marks the 150th anniversary of the publication of Dmitri Mendeleev's first periodic table, shown on the right. Unlike our modern tables, in this version the Groups of elements are arranged in horizontal rows.

Since the structure of the atom was completely unknown at the time, there was no concept of atomic number and the elements were ordered by their atomic masses. The numbers shown in the table are the atomic masses as known at the time. Before the 1860s, atomic masses were not accurate enough for all the trends and patterns in any arrangement of the elements to be discovered.

Mendeleev's table is pretty impressive, but there are a number of errors...



ОПЫТЪ СИСТЕМЫ ЭЛЕМЕНТОВЪ,

ОСНОВАННОЙ НА ИХЪ АТОМНОМЪ ВѢСѢ И ХИМИЧЕСКОМЪ СХОДСТВѢ.

			Ti=50	Zr=90	?=180.
			V=51	Nb=94	Ta=182.
			Cr=52	Mo=96	W=186.
			Mn=55	Rh=104,4	Pt=197,4.
			Fe=56	Ru=104,4	Ir=198.
			Ni=Co=59	Pl=106,6	Os=199.
H=1			Cu=63,4	Ag=108	Hg=200.
	Be=9,4	Mg=24	Zn=65,2	Cd=112	
	B=11	Al=27,4	?=68	Ur=116	Au=197?
	C=12	Si=28	?=70	Sn=118	
	N=14	P=31	As=75	Sb=122	Bi=210?
	O=16	S=32	Se=79,4	Te=128?	
	F=19	Cl=35,5	Br=80	I=127	
Li=7	Na=23	K=39	Rb=85,4	Cs=133	Tl=204.
		Ca=40	Sr=87,6	Ba=137	Pb=207.
		?=45	Ce=92		
		?Er=56	La=94		
		?Yt=60	Di=95		
		?In=75,6	Th=118?		

Section I – the atomic mass of indium

One error is the mass of the element indium (In). To determine the atomic mass of indium, a known quantity of the metal was dissolved in acid, a solution of sodium hydroxide was added to precipitate indium hydroxide and then this was heated to form indium oxide, In_2O_3.

(a) (i) What is the oxidation state of the indium in In_2O_3?

(ii) In dilute mineral acids, indium metal slowly reacts and gives out a flammable gas. Give the equation for the reaction between indium metal and dilute nitric acid.

(iii) Which species is oxidised and which is reduced during this reaction?

(iv) With hot nitric acid, or with more concentrated nitric acid, the only gases formed are oxides of nitrogen. Give the equation for the reaction of indium metal with nitric acid forming nitric oxide, NO.

(v) Give the equation for the formation of indium hydroxide from aqueous indium nitrate and sodium hydroxide.

(vi) Give the equation for the formation of indium oxide from the hydroxide.

(vii) Using the modern atomic mass of indium, calculate the maximum mass of indium oxide that could be formed from 1.00 g of indium metal.

When Mendeleev created his first table indium had only just been discovered and its chemical properties had not been fully studied. The error in the mass arose from the fact that the correct formula for indium oxide was not known.

(b) In one experiment to determine the atomic mass of indium, 0.5135 g of indium metal was converted to 0.6243 g of the oxide. Using these data, and the modern relative atomic mass of oxygen, calculate the apparent atomic mass of indium assuming:

(i) the formula for indium oxide is InO.

(ii) the formula for indium oxide is InO_2.

Section II – the tellurium-iodine problem

Although the elements in Mendeleev's table are primarily arranged by atomic mass, this was not the case with tellurium (Te) and iodine. Mendeleev realised that the chemical properties of the elements meant that tellurium had to come before iodine, but the atomic masses did not support this order. He marked the mass of tellurium with a question mark to highlight its suspicious value.

The modern value for the relative atomic mass of tellurium is one of the least precise: 127.60 ± 0.03. The reason for the uncertainty is that naturally occurring tellurium is a mix of 8 different isotopes whose proportions can vary depending on the sample. In contrast, naturally occurring iodine consists of a single isotope – iodine 127 – and so its relative mass is known to a high precision: 126.904472 ± 0.000003.

(c) How many protons, neutrons and electrons does an iodide ion contain?

The heaviest of the isotopes found in naturally-occurring tellurium is tellurium-130 which has a relative mass of 129.906223. Technically, tellurium-130 is very slightly radioactive and if there were none in the naturally occurring element, the relative atomic mass of tellurium would be 126.412449 (which would make it less than iodine).

(d) Calculate the percentage of tellurium-130 present in naturally-occurring tellurium.

Section III – the misplacement of thallium

Mendeleev also misplaced the highly toxic element thallium (Tl) with the elements from Group 1 rather than in Group 13. There are good reasons for this error. Thallium *can* form salts in the +3 oxidation state like other members of its group, but Tl^{3+} ions are oxidising and the most stable oxidation state is +1. For example, adding iodide ions to solutions of Tl^{3+} actually gives a precipitate of thallium(I) iodide.

(e) Give the equation for the reaction of aqueous thallium(III) nitrate with potassium iodide.

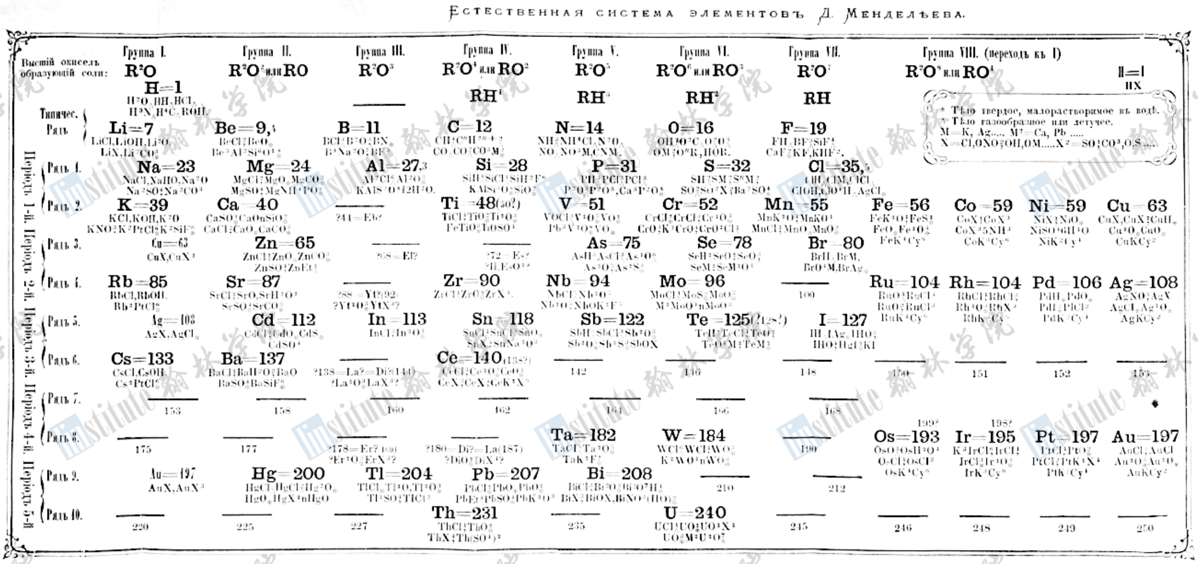
An iodide of thallium with the formula TlI_3 is known and has exactly the same structure as CsI_3.

(f) **(i)** What is the oxidation state of Cs in CsI_3?

(ii) What is the average oxidation state of the iodine in these compounds?

(iii) Draw a dot-and-cross diagram showing the structure of the anion present in CsI_3 and TlI_3.

(iv) What is the bond angle in the anion present in the compounds?



Mendeleev's second periodic table from 1871

Section IV – Mendeleev's short-form table

In the second version of his table, Mendeleev updated the mass of indium and correctly positioned both it and thallium. He also arranged the Groups of similar elements vertically but there are too many elements within each Group; Mendeleev mixed elements from the transition metals with those from the main block of the periodic table. There is sense to this since the elements which Mendeleev places in a given Group form similar compounds – notably their oxides and their hydrides.

(g) All of the elements from Mendeleev's Group V, including nitrogen and niobium (Nb), form oxides with the elements in the +5 oxidation state.

(i) Give the formula for nitrogen(V) oxide and niobium(V) oxide.

(ii) Suggest a structure for a molecule of nitrogen(V) oxide.

(iii) Solid nitrogen(V) oxide has a different structure from the gaseous form and consists of linear cations, and trigonal-planar anions. Suggest the formula of the cation and anion in solid nitrogen(V) oxide.

(iv) In the gas phase, N_2O_5 decomposes to oxygen and nitrogen dioxide. Use the data below (determined at 298 K) to calculate the standard enthalpy change at 298 K for the reaction:

$$2\,N_2O_5\,(g) \longrightarrow 4\,NO_2\,(g) + O_2\,(g)$$

	value / kJ mol^{-1}
$\Delta_f H^\circ$ of N_2O_5 (g)	11.3
$\Delta_r H^\circ$ for NO (g) + ½O_2 (g) $\longrightarrow$ NO_2 (g)	–58.1
bond strength in N_2 (g)	945
bond strength in O_2 (g)	498
bond strength in NO (g)	631

(v) Two different lithium niobate(V) salts exist. One is analogous to the salt formed when one mole of lithium hydroxide neutralises one mole of nitric(V) acid; the other is analogous to the lithium salt formed when three moles of lithium hydroxide neutralise one mole of phosphoric(V) acid. Give the two formulae of lithium niobate(V).

Section V – electron configurations

We now know that elements in the same Group of the periodic table have similar properties because they have the same number of electrons in their outermost (valence) shell. In Mendeleev's second table, elements in the same Group have the same number of valence electrons, even though some elements are from the main block of the periodic table, and some from the transition metals.

Our modern periodic table is based on the electronic configurations of the elements.

For elements from Groups 1 and 2, the valence electrons are in s orbitals whereas for elements in Groups 13-18, they are in s and p orbitals. In both cases the orbitals have principal quantum numbers the same as the period number.

For elements in Groups 3-12, the electrons are filling d orbitals in shells with principal quantum numbers one less that the period number. The valence electrons are the s electrons and perhaps some / all of the d electrons.

For the lanthanoids and actinoids, the electrons are filling f orbitals in shells with principal quantum numbers two less than the period number.

St Catharine's Periodic Spiral, based on the electronic arrangement of the elements.

(h) **(i)** Give the full electron configurations of calcium and zinc in s, p, d notation.

(ii) Given the maximum oxidation states of elements in Groups 2 and 12 are +2, what are the valence electrons of barium and mercury?

(iii) Given the maximum oxidations states of elements from Groups 7 and 17 (except fluorine) are +7, what are the valence electrons of manganese and bromine?

(iv) Use the periodic table to write down the full electronic configuration of oganesson (Og), the last element of the periodic table.

It is predicted that in order to complete the next row of the periodic table starting with electrons in the 8s shell, it will also be necessary to fill elements in the first row of the g-block.

(j) **(i)** How many 5g orbitals will need to be filled?

(ii) Assuming no orbitals from any shells in the 9^{th} period are occupied, predict the atomic number of the element beneath oganesson (Og).

2. This question is about periodic acid

Sugars are important as fuels for our cells and are also being developed as biofuels for manufacturing. An enormous variety of sugars exists in nature. In particular, sugars have many structural isomers, each of which has different properties. **Periodic acid** is a useful reagent for helping to determine which isomer of sugar is present in a sample.

Chem-cat, shown here helping write the paper, comments:

"*Please note it's pronounced purrr-I-odic acid!*"

Periodic acid exists in two forms: **orthoperiodic acid**, H_5IO_6, and **metaperiodic acid**, HIO_4. **Metaperiodic acid** can be formed by heating **orthoperiodic acid.**

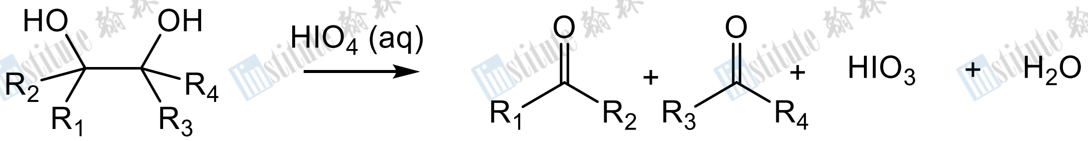
(a) **(i)** Give the oxidation state of iodine in **periodic acid**.

(ii) Write a balanced chemical equation for the formation of **metaperiodic acid** from **orthoperiodic acid**.

(iii) Suggest a structure for **orthoperiodic acid**.

(iv) Suggest a structure for **metaperiodic acid**.

Periodic acid reacts with molecules that have two adjacent alcohol groups. The reaction results in cleavage of the carbon-carbon bond between the two alcohols as shown below:

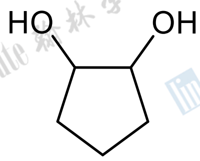


(b) Circle the term that best describes the role of **periodic acid** in this reaction in your answer booklet:

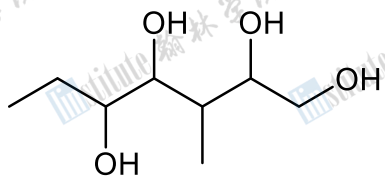
Oxidising agent   Reducing agent   Dehydrating agent   Catalyst

(c) Suggest structures for the products formed when the compounds below react with an excess of **periodic acid**:

(i)



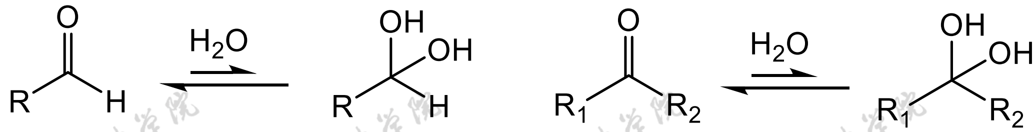
(ii)



The reaction proceeds by first forming a cyclic intermediate species in which the oxygens of both alcohol groups are bonded to the iodine.

(d) Suggest the structure of the intermediate formed when **butane-2,3-diol** reacts with **periodic acid**.

Periodic acid also reacts with a wide range of other compounds, including those where a carbonyl group is adjacent to an alcohol. The reaction has the same mechanism in molecules with two alcohols. This is possible because both aldehydes and ketones are in equilibrium with a small amount of a hydrate in aqueous solution, as shown below. It is the hydrate that reacts with **periodic acid**.



aldehyde ketone

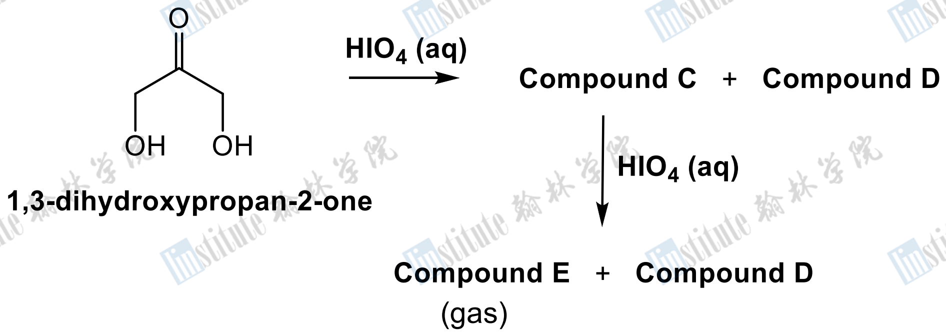
Aldehyde A and **Ketone B** both react with **periodic acid**.

Aldehyde A **Ketone B**

(e) **(i)** Suggest structures for the hydrated forms of **Aldehyde A** and **Ketone B.**

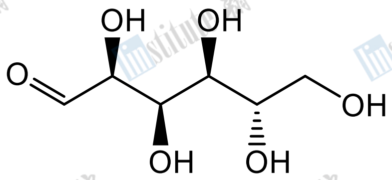
(ii) Suggest structures for the products resulting from reaction of **Aldehyde A** and **Ketone B** with **periodic acid**.

The many alcohol functional groups present in sugar molecules result in one sugar molecule reacting with multiple molecules of periodic acid. **1,3-dihydroxypropan-2-one** is the simplest sugar that has a ketone functional group. One molecule of **1,3-dihydroxypropan-2-one** reacts with two molecules of periodic acid:

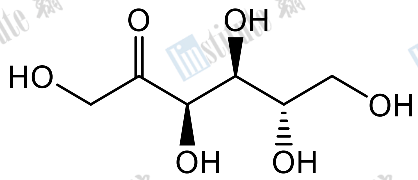


(f) Suggest structures for Compounds **C, D,** and gas **E**.

In nature, sugars exist as a wide range of structural isomers. Analysis of the products formed when sugars react with **periodic acid** is one way to distinguish between isomers. The structures of the isomeric sugars **glucose** and **fructose** are shown:



glucose

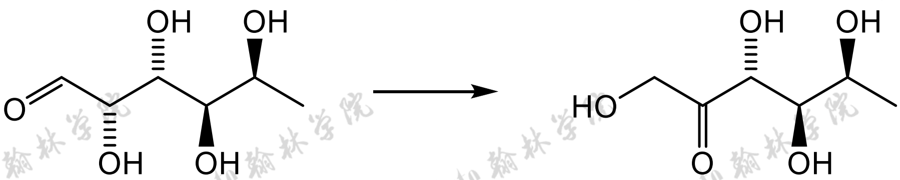


fructose

(g) **(i)** Draw all of the carbon-containing products resulting from the complete reaction of **glucose** with an excess of **periodic acid**. You may ignore stereochemistry but should show the number of moles of each produced.

(ii) Draw all of the carbon-containing products resulting from the complete reaction of **fructose** with an excess of **periodic acid**. You may ignore stereochemistry but should show the number of moles of each produced.

In the search for renewable energy, plants and algae are of great interest as a source of carbohydrates for biofuel production. **Fucose** is the major sugar in the carbohydrates of brown algae (seaweed), and it can be broken down into smaller building blocks using bacteria such as *Escherichia coli*, where the first step is conversion to **fuculose**:



fucose **fuculose**

The next step is addition of a phosphate group to one of the alcohol groups on **fuculose**, catalysed by the enzyme fuculose kinase. When this metabolic pathway was characterised in 1962 **periodic acid** was used to determine which alcohol group becomes phosphorylated.

(h) **(i)** **Fuculose phosphate** was shown to react with **periodic acid** in a molar ratio of 1:3. Suggest the structure(s) for fuculose phosphate that is (are) consistent with this observation.

(ii) Indicate on your structure(s) which C–C bonds would be broken in the reaction with periodic acid.

The phosphorus-containing product was isolated and found to contain 15.4% carbon by mass. (You should assume the product is protonated to give a neutral species, not an anion.)

(j) **(i)** Suggest the structure for the phosphorus-containing product.

(ii) Hence, suggest the structure(s) from **part (h)** that is (are) consistent with this observation.

Acknowledgements

We would like to thank those who support C3L6:

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The pictures of the first published edition of Mendeleev's Periodic Table, and the silver St Catharine's Periodic Spiral are reproduced by permission of the Master and Fellows of St Catharine's College.

As part of the celebrations of the International Year of the Periodic Table, these original publications of Mendeleev's Periodic Table, earlier versions from other chemists, the Silver Periodic Spiral and much more, will be on display at a free exhibition hosted jointly by the Royal Society of Chemistry and St Catharine's College at Burlington House, Piccadilly, London from August 13th – August 30th 2019.