

A Level Chemistry B (Salters)

H433/02 Scientific literacy in chemistry

Monday 19 June 2017 - Morning

Time allowed: 2 hours 15 minutes

You must have:

- the Insert (inserted)
- the Data Sheet for Chemistry B (Salters) (sent with general stationery)

You may use:

• a scientific or graphical calculator

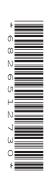
First name	
Last name	
Centre number	Candidate number

INSTRUCTIONS

- The Insert will be found inside this document.
- Use black ink. You may use an HB pencil for graphs and diagrams.
- Complete the boxes above with your name, centre number and candidate number.
- Answer all the questions.
- Write your answer to each question in the space provided. If additional space is required, use the lined page(s) at the end of this booklet. The question number(s) must be clearly shown.
- · Do **not** write in the barcodes.

INFORMATION

- The total mark for this paper is 100.
- The marks for each question are shown in brackets [].
- Quality of extended responses will be assessed in questions marked with an asterisk (*).
- This document consists of 20 pages.



Answer **all** the questions.

Sodium ethanoate is used as an 'acidity regulator' in foods.

(a)	Soc CH ₂	dium ethanoate, $\mathrm{CH_3COONa}$, can be mad $\mathrm{H_3COOH}$, and sodium carbonate, $\mathrm{Na_2CO_3}$, in t	le by reacting solutions of ethanoic acid
	(i)	Write an equation for this reaction.	
	(ii)	Calculate the volume (in cm ³) of 0.500 mol of 0.450 mol dm ⁻³ CH ₃ COOH.	[2] dm ^{–3} Na ₂ CO ₃ that would react with 25.0 cm ³
(b)		volume of Na ₂ CC e ethanoate ion forms an alkaline solution in v ite an equation to show this.	O ₃ =cm ³ [2] vater.
(0)	Eth	capaig acid is a weak acid. $K = 1.7 \times 10^{-5}$ ms	[1]
(c)	(i)	nanoic acid is a weak acid. $K_a = 1.7 \times 10^{-5}$ mc Write an equation for the reaction of ethano	
	(ii)	Calculate the pH of a 0.030 mol dm ⁻³ solution	[1] on of ethanoic acid.
		р	H =[2]

1

(d)		en sodium ethanoate is acting as an acidity regulator in food, a buffer solution is set up. s buffer involves sodium ethanoate and ethanoic acid.
		blain, with the help of an appropriate equation, how this buffer solution works when acid is led.
		[3]
(e)	Sor	me students investigate buffers involving sodium ethanoate and ethanoic acid.
	(i)	They make a solution containing equal amounts of ethanoic acid and sodium ethanoate.
		Calculate the pH of this solution.
		$K_a = 1.7 \times 10^{-5} \mathrm{mol}\mathrm{dm}^{-3}$ for ethanoic acid.
		pH =[1]
	(ii)	The students then set out to make a buffer solution of a known pH. They have 25.0 cm ³ of a 0.100 mol dm ⁻³ solution of ethanoic acid.
		Calculate the mass of sodium ethanoate they need to add to the acid solution to make a solution of pH = 5.00.

mass of sodium ethanoate =g [4]

2 Paracetamol is a pain-relieving medicine.

paracetamol

(a) Name two functional groups in paracetamol, apart from the benzene ring.	(a)	Name two functiona	I groups in paracetamo	ol, apart from the	benzene ring.
--	-----	---------------------------	------------------------	--------------------	---------------

.....

.....[2]

(b) Some students set out to make paracetamol by the method shown below.

(i) The students want to make 5.0 g of 4-nitrophenol in **step 1**.

Calculate the mass of phenol they should start with.

Give your answer to an **appropriate** number of significant figures.

mass of phenol =g [2]

(ii)	The two nitrophenols formed can be separated since they have different boiling points. 2-nitrophenol has a lower boiling point than 4-nitrophenol. This is because internal hydrogen bonding can occur in 2-nitrophenol.
	Draw the structure of 2-nitrophenol with the -OH and -NO ₂ groups shown as full structural formulae; show where the internal hydrogen bond would form.
	[2]
(iii)	Name the type of reaction that occurs in step 2 and name the functional group that has been formed.
	Type of reaction
	Functional group formed[1]
(iv)	Write an equation for the reaction in step 3 . Use skeletal formulae for the organic compounds.

[2]

	(v)	(v)	The students	purify	the	product from	step 3	by re	ecrystallisation	from	wat	er
--	-----	---	----	--------------	--------	-----	--------------	--------	-------	------------------	------	-----	----

			[4 1
soluble impurities	a soliu produc	t iioiii watei. ii	idicate flow

(c) Paracetamol is thought to be converted to AM404 in the body.

AM404 is thought to inhibit the enzyme-catalysed breakdown of anandamide. Anandamide reduces pain responses.

(i) Suggest how AM404 inhibits the breakdown of anandamide.

(ii)	Describe the stereochemistry of the double bonds in AM404.				
		[1]			
(iii)	Explain how the double bonds in AM404 hold the carbon chain in shape.				
		[1]			

3 Deoxyribose, C₅H₁₀O₄, has a vital role in our biochemistry as a component of DNA.

Deoxyribose exists in solution as several forms, two of which are shown below.

(a)	(i)	Circle all the chiral centres on both structures above.
-----	-----	---

(ii) Name the functional group that is present in the linear form only.

.....[1]

(iii) Describe a laboratory test for the functional group identified in (a)(ii).

(iv) Circle a primary alcohol group on each structure below, giving a reason for your choice.

$$HO$$
 OH OH OH OH

Reason.....

.....[2]

(v) Explain why the reaction in which the linear form changes to the ring form is **not** condensation.

.....

.....[1]

(vi) Complete the equation that shows the reaction when the linear form changes to the ring form.

[1]

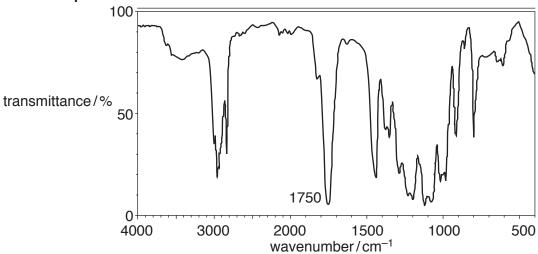
Draw a section of the sugar-phosphate backbone. Show one deoxyribose and two phosphate groups.	
Show one deoxyribose and two phosphate groups.	
	[2]
(c) The structure of a fragment of DNA is sometimes represented by a sequence of le.g. GCA. The letters stand for guanine, cytosine and adenine.	etters,
(i) What single term describes guanine, adenine and cytosine? How and where do they attach to the sugar-phosphate backbone?	
term	
	[2]
(ii) Give the DNA sequence that would produce the CUG sequence in RNA.	
	[1]
(iii) The sequence given in (c)(ii) codes for an amino acid in a protein chain.	
Name the amino acid. Use the <i>Data Sheet</i> to help you.	
	[1]
(iv) Explain how a sequence in DNA codes for an amino acid.	[•]

.....[2]

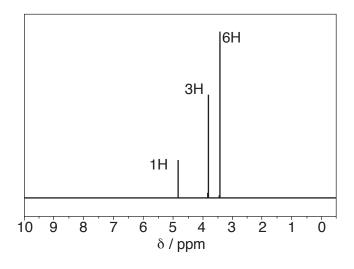
(d)* Compound ${\bf B}$ is a structural isomer of deoxyribose with the molecular formula ${\rm C_5H_{10}O_4}.$

The infrared, ¹H and ¹³C NMR spectra of compound **B** are shown below.

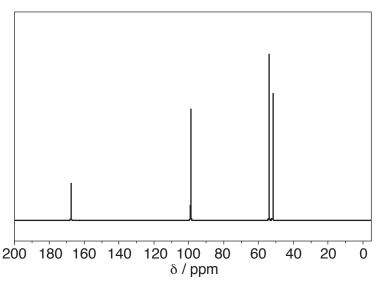




¹H NMR spectrum



¹³C NMR spectrum



You may do rough working on this page but only information written on page 11 opposite will score marks.

Work out the structure of compound B .
Give evidence from each spectrum and show how it relates to the structure you have given.
[6]

- 4 Chromium is a metal with many uses, one of which is the production of a shiny chromium plating on steel.
 - (a) Chromium is made from its ore chromite, FeCr₂O₄, by the following reactions. Iron has one of its common oxidation states in chromite.

$$\begin{array}{lll} {\rm 4FeCr_2O_4 + 8Na_2CO_3 + 7O_2} & \rightarrow {\rm 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2} & & {\rm equation \ 4.1} \\ {\rm 2Na_2CrO_4 + H_2SO_4} & \rightarrow {\rm Na_2Cr_2O_7 + Na_2SO_4 + H_2O} & & {\rm equation \ 4.2} \\ {\rm Na_2Cr_2O_7 + 2C} & \rightarrow {\rm Cr_2O_3 + Na_2CO_3 + CO} & & {\rm equation \ 4.3} \\ {\rm Cr_2O_3 + 2A}l & \rightarrow {\rm A}l_2{\rm O_3} + 2{\rm Cr} & & {\rm equation \ 4.4} \\ \end{array}$$

(i) Complete the table below showing the oxidation states of chromium species in the equations above.

For each equation state whether chromium has been reduced, oxidised or neither.

Equation no.	Oxidation state of Cr in reactant	Oxidation state of Cr in product	Has Cr been oxidised, reduced or neither?
4.1			
4.2			
4.3			
4.4			

[4]

(ii) Calculate the maximum mass of chromium (in kg) that could be obtained from 1000 g of chromite.

mass =kg [2]

(b)	Chromium plating is carried out using a solution of chromium(III) chloride with a graphite anode.		
	(i)	Write the electron configuration of a Cr ³⁺ ion, using sub-shells and atomic orbitals.	
	(ii)	Draw a labelled diagram of a simple apparatus to carry out chromium plating of a steel object in a student laboratory.	
	(iii)	[3] Write a half-equation for the cathode reaction in the cell in (b)(ii).	
	(111)	write a Hall-equation for the cathode reaction in the centif (b)(ii).	
		[1]	
	(iv)	A 'mole of electrons' is 96 500 coulombs and a coulomb is a current of 1 amp flowing for 1 second.	
		Calculate the time (in hours) needed to deposit 26 g of chromium at a current of 5.0 amps in the cell in (b)(ii) .	
		time =hours [3]	

(c) In a solution of chromium (${ m III}$) chloride an equilibrium exists, as shown in equation						
		$ [\operatorname{CrC} l_2(\operatorname{H}_2\operatorname{O})_4]^+ + 2\operatorname{H}_2\operatorname{O} \iff [\operatorname{Cr}(\operatorname{H}_2\operatorname{O})_6]^{3+} + 2\operatorname{C} l^- \text{ equation 4.5} $ green violet				
(i) Name the ligands in the green complex.						
		[1]				
(ii) Some students have a violet solution of chromium(III) chloride.						
	Use your knowledge of equilibria to suggest and explain how they might make the vic solution turn green.					
	Give the name of any reagent required.					
		[2]				

- (d) The concentration of an ethanol solution can be measured using the following steps.
 - add excess acidified dichromate, $\mathrm{Cr_2O_7^{2-}}$, some of which reacts with the ethanol. add excess iodide that reacts with the remaining dichromate.

 - titrate the iodine produced with sodium thiosulfate.

$$\begin{array}{ll} 3 \text{C}_2 \text{H}_5 \text{OH} + 2 \text{Cr}_2 \text{O}_7^{2-} + 16 \text{H}^+ \rightarrow 3 \text{CH}_3 \text{COOH} + 4 \text{Cr}^{3+} + 11 \text{H}_2 \text{O} & \textbf{equation 4.6} \\ \\ \text{Cr}_2 \text{O}_7^{2-} + 6 \text{I}^- + 14 \text{H}^+ \rightarrow 2 \text{Cr}^{3+} + 3 \text{I}_2 + 7 \text{H}_2 \text{O} & \textbf{equation 4.7} \\ \\ \text{I}_2 + 2 \text{Na}_2 \text{S}_2 \text{O}_3 \rightarrow \text{Na}_2 \text{S}_4 \text{O}_6 + 2 \text{I}^- & \textbf{equation 4.8} \\ \end{array}$$

(i) Some students add acid and $20.0\,\mathrm{cm^3}$ of $0.200\,\mathrm{mol\,dm^{-3}}$ $\mathrm{Cr_2O_7^{2-}}$ to $25.0\,\mathrm{cm^3}$ of a 'low-alcohol' beer.

They add excess iodide ions and find that the iodine produced reacts with $27.6\,\mathrm{cm}^3$ of $0.100 \, \text{mol dm}^{-3} \, \text{Na}_2 \, \text{S}_2 \, \text{O}_3$.

Calculate the concentration of the ethanol in the beer (in moldm⁻³) and then the percentage of ethanol (in g per 100 cm³).

concentration of ethanol = mol dm	ı ^{–3}
% ethanol = g/100 cm ³ [[6]
i) Suggest one assumption the students have to make when giving their result.	
r	41

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- 5 This question is based on the article **Saving paper** from *Education in Chemistry*, March 2013, published by the Royal Society of Chemistry which comes as an insert with this paper.
 - (a) The article says that hydroxyl groups in cellulose can be oxidised to aldehydes, ketones and carboxylic acids. The structures below each show part of a cellulose chain.

On each chain, **circle** the hydroxyl group(s) that can be oxidised to give the named group.

(b) (i)* Lignin contains chromophores that absorb in the uv, whereas the decomposition products look yellow.

[3]

products look yellow.
[6]

		17			
	(ii)	Calculate the energy (in kJ mol ⁻¹) that corresponds to a wavelength of 350 nm absorbed by lignin. $(1 \text{ nm} = 10^{-9} \text{ m})$			
		(1mm = 10 ·m)			
		energy =kJ mol ⁻¹ [3]			
(c)	(i)	What is acting as the acid in the equation shown below?			
		$[Al(H_2O)_6]^{3+} + H_2O \rightarrow [Al(OH)(H_2O)_5]^{2+} + H_3O^+$			
		[1]			
	(ii)	Draw a diagram to illustrate the shape of the $[Al(OH)(H_2O)_5]^{2+}$ ion, naming the shape.			
		name of shape[2]			
(d)	The	article gives two equations for the 'Fenton mechanism'.			
	Giv	Give the overall equation represented by the two equations.			
	Exp	lain why the two equations alone do not show that Fe ²⁺ is acting as a catalyst.			
	Ove	erall equation:			
	Exp	lanation:			
		[2]			

(e)	The article describes several methods of neutralising the acidity in paper. One of these is 'washing in a bath of mild alkali'.
	Describe two other methods given in the article.
	Write equations where appropriate.
	[3]

END OF QUESTION PAPER

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ADDITIONAL ANSWER SPACE

If additional space is required, you should use the following lined page(s). The question number(s) must be clearly shown in the margin(s).			
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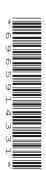
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H433/02 Scientific literacy in chemistry

Insert

Monday 19 June 2017 - Morning

Time allowed: 2 hours 15 minutes

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INFORMATION

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Saving paper

Adapted from an article of the same name in Education in Chemistry, March 2013, www.rsc.org/eic.

History is written on paper and we face an ever-growing urgency to preserve paper-based artefacts before they are lost forever. Chemistry is at the heart of paper conservation and *Michael Seery* finds out more.

In the digital age of the 21st century, our reliance on paper is rapidly declining. Smartphone or tablet screens and electronic paper displays like those of Amazon's Kindle are becoming the norm for everything from cinema tickets to best-selling books. But our history is written on paper and we face an ever-growing urgency to preserve paper-based artefacts before they are lost forever.

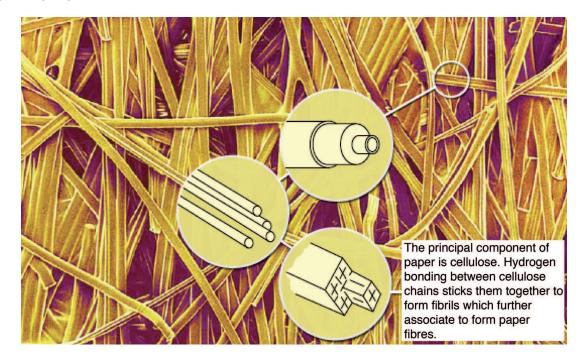


Fig. 1

About one third of the paper items in large libraries are too brittle to handle, with another third in need of attention over the coming century. Chemistry is at the heart of paper conservation, but as a science, paper conservation is a relatively new field. As educators we must include paper chemistry and conservation in our curricula to encourage future generations of chemists to take up the challenge.

What is paper?

The principal component of paper is cellulose, which is effectively a polymer of β -D-glucose. Hydrogen bonding between cellulose chains sticks them together to form fibrils, which further associate to form fibres, the basis of the structure of paper. Raw cellulose fibres are extracted from plant sources and suspended in baths of water. Pulling an appropriately sized mesh through the suspension forms a mat of interwoven cellulose fibres as the water drains away. The remaining water is removed through drying and pressing, which bonds the fibres together into a sheet.

Laboratory filter paper consists of almost pure cellulose, but anyone who has ever tried writing on it will know how poor it is for this purpose, and how weak it is when wet. Additives are therefore included to strengthen the interaction between the fibres. Traditional additives include gelatine and aluminium sulfate, which strengthen the paper and prevent ink from running.

Paper in Europe was originally made from cellulose sourced from linen and cotton rags. This made strong paper structures, owing to the long cellulose chains. The degree of polymerisation – a measure of the average number of glucose molecules in a polymer chain – is high for papers made from linen (3500) and cotton (1000–3000), and this means the chains are tightly bound into the fibrils and fibres by extensive hydrogen bonding.

However, following the invention of the printing press and the enormous surge in demand for paper in the nineteenth century, most paper in our hands today is made from cellulose extracted from wood pulp. Cotton and linen sourced cellulose are now usually reserved for special purposes such as banknotes and artists' materials. While wood is a much more readily available source, the resulting paper has shorter cellulose chains (with a degree of polymerisation around 600–1000) and a weaker structure.

Wood also contains a variety of other carbohydrates and lignin. Lignin is a three-dimensional polymeric material that gives woody plants their physical strength. However, it reduces the strength of paper by interfering with the way the cellulose fibres assemble. For low value paper items, such as newspapers, cheap books and ephemera (material produced for one-off use but now of historical importance), the wood pulps would only be minimally purified to remove lignin. This means they are often the most fragile and rapidly deteriorating materials.

Fig. 2

Acid attack

There are two principal chemical degradation pathways of paper: acid-catalysed hydrolysis and oxidation. The pH of 1 g of a piece of paper in 50 cm³ of water gives a measure of its acidity. Early work on paper conservation chemistry found that old paper that was alkaline was much stronger than acidic paper.

Paper can become acidic either by absorbing pollutants such as sulfur dioxide and nitrogen oxides, or during manufacture. Traditionally, aluminium sulfate (or 'papermaker's alum') was added to harden, or 'size', the paper. While this gave initial strength, it was also a source of acidity with the aluminium ions undergoing hydrolysis as shown below:

$$[\mathrm{A}\mathit{l}(\mathrm{H_2O})_6]^{3+} + \mathrm{H_2O} \mathop{\Longrightarrow}\limits_{} [\mathrm{A}\mathit{l}(\mathrm{OH})(\mathrm{H_2O})_5]^{2+} + \mathrm{H_3O^+}$$

Most paper made in the century from 1850 is acidic due to manufacturing additives.

The β -acetal oxygen bridge joining the glucose molecules of cellulose together is susceptible to acid hydrolysis. This breaks the chains and weakens the fibres. Paper that decomposes this way becomes hard and brittle, and disintegrates easily.

Oxidation, usually initiated by light, discolours the paper. Both cellulose (and its derivatives) and lignin within the paper can be oxidised. In cellulose, oxidising the hydroxyl groups to aldehydes, ketones and carboxylic acids leads to discolouration. But it is lignin that is the main cause of photo-yellowing

of paper. It contains several chromophores with conjugated aromatic rings and carbonyl groups that absorb in the near UV spectrum (300–400 nm). When these chromophores absorb light they can decompose into yellow coloured ketones and quinones, turning the paper yellow. Since these molecules themselves absorb visible light, they act as secondary chromophores and can react further, exacerbating the yellowing and degradation processes.

Fig. 3

Paper preservation

Understanding the degradation pathways reveals preservation methods. From an elementary chemical point of view, if acid is causing decomposition, the solution is to deacidify it. This involves washing paper in a bath of mild alkali such as calcium hydroxide, calcium hydrogen carbonate or magnesium hydrogen carbonate. The benefit is two-fold. Firstly, soaking up water into the cellulose and then drying it re-forms the hydrogen bonds between the fibres, which can restore some of the paper's strength. Secondly, the acid in the paper is neutralised, and reserves of the alkali remain, ready to act against future acidification. Of course this is a process with which conservators need to take great care. Paper may simply disintegrate, or its contents may be removed when added to water. Fragile materials often need to be mounted on mesh for the alkaline wash. However, despite the risks, this method is the mainstay of the conservation of paper that is degrading due to acid.

Mountains of paperwork

One of the significant challenges to libraries is that they have very large volumes of material. This is especially true for copyright libraries like the British Library, which has over 57 million items. The largest library in the world, the US Library of Congress, has over 150 million items – including a staggering 66 million manuscripts. Alkaline washing is effective, but time-consuming and labour intensive. The challenge in an environment with limited funding is to find ways to deacidify such massive stocks.

The goal of mass deacidification is the same: restore the pH of the paper to a neutral range (6.5–8) and leave an alkaline reserve to act against future acidification. One method examined by the US Library of Congress was using diethylzinc gas to neutralise the acid and leave an alkaline deposit of zinc oxide. While this appeared to be perfect as it involved no solvent and worked well in principle, it was abandoned owing to the pyrophoric nature of diethylzinc and the cost of establishing a plant.

Acid neutralisation

$$(C_2H_5)_2Zn + 2H^+ \longrightarrow Zn^{2+} + 2C_2H_6$$

Formation of ZnO deposits

$$(C_2H_5)_2Zn + H_2O \rightarrow ZnO + 2C_2H_6$$

Conservation science is understandably a conservative area that is slow to change, given the nature of the materials involved. One area of current research showing promise is using dispersions of metal hydroxide nanoparticles to neutralise acidity. There are existing commercial products that use microparticles – such as one called Bookkeeper that contains microscopic MgO particles, which form alkaline Mg(OH)₂ on application. However, nanoparticles of calcium and magnesium hydroxide can penetrate the paper structure more easily, resulting in more complete deacidification.

While the deacidification washes may also remove some yellowing, more persistent discolouring can be removed by bleaching. The most common reagent is hydrogen peroxide (0.5–3%), since hypochlorites can damage the cellulose fibres. The active bleaching agent is probably the peroxide anion, ^{-}OOH , which is formed by dissociation of peroxide in water:

$$H_2O_2 + H_2O \rightleftharpoons H_3O^+ + -OOH$$

This reaction only produces an appreciable amount of peroxide anion in the pH range of 8–10, and, while slow, is considered among the most effective bleaching strategies.

More than blank pages

Of course, very little paper is blank, and if it was, it wouldn't be of historic interest. While treating paper, conservators need to consider that inks and pigments themselves can degrade paper. Iron gall ink was popular for several centuries until the mid-nineteenth century, so no one considering paper conservation should ignore its effect on paper structure. This ink was formed by reacting gallic acid (derived from tannins extracted from gall-nuts) with iron(II) sulfate. The presence of excess Fe(II) ions can catalyse the oxidation of cellulose through the production of hydrogen peroxide according to the Fenton mechanism:

$$Fe^{2+} + O_2 + H^+ \longrightarrow Fe^{3+} + HOO^{\bullet}$$

$$Fe^{2+} + HOO^{\bullet} + H^{+} \longrightarrow Fe^{3+} + H_{2}O_{2}$$

This can lead to significant destruction of the paper along the lines of the ink, so much so that the paper can fall out of the structure leaving a lace-like pattern. This decomposition can be stopped by introducing chelating agents to complex the Fe(II) in the ink. The paper is washed in a solution of calcium phytate, which chelates any iron(II) present, blocking the Fenton pathway.



Fig. 4

A call to arms

The challenge of mass deacidification is still unaddressed, and with institutions such as the British Library committing to conservation research, there is a role and responsibility for chemists of this generation and the next to help find a solution.

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