UNIVERSITY OF CAMBRIDGE INTERNATIONAL EXAMINATIONS
General Certificate of Education Advanced Level

CANDIDATE NAME

CENTRE NUMBER

CANDIDATE NUMBER

CHEMISTRY **9701/43**

Paper 4 Structured Questions **October/November 2011**

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Centre number and candidate number on all the work you hand in.
Write in dark blue or black pen.
You may use a pencil for any diagrams, graphs, or rough working.
Do not use staples, paper clips, highlighters, glue or correction fluid.
DO **NOT** WRITE ON ANY BARCODES.

Section A
Answer **all** questions.

Section B
Answer **all** questions.

You may lose marks if you do not show your working or if you do not use appropriate units.
A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.
The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	
2	
3	
4	
5	
6	
7	
8	
Total	

This document consists of **17** printed pages and **3** blank pages.

Section A

For Examiner's Use

Answer **all** questions in the spaces provided.

1 **(a)** Complete the electronic configurations of the following ions.

Cr^{3+}: $1s^2 2s^2 2p^6$.....

Mn^{2+}: $1s^2 2s^2 2p^6$.....

[2]

(b) Both $KMnO_4$ and $K_2Cr_2O_7$ are used as oxidising agents, usually in acidic solution.

(i) Use information from the *Data Booklet* to explain why their oxidising power increases as the $[H^+(aq)]$ in the solution increases.

.....

.....

.....

(ii) What colour changes would you observe when each of these oxidising agents is completely reduced?

- $KMnO_4$
  from ..... to .....
- $K_2Cr_2O_7$
  from..... to .....

[4]

(c) Manganese(IV) oxide, MnO_2, is a dark brown solid, insoluble in water and dilute acids. Passing a stream of $SO_2(g)$ through a suspension of MnO_2 in water does, however, cause it to dissolve, to give a colourless solution.

(i) Use the *Data Booklet* to suggest an equation for this reaction, and explain what happens to the oxidation states of manganese and of sulfur during the reaction.

.....

.....

.....

(ii) The pH of the suspension of MnO_2 is reduced.
Explain what effect, if any, this would have on the extent of this reaction.

.....

.....

[4]

(d) The main ore of manganese, pyrolusite, is mainly MnO_2. A solution of $SnCl_2$ can be used to estimate the percentage of MnO_2 in a sample of pyrolusite, using the following method.

- A known mass of pyrolusite is warmed with an acidified solution containing a known amount of $SnCl_2$.
- The excess $Sn^{2+}(aq)$ ions are titrated with a standard solution of $KMnO_4$.

For Examiner's Use

In one such experiment, 0.100 g of pyrolusite was warmed with an acidified solution containing 2.00×10^{-3} mol Sn^{2+}. After the reaction was complete, the mixture was titrated with 0.0200 mol dm^{-3} $KMnO_4$, and required 18.1 cm^3 of this solution to reach the end point.

The equation for the reaction between $Sn^{2+}(aq)$ and $MnO_4^-(aq)$ is as follows.

$$2MnO_4^- + 5Sn^{2+} + 16H^+ \longrightarrow 2Mn^{2+} + 5Sn^{4+} + 8H_2O$$

(i) Use the *Data Booklet* to construct an equation for the reaction between MnO_2 and Sn^{2+} ions in acidic solution.

.....

(ii) Calculate the percentage of MnO_2 in this sample of pyrolusite by the following steps.

- number of moles of MnO_4^- used in the titration

- number of moles of Sn^{2+} this MnO_4^- reacted with

- number of moles of Sn^{2+} that reacted with the 0.100 g sample of pyrolusite

- number of moles of MnO_2 in 0.100 g pyrolusite. Use your equation in **(i)**.

- mass of MnO_2 in 0.100 g pyrolusite

- percentage of MnO_2 in pyrolusite

percentage = ...%

[6]

[Total: 16]

2 **(a)** **(i)** What is meant by the term *ligand* as applied to the chemistry of the transition elements?

For Examiner's Use

.....

(ii) Describe the type of bonding that occurs between a ligand and a transition element.

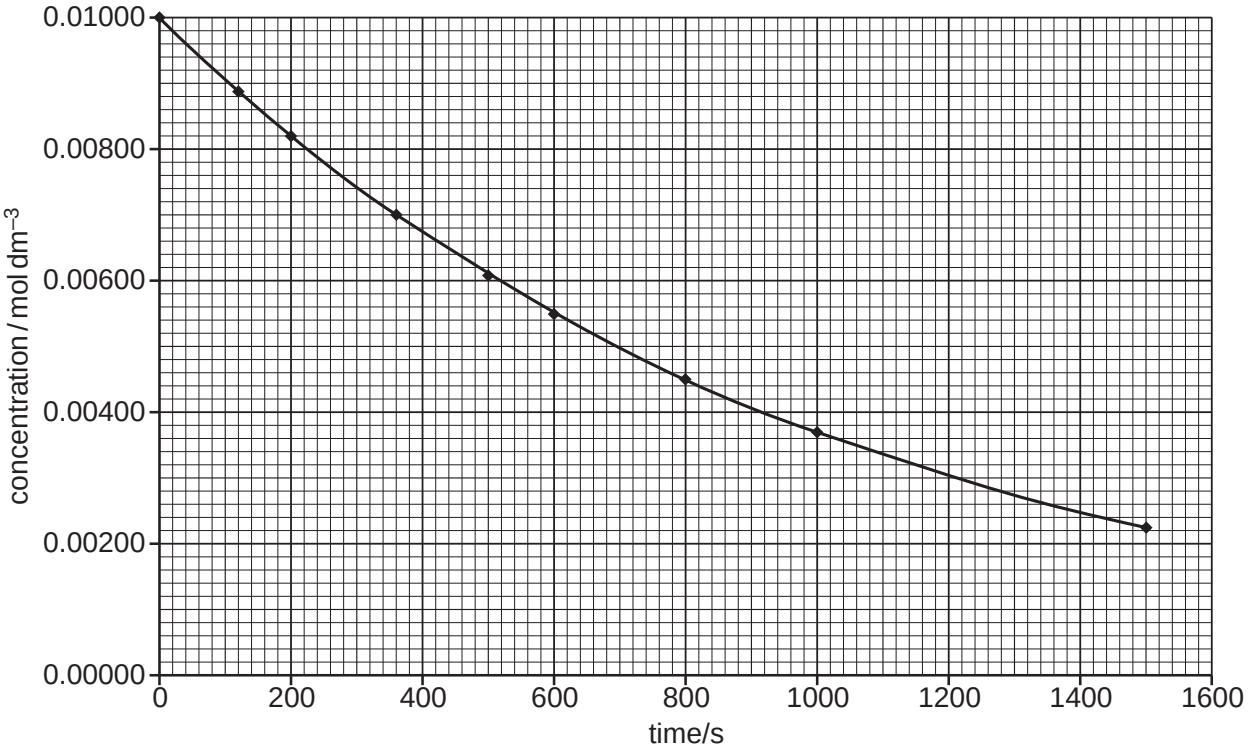
.....

[2]

(b) Chromium hexacarbonyl undergoes the following ligand replacement reaction.

$$Cr(CO)_6 + PR_3 \longrightarrow Cr(CO)_5PR_3 + CO$$

Two separate experiments were carried out to study the rate of this reaction.
In the first experiment, the ligand PR_3 was in a large excess and $[Cr(CO)_6]$ was measured with time. The results are shown on the graph below.



In the second experiment, $Cr(CO)_6$ was in a large excess, and $[PR_3]$ was measured with time. The following results were obtained.

time / s	$[PR_3]$ / mol dm^{-3}
0	0.0100
120	0.0076
200	0.0060
360	0.0028

(i) Plot the data in the table on the graph above, using the same axis scales, and draw the best-fit line through your points.

(ii) Use the graphs to determine the order of reaction with respect to $Cr(CO)_6$ and PR_3. In each case explain how you arrived at your answer.

For Examiner's Use

$Cr(CO)_6$

.....

.....

PR_3

.....

.....

(iii) Write the rate equation for the reaction, and calculate a value for the rate constant, using the method of initial rates, or any other method you prefer.

.....

.....

.....

.....

(iv) State the units of the rate constant.

.....

(v) Four possible mechanisms for this reaction are given below. Draw a **circle** around the letter next to the **one** mechanism which is consistent with the rate equation you have written in **(iii)**.

A $Cr(CO)_6 \longrightarrow Cr(CO)_5 + CO$ fast
$Cr(CO)_5 + PR_3 \longrightarrow Cr(CO)_5PR_3$ slow

B $Cr(CO)_6 \longrightarrow Cr(CO)_5 + CO$ slow
$Cr(CO)_5 + PR_3 \longrightarrow Cr(CO)_5PR_3$ fast

C $Cr(CO)_6 + PR_3 \longrightarrow [OC\text{---}Cr(CO)_4\text{---}PR_3] \longrightarrow Cr(CO)_5PR_3 + CO$
(transition state)

D $Cr(CO)_6 + PR_3 \longrightarrow Cr(CO)_6PR_3$ slow
$Cr(CO)_6PR_3 \longrightarrow Cr(CO)_5PR_3 + CO$ fast

Explain your answer.

.....

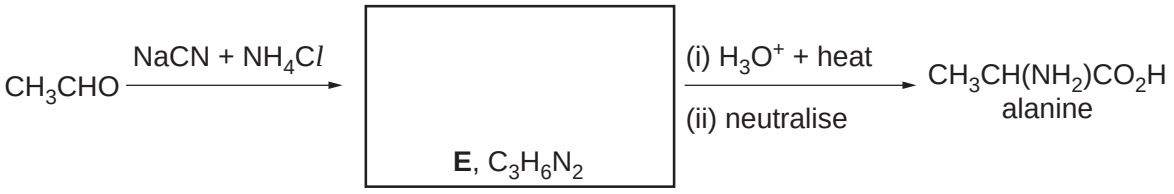
.....

[9]

[Total: 11]

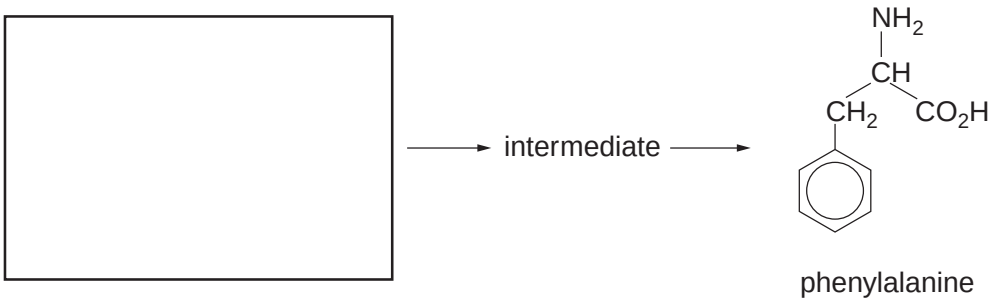
3 **(a)** Amino acids such as alanine are essential building blocks for making proteins. They can be synthesised by a general reaction of which the following is an example.

For Examiner's Use



(i) Suggest the structure of the intermediate compound **E** by drawing its structural formula in the box above.

(ii) Suggest, in the box below, the structural formula of the starting material needed to synthesise phenylalanine by the above general reaction.



phenylalanine

[2]

(b) **(i)** What is a *protein*?

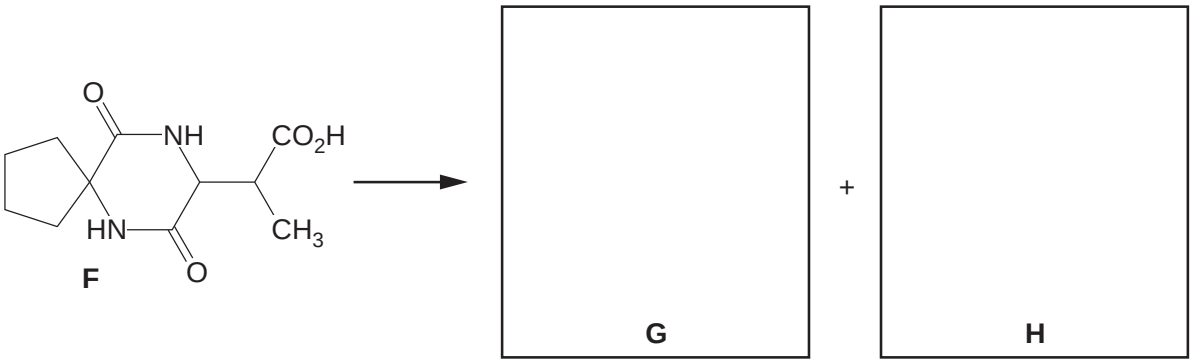
.....

(ii) Using alanine as an example, draw a diagram to show how proteins are formed from amino acids. Show two repeat units in your answer.

[3]

(c) The hydrolysis of compound **F** produces two compounds **G** and **H**.

For Examiner's Use



(i) State the reagents and conditions needed for this hydrolysis.

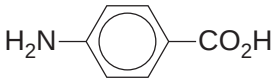
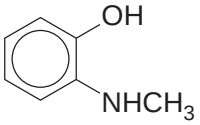
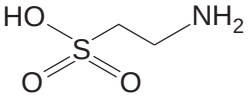
.....

(ii) Draw the structures of the two products **G** and **H** in the boxes above.

[3]

(d) **(i)** Draw the zwitterionic structure of alanine.

(ii) Suggest the structural formulae of the zwitterions that could be formed from the following compounds.

compound	zwitterion
	
	
	

[4]

(e) Solutions of amino acids are good buffers.

For Examiner's Use

(i) What is meant by the term *buffer*?

.....

(ii) Write an equation to show how a solution of alanine, $CH_3CH(NH_2)CO_2H$, behaves as a buffer in the presence of an acid such as HC*l*(aq).

.....

(iii) Briefly describe how the pH of blood is controlled.

.....

.....

.....

(iv) Calculate the pH of the buffer formed when 10.0 cm^3 of 0.100 mol dm^{-3} NaOH is added to 10.0 cm^3 of 0.250 mol dm^{-3} CH_3CO_2H, whose pK_a = 4.76.

pH = ...
[7]

[Total: 19]

4 **(a)** Write an equation representing the action of heat on calcium nitrate, $Ca(NO_3)_2$.

For Examiner's Use

.....

[1]

(b) Describe and explain the trend in the thermal stabilities of the nitrates of the Group II elements.

.....

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.....

[3]

(c) Sodium carbonate is stable to heat, but heating lithium carbonate readily produces $CO_2(g)$.

(i) Suggest an equation for the action of heat on lithium carbonate.

.....

(ii) Suggest a reason for the difference in reactivity of these two carbonates.

.....

.....

(iii) Predict what you would see if a sample of lithium nitrate was heated. Explain your answer.

.....

.....

.....

[4]

[Total: 8]

5 Alkanes are generally considered to be unreactive compounds, showing an inertness to common reagents such as NaOH, H_2SO_4, and $K_2Cr_2O_7$.

For Examiner's Use

(a) Suggest a reason why these reagents **do not** attack an alkane such as CH_4.

.....

[1]

(b) When a mixture of chlorine and ethane gas is exposed to strong sunlight, an explosion can occur due to the fast exothermic reaction.
Under more controlled conditions, however, the following reaction occurs.

$$C_2H_6 + Cl_2 \longrightarrow C_2H_5Cl + HCl$$

(i) What is the name of this type of reaction?

.....

(ii) Use equations to describe the mechanism of this reaction, naming the steps involved.

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(iii) This reaction can produce organic by-products, in addition to C_2H_5Cl.
Draw the structural formulae of three possible organic by-products. Two of your by-products should contain 4 carbon atoms per molecule.
Briefly describe how each by-product could be formed.

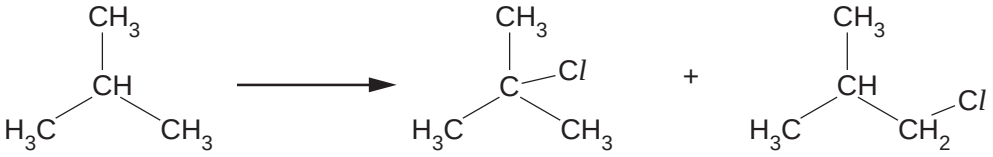
structural formula of by-product	formed by

(iv) It is found by experiment that, during this type of reaction, primary, secondary and tertiary hydrogen atoms are replaced by chlorine atoms at different rates, as shown in the following table.

For Examiner's Use

reaction	relative rate
$RCH_3 \rightarrow RCH_2Cl$	1
$R_2CH_2 \rightarrow R_2CHCl$	7
$R_3CH \rightarrow R_3CCl$	21

Using this information, and considering the number of hydrogen atoms of each type (primary, secondary or tertiary) within the molecule, predict the relative ratio of the two possible products **J** and **K** from the chlorination of 2-methylpropane. Explain your answer.



2-methylpropane **J** **K**

ratio **J**/**K** = ...

explanation:

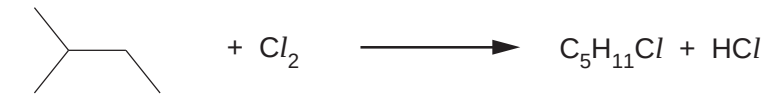
.....

.....

.....

[10]

(c) In the boxes below draw the **skeletal** formulae of **four** different structural isomers of $C_5H_{11}Cl$ that could be obtained from the chlorination of 2-methylbutane. Indicate any chiral centres in your structures by an asterisk (*).



2-methylbutane

[5]

[Total: 16]

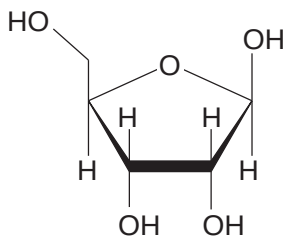
Section B

For Examiner's Use

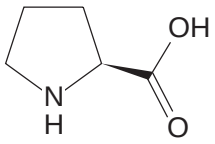
Answer **all** questions in the spaces provided.

6 The formation of proteins is a key process in the growth and repair of tissues in living organisms.

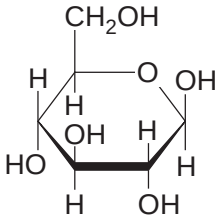
(a) (i) Study the structures of the three molecules below. One of the molecules could be a building block for a protein while the other two could be building blocks for other biological polymers.



J



K



L

Which of the three could be a building block for a protein? Explain your answer.

.....

.....

(ii) For which biological polymer could **one** of the other molecules form a building block?

molecule ..... **polymer** .....

[2]

(b) Protein molecules have four levels of structure as the long molecules fold and take shape.

(i) The primary structure is the sequence of amino acids in the protein chain. What type of bonding exists between the amino acids in this chain?

.....

(ii) What type of bonding can exist in **all** of the other types of structure?

.....

(iii) Name one type of bonding that does **not** occur in the primary or secondary structure of the protein.

.....

[3]

(c) Many proteins play an important role in catalysing chemical reactions in living organisms.

For Examiner's Use

(i) What name is given to these catalysts?

.....

(ii) Give **two** changes in conditions under which these catalysts may be inactivated, explaining the chemical reason for this in each case.

.....

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.....

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.....

.....

[4]

[Total: 9]

[Turn over

7 Different analytical techniques are used to build up a picture of complex molecules. Each technique on its own provides different information about complex molecules but together the techniques can give valuable structural information.

For Examiner's Use

(a) Complete the table, identifying the technique which can provide the appropriate structural information.

structural information	analytical technique
three-dimensional arrangement of atoms and bonds in a molecule	
chemical environment of protons in a molecule	
identity of amino acids present in a polypeptide	

[3]

(b) One general method of separating organic molecules is chromatography. Briefly explain the chemical principles involved in each of the following techniques.

(i) paper chromatography

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.....

.....

(ii) thin-layer chromatography

.....

.....

.....

[2]

(c) A combination of mass spectrometry and NMR spectroscopy is often enough to determine the structure of a simple organic compound.
The organic compound **N** produced a mass spectrum in which the ratio of the M:M+1 peaks was 5.9:0.20, and which had an M+2 peak of similar height to the M peak.

For Examiner's Use

(i) Calculate how many carbon atoms are present in one molecule of **N**.

(ii) Deduce which element, other than carbon and hydrogen, is present in **N**.

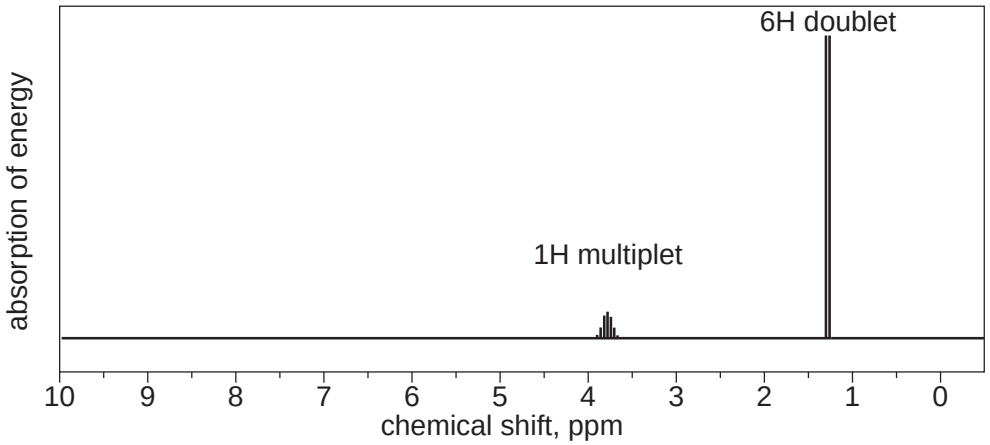
.....

(iii) Explain how many atoms of this element are present in one molecule of **N**.

.....

.....

The NMR spectrum of **N** is shown.



(iv) State the empirical formula of **N** and, using the NMR data, suggest the structural formula of **N**, explaining your reasons.

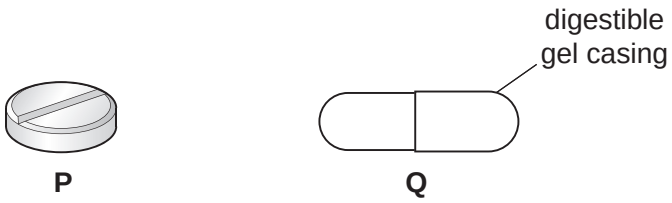
[6]

[Total: 11]

8 Drugs can be delivered in a number of ways. The method chosen depends both on the nature of the drug, and the problem it is being used to treat.

For Examiner's Use

(a) Many common drugs are taken by mouth in forms similar to those shown.



(i) Some drugs are available in solution. How would the speed of action of this form compare with **P** and **Q**? Explain your answer.

.....

.....

(ii) Explain which of the two forms, **P** or **Q**, would act the most rapidly when taken by mouth.

.....

.....

(iii) Some drugs are broken down before they can be absorbed by the intestine. Suggest how the design of **Q** prevents this.

.....

.....

[3]

(b) After an abdominal operation drugs are often delivered by means of a 'drip' inserted into a blood vessel in the patient's arm. Explain why this is more effective than taking painkillers by mouth.

.....

.....

.....

[2]

(c) One of the molecules that has found a variety of uses in drug delivery is poly(ethylene glycol) or PEG. It is formed from dihydroxyethane, $HOCH_2CH_2OH$.

For Examiner's Use

$$2n\ HOCH_2CH_2OH \longrightarrow H–(OCH_2CH_2OCH_2CH_2)_n–OH + (2n–1)\ H_2O$$

(i) What type of reaction is this?

.....

Attaching a PEG molecule to a drug increases the time that it takes for the drug to be broken down and flushed from the body. There are thought to be two major reasons for this: firstly the PEG can form bonds to slow the passage of the drug around the body; secondly it may reduce the efficiency of breakdown of the drug by enzymes.

(ii) What type of bonds would the PEG part of the molecule form with molecules in the body?

.....

(iii) Suggest why attaching a PEG molecule to a drug molecule would reduce the rate of the drug's decomposition by enzymes.

.....

.....

.....

(iv) Drugs are often protein or polypeptide molecules. What type of reaction might occur in the breakdown of such a drug?

.....

[5]

[Total: 10]

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