Write your name here

Pearson Edexcel
International
Advanced Level

Chemistry
Advanced
Unit 4: General Principles of Chemistry I – Rates, Equilibria and Further Organic Chemistry (including synoptic assessment)

Monday 19 January 2015 – Afternoon
Time: 1 hour 40 minutes

You must have: Data Booklet
Candidates may use a calculator.

Instructions
• Use black ink or ball-point pen.
• Fill in the boxes at the top of this page with your name, centre number and candidate number.
• Answer all questions.
• Answer the questions in the spaces provided – there may be more space than you need.

Information
• The total mark for this paper is 90.
• The marks for each question are shown in brackets – use this as a guide as to how much time to spend on each question.
• Questions labelled with an asterisk (*) are ones where the quality of your written communication will be assessed – you should take particular care with your spelling, punctuation and grammar, as well as the clarity of expression, on these questions.
• A Periodic Table is printed on the back cover of this paper.

Advice
• Read each question carefully before you start to answer it.
• Keep an eye on the time.
• Try to answer every question.
• Check your answers if you have time at the end.

Turn over
SECTION A

Answer ALL the questions in this section. You should aim to spend no more than 20 minutes on this section. For each question, select one answer from A to D and put a cross in the box. If you change your mind, put a line through the box and then mark your new answer with a cross.

1 Sulfuryl chloride, SO₂Cl₂, decomposes in a first order reaction.
   The half-life for this reaction is 2300 s.
   In an experiment, the initial concentration of sulfuryl chloride is 1.0 mol dm⁻³.
   What is the concentration, in mol dm⁻³, of sulfuryl chloride after 4600 s?
   □ A 0.75
   □ B 0.50
   □ C 0.25
   □ D 0.125
   (Total for Question 1 = 1 mark)

2 Which classes of halogenoalkane can react with alkali by an S_N₂ mechanism?
   □ A Primary and secondary.
   □ B Secondary and tertiary.
   □ C Primary and tertiary.
   □ D Primary, secondary and tertiary.
   (Total for Question 2 = 1 mark)

3 Which of the following is the correct order of decreasing entropy?

<table>
<thead>
<tr>
<th>Highest entropy</th>
<th>Middle entropy</th>
<th>Lowest entropy</th>
</tr>
</thead>
<tbody>
<tr>
<td>□ A ice at 0°C</td>
<td>water at 0°C</td>
<td>steam at 120°C</td>
</tr>
<tr>
<td>□ B ice at 0°C</td>
<td>steam at 120°C</td>
<td>water at 100°C</td>
</tr>
<tr>
<td>□ C steam at 100°C</td>
<td>water at 0°C</td>
<td>ice at –20°C</td>
</tr>
<tr>
<td>□ D steam at 100°C</td>
<td>ice at –20°C</td>
<td>water at 100°C</td>
</tr>
</tbody>
</table>
   (Total for Question 3 = 1 mark)
4  Ethanol burns in excess oxygen to produce carbon dioxide and water.

\[
\text{C}_2\text{H}_5\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 3\text{H}_2\text{O}(l)
\]

The standard molar entropies of the reactants and products at 298 K are given in the table below.

<table>
<thead>
<tr>
<th>Substance</th>
<th>(S^\circ/\text{J mol}^{-1} \text{ K}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)H(_5)OH(l)</td>
<td>161</td>
</tr>
<tr>
<td>O(_2)(g)</td>
<td>205</td>
</tr>
<tr>
<td>CO(_2)(g)</td>
<td>214</td>
</tr>
<tr>
<td>H(_2)O(l)</td>
<td>70</td>
</tr>
</tbody>
</table>

The value of \(\Delta S^\circ_{\text{system}}\) for this reaction, in J mol\(^{-1}\) K\(^{-1}\), is

- A  -138
- B  -82
- C  +82
- D  +138

(Total for Question 4 = 1 mark)

5  Nitrogen reacts with hydrogen to form ammonia.

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g) \quad \Delta H = -92.2 \text{ kJ mol}^{-1}
\]

What is the value of \(\Delta S^\circ_{\text{surroundings}}\), in J mol\(^{-1}\) K\(^{-1}\), for this reaction at 25°C?

- A  -3688
- B  -309.4
- C  +309.4
- D  +3688

(Total for Question 5 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.
6. The signs of $\Delta H_{\text{reaction}}$ and $\Delta S_{\text{system}}$ for four different gaseous reactions are shown in the table. Which reaction must be thermodynamically feasible at all temperatures?

<table>
<thead>
<tr>
<th></th>
<th>$\Delta H_{\text{reaction}}$</th>
<th>$\Delta S_{\text{system}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>negative</td>
<td>negative</td>
</tr>
<tr>
<td>B</td>
<td>negative</td>
<td>positive</td>
</tr>
<tr>
<td>C</td>
<td>positive</td>
<td>negative</td>
</tr>
<tr>
<td>D</td>
<td>positive</td>
<td>positive</td>
</tr>
</tbody>
</table>

(Total for Question 6 = 1 mark)

7. Use the data in the table to calculate the enthalpy change of solution of calcium chloride, CaCl$_2$.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Lattice energy of calcium chloride</td>
<td>–2258 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>Hydration enthalpy of Ca$^{2+}$</td>
<td>–1650 kJ mol$^{-1}$</td>
</tr>
<tr>
<td>Hydration enthalpy of Cl$^-$</td>
<td>–364 kJ mol$^{-1}$</td>
</tr>
</tbody>
</table>

The enthalpy change of solution of calcium chloride, in kJ mol$^{-1}$, is

- A $-244$
- B $-120$
- C $+120$
- D $+244$

(Total for Question 7 = 1 mark)

8. The expression that relates $\Delta S_{\text{system}}$ to the equilibrium constant, $K$, for a reaction is

- A $\Delta S_{\text{system}} = R \ln K + \Delta H/T$
- B $\Delta S_{\text{system}} = R \ln K - \Delta H/T$
- C $\Delta S_{\text{system}} = T \ln K + \Delta H/R$
- D $\Delta S_{\text{system}} = T \ln K - \Delta H/R$

(Total for Question 8 = 1 mark)
9  Dinitrogen tetroxide forms an equilibrium mixture with nitrogen dioxide.

\[ \text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g}) \]

At equilibrium, when the temperature is 400 K, the equilibrium partial pressures are shown in the table below.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Equilibrium partial pressure / atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(_2)O(_4)</td>
<td>0.365</td>
</tr>
<tr>
<td>NO(_2)</td>
<td>4.18</td>
</tr>
</tbody>
</table>

The numerical value for the equilibrium constant, \(K_p\), is

- A 0.0209
- B 11.5
- C 31.4
- D 47.9

(Total for Question 9 = 1 mark)

10 A buffer solution is 0.1 mol dm\(^{-3}\) with respect to ethanoic acid and 0.05 mol dm\(^{-3}\) with respect to sodium ethanoate.

\(K_a\) for ethanoic acid = \(1.7 \times 10^{-5}\) mol dm\(^{-3}\)

The pH of this buffer solution is

- A 2.88
- B 4.47
- C 4.77
- D 5.07

(Total for Question 10 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.
11 The equation for the reaction between a weak acid, HX, and sodium hydroxide is

\[ \text{HX(aq)} + \text{NaOH(aq)} \rightarrow \text{NaX(aq)} + \text{H}_2\text{O(l)} \]

The pH of the solution of the salt NaX is most likely to be

- [ ] A 5.5
- [ ] B 7.0
- [ ] C 8.5
- [ ] D 13.0

(Total for Question 11 = 1 mark)

12 When a small amount of hydrochloric acid is added to a buffer solution, the change in pH is very small.

What is the best explanation for this?

- [ ] A The dissociation of the acid in the buffer solution is small.
- [ ] B The concentration of the buffer solution only changes a little.
- [ ] C The ratio of the concentration of acid to conjugate base in the buffer solution does not change.
- [ ] D The ratio of the concentration of acid to conjugate base in the buffer solution only changes a little.

(Total for Question 12 = 1 mark)

13 How many structural isomers have the formula \( \text{C}_5\text{H}_{12} \)?

- [ ] A 2
- [ ] B 3
- [ ] C 4
- [ ] D 5

(Total for Question 13 = 1 mark)

Use this space for any rough working. Anything you write in this space will gain no credit.
14 What types of stereoisomerism (if any) can exist in molecules of the following substance?

\[ \text{C} = \text{C} - \text{C} = \text{C} - \text{C} \]

\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]

\[ \text{H} \quad \text{H} \quad \text{OH} \quad \text{H} \]

☐ A  E-Z isomerism only.
☐ B  E-Z and optical isomerism.
☐ C  Neither E-Z nor optical isomerism.
☐ D  Optical isomerism only.

(Total for Question 14 = 1 mark)

15 An organic compound gave a pale yellow precipitate when warmed with a solution of iodine in sodium hydroxide. It also gave steamy fumes when tested with phosphorus(V) chloride.

The organic compound consistent with these results is

☐ A  BrCH\_2CH\_2CH\_2COOH
☐ B  BrCH\_2CH\_2COCH\_3
☐ C  HOCH\_2CH\_2CH\_2COOH
☐ D  HOCH\_2CH\_2COCOH

(Total for Question 15 = 1 mark)

16 Which type of radiation is used in nmr spectroscopy?

☐ A  Infrared
☐ B  Microwaves
☐ C  Radio waves
☐ D  Ultraviolet

(Total for Question 16 = 1 mark)
17 Which of these gases is normally used as the mobile phase in gas chromatography?

- A  Argon
- B  Chlorine
- C  Radon
- D  Steam

(Total for Question 17 = 1 mark)

18 The molecule shown below was reacted with excess lithium tetrahydridoaluminate(III) (lithium aluminium hydride) in dry ether, followed by the addition of acid.

![Molecule structure]

The product of the reaction is

- A  HO\(\text{-}C\text{-}C\equiv\text{C}\text{-}C\text{-}CO\text{OH}\)
- B  O\(\text{-}C\text{-}C\equiv\text{C}\text{-}C\text{-}\text{OH}\)
- C  O\(\text{-}C\text{-}C\equiv\text{C}\text{-}\text{CO}\text{OH}\)
- D  HO\(\text{-}C\text{-}C\equiv\text{C}\text{-}\text{CO}\text{OH}\)

(Total for Question 18 = 1 mark)
19 The molecule CH₃CH₂CONHCH₂CH₃ can be made in a single step at room temperature from

- A  CH₃COCl and CH₃CH₂CH₂NH₂
- B  CH₃CH₂COCl and CH₃CH₂NH₂
- C  CH₃COOH and CH₃CH₂CH₂NH₂
- D  CH₃CH₂COOH and CH₃CH₂NH₂

(Total for Question 19 = 1 mark)

20 The products of the hydrolysis of an ester were propan-2-ol and 2-methylpropanoic acid.

The ester was

- A
- B
- C
- D

(Total for Question 20 = 1 mark)

TOTAL FOR SECTION A = 20 MARKS
21 (a) Iodine reacts with propanone, CH₃COCH₃, in the presence of a catalyst of dilute hydrochloric acid.

\[
\text{CH}_3\text{COCH}_3(\text{aq}) + \text{I}_2(\text{aq}) \rightarrow \text{CH}_3\text{COCH}_2\text{I}(\text{aq}) + \text{HI}(\text{aq})
\]

Students carried out a rate investigation of this reaction. In each set of experiments, the initial concentration of one substance was varied and the initial concentrations of the other two substances were kept constant.

**First set of experiments**

The initial concentration of propanone was varied.

**Second set of experiments**

The initial concentration of iodine was varied.

**Third set of experiments**

The initial concentration of hydrochloric acid was varied.

The results of each set of experiments are shown in the graphs below.
(i) For the second set of experiments, state a practical method for following the progress of this reaction. Indicate which substance is being monitored by your method.

(ii) Use the graphs to deduce the orders of reaction with respect to propanone, iodine and H⁺ ions. Explain your reasoning.

(iii) Write the rate equation for the reaction.
(iv) In one of the experiments, the following data were collected:

\[
\begin{align*}
[\text{CH}_3\text{COCH}_3(\text{aq})] &= 0.667 \text{ mol dm}^{-3} \\
[I_2(\text{aq})] &= 1.67 \times 10^{-3} \text{ mol dm}^{-3} \\
[H^+(\text{aq})] &= 0.667 \text{ mol dm}^{-3} \\
\text{Initial rate} &= 8.80 \times 10^{-6} \text{ mol dm}^{-3} \text{ s}^{-1}
\end{align*}
\]

Use the data to calculate the value for the rate constant. Include units in your answer.

(2)

(v) Use the rate equation to suggest a possible rate-determining step in the mechanism for the reaction between iodine and propanone in the presence of dilute hydrochloric acid.

Explain your reasoning.

(2)
(b) Iodine also forms hydrogen iodide by direct reaction with hydrogen.

\[ \text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI(}g) \]

A graph of \(\ln k\) against \(1/T\) for this reaction is shown below.

(i) Calculate the gradient of the graph. Include a sign and units in your answer.

(2)
(ii) Use your value for the gradient of the graph to calculate the activation energy, $E_a$. Include units and give your answer to **three** significant figures.

The Arrhenius equation is

$$\ln k = -\frac{E_a}{R} \times \frac{1}{T} + \text{a constant}$$

[Gas constant, $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$]

(Total for Question 21 = 15 marks)
22 Butanone, CH₃CH₂COCH₃, is used as an industrial solvent.

(a) State each stage in the procedure in which 2,4-dinitrophenylhydrazine is used to confirm the identity of a carbonyl compound thought to be butanone.

Detailed practical descriptions are not required. (3)

(b) Butanone can be converted into 2-hydroxy-2-methylbutanoic acid, CH₃CH₂C(OH)(CH₃)COOH, in two steps:

\[
\begin{align*}
\text{Step 1:} & \quad \text{HCN/KCN} \\
\text{Step 2:} & \quad \text{OH} \\
\end{align*}
\]

(i) Classify the type and mechanism of the reaction taking place in Step 1. (2)

(ii) Identify the reagent(s) and conditions for the reaction taking place in Step 2. (2)
(iii) The incomplete mechanism for Step 1 is shown below.

\[
\begin{align*}
\text{Step A:} & \\
\text{CH}_3\text{CH}_2\text{C} & \text{CH}_3 + \text{CN}^- \rightarrow \text{CH}_3\text{CH}_2\text{C} & \text{CH}_3 \text{CN}^- \\
\end{align*}
\]

\[
\begin{align*}
\text{Step B:} & \\
\text{CH}_3\text{CH}_2\text{C} & \text{CH}_3 \text{CN}^- + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{C} & \text{CH}_3 \text{OH}^- + \text{CN}^- \\
\end{align*}
\]

On the incomplete mechanism above, draw the curly arrows and the relevant lone pairs of electrons to complete the mechanism.

(iv) Explain why the 2-hydroxy-2-methylbutanoic acid produced in this reaction is not optically active.
(c) Draw two repeat units of the polymer that could be formed from 2-hydroxy-2-methylbutanoic acid. (2)

(Total for Question 22 = 15 marks)
23 Ethanoic acid, CH$_3$COOH, is a weak acid found in vinegar. Successive replacement of the methyl hydrogen atoms by chlorine atoms gives

- chloroethanoic acid, CH$_2$ClCOOH
- dichloroethanoic acid, CHCl$_2$COOH
- trichloroethanoic acid, CCl$_3$COOH

(a) (i) Explain the term **weak acid**.

(ii) Write the expression for the acid dissociation constant, $K_a$, of dichloroethanoic acid, CHCl$_2$COOH.

(iii) Use the $K_a$ data from page 18 in the Data Booklet to place the four acids, named in the introduction to the question, in order of increasing strength. State how the order that you have given can be deduced from the $K_a$ data.
(b) (i) Calculate the pH of a solution of 0.10 mol dm$^{-3}$ ethanoic acid.

State clearly any assumptions you have made.

(4)
(ii) Draw the titration curve, showing the change in pH when 0.10 mol dm\(^{-3}\) sodium hydroxide solution is added to 25 cm\(^3\) of 0.10 mol dm\(^{-3}\) ethanoic acid, until 40 cm\(^3\) of sodium hydroxide has been added.

*(iii) Select a suitable indicator for this titration.

Justify your selection.

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*(iii) Select a suitable indicator for this titration.

Justify your selection.

.......................................................................................................................... ... ........................
.......................................................................................................................... ... ........................
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.......................................................................................................................... ... ........................
.......................................................................................................................... ... ........................
(c) Ethanoic acid and trichloroethanoic acid react together in an acid-base reaction.

Complete the equation by writing the formulae of the acid and base produced in this reaction.

Identify the conjugate acid-base pairs in the spaces under the formulae.

\[ \text{CH}_3\text{COOH} + \text{CCl}_2\text{COOH} \rightarrow \text{..................................................} + \text{..................................................} \]

\[ \text{..................................................} \quad \text{..................................................} \quad \text{..................................................} \quad \text{..................................................} \]

(Total for Question 23 = 17 marks)
SECTION C

Answer ALL the questions. Write your answers in the spaces provided.

24 (a) Ethanoic acid and ethanol react together to form the ester ethyl ethanoate, CH₃COOC₂H₅, and water.

\[ \text{CH}_3\text{COOH}(l) + \text{CH}_3\text{CH}_2\text{OH}(l) \rightleftharpoons \text{CH}_3\text{COOCH}_2\text{CH}_3(l) + \text{H}_2\text{O}(l) \quad \Delta H = -3.5 \text{ kJ mol}^{-1} \]

(i) Give the expression for the equilibrium constant, \( K_c \), for this reaction. 

\( (1) \)

(ii) By considering the effect of temperature on the entropy change of the surroundings, suggest why changing the temperature has little effect on this equilibrium.

\( (3) \)
(iii) An experiment was carried out to determine the value of $K_c$ for this reaction.

- 0.120 mol of ethanoic acid was added to 0.220 mol of ethanol.
- 5.00 cm$^3$ of 1.00 mol dm$^{-3}$ hydrochloric acid was added as a catalyst. This contains 0.278 mol of water.
- The mixture was left to reach equilibrium.
- The mixture was titrated with 1.00 mol dm$^{-3}$ sodium hydroxide, which reacted with both of the acids.
- The titre was 45.0 cm$^3$.

Use these data to determine the value for $K_c$. (6)
(b) Ethanoic acid reacts with another alcohol, Y, to produce an ester Z.

(i) Alcohol Y has molar mass 74 g mol⁻¹ and the following composition by mass:

- carbon, C = 64.9%
- hydrogen, H = 13.5%
- oxygen, O = 21.6%.

Use all these data to confirm that the molecular formula for Y is C₄H₁₀O. Show your working.

(ii) Draw the displayed formulae of the four possible structures of alcohol Y.

<table>
<thead>
<tr>
<th>Alcohol 1</th>
<th>Alcohol 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alcohol 3</th>
<th>Alcohol 4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>
(iii) The mass spectrum of alcohol $Y$ has a major peak at $m/e = 45$. Suggest the structures of two species that could give this peak.

(iv) Use your answers to (b)(ii) and (b)(iii) to identify which two of the alcohols you have drawn in (b)(ii) could be alcohol $Y$.

(v) Complete the displayed formulae for the two possible esters that could be $Z$. 

\[
\begin{align*}
  &\text{H} - \text{C} - \text{C} - \text{O} - \\
  &\text{H} \\
  &\text{H} - \text{C} - \text{C} - \text{O} - \\
  &\text{H}
\end{align*}
\]
*(vi) The high resolution proton nmr spectrum of ester $Z$ is shown below.

The relative number of protons causing the peaks shown are: $A = 1$, $B = 3$, $C = 2$, $D = 3$ and $E = 3$.

Use the nmr spectrum to determine the structural formula for ester $Z$ that is consistent with this data.

Draw your formula below and on it label the protons responsible for the peaks $A$ to $E$.

Explain the splitting patterns of the spectrum.
Explanation of splitting patterns

(Total for Question 24 = 23 marks)

TOTAL FOR SECTION C = 23 MARKS
TOTAL FOR PAPER = 90 MARKS
The Periodic Table of Elements

<table>
<thead>
<tr>
<th>1</th>
<th>2</th>
<th>Key</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>H</td>
<td>hydrogen 1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>(1)</th>
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<th>(3)</th>
<th>(4)</th>
<th>(5)</th>
<th>(6)</th>
<th>(7)</th>
<th>(8)</th>
<th>(9)</th>
<th>(10)</th>
<th>(11)</th>
<th>(12)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
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<td>6.9</td>
<td>Be</td>
<td>4.0</td>
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<td>23.0</td>
<td>Mg</td>
<td>24.3</td>
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<tr>
<td>lithium</td>
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<td>3</td>
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</tr>
<tr>
<td>K</td>
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<td>39.1</td>
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<td>Ti</td>
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<td>V</td>
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<td>vanadium</td>
<td>23</td>
<td>chromium</td>
<td>24</td>
</tr>
<tr>
<td>Rb</td>
<td>85.5</td>
<td>37</td>
<td>Sr</td>
<td>87.6</td>
<td>Zr</td>
<td>91.2</td>
<td>Nb</td>
<td>92.9</td>
<td>Mo</td>
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<td>Ru</td>
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<tr>
<td>rubidium</td>
<td>37</td>
<td>strontium</td>
<td>87</td>
<td>yttrium</td>
<td>89</td>
<td>zirconium</td>
<td>92</td>
<td>niobium</td>
<td>93</td>
<td>molybdenum</td>
<td>94</td>
</tr>
<tr>
<td>Cs</td>
<td>132.9</td>
<td>55</td>
<td>Ba</td>
<td>137.3</td>
<td>La*</td>
<td>138.9</td>
<td>Hf</td>
<td>178.5</td>
<td>Ta</td>
<td>180.9</td>
<td>W</td>
</tr>
<tr>
<td>caesium</td>
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<td>tantalum</td>
<td>73</td>
<td>tungsten</td>
<td>74</td>
</tr>
</tbody>
</table>

Elements with atomic numbers 112-116 have been reported but not fully authenticated.