Past-paper walk-through

Colour of complexes ▪ 28.3

eXercise

Questions in this set

- 9701/41 N25 Q5 ▪ 14 marks
- 9701/42 N25 Q5 ▪ 15 marks
- 9701/44 N25 Q1 ▪ 19 marks

Reading the mark scheme

- **B1** a mark that stands on its own – the point is either made or not.
- **M1** a *method* mark: the right approach, even if the number is wrong.
- **A1** an *answer* mark, and it usually needs its M mark first.
- **C1** a working mark on the way to the answer.
- // separates answers the examiner accepts equally.
- **ecf** = error carried forward: a later part is marked on your own earlier answer.
- **owtte** = "or words to that effect" – the wording need not match.

Question 5

9701/41 N25 ▪ Q5 ▪ 14 marks

5 **(a)** Copper shows typical properties of transition elements, including its behaviour as a catalyst.

Complete Table 5.1 to show the total number of **unpaired** electrons in the 3d and 4s orbitals of an isolated gaseous Cu atom and a Cu^{2+} ion.

Table 5.1

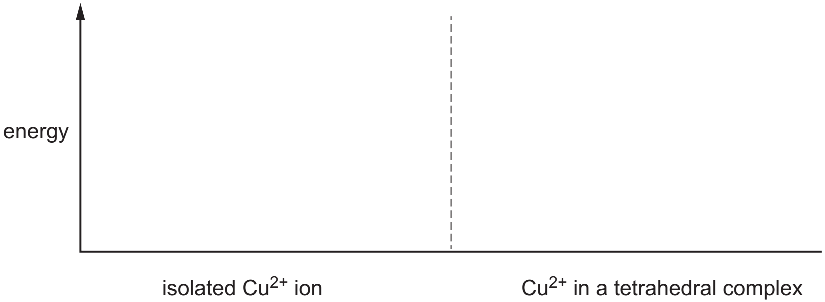
species	number of **unpaired** electrons	
	3d	4s
Cu		
Cu^{2+}		

[1]

(b) The 3d orbitals in an isolated Cu^{2+} ion are degenerate.

Question 5

Complete the diagram to show the relative energies of the 3d orbitals in an isolated Cu^{2+} ion and in Cu^{2+} in a tetrahedral complex.



[2]

(c) Explain why transition elements behave as catalysts.

Question 5

(d) CN^- is a monodentate ligand.

Table 5.2 shows information about two complex ions that contain only CN^- ions as ligands.

Complete Table 5.2.

Table 5.2

metal ion	coordination number	formula of complex ion	charge of complex ion
Ag^+	2		
Fe^{2+}			4–

[2]

(e) The complex ion $[Au(CN)_2Br_2]^-$ displays geometrical (cis / trans) isomerism.

Draw the structure of *trans*-$[Au(CN)_2Br_2]^-$. State its shape and the Br-Au-Br bond angle.

Question 5

Draw the structure of *trans*-$[Au(CN)_2Br_2]^-$. State its shape and the Br–Au–Br bond angle.

Question 5

[2]

(f) An impure sample of a vanadium(V) compound of mass 0.250 g is dissolved in aqueous acid. This solution contains VO_3^- ions.

An excess of zinc is added to this solution. All the VO_3^- ions are reduced to V^{2+} ions and Zn atoms are oxidised to Zn^{2+} ions.

The unreacted zinc is removed and the resulting solution is titrated with acidified MnO_4^-.

The end-point is reached when 22.5 cm^3 of 0.0750 mol dm^{-3} MnO_4^- is added.

A redox reaction takes place and all the V^{2+} reacts forming VO_3^-.

$$3MnO_4^- + 5V^{2+} + 3H_2O \rightarrow 3Mn^{2+} + 5VO_3^- + 6H^+$$

(i) Calculate the percentage by mass of vanadium in the 0.250 g of impure sample.

Assume the impurities do not contain any vanadium ions.

Question 5

Question 5

Show your working.

Question 5

(ii) Complete the equation for the reaction between acidified VO_3^- ions and Zn metal.

Question 5

[2]

[Total: 14]

Solution 5

(a)

Mark scheme

- 1

Solution 5

(b) Mark scheme

- ▪
- five 3d orbitals (lines, boxes) in the isolated Cu2+ ion of the same energy
- ▪
- splitting: three higher and two lower d orbitals
- ▪
- energy of all five d orbitals in complex higher than all d orbitals in isolated ion
- any two [1], all three [2]
- 2

Solution 5

(c)

Mark scheme

- M1: more than one (stable) oxidation state / exist in variable oxidation states
- M2: vacant / empty (d) orbitals are energetically accessible
- OR vacant / empty (d) orbitals can form dative bonds with ligands
- 2

Solution 5

(d)

Mark scheme

- each row [1]
- 2
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Solution 5

(e)

Mark scheme

- M1:
- M2: (shape) square planar AND (bond angle) 180o
- 2

Solution 5

(f)(i)

Mark scheme

- M1: moles MnO4– $= 0.075 \times 0.0225 = 1.6875 \times 10–3$
- M2: moles V2+ $= 5\,/\,3 \times 1.6875 \times 10–3 = 2.8125 \times 10–3$
- M3: mass V $= 50.9 \times 2.8125 \times 10–3 = 0.143\,\text{g}$
- % of V $= 0.143\,/\,0.250 \times 100 = 57.3$ min 2sf
- 3

Solution 5

(f)(ii)

Mark scheme

- $2VO3– + 3Zn + 12H+ \rightarrow 2V2+ + 3Zn2+ + 6H2O$
- M1: 2 : 3 ratio on both sides
- M2: rest of the equation correct
- 2

Question 5

9701/42 N25 ▪ Q5 ▪ 15 marks

5 Cobalt is a transition element which forms compounds containing Co^{2+} and Co^{3+} ions. Cobalt(II) sulfate dissolves in water to form a solution containing the $[Co(H_2O)_6]^{2+}$ complex ion.

(a) **(i)** Complete the electronic configurations of a Co^{2+} ion and a Co^{3+} ion.

Question 5

Question 5

[1]

(ii) Explain why transition elements can form complex ions.

Question 5

(iii) An excess of concentrated HCl is added to a solution containing $[Co(H_2O)_6]^{2+}$.

Describe the colour change observed and the state of the cobalt-containing product.

Question 5

Question 5

[2]

(iv) Write an equation for the reaction occurring in **(a)(iii)**.

Question 5

(v) Name the type of reaction occurring in **(a)(iii)**.

Question 5

(vi) Write an equation for the reaction that occurs when an excess of NaOH(aq) is added to a solution containing $[Co(H_2O)_6]^{2+}$.

Question 5

(b) Cobalt metal can be oxidised by acidified $K_2Cr_2O_7$. The relevant half-equations, and their $E^\ominus$ values, are shown.

$$Co^{2+} + 2e^- \rightleftharpoons Co \qquad E^\ominus = -0.28\,V$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O \qquad E^\ominus = +1.33\,V$$

(i) A Co^{2+}/Co electrode is constructed in which $[Co^{2+}]$ is 0.020 mol dm^{-3} at 298 K.

Use the Nernst equation to show that the E value for this Co^{2+}/Co electrode is –0.33 V.

Question 5

[2]

(ii) An electrochemical cell is constructed using the Co^{2+}/Co electrode described in **(b)(i)** and a $Cr_2O_7^{2-}/Cr^{3+}$ electrode in which all conditions are standard.

Calculate the value of E_{cell}.

Question 5

(iii) A current is drawn from the electrochemical cell described in **(b)(ii)**.

Write an equation for the reaction taking place in the cell.

Question 5

(iv) Complete the sentences to identify the negative electrode and the direction of electron flow when a current is drawn from the cell described in **(b)(ii)**.

Question 5

[1]

(c) A molten Co^{2+} salt is electrolysed using a current of 0.500 A.

0.547 g of cobalt metal forms at the cathode. Under the conditions used no other reduction reaction occurs at the cathode.

Calculate the time in minutes for which the current flows to produce this mass of cobalt.

Give your answer to **three** significant figures.

Question 5

[Total: 15]

Solution 5

(a)(i)

Mark scheme

- $Co2+ = [Ar]$ 3d7 AND $Co3+ = [Ar]$ 3d6
- 1

(a)(ii)

Mark scheme

- has vacant d orbitals that are energetically accessible
- 1

Solution 5

(a)(iii) Mark scheme

- ▪
- pink
- ▪
- blue
- ▪
- aqueous
- Any two [1], all three [2]
- 2

Solution 5

(a)(iv)

Mark scheme

$Co(H_2O)_6$ 2+ + 4HCl → [CoCl4]2– + 6H2O + 4H+ OR [Co(H2O)6]2+ + 4Cl– → [CoCl4]2– + 6H2O

- 1
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Solution 5

(a)(v)

Mark scheme

- ligand exchange
- 1

Solution 5

(a)(vi)

Mark scheme

$Co(H_2O)_6^{2+} + 2OH^- \rightarrow Co(OH)_2(H_2O)_4 + 2H_2O$ OR

$Co(H_2O)_6^{2+} + 2OH^- \rightarrow Co(OH)_2 + 6H_2O$

- 1

Solution 5

(b)(i)

Mark scheme

- M1: Nernst equation E = Eo + (0.059 / z) × log([oxidised]
reduced)
- M2: E = –0.28 + (0.059 / 2) × log(0.02)
- 2

Solution 5

(b)(ii)

Mark scheme

- 1.66 V
- 1

(b)(iii)

Mark scheme

- $3\mathrm{Co} + \mathrm{Cr2O72}– + 14\mathrm{H}+ \rightarrow 3\mathrm{Co2}+ + 2\mathrm{Cr3}+ + 7\mathrm{H2O}$
- 1

Solution 5

(b)(iv)

Mark scheme

- Co^{2+} / Co, Co^{2+} / Co, $Cr_2O_7^{2-} / Cr^{3+}$
- 1

Solution 5

(c)

Mark scheme

- M1: moles of cobalt $= 0.547 \,/\, 58.9 = 0.00929$
- M2: coulombs required $= 0.00929 \times 96500 \times 2 = 1792$
- M3: time required $= 1792 \,/\, 0.50 = 3584.8\,\text{s} = 59.7$ minutes 3sf
- 3

Question 1

9701/44 N25 ▪ Q1 ▪ 19 marks

1 **(a)** Define a transition element.

Question 1

(b) The 3d orbitals in an isolated gaseous Cu^{2+} ion are degenerate.

(i) Define the term degenerate.

Question 1

(ii) Complete the electronic configuration of Cu^{2+}.

Question 1

(c) **(i)** State the colours of the aqueous solutions for the **two** copper(II) complex ions shown.

Question 1

Question 1

[1]

(ii) Explain why aqueous complex ions of transition elements are usually coloured.

Question 1

(d) (i) When an excess of NH_3(aq) is added to a solution of $[CuCl_4]^{2-}$(aq), $[Cu(NH_3)_4(H_2O)_2]^{2+}$(aq) is formed.

State the type of reaction.
Complete the equation for this reaction. State symbols are **not** required.

Question 1

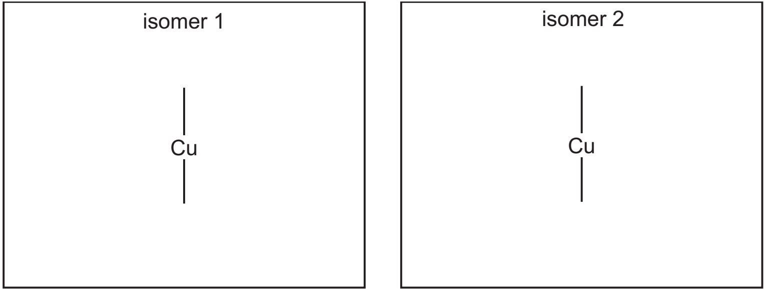
equation

Question 1

[2]

(ii) The $[Cu(NH_3)_4(H_2O)_2]^{2+}$ complex ion shows stereoisomerism.

Complete the three-dimensional diagrams in Fig. 1.1 to show the **two** different stereoisomers of $[Cu(NH_3)_4(H_2O)_2]^{2+}$.



Question 1

Fig. 1.1

Question 1

Fig. 1.1

[2]

(iii) Deduce which stereoisomer in **(d)(ii)** is polar.

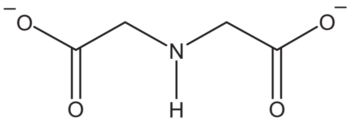
Explain your answer.

Question 1

[1]

(e) The dianion **P** can act as a tridentate ligand.

P



(i) Suggest how **P** can form **three** dative covalent bonds.

Question 1

(ii) 2 moles of dianion **P**, $C_4H_5NO_4^{2-}$, react with 1 mole of aqueous cobalt(III) ions, $[Co(H_2O)_6]^{3+}$ to form 1 mole of complex ion **Q**.

Deduce the formula and charge of **Q**.

Question 1

(f) Table 1.1 shows values for the stability constants, K_{stab}, of some silver(I) complexes.

Table 1.1

complex	value of K_{stab}
$[Ag(CN)_2]^-(aq)$	1.1×10^{18}
$[Ag(NH_3)_2]^+(aq)$	1.2×10^{7}
$[Ag(S_2O_3)_2]^{3-}(aq)$	2.9×10^{13}

(i) Define the stability constant of a complex.

Question 1

(ii) Use the information in Table 1.1 to identify the most stable silver(I) complex.

Explain your answer.

Question 1

Question 1

Question 1

[1]

(g) Sodium sulfite, Na_2SO_3, is used as a food preservative.

A 3.75 g sample of impure Na_2SO_3 is dissolved in distilled water and made up to 250 cm^3 in a volumetric flask.

10.0 cm^3 of this solution requires 18.70 cm^3 of acidified 0.0150 mol dm^{-3} $MnO_4^-(aq)$ to reach the end-point.

The equation for the reaction is shown.

$$2MnO_4^- + 5SO_3^{2-} + 6H^+ \rightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

Calculate the percentage by mass of Na_2SO_3 in the sample.

Question 1

Question 1

[Total: 19]

Solution 1

(a)

Mark scheme

- forms (one or more) stable ions / compounds / oxidation states
- with incomplete / partially filled (3)d orbital(s) / d shell / d sub-shell
- 1

Solution 1

(b)(i)

Mark scheme

- (orbitals) are at the same energy
- 1

(b)(ii)

Mark scheme

- (1s2) 2s2 2p6 3s2 3p6 3d9
- 1

Solution 1

(c)(i)

Mark scheme

H3)4(H2O)2 2+(aq) deep / dark / royal blue

- AND

CuCl4 2–(aq)

- yellow
- 1

Solution 1

(c)(ii) Mark scheme

- M1:
- d orbital(s) of different energy / d-d splitting occurs / d sub-shell splits
- M2:
- electron(s) promoted / excited
- M3:
- light / wavelength / frequency / photon absorbed AND complementary colour seen
- 3

Solution 1

(d)(i)

Mark scheme

- M1: ligand exchange / replacement / substitution / displacement
- M2: [CuCl4]2– $+$ 4NH3 $+$ 2H2O $\rightarrow$ [Cu(NH3)4(H2O)2]2+ $+$ 4Cl–
- 2

Solution 1

(d)(ii)

Mark scheme

- M1: one correct 3D structure of [Cu(H2O)2(NH3)4]2+
- M2: correct 3D stereoisomer structure of isomer 1/2

(d)(iii)

Mark scheme

- cis isomer AND dipoles do not cancel
- 1

Solution 1

(e)(i)

Mark scheme

- (two) oxygen and (one) nitrogen (can donate) three lone pair(s) of electrons (to the metal ion)
- 1
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Solution 1

(e)(ii)

Mark scheme

C4H5NO4)2 –

- 1

Solution 1

(f)(i)

Mark scheme

- equilibrium constant for the formation of the complex (ion)
- in a solvent / water / solution OR from its constituent ions or molecules
- 1

Solution 1

(f)(ii)

Mark scheme

$Ag(CN)_2^-$(aq) AND largest (value of) K_{stab}

- 1

Solution 1

(g) Mark scheme

- M1 M2: any two [1], all four [2]
-
  -
- moles MnO4– $= 0.015 \times 18.70/1000 = 2.805 \times$ 10–4
-
  -
- moles SO32– $= 2.805 \times$ 10–4 $\times 5/2 = 7.0125 \times$ 10–4 (in 10 cm3)
-
  -
- moles SO32– $= 1.753 \times$ 10–2 (in 250 cm3)
-
  -

Solution 1

- mass Na2SO3 $= 1.753 \times 10–2 \times 126.1 = 2.21$ g
- M3: % purity $= 100 \times 2.21 / 3.75 = 58.9 - 59.0$ % min 2sf
- 3