Surname	Centre Number	Candidate Number
Other Names		2

GCE A LEVEL – NEW

1410U30-1

S17-1410U30-1

CHEMISTRY – A2 unit 3
Physical and Inorganic Chemistry

TUESDAY, 13 JUNE 2017 – AFTERNOON

1 hour 45 minutes

	For Examiner's use only		
	Question	**Maximum Mark**	**Mark Awarded**
Section A	**1. to 6.**	**10**	
Section B	**7.**	**7**	
	8.	**10**	
	9.	**15**	
	10.	**11**	
	11.	**10**	
	12.	**17**	
	Total	**80**	

1410U301 01

ADDITIONAL MATERIALS

In addition to this examination paper, you will need a:
- calculator;
- **Data Booklet** supplied by WJEC.

INSTRUCTIONS TO CANDIDATES

Use black ink or black ball-point pen. Do not use gel pen or correction fluid.

Write your name, centre number and candidate number in the spaces at the top of this page.

Section A Answer **all** questions in the spaces provided.
Section B Answer **all** questions in the spaces provided.

Candidates are advised to allocate their time appropriately between **Section A (10 marks)** and **Section B (70 marks)**.

INFORMATION FOR CANDIDATES

The number of marks is given in brackets at the end of each question or part-question.

The maximum mark for this paper is 80.

Your answers must be relevant and must make full use of the information given to be awarded full marks for a question.

The assessment of the quality of extended response (QER) will take place in **Q.8***(b)*.

If you run out of space, use the additional page(s) at the back of the booklet, taking care to number the question(s) correctly.

SECTION A

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

1. When aqueous iodide ions are added to an aqueous solution of lead(II) nitrate, a precipitate is formed.

(a) Give the colour of the precipitate. [1]

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(b) Write an **ionic** equation for the reaction that occurs, including state symbols. [1]

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2. Give an example of a transition metal used as a catalyst. You should name the metal and identify the reaction it catalyses. [1]

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3. Calcium chloride, $CaCl_2$, is soluble in water. Use the values below to explain why this is the case. [2]

Equation 1 $Ca^{2+}(g) + 2Cl^-(g) \longrightarrow CaCl_2(s)$ $\Delta H^\theta = -2237\ \text{kJ mol}^{-1}$

Equation 2 $Ca^{2+}(g) + 2Cl^-(g) + aq \longrightarrow CaCl_2(aq)$ $\Delta H^\theta = -2378\ \text{kJ mol}^{-1}$

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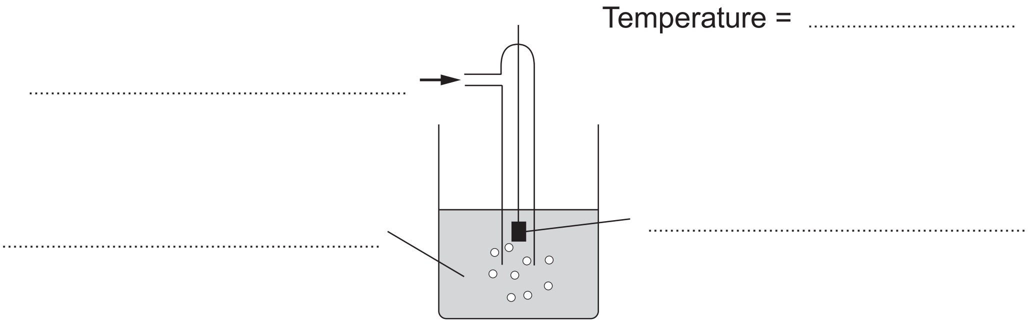
4. Label the diagram of the standard hydrogen electrode below, including all relevant conditions. [2]



5. Reaction rates can be measured using an iodine clock reaction. The data below shows the results obtained by a student in an iodine clock experiment. The concentration of iodide ions was the only difference between the experiments.

Concentration of iodide, [I$^-$] / mol dm^{-3}	Time taken for colour change / s				Mean time taken / s
	1st run	2nd run	3rd run	4th run	
0.200	35	46	36	34	
0.400	18	17	18	17	

(a) Complete the table with appropriate values of mean time taken. [1]

(b) Calculate the rate of reaction for these two concentrations. [1]

Rate for 0.200 mol dm^{-3} [I$^-$] = ... s^{-1}

Rate for 0.400 mol dm^{-3} [I$^-$] = ... s^{-1}

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6. Place the following substances in order of increasing entropy under standard conditions. [1]

nitrogen gas copper metal water air

Lowest .... *Highest*

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SECTION B

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

7. *(a)* Ammonia is an example of a weak base. Describe what is meant by the term *weak base*. [1]

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(b) A mixture of ammonia and ammonium chloride in aqueous solution can be used as a basic buffer solution. Explain what is meant by a *buffer solution* and how this mixture can act as a buffer solution. [3]

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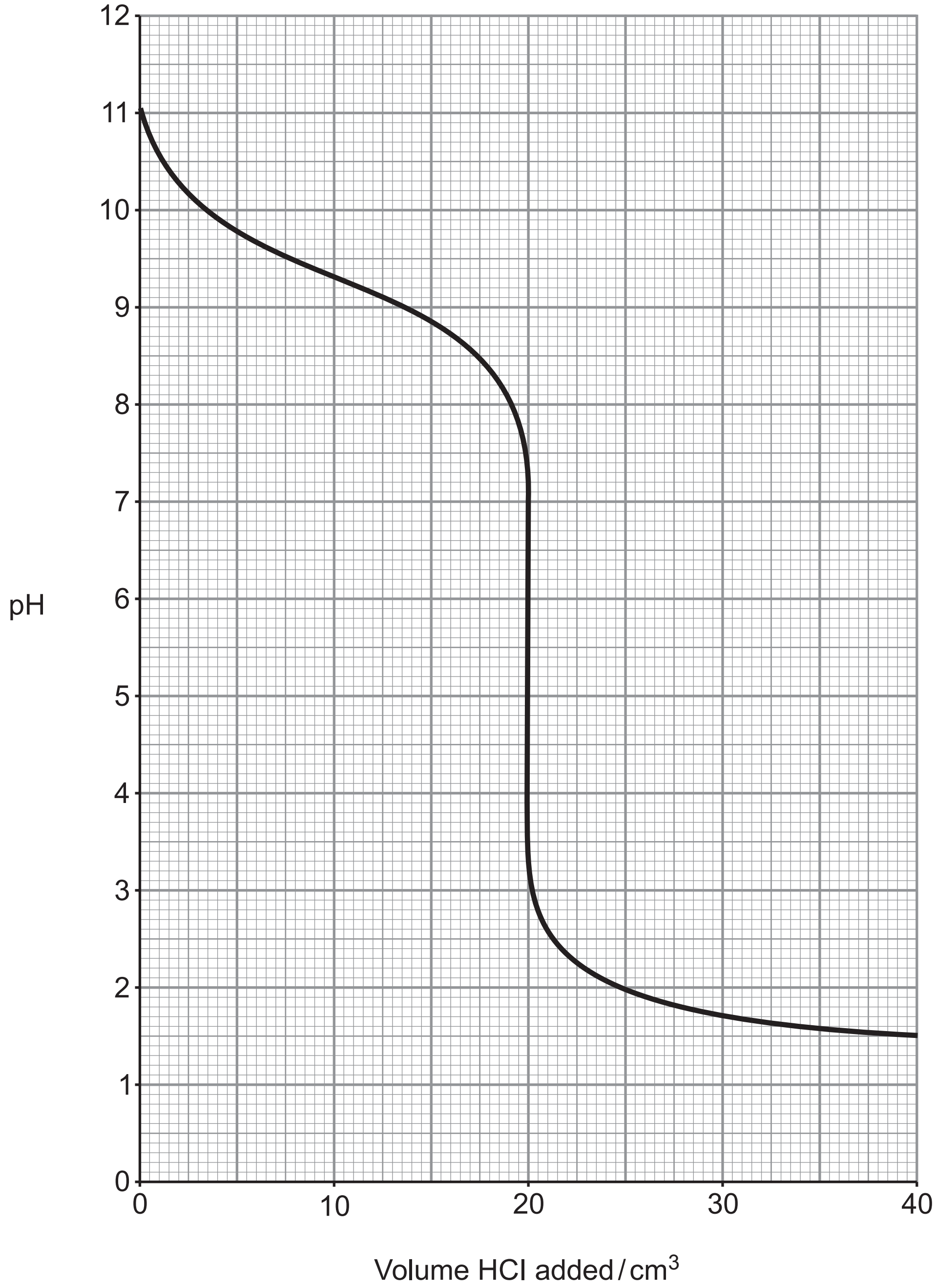
(c) The pH curve for titration of a solution of ammonia against hydrochloric acid of an equal concentration is given below.



(i) Calculate K_a for the ammonium ion. [2]

K_a = ... mol dm^{-3}

(ii) Select an appropriate indicator for this titration from the list below, giving a reason for your answer. [1]

Indicator	pH range
bromothymol blue	6.0 – 7.6
4-nitrophenol	5.0 – 7.0
methyl yellow	2.9 – 4.0
phenolphthalein	8.2 – 10.0

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8. *(a)* Some elements in the *p*-block form compounds where the *p*-block atom does not have eight electrons in its outer shell.

(i) Explain why nitrogen can only form a chloride with eight outer shell electrons, but phosphorus can form a chloride with a different number of outer shell electrons. [2]

You should give the chemical formulae of relevant compounds in your answer.

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(ii) Explain why aluminium forms compounds that are electron deficient. Show how one of these compounds can act to gain a full outer shell. [2]

You should give the dot and cross diagrams of the electron deficient species.

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(b) Below is some information about the oxides of two Group 4 elements.

Carbon	There are two common oxides of carbon. Carbon dioxide is an acidic oxide and carbon monoxide can be used as a reducing agent. Both of these are gases with very low boiling temperatures.
Lead	There are two common oxides of lead. Lead(II) oxide is an amphoteric oxide and lead(IV) oxide can be used as an oxidising agent. Both of these are solids that exhibit a large degree of ionic character.

Explain the differences between the oxides of carbon and lead, giving chemical equations to illustrate their acid/base and redox properties. [6 QER]

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9. The reversible reaction shown below was one of the first to be studied in detail in the gas and liquid phases and in solution.

$$N_2O_4 \rightleftharpoons 2NO_2$$

(a) One study of the liquid mixture showed that it contained 0.714 % NO_2 by mass. Calculate how many moles of NO_2 would be present in 25.0 g of this liquid. Give your answer to an appropriate number of significant figures. [2]

n(NO_2) = ... mol

(b) Both N_2O_4 and NO_2 are soluble in a range of solvents and the equilibrium constant, K_c, can be measured in these.

(i) Give the expression for the equilibrium constant, K_c, for this equilibrium, giving its unit if any. [2]

K_c =

Unit = ...

(ii) The equilibrium constants for the N_2O_4/NO_2 equilibrium measured at room temperature in some different solvents are listed below.

Solvent	Equilibrium constant, K_c (Unit not shown)
CS_2	17.8
CCl_4	8.05
$CHCl_3$	5.53
C_2H_5Br	4.79
C_6H_6	2.03
$C_6H_5CH_3$	1.69

I. Samples of 0.4000 mol of N_2O_4 are dissolved separately in 1 dm^3 of each of these solvents at room temperature and the reactions allowed to reach equilibrium. In one solution the concentration of N_2O_4 present at equilibrium is 5.81×10^{-2} mol dm^{-3}. Find the value of the equilibrium constant in this solution and hence identify the solvent. [3]

Solvent ....

II. The Gibbs free energy change, ΔG, of this reaction is different in different solvents. Explain how the data shows this and state, with a reason, which solvent would have the most negative ΔG value for this reaction. [2]

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(c) Nitrogen dioxide is used in the production of nitric acid. It is produced in two stages.

Stage 1 $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ $\Delta H^\theta = -900\ \text{kJ mol}^{-1}$

Stage 2 $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$ $\Delta H^\theta = -115\ \text{kJ mol}^{-1}$

(i) Explain why the use of a catalyst is essential in industrial processes involving exothermic equilibria such as stage 1. [2]

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(ii) A student attempted to perform stage 2 using a temperature of 450 K and a pressure of 5 atm. He obtained only a small yield. Suggest how the yield could be improved, explaining your reasons. [4]

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10. Aqua regia is an acidic liquid that can dissolve unreactive metals such as gold. It can be formed by bubbling hydrogen chloride gas through concentrated nitric acid.

$$HNO_3(l) + 3HCl(g) \longrightarrow NOCl(g) + Cl_2(g) + 2H_2O(l) \qquad \Delta H^\theta = -69\ kJ\ mol^{-1}$$

Substance	Standard enthalpy change of formation, $\Delta_f H^\theta$ / kJ mol^{-1}	Standard entropy, S^θ / J K^{-1} mol^{-1}
$HNO_3(l)$	−173	156
$HCl(g)$		187
$NOCl(g)$	53	264
$Cl_2(g)$	0	223
$H_2O(l)$	−286	70

(a) Show that this is a redox reaction. [1]

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(b) State why the enthalpy change of formation of $Cl_2(g)$ is zero. [1]

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(c) Calculate the standard enthalpy change of formation of $HCl(g)$. [2]

$\Delta_f H^\theta$ = ... kJ mol^{-1}

(d) (i) Calculate the free energy change, ΔG^{θ}, for this reaction at 25 °C. [3]

ΔG^{θ} = ... kJ mol^{-1}

(ii) An alternative method of preparing aqua regia is to use concentrated hydrochloric acid with concentrated nitric acid. State, giving a reason, the effect of this on the value of ΔG^{θ} at 25 °C. [1]

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(e) (i) The pH of a dilute solution of nitric acid is measured using a pH probe and has a value of 0.3. Calculate the concentration of this solution. [1]

Concentration = ... mol dm^{-3}

(ii) An alternative way of measuring the concentration of the solution is by titration against a standard solution of sodium hydrogencarbonate of concentration 0.500 mol dm^{-3}.

State and explain which of these two methods will give the more precise value for the concentration. [2]

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11. A hydrated compound $M_aAl_bZ_c.dH_2O$ contains an *s*-block metal ion, M, and a halide ion, Z.

The following tests were undertaken.

Test	Result
Heating to constant mass	A 0.0200 mol sample lost 1.44 g when heated
Adding concentrated sulfuric acid	Observations included coloured fumes, an orange-brown solution, steamy fumes and a choking gas; there was no smell of rotten eggs
Adding excess silver nitrate to a solution	A 25.0 cm^3 sample of a solution of concentration 0.203 mol dm^{-3} produced a precipitate with a dry mass of 3.814 g
Adding excess sodium hydroxide to a solution	A white precipitate formed which dissolved in excess sodium hydroxide
Elemental analysis	The hydrated compound was found to contain 1.63 % by mass of *s*-block metal and 6.34 % by mass of aluminium

(a) Calculate the value of *d* in the formula $M_aAl_bZ_c.dH_2O$. [2]

d = ...

(b) (i) Identify the halide present in the compound, explaining fully all observations that led to your conclusion. [2]

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Examiner only

(ii) Calculate the value of c in the formula $M_aAl_bZ_c.dH_2O$. [2]

c = ...

(c) State what the observations with sodium hydroxide indicate about the acidity/basicity of the aluminium ions. [1]

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(d) The M_r of the original **hydrated** compound is 425.62. Use all the information above to find the formula of the hydrated compound. Explain your reasoning. [3]

Formula of the **hydrated** compound ....

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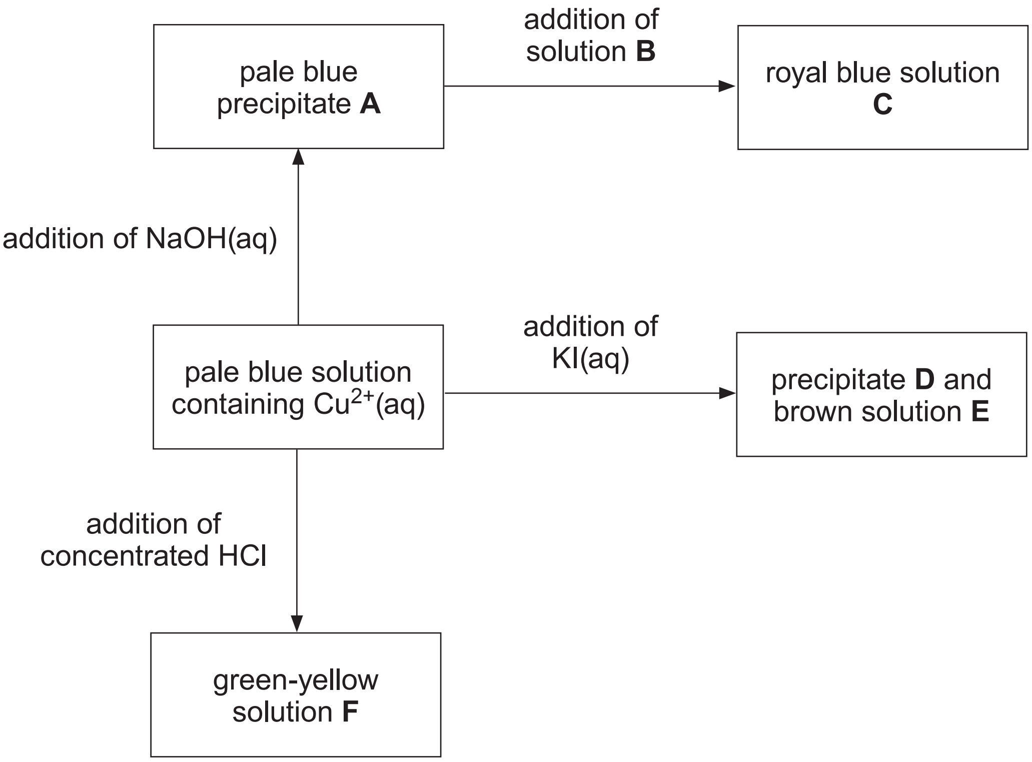
Turn over.

12. *(a)* The diagram below shows some reactions of copper(II) ions in solution.



Identify the species present in each of the following. [3]

A ....

B ....

C ....

D ....

E ....

F ....

(b) Vanadium exhibits the properties of a typical transition element, such as having variable oxidation states and forming coloured complexes. Explain why transition elements have variable oxidation states. [1]

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(c) Blue oxovanadium(IV) cations, VO^{2+}, can be oxidised to yellow oxovanadium(V) ions, VO_2^+, by bromate(V) ions, BrO_3^-.

	Standard electrode potential, E^θ / V
$VO_2^+ + 2H^+ + e^- \rightleftharpoons VO^{2+} + H_2O$	+1.00
$Br_2 + 2e^- \rightleftharpoons 2Br^-$	+1.09
$BrO_3^- + 6H^+ + 6e^- \rightleftharpoons Br^- + 3H_2O$	+1.44

Use these standard electrode potentials to identify the main bromine-containing product formed when excess bromate(V) ions are added to a solution containing VO^{2+} ions. Give reasons for your answer. [3]

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Turn over.

(d) The effect of the concentration of H^+ ions on the rate of the reaction in part *(c)* was studied using the same concentrations and volumes of all other reactants. The following data were collected.

pH	Rate / mol dm^{-3} s^{-1}
1.0	3.287×10^{-3}
1.4	1.308×10^{-3}
1.8	5.193×10^{-4}
2.2	2.071×10^{-4}

Find the order of the reaction with respect to H^+. You **must** show your working. [3]

Order with respect to H^+ = ...

(e) The value of the rate constant, *k*, for this reaction at two temperatures is given below.

Temperature / K	Rate constant (unit not shown)
288	0.0761
300	0.2873

The activation energy for this reaction is 79.333 kJ mol^{-1} and the Arrhenius equation is:

$$k = Ae^{-\left(\frac{E_a}{RT}\right)}$$

Calculate the value of the rate constant, *k*, at a temperature of 295 K. [4]

k at 295 K = ...

(f) VO^{2+} ions may also be oxidised to VO_2^{+} ions using coloured Ce^{4+}, which is itself reduced to colourless Ce^{3+}. A titration using this reaction does not usually include an indicator and colorimetry is sometimes used.

State why an indicator may not be useful in this reaction and explain how colorimetry can be used to find the end point of the titration. [3]

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