THE COLLEGE OF THE BAHAMAS



EXAMINATION

SEMESTER 01-2012

FACULTY OF PURE AND APPLIED SCIENCES

SCHOOL OF CHEMISTRY, ENVIRONMENTAL & LIFE SCIENCES

X NASSAU X FREEPORT EXUMA ELEUTHERA

DATE AND TIME OF EXAMINATION: 9:00 am Monday 23rd April 2012 in rooms F1, F2 and F3 **DURATION: 3 HOURS**

COURSE NUMBER: CHEM 225

COURSE TITLE: COLLEGE CHEMISTRY II

STUDENT NAME:

STUDENT NUMBER:

LECTURER'S NAME

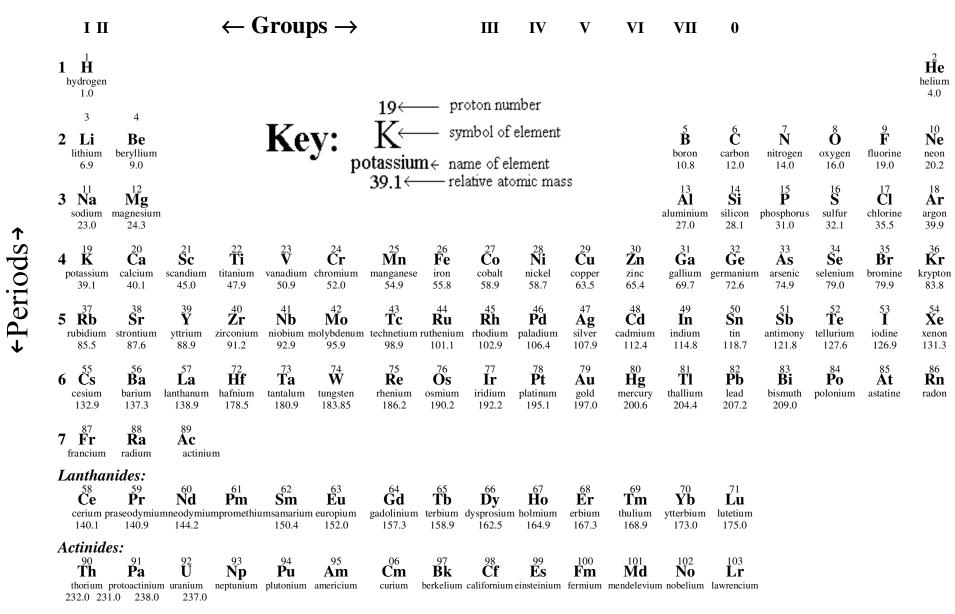
INSTRUCTIONS TO CANDIDATES: This paper has 14 pages and 3 sections. Please follow the instructions given with each section. There is a total of 100 marks for the paper.

Information for students

PV=nRTR=0.0821 L atm mol⁻¹K⁻¹ = 8.31 J mol⁻¹ K⁻¹ = 8.31 Pa m³ mol⁻¹ K⁻¹ Avogadro's number, L = 6.02×10^{23} mol⁻¹ Faraday's constant, F = 96 500 C mol⁻¹

CHEMISTRY 225 FINAL EXAMINATION SEMESTER 01-2012 CONTINUED

PERIODIC TABLE OF THE ELEMENTS



Note: relative atomic masses are omitted for highly unstable elements.

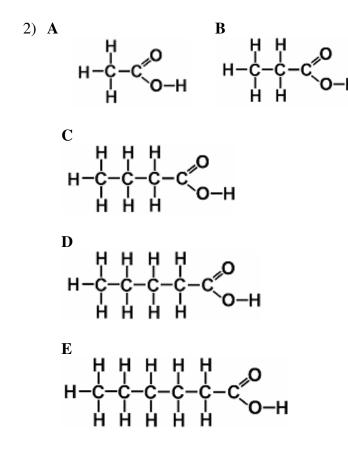
SECTION I: Multiple Choice Questions

Select the SINGLE best alternative in each of the following cases and indicate your answer by marking the corresponding letter on the answer sheet provided. You may place any working on these pages if you wish. It will not be considered during marking.

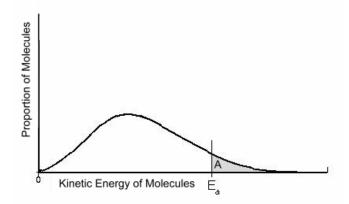
Do not spend more than $1\frac{1}{2}$ minutes on any question in this section: if the question takes more time, guess the answer and mark the question for later consideration if time allows.

There is a total of 40 marks for this section.

- Questions 1) and 2) concern various acids. Using the rules that relate acid strength to structure, pick the strongest acid in each case.
- 1) **A** HClO **B** HClO₂ **C** HClO₃ **D** HClO₄ **E** HBrO



Questions 3) and 4) involve the following graph showing the kinetic energy of the molecules involved in a reaction:



- 3) The area A represents the proportion of:
 - A molecules with at least the activation energy.
 - B molecules with exactly the activation energy.
 - C molecules with less than the activation energy.
 - D slow-moving molecules.
 - E average-speed molecules.

- 4) Upon the introduction of a catalyst, the shaded area A
 - A is increased.
 - B is decreased.
 - C is unaffected
 - D is increased by homogeneous catalysts only.
 - E is decreased by heterogeneous catalyst only.

5) The reaction between propanone and iodine in acidified aqueous solution is described by the following equation:

$$CH_{3}COCH_{3}(aq) + I_{2}(aq) + H^{+}(aq)$$

$$\rightarrow CH_{2}ICOCH_{3}(aq) + 2H^{+}(aq) + I$$

(aq)

The reaction is also found to be first order with respect to both propanone and hydrogen ion, but zero order with respect to iodine. If the concentration of the reactants is doubled, the rate is

- A doubled.
- B tripled.
- C quadrupled.
- D multiplied by $\frac{1}{2}$.
- E multiplied by $\frac{1}{4}$.
- 6) The rate of a chemical reaction depends strongly on temperature. Which statement best explains this observation?
 - A At high temperatures the activation energy of the reaction is lower.
 - B At high temperatures almost all molecules are present as activated complexes.
 - C At high temperatures the concentrations of reactants is higher.
 - D At high temperatures the partial pressures of the reactants are higher.
 - E At high temperatures a much larger proportion of molecules have sufficient energy to react.
- 7) Solutions of magnesium sulphate in water are weakly acidic because:
 - A Water molecules bound to the magnesium ion lose protons more readily than free water molecules.
 - B Sulphuric acid is not a very strong acid.
 - C The second proton of sulphuric acid is lost with some difficulty.
 - D Magnesium ions react readily with protons.
 - E Such solutions are usually impure.

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- The K_b value for a certain base X⁻ is 10⁻⁶ at 25°C. The K_a value for HX at the same temperature is therefore:
 - A 10⁻⁸
 - B 10⁻⁶
 - C 10^{6}
 - D 10^8
 - E 6
- 9) The decomposition of dinitrogen pentoxide in tetrachloromethane solution (tcm) may be represented by the equation:

 $2N_2O_5(tcm) \rightarrow 4NO_2(tcm) + O_2(g)$ The nitrogen dioxide is soluble in

tetrachloromethane whilst the oxygen is not. Measurement of which physical property could most easily be used for determining the rate of this reaction?

- A Electrical conductivity of the solution.
- B Volume of oxygen evolved.
- C pH of the solution.
- D Total mass of reactants and products.
- E Volume of the solution.
- 10) The experimentally determined rate equation for the reaction represented by the equation: $BrO_3(aq) + 5Br(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) +$

 $3H_2O(aq)$

- is rate = $k[BrO_3^{-}][Br^{-}][H^{+}]^2$ The units of the rate constant are:
- A Ms^{-1}
- $\begin{array}{c} \mathbf{A} \quad \mathbf{MS} \\ \mathbf{B} \quad \mathbf{s}^{-1} \end{array}$
- $C M^{-1}s^{-1}$
- $\begin{array}{c} \mathbf{D} \quad \mathbf{M}^{-2}\mathbf{s}^{-1} \\ \mathbf{D} \quad \mathbf{M}^{-2}\mathbf{s}^{-1} \end{array}$
- $E M^{-3}s^{-1}$
- 11) At a certain temperature the partial pressures of carbon monoxide, chlorine and carbon oxide dichloride in the equilibrium mixture defined by the equation:

 $CO(g) + Cl_2(g) \Rightarrow COCl_2(g)$

carbon oxide dichloride were 2, 4 and 48 atm respectively. What is the value of K_p ?

- A 0.167
- B 6
- C 24
- D 54
- E 86
- 12) Consider the following system at equilibrium: $CaCO_3(s) \Rightarrow CaO(s) + CO_2(g) \qquad \Delta H + ve$ Which operation would displace the equilibrium position to the right?
 - A Adding more $CaCO_3$ to the system.
 - B Adding more CaO to the system.
 - C Increasing the partial pressure of CO₂.
 - D Heating the system.
 - E Adding an inert gas at constant volume. (Assume ideal behaviour.)

- 13) Which one of the following changes the value of the *equilibrium constant* for a reaction?
 - A Reducing the pressure of the reaction mixture.
 - B Increasing the volume of the reaction mixture.
 - C Increasing the concentration of reactants.
 - D Reducing the temperature of the system.
 - E Removing one of the products.
- 14) Given that the K_a values of the following five acids decrease in the order: HI > HCl > $C_6\text{H}_5\text{COOH} > \text{CH}_3\text{COOH} > \text{HPO}_4^{2-}$, which salt is expected to give the highest pH value when in 0.1 M solution?
 - A NaCl
 - B NaI
 - C C₆H₅COONa
 - D CH₃COONa
 - E Na₃PO₄
- 15) Which statement regarding the ionic product of water (K_w) is **NOT** true?
 - A K_w is the equilibrium constant for the reaction:

 $2H_2O(l) \Rightarrow H_3O^+(aq) + OH^-(aq)$

- B K_w is decreased by the addition of an acid to an aqueous solution.
- C K_w is altered by a change in temperature.
- D K_w is constant for any dilute aqueous solution at constant temperature.
- E K_w is approximately 10^{-14} at 25°C.
- 16) A certain weak monoprotic acid has a pK_a value of 4.8. What is the pH of a buffer solution containing 0.2 mol of the weak acid, together with 0.2 mol of the sodium salt of the acid, all dissolved in 250cm³ of water?
 - A 2.8
 - B 3.8
 - C 4.8
 - D 5.8
 - E 6.8
- 17) Which statement regarding a 10⁻⁸M solution of hydrochloric acid in water is correct?
 - A The solution is a buffer solution.
 - B The solution has a pH of 8.
 - C Such a solution cannot be prepared.
 - D The solution is very slightly acidic.
 - E The solution is extremely acidic.
- 18) Which one of the following pairs of species is an acid-base conjugate pair?
 - A H_3O^+ and OH^-
 - B CH₃NH₄⁺ and CH₃NH₂
 - C $H_2PO_4^-$ and HPO_4^2
 - D H_3PO_4 and PO_4^{3-1}
 - $E \quad CO_2 \text{ and } H_2CO_3$
- 19) Which one of the following is **NOT** a redox reaction?
 - A $SO_2 + OH^- \rightarrow HSO_3^-$
 - B $2Na + Cl_2 \rightarrow 2NaCl$
 - C $2Mg + O_2 \rightarrow 2MgO$
 - D SO₂ + $\frac{1}{2}O_2 \rightarrow SO_3$
 - $E \quad Fe + Cu^{2+} \rightarrow Cu + Fe^{2+}$

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- 20) Phenolphthalein is a better indicator for the titration of ethanoic acid with sodium hydroxide solution than is methyl orange. Which statement is the best explanation for this?
 - A Phenolphthalein gives a more vivid colour change than does methyl orange.
 - B Phenolphthalein changes colour in slightly alkaline solution.
 - C Phenolphthalein changes colour in slightly acidic solution.
 - D Methyl orange would not change colour during this titration.
 - E Methyl orange changes colour over a much greater pH range than does phenolphthalein.
- 21) $H_2PO_4^-$ has $pK_a = 7.2$ and $pK_b = 11.9$. A
 - solution of NaH₂PO₄ is therefore:
 - A Strongly basic.
 - B Weakly basic.
 - C Neutral.
 - D Weakly acidic.
 - E Strongly acidic.
- 22) The following equilibrium is established when solid lead(II) chloride is shaken with water: $PbCl_2(s) \Rightarrow Pb^{2+}(aq) + 2Cl^{-}(aq)$

If K_{sp} is the solubility product of lead chloride at 25°C, and the solubility of lead chloride is *x* mol dm⁻³ at this temperature, then:

- A $K_{sp} = 2x^2$
- **B** $K_{sp} = x^2$
- C $K_{sp} = 2x^3$
- $D \quad K_{sp} = 4x^3$
- $E \quad K_{sp} = 27x^4$
- 23) Which equation shows nitric acid acting as an oxidizing agent?
 - A $P_4O_{10} + 4HNO_3 \rightarrow 4HPO_3 + 2N_2O_5$
 - B $6Fe^{2+} + 8HNO_3 \rightarrow 6Fe^{3+} + 2NO + 4H_2O + 6NO_3^{-}$
 - $C \quad CO_3^{2-} + 2HNO_3 \rightarrow CO_2 + H_2O + 2NO_3^{--}$
 - D $HNO_3 + NaCl \rightarrow NaNO_3 + HCl$
 - $E \quad 2HNO_3 + Na_2SO_3 \rightarrow 2NaNO_3 + SO_2 + H_2O$
- 24) Given the equations:

 $S_2O_8^{2^-} + 2e^- \rightarrow 2SO_4^{2^-}$ Mn²⁺ + 4H₂O \rightarrow MnO₄⁻ + 8H⁺ + 5e⁻ which figure expresses the correct number of moles of S₂O₈²⁻ ions required to oxidize 1 mole of Mn²⁺ ions?

- A 0.4
- B 0.5
- C 1.0
- D 2.0
- E 2.5
- 25) In which compound is the oxidation number of vanadium equal to +3?
 - A VCl₄
 - B H₃VO₄
 - C H₄V₂O₇
 - D NH₄VO₃
 - E K₃VF₆

- 26) The e.m.f. of the cell: Pt $| H_2(g) | HCl(aq) || CuSO_4(aq) | Cu$
 - is **INDEPENDENT** of which one of the following?
 - A temperature
 - B concentration of hydrochloric acid
 - C concentration of copper(II) sulphate solution
 - D mass of the platinum electrode
 - E pressure of hydrogen
- 27) Standard electrode potentials for the gain of one electron by the ions Cu⁺(aq) and Cu²⁺(aq) are as follows:

Cu⁺(aq) + e⁻ \rightarrow Cu(s) $E^{\Theta} = +0.52v$ Cu²⁺(aq) + e⁻ \rightarrow Cu⁺(aq) $E^{\Theta} = +0.17v$ The standard electrode potential in volts for the reaction: 2Cu⁺(aq) \rightarrow Cu²⁺(aq) + Cu(s) is: A -0.69 B -0.35 C +0.52

- D +0.69
- E +0.35
- 28) The equilibrium constant for the reaction $A(aq) \Rightarrow B(aq)$ is 3.75×10^{-7} .

Which statement is TRUE?

- A The equilibrium concentration of A is less than that of B.
- B The equilibrium concentration of A is greater than that of B.
- C Adding a suitable catalyst will increase the equilibrium concentration of A.
- D Adding a catalyst will increase the value of the equilibrium constant.
- E Adding more A will increase the value of the equilibrium constant.

29) Consider the reaction

 $NO(g) + O_3(g) \Rightarrow NO_2(g) + O_2(g)$ The activation energy for this reaction is 10 kJ, whilst the activation energy for the reverse reaction is 210 kJ. What is the enthalpy change for the forward reaction, in kJ?

- A -200
- B -210
- C -220
- D -2000
- E -20

30) For the reaction

 $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$ the average rate with respect to the production

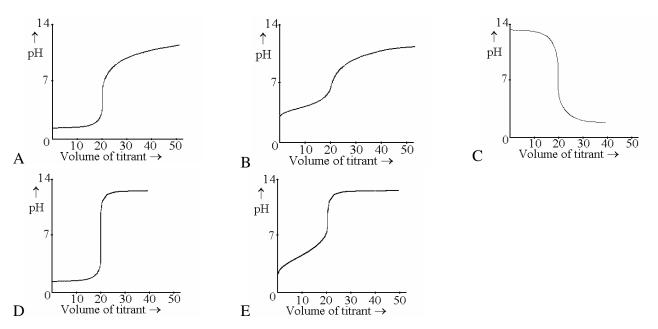
of ammonia is expressed as

$$\Delta[NH_3]$$

An expression whose value is the same is:

$$A \quad \frac{-\Delta[N_2]}{\Delta t} \qquad B \quad \frac{\Delta[H_2]}{2\Delta t}$$
$$C \quad \frac{\Delta[N_2]}{\Delta t} \quad D \quad \frac{\Delta[H_2]}{3\Delta t}$$
$$E \quad \frac{-2\Delta[N_2]}{\Delta t}$$

CHEMISTRY 225 FINAL EXAMINATION SEMESTER 01-2012 CONTINUED **Questions 31) -35).** The diagrams A to E represent titration curves for the reaction between various acids and bases.



Given that each curve may be used once, more than once or not at all, choose from A to E the curve which best represents

- 31) the titration of 20 cm^3 of 0.1M HCl with 0.1M NaOH.
- 32) the titration of 20 cm³ of 0.1M CH₃COOH with 0.1M NaOH.
- 33) the titration of 20 cm³ of 0.1M CH₃COOH with 0.1M NH₃.
- 34) the titration of 20 cm^3 of 0.1M NaOH with 0.1M HCL 35) the titration of 20 cm^3 of 0.1M HCl with 0.1M NH₃.

Questions 36) to 40) concern the following experimental situation.

Six equilibrium mixtures (1) were made up with various volumes of $0.10 \text{ M Fe}(NO_3)_2$ solution, dilute HNO₃(aq) and 0.10 M AgNO₃ (aq). The solutions were stirred for 15 minutes until a precipitate (2) formed, and then filtered into separate test tubes. 5.00 cm³ aliquots were each mixed with about 1 cm³ of 1 M Fe(NO₃)₃ (3) and titrated (4) with 0.010 M KSCN(aq). The titre values were used to calculate the concentrations of the various species present at equilibrium and hence the equilibrium constant.

- 36) The equilibrium studied, referred to in (1),
 - involves an equilibrium between
 - A NO_3^- ions, H_3O^+ ions and HNO_3 molecules.
 - R Fe^{3+} ions, SCN⁻ ions and [FeSCN]²⁺ complex.
 - C Fe^{2+1} ions, Ag^+ ions, Fe^{3+} ions and solid Ag. D Fe^{3+} ions and Fe^{2+} ions.

 - E Ag^+ ions, Fe^{2+} ions, NO_3^- ions and Ag.

37) Precipitate (2) was

- A AgNO₃
- В AgCl
- С AgSCN
- D Ag
- E Fe(SCN)₃

38) The $Fe(NO_3)_3$ (3) was added in order to

- A oxidise any silver still present to silver ions. B react with excess thiocyanate ions to form a
- coloured complex. С catalyse the reaction between titrant and
- titrand in (4). prevent the forward reaction in the D equilibrium from occurring.

- E prevent the precipitation of silver thiocyanate.
- 39) The precipitate (2) was filtered off in order to
 - A prevent the equilibrium concentration of silver ions from changing during the titration (4).
 - B make the solution clear so that the end-point in (4) could be seen more clearly.
 - С prevent solid matter interfering with the equilibrium reactions.
 - remove excess Ag⁺ ions from the solution. D
 - E collect it for weighing.
- 40) Dilute HNO₃ is added to:
 - A Form a complex with the silver ion.
 - Act as an indicator В
 - С Lower the pH at the end-point.
 - Displace equilibrium to the right. D
 - Suppress hydrolysis of the hydrated Fe³⁺ E ion.

SECTION II

Answer all questions in this section in the spaces provided on the question paper. Numerical answers must be supported by working, and, where appropriate, must be displayed to the correct number of significant figures or decimal places. Underline your final answers. There are 32 marks for this section.

1) This question concerns oxidation and reduction. (Total marks: 8) The balanced half-reaction for the reduction of $X_2O_7^{m-}(aq)$ to $X^{3+}(aq)$ (X represents an element, and m an integer) in acidified aqueous solution is

 $X_2O_7^{m-}(aq) + 14H^+(aq) + 6e^- \rightarrow 2X^{3+}(aq) + 7H_2O(l)$

a) Determine the value of m. Explain your reasoning.

b) Deduce the overall balanced net ionic equation for the reaction in which potassium chlorate, $KClO_3(aq)$, oxidizes $Mn^{2+}(aq)$ to $MnO_2(s)$ in acid solution. The chlorate ion is reduced to chlorine gas. (5 marks)

2) Fill in the blanks in the following table with the appropriate hydrolysis reaction.

(8 marks)

(3 marks)

Salt	Acid/base propertie s of aqueous solution	Hydrolysis equation
KHCO ₃	basic	
KCN	basic	
Al(NO ₃) ₂	acidic	
NH ₄ NO ₃	acidic	

3) The following question deals with chemical equilibrium. A student studied the following equilibrium system

$Fe^{3+}(aq) + SCN^{-}(aq) \Rightarrow FeSCN^{2+}(aq)$ pale yellow colourless reddish brown

which she made up by mixing 20.0 cm³ of 0.100 M Fe(NO₃)₃(aq) with 20.0 cm³ of 0.100 M KSCN(aq) diluted to 1.00 L with distilled water.

- a) What is the initial concentration (in mol dm⁻³) of the Fe³⁺ and SCN⁻ in the mixture of solutions? (1 mark)
- b) Is the equilibrium of a heterogeneous or homogeneous type?
- c) Write the expression for the equilibrium constant.
- d) Calculate the concentration of the complex (FeSCN²⁺)at equilibrium, given that the equilibrium constant for the above reaction is 891 at the temperature of the mixture. (3 marks)

e) Write a net ionic equation describing the formation of a precipitate when sodium hydroxide is added to the equilibrium mixture. (1 mark)

(1 mark)

(1 mark)

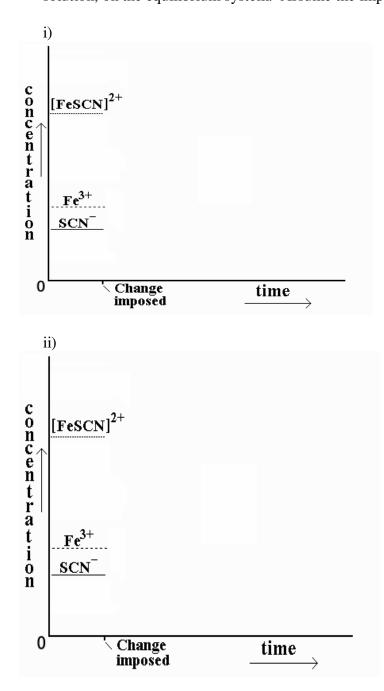
f) What colour change occurs to the remaining *solution* (the *supernatant*) as a result of adding the sodium hydroxide?

(1 mark)

g) Explain the colour change in f) above by referring to Le Chatelier's principle.

(2 marks)

h) Given that the reaction $Fe^{3+}(aq) + SCN^{-}(aq) \Rightarrow FeSCN^{2+}(aq)$ is exothermic, complete the graphs below to show the effect of (i) increasing the concentration of SCN⁻ and (ii) increasing the temperature of the solution, on the equilibrium system. Assume the imposed changes occur instantaneously. (6 marks)



SECTION III

Students' Choice

Answer TWO questions from this section in the spaces provided on the question paper. If more than two questions are answered, only the first two will be marked!

Numerical answers must be supported by working, and, where appropriate, must include units and be displayed to the correct number of significant figures or decimal places. Underline your final answers. There is a total of 28 marks for this section.

- 1) The following electrochemical cell is constructed at 25°C: $Cu(s) | Cu^{2+}(aq, 1 M) || H^{+}(aq, 1 M) || H_2(g, 1 atm) || Pt(s)$ The standard reduction potential for the Cu²⁺ | Cu couple is +0.34 v.
 - a) Write down the chemical equation which corresponds to the cell notation above. (1 mark)
 - b) Calculate the standard e.m.f. for the cell and deduce which way the above equation will proceed spontaneously. (2 marks)
 - c) Define the term "cathode". Which half-cell contains the cathode if the reaction of part (a) goes left to right. (2 marks)
 - d) Calculate the pH of the solution in the half-cell on the right. (2 marks)
 - e) Explain how the pH changes in the right-hand half cell as current is draw from the cell. (2 marks)
 - f) What does the double vertical line in the cell-notation indicate? Mention one function of this part of the cell.
 (2 marks)

(Total marks = 14)

g) If the concentration of H⁺ in the right-hand half-cell is maintained at exactly 1 M, and the supply of copper and hydrogen gas (at 1 atm) is likewise maintained constant, what is the molarity of the Cu²⁺ in the left-hand half-cell when the cell e.m.f. has declined to zero? You may use the Nernst equation,

$$E = E^{\circ} - \frac{RT}{nF} \ln Q \tag{3 marks}$$

2) This question concerns the properties of acids and bases. (Total marks = 14)

a) Hypochlorous acid (HOCl) is a weak monobasic acid whose K_a value at 25°C is 2.88×10⁻⁸.
i) By drawing up the "ICE" table, find the pH of a 0.025 M solution of HOCl at 25°C. (6 marks)

ii) How many moles of NaOCl should be added to 800cm^3 of 2.0×10^{-2} M HOCl in order to obtain a solution of pH 7.0, assuming no change in volume? (Na = 23.0, O = 16.0, Cl = 35.5). You may use the buffer equation.

$$pH = pK_a + \log \frac{C_b}{C_a}$$
(5 marks)

iii) At what pH value would an NaOCl/HOCl buffer achieve its maximum buffer capacity? (1 mark)

b) The pH of a 0.10M solution of sodium carbonate (Na₂CO₃) is 11.65 at 25°C. Calculate the concentration of the hydroxide ion. (2 marks)

3) This question concerns the reaction

 $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O(g)$

for which the following experimental rate data were collected in three experiments carried out at the same temperature. (Total marks = 14)

Experiment Number	INITIAL [NO] /M	INITIAL [H ₂] /M	INITIAL RATE OF N ₂ O FORMATION /M min ⁻¹
1	0.60	0.37	0.18
2	1.80	0.37	1.62
3	1.80	1.11	4.86

a) Derive the rate law for the reaction showing your reasoning.

b) Calculate the rate constant for the reaction.

c) Calculate the initial rate of formation of N_2O when the concentration of NO is 0.70 M, and the concentration of H_2 is 0.50 M. (2 marks)

d) Calculate the initial rate of formation of N_2O when the initial rate of consumption of NO is 2.16 M min⁻¹.

(2 marks)

(2 marks)

(3 marks)

e) The following mechanism is proposed for the above reaction:

$NO + H_2 \rightarrow NOH_2$	Slow step A	
$NOH_2 + NO \rightarrow N_2O + H_2O$	Fast step B	
Identify the rate-determining step.		(1 mark)

i) Identify the rate-determining step.

- ii) Write the rate law implied by the mechanism.
- iii) By referring to part (a) above, explain why the proposed mechanism cannot be correct. (1 mark)

iv) Describe what you would need to measure, and what factor(s) would need to be kept constant, to find the activation energy of the reaction. (2 marks)

(1 mark)