**CHEMISTRY**

**DATE:** 12 June2012

**DURATION OF THE EXAM :**

3 hours (180 minutes)

**PERMITTED MATERIAL :**

Calculator (not graphical and not programmable)

**INSTRUCTIONS :**

* Answer two A questions and two B questions.
* Indicate which four questions you have answered by putting crosses in the appropriate place on the sheet supplied.
* Use a separate answer sheet for each of the four main questions.

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| Question A1 | | **Page 1/2** |
|  | | **Marks** |
| a) | The pH of a 1.00 x 10-1 mol dm-3 aqueous solution of ammonia, A1, NH3(aq),  is equal to 11.1 at 25oC. |  |
|  | 1. Give the equation for the reaction between ammonia and water. | 2 marks |
|  | 1. Calculate the molar concentration of the three main chemical species  (apart from water) present in solution A1. | 3 marks |
|  | 1. Deduce the value of the acidity constant, *K*a, of the couple  NH4+(aq)/NH3(aq) and show that the p*K*a value of the couple equals 9.2. | 4 marks |
| b) | Solid ammonium chloride, NH4Cl(s), is added to 1.00 dm3 of solution A1.  It is assumed that the volume of the solution remains unchanged.  The pH of the solution B1 thus obtained is equal to 9.2.  Compare the molar concentrations, [NH4+(aq)] and [NH3(aq)], in solution   B1 and explain your answer. | 2 marks |
| c) | The same quantities of solid ammonium chloride are added to the same   volumes of solutions A1 and B1 to give solutions A2 and B2.  The volumes of both solutions remain constant. |  |
|  | 1. For each of the solutions A1 and B1 state and explain whether you  would expect the pH to increase or to decrease when the ammonium  chloride is added. | 2 marks |
|  | The pH of one of the solutions changes by 0.1 unit, the other by 1.3 units.   1. In each case identify the solution concerned and explain the difference in the variation in the observed pH values | 2 marks |
| d) | 1. The following four solutions, each with the same concentration of 2. 1.00 x 10-1 mol dm-3, are available in a laboratory.   W : an aqueous solution of hydrochloric acid, HCl(aq).  X : an aqueous solution of methanoic acid, HCOOH(aq).  Y : an aqueous solution of sodium methanoate, NaHCOO(aq).  Z : an aqueous solution of sodium hydroxide, NaOH(aq).    Outline two different methods, using any of W, X, Y and Z, to prepare  30.0 cm3 of a buffer solution with a pH of 3.7 at 25 oC.  Given : p*K*a of methanoic acid at 25 oC : 3.7 | 4marks |

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| Question A1 | | **Page 2/2** |
|  | | **Marks** |
| e) | The graph below shows the variation in pH as a volume *V*a of 2.00 x 10-1   mol dm-3 hydrochloric acid solution, HCl(aq), is progressively added to 40.0   cm3 of a solution of a weak monoprotic base, B, of unknown concentration at 25 oC.  pH  Graphe A1 a).jpg  *V*a / cm3  With the aid of this graph : |  |
| 1. Determine the pH at the equivalence point. | 1 mark |
| 1. Calculate the initial concentration of the solution of the weak base, B. | 3 marks |
| 1. Calculate the pKb of the base B. | 2 marks |
| **Given :** p*K*w of water at 25oC : 14.0 |  |

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| Question A2 | | **Page 1/3** |
|  | | **Marks** |
| a) | Fuel cells provide electrical energy directly from chemical reactions.    A diagram of a fuel cell is shown below.    Pile à combustible (H2 + O2 sol alcaline).jpg  **H2(g) O2(g)**  **H2O(l)**  **KOH(aq)**  In this fuel cell, hydrogen, H2(g) reacts at one electrode, whilst oxygen, O2(g)   reacts at the other electrode.  The two electrodes are separated by an aqueous solution of potassium   hydroxide, KOH(aq).  The electrodes are inert and permeable to gas.  Given :  The standard electrode potentials for the two relevant couples :   |  |  | | --- | --- | | Couples | *E*θ / V | | O2(g) / OH–(aq) | + 0.40 | | H2O(l) / H2(g) | – 0.83 | |  |
|  | 1. Explain the polarity of the electrodes as shown in the diagram. | 2 marks |
|  | 1. Give the half-equations for the reactions taking place at each electrode and the equation for the overall reaction in the cell. | 3 marks |
|  | 1. Calculate the e.m.f. of this cell operating under standard conditions. | 1 mark |

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| Question A2 | | **Page 2/3** |
|  | | **Marks** |
| b) | The hydrogen used in a fuel cell can be made by steam reforming of methane, CH4(g), according to the equation:  **CH4(g) + H2O(g) → CO(g) + 3H2(g)** |  |
|  | 1. Determine the oxidation numbers of each element in this reaction. | 3 marks |
|  | 1. Use the oxidation numbers to explain that the steam reforming of methane is a redox reaction and identify the oxidizing agent and the reducing agent. | 2 marks |
| c) | Hydrogen can also be made by the electrolysis of water. |  |
|  | 1. Give the half-equation for the reaction occurring at the negative electrode during the electrolysis of water. | 1 mark |
|  | 1. Calculate the volume of hydrogen gas that would be produced during the electrolysis of water at 25oC and a pressure of 1.01 x 105 Pa when a current of 12.0 A is passed for a period of 12 hours. | 3 marks |
|  | **Given:**  The molar volume of a gas at 25 oC and 1.01 x 105 Pa: 24.5 dm3 mol-1  1 Faraday : 9.65 x 104 C mol-1 |  |
| d) | Alternative production methods for hydrogen include the cerium oxide cycle and the iron oxide cycle.  In the cerium oxide cycle, the two reactions taking place can be represented by the (unbalanced) equations:  **CeO2(s) → Ce2O3(s) + O2(g)**  **Ce2O3(s) + H2O(g) → CeO2(s) + H2(g)** |  |
|  | 1. Balance these two equations, and hence find the overall equation for the reaction during this cycle. | 3 marks |
|  | A similar cycle exists for the Fe3O4(s)/FeO(s) system. |  |
|  | 1. Write the equations for the formation of oxygen from Fe3O4(s) and hydrogen from FeO(s) and H2O(g). | 4 marks |

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| Question A2 | | **Page 3/3** |
|  | | **Marks** |
| e) | An alternative type of fuel cell is the solid oxide fuel cell.  In this cell, the electrolyte is a solid oxide such as cerium(III) oxide, Ce2O3(s).  The reaction taking place at the positive electrode is the reduction of oxygen gas to oxide ions, O2-, (in the form of a metallic oxide). |  |
|  | 1. Give the half-equation for the reduction of oxygen.   One advantage of this type of cell is the possibility of replacing hydrogen by another fuel such as methane which can combine with oxide ions to form carbon dioxide, CO2(g) and water. | 1 mark |
|  | 1. Give the half-equation for the corresponding oxidation. | 2 marks |

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| Question A3 | | **Page 1/2** |
|  | | **Marks** |
| a) | Bromine, Br2(l) can be produced by a variety of methods   * The first method involves reacting chlorine gas, Cl2(g), with a solution of potassium bromide, KBr(aq). * A second method uses manganese(IV) oxide, MnO2(s), with a solution of potassium bromide, KBr(aq), in acidic conditions. * The third is the electrolysis of a solution of potassium bromide using platinum electrodes. Bromine is produced at the positive electrode, with a flammable gas being produced at the negative electrode. |  |
|  | 1. Give the equation for the reaction of the first method, and indicate the changes in oxidation numbers for bromine and chlorine during the reaction. | 2 marks |
|  | The second method involves the two redox couples  Br2(aq)/Br–(aq) and MnO2(s)/Mn2+(aq) |  |
|  | 1. Use these couples to write the chemical equation for the reaction, and give the changes in oxidation numbers for bromine and manganese during the reaction. | 3 marks |
|  | The table below gives the electrode potentials for the likely couples involved under the conditions experienced in the third method using the electrolysis cell.   |  |  | | --- | --- | | Couples | *E*/ V | | K+(aq) / K(s) | – 2.93 | | H2O(l) / H2(g) | – 0.41 | | O2(g) / H2O(aq) | + 0.81 | | Br2(aq) / Br-(aq) | + 1.09 | |  |
|  | 1. Draw a labelled diagram of the electrolysis experiment as described for the third method. Include arrows to show the movement of ions and of electrons during the electrolysis. | 3 marks |
|  | 1. Using the data from the table, identify the substances that should be theoretically produced at each electrode and explain your answer. | 2 marks |

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| Question A3 | | **Page 2/2** |
|  | | **Marks** |
|  | In practice, it is found that bromine is one of the substances. |  |
|  | 1. Write the overall equation for the reaction taking place during this electrolysis and calculate the minimum voltage that must be applied during the electrolysis to produce bromine. | 2 marks |
|  | 1. Calculate the time taken for the electrolysis to produce a mass of 1.00 kg of bromine, Br2(l), if a steady current of 12.0 A is passed. | 2 marks |
|  | **Given:** 1 Faraday= 9.65 x 104 C mol-1  Molar atomic mass (in g mol-1) : Br : 79.9 |  |
| b) | Bromine, Br2(l), is used in the manufacture of potassium hypobromite, KBrO(aq), which is used as a disinfectant.  The process involves two stages.   * Step 1: bromine reacts with water to produce hydrobromic acid, HBr(aq), and hypobromous acid, HBrO(aq). * Step 2: the hypobromous acid from step1 reacts with an aqueous solution of potassium hydroxide, KOH(aq). |  |
|  | Give the equations for the reactions occurring in step 1 and in step 2. | 2 marks |
| c) | 25.0 cm3 of 1.00 x 10-1 mol dm-3 hypobromous acid solution is titrated with an aqueous solution of sodium hydroxide, NaOH(aq) with a concentration of 8.00 x 10-2 mol dm-3. |  |
|  | 1. Give the equation for the reaction taking place during the titration. | 1 mark |
|  | 1. Calculate the volume of the sodium hydroxide solution that must be added to reach the equivalence point. | 2 marks |
|  | 1. Calculate the initial pH of the solution of hypobromous acid at 25 oC. | 2 marks |
|  | 1. Calculate the pH at the equivalence point of the titration at 25 oC. | 4 marks |
|  | **Given:** *K*a, for hypobromous acid at 25 oC : 2.00 x 10-9.  p*K*w of water at 25 oC : 14.0 |  |

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| Question B1 | | **Page 1/2** |
|  | | **Marks** |
| a) | A secondary alcohol has the molecular formula C5H12O. |  |
|  | 1. Give the three possible structural formulas of the secondary alcohol isomers of C5H12O. | 3 marks |
|  | One of the isomers you have drawn is not optically active. |  |
|  | 1. Give the IUPAC name of this isomer and explain why it is not optically active. | 3 marks |
|  | The alcohol pentan-2-ol is oxidized by an acidified aqueous solution of   potassium dichromate, K2Cr2O7(aq). |  |
|  | 1. Give the equation for the reaction and give the IUPAC name of the organic product. | 3 marks |
|  | Given: The half-equation for the oxidizing agent is:  Cr2O72-(aq) + 14H+(aq) + 6e- → 2Cr3+(aq) + 7H2O(l) |  |
|  | 1. Calculate the minimum volume of 2.00 x 10-1 mol dm-3 aqueous potassium dichromate solution required to oxidize 25.0 cm3 of pentan-2-ol. | 3 marks |
|  | Given: The density of pentan-2-ol : 8.09 x 10-1 g cm-3.  Molar atomic masses (in g mol-1) :  H : 1.01 C : 12.0 O : 16.0 |  |
| b) | Esterification reactions, represented by the general equation below, are reversible:  **acid + alcohol ⇄ ester + water** |  |
|  | 1. Suggest two different ways in which the yield of ester could be increased. | 2 marks |
|  | 1. Give the mechanism for the esterification reaction between ethanoic acid and methanol. | 4 marks |
|  | 1. Explain why a strong acid is used to catalyze this reaction. | 1 mark |

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| Question B1 | | **Page 2/2** |
|  | | **Marks** |
| c) | An organic compound, X is a liquid at room temperature and is produced by   oxidizing a saturated alcohol.  9.70 g of compound X is totally combusted in air to give 9.01 g of water and 12.3 dm3 of carbon dioxide, measured at 25 oC and a pressure of 1.01 x 105 Pa. |  |
|  | 1. Calculate the molar ratio of carbon to hydrogen in compound X. | 3 marks |
|  | 1. Assuming that the molar mass is 58.1 g mol-1 give the molecular formula of X. | 1 mark |
|  | 1. Give the structural formulas and the names of the two isomers of X. | 2 marks |
|  | Given: Molar atomic masses (g mol-1):  H : 1.01 C : 12.0 O : 16.0  Molar volume of a gas at 25 oC and 1.01 x 105 Pa : 24.5 dm3 mol-1 |  |

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| Question B2 | | **Page 1/2** |
|  | | **Marks** |
| a) | Piperidine, coniine and sedamine are alkaloids. Alkaloids are organic compounds which can be found in plants. Many of them are poisonous. The death of Socrates was due to absorption of coniine. Coniine and sedamine are derivatives of piperidine. Sedamine is present in some sleeping pills. |  |
|  | Coniine.jpg  Pipéridine.jpg  Sédamine.jpg |  |
|  | piperidine coniine sedamine |  |
|  | All three compounds are amines. |  |
|  | 1. Explain why amines can act as bases. | 2 marks |
|  | 1. Classify each of the three amines represented above as primary, secondary or tertiary amines. | 2 marks |
|  | 1. Explain why piperidine and coniine are stronger bases in aqueous solution than ammonia, NH3(aq). | 2 marks |
|  | 1. Other than the amine group, identify another functional group present in sedamine. | 1 mark |
|  | 1. Which of these three compounds is/are optically active?   Justify your answer | 2 marks |
|  | Even if the higher molar mass is taken into account the boiling point of   sedamine is considerably higher than that of coniine.   |  |  | | --- | --- | | **Compound** | **Boiling point / °C** | | piperidine | 106 | | coniine | 166 | | sedamine | 331 |   . |  |
|  | 1. Suggest, with an explanation, one other reason why there is such a difference in the boiling points of these two compounds. | 2 marks |

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| Question B2 | | **Page 2/2** |
|  | | **Marks** |
| b) | Cadaverine can be made from the amino acid lysine.  Lysine.jpg  Cadavérine.jpg  cadaverine lysine |  |
|  | 1. Give the IUPAC names for lysine and cadaverine | 2 marks |
|  | The isoelectric point of lysine is 9.59. |  |
|  | 1. Draw the simplified structural formulas of lysine in strongly acidic, and strongly alkaline solutions. | 2 marks |
|  | Amino acids form a peptide bond when they react with another amino acid. |  |
|  | 1. Write the simplified structural formula of a dipeptide formed from two lysine molecules. | 2 marks |
|  | Cadaverine can form a polymer by reaction with oxalic acid.  oxalic acid  oxalic acid |  |
|  | 1. Draw a repeating unit of the polymer formed. | 2 marks |
| c) | [Pyrrolidine](http://en.wikipedia.org/wiki/Pyrrolidine) is another alkaloid with a cyclic structure which includes a nitrogen atom. It has the molecular formula C4H9N. It is a saturated secondary amine and does not contain any carbon side chains.  Pyrrolidine is very soluble in water. |  |
|  | 1. Draw the structural formula of [pyrrolidine](http://en.wikipedia.org/wiki/Pyrrolidine). | 2 marks |
|  | 1. Give two reasons to explain the high solubility of pyrrolidine in water. | 2 marks |
|  | 1. Draw the structural formulas of two structural isomers of pyrrolidine | 2 marks |

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| Question B3 | | **Page 1/2** |
|  | | **Marks** |
| a) | Dopamine, noradrenaline and adrenaline all function as neurotransmitters in mammals. Their structures are shown below:  Dopamine.jpg  Noradrénaline.jpg  Adrénaline.jpg    **dopamine noradrenaline adrenaline**  All three compounds belong to a family of compounds called catecholamines.  These three compounds can be classified as Brønsted-Lowry bases. |  |
|  | 1. Explain, by referring to their molecular structures, why these three compounds can also show acidic properties. | 2 marks |
|  | 1. What name is given to such compounds that exhibit both acid and base properties? | 1 mark |
| b) | One molecule of the triglyceride, **A**, is synthesized from one molecule of propane-1,2,3-triol, two molecules of hexadecanoic acid and one molecule of octadec-9-enoic acid. |  |
|  | 1. Draw one simplified possible structural formula of the triglyceride, A. | 3 marks |
|  | 1. What is the physical state of A at room temperature?   Explain your answer. | 2 marks |
|  | The triglyceride, **A**, is heated with a concentrated solution of aqueous potassium hydroxide, KOH(aq). |  |
|  | 1. Using simplified structural formulas, write the equation for the reaction of A with the aqueous potassium hydroxide. | 3 marks |
|  | 1. Name the type of reaction involved and state its industrial importance. | 2 marks |

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| Question B3 | | **Page 2/2** |
|  | | **Marks** |
| c) | Benzocaine is the active ingredient in many anaesthetic creams. It can be prepared from 4-aminobenzoic acid.  Acide 4-aminobenzoïque.jpg      **4-aminobenzoic acid**  In a laboratory experiment to prepare benzocaine, 17.5 cm3 of ethanol and 1.30 g of 4-aminobenzoic acid were placed in a 100 cm3 round-bottomed flask. 2.00 cm3 of concentrated sulphuric acid were slowly added. The mixture was heated under reflux for one hour. |  |
|  | 1. 4-aminobenzoic acid can exist as a zwitterion. Draw the structural formula of the zwitterionic form. | 1 mark |
|  | 1. Using simplified structural formulas of reactants and products, write the equation for the reaction taking place to produce benzocaine. | 2 marks |
|  | 1. Which of the two reactants was present in excess? Justify your answer by means of relevant calculations. | 3 marks |
|  | **Given:** Density of ethanol : 7.89 x 10-1 g cm-3  Molar atomic masses (in g mol-1):  H: 1.01 C: 12.0 N : 14.0 O: 16.0 |  |
| d) | Glucose, C6H12O6, is a saccharide.  Glucose.jpg  The chain form of glucose is given : |  |
|  | 1. Explain why glucose has a high melting point. | 2 marks |
|  | 1. Draw the cyclic form of glucose. | 2 marks |
|  | 1. Using molecular formulas, give the equation for the synthesis of maltose starting from glucose. | 2 marks |