

**2014**

# Scholarship Chemistry

**93102**

NAME

**Time allowed: 3 hours**

**Marks: 48**

**Answer all questions**

**A periodic table is included at the back of this booklet**

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**QUESTION ONE**

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To launch the space shuttle, two propulsion systems are used. Most of the thrust for the first two minutes of flight comes from the two reusable solid rocket boosters. The so-called ‘external tank’ provides the remainder of the thrust needed to get the shuttle into orbit.

The external tank is filled with liquid hydrogen and liquid oxygen which react to form water. The solid rocket boosters use a mixture of aluminium powder and ammonium perchlorate, NH4ClO4, together with an iron oxide catalyst and an organic binder.

**(a)** Write the equation for the reaction between hydrogen and oxygen.

**(b)** The external tank has a mass of 27 tonnes (27,000 kg) when empty and 745 tonnes when full. Assuming these are present in the correct stoichiometric proportions, calculate the masses of hydrogen and oxygen in the external tank.

**(c)** In practice, the actual masses of hydrogen and oxygen used are 104 and 614 tonnes respectively. Given that the densities of liquid hydrogen and oxygen are 0.0708 and 1.141 g cm–3, calculate the volumes of these liquids needed and hence the total capacity of the external tank in m3.

The reaction that takes place during the combustion of the solid rocket booster fuel has been summarized as:

 10Al(s) + 6NH4ClO4(s)  4Al2O3(s) + 2AlCl3(s) + 12H2O(*l*) + 3N2(g)

 **(d)** Given the following standard enthalpies of formation, calculate the standard enthalpy change for this reaction as given.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | NH4ClO4(s) | Al2O3(s) | AlCl3(s) | H2O(*l*) |
| ∆f*H*°/ kJ mol–1 | –295.3 | –1675.7 | –704.2 | –285.8 |

 **(e)** Given that 450 tonnes of solid propellant are used in the solid rocket boosters in total, and that aluminium is the limiting reagent present at 16% in the mixture, calculate the energy released when this is reacted according to the above equation. *M*(Al) = 27.0 g mol–1

**QUESTION TWO**

**Part A**

The IUPAC name for vitamin A is:

9-(2,6,6-trimethylcyclohex-1-enyl)-3,7-dimethylnona-2,4,6,8-tetraen-1-ol

Draw its structural formula.

**Part B**

Compound **A**, C5H12O, on oxidation with acidified potassium dichromate forms **B**, C5H10O, which does not react with Tollens’ reagent. **A** reacts with SOCl2 to form **C**, C5H11Cl, which forms two alkenes **D** and **E**, C5H10, on reaction with alcoholic KOH. Neither **D** nor **E** can exist as geometrical isomers. On addition of HCl **D** forms **F** as the major product which is an isomer of **C**, while addition of HCl to **E** generates **C** as the major product. Deduce the structure of compounds **A** to **F**.

**Part C**

Propose a synthesis to make Compound X from Compounds Y and Z using any reagents. Consider major and minor products where relevant.

**QUESTION THREE**

**Part A**

1. Write half-equations and a balanced net ionic equation for the conversion of arsenious acid, H3AsO3 into arsenic acid, H3AsO4 by hydrogen peroxide.

(b) When the reaction is carried out in the presence of methyl orange indicator the colour changes from yellow to red. All species remain in solution.

(Methyl orange changes from red in acid to yellow in a pH range of 3 to 4.)

Account for change in pH assuming the H2O2 does not, on its own, influence the pH.

(c) Adding silver nitrate solution to solutions of the sodium salts of the two acids gives precipitates of Ag3AsO3 and Ag3AsO4. The yellow precipitate of Ag3AsO3 dissolves in dilute ethanoic acid but the brown precipitate of Ag3AsO4 remains insoluble. However Ag3AsO4 dissolves in dilute HNO3. Explain these observations using relevant equations.

**Part B**

Aluminium anodising is the process of using electrolysis to create a protective layer of aluminium oxide on the surface of aluminium metal.



Different uses of the aluminium require different amounts of the aluminium oxide layer to be made. The following three relationships can be used in determining the amount formed from the electrolysis:

 1 mole of electrons (**e**) = 1 Faraday (**F**)

1 Farady (**F**) = 96485 Coulombs (**C**)

Coulombs (**C**) = current in amperes (**I**) × time in seconds (**t**)

A 46.0 g pure aluminium machine roller needs to be anodised. It requires 0.70% to be converted to the oxide at a slow rate for a hard and durable use. Write a balanced half equation for the anode reaction of aluminium metal forming aluminium oxide, and determine how long must it be anodised for at a current of 0.850 amps?
 *M*(Al) = 27.0 g mol–1, *M*(O) = 16.0 g mol–1

**Part C**

(c) Disproportionation is an oxidation-reduction reaction where one reactant species simultaneously oxidises and reduces itself.

Comproportionation is an oxidation-reduction reaction where an element from two different reactant species forms the same product species.

Using the electrode potential data provided, determine, a combination of redox couples that could undergo disproportionation and a combination that could undergo comproportionation. Show ion-electron-half equations and balanced net ionic equation.

|  |  |
| --- | --- |
| *E*°(HOCl/Cl2) = +1.63 V | *E*°(I2/I-) = +0.54 V |
| *E*°(ClO3–/HOCl) = +1.43 V | *E*°(SO2/S) = +0.50 V |
| *E*°(IO3–/I2) = +1.20 V | *E*°(S/H2S) = +0.17 V |

**QUESTION FOUR**

**Part A**

Nitrogen and oxygen form several different molecules and ions. The bond angles (O-N-O) in some of these species are shown in the table below.

|  |  |  |
| --- | --- | --- |
| Species | Bond angle  | Lewis diagram and discussion |
| NO2 | 134° |  |
| NO2+ | 180° |  |
| NO2– | 115° |  |
| NO3– | 120° |  |

1. Complete the table by drawing Lewis diagrams for the species shown. In each case, N is the central atom.

2. Discuss how your diagrams can be used to explain the measured bond angles.

**Part B**

At low temperatures, nitrogen dioxide (NO2) is converted to the dimer dinitrogen tetroxide (N2O4).

The equilibrium reaction between dinitrogen tetroxide and nitrogen dioxide can be represented by the equation:

N2O4(g)  2NO2(g)

(a) If 1.00 mole of N2O4 is introduced into a 1.00 litre container and allowed to come to equilibrium at 120 °C, the concentration of N2O4 in the equilibrium mixture is 0.070 mol L–1. Calculate the value of *K*c for the equilibrium at 120 °C.

(b) The value of *K*c at 25°C is 0.00590. If 1.00 mole of N2O4 is introduced into a 1 litre container and allowed to come to equilibrium at 25°C, what would be the concentrations of N2O4 and NO2 in the equilibrium mixture?

(c) Using the information above and your answer to (a) state whether the reaction is exothermic or endothermic and justify your answer using two different arguments .

**QUESTION FIVE**

**Part A**

(a) 15.00 mL of 0.100 mol L–1 HOCl solution reacts completely with 30.00 mL of NaOH solution. Determine the pH of the final solution. *K*a(HOCl) = 2.95 × 10–8.

(b) Determine the percentage reaction of the hypochlorite ion, OCl–, with water.

**Part B**

Phosphoric acid is a triprotic acid. The successive proton transfer reactions and the associated p*K*a values are listed below.

(1) H3PO4 + H2O  H3O+ + H2PO4– p*K*a1 = 2.12

(2) H2PO4– + H2O  H3O+ + HPO42– p*K*a2 = 7.21

(3) HPO42– + H2O  H3O+ + PO43– p*K*a3 = 12.67

A student made a buffer solution by adding 1.00 mol L–1 sodium hydroxide solution to 1 litre of a 0.100 mol L–1 solution of phosphoric acid in water until the pH of the solution was exactly 7.00.

(a) Calculate the volume of sodium hydroxide solution that the student added to make the buffer solution. Explain any assumptions that you make in your calculation.

(b) Calculate the concentration of sodium ions and of the four phosphorus-containing species in the buffer solution.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **1** |  | **Periodic Table of the Elements** |  |  |  |  |  | **18** |
| Hydrogen1**H**1.008 | **2** |  | **13** | **14** | **15** | **16** | **17** | Helium2**He**4.003 |
| Lithium3**Li**6.943 | Beryllium4**Be**9.012 |  |  |  |  |  |  |  |  |  |  | Boron5**B**10.81 | Carbon6**C**12.01 | Nitrogen7**N**14.01 | Oxygen8**O**16.00 | Fluorine9**F**19.00 | Neon10**Ne**20.18 |
| Sodium11**Na**22.99 | Magnesium12**Mg**24.31 | **3** | **4** | **5** | **6** | **7** | **8** | **9** | **10** | **11** | **12** | Aluminium13**Al**26.98 | Silicon14**Si**28.09 | Phosphorus15**P**30.97 | Sulfur16**S**32.07 | Chlorine17**Cl**35.45 | Argon18**Ar**39.95 |
| Potassium19**K**39.10 | Calcium20**Ca**40.08 | Scandium21**Sc**44.96 | Titanium22**Ti**47.88 | Vanadium23**V**50.94 | Chromium24**Cr**52.00 | Manganese25**Mn**54.94 | Iron26**Fe**55.85 | Cobalt27**Co**58.93 | Nickel28**Ni**58.69 | Copper29**Cu**63.55 | Zinc30**Zn**65.39 | Gallium31**Ga**69.72 | Germanium32**Ge**72.59 | Arsenic33**As**74.92 | Selenium34**Se**78.96 | Bromine35**Br**79.90 | Krypton36**Kr**83.80 |
| Rubidium37**Rb**85.47 | Strontium38**Sr**87.62 | Yttrium39**Y**88.98 | Zirconium40**Zr**91.22 | Niobium41**Nb**92.91 | Molybdenum42**Mo**95.94 | Technetium43**Tc**(98) | Ruthenium44**Ru**101.1 | Rhodium45**Rh**102.9 | Palladium46**Pd**106.4 | Silver47**Ag**107.9 | Cadmium48**Cd**112.4 | Indium49**In**114.8 | Tin50**Sn**118.7 | Antimony51**Sb**121.8 | Tellurium52**Te**127.6 | Iodine53**I**126.9 | Xenon54**Xe**131.3 |
| Caesium55**Cs**132.9 | Barium56**Ba**137.3 | Lanthanum57 **La**†138.9 | Hafnium72**Hf**178.5 | Tantalum73**Ta**180.9 | Tungsten74**W**183.9 | Rhenium75**Re**186.2 | Osmium76**Os**190.2 | Iridium77**Ir**192.2 | Platinum78**Pt**195.1 | Gold79**Au**198.0 | Mercury80**Hg**200.6 | Thallium81**Tl**204.4 | Lead82**Pb**207.2 | Bismuth83**Bi**209.0 | Polonium84**Po**(209) | Astatine85**At**(210) | Radon86**Rn**(222) |
| Francium87**Fr**(223) | Radium88**Ra**226.0 | Actinium89 **Ac**‡227.0 | Rutherfordium104**Rf**(261) | Dubnium105**Db**(262) | Seaborgium106**Sg**(263) | Bohrium107**Bh**(264) | Hassium108**Hs**(265) | Meitnerium109**Mt**(266) | Darmstadtium110**Ds**(271) | Roentgenium111**Rg**(272) | Copernicium112**Cn**(277) |  | 114(289) |  | 116(289) |  |  |
|  |  |  |
|  |  |  |
|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
|  | † | Cerium58**Ce**140.1 | Praseodymium59**Pr**140.9 | Neodymium60**Nd**144.2 | Promethium61**Pm**(145) | Samarium62**Sm**150.4 | Europium63**Eu**152.0 | Gadolinium64**Gd**157.3 | Terbium65**Tb**158.9 | Dysprosium66**Dy**162.5 | Holmium67**Ho**164.9 | Erbium68**Er**167.3 | Thulium69**Tm**168.9 | Ytterbium70**Yb**173.0 | Lutetium71**Lu**175.0 |  |
|  | ‡ | Thorium90**Th**232.0 | Protactinium91**Pa**231.0 | Uranium92**U**238.0 | Neptunium93**Np**237.0 | Plutonium94**Pu**(244) | Americium95**Am**(243) | Curium96**Cm**(247) | Berkelium97**Bk**(247) | Californium98**Cf**(251) | Einsteinium99**Es**(252) | Fermium100**Fm**(257) | Mendelevium101**Md**(258) | Nobelium102**No**(259) | Lawrencium103**Lr**(260) |  |