2022/2023 學年澳門高中學生化學競賽

High school chemistry competition – Macau 2022/2023

Question	1	2	3	4	5	6	7	8	9		Point total
Points	30	10	10	10	10	8	6	8	8		100
Scores											
Grader											

Question 1	1-1	1-2	1-3	1-4	1-5	1-6	1-7	1-8
Answer(s)								
Question 1	1-9	1-10	1-11	1-12	1-13	1-14	1-15	
Answer(s)								

H 1.008																	He 4.003
Li 6.941	Be 9.012											B 10.81	C 12.01	N 14.01	O 16.00	F 19.00	Ne 20.18
Na 22.99	Mg 24.31											Al 26.98	Si 28.09	P 30.97	S 32.07	Cl 35.45	Ar 39.95
K 39.10	Ca 40.08	Sc 44.96	Ti 47.88	V 50.94	Cr 52.00	Mn 54.94	Fe 55.85	Co 58.93	Ni 58.69	Cu 63.55	Zn 65.39	Ga 69.72	Ge 72.61	As 74.92	Se 78.96	Br 79.90	Kr 83.80
Rb 85.47	Sr 87.62	Y 88.91	Zr 91.22	Nb 92.91	Mo 95.94	Tc 98.91	Ru 101.1	Rh 102.9	Pd 106.4	Ag 107.9	Cd 112.4	In 114.8	Sn 118.7	Sb 121.8	Te 127.6	I 126.9	Xe 131.3
Cs 132.9	Ba 137.3	La-Lu	Hf 178.5	Ta 180.9	W 183.9	Re 186.2	Os 190.2	Ir 192.2	Pt 195.1	Au 197.0	Hg 200.6	Tl 204.4	Pb 207.2	Bi 209.0	Po [210]	At [210]	Rn [222]
Fr [223]	Ra [226]	Ac-Lr	Rf	Db	Sg	Bh	Hs	Mt									

Relative molecular mass, g/mol

Student full name: _____

Seat number: _____

Student ID number: _____

High school: _____

Contact phone number: _____

Question 1 (30 points)

Multiple choice questions: each question has 1 to 2 good answers; write your answers in the table on the first page.

1-1. Concerning the applications of chemistry in some of the advancement in sciences and technologies, which of the following statements is/are correct?

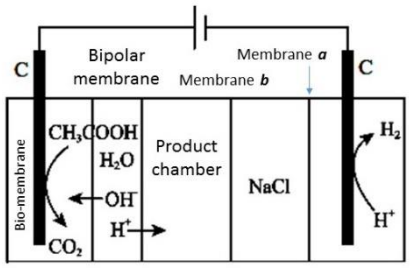
A · Aluminum anti-corrosive plating as the 'exterior cathodic galvanization' method used in the subsurface steel columns of Hong Kong–Zhuhai–Macau Bridge

B · The principal component for the fiber optics used in high speed telecommunication of The Five-hundred-meter Aperture Spherical radio Telescope (FAST) is a silicate

C · The critical polymer component used in the carriage joints for China Railway High-speed, 'Fuxing", is reinforced polytetrafluoroethylene sheet

D · Ultra high-pressure titanium alloy used in exterior casing of the manned submersible vehicle, 'Jiaolong', is a type of titanium alloy material

1-2. Coupled with electrochemical treatment, organic wastewater may be used to desalinate seawater and obtain acids and alkalines. Consider NaCl solution as seawater test model, the following schematic of a device is used to treat organic solution containing CH_3COOH. Under direct current, hydrolysis of water within the bipolar membrane forms H^+ and OH^-. The correct statement(s) is/are



A · Membrane ***a*** is a cationic exchange membrane, membrane ***b*** is an anionic exchange membrane.

B · Sodium hydroxide is the product in the product chamber

C · When 11.2 L-H_2 is formed, the theoretic processed amounts to 23 g Na^+ of the model seawater

D · Anodic reaction is: $CH_3COOH + 8OH^- + 8e \leftrightarrows 2CO_2\uparrow + 6H_2O$

1-3. When an electronic arrangement of valence electrons in neutral gaseous state atoms undergoes a certain change, the maximum amount of energy for absorption occurs with reaction(s)

A · $1s^22s^1 \longrightarrow 1s^2$ B · $1s^22s^2 \longrightarrow 1s^22s^1$

C · $1s^22s^22p^1 \longrightarrow 1s^22s^2$ D · $1s^22s^22p^2 \longrightarrow 1s^22s^22p^1$

1-4. In an experiment, the same quantity of H_2O and D_2O sample is reacted completely with a small quantity of potassium. If the number of electron transfer is the same, which of the following statements about the physical quantities are not equivalent?

A · The same amount of H_2O and D_2O are used

B · The volume of gas products under the same reaction condition

C · The yield fraction of the aqueous products after reaction

D · The amount of potassium used in the two chemical reactions

1-5. Which of the following statement(s) is/are false?

A · The boiling point of H_2O is higher than that of H_2S because O has the greater non-metallic character than S

B · When solid $NaHSO_4$ dissolves in water, there are both ionic and covalent bond dissociations

C · Since the bond dissociation of carbon dioxide releases a large amount of heat, it can be used to create 'scene

of fog' using dry ice

D · As covalent bonds exist in N_2, CO_2, and PCl_3, they are substances made up of molecules, and all satisfy the octet stable structure

1-6. Novel corona virus constitutes positive single strand RNA protected by some fatty acid and nucleoprotein coating. The virus is ultraviolet radiation- and heat- sensitive. Lipid solvents, such as medical alcohol, chlorine containing disinfectant, peracetic acid, and chloroform, can effectively inactivate viruses. The following statement(s) is/are correct

A · Peracetic acid is a strong oxidizing agent. At high concentrations, it is corrosive, irritant substance. An accidental spillage on skin should be treated with flushing with water immediately

B · '84 Disinfectant liquid' and alcohol should not be mixed together because the mixture may burn spontaneously

C · Medical alcohol is constituted of 75% ethanol

D · Trichlorosiocyanuric acid (TCCA, $C_3N_3O_3Cl_3$) is a chlorine containing disinfectant. Compared to '84 Disinfectant liquid' constituting 60 g/L effective chlorine, TCCA contains a higher chlorine content and longer release time

1-7. Carbonyl chloride (phosgene) may be synthesized by the following reaction: $CO + Cl_2 \leftrightarrows COCl_2$

Experimental results of the reaction is as follows:

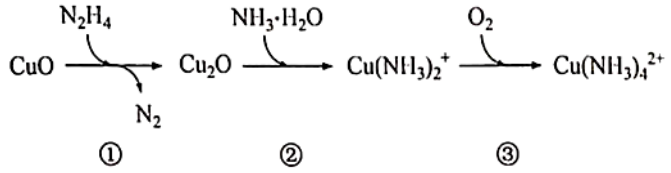
Test	Initial concentration / $mol \cdot L^{-1}$		Initial rate/ $10^{-3} mol \cdot L^{-1} \cdot s^{-1}$
	CO	Cl_2	
1	0.100	0.100	12
2	0.100	0.050	4.26
3	0.050	0.100	6.0
4	0.050	0.050	2.13

The overall order of the reaction is

A · 1.5 B · 2

C · 2.5 D · 3 E · None of the above

1-8. Hydrazine can be used to treat dissolved oxygen in boilers to prevent corrosion. One of the reaction mechanisms is shown in the following figure. The correct statement(s) is/are



A · At room temperature, hydrazine is a liquid

B · 2 mol N_2H_4 can treat 1 mol O_2 in water

C · Both ionic and covalent bonds exist in $[Cu(NH_3)_4]^+$

D · Both N_2H_4 and NH_3 are polar molecules

1-9. Oxalic acid is a diprotic weak acid. Given that $K_{a1}(H_2C_2O_4) = 5.4\times10^{-2}$, $K_{a2}(H_2C_2O_4) = 5.4\times10^{-5}$ at room temperature, in a titration, 0.2000 $mol\cdot L^{-1}$ NaOH requires 20.00 mL 0.1000 $mol\cdot L^{-1}$ $H_2C_2O_4$ to reach the end-point. During the titration, the correct statement(s) is/are

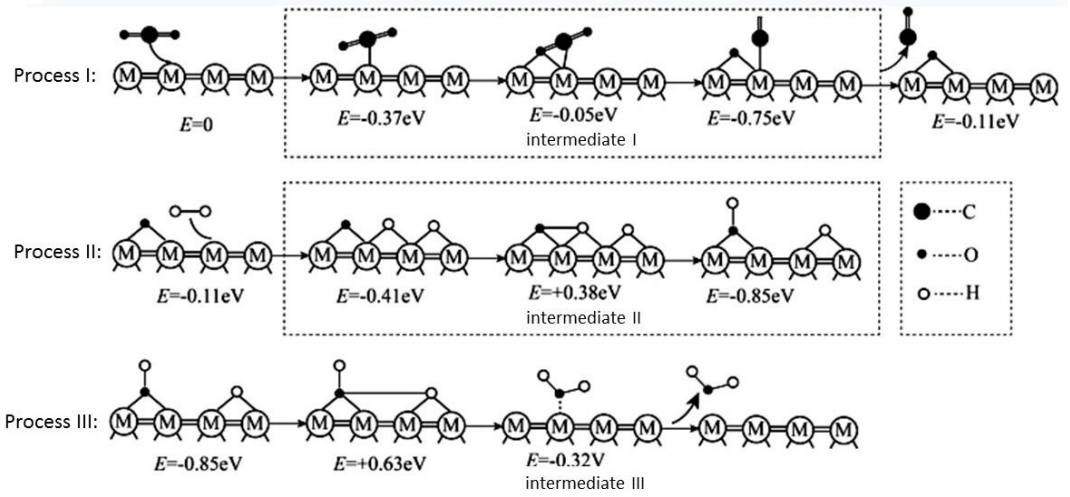
A · After the addition of 10.00 mL NaOH, the solution mixture has a pH greater than 7

B · In the solution, there always exists $c(Na^+) < c(HC_2O_4^-) + 2c(C_2O_4^{2-})$

C · When phenolphthalein is used as the indicator, the solution turns to red at the end point

D · In the solution, $c(HC_2O_4^-)/c(C_2O_4^{2-})$ continues to diminish

1-10. When appropriate metal catalyst is used, it is possible to reverse the conversion of CO hydration process: $CO_2(g) + H_2(g) \rightleftharpoons CO(g) + 2H_2O(g)$ The microscopic reaction process and corresponding relative energy (E) are shown in the following figure, where '*' denotes the adsorption on the surface of the catalyst.



The following statement(s) that is/are false

A · Reaction process I can be represented as $CO_2(g) \rightarrow CO(g) + O^*$

B · Rate of the overall reaction cannot be determined in process II

C · Reaction process III involves the formation of CO_2

D · ΔH of the overall reaction becomes smaller owing to the metal catalyst

1-11. Under various pH, the particle sizes of +5 valence of V +5 vary. The variation of particle sizes with pH is given in the following table.

Vanadium ions	VO_2^+	VO_3^-	$V_2O_7^{4-}$	VO_4^{3-}
pH	4~6	6~8	8~10	10~12

In addition, the solution of V at various valence states appear in different colors, for instances, V^{2+}(lilac), V^{3+}(green), VO^{2+}(blue), VO_2^+(yellow), VO_4^{3-} (colorless), $V_5O_{14}^{3-}$ (brownish red). The following statement(s) is/are correct

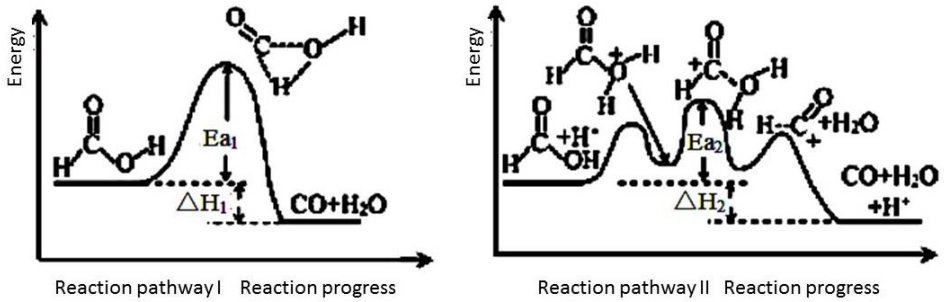
A · The ionic reaction equation for which VO_3^- is converted to $V_2O_7^{4-}$ is $2VO_3^- + H_2O \leftrightarrows V_2O_7^{4-} + 2H^+$

B · On addition of dropwise ammonia solution, the solution with VO_2^+ will precipitate NH_4VO_3, where V species is reduced

C · The ionic reaction equation for the dropwise addition of caustic soda to acidified VO_2^+ to form brown red solution is $5VO_2^+ + 8OH^- \leftrightarrows V_5O_{14}^{3-} + 4H_2O$

D · To acidified lilac VSO_4 solution, potassium permanganate is added. The solution appears to undergo color change from green to blue to yellow. During the reactions, 1 mole of electron is lost

1-12. Formic acid is commonly used in rubber, medical and other industries. Under a certain condition, it can decompose to form CO and H_2O. The variations of energy with reaction coordinate with or without catalyst are shown in the following figures. The statement(s) that are false is/are



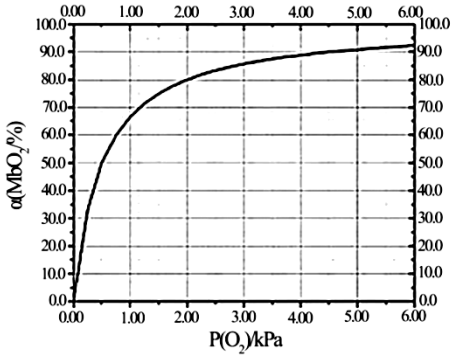
A · As no catalyst is used in reaction pathway 1, the conversion rate is higher in pathway 2 than pathway 1

B · $\triangle H_1 > \triangle H_2$，$E_{a1} > E_{a2}$

C · In pathway 2, H^+ participates in the reaction, altering the pathway and thus enhances the reaction rate

D · The unit production rate of CO increases with temperature

1-13. Myoglobin (Mb), comprised of peptides and heme prosthetic groups, is a protein which can bind with oxygen molecules. Myoglobin are commonly present in muscles. The binding ratio (α) between Mb and O_2 is related to the partial pressure, $P(O_2)$. At 37°C the equilibrium (a), $Mb(aq) + O_2(g) \underset{k_B}{\overset{k_A}{\rightleftharpoons}} MbO_2(aq)$, where k_A and k_B are the forward [$v_f = k_A(Mb)P(O_2)$] and reverse [$v_{逆} = k_B(MbO_2)$] reaction rates respectively, a set of test results is plotted in the following figure.



The following statement(s) is/are correct

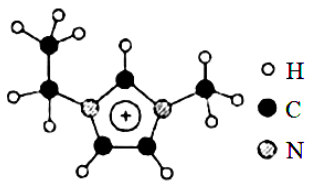
A · At 37°C, the equilibrium constant for (a) is $K = 2.00\ kPa^{-1}$

B · If the partial pressure of oxygen in air is 20.0 kPa, the maximum binding ratio between Mb and O_2 in a man is 97.6%

C · Given that $k_B = -60\ s^{-1}$, $k_A = 1.2 \times 10^2\ s^{-1} \cdot Pa^{-1}$

D · If the partial pressure of oxygen is maintained at 20.0 kPa, the time required to achieve a 50% binding ratio depends on the initial concentration of Mb

1-14. The structure of a certain cation, EMIM, is shown in the following figure. The statement(s) that is/are false



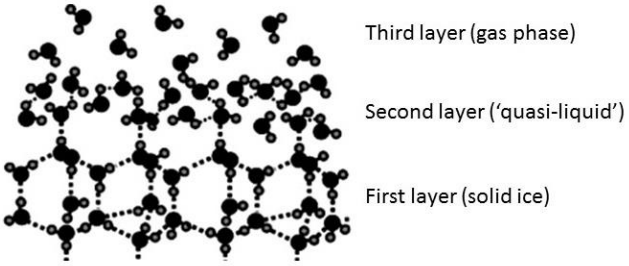
A · The resulting mixture between $EMIM^+$ and Cl^- is an electrical conductor

B · A large π-bond is present in $EMIM^+$

C · Electrostatic interactions are present between cations and anions of the liquid. Because of the large difference in size between the cations and anions, the strength of the interaction is weak

D · There are five different hydrogen environments in $EMIM^+$

1-15. 'Why is ice slippery?' This phenomenon is attributed to the structure of ice surface layer (see figure). The correct statement(s) is/are



A · The stability of water molecules is enhanced by the presence of hydrogen bonds. Even at elevated temperature, the bonds are still strong

B · In the first solid state ice layer, spatial network structure is formed owing to the hydrogen bonds between water molecules

C · In the 'quasi-liquid' second layer, there are no hydrogen bonds between water molecules

D · As temperature rises over a certain point, the hydrogen bonds between water molecules in 'quasi-liquid' and those in its lower layer are broken, allowing 'mobile water molecules', resulting in slippery ice surface

Question 2 (10 points)

Write the corresponding ionic equation according to the information provided.

2-1. To acidified potassium dichromate, add ethanol.

2-2. Reaction between N_2O_3 and concentrated sulfuric acid results in acid salt and sulfate monohydrate products.

2-3. Ammonium paratungstate is a polyprotic salt. The paratungstate contains 12 W atoms, with -10 charge. By concentrating ammonium tungstate $(NH_4)_2WO_4$ solution, the less soluble ammonium paratungstate pentahydrate crystallizes from the solution.

2-4. To NaOH solution, potassium permanganate is added. The mixture is gently heated. A transparent green solution is formed.

2-5. Mix $ZnSO_4$, H_3PO_4 with urea, Zinc phosphate tetrahydrate is formed (not a redox reaction). While ammonia is not a product in this reaction, another common gas is formed.

Question 3 (10 points)

Briefly answer the following questions.

3-1. Explain why CCl_4 can hydrolyze, whereas $SiCl_4$ cannot hydrolyze.

3-2. Explain the reason(s) the bond angle in NH_3 is greater than that in PH_3.

3-3. Based on the bond formation, explain why SF_6 is a very good liquid insulator.

3-4. The reaction between methane and chlorine is classified as a radical reaction. When I_2 is added to the reaction mixture, the reaction is inhibited. Explain.

3-5. At 298K, 101 kPa, the reaction $\frac{3}{2}H_2(g) + \frac{1}{2}N_2(g) \leftrightarrows NH_3(g)$ can occur spontaneously.
(Given that $\Delta_f G^{0}_{m,298}(NH_3) = -16.5\ kJ \cdot mol^{-1}$)

Question 4 (10 points)

The ideal packing model for metallic copper is face-centered cubic close packing (CCP). The atomic radius of copper is 128.0 pm.

4-1. Draw the unit cell for copper (use ○ to denote copper atom). Highlight an atom on the (1,1,1) face as a representing copper atom, state its coordinate in your diagram.

4-2. Calculate the density of copper **and** its spatial occupancy in the unit cell.

4-3. In an electrolytic cell containing $CuSO_4$ solution, copper is electroplated. The cathode is pretreated such that only the (1,1,1) plane is exposed in the electrolyte, while all other planes are protected. The exposed area measured to 100 cm^2, current is maintained at 1 A. Cu^{2+} ions are cathode deposited constantly and completely for 2 minutes. Calculate the number of copper layers which has been deposited.

Question 5 (10 points)

Important iron complexes include iron hexacyanide complexes: Potassium ferrocyanide, $K_4[Fe(CN)_6]$ (commonly known as yellow Prussiate of Potash) and Potassium ferricyanide $K_3[Fe(CN)_6]$ (commonly known as red Prussiate of Potash)

5-1. It is more difficult to synthesize red Prussiate of Potash directly from Fe^{3+} ions and CN^-. The synthesis is carried out using yellow Prussiate of Potash reacting with oxidizing agents such as H_2O_2 instead. Explain.

5-2. One way to generate a photograph uses papers which have been previously soaked and dried with the mixture of $K_3[Fe(CN)_6]$ and $K_3[Fe(C_2O_4)_3]$. After a short exposure with intense light, the paper is submerged in water. The area where lines were drawn on the paper is colorless, where there were no lines drawn appear blue. Write the chemical reaction that gives the blue appearance on the paper.

5-3. To $K_4[Fe(CN)_6]$ solution, add nitric acid, and heat the mixture. After the addition of sodium carbonate to remove excess nitric acid and potassium nitrate, it is followed by recrystallization. The product is a red diamagnetic disodium salt hydrate, X. The anion of X is a six-coordinate ion, with a quadruple axis, but without a symmetric center. There are two types of ligands in the compound.

5-3-1. State the valence electron configuration, spin state (high or low) and oxidation states of the central ion X.

5-3-2. The decomposition of X at 120°C results in 12.1% weight loss. Show calculation steps and propose the chemical formula of X.

Question 6 (8 points)

At -30°C, the reaction between thionyl chloride and sodium azide forms colorless crystals, $[NS(O)Cl]_3$. The structural formula of the crystal consists of a ring structure.

6-1. Draw the two possible stereoisomers of $[NS(O)Cl]_3$.

6-2. $[NS(O)Cl]_3$ and SbF_3 react to form a colorless liquid, X. React 1.00 g X with excess amount of barium acetate to form 3.96 g precipitate. Determine the chemical formula of X and write the chemical reaction equation.

6-3. Substitution reaction occurs between X and nucleophilic agents, such as methylamine. Write chemical formula of the products for the reaction between X and excess amount of methylamine.

6-4. An isoelectronic form of X, at trace amount of water, undergoes polymerization to become Y. Dissolve 1

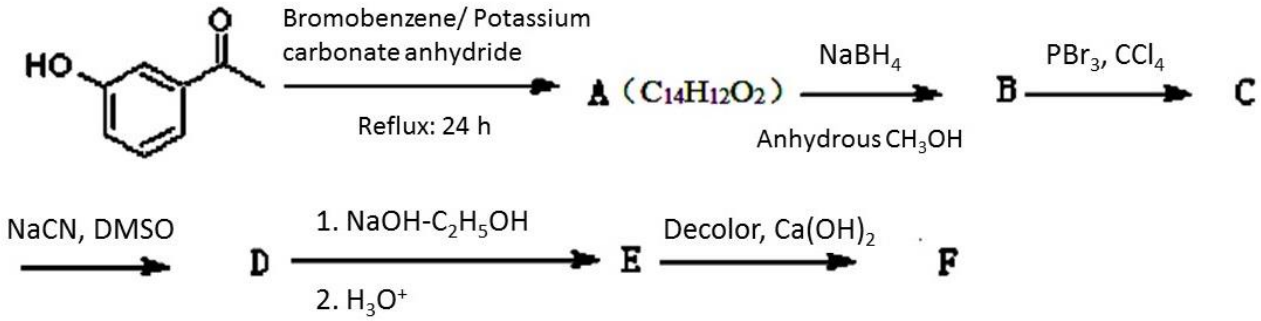
g of Y in water, the resultant solution is reacted with excess amount of barium acetate, 2.91 g precipitate is formed. Determine the chemical and structural formula of Y.

Question 7 (6 points)

A 0.6050 g sample was used to analyze the iron, aluminum, and titanium content in silicate rock. After the removal of SiO_2, ammonia solution is used to precipitate iron, aluminum, and titanium hydroxides. The precipitates are oxidized by combustion, weighed 0.4120 g afterward. The oxides are subsequently reacted with $K_2S_2O_7$, then resultant product is volumetrically made up to 100 mL. 25.00 mL of this solution is reduced with zinc-mercury amalgam, where $Fe^{3+} \rightarrow Fe^{2+}$，$Ti^{4+} \rightarrow Ti^{3+}$ occur. This reduced solution is then titrated against $K_2Cr_2O_7$, using up 0.01388 mol·L^{-1} $K_2Cr_2O_7$ 10.05 mL. Another portion of 25.00 mL solution is reacted with $SnCl_2$ to form Fe^{3+}. Again titrate against 8.02 mL $K_2Cr_2O_7$. Calculate the amount of Fe_2O_3, Al_2O_3, and TiO_2 in the original sample.

Question 8 (8 points)

There are many routes to synthesize fenoprofen calcium hydrate (F). One of routes is shown below:



8-1. What is the decoloring agent commonly used in the last step of this reaction sequence?

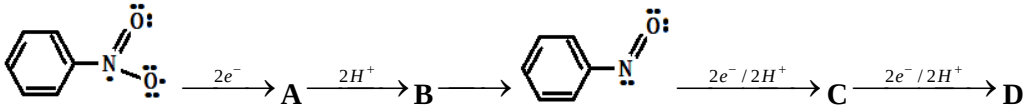
8-2. Write the structural formula for compounds A to F.

8-3. State the presence of optical isomers amongst compounds A to E.

8-4. Write the IUPAC name for compound A.

Question 9 (8 points)

In the laboratory, nitrobenzene can be reduced with metals and hydrochloric acid to form aniline. However, nitrobenzene is not easily reduced in nature. It is commonly removed by electrolytic reduction. In a study, the reduction reaction of nitrobenzene on a copper electrode is found to follow the steps shown below:



9-1. Based on its structure, why is nitrobenzene stable.

9-2. Write the structural formula for compounds A to D.

9-3. Write the overall chemical reaction equation for nitrobenzene on the copper electrode.

9-4. In the nitrobenzene reduction reaction, apart from the final product D, there is also a stable by-product. What is it?

【End】