

National Examination for 2013 IChO

Taiwan (Chinese Taipei)

Round 3 (3 h)

1. When metal reacts with nitric acid, depends on the amount of nitric acid, it produces NO or NO₂. With a highly active metal or very small amount of nitric acid, the reaction may give unexpected products. Magnesium powder was weighted out (1 g) from an old bottle and reacted with 400 mL of 2.1% of diluted nitric acid ($d = 1.01$). The evolved gas was collected in a pre-evacuated 1 L vessel. The pressure was 0.54 atm at room temperature. The vessel was heated to high temperature and then cooled back down to room temperature. The pressure increased during the heating, but back to its original value after cooled. Adding oxygen to the vessel until the total pressure reached 0.85 atm. The vessel was heated again. Explosion happened. After the reaction and cooled back to room temperature, the pressure was 0.134 atm.

Hint: NO_x will be reduced by hydrogen at high temperature. Water pressure can be neglected.

- (a) Write the reaction of magnesium and nitric acid. Calculate the amount of all products. (24 pts)
(b) What is the purity of this magnesium powder? (6 pts)

2. Chromium Chemistry

(a) The chromium redox couple ($E^\circ(\text{Cr}^{3+}|\text{Cr}_2\text{O}_7^{2-}) = +1.380 \text{ V}$) are often used in analytical chemistry.

(i) Write the balance equation for this redox reaction. (2 pts)

(ii) At neutral pH and $[\text{Cr}^{3+}] = [\text{Cr}_2\text{O}_7^{2-}] = 1 \text{ M}$, will it react with I⁻ and produces iodine ($E^\circ(\text{I}^-|\text{I}_2) = +0.54 \text{ V}$)? (4 pts)

Deep yellow CrO_4^{2-} and orange $\text{Cr}_2\text{O}_7^{2-}$ are often used to detect Cr^{3+} ions. In aqueous solution, addition of hydrogen peroxide or bromine can determine the existence of Cr^{3+} ions.

(iii) Write all the balanced reaction equations. (8 pts)

According to the potential of bromine, $E^\circ(\text{Br}^-|\text{Br}_2) = +1.065 \text{ V}$, it should not be able to detect Cr^{3+} ions.

(iv) Why is bromine a reagent to detect Cr^{3+} ions? Calculate the condition from redox potential. (4 pts)

(b) Measuring the magnetic moment is important to determine the oxidation state of the metal ions. Bohr magneto, $\mu_{\text{BM}} = \sqrt{n(n+2)}$ ($n = \text{number of unpaired electrons}$) °

Octahedral chromium-cyanide complex readily dissolves in water and is a good reductant. It has magnetic moment of $2.83 \mu_{\text{BM}}$.

(i) What is the oxidation state of the chromium in this complex? Give your reason. (6 pts)

Replacing the cyanides to amines results a paramagnetic complex.

(ii) What is the magnetic moment you expected for this complex? Explain your answer. (12 pts)

3. Element **X** has allotropes, its oxoanions are indicators of water pollution. The electronegativity of the element **X** is lower than that of oxygen. It forms only molecular compounds with halogens. Element **X** is important in biochemistry. It has half-filled *p*-orbitals.

(a) What is element X? Write its electronic configuration. (4 pts)

Element **X** forms many covalent compounds with hydrogen and has a general formula of X_aH_b . The series of compounds are like alkanes.

(b) (i) Sketch the structure formula for the first four compounds of the **X-H** series. (8 pts)

One of the above four compounds has 3 diastereomers (similar to tartaric acid).

(ii) Cycle the one with diastereomers in your answer sheets. (2 pts)

(iii) Sketch the structure of all diastereomers. (9 pts)

The plane heterocyclic compound, $(NXCl_2)_3$, was synthesized by J. Liebig and F. Wöhler in 1834 from the reaction of NH_4Cl and pentachloride compound of **X**. There is a gaseous by-product which is very easy to dissolve in water and reacts similar to strong acids.

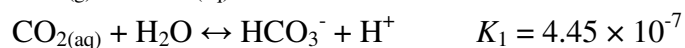
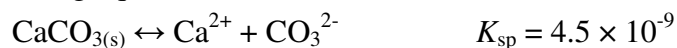
(c) (i) Write the balanced reaction equation of the synthesis of $(NXCl_2)_3$. (3 pts)

(ii) Sketch the structure of $(NXCl_2)_3$! (4 pts)

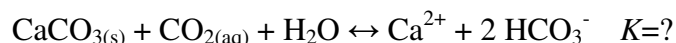
Heating the above compound shows a peculiar behaviour. The compound boils when heated quickly to $256^\circ C$. If heated slowly, the compound starts to melt at $250^\circ C$. Quickly cool the liquid results in a rubble-like material.

(iii) Use structure to explain this peculiar behaviour ! (4 pts)

4. If river water is saturated with calcite ($CaCO_3$), the concentration of Ca^{2+} is governed by the following equilibria:



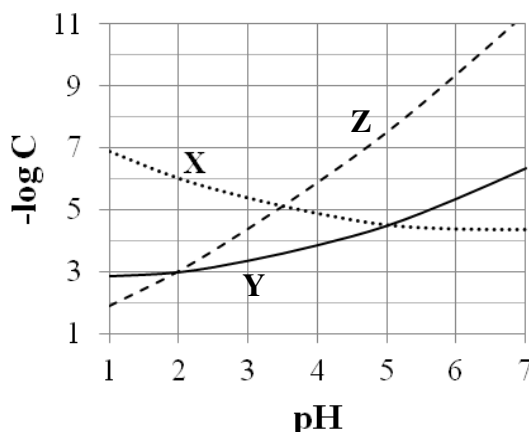
(a) Please find the equilibrium constant for the following reaction:



(b) Find the concentration (in ppm) of Ca^{2+} in river if the partial pressure of atmospheric CO_2 is $P_{CO_2} = 3.6 \times 10^{-4}$ bar.

5. A buffer solution containing 0.025M KH_2PO_4 and 0.025 M Na_2HPO_4 has a pH of 6.865 at 25°C. $\text{p}K_a$ of H_3PO_4 : $\text{p}K_1=2.148$, $\text{p}K_2=7.199$, $\text{p}K_3=12.15$
- (a) Show the ionic strength of the buffer is $\mu=0.100\text{M}$.
- (b) Find the quotient of activity coefficients, $\gamma_{\text{HPO}_4^{2-}}/\gamma_{\text{H}_2\text{PO}_4^-}=?$ At $\mu=0.100\text{M}$.
- (c) What molarities of KH_2PO_4 and Na_2HPO_4 should be mixed to obtain a pH 7.000 buffer at $\mu=0.100\text{M}$. You need to consider the activity coefficients, but you do not need to use Debye-Huckel equation and activity coefficient table.

6. Calcium oxalate (CaC_2O_4) is found in many plants and is a major constituent of kidney stones. The solubility of calcium oxalate in water is strongly pH-dependent, because oxalic acid exists in three different forms in aqueous solution: $\text{H}_2\text{C}_2\text{O}_4$, HC_2O_4^- , and $\text{C}_2\text{O}_4^{2-}$. When studying the solubility of calcium oxalate in water at different pH, it is found that the concentrations of Ca^{2+} and the three oxalate species vary considerably over the pH range studied. The following figure shows the plots of $-\log C$ vs. pH for the three oxalate species over pH 1~7, where C is the molarity of solute. Answer the following questions.



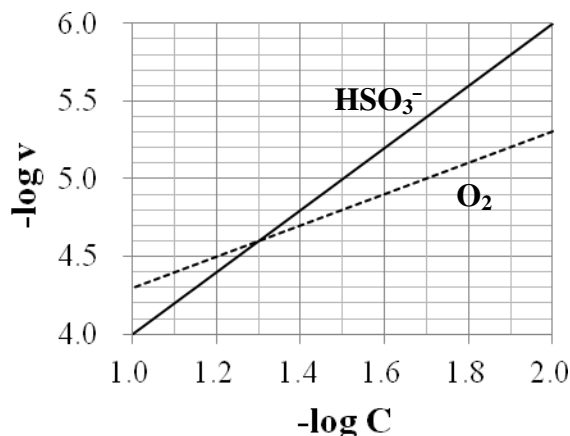
- (a) Assign the three curves (X, Y, Z) to the three oxalate species. 6 pts
- (b) Determine the two acid dissociation constants (K_1 , K_2) for oxalic acid. 6 pts
- (c) Give the relation for the concentrations of Ca^{2+} and the three oxalate species. 3 pts
- (d) Determine the solubility product constant (K_{sp}) for CaC_2O_4 . 4 pts
- (e) Find the solubility of $\text{CaC}_2\text{O}_4(\text{s})$ at pH 2.0. 4 pts
- (f) Find the ratio $[\text{H}_2\text{C}_2\text{O}_4]:[\text{HC}_2\text{O}_4^-]:[\text{C}_2\text{O}_4^{2-}]$ at pH 5.0. 3 pts
- (g) Find the mass of precipitate when the pH of 10 liters of the saturated solution of $\text{CaC}_2\text{O}_4(\text{s})$ at pH 2.0 is raised to 5.0. ($\text{CaC}_2\text{O}_4 = 128$) 6 pts

7. The oxidation of hydrogen sulfite ion (HSO_3^-) by dissolved oxygen (O_2) to form sulfate ion (SO_4^{2-}) in aqueous solution (given below) is a reaction of importance in acid rain formation and flue gas desulfurization.



To determine the rate law for the above reaction, a series of experiments has been conducted at 300

K in aqueous solution buffered at pH 4.0 by varying the concentrations (denoted as C in M) of either HSO_3^- or O_2 , while keeping the other reactant at a fixed concentration of 0.050 M. The initial rate for the consumption of oxygen (v) for each experiment was measured and then plotted as $-\log v$ vs. $-\log C$ (shown in the following figure). Answer the following questions.



- (a) Give the rate law and determine the rate constant. 6 pts
- (b) In an experiment conducted with an initial concentration of 0.20 M HSO_3^- and 1.0×10^{-3} M O_2 at pH 4.0 and 300 K, find the initial rate. 4 pts
- (c) Estimate the time elapsed when the concentration of O_2 in (B) is halved. 6 pts
- (d) If the rate constant increases 50% when the temperature is raised from 300 K to 306 K, calculate the activation energy of the reaction. 4 pts
- (e) Estimate the activation energy of the reverse reaction. 4 pts
- (f) The catalyst Fe^{2+} can accelerate the reaction 1000-fold of its initial (un-catalyzed) value at 300 K. Estimate the activation energy of the catalyzed reaction. 4 pts
- (g) A two-step mechanism was proposed for the reaction. The first step is
 $2 \text{HSO}_3^-(\text{aq}) + \text{O}_2(\text{aq}) \rightarrow \text{S}_2\text{O}_7^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l})$
 Give the second step of the mechanism. 4 pts

8. The vapor pressure at different temperatures can be described by the Clausius-Clayperon equation:

Clausius-Clayperon eq.:

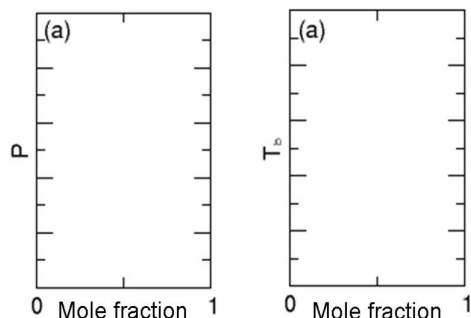
$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

At 25 °C, the vapor pressures of ethanol and water are 58.9 Torr and 23.8 Torr, respectively.

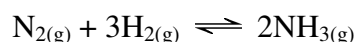
- (a) What is the boiling point of ethanol at 1 atm? ($\Delta H_{\text{vap}}^\circ = 43.5$ kJ/mol for ethanol)
- (b) What is a vapor pressure of a 95.5% (wt) ethanol aqueous solution at 25 °C? (Assume ideal solution.)
- (c) What is the mole fraction of ethanol in vapor?
- (d) Actually, the purity of ethanol cannot exceed 95.5% (wt) by distillation. Ethanol and water

forms an azeotrope system at 95.5%. What is an azeotrope?

- (e) Draw schematically $P(X)$, the vapor pressure as a function of composition (X =mole fraction) for ethanol-water mixture.
- (f) Draw schematically $T_b(X)$, the boiling point as a function of composition (X =mole fraction) for ethanol-water mixture.



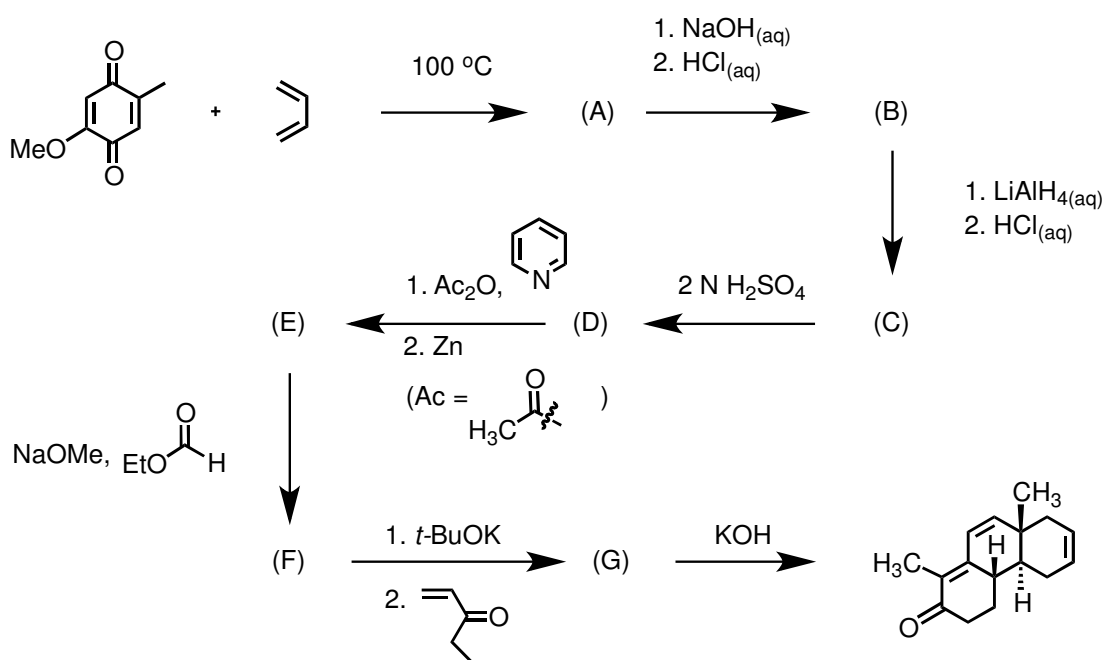
9. The chemical reaction for the synthesis of ammonia is as following:



Consider a closed system containing the mixture of $\text{N}_{2(\text{g})}$, $\text{H}_{2(\text{g})}$, and $\text{NH}_{3(\text{g})}$, the H: N atom ratio in the system is 3:1.

- (a) The equilibrium constant for the reaction at 25 °C is $K = 6.78 \cdot 10^5$. The total pressure of the system is 1 atm. Calculate the partial pressures of $\text{N}_{2(\text{g})}$, $\text{H}_{2(\text{g})}$, and $\text{NH}_{3(\text{g})}$.
- (b) If the closed system (the volume doesn't change) is heated up to 400 °C ($K = 3.19 \cdot 10^{-4}$), what is the total pressure and the partial pressures of $\text{N}_{2(\text{g})}$, $\text{H}_{2(\text{g})}$, and $\text{NH}_{3(\text{g})}$ after equilibrium?
- (c) What is the sign of enthalpy and entropy change for this reaction?
- (d) How does the reaction Gibbs free energy change with temperature? Explain the physical meaning.

10. Steroid is a very important class of pharmaceutical compounds. The following steroid synthesis is selected partially from 1965 Nobel laureate – R. B. Woodward's work. The reaction starts with a stereoselective Diels-Alder reaction.



Hint:

Compounds (A) and (B) are stereoisomers.

Compound (E): No hydroxyl group presenting in the molecules as evidenced by NMR and IR spectroscopies.

Compound (G): A chemical shift at 9.2 ppm (1 H) on ^1H NMR spectroscopy observed.

Questions: Draw structures of (A) to (G)

11. Organic halides are versatile reagents in Organic Synthesis. They are capable of transforming into various organic functional groups. The following reactions are examples of organic halides in Organic Synthesis.

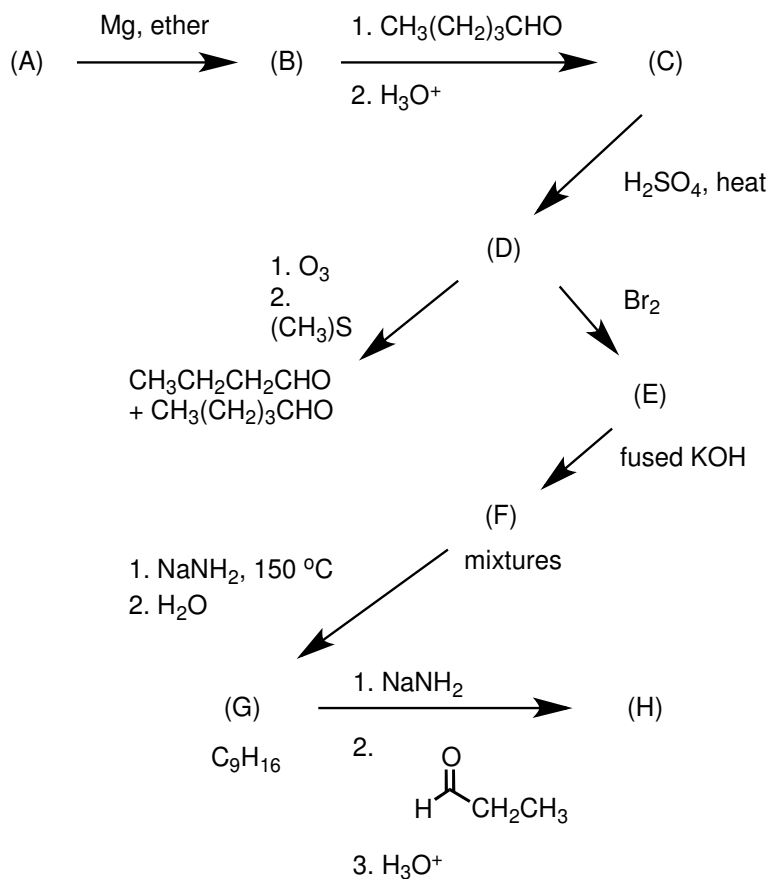
A monobrominated hydrocarbon (A) shows weight percentages as follows:

Weight % C: 35%

Weight % H: 6.6%

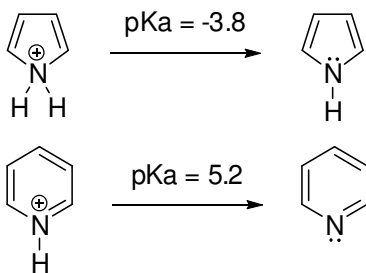
Weight % Br: 58.4%

Compound (A) can be used for the following reaction:



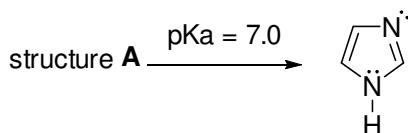
Questions: Draw structures of (A) to (H)

12. The pKa for the conjugated acids of pyrrole and pyridine are shown below: (35 pts)

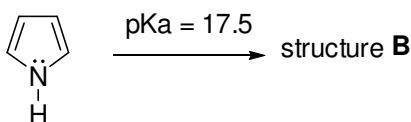


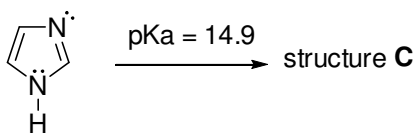
(a) Explain why pyridine is more basic than pyrrole. (5 pts)

(b) The pKa for the conjugated acid of imidazole (structure **A**) is 7.0. Draw the structure of **A**.

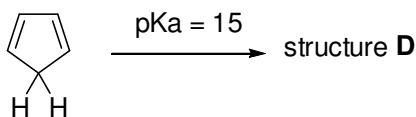


(c) The pKa of pyrrole and imidazole are 17.5 and 14.9, respectively. Draw the structures for the conjugated bases of pyrrole (structure **B**) and imidazole (structure **C**). (6 pts)





(d) The pKa of cyclopentadiene is 15. Draw the structure for the conjugated base of cyclopentadiene (structure **D**). (3 pts)

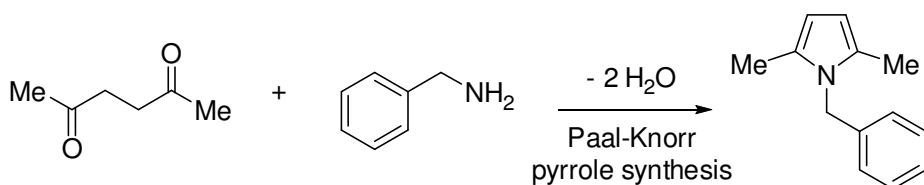


(e) Which of them is aromatic? cyclopentadiene and its conjugated base. (3 pts)

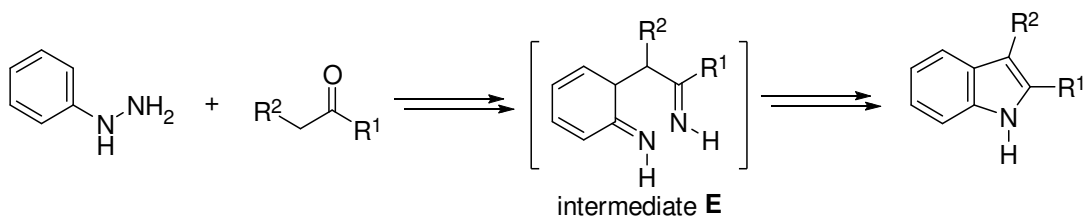
(f) Briefly explain why it is aromatic. (5 pts)

(g) Draw the reaction mechanisms for the following reactions: (10 pts)

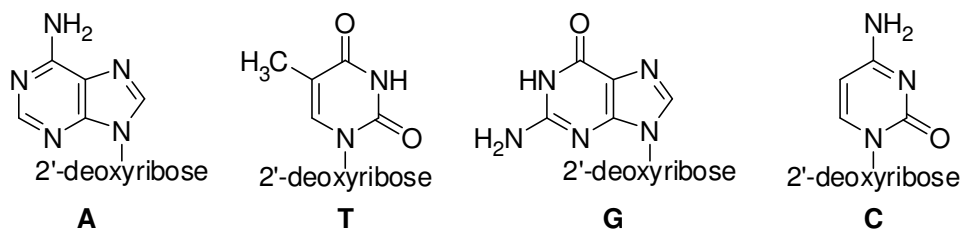
(i) Paal-Knorr pyrrole synthesis:



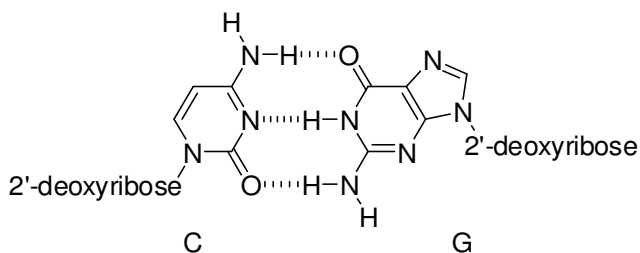
(ii) Fischer indole synthesis:



13. The following structures are the 4 bases in DNA: (15 pts)



(a) In double-strand DNA, G-C pairing forms 3 hydrogen bonds as shown below:



Mark the hydrogen-bond donors (D) and acceptors (A).

(b) A-T pairing forms 2 hydrogen bonds. Draw the base-pairing structure between A and T.

Round 3 Answers

1. (a) 24 pts

Mg and H⁺ react must produce H₂, If 0.54 atm is only H₂, then H₂ = 0.022 mol,
 Check HNO₃, 400 x 1.01 x 0.021 = 8.484 g ~ 8.48 mol (more than H₂), possible.
 1 g Mg (0.042 mol) should be okay.

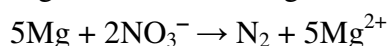
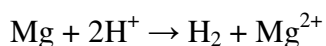
No NO or NO₂ formation, since heating show no reaction.

O₂ added: 0.85 - 0.54 = 0.31 atm ~ 0.0126 mol enough to complete 2H₂ + O₂ → H₂O reaction if
 0.54 is only H₂. In this case, leaves 0.04 atm O₂ which is not the situation.

But vessel remains 0.134 atm after explosion reaction, Mg and H⁺ reaction must produce other gas
 that is not reacting with H₂ or O₂.

It could be N₂ formation.

Reactions:



$$\text{H}_2: (2/3)(0.85 - 0.134)/RT = 19.53 \text{ mmol}$$

$$\text{Need O}_2 \text{ 9.765 mmol (0.239 atm)}$$

$$\text{N}_2: (0.134 - (0.31 - 0.239))/RT = 2.58 \text{ mmol}$$

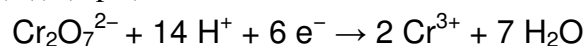
(b) (6 pts)

$$\text{Mg} = 19.53 + 5(2.58) = 32.43 \text{ mmol}$$

$$0.03243 \times 24.03 = 0.779 \text{ g}$$

$$\text{purity: } 77.9/1 \times 100\% = 77.9\%$$

2. (a) (i) (2 pts)



(ii) (4 pts)

in neutral solution:

$$E = 1,38 \text{ V} + \frac{R \cdot T}{6 \cdot F} \cdot \ln \frac{c(\text{Cr}_2\text{O}_7^{2-}) \cdot c(\text{H}^+)^{14}}{c(\text{Cr}^{3+})^2} \quad E = 1,38 \text{ V} + \frac{8,314 \cdot 298}{6 \cdot 96485} \text{ V} \cdot \ln (10^{-7})^{14}$$

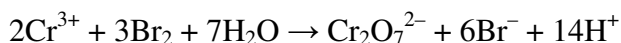
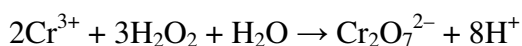
$$E = 0,414 \text{ V}$$

$$\text{or : } E = E^\circ - (0.059/n) \log(1/[\text{H}^+]^{14}) \equiv 1.38 - (0.059/6) \log(1/10^{-98}) = 0.416$$

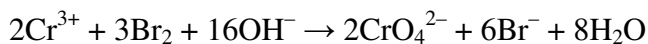
$$E^\circ: 2\text{I}^- + 2\text{e}^- \rightarrow \text{I}_2 = -0.54 \quad \text{No reaction}$$

(iii) (8 pts)

in acidic solution



In basic solution



(iv) (4 pts)

$$1.065 > 1.38 + \frac{8.314 \cdot 298}{6.96485} \cdot \ln c(\text{H}^+)^{14} \quad \Leftrightarrow \quad -73.60 > \ln c(\text{H}^+)^{14}$$

$$\sqrt[14]{e^{-73.60}} = 5.21 \cdot 10^{-3} > c(\text{H}^+) \quad 2.28 < \text{pH}$$

Only works when $\text{pH} > 2.28$.

(b) (i) (6 pts)

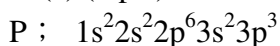
+2. To meet $(t_{2g})^4$ electronic configuration

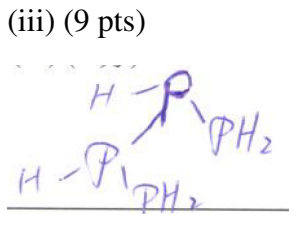
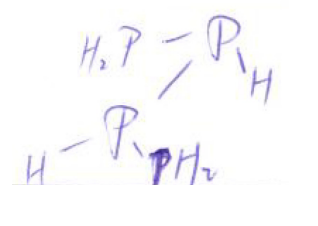
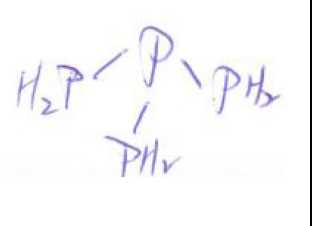


(ii) (12 pts)

Replace ligands to NH_3 reduces the ligand field and gives high spin complex of $(t_{2g})^3(e_g)^1$.

The magnetic moment is $4.9 \mu_{\text{BM}}$.

3. (a) (4 pts)



(b) (i) (8 pts) PH_3	P_2H_4 $\text{H}_2\text{P}-\text{PH}_2$	P_3H_5 $\text{H}_2\text{P}-\text{PH}-\text{PH}_2$	P_4H_6 $\text{H}_2\text{P}-\text{PH}-\text{PH}-\text{PH}_2$
(ii) (2 pts) 在(i)中圈選	(iii) (9 pts) 		
(c)(i) (3 pts) $3\text{NH}_4\text{Cl} + 3\text{PCl}_5 \rightarrow (\text{NPCl}_2)_3 + 12\text{HCl}$			
(ii) (4 pts) 	(iii) (4 分) Polymerized 		

<p>4. (a) (24 pts)</p> $\text{CaCO}_3(\text{s}) \leftrightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$ <p>+) $\text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- + \text{H}^+$ -) $\text{HCO}_3^- \leftrightarrow \text{CO}_3^{2-} + \text{H}^+$</p> <hr/> $\text{CaCO}_3(\text{s}) + \text{CO}_2(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{Ca}^{2+} + 2 \text{HCO}_3^-$ $K = K_{\text{sp}} \times K_1 / K_2 = 4.27 \times 10^{-5}$	<p>(b) (10 pts)</p> <p>from (a), $\frac{[\text{Ca}^{2+}][\text{HCO}_3^-]^2}{[\text{CO}_2(\text{aq})]} = K = 4.27 \times 10^{-5}$,</p> <p>$[\text{HCO}_3^-] = 2[\text{Ca}^{2+}]$ and $[\text{CO}_2(\text{aq})] = K_{\text{CO}_2} \times P_{\text{CO}_2}$</p> $\frac{[\text{Ca}^{2+}](2[\text{Ca}^{2+}])^2}{K_{\text{CO}_2} P_{\text{CO}_2}} = K = 4.27 \times 10^{-5}$ <p>$[\text{Ca}^{2+}] = 4.97 \times 10^{-4} \text{ M} = 20 \text{ mg/L (ppm)}$</p>
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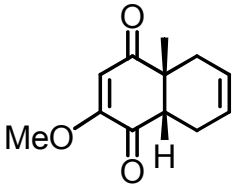
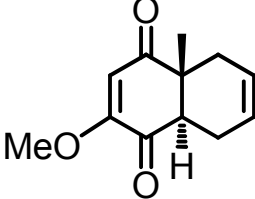
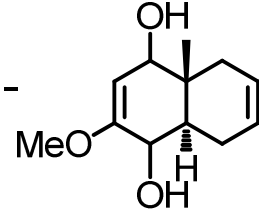
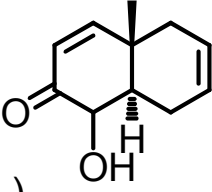
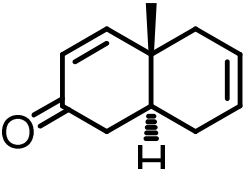
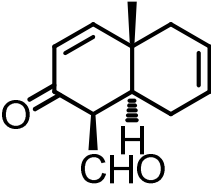
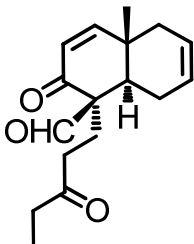
<p>5. (a) (10 pts)</p> <p>0.025M KH_2PO_4, $\mu = 0.025\text{M}$, 0.025 M Na_2HPO_4, (2:1 ions) $\mu = 0.075\text{M}$, $0.025 + 0.075 = 0.100\text{M}$</p>
<p>(b) (10 pts)</p> $K_2 = \frac{[\text{H}^+]\gamma_{\text{H}^+}[\text{HPO}_4^{2-}]\gamma_{\text{HPO}_4^{2-}}}{[\text{H}_2\text{PO}_4^-]\gamma_{\text{H}_2\text{PO}_4^-}}, \quad K_2 = 10^{-7.199}, [\text{H}^+]\gamma_{\text{H}^+} = 10^{-\text{pH}} = 10^{-6.865}$ $\frac{\gamma_{\text{HPO}_4^{2-}}}{\gamma_{\text{H}_2\text{PO}_4^-}} = \frac{K_2[\text{HPO}_4^{2-}]}{[\text{H}^+]\gamma_{\text{H}^+}[\text{H}_2\text{PO}_4^-]} = \frac{10^{-7.199}[0.025]}{10^{-6.865}[0.025]} = 0.463$
<p>(c) (14 pts)</p> $K_2 = \frac{[\text{H}^+]\gamma_{\text{H}^+}[\text{HPO}_4^{2-}]\gamma_{\text{HPO}_4^{2-}}}{[\text{H}_2\text{PO}_4^-]\gamma_{\text{H}_2\text{PO}_4^-}}, \quad 10^{-7.199} = \frac{10^{-7.000}[0.025 + x]}{[0.025 - 3x]} \times (0.463)$ <p>$x = 0.0018\text{M}$, $\text{Na}_2\text{HPO}_4 = 0.0268\text{M}$, $\text{KH}_2\text{PO}_4 = 0.0196\text{M}$</p>


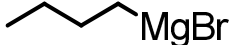
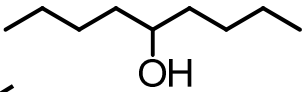

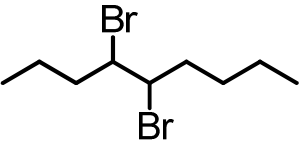

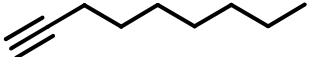
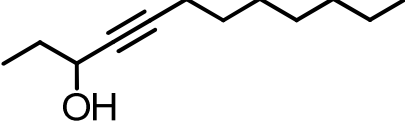
6. (a)(6 pts) $X = C_2O_4^{2-}$; $Y = HC_2O_4^-$; $Z = H_2C_2O_4$
(b) (6 pts) $K_1 = 1.0 \times 10^{-2}$ (intersection of Y & Z); $K_2 = 1.0 \times 10^{-5}$ (intersection of X & Y)
(c) (3 pts) $[Ca^{2+}] = [H_2C_2O_4] + [HC_2O_4^-] + [C_2O_4^{2-}]$
(d) (4 pts) $K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = 2.0 \times 10^{-9}$ (from the data in (E))
(e) (4 pts) $[H_2C_2O_4] = [HC_2O_4^-] = 1.0 \times 10^{-3} M$; $[C_2O_4^{2-}] = 1.0 \times 10^{-6} M$ Solubility = $[Ca^{2+}] = 2.0 \times 10^{-3} M$
(f) (3 pts) $[H_2C_2O_4]:[HC_2O_4^-]:[C_2O_4^{2-}] = [H^+]^2:K_1[H^+]:K_1K_2 = 10^{-3}:1:1$
(g) (6 pts) $[Ca^{2+}] = 2[C_2O_4^{2-}]$; $K_{sp} = [Ca^{2+}]^2/2$; $[Ca^{2+}] = 6.3 \times 10^{-5} M$ $(2.0 \times 10^{-3} - 6.3 \times 10^{-5}) \times 10 \times 128 = 2.5 g$

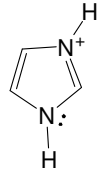
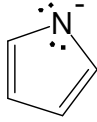
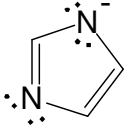
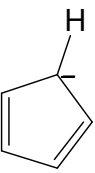
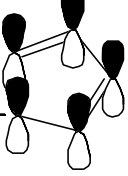
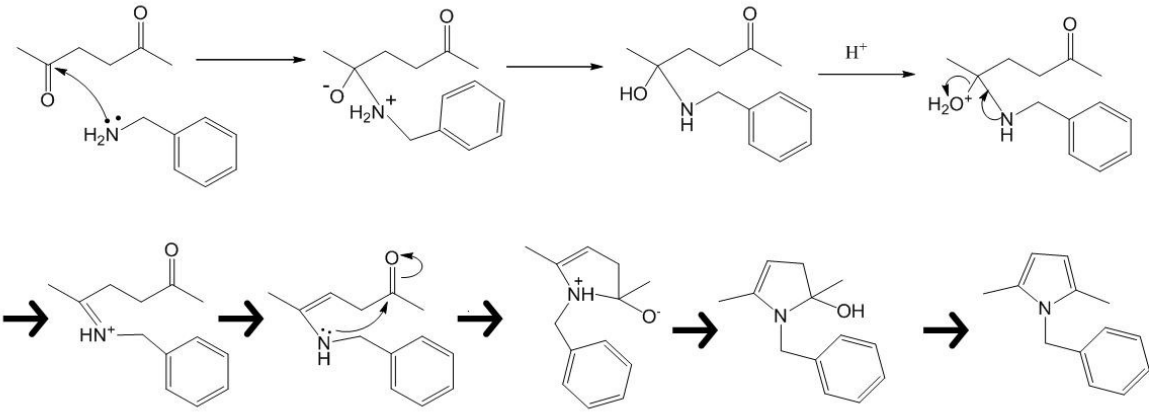
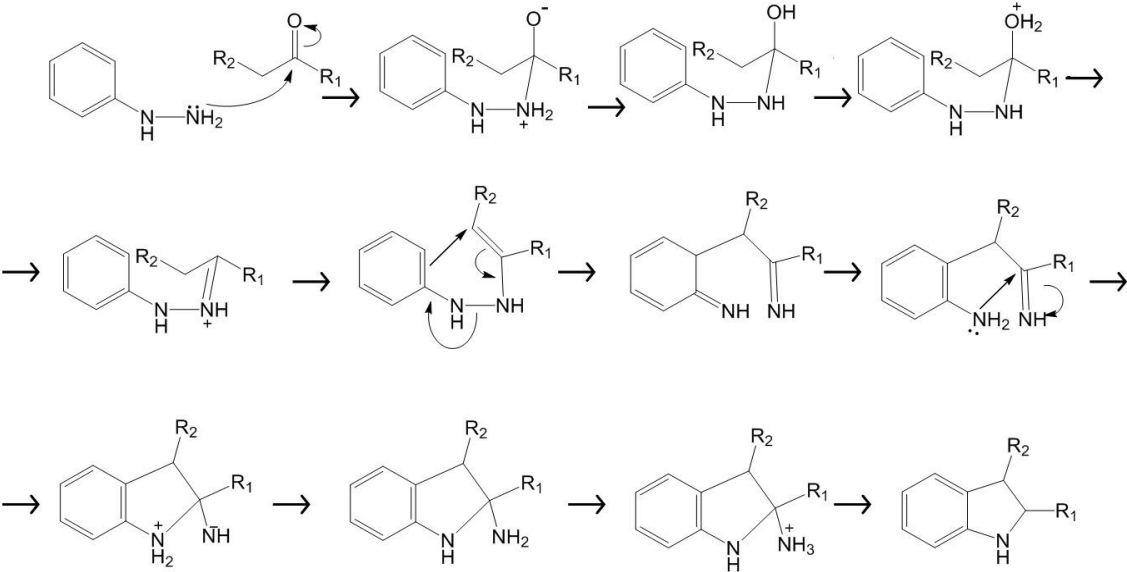
7. (a) (6 pts) Reaction order = slope = 2 for HSO_3^- and 1 for O_2 . rate = $k[HSO_3^-]^2[O_2]$; $v = 1.0 \times 10^{-4} M \cdot s^{-1}$; $[HSO_3^-] = 0.10 M$ (from the figure); $[O_2] = 0.050 M$ $k = 0.20 M^{-2} \cdot s^{-1}$	(b) (4 pts) $v = 0.20 \times (0.20)^2 \times 1.0 \times 10^{-3}$ $= 8.0 \times 10^{-6} M \cdot s^{-1}$
(c) (6 pts) $[HSO_3^-] \gg [O_2]$; $[HSO_3^-] \approx \text{constant}$; rate = $(k[HSO_3^-]^2)[O_2]$ $= 8.0 \times 10^{-3} [O_2] = k'[O_2]$; pseudo-first order in O_2 ; $t_{1/2} = \frac{0.693}{k'} = \frac{0.693}{8.0 \times 10^{-3}} = 87 s$	(d) (4 pts) $\ln \frac{k_2}{k_1} = \ln 1.5 = \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$; $E_a = 52 \text{ kJ/mol}$
(e) (4 pts) E_a (reverse) = E_a (forward) - ΔH° $= 52 + 96 = 148 \text{ kJ/mol}$	(f) (4 pts) $\ln \frac{k_2}{k_1} = \ln 1000 = \frac{(E_a - E'_a)}{R} \cdot \frac{1}{300}$ $E'_a = 38$ kJ/mol (catalyzed reaction)
(g) (4 pts) Second step = net reaction - first step $S_2O_7^{2-}(aq) + 3 H_2O(l) \rightarrow 2 SO_4^{2-}(aq) + 2 H_3O^+(aq)$	

<p>8. (a) (6 pts)</p> $\ln \frac{760}{58.9} = \frac{43.5 \cdot 1000}{8.314} \left(\frac{1}{298.15} - \frac{1}{T_b} \right)$ $T_b = 349.01K = 75.9^\circ C$	<p>(b) (6 pts)</p> $\chi_{ethanol} = \frac{95.5/46}{95.5/46 + 4.5/18} = 0.89$ $\chi_{water} = \frac{4.5/18}{95.5/46 + 4.5/18} = 0.11$ $P = 0.89 \cdot 58.9 + 0.11 \cdot 23.8 = 55.04 Torr$
<p>(c) (6 pts)</p> $\chi_{ethanol}^{vapor} = \frac{0.89 \cdot 58.9}{55.04} = 0.95$	<p>(d) (6 pts)</p> <p>The mole fraction of ethanol in the gas phase is the same as the one in the liquid phase.</p>
<p>(6 pts)</p>	<p>(6 pts)</p>

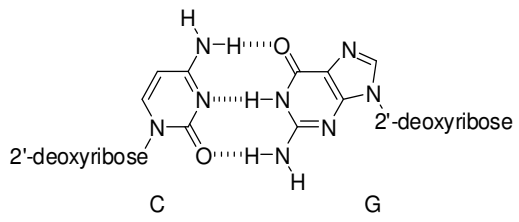
<p>9. (a) (10 pts)</p> $P_{N_2} + P_{H_2} + P_{NH_3} = 1.013bar$ $\frac{2P_{N_2} + P_{NH_3}}{2P_{H_2} + 3P_{NH_3}} = \frac{1}{3}$ $\frac{P_{NH_3}^2}{P_{N_2}P_{H_2}^3} = K = 6.78 \cdot 10^5$ $\Rightarrow \frac{2P_{N_2} + P_{NH_3}}{2P_{H_2} + 3P_{NH_3}} = \frac{1}{3} \Rightarrow 3P_{N_2} = P_{H_2}$ $\frac{P_{NH_3}^2}{27P_{N_2}^4} = 6.78 \cdot 10^5 \Rightarrow P_{NH_3} = 4.28 \cdot 10^3 P_{N_2}^2$ $4P_{N_2} + P_{NH_3} = 1.013bar$ $\Rightarrow 4P_{N_2} + 4.28 \cdot 10^3 P_{N_2}^2 = 1.013bar$ $P_{N_2} = 0.0149bar = 0.0147atm$ $P_{H_2} = 0.0447bar = 0.0441atm$ $P_{NH_3} = 0.953bar = 0.941atm$	<p>(b) (10 pts)</p> $298K \Rightarrow 673K$ <p>Initial condition:</p> $P_{total} = 1 \cdot 673 / 298 = 2.26atm = 2.288bar$ $P_{N_2} = 0.0149 \cdot 673 / 298 = 0.0337bar$ $P_{H_2} = 0.0447 \cdot 673 / 298 = 0.101bar$ $P_{NH_3} = 0.953 \cdot 673 / 298 = 2.152bar$ <p>at equilibrium</p> $P_{N_2} = 0.0337 + x$ $P_{H_2} = 0.101 + 3x$ $P_{NH_3} = 2.152 - 2x$ $\frac{(2.152 - 2x)^2}{(0.0337 + x)(0.101 + 3x)^3} = 3.19 \cdot 10^{-4} \square \frac{(2.152 - 2x)^2}{27(0.0337 + x)^4}$ $\frac{(2.152 - 2x)}{(0.0337 + x)^2} = 9.28 \cdot 10^{-2}$ $\Rightarrow x = 1.027$ $P_{N_2} = 0.0337 + 1.027 = 1.061bar$ $P_{H_2} = 0.101 + 3 \cdot 1.027 = 3.183bar$ $P_{NH_3} = 2.152 - 2 \cdot 1.027 = 0.098bar$ $P_{total} = 4.408bar$
<p>(c) (6 pts) When $T \uparrow$, $K \downarrow$, reaction shifts to the left, so it is an exothermic reaction, $\Delta H < 0$. Reaction from 4 molecules to 2 molecules, so $\Delta S < 0$.</p>	<p>(d) (4 pts) $\Delta G = \Delta H - T \Delta S$, when $T \uparrow$, ΔG more positive. Indicates at high T, this reaction is less spontaneous. $\Delta G = -RT \ln K$, K become smaller, same as experimental results.</p>

<p>10. (4 pts each, total 28 pts)</p> <p>Structure of compound (A)</p> 	<p>Structure of compound (B)</p> 	<p>Structure of compound (C)</p> 
<p>Structure of compound (D)</p> 	<p>Structure of compound (E)</p> 	<p>Structure of compound (F)</p> 
<p>Structure of compound (G)</p> 		

<p>11. (3 pts each, total 24 pts)</p> <p>Structure of compound (A)</p> 	<p>Structure of compound (B)</p> 	<p>Structure of compound (C)</p> 
<p>Structure of compound (D)</p> 	<p>Structure of compound (E)</p> 	<p>Structure of compound (F)</p> 
<p>Structure of compound (G)</p> 	<p>Structure of compound (H)</p> 	

<p>12. (a) (5 pts)</p> <p>The lone pair electrons on Pyridine are not involved in the aromatic resonance, therefore, a better Lewis base.</p>	<p>(b) structure A (3 pts)</p> 	
<p>(c) structure B (3 pts)</p> 	<p>structure C (3 pts)</p> 	
<p>(d) structure D (3 pts)</p> 	<p>(e) (3 pts) cyclopentadiene conjugated base</p>	<p>(f) (5 pts) 6 p electron involve in resonance</p> 
<p>(g) (i) (5 pts)</p> 		
<p>(ii) (5 pts)</p> 		

13 (15 pts) (a)



(b) A-T base-pair

