

General Chemistry C

Final Examination

(2 hours)

You may find the following equations and physical constants useful. However, it does not mean they are required in answering the questions.

$$[A] = [A]_0 - kat$$

$$\ln[A] = \ln[A]_0 - akt$$

$$\frac{1}{[A]} = \frac{1}{[A]_0} + akt$$

$$x = \frac{\sqrt{K_a^2 + 4(K_a c)} - K_a}{2}$$

$$ax^2 + bx + c = 0 \quad \Rightarrow \quad x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$K_{eq} = e^{-\frac{\Delta G^0}{RT}}$$

$$\Delta G^0 = -nFE_{cell}^0$$

$$E_{cell} = E_{cell}^0 - \frac{RT}{nF} \ln C$$

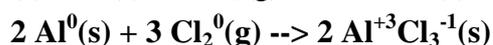
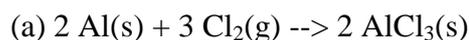
$$\Delta G = \Delta G^0 + RT \ln C$$

Gas constant $R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$

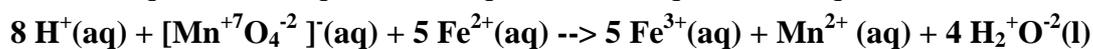
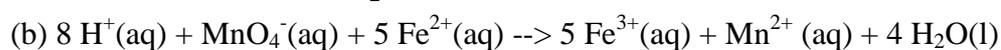
Faraday Constant = 96489 C

Section A (50 marks)

1. (10 marks) In each of the following chemical reactions, state which substance is oxidized and which is reduced. In addition, state how many electrons (n) are involved in the reaction. [Hints: you can write down the half-reaction to deduce n]



Al is oxidized and Cl in Cl_2 is reduced. There are 6 electrons involved.



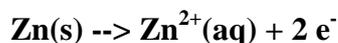
Fe^{2+} is oxidized, Mn in MnO_4^- is reduced. There are 5 electrons involved.

2. (10 marks) Using standard reduction potentials, calculate the potential for the following cell at 298 K: Zn / Zn²⁺(aq), 0.1 M // Cu²⁺(aq), 1.0 M / Cu

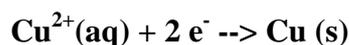
Standard reduction potential at 298 K



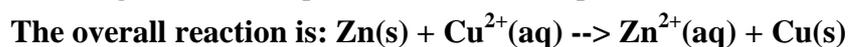
(a) Write down the half-reaction at the anode.



(b) Write down the half-reaction at the cathode.



(c) Using the Nernst equation, calculate the potential of the cell.



$$Q = [\text{Zn}^{2+}] / [\text{Cu}^{2+}]$$

Nernst equation: $E = E^0 - (0.0592/n) \log Q$

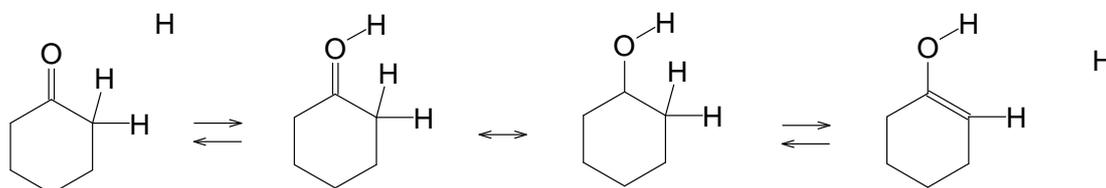
For the above reaction, n = 2, and $E^0 = E^0(\text{cathode}) - E^0(\text{anode})$ [using standard reduction potentials]

$$E^0 = 0.34 \text{ V} - (-0.76 \text{ V}) = 1.10 \text{ V}$$

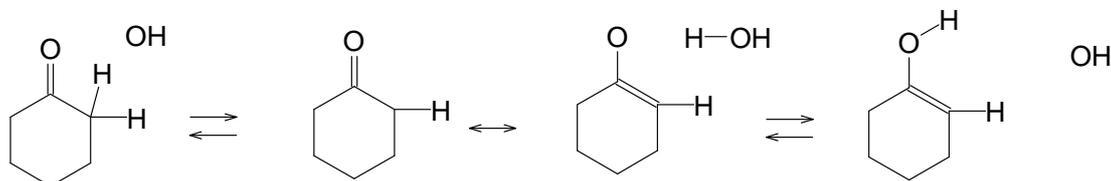
$$E = 1.10 \text{ V} - (0.0592/2) \log (0.1/1.0) = 1.13 \text{ V}$$

3. (10 marks) Ketones in acidic or alkaline media will undergo the following transformation. Add arrows and charges to complete the mechanisms shown below:

(a) in acidic medium

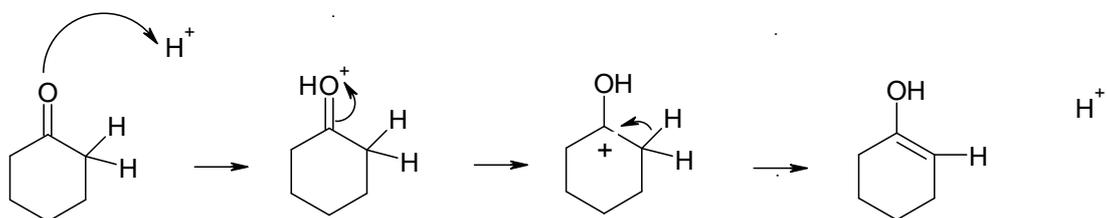


(b) in alkaline medium

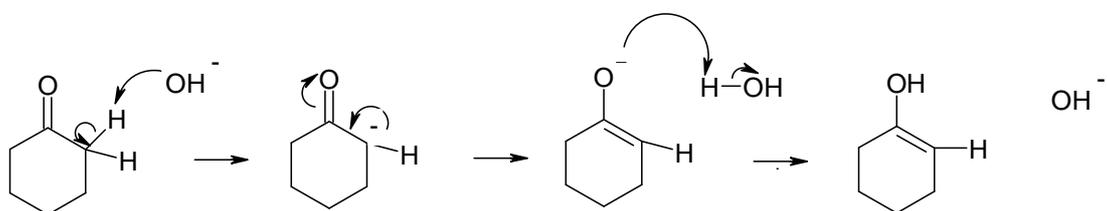


Answer

(a)

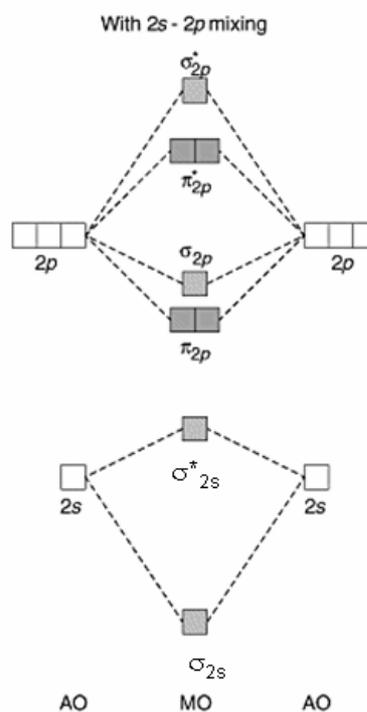
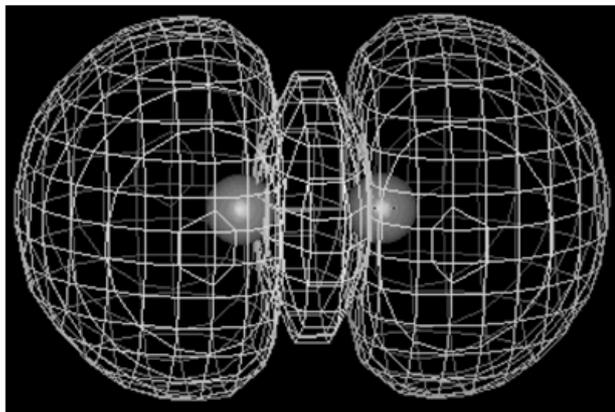


(b)



4. (10 marks) Referring to the following figure, we have shown eight molecular orbitals for a nitrogen molecule. One of these eight molecular orbital is shown on the left hand side.

Nitrogen Molecule



(a) What is the bond type of this MO? [Hints: σ or π bond]

σ

(b) What kind of bonding orbital is this MO? [Hints: non-bonding, bonding, anti-bonding]

Bonding

(c) Is this MO an OMO or HOMO or LUMO or SOMO or UMO?

HOMO

(d) What is the bond order of N_2^{2+} (g)?

2

(e) Is N_2^{2+} (g) paramagnetic or diamagnetic?

Diamagnetic

5. (10 marks) The amino acid glycine, $\text{H}_2\text{N}-\text{CH}_2-\text{COOH}$, can undergo the following equilibria in water:



$$K_a = 4.3 \times 10^{-3}$$



$$K_b = 6.0 \times 10^{-5}$$

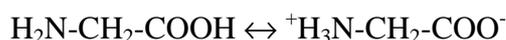
THIS QUESTION IS NOT COUNTED IN YOUR FINAL MARKS.

THAT IS, YOU GET 50 MARKS IF YOU ANSWER THE PREVIOUS

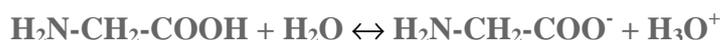
FOUR QUESTIONS CORRECTLY.

One of you get the part a done correctly and he/she will get extra 5 marks as bonus. Very impressive!

(a) Use the values of K_a and K_b to estimate the equilibrium constant for the intramolecular proton transfer to form a zwitterion:



We can imagine that the formation of a zwitterion occurs as a series of steps:



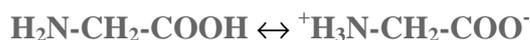
$$K_a = 4.3 \times 10^{-3}$$



$$K_b = 6.0 \times 10^{-5}$$



$$1/K_w = 1.0 \times 10^{14}$$



$$K_a \times K_b / K_w = 2.6 \times 10^7$$

Since K is large, it means that glycine will exist predominantly as a zwitterion. The assumption we made here is that the same glycine molecule acts in the first two reactions.

(b) What is the pH of a 0.050 M aqueous solution of glycine?

Since glycine will exist as the zwitterion, we need to consider how this ion will behave in aqueous solution. First, in case you have not noticed, glycine is stronger as an acid than as a base. (Compare K_a and K_b) This means that the zwitterion is more likely to give a proton away than take another proton ($1/K_b > 1/K_a$). Therefore, we need to consider the following reaction:



$$K = K_w/K_b$$

And from this point, this becomes a simple "weak-acid" problem where

$$[\text{H}^+] = (K_a c)^{1/2}$$

$$= ((1.7 \times 10^{-10})(0.050))^{1/2}$$

$$= 2.9 \times 10^{-6}$$

$$\text{pH} = 5.54$$

Does our answer make sense?

Yes, since glycine is stronger as an acid than as a base.

Section B (50 marks)

1. If the half life of a reaction with respect to a reactant concentration is $\frac{0.693}{k}$,

what is the reaction order of the reactant?

- a. **First order** b. Second order c. Third order d. Zero order

2. For any spontaneous chemical reactions in a beaker (燒杯) at constant temperature, which of the following condition must be satisfied?

a. $\Delta S_{\text{system}} \geq 0$ b. $\Delta H - T\Delta S_{\text{system}} < 0$

c. $\Delta G \geq 0$ d. $\Delta S_{\text{universe}} < 0$

3. What is the oxidation number of Mn in MnO_4^- ?

- a. +5 b. +7 c. -5 d. -7

4. What is the formal charge of P in the most stable Lewis structure of PO_4^{3-} ?

- a. +1 b. +2 c. -1 d. 0

5. Calculate the potential for the following cells at 25°C: $\text{Cr(s)} / \text{Cr}^{3+}(0.040 \text{ M}) // \text{Cr}^{3+}(2.0 \text{ M}) / \text{Cr(s)}$

- a. 0.014 V b. 0.024 V c. 0.034 V d. 0.044 V

6. What would be the predominant (主要) form of glycine in a solution with pH 13 and with pH 1?

a. At pH 13, $\text{H}_2\text{N-CH}_2\text{-COO}^-$ and at pH 1, $^+\text{H}_3\text{N-CH}_2\text{-COOH}$

b. At pH 13, $^+\text{H}_3\text{N-CH}_2\text{-COOH}$ and at pH 1, $\text{H}_2\text{N-CH}_2\text{-COO}^-$

c. At pH 13, $^+\text{H}_3\text{N-CH}_2\text{-COOH}$ and at pH 1, $\text{H}_2\text{N-CH}_2\text{-COOH}$

d. At pH 13, $^+\text{H}_3\text{N-CH}_2\text{-COO}^-$ and at pH 1, $\text{H}_2\text{N-CH}_2\text{-COO}^-$

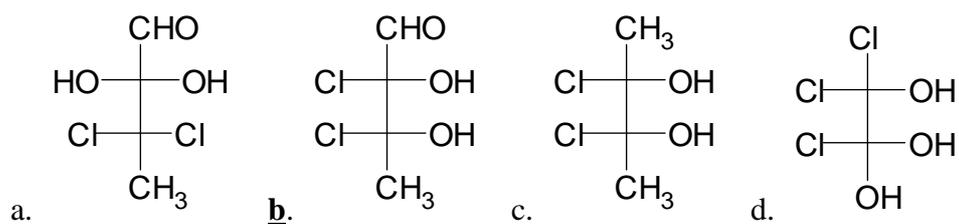
7. Predict the shape of a chlorine trifluoride (ClF_3) molecule.

- a. Trigonal planar b. Linear c. **T-shaped** d. tetrahedral

8. Which of the following molecule does not have a C_2 symmetry axis?

- a. CH_4 b. PCl_5 c. **CH_3Cl** d. SF_6

9. Which of the following molecule has optical activity?



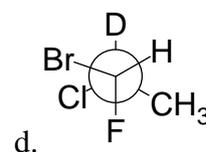
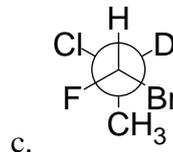
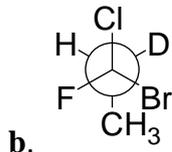
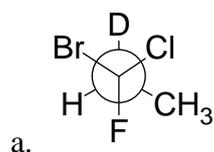
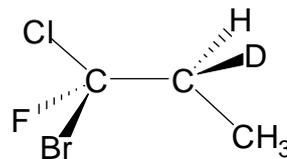
10. Which of the following statement is WRONG?

- a. We have to do experiments to determine the optical activity, $d(+)$ or $l(-)$, for the twenty L-amino acids.
- b. If L-alanine has a specific rotation of $+15^\circ$, the corresponding value for D-alanine must be -15°
- c. If we have equal amount of a pair of enantiomers in a solution, we will not observe any optical rotation.
- d. A molecule containing more than two chiral carbons must be optically active.**

11. For a $[\text{H}^+]$ concentration of 0.02040 M, the pH value should read

- A. 1.69036 B. 1.6904 C. 1.690 D. 1.69

12. For the given molecule on the right hand side, which of the following is the correct Newman projection?



13. Referring to the molecule shown in the previous question, which of the following is correct?

- a. Both chiral carbons have R configuration.
- b. The chiral carbon on the left has S configuration and that on the right has R configuration.
- c. Both chiral carbons have S configuration.**
- d. The chiral carbon on the left has R configuration and that on the right has S configuration.

14. What is the shape of the molecule ClF_4^- ?

- a. Tetrahedral
- b. Octahedral
- c. Square planar**
- d. Seesaw

15. Which of the following is NOT a correct description for a peptide bond?

- a. A peptide bond is chemically inactive compared with similar carbonyl or amine groups.
- b. A plane is always associated with a peptide bond.
- c. Due to the strong dipole moment of a peptide bond, it is easy to form H-bonding with other peptide bond.
- d. A peptide bond has higher HOMO than a similar amine group.**

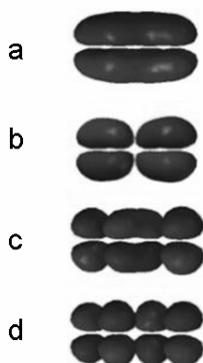
16. For proteins (蛋白質) or polypeptides (多肽), the descriptions of β -sheets, α -helices or turns belong to the category of

- a. primary structure
- b. secondary structure**
- c. tertiary structure
- d. quaternary structure

17. Which of the following species (東西) has the highest HOMO?

- a. NH_3
- b. CH_3OH
- c. OH^-**
- d. H_2O

18. Which of the following is the LUMO for 1,3-butadiene ($\text{H}_2\text{C}=\text{CH}-\text{CH}=\text{CH}_2$)?

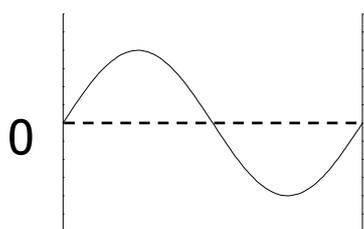


Answer is c.

19. Which of the following statement is CORRECT?

- a. Orbital means electron density
- b. For orbitals with the same l quantum number (same shape), the larger the orbital, the higher the energy**
- c. Experimentally we can measure the shape of an orbital
- d. The 2s and 2p orbitals are degenerate for a carbon atom

20. Referring to the following wavefunction calculated for a particle in a one-dimensional box.



The probability that a particle will appear in the middle of the box will be

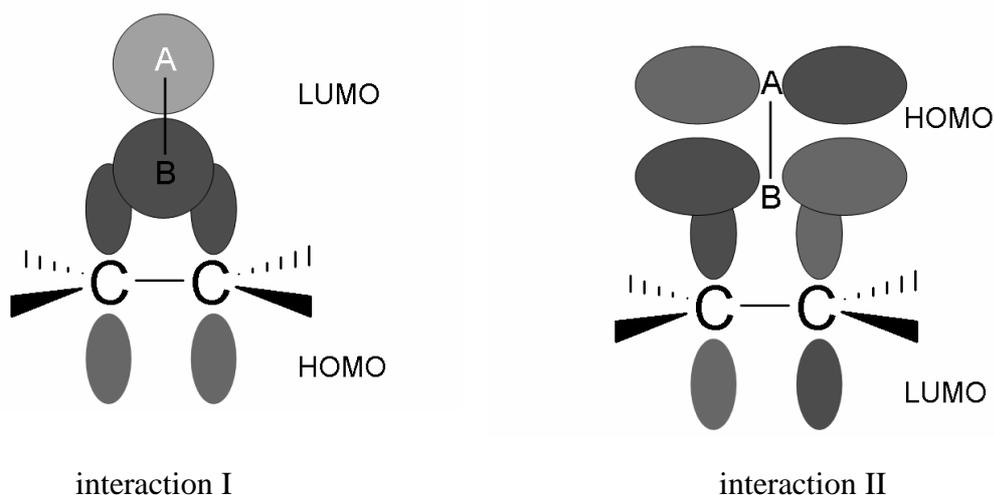
- a. 0.5
- b. 1.0
- c. 0.0**
- d. 0.25

21. Which of the following statement is CORRECT. [Hints: You may get a wrong answer if you think in terms of Lewis concepts]. **What you need is a MO diagram for a diatomic molecule. See Question 4 of Section A.**

- a. The HOMO of a Br_2 molecule is non-bonding.
- b. The HOMO of a Br_2 molecule is anti-bonding**

- c. The LUMO of a Br₂ molecule is non-bonding.
- d. A Br₂ molecule does not have HOMO.

Question 22-24: Assume a molecule A-B will react with an alkene molecule (an example of electrophilic addition). The reaction involves (包含) the mixing (混合) of the LUMO of A-B with the HOMO of the alkene, and at the same time the HOMO of A-B and the LUMO of the alkene:



22. Consider the bond strength between A and B, which of the following statement is CORRECT?

- a. **The interaction I will weaken (弱化) the bond between A and B while the interaction II will strengthen (強化) the bond between A and B.**
- b. Both interaction I and II will weaken the bond between A and B.
- c. Both interaction I and II will strengthen the bond between A and B.
- d. Both interaction I and II will have no effect (無影響) on the bond strength between A and B.

23. Consider the bond strength between B and the two carbons, which of the following statement is CORRECT?

- a. The interaction I will weaken the bond between B and the carbons while the interaction II will strengthen the bond between B and the carbons.
- b. Both interaction I and II will weaken the bond between B and the carbons.
- c. **Both interaction I and II will strengthen the bond between B and the carbons.**
- d. Both interaction I and II will have no effect on the bond strength between B and the carbons.

24. Consider the bond strength between the two carbons, which of the following statement is CORRECT?

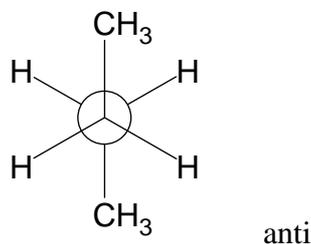
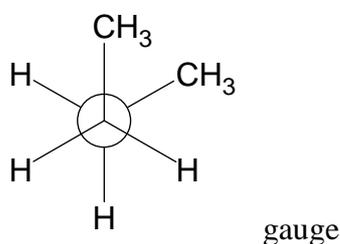
a. The interaction I will weaken the bond between the carbons while the interaction II will strengthen the bond between the two carbons.

b. Both interaction I and II will weaken the bond between the two carbons.

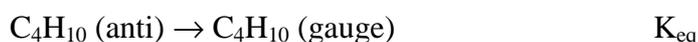
c. Both interaction I and II will strengthen the bond between the two carbons.

d. Both interaction I and II will have no effect on the bond strength between the two carbons.

25. The following two different configurations of a butane molecule are known as gauge and anti forms.



Experimentally the anti form is 7.53 kJ/mol lower in energy. What is the equilibrium constant for their conversion (轉化) at room temperature?



[Hints: the entropy change of this transformation is NOT equal to zero. Instead of determining ΔS directly, you should try to think about the meaning of equilibrium constant. Don't spend too much time – it worths two marks only] **First you can assume entropy change is zero and then based on the enthalpy term you can obtain the value 0.048. Next, the entropy change is due to the fact that there are actually two possible gauge forms. Therefore, you have to multiply 0.048 by 2 in order to get the correct answer. In fact, the entropy change is equal to $R \times \ln(2)$!**

a. 0.096 b. 0.048 c. 0.024 d. 0.19

Those who answer this question correctly should feel happy because only eight of you guys make it.

Good Luck! ☺