

國立中山大學 104 學年度碩士暨碩士專班招生考試試題

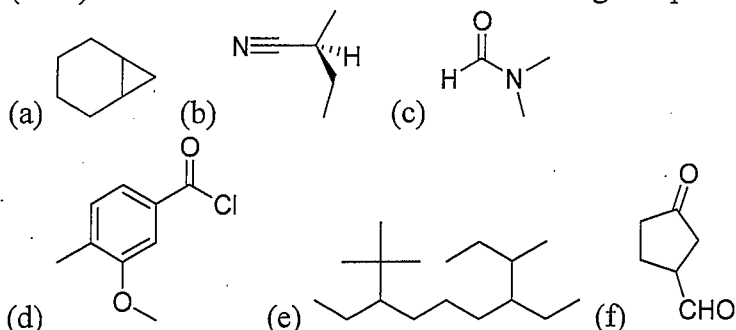
科目名稱：有機化學及無機化學【化學系碩士班】

題號：422001

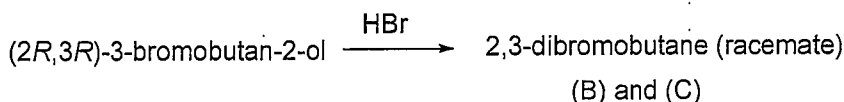
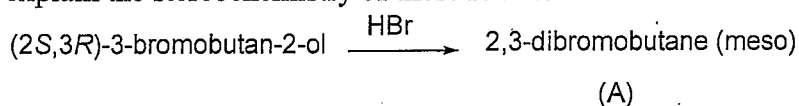
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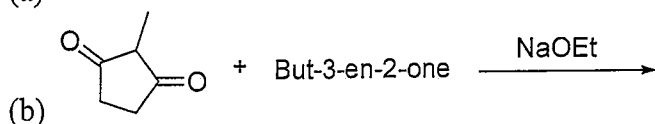
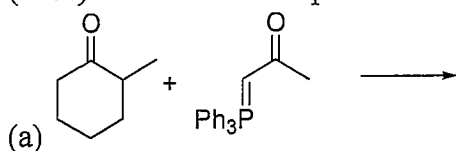
1. (10%) Chlorine trifluoride could be produced from fluorination of chlorine. (1) Give a balanced chemical equation for this reaction. (2) What is the molecular geometry of chlorine trifluoride? (3) Is this molecule polar or non-polar? (4) Are the bond distances between chlorine and fluorine atoms all identical, and why or why not? (5) Are the bond angles of chlorine trifluoride larger or smaller than or equal to those of iodine trifluoride, and why?
2. (14%) (1) Give the Lewis structure of CO. (2) In $\text{Cr}(\text{CO})_6$, explain why CO binds to Cr at C instead of O. (3) How many CO stretching bands can be observed in the IR spectrum of $\text{Cr}(\text{CO})_6$? (4) Assign Mulliken symbol(s) to the IR band(s). (5) Compounds $[\text{X}(\text{CO})_6]^{2-}$ and $[\text{Z}(\text{CO})_6]^+$ are isoelectronic to $\text{Cr}(\text{CO})_6$; what are X and Z? (6) Arrange the increasing order of C-O bond distances in $\text{Cr}(\text{CO})_6$, $[\text{X}(\text{CO})_6]^{2-}$ and $[\text{Z}(\text{CO})_6]^+$.
3. (16%) Water coordinates to transition metals to give aqua complexes. (1) Give the Lewis structure of water. (2) Is water a pure sigma-donor, pi-base or pi-acid ligand? (3) The crystal field stabilization energy of $[\text{Co}(\text{H}_2\text{O})_6]^{2+} = xDq$, $x = ?$ (4) Give the d -orbital diagram of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ with complete electron filling and orbital labeling. (5) Estimate the spin-only magnetic moment of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ in Bohr Magneton. (6) What is the point group in determining the electronic structure of $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$. (7) How many $d-d$ transitions can be found for $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$?
4. (10%) Complex $\text{Ta}(\text{CH}_2\text{Ph})_5$ is a stable, deep red crystalline solid while $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ is a short-lived species that decomposes to give an orange, sublimable, crystalline product. (1) Explain why the stability difference in these complexes occurs. (2) Interpret how $\text{Ta}(\text{CH}_2\text{CMe}_3)_5$ decomposes. (3) Give the structure of the orange crystalline complex. (4) Calculate the electron count of this orange complex. (5) What is (are) the significant feature(s) of this orange complex?
5. (12%) Give the IUPAC names of the following compounds.



6. (12%) Please write the structures of products (A), (B) and (C) with specific stereochemistry and explain the stereochemistry of these reactions with reasonable mechanisms.



7. (15%) Predict the main products of the following reactions.



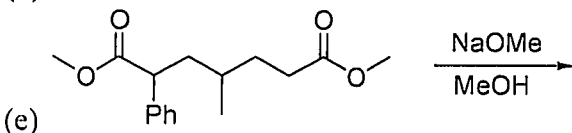
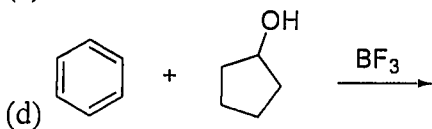
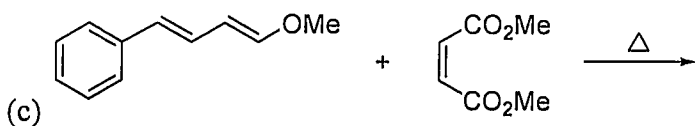
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8. (11%) In an addition reaction, HBr adds to 1,3-butadiene to form a mixture of 3-bromobut-1-ene (1,2-addition) and 1-bromobut-2-ene (1,4-addition). At -80°C , 3-bromobut-1-ene is the major product, and at 40°C 1-bromobut-2-ene is the major product. Please answer the following questions according to the above description.

- Please indicate which the thermodynamic product is and which the kinetic product is. And explain why.
- According to the allyl cation intermediate, please explain the thermodynamic and kinetic control of the reaction.
- The reaction is known as an exothermic reaction. Please draw a energy-coordinate diagram to represent this reaction.

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Part I. Physical Chemistry (50%)

There is one answer to every problem. Each is worth 2%.

1. Which statement is incorrect?

(a) $\frac{\partial^2 \Psi}{\partial t^2} = \frac{1}{v^2} \frac{\partial^2 \Psi}{\partial x^2}$ ($v = \lambda v$) is the classical wave equation.

(b) $\frac{\partial^2 \psi}{\partial x^2} + \frac{4\pi^2}{\lambda^2} \psi = 0$ is the classical wave equation for the standing waves.

(c) $\left[-\frac{\hbar^2}{2m} \nabla^2 + V \right] \Psi = i\hbar \frac{\partial \Psi}{\partial t}$ is the time-dependent Schrödinger equation.

(d) the function of $e^{i(kx - \omega t)}$, where $k = \frac{2\pi}{\lambda}$ and $\omega = 2\pi v$, satisfies the classical wave equation.

2. Given a free particle in a box, which of the following conditions is incorrect?

(a) Shifting the box in space will change the wavefunction.

(b) The precise position of the particle is unpredictable.

(c) If the size of the box is infinite, the energy of the particle is not quantized.

(d) Shifting the box in space will change the energy of the particle.

(e) The energy of the particle depends on the shape of the box.

3. Which of the following functions is acceptable (well-behaved) as quantum mechanical wavefunction over the indicated intervals.

(a) $\frac{1}{x}, (0, \infty)$ (b) $\sin|x|, (-\infty, \infty)$ (c) $e^{-x}, (-\infty, \infty)$ (d) $e^{-x^2}, (-\infty, \infty)$

4. Which statement about the integral $\int_{\text{all}} g^* \hat{A} g dx$ is true, where \hat{A} is a Hermitian operator and g is its eigenfunction.

(a) It must be zero (b) It must be a real number (c) It is equal to $\int_{\text{all}} g \hat{A}^* g dx$. (d) It is equal to

$\hat{A} \int_{\text{all}} g^* g dx$.

5. A wavefunction $\psi(x) = \sin kx$ is defined in the region $-\frac{\pi}{k} \leq x \leq \frac{\pi}{k}$.

Which of the following wavefunctions is not orthogonal to $\psi(x)$?

(a) 1 (b) $\sin kx$ (c) $\cos kx$ (d) $\cos 2kx$ (e) $\sin 2kx$

6. Which of the following statements is true for a given set of harmonic oscillator wavefunctions corresponding to the same potential V ?

(a) The ground-state energy is called zero-point energy and its value is zero. (b) The number of

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nodes at each energy level is equal to $\nu-1$, where ν is the vibration quantum number. (c) The wavefunctions must have zero amplitude beyond the classical turning points. (d)

$\int_{-\infty}^{\infty} \psi_{\nu}^* \psi_{\nu'} dx = 0, \nu \neq \nu'$ (e) The wavefunctions involve Gaussian-type functions and thus are all even functions.

7. Which one of the following systems has the greatest degeneracy?

- (a) Rigid rotator, $J=3$ (b) Particle in a one-dimensional box, $n=10$ (c) Harmonic oscillator, $\nu=10$
(d) Hydrogen atom, $n=3$ (e) All the above are singly degenerate.

8. Which of the following about the spherical harmonics Y_l^m is incorrect?

- (a) The number of angular nodes in Y_l^m is l . (b) The complex Y_l^m give non-zero eigenvalues of \hat{L}_z
(c) Y_0^0 is a constant everywhere in space (d) Y_l^m serves as eigenfunctions for \hat{L}_x (e)

$Y_1^0 = \left(\frac{3}{4\pi}\right)^{1/2} \cos\theta$ correlates with all p_z orbitals.

9. Which statement about H-atom is incorrect?

- (a) Spherical polar coordinates are the natural choice for H-atom Schrödinger equation because the potential term is spherically symmetric. (b) H-atom Schrödinger equation can be solved by separation of variables where $R(r)$ and $\Theta(\theta)$ are linked through $l(l+1)$ while $\Theta(\theta)$ and $\Phi(\phi)$ are linked through m^2 . (c) The operator for the z -component of angular momentum has the simplest form in spherical polar coordinates as opposed to the x - and y -components. (d) The rules for allowed angular momentum magnitudes and orientations are shared by the rigid rotor and the H-atom. (e) By changing the variable $\sin\theta$ into x , the Θ differential equation can be recognized as being the associated Legendre equation.

10. Which is the correct Hamiltonian for the He atom?

(a) $\frac{\hbar^2}{2m_e} \nabla_1^2 + \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$

(b) $\frac{\hbar^2}{2m_e} \nabla_1^2 + \frac{\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} - \frac{e^2}{4\pi\epsilon_0 r_{12}}$

(c) $\frac{-\hbar^2}{2m_e} \nabla_1^2 + \frac{-\hbar^2}{2m_e} \nabla_2^2 + \frac{2e^2}{4\pi\epsilon_0 r_1} + \frac{2e^2}{4\pi\epsilon_0 r_2} - \frac{e^2}{4\pi\epsilon_0 r_{12}}$

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$$(d) \frac{-\hbar^2}{2m_e} \nabla_1^2 + \frac{-\hbar^2}{2m_e} \nabla_2^2 - \frac{e^2}{4\pi\epsilon_0 r_1} - \frac{e^2}{4\pi\epsilon_0 r_2} + \frac{2e^2}{4\pi\epsilon_0 r_{12}}$$

$$(e) \frac{-\hbar^2}{2m_e} \nabla_1^2 + \frac{-\hbar^2}{2m_e} \nabla_2^2 - \frac{Ze^2}{4\pi\epsilon_0 r_1} - \frac{Ze^2}{4\pi\epsilon_0 r_2} + \frac{(Z-2)e^2}{4\pi\epsilon_0 r_1} + \frac{(Z-2)e^2}{4\pi\epsilon_0 r_2} + \frac{e^2}{4\pi\epsilon_0 r_{12}}$$

11. Which of the following is not a possible value of \bar{S}° for a pure substance?

- (a) $-31.0 \text{ J K}^{-1} \text{ mole}^{-1}$ (b) $85.0 \text{ J K}^{-1} \text{ mole}^{-1}$ (c) $1.856R$ (d) All of these are possible. (e) None of these is possible.

12. For which of the following standard enthalpies of formation is not zero $\Delta\bar{H}_f^\circ(25^\circ\text{C})$?

- (a) $\text{Na}_{(s)}$ (b) $\text{N}_{2(g)}$ (c) $\text{I}_{2(g)}$ (d) $\text{C}_{(s, \text{graphite})}$ (e) none of these

13. In an adiabatic expansion of an ideal gas, which of the following is always true?

- (a) The work done by the gas is equal to the decrease in the internal energy of the gas.
 (b) The work done by the gas is equal to the heat absorbed by the gas.
 (c) The temperature of the gas will rise.
 (d) The temperature of the gas will remain the same.
 (e) No work is done by the gas to the surroundings.

14. For which statement about the Joule-Thomson (J-T) experiment is not true?

- (a) J-T expansion is an isenthalpic process ($\Delta H = 0$).
 (b) $\left(\frac{\partial T}{\partial P}\right)_H$ is called the J-T coefficient μ_{JT} .
 (c) Any gas will be cooled by J-T expansion.
 (d) For ideal gases $\mu_{JT} = 0$

15. Using one of the Maxwell relations and the ideal-gas equation of state, determine $\left(\frac{\partial S}{\partial V}\right)_T = ?$

- (a) $\frac{R}{P}$ (b) nR (c) $\frac{R}{\bar{V}}$ (d) 0 (e) None of these.

16. Which statement about the compressibility factor Z is incorrect?

- (a) $Z = \frac{RT}{P\bar{V}}$ (b) Z is temperature and pressure dependent. (c) Z is equal to one for ideal gases. (d)

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When $Z > 1$, the real gas is more difficult to be compressed than the ideal gas. (e) For real gases, Z can be expressed by using virial expansion.

17. Which of the following is true?

- (a) An increase of pressure always leads to a boiling point elevation for all substances.
- (b) An increase of pressure always leads to a melting point depression for all substances.
- (c) The slope of the solid-liquid coexistence curve in the P-T phase diagram is positive if the solid is less dense than the liquid.
- (d) In the P-V phase diagram, the solid-liquid coexistence region is broader than the gas-liquid coexistence region.

18. Which of the following is not true?

- (a) At phase equilibrium, a substance that occurs in two phases will have the same concentration in both phases.
- (b) For a single component substance at a fixed value of pressure, the change of slopes in the plot of the chemical potential versus temperature across different phases represents the variation of the molar entropies of phases.
- (c) $\Delta_r G$ is the change of Gibbs energy for a reaction and $\Delta_r G = -RT \ln K_p + RT \ln Q$ where Q represents the reaction quotient.
- (d) The mixing of reactants and products results in a minimum in the plot of the Gibbs energy against the extent of reaction. This minimum corresponds to the equilibrium position.

19. The unit of the rate constant must be

- (a) $\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
- (b) $\text{dm}^{-3} \text{mol s}^{-1}$
- (c) s^{-1}
- (d) equivalent to the pre-exponential factor
- (e) a value of no dimension

20. Which of the following kinetic plots is not a straight line theoretically?

- (a) $[A]$ as a function of t for a reaction zero order in A.
- (b) $1/[A]$ as a function of t for a reaction second order in A.
- (c) $\ln[A]$ as a function of t for a reaction first order in A.
- (d) $[A]^{1/2}$ as a function of t for a reaction 1/2 order in A.
- (e) All the above is linear.

21. Which of the following statements is true concerning the Arrhenius relation between the rate constant, k , the activation energy E_a , and the temperature?

- (a) A plot of $\ln k$ vs. T is a straight line with slope E_a/R .
- (b) A plot of $\ln k$ vs. $\ln T$ is a straight line with slope E_a/R .

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- (c) A plot of $\ln k$ vs. $\ln T$ is a straight line with slope $-E_a/R$.
 (d) A plot of $\ln k$ vs. $1/T$ is a straight line with slope $-E_a/R$.
 (e) A plot of $\ln k$ vs. $1/T$ is a straight line with intercept E_a/R .

22. The gaseous isomerization reaction, $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$, displays first-order kinetics, namely rate = $k[\text{CH}_3\text{NC}]$. Measurements at 500K show that the concentration of the reactant has declined to 75% of its initial value after 440 s. How much time will be required for the concentration of CH_3NC to drop to 25% of its initial value?

- (a) 440 s (b) 880 s (c) 1320 s (d) 1680 s (e) 2120 s

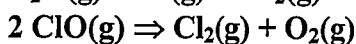
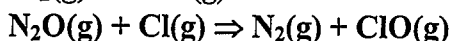
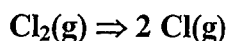
23. Consider a reversible reaction $\text{A} \rightleftharpoons \text{B}$ with a forward rate constant k_f and a backward rate constant k_b . If the initial concentration of A is $[A]_0$ and the initial concentration of B is zero, then the equilibrium concentration of B is

- (a) $\frac{k_b}{k_f}[A]_0$ (b) $\frac{k_f}{k_b}[A]_0$ (c) $\frac{k_b}{k_f + k_b}[A]_0$ (d) $\frac{k_f}{k_f + k_b}[A]_0$ (e) $(k_f - k_b)[A]_0$.

24. For a reversible reaction $\text{A} \rightleftharpoons \text{Y} + \text{Z}$, the rate constants k_1 (forward) and k_{-1} (reverse) can be obtained by the T-jump relaxation method. Suppose x_e is the concentration of Y and Z at equilibrium. The relaxation time $\tau =$

- (a) $\frac{1}{k_1 + k_{-1}}$ (b) $\frac{1}{2k_1x_e + k_{-1}}$ (c) $\frac{1}{2k_{-1}x_e + k_1}$ (d) $\frac{1}{4k_1x_e + k_{-1}}$

25. The decomposition of gaseous N_2O (laughing gas) in the presence of Cl_2 at high temperature is thought to follow the mechanism,



In the net overall reaction, the second step occurs *twice* for each occurrence of the first and third steps.

- (a) The net overall reaction is $\text{N}_2\text{O} + \text{ClO} \rightarrow \text{N}_2 + \text{O}_2 + \text{Cl}$.
 (b) ClO is the only intermediate involved in the mechanism.
 (c) The mechanism is purely imaginary, and cannot be experimentally proved.
 (d) Knowledge of the rate law can imply one and only one mechanism.
 (e) Cl_2 is a catalyst.

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Part II. 分析化學 (50%)

26. Define the following terms

- (a) standard addition calibration method
 - (b) effective bandwidth of a filter
 - (c) Doppler broadening of spectral line profile
 - (d) Stokes shift in Raman Spectroscopy
 - (e) tandem-in-time mass spectrometer
 - (f) isocratic and gradient elution in liquid chromatography
- (5% each, 30% total)

27. Describe the preparation of 100 mL of 1.00 M HCl from a concentrated solution that has a specific gravity of 1.18 and is 37 wt% HCl (36.5 g/mol). (5%)

28. (a) Find the pH of a solution prepared by dissolving 12.43 g of Tris [(HOCH₂)₃CNH₂, 121.135 g/mol] plus 4.67 g of Tris hydrochloride [(HOCH₂)₃CNH₃⁺Cl⁻, 157.596 g/mol] in 1.00 L of water. $pK_{\text{Tris} \cdot \text{HCl}} = 8.072$ (5%)
(b) If we add 12.0 mL of 1.00 M HCl to the solution in (a), what will be the new pH. (4%, 9% total)

29. A solution contains 35.3 μg/mL Cr (51.996 g/mol). The Cr is present only as dichromate (Cr₂O₇²⁻) in 1.0 M H₂SO₄. The transmittance of this solution was 76.2% at 440 nm in a 1-cm pathlength cell. What is the molar absorptivity of dichromate at 440 nm? (6%)