

國立中山大學100學年度碩士班招生考試試題

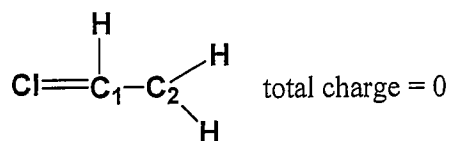
科目：有機化學及無機化學【化學系碩士班】

有機化學 (50 points)

(一) Multiple choice questions, choose only one answer. (3% x 10 = 30%)

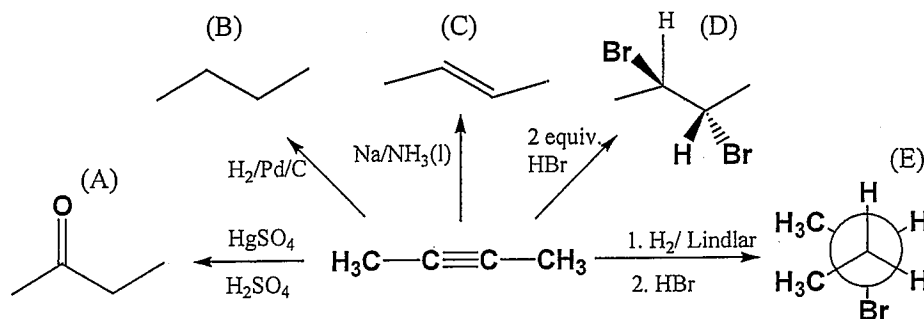
1. Which of the following is NOT a reactions between Lewis acid-base

- (A) $(\text{CH}_3)_3\text{N} + \text{BF}_3 \rightarrow (\text{CH}_3)_3\text{NBF}_3$ (B) $\text{H}_2\text{O} + \text{H}^+ \rightarrow \text{H}_3\text{O}^+$
 (C) $\text{PF}_3 + \text{F}_2 \rightarrow \text{PF}_5$ (D) $\text{SnCl}_2 + \text{Cl}^- \rightarrow \text{SnCl}_3^-$ (E) $\text{Al}(\text{OH})_3 + \text{HO}^- \rightarrow \text{Al}(\text{OH})_4^-$

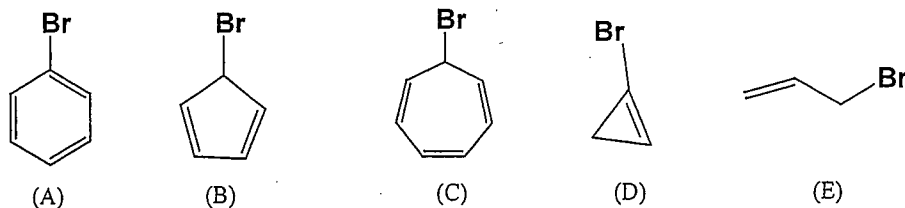
2. The formal charge on C_1 and C_2 for the molecule below are:

- (A) $\text{C}_1 = \text{C}_2 = 0$ (B) $\text{C}_1 = -1, \text{C}_2 = +1$ (C) $\text{C}_1 = 0, \text{C}_2 = +1$
 (D) $\text{C}_1 = +1, \text{C}_2 = 0$ (E) $\text{C}_1 = 0, \text{C}_2 = -1$

3. Which of these reactions below will not give the product shown.



4. Which of the following bromides would ionize most rapidly to form a carbocation?



5. Which of the following compound(s) below can be oxidized by PCC (pyridinium chlorochromate) in dry dichloromethane as solvent to give carbonyl product.

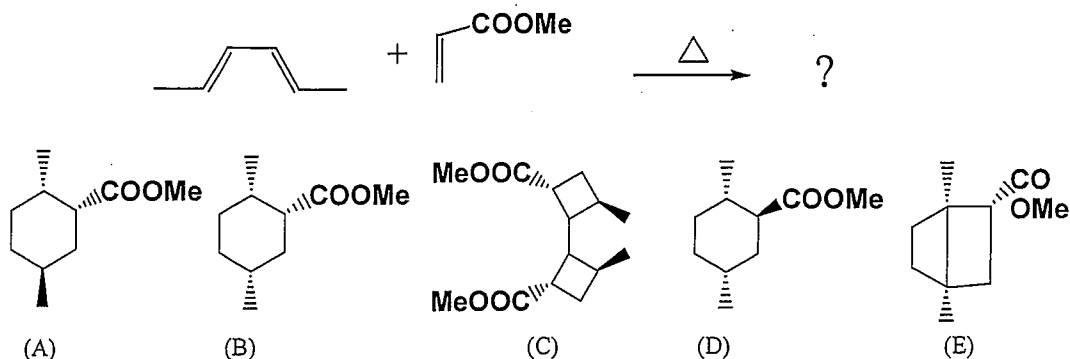
- (I) 1-methylcyclopentanol (II) 4-hydroxy-4-methyl-2-pentanone
 (III) cyclohexanecarbaldehyde (IV) cyclohexyl ethyl ether

- (A) (I) (B) (I) and (II) (C) (I), (II) and (III) (D) (II) (E) (IV)

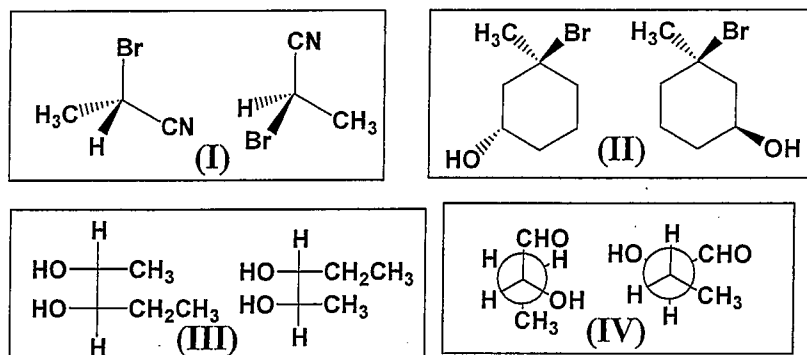
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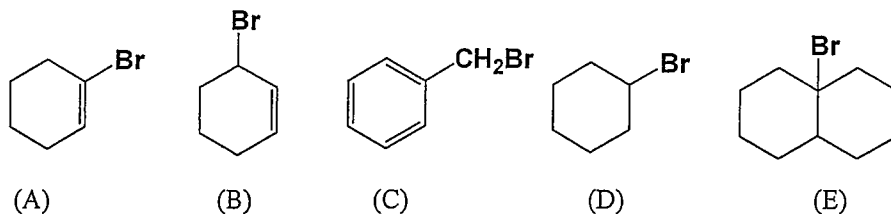
6. Choose the correct product for the Diels-Alder reaction below:



7. Which set of compounds below is enantiomeric?



(A) (I) (B) (I), (II) (C) (I), (III) (D) (I), (IV) (E) (IV)

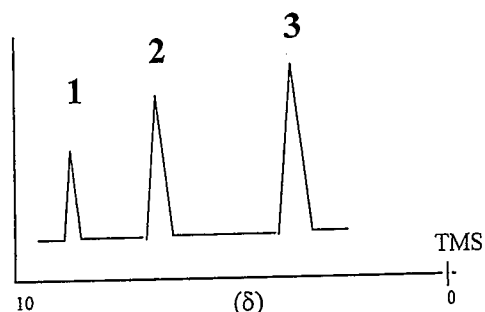
8. Which of the following **cannot** undergo nucleophilic substitution9. Which statement is **correct** for S_N1 reaction at the chiral carbon atom?

- (A) The product will be optically active, but with Walden inversion
- (B) A carbanion is formed as an intermediate
- (C) The product will be a racemic mixture
- (D) The rate of reaction is a function of the concentration of the nucleophile
- (E) The attacking group will be a strong electrophile

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10. Base on the low-resolution proton NMR spectrum of a particular compound shown below, which of the following is (are) true?

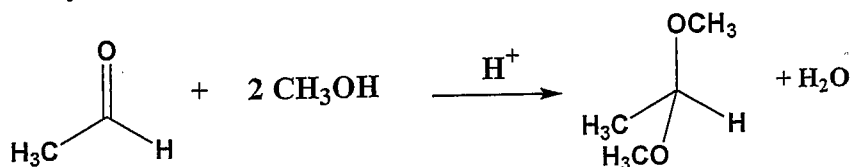


- I. There are at least three different types of protons in this compound
- II. Protons at peak 2 are more shielded than those in peak 1
- III. Proton in peak 3 is most deshielded in this compound
- IV. Proton in peak 1 is most shielded in this compound

- (A) I (B) (I) and (II) (C) (I) and (III) (D) (I) and (IV) (E) (III)

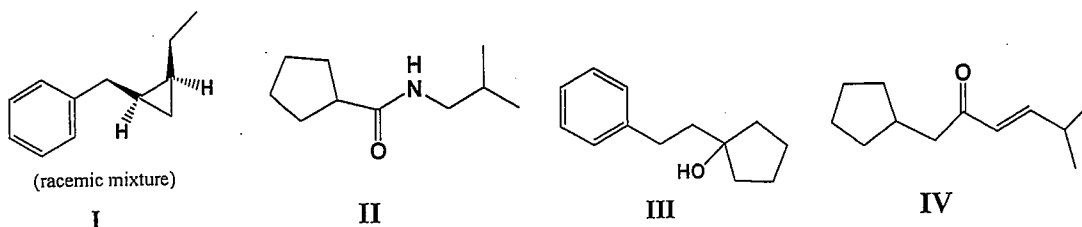
(二). Mechanism question (5% x 1 = 5%)

Propose mechanisms for the following reaction. Be sure that your diagrams clearly show what you want your answer to mean.

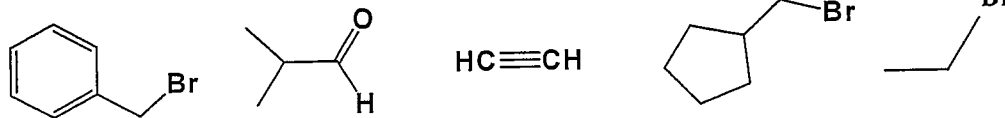


(三). Synthetic question (5% x 3 = 15%)

Choose **THREE** compounds below, **I**, **II**, **III** and **IV**; and design the synthesis of each of the compound from the given starting materials (carbon containing). Give a detail step by step synthesis, showing all the product form in each step. Also, indicate clearly all the other common reagents needed for the transformation in each step.



Starting Materials You may choose from to synthesis I, II, III, IV



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無機化學 (50 points)

(四) Answer the following questions: (30 points; 3 points for each question)

1. Give the IUPAC name of $K_3[Fe(CN)_6]$.
2. Determine the metal-metal bond order consistent with the 18-electron rule for the compound of $[(\eta^5-C_5H_5)Mo(CO)_2]_2^{2-}$.
3. Determine the point group for stagger ferrocene $((\eta^5-C_5H_5)_2Fe)$.
4. **Explain briefly** the trend of π bonding characteristics (B-X bond distances in BF_3 (131 pm), BCl_3 (174 pm), BBr_3 (189 pm), and BI_3 (210 pm)).
5. Consider the molecule $CH_3C \equiv CH$. Apply Bent's rule to predict whether the bond angles, H-C-H, are greater or less than 109.5° . **Please give brief explanation.**
6. Of the compounds $[Cr(CN)_5(NO)]^{4-}$, $[Mn(CN)_5(NO)]^{3-}$, and $[Fe(CN)_5(NO)]^{2-}$, which would you expect to have the highest energy $\nu(NO)$ stretching band in the IR spectrum. **Please give brief explanation.**
7. Determine the metal-metal bond order for $[Re_2Cl_4(PMe_2Ph)_4]^+$.
8. **Briefly explain** the band theory.
9. Which ion, Mg^{2+} or Ba^{2+} , will exhibit the greater polarizing power? **Please give brief explanation.**
10. **Briefly explain** the trans-effect.

(五) Give the most stable molecular structure of $P(CH_3)_2F_3$? What would the variable temperature ^{19}F -NMR spectra of $P(CH_3)_2F_3$ look like under the condition of very slow fluorine exchange. Only consider the spin-spin interactions of F-F and F-P. **Give your explanation.** (10 points)

(六) Answer the following questions for the octahedral high-spin complex of $[FeL_6]^{2+}$ (L = neutral mono-dentate ligand):

1. Determine the ground-state term symbol for the free iron (Fe) ion. **Give your explanation.** (2 points)
2. What is the electronic ground-state irreducible representation for this complex? **Give your explanation.** (4 points)
3. Would you expect the contribution of Jahn-Teller effect for this complex? **Give your explanation.** (4 points)

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Physical Chemistry (50 points)

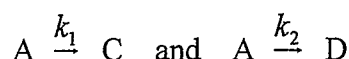
Single choice, 2 points for each question

- For a ground state free particle in one-dimensional box ($0 \leq x \leq a$) the expectation value of the physical quantity p^4 is
 - $8h^4/a^4$
 - $h^4/16a^4$
 - $h^2/2a^4$
 - 0
 - none is correct
- Convert the energy $E = 1.5$ erg into wave number (cm^{-1})
 - 3.88×10^{26}
 - 5.0348×10^{22}
 - 4.32×10^5
 - 7.5522×10^{15}
 - none is correct
- Which of the following statements is correct?
 - The electron spin has no angular momentum
 - One can measure all three components of angular momentum simultaneously.
 - Quantum mechanical expression of angular momentum operator has only angular dependence.
 - Electrons at same atomic orbital have identical angular momentum.
 - All answers are correct.
- The ground state wave function of hydrogen atom is $\psi = \frac{1}{\pi^{1/2}} \left(\frac{1}{a}\right)^{3/2} e^{-r/a}$, where a is Bohr radius. According to this wave function, the average distance of r for hydrogen atom is
 - a
 - $3a/2$
 - $a/2$
 - $2a$
 - none is correct
- Which of the following statements about harmonic oscillator is true?
 - The vibration of a diatomic molecule is exact harmonic oscillation.
 - The average kinetic energy is equal to the average of potential energy.
 - The frequency of harmonic oscillation depends on the equilibrium position.
 - The ground state energy, $E_0 = h\nu/2$, can be measured experimentally.
 - None is correct
- The microwave spectrum of HCl consists of a series of lines with approximately equally spaced. The lines are separated by 6.26×10^{11} Hz. The microwave spectrum of DCl should display lines separated by

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- a. 3.13×10^{11} Hz b. 3.22×10^{11} Hz c. 4.27×10^{11} Hz
d. 4.56×10^{11} Hz e. none is correct
7. Which of the following statement is correct?
- a. Hamiltonian operator commutes with all operators.
b. Quantum mechanical operators are always commute.
c. For two commute operators \hat{A} and \hat{B} , one can always measure their corresponding physical properties simultaneously.
d. $[\hat{A}, \hat{B}\hat{C}] = [\hat{A}, \hat{B}]\hat{C} = \hat{A}[\hat{B}, \hat{C}]$
e. None is correct
8. Evaluate $[\hat{x}, \hat{p}_x^2] =$
- a. $i\hbar$ b. $-i\hbar \frac{\partial^2}{\partial x^2}$ c. 0 d. $2\hbar^2 \frac{\partial}{\partial x}$
e. none is correct
9. The fundamental of HBr is around 2640 cm^{-1} , then the fundamental of DBr should be around
- a. 1892 cm^{-1} b. 1320 cm^{-1} c. 1867 cm^{-1} d. 3683 cm^{-1}
e. None is correct.
10. In aqueous ionic solution, the rate constant is
- a. has no relation to ionic strength
b. proportional to the square root of ionic strength
c. proportional to the inverse of ionic strength
d. proportional to the square of ionic strength
e. proportional to ionic strength
11. For a system with the two competing elementary reactions



In which E_1 and E_2 are the activation energies correspond to k_1 and k_2 respectively. Then the observed activation energy E_a of the system is

- a. $E_a = \ln(k_1 e^{-E_1/RT} + k_2 e^{-E_2/RT})$ b. $E_a = E_1 + E_2$
c. $E_a = (k_1 e^{-E_1/RT} + k_2 e^{-E_2/RT}) / (k_1 + k_2)$ d. $E_a = (k_1 E_1 + k_2 E_2) / (k_1 + k_2)$

e. none is correct

12. The reaction between X and Y is second order. If Y is in large excess than X, the following data were obtained:

T(K)	[Y] (mol/dm ³)	rate constant (s ⁻¹)
300	2.5×10 ⁻⁶	5.0×10 ⁻⁴
500	1.0×10 ⁻⁶	7.5×10 ⁻³

According to Arrhenius law, the pre-exponential factor for this reaction is

- a. 7.5×10^6 b. 4.42×10^6 c. 3.18×10^6 d. 5.74×10^6
 e. None is correct
13. In usual condition, which is the correct order of molecular energies?
 (E_{elec} : electronic energy, E_{trans} : translational energy, E_{vib} : vibrational energy, E_{rot} : rotational energy)
- a. $E_{elec} > E_{trans} > E_{rot} > E_{vib}$ b. $E_{elec} > E_{vib} > E_{rot} > E_{trans}$
 c. $E_{vib} > E_{elec} > E_{rot} > E_{trans}$ d. $E_{trans} > E_{vib} > E_{rot} > E_{elec}$
 e. none is true

14. The following data relate to an enzyme reaction

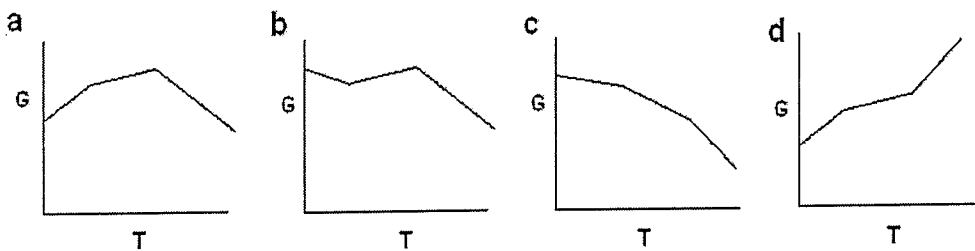
$10^3 [S] / \text{mol dm}^{-3}$	$10^5 V / \text{mol dm}^{-3} \text{ s}^{-1}$
2.0	13
4.0	20
8.0	29
12.0	33
16.0	36
20.0	38

Base on the data, the Michaelis constant is approximately

- a. $8.0 \times 10^{-3} \text{ mod dm}^{-3}$ b. $4.0 \times 10^{-3} \text{ mod dm}^{-3}$ c. $9.5 \times 10^{-3} \text{ mod dm}^{-3}$
 d. $10.0 \times 10^{-3} \text{ mod dm}^{-3}$ e. None is true
15. Which of the following relation is correct?

- a. $\left[\frac{\partial}{\partial T} \left(\frac{\Delta G^0}{T} \right) \right]_P = -\frac{\Delta H^0}{T^2}$ b. $\left[\frac{\partial}{\partial T} \left(\frac{\Delta H^0}{T} \right) \right]_P = -\frac{\Delta G^0}{T^2}$
 c. $\left[\frac{\partial}{\partial T} \left(\frac{\Delta G^0}{T} \right) \right]_P = -\frac{\Delta H^0}{T}$ d. $\left[\frac{\partial}{\partial T} \left(\frac{\Delta H^0}{T} \right) \right]_P = \frac{\Delta S^0}{T^2}$
 e. all answers are wrong

16. Which of the following diagram gives correct behavior of G vs. T for a single component system?

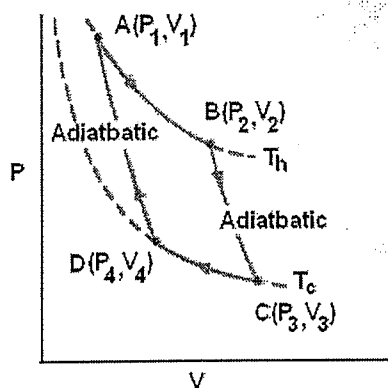


e. none is correct

17. If 3.0 mole of argon is expanded reversibly and isothermally from a volume of 500.0 dm³ to a volume of 2500.0 dm³ at 298.15 K, what is the entropy change of the system?

- a. 13.38 J K⁻¹ b. 40.14 J K⁻¹ c. 31.32 J K⁻¹ d. Zero
e. All answers are wrong

18. For an ideal gas, a typical Carnot cycle undergoes four reversible steps: I. isothermal expansion at T_h from V₁ to V₂, II. adiabatic expansion from T_h to T_c and volume from V₂ to V₃, III. Isothermal compression from V₃ to V₄, IV. adiabatic compression from V₄ to V₁.



The enthalpy change of step II is

- a. Zero b. C_p(T_c - T_h) c. C_v(T_c - T_h) d. C_pln(V₃/V₂)
e. All answers are wrong

19. Which of the following is the correct expression of thermodynamic equation of state?

- a. $\left(\frac{\partial U}{\partial P}\right)_V = -P + T\left(\frac{\partial T}{\partial P}\right)_P$ b. $\left(\frac{\partial U}{\partial P}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_P$

- c. $\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$ d. $\left(\frac{\partial U}{\partial V}\right)_T = -P + T\left(\frac{\partial P}{\partial T}\right)_V$
- e. All answers are wrong

20. The heat of fusion of water is 333 J/g. The entropy change for melting of 10 g of ice is

- a. 12.2 J K⁻¹ b. 23.6 J K⁻¹ c. 8.7 J K⁻¹ d. 10.4 J K⁻¹
- e. none is correct

21. Which is the correct conclusion of Joule-Thompson experiment?

- a. Internal energy of ideal gas is zero.
- b. The Joule-Thompson coefficient is always greater than zero.
- c. The adiabatic expansion has no enthalpy change.
- d. A gas has positive Joule-Thompson coefficient will heat during a Joule-Thompson expansion.
- e. None is correct.

22. The molar heat capacity (JK⁻¹mol⁻¹) at constant pressure of Al₂O₃ is

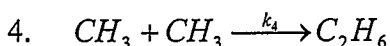
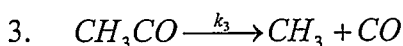
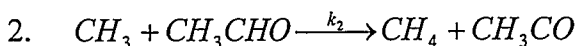
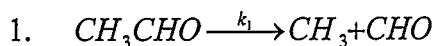
$$C_p = a + bT + (c/T^2)$$

$$\text{Where } a = 114.8, b = 12.8 \times 10^{-3} \text{ and } c = -35.4 \times 10^5$$

The enthalpy change for heating one mole Al₂O₃ from 300 K to 500 K is

- a. 19.56 kJ b. 19.26 kJ c. 11.28 kJ d. 35.6 kJ
- e. none is correct

23. When acetaldehyde decomposed thermally the main products are methane and carbon monoxide. The experimental evidence has shown that the reaction occurs by the mechanism



Using steady state approximation, the rate of change of the concentration of acetaldehyde is

- a. $v = k_2 \left(\frac{k_1}{k_4} \right) [CH_3CHO]^{1/2}$ b. $v = k_1 \left(\frac{k_2}{k_4} \right) [CH_3CHO]^{1/2}$
- c. $v = k_2 \left(\frac{k_1}{k_4} \right)^{1/2} [CH_3CHO]^{3/2}$ d. $v = k_4 \left(\frac{k_2}{k_4} \right) [CH_3CHO]^{1/2}$
- e. none is correct

24. A mole of gas at P_1, V_1, T_1 is expanded isothermally to the condition $P_1/2, 2V_1, T_1$. The collision number after expansion is

- a. 1/2 as large as before expansion b. $\sqrt{2}$ as large as before expansion
- c. 1/4 as large as before expansion d. $1/\sqrt{2}$ as large as before expansion
- e. none is correct

25. The Maxwell distribution function of gaseous molecule is

$$F(v) = \left(\frac{m}{2\pi kT} \right)^{3/2} \exp\left(-\frac{mv^2}{2kT} \right) \cdot 4\pi v^2$$

The average velocity is

- a. $\sqrt{\frac{2kT}{\pi m}}$ b. $\sqrt{\frac{3kT}{\pi m}}$ c. $\sqrt{\frac{8kT}{\pi m}}$ d. $\sqrt{\frac{kT}{\pi m}}$
- e. none is correct

Gas constant: $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 82.057 \text{ cm}^3 \text{ atm mol}^{-1} = 1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$

1 cal = 4.184 Joule = 41.29 cm³ atm

	Nm ⁻²	atm	torr	bar
1 pa =	1	9.869×10^{-6}	7.501×10^{-3}	10^{-5}
1 atm =	101325	1	760	1.01325
1 torr =	133.32	1.316×10^{-3}	1	1.3332×10^{-3}
1 bar =	10^5	0.9869	750.1	1

1 bar = 10^5 pa

Planck constant $h = 6.626 \times 10^{-34} \text{ J s}$

$$\int_0^{\infty} x^n e^{-qx} dx = \frac{n!}{q^{n+1}} \quad n > -1, \quad q > 0$$

Analytical Chemistry (50 points)

Note: Always use the correct significant figures in your calculation.

26. Define and distinguish between the following;

- (a) t-test and F-test
- (b) standard addition method and internal standard method
- (c) fluorescence and phosphorescence
- (d) Quadrupole ion-trap mass spectrometer and Fourier transform ion cyclotron resonance mass spectrometer (4% each, 16% total)

27. Use van Deemter equation to describe peak broadening in capillary electrophoresis, high-performance liquid chromatography, and gas chromatography. (8%)

28. A typical ICP-MS system has a mass range of 250 amu, whereas a typical GC-MS system has a mass range of 1000 amu. Explain this difference. (4%)

29. Consider the diprotic acid H_2A with $pK_1 = 5.00$ and $pK_2 = 9.00$. Find the pH and concentrations of H_2A , HA^- , and A^{2-} in the 0.100 M NaHA. (4%)

30. Use activities to calculate the solubility of $Ba(IO_3)_2$ in a 0.1 M solution of NaCl. The thermodynamic solubility product for $Ba(IO_3)_2$ is 1.57×10^{-9} . (4%)

Ionic strength (M)	Activity coefficient of Ba^{2+}	Activity coefficient of IO_3^-
0.001	0.869	0.965
0.005	0.743	0.926
0.01	0.668	0.900
0.05	0.46	0.81
0.1	0.38	0.76

31. Describe the operating principle of a pH glass-electrode. (4%)

32. What information can be obtained from the following analytical methods?

- (a) XPS, (b) FTIR, (c) NMR, (d) MALDI-TOF-MS, (e) cyclic voltammetry. (10%)