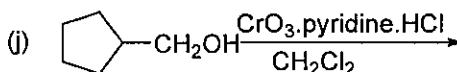
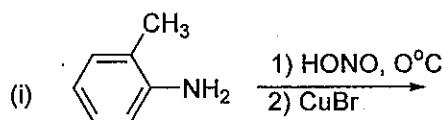
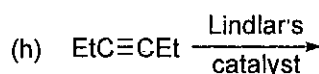
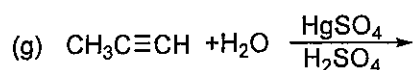
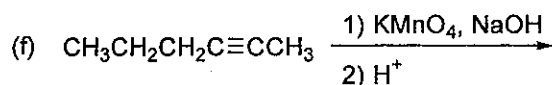
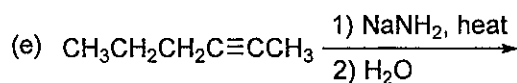
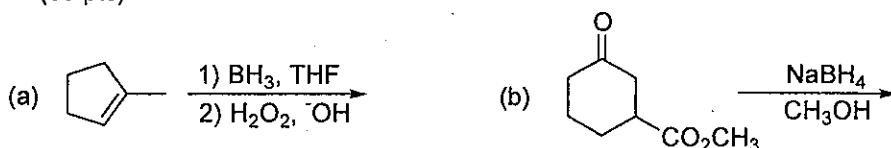


1. Define and give an example for each of the following terms. (20 pts.)

- (a) Hydride reagent (b) Diastereomers (c) Huckel's rule on aromaticity
 (d) Extended Markovnikov's rule (e) Concerted reaction

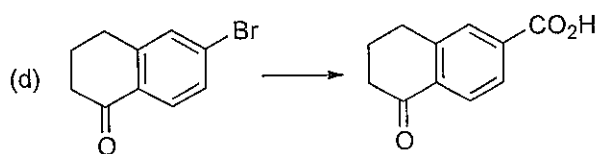
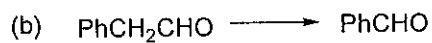
2. Predict the major products (including stereochemistry) of the following reactions. (30 pts)



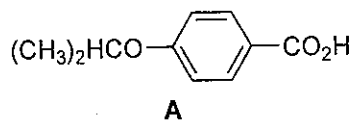
3. Give the structures of the following compounds. (15 pts.)

- (a) *cis*-4-Methyl-1,2-epoxycyclohexane (b) (*R*)-3-Methyl-1-penten-4-yne
 (c) 2,4-,*N,N*-Tetramethyl-3-hexanamine (d) 2-Bromo-3-methoxyfuran
 (e) 3-Methylene-5-chlorocyclohexene

4. Accomplish the following syntheses. (you may use any necessary reagents) (20 pts.)

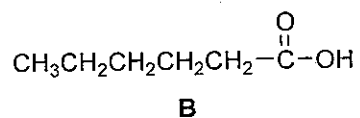


5. (a) Sketch your prediction of the ^1H NMR spectrum of A. (5 pts.)



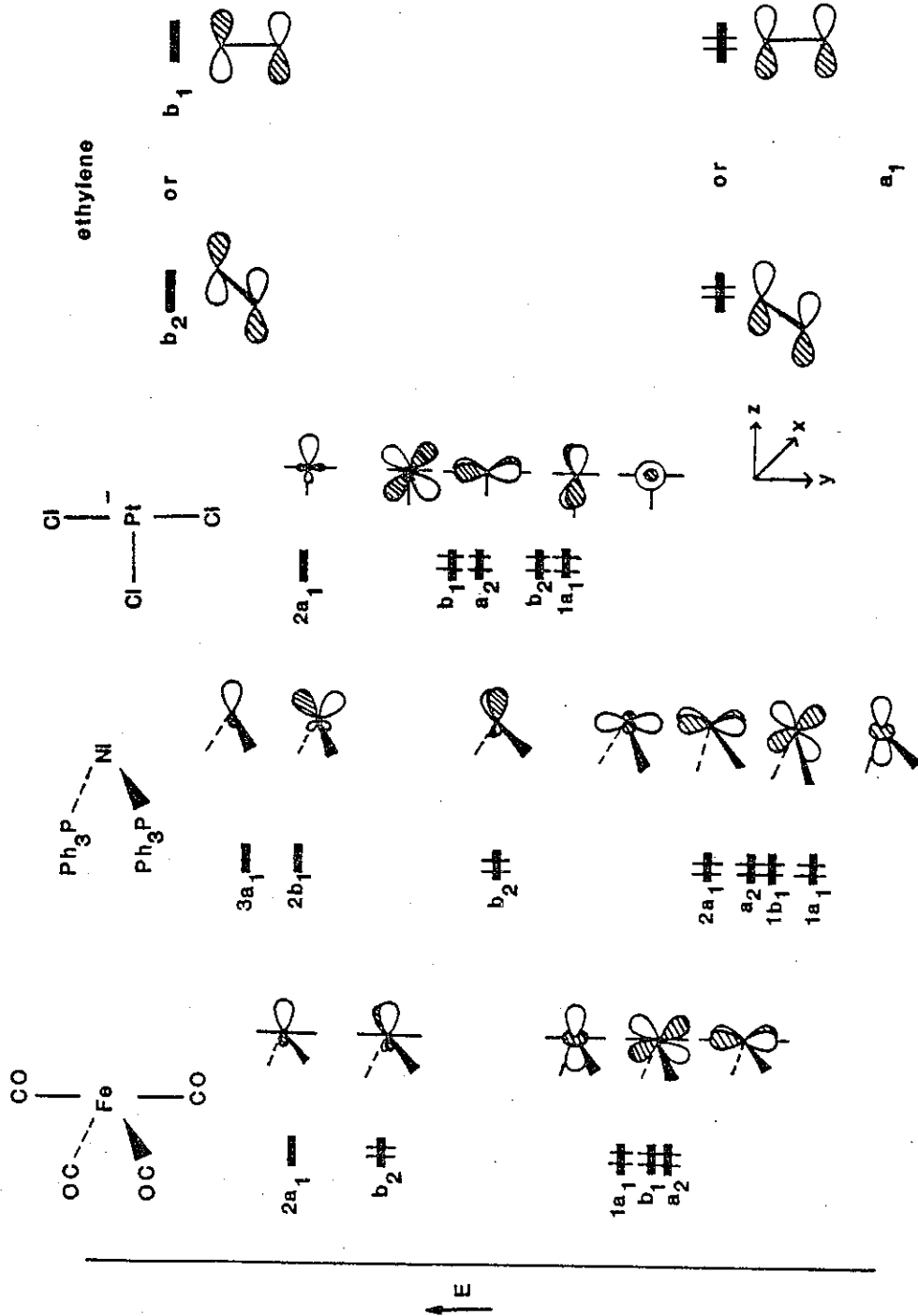
(b) How many ^{13}C NMR peaks will you expect for compound A? (5 pts.)

6. Predict the mass and the structure of the most abundant fragment observed in the mass spectrum of compound B. (5 pts)



Inorganic Chemistry

- (1) (15%) What is the physical meaning of spin-orbital coupling? In the octahedral complexes of $[\text{FeL}_6]^{3+}$ (Fe(III), high spin) and $[\text{FeL}_6]^{3+}$ (Fe(III), low spin), would you expect contributions from spin-orbital coupling? (Explain briefly)
- (2) (15%) Give the molecular structure of $\text{P}(\text{CH}_3)_2\text{F}_3$? What would the variable temperature ^{19}F -NMR spectra of $\text{P}(\text{CH}_3)_2\text{F}_3$ look like under the following conditions? (i) Very slow fluorine exchange (ii) Faster fluorine exchange
- (3) (15%) Show the molecular structures of the following compounds. Furthermore, describe the bonding in the molecules. (i) $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2]_2$ (contains two terminal CO) (ii) $\text{Cr}(\text{CO})_5[\text{C}(\text{OCH}_3)(\text{CH}_3)]$ (iii) $\text{Ni}(\text{CO})_4$
- (4) (15%) Draw the MO diagram of CO. On the basis of this diagram, explain the metal-to-CO back bonding in $\text{Fe}(\text{CO})_5$ complex.
- (5) (20 %) Consider the molecule $\text{CH}_3\text{C}\equiv\text{CH}$. Applying Bent's rule in its classical form, predict whether the bond angles, H-C-H, are greater or less than 109.5° .
- (6) (20 %) Using the Dewar-Chatt-Duncanson model of bonding, predict the orientation of the ethylene in each of the following complexes. The metal fragment orbitals and the π orbitals of ethylene are shown on the following page. Explain reason.
 - (a) $(\text{ethylene})\text{Ni}(\text{PPh}_3)_2$
 - (b) $(\text{ethylene})\text{Fe}(\text{CO})_4$
 - (c) $[(\text{ethylene})\text{PtCl}_3]^-$



Symbols and constants:

P: pressure, V: volume, T absolute temperature, C_v : heat capacity at constant volume,
q: heat, G: Gibbs free energy

ϵ_0 : permittivity in free space: $8.85419 \times 10^{-12} C^2 N^{-1} m^{-2}$

h : Planck constant $6.626 \times 10^{-27} \text{ erg} \cdot \text{sec}$

R : ideal gas constant $1.987 \text{ cal/mol-deg K}$

k_B : Boltzmann constant $1.3806 \times 10^{-16} \text{ erg/molecule-deg K}$

Find the right answer for the following questions (2.5 points for each)

- The magnitude of interaction potential for a proton and an electron separated by 1 \AA is?
 - 13.6 eV
 - $1.16 \times 10^5 \text{ cm}^{-1}$
 - $5.802 \times 10^4 \text{ cm}^{-1}$
 - 7.194 eV
 - none is correct
- Which of the following is true to expand ideal gas adiabatically from state 1 to state 2?
 - $5 \ln(P_2/P_1) = 2 \ln(T_2/T_1)$
 - $2 \ln(P_1/P_2) = 5 \ln(V_2/V_1)$
 - $3 \ln(T_1/T_2) = 2 \ln(V_2/V_1)$
 - $3 \ln(P_2/P_1) = 2 \ln(V_1/V_2)$
 - None is correct
- Which of the following statement about a free particle in an one-dimensional box is correct?
 - The maximum momentum can be observed at the center of the box.
 - The particle has equal probability appeared in the box.
 - The quantum number is ranged from $n = 0$ to infinity.
 - The wavelength of the particle is larger at high quantum number.
 - None is correct.
- Which of the following statement is correct?
 - Spectroscopic method is useful to measure the ground state energy of a molecule.
 - No instrument can simultaneously measure the momentum and position precisely of a moving particle.
 - Measuring the momentum of a particle always get discrete values.
 - One can measure any type of angular momentum and all the components simultaneously.
 - All answers are correct.

5. Which of the following statement about two quantum mechanical operators \hat{A} and \hat{B} is correct?
- If $[\hat{A}, \hat{B}] \neq [\hat{B}, \hat{A}]$, eigenvalues associated to the two operators will be different.
 - If $[\hat{A}, \hat{B}] = [\hat{B}, \hat{A}]$, the two operators have common eigenvalues.
 - If $[\hat{A}, \hat{B}] = [\hat{B}, \hat{A}]$, eigenfunctions associated to the two operators are the same.
 - If $[\hat{A}, \hat{B}] = [\hat{B}, \hat{A}]$, eigenvalues associated to the two operators can be measured simultaneously.
 - None is correct.
6. X_2 and Y_2 are two diatomic molecules. The bond length of X_2 is 1.5 times than bond length of Y_2 , and the mass of X_2 is 0.8 of Y_2 . The rotation constants of two molecules are B_{X_2} and B_{Y_2} , then
- $B_{X_2} = 1.5 B_{Y_2}$
 - $B_{X_2} \sim 0.55 B_{Y_2}$
 - $B_{X_2} \sim 0.67 B_{Y_2}$
 - $B_{X_2} \sim 2.25 B_{Y_2}$
 - none is correct
7. In the temperature range from 300 to 500 K, the standard equilibrium constant, K_p^0 , for the equation $A + B = C$ can be expressed as $\ln K_p^0 = a/T - b$ where a and b are constants. What is the ΔS^0 at 400 K?
- $\Delta H^0 = aR$
 - $\Delta H^0 = aR/1600$
 - $\Delta G^0 = aR/T^2 - b/T$
 - $\Delta S^0 = -bR$
 - None is correct
8. Assuming that harmonic oscillator model is valid for molecular vibration. Let ν denotes vibration frequency and n denotes vibration quantum number, which of the following statement is correct?
- The dissociation energy is $(n+1/2)h\nu$.
 - Isotopic diatomic molecules have identical vibration energy levels.
 - At zero temperature the kinetic energy of the oscillator is vanished, only potential energy has nonzero value.
 - The total energy is always larger or equal to the potential energy.
 - None is correct.

13. The following are measured Joule-Thompson coefficients of four substances within temperature range from T_1 to T_2 ($T_2 > T_1$).

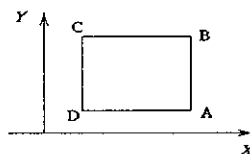
A: -0.06 B: 0.15 C: 4.3 D: 0.20

Which of the following statement in this given temperature range is correct?

- C is more close to ideal gas
- Temperature increases as volume of B decreases
- Volume of A decreases as pressure increases
- Temperature decreases as volume of A increases
- None is correct

14. A usual Carnot cycle is composed of 4 processes: isothermal expansion from A to B, adiabatic expansion from B to C, isothermal compression from C to D and adiabatic compression from D to A. For an ideal gas, the following diagram represents the change of which of two coordinates X and Y ?

- temperature vs. pressure
- pressure vs. temperature
- temperature vs. Internal energy
- internal energy vs. entropy
- none is correct



15. A one-phase two-component system contains A and B substances. If one adds n moles of A into the system the Gibbs energy changes from G_1 to G_2 . If one removes n moles of B, the Gibbs energy also changes from G_1 to G_2 . Assume all other conditions, such as temperature, pressure, are fixed, which of the following statement is correct?

- The chemical potential of A is equal to the chemical potential of B.
- The chemical potential of A is twice as the chemical potential of B.
- If one adds n moles of A and removes n moles of B simultaneously from the system, the Gibbs energy of the system is unchanged.
- The chemical potential of A is positive and of B is negative.
- None is correct.

16. One may use temperature, C_v , and pressure data to estimate which of the following quantity?

- variation of entropy
- variation of enthalpy
- variation of internal energy
- variation of Gibbs energy
- none of above

17. Solution 1 contains 2 moles A and 1 moles of B. Solution 2 contains 1.5 moles of B and 1.5 moles of A. If one finds that $P_A = 2/3 P_A^0$ for solution 1, and $P_B = 0.5 P_B^0$ for solution 2, where P_A and P_B are partial pressures and P_A^0 and P_B^0 are pressures for the pure component. Which of the following about the entropy of mixing for solutions 1 and 2 is correct?

- $\Delta S_1 = \Delta S_2$
- $\Delta S_1 = 2\Delta S_2$
- $\Delta S_1 > \Delta S_2$
- $\Delta S_1 < \Delta S_2$
- can not compare

18. The heat capacity of a gas can be estimated from the degree of freedom of molecules. At normal temperature, which type of the molecular motion has the largest deviation from this rule?
- translation
 - vibration
 - rotation
 - translation and rotation
 - vibration and rotation
19. Given the following three energy states, $E_1 = 0$, $E_2 = C$, $E_3 = 2C$, where $C = k_B T$. Let n_1 , n_2 and n_3 denote the numbers of molecules populated in these states, which of the following is correct?
- $n_2^2 = n_1 \cdot n_3$
 - $2n_1 = n_2 + n_3$
 - $n_1 = 2n_3$
 - $n_3 = n_1 - n_2$
 - none is correct
20. A diatomic molecular ion with a ground state electron configuration, $(1\sigma_g)^2(1\sigma_u)^2(2\sigma_g)^1$, which of the following is correct?
- The molecular ion has double bond.
 - The configuration corresponds to Σ term.
 - The wave function of this molecular ion must be symmetric.
 - There is no effect when the ion was placed in a magnetic field.
 - None is correct.
21. For a real gas $P(v-b) = RT$, $C_p - C_v =$
- bR
 - R
 - R/b^2
 - R/b
 - none is correct
22. The measured activity coefficients of a two-component solution are $\gamma_1 = 0.3$ and $\gamma_2 = 0.5$. Which of the following is correct?
- The mole fractions of the components are $3/8$ and $5/8$.
 - There is no interaction between component 1 and 2.
 - The activity of component 1 is less than component 2.
 - Component 1 is less ideal than component 2.
 - None is correct
23. Which of the following is correct?
- The magnitude of the orbital magnetic moment of an electron is proportional to the magnitude of orbital angular momentum.
 - Increases the strength of external magnetic field will increase the splitting of proton signals in NMR spectrum.
 - Total angular momentum of an electron is the sum of the orbital angular momentum and spin angular momentum.
 - The Bohr magneton is inversely proportional to the electron mass
 - All answers are correct

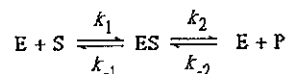
24. According to the second law of thermodynamics, which of the following statement is correct?
- The entropy of an isolated system increases for any spontaneous process.
 - The change of Gibbs energy is always negative for any process.
 - The change of energy alone is sufficient to determine the direction of a spontaneous process.
 - At equilibrium the quantity (dq/T) is always larger than zero.
 - None is correct

25. For CO and N₂ gases at same temperature and volume, which of the following properties of two gases are about the same?
- Van der waals radius
 - root mean square speed
 - collision frequency
 - rotation constant
 - all properties are about the same

26. The speed distribution functions of molecules A and B are $f_A(v_A) = C v_A^2 e^{-b v_A^2}$, $f_B(v) = D v_B^2 e^{-2b v_B^2}$ where C, D and b are constants. Find the ratio of averaged

$$\text{speed } \langle v_A \rangle : \langle v_B \rangle. \left(\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}, \int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4} \left(\frac{\pi}{a^3} \right)^{1/2} \right)$$

- $1/\sqrt{2}$
 - $1/2$
 - 4
 - $\sqrt{2}$
 - none is correct
27. For the simple enzyme catalytic reaction:



Where E is the free enzyme, S is the substrate, ES is the enzyme-substrate complex and P is the product. The reaction rate $r = -d[S]/dt$ can be derived as

$$r_0 = \frac{k_1[E]_0[S]_0}{k_M + [S]_0}, \text{ where the subscript 0 refers to the initial condition and } k_M \text{ is}$$

the so-called Michaelis constant. Which of the following is not correct?

- To reach the derived formula, one must use steady state approximation for ES
- $k_M = (k_{-1} + k_2)/k_1$
- In the limit of high concentration of substrate, the reaction rate becomes maximum that independent of substrate concentration
- K_M can be determined by measuring r_0 as function of $[S]_0$
- All answers are correct

28. For the given gaseous molecules, oxygen, nitrogen, benzene and butane, at same pressure and temperature, which of the following statement is correct?

- butane has the largest collision frequency
- oxygen has the smallest mean free path
- benzene has the largest diffusion coefficient
- nitrogen has the largest intermolecular force
- none is correct

29. In the gaseous mixture, which of the following pair of molecules may have the largest averaged relative velocity?

- N_2 and O_2
- H_2 and D_2
- O_2 and NH_3
- CO and O_2
- all equal to each other

30. Which of the following statement is correct?

- A bullet fired from a gun has wave nature more than a particle.
- Break the symmetry reduces the degeneracy of energy levels.
- One usually observes quantum behavior of molecules at high temperature condition
- Infrared spectroscopy is used to approach the electronic transition of molecules.
- None is correct

31. The matrix elements of an operator \hat{A} are:

$$A_{11} = A_{22} = \dots = A_{mm} = \int \phi_n \hat{A} \phi_n d\tau = a, (n = m)$$

$$A_{nm} = \int \phi_n \hat{A} \phi_m d\tau = b \quad (n = m \pm 1),$$

$$A_{nm} = 0 \quad (n \neq m \text{ and } n \neq m \pm 1)$$

The averaged value of A for a state $\psi = \frac{1}{2}(\phi_1 - \phi_2 - \phi_3 + \phi_4)$ is

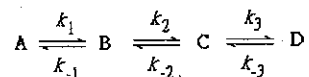
- $(a-b)/2$
- $(a+b)/4$
- $a-b/2$
- $2a-b$
- none is correct

32. The hydrogenlike 2s and 2p wavefunctions have the same energy. In spite of the normalization constant, which of the following statement about He atoms is correct?

- $[1s(1)2s(2)][\alpha(1)\beta(2)-\alpha(2)\beta(1)]$ is the first excited state wavefunction
- $[1s(1)2p_x(2)+1s(2)2p_x(1)][\alpha(1)\beta(2)]$ is the first excited state wavefunction
- $[1s(1)1s(2)][\alpha(1)\beta(2)+\alpha(2)\beta(1)]$ is the ground state wavefunction
- $[1s(1)2s(2)][\alpha(1)\alpha(2)]$ is the first excited state wavefunction
- none is correct

33. The ionic strength of a solution contains 0.1 mol/kg NaCl and 0.05 mol/kg Na_2SO_4 is
- 0.50
 - 0.25
 - 0.125
 - 0.05
 - none is correct
34. Which of the following statement may be true?
- Harmonic oscillator model is useful to estimate the dissociation energy of a diatomic molecule.
 - Within Born-Oppenheimer approximation, isotopic molecules have different electrostatic interaction energies.
 - The quantum mechanical result of harmonic oscillator indicates that the wavefunction may appear in classical forbidden region.
 - The absorption frequencies of overtones in the infrared spectrum are exactly the multiples of fundamental.
 - None is correct
35. Which of the following form is the Clausius-Clapeyron equation?
- $\frac{d \ln P}{d(1/T)} = -\frac{\Delta H}{R}$
 - $\frac{d \ln P}{dT} = \frac{\Delta H}{R}$
 - $\frac{dP}{dT} = \frac{T\Delta H}{\Delta V}$
 - $\frac{d \ln H}{dT} = \frac{P}{RT}$
 - none is correct
36. For degenerate states which of the following may be different?
- energies
 - number of nodes
 - symmetry properties
 - wavefunctions
 - all the same
37. At 298 K and one bar pressure, heat of combustion of butane is ΔH_1 ; heat of formation of liquid water is ΔH_2 and heat of formation of carbon dioxide is ΔH_3 , then, the heat of formation of butane is
- $4\Delta H_3 + \Delta H_2 + \Delta H_1$
 - $2\Delta H_3 + \frac{5}{2}\Delta H_2 - \Delta H_1$
 - $4\Delta H_1 + 5\Delta H_2 - \Delta H_3$
 - $4\Delta H_3 + 5\Delta H_2 - \Delta H_1$
 - none is correct
38. The spherical harmonics $Y_{1,0} = N \cos \theta$ is an eigenfunction of rigid rotator. The constant N is
- $N = \sqrt{5/8}$
 - $N = \sqrt{3/4\pi}$
 - $N = \sqrt{3\pi/2}$
 - $N = \sqrt{2\pi/3}$
 - None is correct

39. For the overall reaction composed of following elementary reactions



If the rate-determine step is step 2, and $E_{a,1}$, $E_{a,-1}$, $E_{a,2}$... are the activation energies for the corresponding steps, then the overall activation energy is

- a. $E_{a,1} + E_{a,-1} + E_{a,2}$ b. $E_{a,2} - E_{a,-2}$
 c. $E_{a,1} + E_{a,2} - E_{a,-1}$ d. $E_{a,1} + E_{a,2}$
 e. None is correct

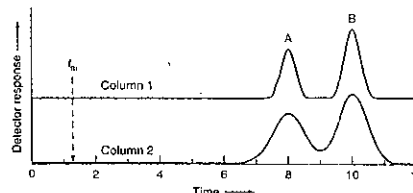
40. For a free particle of mass m in a cubic box with dimension a , the wave function $\psi_{n_x, n_y, n_z}(x, y, z)$ has three quantum numbers n_x , n_y and n_z . If

$\psi = 0.8165\psi_{1,1,2} - 0.4082\psi_{1,2,1} - 0.4082\psi_{2,1,1}$, the energy of ψ is

- a. $\frac{3}{2} \frac{h^2}{ma}$ b. $(c_1^2 + c_2^2 + c_3^2) \frac{h^2}{2ma^2}$
 c. $\frac{3}{4} \frac{h^2}{ma^2}$ d. can not be determined
 e. none is correct

I. Briefly answer the following questions: (60 %, 10 % each)

1. Explain why the solubility of an ionic compound increases as the ionic strength of the solution increases (at least up to ~ 0.5 M).
2. Write a charge balance equation for a solution containing H^+ , OH^- , Ca^{2+} , HCO_3^- , CO_3^{2-} , $Ca(HCO_3)^+$, $Ca(OH)^+$, K^+ and ClO_4^- .
3. What will be the effects of increasing cross-linking on an ion-exchange column?
4. Chromatograms of compounds A and B were obtained at the same flow rate with two columns of equal length.



- (a) Which column has more theoretical plates? _____
 - (b) Which column gives higher resolution? _____
 - (c) Which column has a larger plate height? _____
 - (d) Which compound has a higher capacity factor? _____
 - (e) Which compound has a greater partition coefficient? _____
5. Explain the difference between charging current and faradaic current.
 6. What do DAC and ADC abbreviate for? What will be the resolution of a 10-bit DAC with $V_{Ref} = 10$ V?

II. Multiple choice: (40 %) There may have more than one correct answer for each problem. (2% for each correct answer and -1 % for each wrong answer)

1. Sodium hypochlorite was dissolved in a solution buffer to pH 5.53. Find the ratio $[OCl^-]/[HOCl]$ in this solution. ($pK_a = 7.53$ for $HClO$) (a) 0.10 (b) 0.01 (c) 1.00 (d) 10.0 (e) 2.00
2. The absorbance of a 2.31×10^{-5} M solution of a compound is 0.822 at a wavelength of 266 nm in a 0.10 cm cell. The molar absorptivity at 266 nm is (a) 2.03×10^{-5} (b) 2.03×10^{-4} (c) 3.56×10^4 (d) 3.56×10^5 (e) 3.56×10^3 $M^{-1}cm^{-1}$.
3. Karl Fischer titration is useful for the analysis of (a) enzyme activity (b) ethanol (c) fat acid (d) water (e) Br_2
4. Which of the following electrode(s) behave(s) like an ideal non-polarizable

- electrode? (a) Pt electrode (b) Ag/AgCl(sat KCl) electrode (c) glass electrode (d) Hg drop electrode (e) Hg/Hg₂Cl₂ (sat. KCl)
5. For the following electrolysis to proceed.
Cathode: $\text{H}_2\text{O}(\text{l}) + \text{e} = 1/2 \text{H}_2(\text{g}, 1.0 \text{ bar}) + \text{OH}^-(\text{aq}, 0.10\text{M})$ $E^\circ = -0.828 \text{ V}$
Anode: $1/2 \text{Br}_2(\text{l}) + \text{e} = \text{Br}^-(\text{aq}, 0.10\text{M})$ $E^\circ = 1.078 \text{ V}$
What voltage is needed to drive the reaction if an ohmic voltage drop of 0.2 V is found. (a) >2.106 V (b) 1.906 V (c) 1.706 V (d) -1.906 (e) <-2.106 V.
[4% for this question]
6. Which of the following detector is appropriate to the GC analysis of halogen containing molecules. (a) thermal conductivity (b) flame ionization (c) electron capture (d) flame photometric (e) atomic emission
7. Which of the following compounds has negative pK_a. (a) HCl (b) NaOH (c) NaHCO₃ (d) H₂SO₄ (e) CH₃COOH
8. Specify the apparatus related to fluorescence spectrometric detection. (a) PM tube (b) Geiger counter (c) thermal couple (d) photodiode array (e) goniometer
9. Which of the following technique(s) provide little information for surface characterization? (a) AFM (b) STM (c) QCM (d) SIMS (e) ICPMS
10. Which of the following noise(s) is (are) frequency dependent? (a) Johnson noise (b) shot noise (c) white line noise (d) flicker noise (e) none of above
11. The mobile phase(s) applicable for supercritical-fluid chromatography include(s) (a) carbon dioxide (b) ethane (c) methanol (d) carbon tetrachloride (e) water
12. What procedure(s) is (are) helpful for minimizing the matrix effect in XRF analysis? (a) Addition of a releasing agent (b) use an internal standard (c) prepare the sample and standards with buffer solutions (d) dilute the sample and standards with light atomic weight substances (e) none of above