

1. (8%) Write (a) the mass-balance expression and (b) the charge-balance equation for a solution that is 0.10 M in Na_2HAsO_4 .
2. (8%) What is peptization (during the gravimetric method) and how is it avoided?
3. (9%) Explain why both the sensitivity and the interference from sample matrix are high for graphite furnace atomic absorption spectroscopy compared to flame atomic absorption spectroscopy.
4. (5%) CCD
Draw how charges are coupled in a CCD detector (*i.e.*, draw how a 3-phase clocking (or potential wells) is changed in the device such that the charge can be dumped into one direction).
5. (5%) FT-ICR-MS (Fourier-Transform Ion Cyclotron Resonance)
 - i. Prior to FT, what do the spectra look like?
 - ii. What kind of signal is measured by the detector of FT-ICR-MS prior to FT? (*i.e.*, the unit of y axis in question (i). For example, current, time, kinetic energy, velocity, electric field, etc.)
6. (6%) ESCA (XPS) or AES
Draw schematic representation of the processes of (i) X-ray photoelectrons, and (ii) Auger electrons.
7. (9%) **Define** the following terms:
 - a. (3%) buffer capacity
 - b. (3%) guard column (HPLC)
 - c. (3%) electrophoretic mobility (CE)
8. (4%) Determine the following thermodynamic quantities extensive or intensive variables: (i) pressure (ii) entropy (iii) chemical potential, and (iv) Gibbs free energy.
9. (6%) Derive the Maxwell relation below

$$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

10. (6%) Write down the mathematical expressions for ΔG and ΔS for mixing 1 mole of H_2 with 2 mole of O_2 at 300 K under conditions where no chemical reaction occurs.
11. (6%) From the thermodynamic statistical mechanics, show that the vibrational energy of a diatom (with a harmonic vibrational frequency ν) is given to be

$$U_{\text{vib}} = \frac{Nh\nu}{e^{h\nu/k_bT} - 1}$$

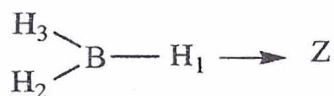
if the zero-point vibrational energy is excluded from the vibrational energy.

12. (3%) Explain why the entropy change of activation for a bimolecular gaseous reaction is generally negative.

13. 填充題：答案勿寫在此處，要寫在答案卷上，見題末答案格式樣本。

(25%)

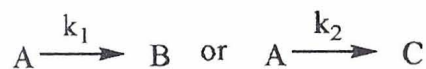
- a. Express the normalization factor N for the molecular orbital $\psi = N(\chi_A + \lambda\chi_B)$ in terms of the parameter λ and the overlap integral S between the two atomic orbitals, χ_A and χ_B . $N =$ _____
- b. Write down the spin part of the wavefunction ϕ_s for the valence-bond wavefunction for H_2 in a excited state with $S_z = 0$. $\phi_s =$ _____
(hint: express it in terms of $\alpha(1)$, $\alpha(2)$, $\beta(1)$ and $\beta(2)$. $\psi_T = \psi\phi_s = (1s_A(1)1s_B(2) - 1s_A(2)1s_B(1))\phi_s$. You may ignore the normalization factor).
- c. Give the coefficient λ for the sp^2 hybrid orbital $\psi_{hy} = (2s + \lambda 2p_z)$ in BH_3 pointing to the H_1 atom. $\lambda =$ _____



- d. The number of normal modes of vibration for H_2O_2 is _____
- e. The value of J of the total angular momentum for the term 1D is _____
- f. For the eigenfunction of L_z , $\phi = Ne^{im\phi}$, give the normalization constant $N =$ _____
- g. For a reaction $A \rightarrow B$, a plot of $1/[A]$ versus t is a straight line of slope k and intercept $1/[A]_0$. therefore the rate law is

$$-\frac{d[A]}{dt} = \text{_____}$$

- h. If A reacts to form either B or C according to



The time dependent concentration of $[A]$ can be expressed as

$$[A] = \text{_____} \quad (\text{hint: express it in terms of } [A]_0, k_1, k_2 \text{ and } t)$$

- i. Write down the eigenvalue of $Y_l^m(\theta, \phi)$ with respect to the

operator $(L_x^2 + L_y^2)$.

$(L_x^2 + L_y^2)Y_l^m(\theta, \phi) = CY_l^m(\theta, \phi)$, $C =$ _____ (hint: express C in

term of l , m and \hbar)

- j. The square of the length of spin angular momentum for α spin state is _____
- k. The bond order of O_2^- is _____ (hint: that of N_2 is 3)
- l. The point group of chlorobenzene is _____; that of *para*-dichlorobenzene is _____, that for 1,3,5-trichlorobenzene is _____. (For example, the point group for H_2S is C_{2v})

答案格式，一小題一行

13. a. xxxxxx

b. xxxxx

c. xxxxx

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l. xxxxx, xxxxx, xxxxx