

八十四學年度 化學研究

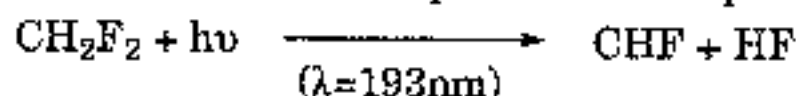
化學系 應用化學組碩士班研究生入學考試

科目 物理化學及分析化學 科號 0603 共 7 頁第 1 頁 *請在試卷【答案卷】內作答

- (6%) 1. (a) Draw the circuit scheme of a photomultiplier including a load resistor (R_L) to show output voltage from light signal.
- (b) When viewing scattered photons (2.2×10^{12} photons S^{-1}) through a filter (transmission 5%) and its quantum efficiency is 20% and its gain 10^6 , (the output is fed across a 50Ω load resistor), calculate the output voltage expected from the scattered photons.
- (c) If a 5 cm diameter photocathode is positioned 10 cm from the light source, calculate the solid angle of the photocathode view.

- (6%) 2. 10 mTorr CH_2F_2 (at room temperature, $T=298K$) is photolyzed at 193 nm by Laser radiation (10 mJ in a 1 cm diameter beam and 1 cm path length), calculate

- (a) the laser radiant flux density
- (b) concentration of CHF produced from photolysis;



- (c) What would be the situation if a 1 J pulse at 193 nm was used?

For the purpose of this calculation we shall assume that the absorption coefficient of CH_2F_2 at this wavelength is $3 \times 10^{-18} cm^2$, and that the quantum yield for CHF production is unity, and that the Beer's Law approximately is

$$I_{abs}/I_0 = \epsilon \cdot c \cdot l$$

- (6%) 3. Define and elaborate the polarization of light as
- (a) linear polarization
- (b) circular polarization
- (c) elliptical polarization

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(7%) 4. For FT-IR Spectroscopy

- (a) how to determine the resolution ($\Delta\bar{\nu}$)
- (b) how to determine the maximum range of frequency ($\bar{\nu}_m$)
- (c) What is the throughput advantage?
- (d) What is the multiplex advantage?

(9%) 5. A new method for the analysis of copper was tested with a sample known to contain 16.68% Cu

Sample	% Cu Found
1	16.54
2	16.64
3	16.30
4	16.67
5	16.70

- (a) Evaluate the mean and the median percentages of copper for these data.
- (b) Apply the Q test (90% confidence level, $Q_{crit} = 0.642$) to the outlying result.
- (c) Which value - the mean or the median - do you prefer as the "best" value for this analysis? Define your answer in a sentence or two.

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(6%) 6. A 1.219 g sample that contained $(\text{NH}_4)_2\text{SO}_4$, NH_4NO_3 , and inert materials was diluted to 250.0 mL in a volumetric flask. A 50.00 mL aliquot was heated with strong NaOH, and the liberated NH_3 was distilled into 30.00 mL of 0.08421 M HCl. The excess HCl required 10.17 mL of 0.08802 M NaOH. A 25.00 mL aliquot of the sample was made basic after the addition of Devarda's alloy to reduce the NO_3^- to NH_3 . The NH_3 from both NH_4^+ and NO_3^- was then distilled into 30.00 mL of the standard acid and back-titrated with 14.16 mL of the standard base. Calculate the percentages of $(\text{NH}_4)_2\text{SO}_4$ and NH_4NO_3 in the sample.

(10%) 7. Briefly define or describe

- (a) Voltammograms.
- (b) Counter-ion layer
- (c) Autoprotolysis
- (d) Faraday
- (e) Volhard method

第 8 題至 24 題為填充題，請連續作答，每題分行作答。如果一題有多格填充，請註明 a,b,c... 之編號。只要答案，不要過程。勿忘答案要寫在答案卷上，不是試題上。

(4%) 8. Give the definition of the Gibbs energy 8a and entropy 8b and the criteria for spontaneous change in terms of the entropy 8c and Gibbs energy 8d.

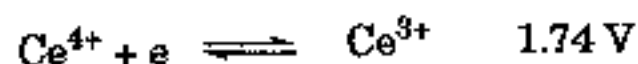
(4%) 9. Derive expression of ΔG for the isothermal expansion at temperature T from V_1 to V_2 of 1 mole of an ideal gas 9a or a van der Waals gas 9b.

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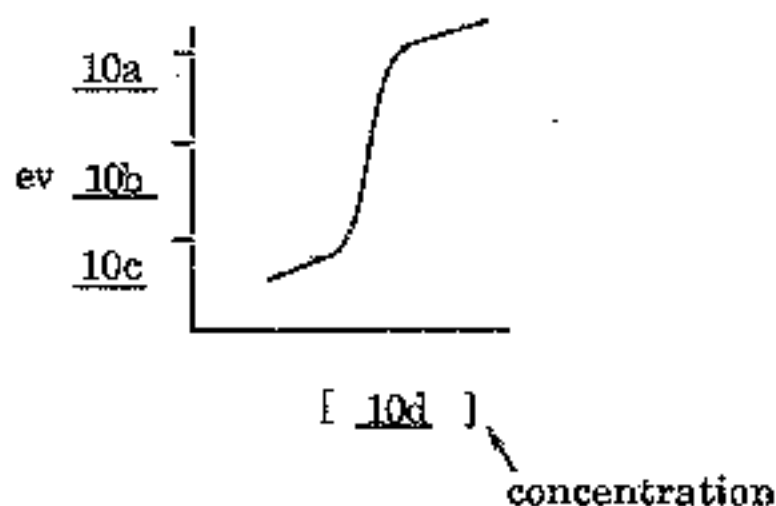
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- (6%) 10. The standard reduction potential at 25°C for Ce^{4+} and Fe^{3+} are listed as follows



Using Ce^{4+} , Ce^{3+} and Fe^{3+} , Fe^{2+} as an example,

- (a) draw the variation of potential as an oxidizing agent is added to a solution of reducing agent (the titration curve)



- (b) give the potential for the equivalent point 10e .
 (c) write down the reaction for the above case 10f .

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- (6%) 11. Give the expression for (a) the vibrational partition function for a diatomic molecule (of T , ν (vibrational frequency)) 11a (b) the translational partition function for a monatomic molecule (of T , V , m (molecular weight)) 11b and (c) estimate the molar heat capacity of constant volume (\bar{C}_v) for an ideal gas consisted of monatomic molecules in terms of $\text{cal deg}^{-1} \text{mol}^{-1}$ 11c.
- (4%) 12. Compare the number of nearest neighbors for each lattice point in the simple cubic 12a and face-centered cubic 12b cases.
- (2%) 13. The rate constant of a bimolecular reaction ($A + B \rightarrow P$) can be derived from simple collision theory as $k_{bi} = ze^{-\epsilon_0/kT}$, please give the form of z in terms of T , m_A and r_A (molecular weight and radius of A), m_B and r_B (molecular weight and radius of B) .
- (2%) 14. Plot the Langmuir adsorption isotherm (θ vs. P) , where θ is the fraction of sites occupied by A for a reaction $A + S \rightleftharpoons As$ and P is the pressure of gas molecules.
- (2%) 15. The probability of finding the particle in a region between $x=L/2$ and $x=3L/4$ for particle-in-a-box system in the state with the quantum number $n=\infty$ is (the probability between 0 and L is 1.0)
- (2%) 16. The term symbol for the N atom in the ground state is (hint: a term symbol gives three pieces of information)

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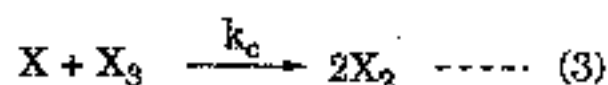
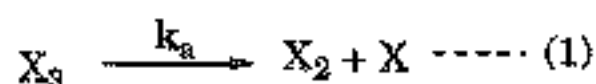
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- (2%) 17. The point group for the twisted, 90° allene, $\text{H}_2\text{C}=\text{C}=\text{CH}_2$ is _____.
- (2%) 18. The ionization energy of the H atom in the ground state is 13.6 eV, therefore its $3d \rightarrow 2p$ transition energy is _____.
- (2%) 19. The vibrational frequency for the diatomic molecule $^1\text{H}_2$ is 4400 cm^{-1} . That for the isotopic species $^1\text{H}^3\text{H}$ is _____ cm^{-1} .
- (2%) 20. The rotational constant (\tilde{B}_e) for $^1\text{H}_2$ is about 60 cm^{-1} . That for the isotopic species $^1\text{H}^3\text{H}$ is _____.
- (2%) 21. Two of the sp^2 hybrid orbitals are given as $h_1 = \frac{1}{\sqrt{3}}s + \sqrt{\frac{2}{3}}p_y$ and $h_2 = \frac{1}{\sqrt{3}}s + \frac{1}{\sqrt{2}}p_x - \sqrt{\frac{1}{6}}p_y$. The form for the third one is $h_3 =$ _____.
- (2%) 22. Write down explicitly the two-electron wavefunction including both the spin part and the spatial part for the 1S state of the He atom with the configuration $1s^1 2s^1$ _____
(hint: express it in terms of $\alpha(1)$, $\alpha(2)$, $\beta(1)$, $\beta(2)$, $1s(1)$, $1s(2)$, $2s(1)$, $2s(2)$).

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(3%) 23. A triatomic molecule X_3 undergoes the following set of reaction:



The reaction (3) is the rate-determining step. Therefore the rate of decomposition for X_3 can be expressed as $k[X_3]^n[X_2]^m$. The value for k is 23a (in terms of k_a, k_b, k_c), n is 23b and m is 23c.

(3%) 24. The reaction rate for the radical reaction $\cdot\text{CH}_3 + \text{CH}_3\text{CN} \rightarrow \text{CH}_4 + \cdot\text{CH}_2\text{CN}$ is dramatically reduced – by a factor 28,000 – when CD_3CN is used in place of CH_3CN . Give your explanation _____ (hint: there is mass effect on potential energy surface with two or more independent contribution).