

八十五學年度 化 學 系 化學，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 0703 共 5 頁第 1 頁 *請在試卷【答案卷】內作答

- (5%) 1. A two dimensional harmonic oscillator has the potential energy function

$$V(x,y) = \frac{k}{2}(x^2 + y^2)$$

- (a) Write the time-independent Schrödinger equation for it.
 - (b) Find the energy eigenvalues and the degeneracies for the third lowest energy level.
- (6%) 2. Explain the following terms and give an example for each one.
- (a) Selection rule of vibrational spectra
 - (b) Fine-structure coupling
 - (c) LS coupling
- (8%) 3. Considering a benzene molecule,
- (a) How many electrons does it have?
 - (b) What is its symmetry?
 - (c) Using localized valence bond for σ bondings and delocalize MO for π bondings, place all the electrons in proper orbitals. You do not have to label the symmetry of each orbital.
- (3%) 4. The standard enthalpy of formation of $N_2O_4(g)$ is $+9.2 \text{ kJmol}^{-1}$, the equilibrium constant of the synthesis of $N_2O_4(g)$ from $N_2(g)$ and $O_2(g)$ is K_1 at 273K, what is the equilibrium constant expressed in term of K_1 at 400°C ?
- (3%) 5. The partition function is the fundamental concept of statistical thermodynamics.
- (a) What is the definition of vibrational partition function?
 - (b) What is the electronic partition function of H_2 at room temperature?

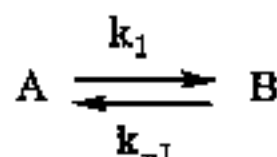
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6. The gas obeys the equation of state

$$(P + \frac{n^2a}{V^2})V = nRT$$

- (2%) (a) Find the reversible expansion work for a mole of gas under isothermal condition from V_1 to V_2 .
- (3%) (b) Find $(\frac{\partial E}{\partial V})_T$, in which E denotes the internal energy.
- (4%) (c) Derive an expression for ΔG for the process in (a).
- (2%) 7. Determine the number of degrees of freedom for the system of ice in a solution of water and alcohol.
- (4%) 8. Show that if a solute follows Henry's law in the form of $P_2=k'x_2$, then the solvent must follow Raoult's law. P_2 and x_2 are vapor pressure and mole fraction of solute, respectively.
9. We consider a reversible elementary reaction

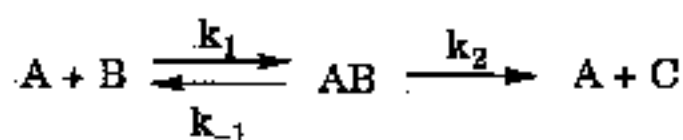


where k_1 is the forward rate constant and k_{-1} is the reverse rate constant.

- (1%) (a) Write down the differential rate equation for this reaction.
- (4%) (b) Assume that the initial concentrations of A and B are A_0 and zero, respectively, solve the concentration of A as a function of time.
- (1%) (c) Under (b) conditions, what is the half-life time constant to reach equilibrium of the reaction. (Time required for $[A]-[A]_{\infty}$ to drop to half of its initial value.)

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(4%) 10. For an enzyme reaction given below



where A is the enzyme, B is the substrate, AB is the enzyme-substrate complex, and C is the product. Draw a Lineweaver-Burk plot of $1/v$ vs. $[B]^{-1}$ for this reaction; v denotes the reaction rate. Indicate the value of slope and intercept of the plot. Apply the steady-state approximation to the concentration of complex AB.

(5%) 11. Define and elaborate on the following terms:

- (a) Internal standard
- (b) Standard addition
- (c) S/N ratio
- (d) Detection limit
- (e) Sensitivity

(5%) 12. Draw the circuit schemes of the operational amplifier doing the following functions for signal processing

- (a) current to voltage converters
- (b) voltage follower
- (c) differentiator
- (d) high pass filter
- (e) inverting voltage amplifier

(5%) 13. (a) Describe the four major parts of the spectrophotometer for a single beam and a double beam design.
 (b) What are the basic principles (or law) used in the spectrophotometry for qualitative and quantitative analysis.

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- (5%) 14. Describe the following instrumentation for the metallic element analysis
- X-ray fluorescence (XRF)
 - Graphite atomiser-Atomic Absorption
 - ICP-Atomic Emission Spectroscopy
 - ICP-Mass Spectrometry
 - Cold Vapor-Atomic Absorption Spectroscopy
- (5%) 15. (a) Describe the basic principle of the two electrochemical methods: polarography and anodic stripping voltammetry.
 (b) What are the advantages of anodic stripping voltammetry over polarography in terms of sensitivity and detection limit?
- (5%) 16. The standard electrode potentials for $\text{Pt}|\text{Fe}^{3+}, \text{Fe}^{2+}$ and $\text{Pt}|\text{Ce}^{4+}, \text{Ce}^{3+}$ are 0.771 and 1.61V, respectively. Calculate
- the potential at the half end point
 - the potential at the end point
 - the potential at $[\text{Ce}^{4+}] = 2 \cdot [\text{Fe}^{2+}]$
- in the titration of 0.050 mol Fe^{2+} with Ce^{4+} solution.
 (Assume total volume of solution at end point is 1 dm³ and that all activity coefficients are unit.)
- (5%) 17. A coastal marine sediment was analyzed for its iron content. Sevent replicate measurements were made on a random sample of the marine sediment. The results were : 3.36, 3.20, 3.15, 3.12, 3.10, 3.09 and 3.06% of iron (wt/wt).
- Calculate the sample mean and the sample standard deviation.
 - Calculate the 90% confidence interval for the iron content of the marine sediment. (Student t values = 2.015, 1.943 and 1.895 for degree of freedom 5, 6, and 7 respectively).

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- (c) Use Q-test to point out the outlying value. (the rejection quotient, $Q_{90}=0.51$ for seven measurements)
- (d) Calculate the 90% confidence interval after Q-test
- (5%) 18. Calculate
- (a) The absorptivity if a sample in a 1 cm path cell with concentration of 0.5×10^{-3} M shows an absorbance of 0.265 absorbance units at 595 nm (λ_{\max}).
- (b) The partition coefficient, $K_D = \frac{(Cs^+)(s)}{(Cs^+)(aq)}$ (weight M^{-1}) after passing 100 ml of 0.005 M Cs^+ solution through an ion-exchange resin and the concentration of Cs^+ in solution was found to be 5 ppm.
- (5%) 19. What types of GC column would be your initial choice for the analysis of
- (a) chlorinated pesticides in a natural water sample
- (b) volatile solvents in waste water
- (c) oil contamination in water
- (5%) 20. (a) Calculate the relative isotope abundance of M^+ with molecular formula $C_{12}H_4O_2Cl_3$ ($m/e = 285, 287, 289, 291$).
- (b) The exact mass of CO is 27.9949 and that of C_2H_4 is 28.0313. What resolution is necessary to just separate CO^+ and $C_2H_4^+$ found in a mixture of carbon monoxide and ethylene? Compare this requirement with that necessary to separate $C_{20}H_{40}^+$ and $C_{19}H_{36}O^+$, both nominally at $m/e = 280$.