國　立　清　華　大　學　命　題　紙

九十三學年度＿＿化學＿＿系（所）＿化學、應用化學＿組碩士班研究生招生考試
科目_物理化學及分析化學_科號_0603, 0703_共＿4＿頁第＿1＿頁 *請在試卷【答案卷】內作答

1. (a) Explain the "Sources of Systematic Errors" of chemical analysis by giving examples.
   (b) How to detect the errors of an analytical method? (13%)

2. A solution contains $NaHCO_3$, Na_2CO_3 and NaOH, either alone or in a permissible combination. Titration of a 50.0 ml portion to a phenolphthalein end point requires 30.0 ml of 0.100 M HCl. A second 50.0 ml aliquot requires 52.0 ml of 0.100 M HCl when titrated to a bromocresol green end point (end point at acidic condition). Deduce the composition and calculate the molar solute concentrations of the original solution. (12%)

3. Suppose that you are a teaching assistant in a university and you have to provide your students the procedures of preparing a buffer solution, please do your best to **write down a step-by-step instruction** for your students. The buffer solution should have the following requirements: 1.0 L, pH 6.2, and 1.0 M phosphate (*i.e.*, $[H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = 1.0$ M). Assuming that your teaching lab has balances, pH meters and electrodes, beakers, volumetric flasks, magnetic stirrers, deionized water, and necessary chemicals including HCl (fw 36.5), NaOH (fw 40.0), H_3PO_4 (fw 98.0), KH_2PO_4 (fw 136.1), K_2HPO_4 (fw 174.2), etc.
   (Note: to answer this question, it is not encouraged to do any calculation involving pKa.) (5%)

4. Please describe the major reason why (a) molecular fluorescence spectroscopy is a very sensitive technique and (b) methods of chemiluminescence have very good detection limits? (The answer is **NOT** the 90-degree angle between the incident and emitting beams.) (5%)

5. Define **matrix effect** in analytical measurements. Describe **one method** (and **no more than one**) that can be used to minimize matrix effect. (5%)

6. Ten analytical techniques are listed in the following. For the obtained spectra, please write down what their *x-axes* are and their *units* (the most commonly used form).
   For example, the correct answers for *Liquid Chromatography* are *x-axis*: retention time; *unit*: min. However, "*x-axis*: time; *unit*: day" will be considered as a wrong answer. (10%)

   a. UV/Vis Spectroscopy　　b. IR Spectroscopy
   c. Atomic Absorption Spectroscopy　　d. Secondary Ion Mass Spectroscopy
   e. X-ray Fluorescence Spectroscopy　　f. NMR
   g. X-ray Photoelectron Spectroscopy　　h. Auger Electron Spectroscopy

i. Capillary Electrophoresis　　j. Cyclic Voltammetry

7. A particle of mass m is placed in a one-dimensional box of length ℓ. At certain time, t_0, the particle is found in the physical state Ψ (6%)

$$\Psi(x) = 5\psi_1 + 6\psi_2 + 8\psi_3 + 10\psi_5$$

where ψ_n are the eigenfunctions of particle in a one-dimensional box with quantum number n.

(a) Normalize the state wavefunction $\Psi(x)$, and write out $\Psi(x)$ explicitly in terms of m, ℓ, and other constants.

(b) What are the possible values of energy measurement and the corresponding probabilities?

(c) What is the average energy of this physical state?

(d) What is the expectation value of momentum? What is the expectation value of position?

8. The partition function is the fundamental concept of statistical thermodynamics. (5%)

(a) How to obtain average energy using the energy partition function?

(b) What is the definition of vibration partition function?

(c) What is the electronic partition function of H_2 at room temperature?

9. The simple treatment of molecular vibration is using the harmonic oscillator model. Use this model for the following questions. (6%)

(a) For $^1H^1H$ molecule, the functional frequency ω_e is 4395.2 cm^{-1}. What is ω_e for $^2D^1H$?

(b) Draw qualitatively the wavefunctions for v = 4 and v = 0.

(c) Can you find the particle outside the potential well in the so called classical forbidden region? Explain.

10. Explain the following terms briefly. (8%)

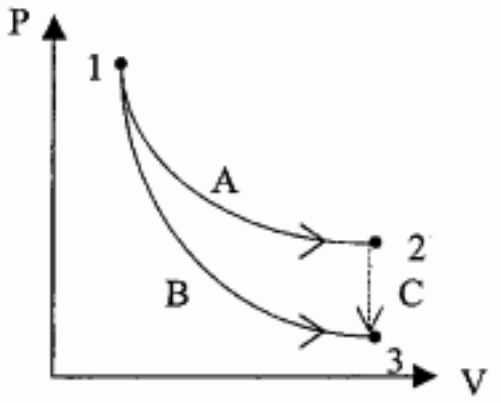
(a) Well behaved state function.

(b) The ground state term of C_6H_6

(c) Bonding and antibonding.

(d) σ bond and π bond.

11. In the drawing below for a simple ideal gas system, line A is a reversible isotherm at temperature T_1, line B is a reversible adiabat from T_1 to T_2, line C is an irreversible constant-volume at V_2. Fill in the blanks with 0, x, y, z, s, T_1, T_2 or any combinations such as x+y, z/T_2, y/z ……. **Just write the answers, e.g. ① = x + y, ② = 0, …….** **(8%)**



	path A rev. 1→2	path B rev. 1→3	path C irrev. 2→3	an irreversible process 1→3 (path not shown)
V				
q	x		y	⑦ = ?
W				s
ΔU	① = ?	③ = ?	⑤ = ?	
ΔS	② = ?	④ = ?	⑥ = ?	⑧ = ?

12. The ionization constant of an ion could be described by the equation

$$\ell n\, K = 50.0 - \frac{1800}{T} - 10\, \ell n\, T$$

between 5°C and 55°C. Calculate values of ΔH° and ΔS° for the ionization at 27°C. (Note: $\ell n\ 300 = 5.70$, $\ell n\ 100 = 4.61$, $\ell n\ 2 = 0.693$)
(6%)

13. A nonideal gas is described by the truncated virial equations of state:

$$P\overline{V} = RT + AP$$

where A, the second virial coefficients, is functions of T. Find expression of pressure dependence for $\overline{S}(T, P) - \overline{S}^{\circ}(T)$
The pressure of the standard state is P^0. (3%)

14. One possible mechanism for the reaction $2NO + O_2 \rightarrow 2NO_2$ is: (4%)

(1) $NO + NO \rightarrow N_2O_2$ k_1

(2) $N_2O_2 \rightarrow 2NO$ k_2

(3) $N_2O_2 + O_2 \rightarrow 2NO_2$ k_3

(a) Apply steady-state approximation to obtain the rate law.

(b) If only a small fraction of N_2O_2 formed in reaction (1) proceeds to form products in reaction (1), whereas most N_2O_2 decomposes to NO via reaction (2), what is the activation energy of the overall reaction? The activation energies for reactions (1) – (3) are $E_1 = 80$ kJ mol^{-1}, $E_2 = 210$ kJ mol^{-1}, and $E_3 = 90$ kJ mol^{-1}, respectively.

15. (a) For competitive reactions

$A + C \xrightarrow{k_a} P$, rate $= k_a[A][C]$

$B + C \xrightarrow{k_b} Q$, rate $= k_b[B][C]$

with initial concentration $[A]_0$, $[B]_0$, and $[C]_0$, what is the slope of the plot of ℓn $([A]/[A]_0)$ vs. ℓn $([B]/[B]_0)$?

(b) For parallel reactions

$A \xrightarrow{k_1} B$, rate $= k_1[A]$

$\xrightarrow{k_2} C$, rate $= k_2[A]$

$\xrightarrow{k_3} D$, rate $= k_3[A]$

with initial concentrations $[A]_0 = a$ and $[B]_0 = [C]_0 = [D]_0 = 0$, what is [B] as a function of time t? (4%)