國立臺灣大學98學年度碩士班招生考試試題

※ 注意：請於試卷上依序作答，並應註明作答之部份及其題號。

Part I. Physical Chemistry

Procedures for all calculations and the units of the final results must be given.

1. One mole of an ideal gas ($C_{v,m} = 3R/2$), initially at 10 atm and 400 K, was allowed to expand adiabatically against a constant pressure of 1 atm to a final pressure of 1 atm. Answer the following questions. ($R = 8.31\ J \cdot K^{-1} \cdot mol^{-1}$) 10%

(a) Find the final temperature of the gas.

(b) Find the change in internal energy (ΔU) and enthalpy (ΔH) of this process.

(c) Find the change in entropy (ΔS) of this process.

(d) Is this process spontaneous? Justify your answer.

2. The excess Gibbs free energy (G^E) of solution of cyclohexane (CH) and tetrahydrofuran (THF) at 300 K and 1 atm was found to fit the expression: $G^E = nRT[0.5x(1-x)(1-x^2)]$, where x is the mole fraction of CH and n is the total moles of CH and THF. Answer the following questions for mixing of 2 moles CH with 3 moles THF. 10%

(a) Find the change in Gibbs free energy for the mixing process.

(b) Find a general expression of the excess entropy for the mixing of CH and THF.

(c) Find the change in entropy for the mixing process.

(d) Find the change in enthalpy for the mixing process.

3. Answer the following questions. 15%

(a) If the wavefunction of a particle in a ring is given by $\Psi = e^{i \cdot 5\phi}$, where $\phi = 0 \sim 2\pi$ and $i = \sqrt{-1}$, find the normalization constant for Ψ. Also find the probability of finding a particle in a ring with $\phi = 0 \sim \pi/3$.

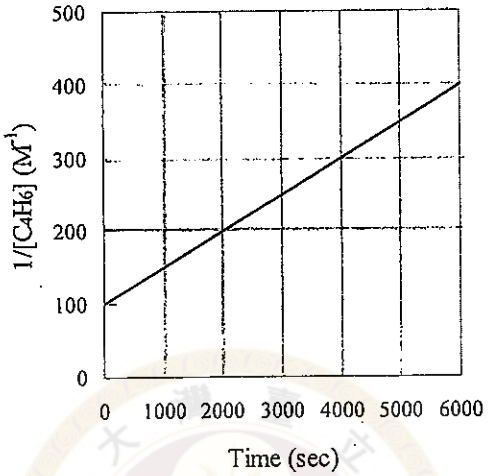
(b) How many possible combinations of quantum numbers are there for the two p-electrons in the ground-state of carbon atom? Justify your answer.

(c) The wave function for a one dimensional particle-in-a-box of length L is given by $\Psi_n = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}$. Find the position of nodes and the probability of finding the particle within L/6 and L/2 for n = 3.

(d) The pure rotational spectrum of $^1H^{131}I$ consists of a series of equally spaced lines with $\Delta \tilde{\nu} = 12.8\ cm^{-1}$. Estimate the internuclear distance of HI.

4. Butadine (C_4H_6) reacts to form its dimer (C_8H_{12}) at 500 K according to the equation: $2\ C_4H_6(g) \rightarrow C_8H_{12}(g)$. The following figure shows a linear plot of $1/[C_4H_6]$ vs. time for the reaction. Answer the following questions. 15%

見背面



(a) What is the order of the reaction?

(b) Find the rate constant of the reaction.

(c) Calculate the initial rate for the disappearance of C_4H_6.

(d) What is the half-life of the reaction when the initial concentration of C_4H_6 is 0.010 M?

(e) Calculate the collision frequency per m^3 of C_4H_6 at t = 0 if the diameter of a C_4H_6 molecule is 0.6 nm.

(f) Estimate the rate constant from the collision theory, assuming that the activation energy for the reaction is 115 kJ/mol.

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Part II. Analytical Chemistry　50%

A. 單選題 (共 10 題，每題 2 分，選最恰當的選項，答錯倒扣 1 分)本大題請作答於試卷內「選擇題作答區」

1. The unit for the equilibrium constant of the reaction of $Hg_2Cl_2(s) \rightleftharpoons Hg_2^{2+}(aq) + 2Cl^-(aq)$ is
   (a) none.　(b) $(mol/L)^2$.　(c) $(mol/L)^3$.　(d) $(mol/L)^4$.　(e) $(mol/L)^3(cm^3/g)$.

2. An indicator for acid-base titration has K_a equal to 2.0×10^{-8}. It is yellow for basic form and blue for acidic form. During the course of titration at pH 8.0, what is the ratio of [HIn]/[In^-] and the color?
   (a) 2, yellow　(b) 2, blue　(c) 1/2, yellow　(d) 1/2, blue　**(e) 1/2, hard to tell the color.**

3. Which of the following terms is *irrelevant* to solution pH?
   (a) isosbestic point　(b) isoelectric point
   (c) isoionic point　(d) acid/base titration end point

4. Which of the following explains how temperature affects the intensity and sensitivity of AES (atomic emission spectroscopy)?
   (a) Beer's law　(b) Boltzmann distribution　(c) Heisenberg uncertainty principle
   (d) Doppler effect　(e) Franck-Condon Principle

5. Which type of detectors in the following is suitable for an FTIR spectrometer?
   (a) photodiode array　(b) photomultiplier tube　(c) interferometer
   (d) charge coupled device　(e) thermocouple transducer

6. The junction 0.10 M HCl(*aq*)|3.5 M KCl(*aq*) develops a liquid junction potential of +3.1 mV at 25 °C because
   (a) the mobility of H^+ is very much faster than the mobility of K^+.
   (b) the mobility of H^+ is very much slower than the mobility of K^+.
   (c) the concentration of K^+ is higher than the concentration of H^+.
   (d) the concentration of Cl^- at the right hand side is a lot higher than that at the left hand side.
   (e) KCl is oversaturated.

7. Which of the following ionization methods is the most suitable to couple with liquid chromatography?
   (a) CI　(b) EI　(c) ESI　(d) FI　(e) MALDI

8. For cyclic voltammetry carried out in a solution containing sufficient amount of supporting electrolyte, the analyte reaches working electrode by
   (a) migration.　(b) diffusion.　(c) convection.　(d) electrostatic attraction.　(e) hydrodynamic flow.

9. Which of the following has the shortest t_R from a column containing a reversed-phase packing?
   (a) benzene　(b) diethyl ether　(c) n-octane　(d) n-hexane　(e) toluene

10. In gas chromatography, which term in van Deemter equation describes the time required for solute to transfer (or equilibrate) in gas phase?
    (a) A　(b) B/u_x　(c) C_m　(d) C_s　(e) H/u_x

B. 填充、簡答題 (共 10 分)

1. Write the answer with the correct number of significant figures. (每題 2 分)
   (a) 105.7 − 4.7002 = 100.999 800
   (b) (26.14 ÷ 3.72) + 4.7002 = 11.727 082
   (c) $\log(1.00 \times 10^5) = 5.000\ 000$

2. Write the equation(s) for the propagation of uncertainty. (每題 2 分；僅需列式，不必計算)
   (a) [26.14 (± 0.14) ÷ 3.72 (± 0.72)] + 4.7002 (± 0.0002) = 11.727 082 (± ?)
   (b) $[8.00\ (\pm\ 0.04)]^{1/3} = 2.000\ 000\ (\pm\ ?)$

見背面

C. 論說題 (共 20 分，每題 10 分)

1. The potassium content of a standard reference material from NIST is 240 mg/L. The same sample is measured by a new developed method which gives 260 (± 10) mg/L (n = 4), in which ± 10 mg/L is the standard deviation and n is the number of measurements. Based on 98% CL, this new method is valid. Please explain why this comment is reasonable. (Both your knowledge and **writing skill** will be graded.)

2. The following is the experimental procedure for HCl(*aq*) standardization. Based on the concept of buffer, explain why the procedure suggests "**Then boil the solution.**". (Both your knowledge and **writing skill** will be graded.)

Standardizing HCl

1. Calculate the volume of ~37 wt% HCl that should be added to 1 L of distilled water to produce 0.1 M HCl and prepare this solution.
2. Dry primary standard grade sodium carbonate for 1 h at 105°C and cool it in a desiccator.
3. Weigh four samples, each containing enough Na_2CO_3 to react with ~25 mL of 0.1 M HCl and place each in a 125-mL flask. When you are ready to titrate each one, dissolve it in ~25 mL of distilled water. Add 3 drops of bromocresol green indicator and titrate one rapidly to a green color to find the approximate end point.
4. Carefully titrate each sample until it turns from blue into green. **Then boil the solution.** The color should return to blue. Carefully add HCl from the buret until the solution turns green again and report the volume of acid at this point.
5. Perform one blank titration of 50 mL of 0.05 M NaCl containing 3 drops of indicator. Subtract the volume of HCl needed for the blank from that required to titrate Na_2CO_3.
6. Calculate the mean HCl molarity, standard deviation, and percent relative standard deviation.

TABLE 4-2 Values of Student's *t*

	Confidence level (%)						
Degrees of freedom	50	90	95	98	99	99.5	99.9
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

In calculating confidence intervals, σ may be substituted for s in Equation 4-3 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s, the value of t to use in Equation 4-3 comes from the bottom row of this table.

Table 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function[a]	Uncertainty[b]
$y = x_1 + x_2$ $y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
		$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\frac{e_x}{x}$
$y = x_1 \cdot x_2$ $y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
		$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\,e_x$
		$y = e^x$	$\frac{e_y}{y} = e_x$

a. x represents a variable and a represents a constant that has no uncertainty.

b. e_x/x is the relative error in x and $\%e_x$ is $100 \times e_x$/x.

TABLE 4-4 Values of *Q* for rejection of data

Q (90% confidence)[a]	Number of observations
0.76	4
0.64	5
0.56	6
0.51	7
0.47	8
0.44	9
0.41	10
0.39	11
0.38	12
0.34	15
0.30	20

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