物理化學 考題

請務必依照考題順序寫答案卷！
此部分佔本科目 50 分
1~9 題為選擇題（單選題），每題 2 分。其餘為問答或填充，配分列於各題號上。

選擇題（單選題）

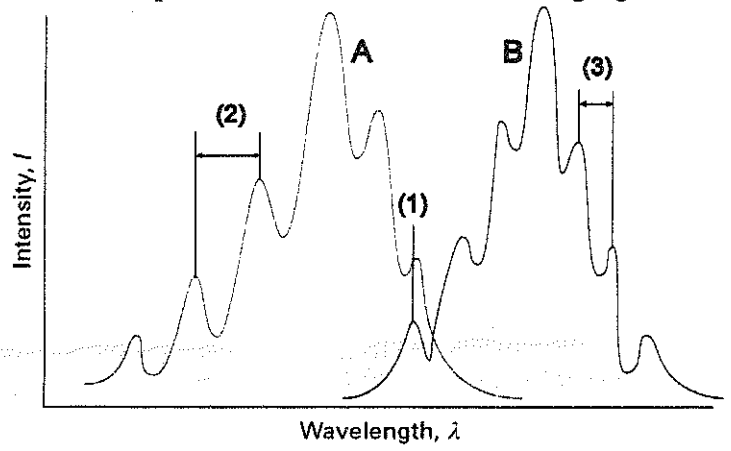
1. Which of the following is known as the Schrödinger equation
   (A) $E = h\nu$　(B) $E = mc^2$　(C) $\lambda = h/p$　(D) $\hat{H}\psi = E\psi$　(E) $-\frac{\hbar^2}{2m}\nabla^2 = E$
2. Which of the following is NOT a correct consequence of the Heisenberg uncertainty principle: (A) The shorter the lifetime of an excited state of an atom, the less accurately can its energy be measured.
   (B) An electron in an atom cannot be described by a well-defined orbit.
   (C) A harmonic oscillator possesses a zero-point energy.
   (D) Measurement of one variable in an atomic system can affect subsequent measurements of other variables.
   (E) The momentum of an electron cannot be measured exactly.
3. Which of the following is NOT a solution of the differential equation $y''(x) + k^2y(x) = 0$
   (A) $\exp(-ikx)$　(B) $\exp(-kx)$　(C) $\sin kx$　(D) $\cos kx$　(E) $\sin(kx-\alpha)$ (α = constant)
4. The energy levels of the linear harmonic oscillator are
   (A) n-fold degenerate　(B) (n+½)-fold degenerate　(C) (2n+1)-fold degenerate
   (D) n^2-fold degenerate　(E) all nondegenerate
5. The Lennard-Jones potential for the interaction of two atoms has the form of
   $V(R) = V_0\left[\left(\frac{\sigma}{R}\right)^{12} - \left(\frac{\sigma}{R}\right)^{6}\right]$
   The value of R_e is given by
   (A) σ　(B) $\sigma^{12} - \sigma^6$　(C) $2^{1/6}\sigma$　(D) $V_0/4\sigma^2$　(E) $(1-e^{-\sigma/2})^2$
6. Which of the following electronic transitions is (or are) allowed in O_2.
   (A) ${}^3\Sigma_g^- \leftrightarrow {}^1\Delta_g$　(B) ${}^3\Sigma_g^- \leftrightarrow {}^3\Sigma_u^-$　(C) ${}^3\Sigma_g^- \leftrightarrow {}^3\Sigma_u^+$　(D) ${}^3\Sigma_g^- \leftrightarrow {}^3\Delta_u$　(E) ${}^3\Sigma_u^- \leftrightarrow {}^3\Sigma_g^-$

The existence of spontaneous endothermic reactions provides an illustration of the role of *G*. Please answer the following questions 7 and 8:

7. What is the value of ΔH for the system?
   (A) $\Delta H > 0$　(B) $\Delta H = 0$　(C) $\Delta H < 0$　(D) $\Delta H \leq 0$　(E) $\Delta H \neq 0$
8. What is the value of ΔG for the system?
   (A) $\Delta G > 0$　(B) $\Delta H = 0$　(C) $\Delta G < 0$　(D) $\Delta G \leq 0$　(E) $\Delta G \neq 0$
9. The van't Hoff equation relates the slope for a plot of the equilibrium constant as a function of temperature. Its expression has the form of
   (A) $\ln K = -\frac{\Delta_r G^0}{RT}$　(B) $\left(\frac{\partial}{\partial T}\frac{\Delta_r G}{T}\right) = -\frac{\Delta_r H}{T^2}$　(C) $\Delta_r H^\circ(T_2) = \Delta_r H^\circ(T_1) + \int_{T_1}^{T_2} \Delta_r C_p{}^\circ \, dT$
   (D) $K = -\frac{\Delta_r G^0}{RT}$　(E) $\frac{d\ln K}{dt} = -\frac{\Delta_r H^0}{RT^2}$

問答、填充或繪圖題

10. (13 pts) On the Beer-Lambert law, A = εb C, please answer the following questions:
    (a) What are the name for individual terms?
    (b) Indicate which term(s) are function of the frequency or wavelength?
    (c) The value of ε represents another form of the transition dipole moment in spectroscopy. Please write the quantum mechanical expression for the transition dipole moment and clearly define each term in it.
    (d) The value of the transition dipole moment determines the probability of a transition between two energy states and forms the basis of "selection rule". There are two different kinds of selection rules, namely "gross selection rule" and "specific selection rule". Please give clear descriptions for these two selection rules. Also, use a diatomic molecule as an example to give the answers for both selection rules in its IR absorption spectroscopy.
11. (7 pts) On the fluorescence spectroscopy of a chromophore in solution, a typical absorption and fluorescence spectra are shown in the following figure.



A is the absorption spectrum and B is the fluorescence spectrum of the same molecule. Please fill the following blanks for the marks shown in the above figure:
    (a) (1) indicates a transition of _____;
    (b) The spacing between two adjacent fine structures in A, such as (2), represents the _____;
    (c) The spacing between two adjacent fine structures in B, such as (3), represents the _____;
    (d) The relative intensities of the fine structures found in both A and B are governed mainly by the _____. Please write down its quantum mechanical expression:
    (Hint: You need to give clear definitions for the major terms)
12. (4 pts) Consider a particle in a 1-dimensional box in which a particle of mass m is confined to a finite region of space between two impenetrable walls. The potential energy is zero inside the box but rises abruptly to infinity at the walls at x=0 and x=L. Its wavefunctions are

$$\psi_n(x) = C \sin\left(\frac{n\pi x}{L}\right) \qquad n=1,2,\ldots$$

The constant C can be determined via normalization to give $C^2 = \frac{2}{L}$

Calculate the probability that the particle will be found in the middle third of the box: $L/3 \leq x \leq 2L/3$. From the general formula for arbitrary n, find the limiting value as $n \rightarrow \infty$.
13. (8 pts) The variation in the partial pressure of azomethane with time in its decomposition reaction

$$CH_3N_2CH_3(g) \rightarrow CH_3CH_3(g) + N_2(g)$$

was monitored at 600 K, with the results given below:

t/s	0	1000	2000	3000	4000
p/Pa	10.9	7.63	5.32	3.71	2.59

Assuming that we already know its reaction follows either first-order or second-order kinetics, please present your verifications to prove its reaction order in terms of the associated integrated rate laws and the half-lives. (Note: Please do not attempt to calculate the above data. Also, you need to show your derivation in detail for the necessary equations.)

分析化學部份(總分 50 分) 計算題須有計算過程

1. Report results of the following calculations to the correct number of significance figures.
   (a) 4.591 + 0.2309 + 67.1 = ? (2 分)
   (b) 1.43/0.026 = ? (2 分)
   (c) 9.23 (±0. 03) + 4. 21 (±0. 02) – 3.26 (±0.06) = ? (±?) (3 分)
   (d) 9.43 (±0.05) x 0.016 (±0.01) = ? (±?) (3 分)

2. Shown in the following data are the results for the determination of acetaminophen (in milligrams) in ten separate tablets of a Pain Reliever.
   224.3, 240.4, 246.3, 239.4, 253.1, 245.5, 229.4, 255.5, 235.5, 249.7
   (a) Report the mean and standard deviation for these data. (2 分)
   (b) Assuming that $\overline{X}$ and s^2 are good approximations for μ and σ^2, and that the population is normally distributed, what percentages of tablets are expected to contain more than the standard amount of 250 mg acetaminophen per tablet? (6 分)

3. (a) Calculate the pH of a buffer that is 0.020 M in NH_3 and 0.030 M in NH_4Cl. (3 分) [K_a (NH_4^+) =5.7×10^{-10}]
   (b) What is the pH after adding 1.00 mL of 0.10 M NaOH to 0.10 L of buffer solution 3(a)? (3 分)
   (c) What is the pH after adding 1.00 mL of 0.10 M NaOH to 0.10 L of water? (2 分)
   (d) Explain the pH difference between the results of 3(b) and 3(c). (2 分)

4. A compound with molecular mass 292.16 g/mol was dissolved in a 5-mL volumetric flask. A 1.00-mL aliquot was withdrawn, placed in a 10-mL volumetric flask, and diluted to the mark. The absorbance at 340 nm was 0.427 in a 1.000-cm cuvet. The molar absorptivity at 340 nm is $\varepsilon_{340} = 6\ 130\ M^{-1}\ cm^{-1}$.
   (a) Calculate the concentration of compound in the cuvet. (5 分)
   (b) How many milligrams of compound were used to make the 5-mL solution? (5 分)

5. The following data were obtained for four compounds separated on a 20-m capillary column. (每一小題 3 分)

Compound	Retention time(min)	Peak width(min)
Nonretained	1.1	-
A	8.04	0.15
B	8.26	0.15
C	8.43	0.16
D	10.6	0.22

(a) Calculate the retention factor of A, B, C, and D. (b) Calculate the average plate height of the column. (c) Calculate the number of plates for the column. (d) Calculate the resolution and selectivity factors for B and C.

TABLE 4–1 Ordinate and area for the normal (Gaussian) error curve, $y = \frac{1}{\sqrt{2\pi}} e^{-z^2/2}$

$\lvert z\rvert^a$	y	Area[b]	$\lvert z\rvert$	y	Area	$\lvert z\rvert$	y	Area
0.0	0.398 9	0.000 0	1.4	0.149 7	0.419 2	2.8	0.007 9	0.497 4
0.1	0.397 0	0.039 8	1.5	0.129 5	0.433 2	2.9	0.006 0	0.498 1
0.2	0.391 0	0.079 3	1.6	0.110 9	0.445 2	3.0	0.004 4	0.498 650
0.3	0.381 4	0.117 9	1.7	0.094 1	0.455 4	3.1	0.003 3	0.499 032
0.4	0.368 3	0.155 4	1.8	0.079 0	0.464 1	3.2	0.002 4	0.499 313
0.5	0.352 1	0.191 5	1.9	0.065 6	0.471 3	3.3	0.001 7	0.499 517
0.6	0.333 2	0.225 8	2.0	0.054 0	0.477 3	3.4	0.001 2	0.499 663
0.7	0.312 3	0.258 0	2.1	0.044 0	0.482 1	3.5	0.000 9	0.499 767
0.8	0.289 7	0.288 1	2.2	0.035 5	0.486 1	3.6	0.000 6	0.499 841
0.9	0.266 1	0.315 9	2.3	0.028 3	0.489 3	3.7	0.000 4	0.499 904
1.0	0.242 0	0.341 3	2.4	0.022 4	0.491 8	3.8	0.000 3	0.499 928
1.1	0.217 9	0.364 3	2.5	0.017 5	0.493 8	3.9	0.000 2	0.499 952
1.2	0.194 2	0.384 9	2.6	0.013 6	0.495 3	4.0	0.000 1	0.499 968
1.3	0.171 4	0.403 2	2.7	0.010 4	0.496 5	∞	0	0.5

a. $z = (x - \mu)/\sigma$.

b. The area refers to the area between $z = 0$ *and* $z =$ *the value in the table. Thus the area from* $z = 0$ *to* $z = 1.4$ *is 0.419 2. The area from* $z = -0.7$ *to* $z = 0$ *is the same as from* $z = 0$ *to* $z = 0.7$. *The area from* $z = -0.5$ *to* $z = +0.3$ *is* $(0.191\ 5 + 0.117\ 9) = 0.309\ 4$. *The total area between* $z = -\infty$ *and* $z = +\infty$ *is unity.*