國立高雄大學九十七學年度研究所碩士班招生考試試題

科目：綜合化學(II)　　系所：應用化學系碩士班　　是否使用計算機：是

考試時間：100 分鐘　　本科原始成績：100 分

Part I (physical chemistry)

1. The van der Waals equation is often written as the following: (5%，複選，答錯倒扣1.25%)

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m^2} \quad (1),$$

where V_m is the molar volume, a and b are called the van der Waals coefficients.

Which terms stated in the kinetic model for ideal gases are corrected as the van der Waals coefficients in equation (1)?

(a) The gas consists of molecules in ceaseless random motion.

(b) The size of the molecule is much smaller than the average distance traveled between collisions.

(c) The molecules interact only through brief, infrequent, and elastic collisions.

(d) The averaged kinetic energy of the molecules depends only on the Kelvin temperature of the gas.

2. Which of the following statement is correct: (5%，複選，答錯倒扣 1%)

(a) The internal energy of an isolated system is constant.

(b) $\Delta U = q + w$: The change of internal energy, heat transferred to and work done on a system are all state functions.

(c) The maximum work that a system can do to a surrounding is by free expansion.

(d) The Linde refrigerator is operated in a temperature range, where a gas system is cooled on expansion.

(e) A perfect gas expands adiabatically from P_i, V_i, T_i, to P_f, V_f, T_f, its change of the internal energy is $C_v(T_f - T_i) + (P_f V_f - P_i V_i)$

3. The vibrational wavenumbers of CO_2 are 1288 cm^{-1}, 667.4 cm^{-1}, and 2349 cm^{-1}, the second being the doubly degenerate bending mode. The vibrational partition function of CO_2 at 1500 K is about:

(a) 0.0007　(b) 0.07　(c) 7　(d) 700　(e) 70000　(5%，單選，答錯倒扣 1%)

4. Fill in the right statement of the following quantum principles from (i) – (v):

____ → (a) Born – Oppenheimer approximation

____ → (b) Quantization of energy by Planck

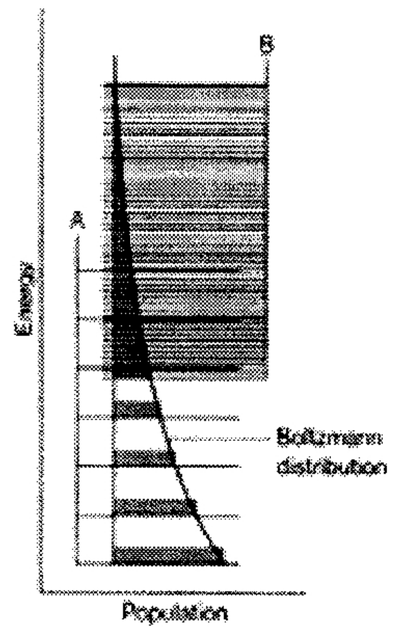
____ → (c) The uncertainty principle by Heisenberg

____ → (d) Hund's multiplicity rule

____ → (e) de Broglie relation. (5%，答錯倒扣 1%)

(i) It is impossible to specify simultaneously, with arbitrary precision, both the momentum and the position of a particle.
(ii) An atom in its ground state adopts a configuration with the greatest number of unpaired electrons.
(iii)The energy of each electromagnetic oscillator is limited to discrete values and can not be varied arbitrarily.
(iv) In the time scale while the electrons move in their field, the nuclei may be treated as stationary.
(v) Any particle, not only photon, travels with a linear momentum p should have a wavelength given by $\lambda = h/p$.

5. According to the right-hand figure for an A → B reaction, which of the following statements are correct? (5%，複選，答錯倒扣 1%)
   (a) The reaction is endothermic.
   (b) The equilibrium compositions always favor the reactant.
   (c) The equilibrium compositions always favor the product.
   (d) Changing the reaction Gibbs energy from positive to negative can be possible by heating up the reaction system.
   (e) The change of entropy is not important in this type of reaction.



6. Which of the following statement are correct? (5%，複選，答錯倒扣 1%)
   (a) The FT-IR method can be used to study O_2 vibration.
   (b) The rotation-vibration spectrum of HCl can be obtained by the FT-IR spectrum.
   (c) The rotation-vibration FT-IR spectrum of DCl shows P, Q, and R branches, which belong to transitions of $\Delta J = -1$, 0, and 1, respectively.
   (d) UV-VIS light can be used to electronically excite C_6H_6.
   (e) In general, the fluorescence life time is longer than the phosphorescence life time.
7. (a) Construct the orbital energies of Period 2 homonuclear diatomic molecules. (b) Explain why no Be_2 molecule can be formed. (c) Explain why B_2 and O_2 are paramagnetic. (3, 1, 1%)
8. Calculate the mean, root mean square, and most probable velocity of N_2 at 25°C.
   (The velocities in an **arbitrary** order are $(2RT/M)^{1/2}$, $(8RT/\pi M)^{1/2}$, and $(3RT/M)^{1/2}$;
   $R = 8.314\ J\ K^{-1}\ mol^{-1}$; and the molar mass of $N_2 = 28\ g\ mol^{-1}$.) (速率定義 3%，速率值 2%)
9. The rate law of the 2A → P reaction was determined as the following:

$$\frac{d[\mathrm{P}]}{d\mathrm{t}} = \frac{a[\mathrm{A}]^2}{b + c[\mathrm{A}]}$$

(a) Proposed the reaction mechanism of the reaction. (b) Derive the rate equation at low-pressure and high-pressure limits. (3, 2%)

10. Calculate the half-life ($t_{1/2}$) of a reaction, A → P, with an initial reactant concentration of $[A]_0$:
    (a) A zeroth-order reaction, rate constant = k^0.
    (b) A second-order reaction, rate constant = k^I.
    (c) A second-order reaction, rate constant = k^{II}. (2, 1, 2%)

Part II (analytical chemistry)

1. (3 points each) Explain the difference between
   a、 systematic error and random error
   b、 sensitivity and detection limit
   c、 activity and ionic strength
   d、 Faradaic current and charging current
   e、 capacity factor (k) and resolution (R) in chromatogram
2. Describe how to prepare an aqueous solution with pH 3.76 by mixing acetic acid ($pK_a = 4.76$) with sodium acetate. (5 points)
3. A solution containing 0.040 M HA and 0.020 M HB gave chromatogram peak areas of A_{HA} = 400 and A_{HB} = 350. To analyze an unknown, 10 mL of 0.200 M HB was added to 10.0 mL of unknown, and the mixture was diluted to 25.0 mL in a volumetric flask. This mixture gave the chromatogram with A_{HA} = 450 and A_{HB} = 575. Find the concentration of HA in the unknown. (5 points)
4. Why the pH is not 7.00 at equivalence point in the titration of weak acid with strong base? (5 points)
5. Describe the advantage for using three-electrode cell over two-electrode cell on electrolysis. (5 points)
6. Describe how to determine the measurement of a spectrometer is absorption or emission on the basis of the alignment among light source, sample cell, and detector. (5 points)
7. You have been request to determine the amount of $CH_3CH_2CH_2CH_2Cl$ and $(CH_3)_3CCl$ in a solution by chromatographic method. Describe which method you are going to use, include the detector equipped with the instrument. (5 points)
8. Describe three common types of noise in electric instruments. (5 points)