一、 Physical Chemistry (5 questions of total 50 points)

(1, 12pts)

The one-dimensional quantum mechanical harmonic oscillator can be used to approximate the nature of vibrational motion of molecules. The harmonic oscillator model has the potential of **V(x) =*(1/2)kx²***, where ***x*** is the bond length and ***k*** is the force constant. Therefore, we should consider this to a mathematically equivalent problem as a single reduced mass μ tethered to a wall of infinite mass of spring with a force constant ***k***. The Schrodinger equation can be written as:

$$-\frac{\hbar^2}{2\mu}\frac{d^2\psi_n(x)}{dx^2}+\left(\frac{1}{2}kx^2\right)\psi_n(x)=E_n\psi_n(x)$$

(1A, 4pts) If $e^{-\beta x^2}$ is the eigenfunction of the above Schrodinger equation, what is β?

(1B, 4pts) What is its corresponding eigenenergy, E?

(1C, 4pts) Compared with the particle-in-a-box model, where V(x) =0 within the box, this harmonic oscillator has a finite potential well. First, plot the potential function (V(x), y-axis) as a function of x (x-axis), and then plot wavefunctions of n=0, 1, 2, 3. Identify where ψ=0 using dash lines (-----).

(2, 8pts)

Chlorine has been found to catalyze ozone's destruction in stratosphere:

$$Cl+O_3 \xrightarrow{k_1} O_2+ClO$$
$$ClO+O \xrightarrow{k_2} O_2+Cl$$

$$O+O_3 \longrightarrow 2O_2$$

(2A, 4pts) Given the initial chlorine concentration is $[Cl]_0$, use steady-state approximation to express the rate of O_2 formation ($d[O_2]/dt$).

(2B, 4pts) One common way to monitor the dynamics of ClO is to use its vibrational band at ~ 830 cm^{-1}. Is this band infrared active? What is the quantum mechanical basis to establish the selection rule in infrared spectroscopy: $\Delta v=\pm 1$?

(3, 10pts)

1 mole of an ideal gas initially at 300 K is expanded from 1 m^3 to 5 m^3. Calculate the values of ***q***, ***w***, ***ΔH***, ΔS_{sur} and ***ΔG***, if the process is carried out isothermally and irreversibly against an external pressure of 10.0 bar.

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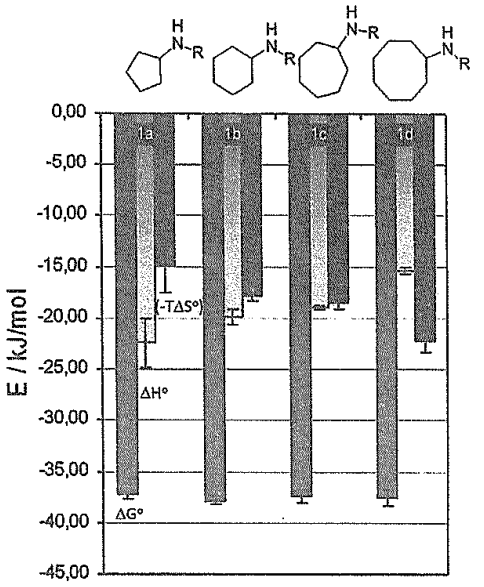
(4, 10pts)

Chemists are capable of modifying different structural moieties on substrates in order to optimize binding to the drug target. For example, a series of substrates were designed to bind to protease to function as protease inhibitors, and their binding thermodynamic properties were determined and summarized here. Three bars under each substrate refer to their values of ΔG°, ΔH°, and (-TΔS°) of binding (adapted from *J. Mol. Bio.* 405, 11070 (2011)).



(4A, 4pts). Propose a set of experiments that allow you to determine ΔG°, ΔH°, ΔS°, and K of the binding reaction. Describe how these thermodynamics parameters are obtained.

(4B, 2pts). If the binding affinity (i.e. association equilibrium constant) increases two-fold, what is the difference on Gibbs free energy of binding?

(4C, 4pts). As seen in the figure, surprisingly, there are no apparent change in Gibbs free energies of binding on all these modified substrates. Please propose a molecular model to explain this set of data.

(5, 10pts)

N distinguishable particles can only exist in one of the 3 non-degenerate energy levels of energies **−ε**, **0** and **+ε**. The system is in contact with a thermal reservoir at temperature T.

(5A, 2pts) What is the canonical partition function?

(5B, 4pts) What is the average energy of the system?

(5C, 4pts) What is the value of $\int_0^\infty \frac{C_V(T)}{T} dT$?

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二、分析試題

Attentions:
a) **Do not** leave your answers in the table on the first page of the answer booklet. Write all your answers in the second and subsequent pages of the answer booklet.
b) Answers should appear in order in the answer booklet. Each answer should be preceded with its question number/code. Answers not preceded with question numbers/codes will not be credited.
c) No explanation or calculation is required in the answer to the multi-select question.
d) Pay attention to the sign and unit of your answers.

I. Multi-select question (12%)

Choose one or more answers from the list of answers provided for each question below. Penalty of 50% credit to the correct answer will be applied for the incorrect choice. No penalty will be applied for failure to choose the correct answer, though.

1. Which of the following statements related to data treatment is (are) correct?
   (A) The *medium* is the most common number in a data set.
   (B) The *coefficient of variation* and *relative standard deviation* have the same value.
   (C) The *standard error of the mean* is given by the standard deviation of the data set divided by the number of measurements.
   (D) The mean is known with more confidence than is a single result.
   (E) As the sample size increases, the confidence interval increases.
   (F) As the standard deviation increases, the confidence interval decreases.

2. Which of the following statements about normal distribution is (are) correct?
   (A) Bell-shaped distributions are normal distributions.
   (B) Approximately 95% of the area of a normal distribution is within three standard deviations of the mean.
   (C) The median and mode are not equal for a normal distribution.
   (D) Normal distributions can differ in their means and in their standard deviations.
   (E) The average of many observations of a random variable with finite mean and variance is itself not a random variable.
   (F) Normal distributions are often used in the natural and social sciences to represent real-valued random variables whose distributions are not known.

3. Which of the following analytical statistics statements is (are) correct?
   (A) A user repetitively reading the volume marking on the pipet from an angle rather than at eye level causes random error.
   (B) Random error causes data to be scattered more or less symmetrically around a mean value.
   (C) The relative error of a measurement is the difference between the measured value and the true value divided by the standard deviation.
   (D) Systematic method errors can be decided by application of the method to the analysis of a standard reference material having one or more analytes at known concentration levels.
   (E) The mean is the middle result when replicate data are arranged according to increasing or decreasing value.
   (F) Proportional systematic errors can be detected by varying the sample size.

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4. Which of the following statements about spectrophotometer is (are) correct?
(A) In a single-beam spectrophotometer, the solvent and solution are irradiated simultaneously or nearly so.
(B) A double-beam spectrophotometer employs a fixed beam of radiation that irradiates the solvent and the analyte solution sequentially.
(C) The single-beam spectrophotometer can be adapted to automatic spectral recording easier than the double-beam spectrophotometer.
(D) Problems arising from fluctuations in the source intensity due to drift in electronic circuits are less in double-beam spectrophotometers than single-beam spectrophotometers.
(E) Diode-array spectrophotometers can detect the entire spectral range essentially simultaneously and can produce a spectrum in less than a second.
(F) The resolution of diode-array spectrophotometers is usually higher than that of conventional spectrophotometers.

5. Which of the following statements about molecular absorption and luminescence spectrometries is (are) correct?
(A) The dissociation, association, and reaction of analytes with the solvent will not cause deviations from Beer's Law.
(B) The most common source of visible and near-IR radiation is the deuterium/hydrogen lamp.
(C) The visible region includes the wavelength range between 200 and 300 nm.
(D) A triplet state is one in which the spins of the electrons of an atom or molecule are paired so that their spin angular moments add to give a net non-zero moment.
(E) Resonance fluorescence is observed when an excited species emits radiation of the same frequency as that used to cause the excitation.
(F) Vibrational relaxation is the process by which a molecule loses its excess vibrational energy without emitting radiation.

6. Which of the following statements about atomic spectrometry is (are) correct?
(A) An ionization suppressor is more easily ionized than the analyte and provides a high concentration of electrons in the flame or plasma.
(B) Pressure broadening refers to the broadening of atomic lines due to sample vaporization and decomposition.
(C) One single lamp is used in flame atomic absorption for analyzing different elements.
(D) An x-ray source is a tube filled with low-pressure argon in which a tungsten filament cathode and a massive anode are mounted.
(E) Atomic emission methods with an ICP source is suited for multielement analysis.
(F) A scintillation counter is an instrument for detecting and measuring non-ionizing radiation by using the excitation effect of incident radiation on a scintillating material.

7. Which of the following statements about mass spectrometry is (are) correct?
(A) An electron multiplier is a vacuum-tube structure, in which a secondary emission process takes place and a single charge can bombard on secondary-emissive material and induce emission of several ions.
(B) Among different ion sources for molecular mass spectrometry, the most fragmentation is encountered with electron ionization, which does not produce the most complex spectra, though.
(C) The selection of sample ions in the quadrupole mass analyzer for detection is only made possible through applying a radio frequency voltage to one fixed pair of rods and a dc offset voltage to the other.
(D) An electric voltage and a magnetic field are needed in both FT ICR and TOF mass spectrometers.
(E) The resolution of a quadrupole is determined by the ratio of the ac to dc voltage and becomes a maximum when this ratio is just slightly less than 6.
(F) ICPMS uses an inductively coupled plasma to separate ions and a mass spectrometer to detect them.

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II. Fill-in-the-blank (14%)

8. The following sentences state the essence of some important/useful equations developed and used in analytical chemistry. In *each* of the blanks of the following question, fill, in English, *one* word only from the list below so as to best complete the sentence that concisely reveals the analytical chemistry concepts behind the equations. Only the singular noun of the possible answer is provided in the list.

salt, matrix, mass, sensitivity, variance, molarity, size, strength, balance, limit, aliquot, dropping, population, equilibrium, parallax, diffusion, eluate, zwitterion, ionic, diameter, standard, formal, rate, buoyant, velocity, error, conjugate, trace, saponification, Levich, Beer–Lambert, Michaelis–Menten, low, high, detection, charge, reduction, oxidation, current, potential, suspension

(a) The Nernst equation relates the _____ potential of an electrochemical reaction (half-cell or full cell reaction) to the ___ electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation.

(b) The Henderson-Hasselbalch equation is used to calculate the pH of the buffer solution based on the concentrations of the acid and of a _____ of its _____ base in the solution.

(c) In polarography, the Ilkovic equation relates the _____ current and the concentration of the depolarizer, which is the substance reduced or oxidized at the _____ mercury electrode.

(d) In cyclic voltammetry, the Randles–Ševčík equation describes the effect of scan _____ on the peak _____.

(e) The _____ law equation relates the attenuation of light to the properties of the material through which the light is travelling.

(f) The Debye-Hückel Limiting Law equation enables one to determine the activity coefficients of ions in a solution of very ___ ionic _____ based on their _____.

(g) The van Deemter equation relates the _____ per unit length of a separation column to the linear mobile phase _____ by considering physical, kinetic, and thermodynamic properties of a separation.

III. Analytical calculations and concepts

9. Assume that the conjugate base, X^-, of an acid can react simultaneously with Hg^{2+} and Cu^{2+}, forming 1:1 complexes that exhibit absorption maxima at 255 nm and 620 nm, respectively. Their molar absorptivity (L/mol-cm) values are as follows:

	255 nm	620 nm
HgE	4.00×10^2	1.00×10^3
CuE	1.00×10^4	2.00×10^3

A solution sample of 10.0 mL containing Hg^{2+} and Cu^{2+} was obtained. It was treated with an excess of X^- and no ions other than Hg^{2+} and Cu^{2+} absorb at 255 nm and 620 nm. Following the treatment, the solution is diluted to 100.0 mL before conducting spectroscopic measurements. The measurements display an absorbance of 0.600 at 255 nm and 0.350 at 620 nm when measured in a 1.00-cm cell. (a) Calculate the molar concentrations of Hg^{2+} and Cu^{2+} in the sample. (b) The spectrophotometric measurements are often limited by the indeterminate errors associated with the spectrophotometer used. A detailed theoretical and experimental study showed that the errors on the precision of concentration measurements fall into three categories: (1) independent of T, (2) proportional to the square root of T^2+T, and (3) proportional to T. (i) Discuss the main sources of error and their relations to the quality and components of spectrophotometers. (ii) Sketch with proper labels a plot of relative concentration error vs. absorbance for the three categories of error and state how absorbance is affected. (10%)

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10. Each electroanalytical method (such as potentiometry, coulometry, and voltammetry) is by itself a group of techniques available from changes in experimental configuration and/or component. For example, there are two basic categories of coulometric techniques: potentiostatic coulometry and coulometric titration. (a) Select two out of the three electrochemical methods (i.e., potentiometry, coulometry, and voltammetry) mentioned above and name one technique for each of the two. (b) For each technique you named in (a), ***sketch*** (with proper labeling of each component – Pay attention to the fact that a component may have different names in different electroanalytical methods) the related experimental setup and ***describe*** (i) the electrical observables measured, (ii) the preferred experimental condition, and (iii) the operation/working principle, and then ***draw*** a representative plot (with proper labeling) produced from analyzing a chemical species of your interest using the named technique. (14%)

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