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國立臺灣大學 107 學年度碩士班招生考試試題

科目: 物化分析

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※ 注意:請於試卷上「非選擇題作答區」內依序作答,並應註明作答之部份及其題號。

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 to questions 1-6 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) The following math may be of some use: exp(1.00)=2.718; exp(2.00)=7.389; exp(3.00)=20.09; exp(5.00)=148.4; ln(2.00)=0.6931; ln(3.00)=1.099; ln(5.00)=1.609	
I. Fill	n-the-blank (10%)
	in each of the blanks in the following sentences with the <u>most proper</u> answer in the list below. Please note that only the singular noun of possible answer is provided in the list. No penalty will be applied for incorrect answers. The answer for a) is provided for your reference.
	eptization, diffusion, Rayleigh scattering, concentration polarization, sampling, evaporation, dead time, bumping, Jones reductor, tandard deviation, Raman scattering, coagulation, solubility product, common-ion effect, confidence level, time of flight, coefficient of ariation, kinetic polarization, Mohr method, confidence limit, limit of linearity, dispersion, migration, electrolyte effect, elution time, tandard deviation about regression, dissolution
a)	Diffusion is the movement of a species under the influence of a concentration gradient.
b)	is the elastic scattering of light or other electromagnetic radiation by particles much smaller than the wavelength fithe radiation.
c)	is the process by which a representative fraction of the material of interest is acquired.
d)	is the time it takes for an unretained species to pass through a chromatographic column.
e)	is a sudden, often violent boiling that tends to spatter solution out of its container.
f)	is the boundary around the mean of a set of replicate analytical results within which the population mean can be xpected to lie within a certain probability.
g)	is the effect that results from the electrostatic attractive and repulsive forces that exist between the ions of an lectrolyte and the ions involved in an equilibrium.
h)	is a band-spreading or mixing phenomenon occurring in continuous flow methods that results from the coupling f fluid flow with molecular diffusion.
i)	is the behavior indicated by the decrease in solubility of an ionic precipitate when a soluble compound containing ne of the ions of the precipitate is added to the solution.
j)	helds the finely divided amalgamated zinc in a narrow, vertical tube through which the solution to be reduced is rawn under a mild vacuum.
k)	occurs because of the finite rate of electron transfer between the reactant and the electrode on one or both

electrodes such that the magnitude of the current is limited.

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II. Multi-select question

(12%)

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

- 2. Which of the following instrumental method (methods) makes (make) use of electrons emitted from samples for analysis?
 - (A) FIA
- (B) TOFMS
- (C) STM
- (D) MALDI
- (E) AES
- (F) Ellipsometry
- 3. Which has (have) these types of electromagnetic radiation arranged from left to right in order of increasing wavelength?
 - (A) ultraviolet, visible, radiowave
- (B) infrared, microwave, radiowave
- (C) microwave, x-ray, gamma ray
- (D) microwave, ultraviolet, gamma ray
- (E) radiowave, infrared, x-ray,
- (F) visible, infrared, radiowave
- 4. Which of the following statement (statements) is (are) true?
 - (A) Absorbance is the reciprocal of transmission.
 - (B) Transmittance is the logarithm of transmission.
 - (C) Absorbance is the logarithm of optical density.
 - (D) Transmittance is directly proportional to the analyte concentration.
 - (E) Molar absorptivity is independent of the irradiation wavelength.
 - (F) none of these
- 5. Which of the following statement (statements) related to Beer's law is (are) true?
 - (A) Beer's law is a limiting law.
 - (B) At a fixed concentration, there is a linear relationship between absorptivity and path length.
 - (C) At a constant path length, deviations from the direct proportionality between absorbance and concentration may occur.
 - (D) Real deviations are fundamental limitations to the law.
 - (E) Absorptivity dependence on the refractive index of the medium is a chemical deviation from the law.
 - (F) The linear variation in absorptivity of the analyte over the absorption band results in little deviation from the law.
- 6. Which of the following statement (statements) is (are) true?
 - (A) The dissolution of ZnS in dilute HCl is due to the decrease in S²-concentration by the formation of H₂S.
 - (B) Adding a strong base can ensure complete precipitation of SnS from a saturated H₂S solution.
 - (C) The concentration of H₂S in its saturated solution varies significantly with pH.
 - (D) The S²-concentration of a saturated H₂S solution varies inversely with the square of the hydrogen ion concentration.
 - (E) The solubility of a divalent metal sulfide increases directly with the hydrogen ion concentration.
 - (F) none of these

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III. Calculation and essay questions

7. An experiment is carried out to determine the amount of manganese in a metal sample. At first, nitric acid is used to dissolve the sample, in which Mn^{2+} ions are produced. They are then oxidized by IO_4^- in acid solution to produce MnO_4^{2-} . (A) Write down the balanced chemical equations and their corresponding E°_{cell} for both nitric acid oxidation and IO_4^- oxidation. (B) Calculate (a) ΔG° of the nitric acid oxidation at 300 K and (b) K_{eq} of the IO_4^- oxidation occurring in the experiment conducted at 300 K. $(E^{\circ}(NO_3^-/NO) = +0.96 \text{ V}; E^{\circ}(IO_4^-/IO_3^-) = +1.60 \text{ V}; E^{\circ}(MnO_4^-/Mn^{2+}) = +1.51 \text{ V}; E^{\circ}(Mn^{2+}/Mn) = -1.18 \text{ V})$ (8%)

- 8. On March 21, 2017, President Donald Trump signed a law that mandates NASA send people to Mars by 2033. It is known that when fully assembled and fueled, the subsystems, scientific instruments, and astronauts (a crew of four in plan at present) on board the spaceship to Mars must weigh in total less than 1,031 kg or the Atlas V launch vehicle will not be able to maneuver the spaceship's trajectory correctly. In addition, for human exploration of Mars and the possible permanent human settlement, water will be a major resource since it is essential to life. Search for accessible water other than Martian polar caps that include water ice has thus actively undertaken. In Jan. 2018, a paper published in *Science* reported exposed subsurface ice sheets in the Martian mid-latitudes.
 - (a) Suggest by naming one spectroscopic analysis method that may be <u>feasibly</u> carried out in the Mars mission for water analysis. (b) With the method of your suggestion, discuss clearly the procedures with which water may be (i) qualitatively confirmed and (ii) quantitatively analyzed (hint: specific calibration method should be named and described in your procedure). (c) For the method of your suggestion, (i) name one each specific probe source, wavelength selector, and detector you would suggest to be used; (ii) discuss the operation principle of each instrument component named in (i), (iii) discuss the advantages and disadvantages of the components you named in (i) over at least one other possible component alternatives; and (iv) summarize why you suggest the use of these components in the Mars mission. (20%)

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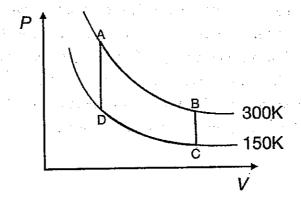
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- (1) (15 pts) An engine is operating between the two heat reservoirs at the temperatures 300K and 150K. The engine contains 1 mole ideal gas and follows the path in the figure below.
 - (a) From point A to point B the gas expands isothermally at 300K from 10L to 30L. Calculate the work done on the gas, the heat, and the entropy change of this process. (R=8.314 JK⁻¹mol⁻¹)
 - (b) From B to C, the volume of the gas is fixed at 30L. The gas is cooled down by transferring heat to the 150K reservoir. The heat capacity of the gas is $C_V = 3R/2$. Calculate the heat, the entropy change of the gas, and the entropy change of the 150K reservoir.
 - (c) From C to D, the gas is compressed isothermally at 150K. From D to A, the volume is fixed at 10L and the gas obtains energy from the 300K reservoir. Calculate the efficiency of this engine. What is the efficiency limit set by the Carnot engine?



(2) (10 pts) A two components solution has the molar Gibbs energy of mixing

$$\Delta_{mix}G = RT[x_A \ln a_A + x_B \ln a_B]$$

where x_A , x_B are the mole fractions of the two species. The activities a_A , a_B approach the mole fractions in the respective dilute limits. Suppose that the activity coefficients obey

$$\ln \gamma_A = \xi x_B^2$$

$$\ln \gamma_B = \xi x_A^2$$

where ξ is an enthalpy parameter.

- (a) Calculate the critical enthalpy parameter ξ_c , above which the solution will phase separate into two phases.
- (b) Suppose that the enthalpy parameter ξ is non-negative, and it is proportional to T^{-1} . Plot the qualitative temperature-mole fraction phase diagram.

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(3) (25 pts) A particle is confined in a box of length L. The 1D motion of the particle is described by the time dependent Schrodinger equation. Inside the box $0 \le x \le L$, the potential is zero, while outside the box the potential is very high (infinite). Suppose that at time zero the particle is described by the wave function $\psi(x, t = 0) = N(2\sin(3\pi x/L) - i\sin(2\pi x/L))$ where $i = \sqrt{-1}$.

(a) Calculate the normalization constant N.

(b) What is the averaged energy of this state?

(c) Given that the momentum operator is $\hat{p}_x = -i\hbar \frac{d}{dx}$, calculate the averaged momentum of this state at t = 0, $\langle \hat{p}_x(0) \rangle$.

(d) What will be the wave function at a later time t?

(e) Using the above wave function to calculate the (quantum) averaged particle position at time t, $\langle x(t) \rangle$. Plot the function $\langle x(t) \rangle$ and compare the quantum result with the classical trajectory.

(Hint: $\int_0^1 x \sin^2(2\pi x) dx = 1/4$, $\int_0^1 x \sin^2(3\pi x) dx = 1/4$, $\int_0^1 x \sin(2\pi x) \sin(3\pi x) dx = -24/25\pi^2$, $\int_0^1 \sin(2\pi x) \cos(3\pi x) dx = -4/5\pi$, $\int_0^1 \cos(2\pi x) \sin(3\pi x) dx = 6/5\pi$)