

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 multiple-choice question. No penalty will be applied for the incorrect choice.
- d) The following math may be of some use: $\exp(1.00)=2.718$; $\exp(2.00)=7.389$; $\exp(3.00)=20.09$; $\exp(5.00)=148.4$; $\ln(2.00)=0.6931$; $\ln(3.00)=1.099$; $\ln(5.00)=1.609$

Questions 1-17 Chemical species of interest can often be analyzed using different methods. Taking the analysis of Fe(II) and/or Fe(III) in a sample as an example (atomic mass: Fe=55.8, O=16.0; formation constant: $K_{\text{Fe(II)-Y}} = 2.1 \times 10^{14}$, $K_{\text{Fe(III)-Y}} = 1.3 \times 10^{25}$; $E^0(\text{Fe}^{2+}/\text{Fe}) = -0.440\text{V}$, $E^0(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.771\text{V}$):

I.(Absorption spectrometry) The complex formed between Fe(III) and thiocyanate has a molar absorptivity of $7.50 \times 10^3 \text{ L cm}^{-1} \text{ mol}^{-1}$ at 580 nm, the wavelength of maximum absorption.

1. A sample solution of the complex in a 2.50-cm cell measured at 580 nm has the absorbance equal to that of a $4.00 \times 10^{-5} \text{ M}$ solution of the complex in a 1.00-cm cell measured at the same wavelength. Calculate the molar concentration of the complex in the sample solution. (2.5%)
2. Which of the following devices can best detect the complex at 580 nm?
(A) photoconductor (B) transmitter-receiver coil (C) proportional counter
(D) photodiode (E) Golay cell (F) electron multiplier (1.5%)
3. Which of the following statements about absorption is not correct?
(A) All spectrometries and spectroscopies, such as UV spectrophotometry, IR photometry, photoacoustic spectroscopy, nuclear magnetic resonance, and electron spin resonance spectroscopy, involve the absorption of radiation.
(B) Radiant energy can only be absorbed in definite units, or quanta.
(C) Upon absorption of light, the Fe(III)-thiocyanate complex undergoes a charge transfer process, causing transfer of an electron from the thiocyanate ion to an orbital largely associated with Fe(III) and producing an excited species involving predominantly iron(II) and the SCN radical.
(D) Light sources in atomic absorption instruments are often chopped so as to eliminate the high-frequency fluctuations inherent in flames and other atomization devices.
(E) A narrow spectral band can be isolated by coupling a cutoff filter with a second filter.
(F) none of these (1.5%)

II.(Neutralization titration) For the reaction $\text{Fe}^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{FeOH}^{2+} + \text{H}^+$, the K_{eq} (i.e., the first acidity constant, K_1 , of Fe^{3+}) is 6.46×10^{-3} .

4. Assume neutralization is the only reaction occurring when Fe^{3+} solution is titrated with NaOH and $\text{Fe}(\text{OH})_3$ is not formed during the titration. (i) Plot as accurately as possible a titration curve (with proper labels; 0.0 to 80.0 mL on x axis with ticks every 10 mL and pH values 0.0 to 14.0 on y axis with 6 ticks in between) for 50.00 mL of 0.100 M Fe^{3+} titrated with 0.100 M NaOH. (ii) Predict by drawing on the same plot of (i) the titration curve obtained when the concentrations of both Fe^{3+} and NaOH are diluted 10 times, instead. (Note: You do not have to show your calculations for this question. Pay attention to the pH values at some key points of the curves.) (5%)

5. For the reaction $\text{Fe}(\text{OH})_3 \rightleftharpoons \text{Fe}^{3+} + 3\text{OH}^-$, the K_{eq} is 1.55×10^{-39} . Calculate the base constant for the reaction $\text{Fe}(\text{OH})_3 \rightleftharpoons \text{FeOH}^{2+} + 2\text{OH}^-$. (3%)

6. In reality, multiple equilibria are established when NaOH is added slowly to pure Fe^{3+} solution. (i) From the analytical chemistry point of view, write down all chemical equations (other than those shown in this test paper) of the reactions that actually occur during the addition. Specify conditions (e.g., early stage in the addition), if needed, for the written reactions to occur. (ii) Write down the general flow chart of a systematic method for solving multiple-equilibrium problems. (5%)

III.(Complexiometric titration) The complexiometric titration of Fe(II) and/or Fe(III) may involve the use of EDTA for quantitative analysis.

7. A chemical effect causes EDTA to be more preferable than NH_3 in complexiometric titrations of Fe(II) and Fe(III). (i) Name the chemical effect and (ii) explain the effect based on thermodynamic arguments. (3.5%)

8. A 50.00-mL aliquot of a solution containing Fe(II) and Fe(III) required 6.00 mL of 0.01500 M EDTA when titrated at pH 2.0 and 8.00 mL of 0.01500 M EDTA when titrated at pH 6.0. Calculate the concentrations of Fe(II) and Fe(III) in ppm. (3.5%)

9. Which of the following statements concerning auxiliary complexing reagent is correct?

- (A) The reagent is used to control the pH.
 - (B) The reagent is used to control the amount of free EDTA.
 - (C) The reagent is used to displace metal from the metal-EDTA complex.
 - (D) The formation constant of the reagent with the analyte must be larger than the constant of EDTA with the analyte.
 - (E) The reagent does not undergo complexation reactions.
 - (F) None of these
- (1.5%)

IV.(Electrochemical method) The electrochemical method is based on redox reactions for quantitative analysis.

10. The potential $E^0(\text{Fe}^{3+}/\text{Fe}^{2+})$ found in the electrode potential table is a formal potential. Define formal potential and explain why the standard potential is not listed in the table for $E^0(\text{Fe}^{3+}/\text{Fe}^{2+})$. (3%)

11. Calculate the K_{eq} and ΔG° of the redox reaction involved in the titration of Fe(II) with KMnO_4 at pH2 at 25°C. ($E^0(\text{MnO}_4/\text{Mn}^{2+}) = +1.51\text{V}$) (5%)

12. Which of the followings cannot be used as auxiliary reducing agent in the determination of iron in a sample?

- (A) Walden reductor (B) Jones reductor (C) Zn(Hg) (D) $\text{H}_2\text{S}(\text{g})$
(E) $\text{SO}_2(\text{g})$ (F) none of these (1.5%)

V.(Mass spectrometry) Mass spectrometry (MS) is a powerful technique for analyzing metals in biological systems.

13. In theory, which of the following mass analyzers is best in terms of throughput and high m/z for use in studying biological systems?

- (A) quadrupole (B) magnetic sector (C) electrostatic sector (D) TOF
(E) quadrupole ion trap (F) ICR (1.5%)

14. Iron is an essential micronutrient for marine microbes. The concentrations of dissolved Fe in the ocean are very low (<1 nM), however. Over 99% of the dissolved Fe are present as complexes with organic ligands. Which of the followings is the best ion source in mass spectrometry for real-time monitoring of the dissolved Fe in the ocean?

- (A) EI (B) FI (C) CI (D) ESI (E) DART (F) MALDI (1.5%)

VI.(Luminescence spectrometry) Iron in our body is involved in numerous physiologically essential processes, such as oxygen transport, DNA synthesis, and metabolic reactions.

15. If the concentration of fluorescing molecules in the sample is C , the fluorescence intensity of the sample is proportional to

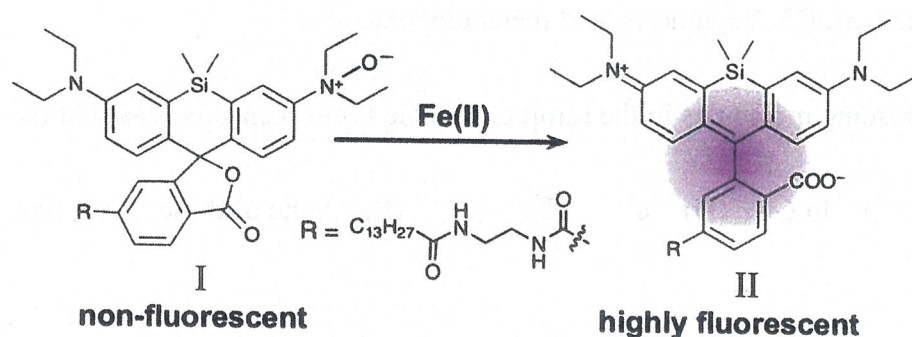
- (A) C (B) $\log C$ (C) $\ln C$ (D) e^C (E) $-e^C$ (F) none of these (1.5%)

16. Which of the following statements about luminescence is not correct?

- (A) The quantum efficiency for fluorescence or phosphorescence is the ratio of the number of molecules that luminesce to the total number of excited molecules.
- (B) The quantum efficiency of most complex molecules is independent of the wavelength of exciting light.
- (C) When the external energy supply is by means of the absorption of infrared, visible or ultraviolet light, the emitted light is called photoluminescence.
- (D) Molecular structure influences whether a substance will or will not luminesce, whereas chemical environment does not influence.
- (E) Oxygen is very effective at destroying triplet states even at low concentrations.
- (F) none of these

(1.5%)

17. Due to factors such as the reductive cellular environment and water solubility, protein-free or weakly protein-bound iron (called labile iron) in living organisms exists as Fe(II) ion rather than Fe(III) ion. Labile Fe(II) is potentially toxic because of its uncontrolled redox activity and its action as a catalyst to generate hydroxyl radicals which causes severe cellular damage. The transport of labile Fe(II) is partially regulated by a protein-sorting system. By probing labile Fe(II), a study published in *Chem. Sci.* in October, 2018 successfully revealed an abnormal cellular iron distribution induced by dysfunction of the protein-sorting system that is known to be involved in the pathogenic mechanisms of severe neurodegenerative diseases including Alzheimer's disease and Parkinson's disease. The success relied in part on the authors' development of a suitable fluorescent probe, Compound I, as shown in the figure below, for detection of Fe(II). The detection was achieved via fluorescence occurring only when Compound I reacted with Fe(II), producing highly fluorescent Compound II. (i) Based on the molecular structures shown in the figure, list the favorable spectroscopic processes and conditions involved in the better luminescence of Compound II than Compound I. (ii) List the favorable experiment conditions in which the research has to be carried out for maximizing luminescence intensity to successfully map the cellular iron distribution. (iii) Discuss the chemical and luminescent rationales behind your answers for (i) and (ii) and explain why the luminescence intensity of Compound II is higher than Compound I.



(7.5%)

18. (10%) Suppose that a person counts out gold atoms at the rate of one each second for the entire span of an 80-year life. Has the person counted enough atoms to be detected with an ordinary balance? Explain.
19. (10%) N_2 has equilibrium bond length of 1.100 Å and bond dissociation energy of 942 kJ mol⁻¹, whereas O_2 has equilibrium bond length of 1.211 Å and bond dissociation energy of 495 kJ mol⁻¹. On the same graph show qualitative sketches of the effective potential energy curve for N_2 and O_2 .
20. (10%) When metallic sodium is dissolved in liquid sodium chloride, electrons are released into the liquid. These dissolved electrons absorb light with a wavelength near 800 nm. Suppose we treat the positive ions surrounding an electron crudely as defining a three-dimensional cubic box of edge L , and we assume that the absorbed light excites the electron from its ground state to the first excited state. Calculate the edge length L in this simple model.
21. (10%) The molecular ion HeH^+ has an equilibrium bond length of 0.774 Å. Draw an electron correlation diagram for this molecule, indicating the occupied MOs. If the lowest energy MO has the form $C_1\psi_{1s}^{\text{H}} + C_2\psi_{1s}^{\text{He}}$, do you expect C_2 to be larger or smaller than C_1 ?
22. (10%) Suppose 60.0 g hydrogen bromide, $\text{HBr}(g)$, is heated reversibly from 300 to 500 K at a constant volume of 50.0 L, and then allowed to expand isothermally and reversibly until the original pressure is reached. Using $c_P(\text{HBr}(g)) = 29.1 \text{ J K}^{-1} \text{ mol}^{-1}$, calculate ΔU , q , w , ΔH , and ΔS for this process. Assume that HBr is an ideal gas under these conditions.

(Electron mass $m_e = 9.1094 \times 10^{-31} \text{ kg}$; Planck's constant $h = 6.6261 \times 10^{-34} \text{ m}^2 \text{ kg/s}$; the speed of light $c = 2.9979 \times 10^8 \text{ m/s}$; Gas constant $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; Boltzmann constant $k_B = 1.3806 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$)

試題隨卷繳回