國立成功大學107學年度碩士班招生考試試題

系　所：化學系

考試科目：分析化學　　　　考試日期：0206，節次：4

※ 考生請注意：本試題不可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

Part I. Single or Multiple choice questions. Each question has one or more answers. (65%, 5 points for each question.)

1. Which of the following statements about the figure of merit for analytical methods is/are correct?
   (A) Calibration sensitivity refers to the slope of a calibration curve and suffers from its failure to take into account the precision of individual measurements.
   (B) Analytical sensitivity refers to the slope of a calibration curve divided by the standard deviation of the measurement and is not concentration dependent.
   (C) Detection limit is the minimum concentration or mass of an analyte that can be detected at a known confidence level.
   (D) Limit of quantitation is the lowest concentration at which quantitative measurement can be made, and is generally taken to be three times the standard deviation of repetitive blank measurement.
   (E) Linear dynamic range of an analytical method refers to the analyte concentration ranging from detection limit to the limit of linearity.
2. Which of the following statement about pH indicators is/are correct?
   (A) The color transition range of an appropriate indicator must fall within the steep equivalence point break of the titration curve.
   (B) Considering the capability to identify color changes of the pH indicator with naked eyes, the difference between the pK_a of the indicator and the pH of the equivalence point must be within ± 0.1
   (C) The color change of a pH indicator is typically insensitive to the presence of colloidal particles.
   (D) To indicate the equivalence point for the titration of a weak base with a strong acid, methyl orange (pK_a 3.46) is a better choice than thymolphthalein (pK_a 9.90).
   (E) The pH interval over which a given indicator exhibits a color change is significantly influenced by the ionic strength of the medium and the presence of organic solvent.
3. Which of the following statements about reported models to describe electrical double layers of colloids in aqueous solution is/are correct?
   (A) In Gouy-Chapman model, the charge distribution of ions from the charged surface of colloids can be described with Maxwell–Boltzmann distribution.
   (B) In Helmholtz model, the potential distribution in the solution is an exponential function of the distance from the colloid surface.
   (C) In Stern model, some ions adhere to the charged surface as suggested by Helmholtz, while some form a Gouy-Chapman diffuse layer.
   (D) In Helmholtz model, the electrical double layer is described as a capacitor-like structure, which consists of two layers of charges with opposite polarity formed at the solid-liquid interface.
   (E) The Gouy-Chapman model overemphasizes the rigidity of the local solution located at the solid-liquid interface.
4. An ion-selective electrode is applied to determine the concentration of a standard calcium (Ca^{2+})

solution. The determined concentration displays a relative error of 3.9%. What is the corresponding error in potential measurement recorded in this measurement?

(A) 0.1 mV
(B) 0.5 mV
(C) 1.0 mV
(D) 1.5 mV
(E) 2.0 mV

5. Which of the following statements about a reference electrode in electrochemical system is/are correct?
(A) The electrode must have a well-known and stable equilibrium potential.
(B) An ideal reference electrode displays almost infinite charge transfer rate.
(C) An ideal polarized electrode is a good candidate as a reference electrode.
(D) For a reference electrode, there is no electrode reaction can occur with a fairly wide applied potential.
(E) The potential of an ideal reference electrode can be maintained at its equilibrium potential with the application of even a large current density.

6. Calculate "y" including the absolute standard deviation and round the result to include only significant figures. $y = \dfrac{187(\pm 6) - 89(\pm 3)}{1240(\pm 1) + 57(\pm 8)}$
(A) 0.075559(±0.005200)
(B) 0.07556(±0.00382)
(C) 0.0756(±0.0038)
(D) 0.076(±0.005)
(E) 0.08(±0.01)

7. Calculate E^0 for the following process $Cu(NH_3)_4^{2+} + e^- \leftrightarrow Cu(NH_3)_2^{+} + 2NH_3$, given that

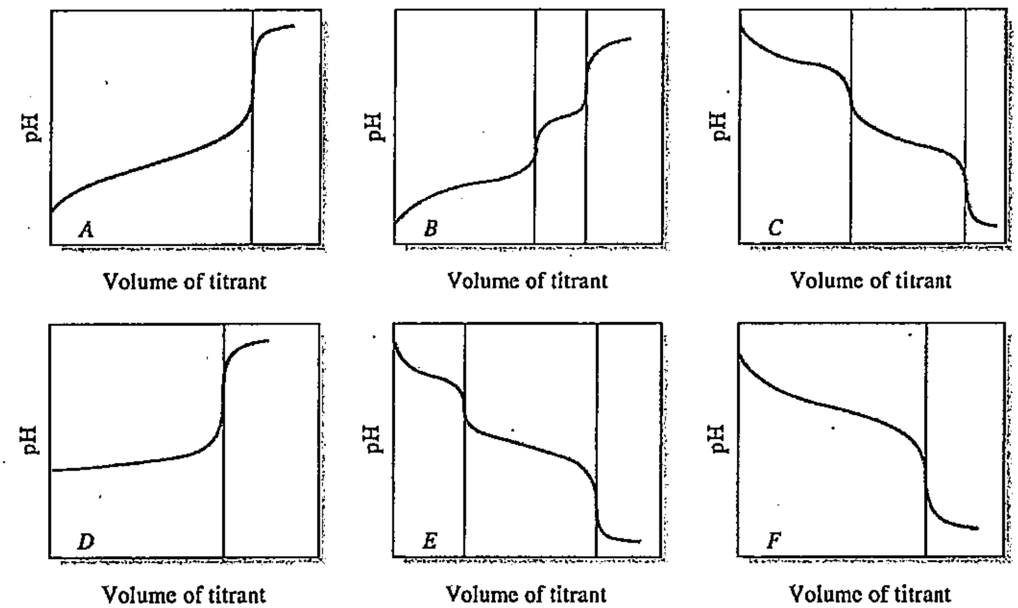
$Cu^+ + 2NH_3 \leftrightarrow Cu(NH_3)_2^+$ $K_f = 7.2\times10^{10}$
$Cu^{2+} + 4NH_3 \leftrightarrow Cu(NH_3)_4^{2+}$ $K_f = 5.62\times10^{11}$

(A) 0.21 V
(B) 0.11 V
(C) 0.22 V
(D) 0.09 V
(E) 0.25 V

8. For the following solutions, which sequence is/are correct to describe their relative buffer capacity?
a. 5 mL of 2.0 M C_2H_5COOH + 10 mL of 0.1 M C_2H_5COON
b. 25 mL of 2.0 M C_2H_5COOH + 10 mL of 0.5 M C_2H_5COONa
c. 20 mL of 2.50 M C_2H_5COOH + 50 mL of 0.96 M C_2H_5COONa
d. 10 mL of 1.0 M C_2H_5COOH + 4 mL of 2.4 M C_2H_5COONa

(A) b>a>c>d
(B) a>c>b>d
(C) c>b>d>a
(D) b>c>a>d
(E) c>d>b>a

9. About the following titrations curves, which statements is/are correct?



(A) A is a typical titration curve for a strong acid titrated with a strong base, while D is related to a weak acid titrated by a strong base.
(B) B could be the curve of an acid mixture composed of 0.75 M CH_3COOH and 0.5 M H_2S titrated by KOH
(C) C could be the titration curve of $Na_2C_2O_4$ with HCl.
(D) E could be the curve of a base mixture composed of equal amount of $NaHCO_3$ and Na_2CO_3 titrated by HCl.
(E) F could be the titration curve of NH_4CN with HCl.

10. Which of the following is/are not factors that influence the band broadening observed in atomic spectrum?
(A) Doppler effect
(B) Pressure effect
(C) Uncertainty effect
(D) Solvent effect
(E) Temperature effect

11. Which of the following statements is true about instrumental noise?
(A) Thermal noise is caused by thermal agitation of charge carries in components of an instrument and does not exist when there is no current flowing in the instrument.

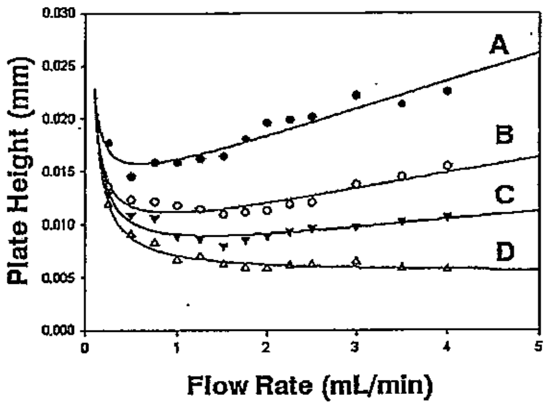
(B) Environmental noise is a combination of different forms of noise that arise from the surroundings.

(C) Jonson noise can be reduced by cooling the instrument.

(D) Shot noise belongs to white noise and can only be decreased by reducing the bandwidth of signal.

(E) The magnitude of flicker noise is proportional to signal frequency and thus shows significantly influence on the measurement with high frequency.

12. Consider the experimental data collected for separation on four columns identical in all ways except for the size of the stationary phase particles. Which of the following statements is/are true?



(A) The particle size of the stationary phase of these four columns shows the following relationship: A<B<C<D

(B) Column D would show the best resolution for two similar solutes.

(C) The relationship between plate height and the flow rate can be described with Van Deemter equation.

(D) Column A shows the heighest efficiency for sample separation.

(E) The relationship between particle size and plate height can be described with Snyder equation.

13. The ion-accelerating voltage in a particular quadrupole mass spectrometer is 5.00 V. How long would it take a singly charged cyclohexane ion to travel the 15.0 cm length of the rod assembly? Assume that the initial velocity of the ion in the z direction is zero.

(A) 31.3 μs

(B) 44.3 μs

(C) 62.6 μs

(D) 54.3 μs

(E) 22.4 μs

Part II. Problem-solving and short answer questions. Please show all work, steps, units and explanation if applicable. (35%)

1. The figure shown below describes the changes of concentration equilibrium constants as a function of electrolyte concentration.

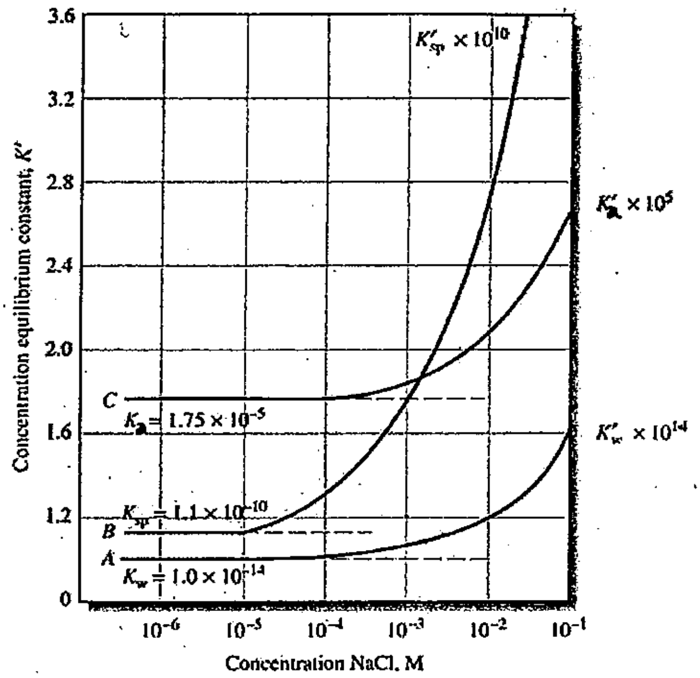
K'_{sp}: concentration-based solubility product of $BaSO_4$

K'_a: concentration-based dissociation constant of HCl

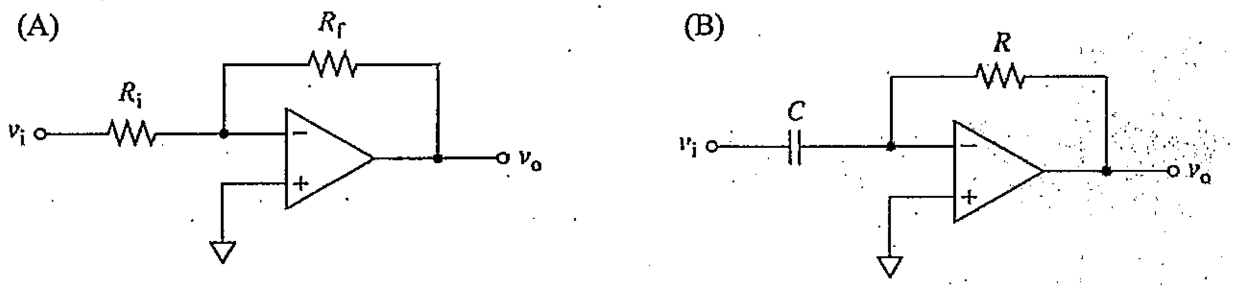
K'_w: concentration-based ionic product of H_2O

(A) Explain why these concentration equilibrium constants change with the concentration of NaCl. (5 points)

(B) What will happen to these curves if the solution electrolyte, NaCl, is replaced with Na_2SO_4? (5 points)



2. For the following operational amplifier circuits, "derive" equations to show the relationship between the input (v_i) and output (v_o) signals. (10 points)



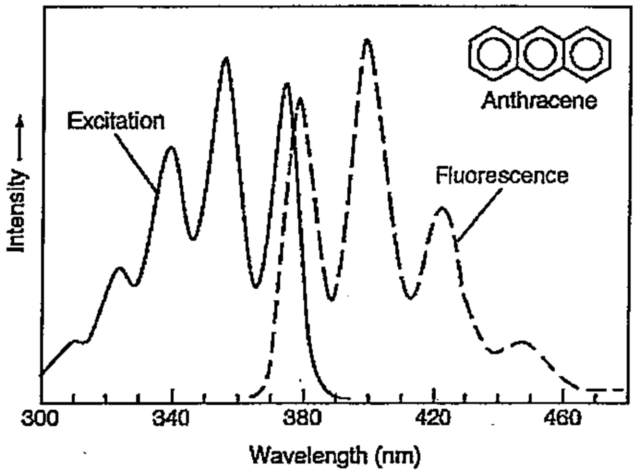
3. The sodium salt of 2-quinizarinsulfonic acid (NAQ) forms a complex with Al^{3+} that absorbs radiation strongly at 560 nm. Use the data shown below to find the formula of the complex. (5 points)

c_Q (M)	A_{560}
1.00×10^{-5}	0.131
2.00×10^{-5}	0.265
3.00×10^{-5}	0.396
4.00×10^{-5}	0.468
5.00×10^{-5}	0.487
6.00×10^{-5}	0.498
8.00×10^{-5}	0.499
1.00×10^{-4}	0.500

4. The figure shown below describes the excitation and emission (fluorescence) spectra of anthracene.

(A) Please explain why the excitation spectrum and the fluorescence spectrum for a compound often appear as approximate mirror images. (5 points)

(B) Based on the excitation and emission (fluorescence) spectra, what excitation and emission wavelength should be chosen to maximized the measured fluorescence intensity. (5 points)



Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		