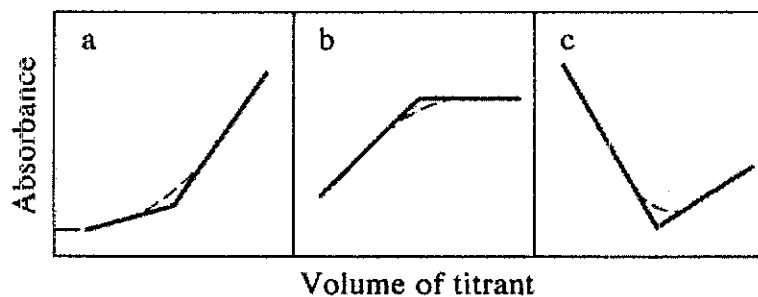※ 考生請注意：本試題不可使用計算機。　請於答案卷(卡)作答，於本試題紙上作答者，不予計分。

Part I.　Single or Multiple choice questions. Each question has one or more answers. (80%, 5 points for each question.)

1.　Which of the following statements about liquid-junction potential is/are not correct?

　　(A) A liquid-junction potential develops across the boundary between two electrolytes with different compositions.

　　(B) The magnitude of liquid-junction potential is determined by the diffusion of more diluted electrolyte.

　　(C) The liquid-junction potential arises from an unequal distribution of cations and anions across the boundary due to differences in the diffusion rates of these ions.

　　(D) In terms of minimizing the liquid-junction potential, the salt bridge containing 1.0 M KCl is more effective than that filled with 1.0 M HCl.

　　(E) The liquid junction potential can be minimized by keeping a low concentration of a salt, which has constituent ions have nearly the same mobility, on one side of the boundary.

2.　Three typical photometric titration curves are shown below. Which combination about the molar absorptivities of each curve is/are correct? The molar absorptivities of the substance titrated, the titrant and the product are represented as ε_s, ε_t, and ε_p.


Volume of titrant

　　(A) a: $\varepsilon_s = \varepsilon_p = 0$, $\varepsilon_t > 0$; b: $\varepsilon_p > \varepsilon_t > 0$, $\varepsilon_s = 0$; c: $\varepsilon_p = \varepsilon_t = 0$, $\varepsilon_s > 0$

　　(B) a: $\varepsilon_t > \varepsilon_p > 0$, $\varepsilon_s = 0$; b: $\varepsilon_p = \varepsilon_t = 0$, $\varepsilon_s > 0$; c: $\varepsilon_s = \varepsilon_p = 0$, $\varepsilon_t > 0$

　　(C) a: $\varepsilon_p > \varepsilon_t > 0$, $\varepsilon_s = 0$; b: $\varepsilon_s = \varepsilon_t = 0$, $\varepsilon_p > 0$; c: $\varepsilon_p = \varepsilon_t = 0$, $\varepsilon_s > 0$

　　(D) a: $\varepsilon_t > \varepsilon_p > 0$, $\varepsilon_s = 0$; b: $\varepsilon_s = \varepsilon_t = 0$, $\varepsilon_p > 0$; c: $\varepsilon_s > \varepsilon_t > 0$, $\varepsilon_p = 0$

　　(E) a: $\varepsilon_s = \varepsilon_p = 0$, $\varepsilon_t > 0$; b: $\varepsilon_t > \varepsilon_p > 0$, $\varepsilon_s = 0$; c: $\varepsilon_s > \varepsilon_t > 0$, $\varepsilon_p = 0$

3.　Which of the following statements is/are true for the electrical double layer (EDL) formed at electrode surface as a result of an applied potential?

　　(A) The EDL consists of a layer of charge accumulated at the electrode surface due to the applied potential and a layer with a net opposite charge in the solution surrounding the electrode.

　　(B) The formation of EDL results from the requirement of electrical neutrality.

　　(C) Increasing the electrolyte concentration increases the thickness of electrical double layer.

　　(D) The structure of EDL includes a compact inner layer and a diffuse layer.

　　(E) The compact inner layer of EDL named Stern layer in which the potential decreases exponentially from the electrode surface.

4. Which of the following statements is/are true for a redox titration using Ce^{4+} to titrate Fe^{2+}?

   (A) A redox indicator is a substance which does not participate in the redox titration but its oxidized and reduced forms differ in color and thus can be used to indicate the endpoint of redox titration.

   (B) When the reaction is over-run, back-titration is required to obtain correct quantitative measurement.

   (C) The equilibrium potential depends on concentration and volume of Ce^{4+} and Fe^{2+}.

   (D) The same titration curve can be obtained although the reactants (Ce^{4+} and Fe^{2+}) are diluted or concentrated by a factor of 10.

   (E) The color transition range of a redox indicator is affected by the number of electron involved in the redox reaction of the indicator.

5. A triprotic acid (H_3A) is titrated by a strong base to obtain the titration curve shown below. Which statement about the titration curve is/are correct? (The dissociation constants of H_3A are K_{a1}, K_{a2} and K_{a3})
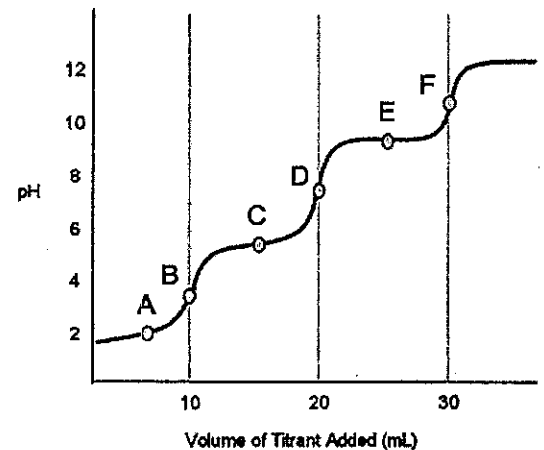
   (A) Point B is the first equivalence point at which the pH value of the solution is determined by K_{a1}.

   (B) At point C, the pH value of the solution is equal to pK_{a2}.

   (C) Beyond point F, the pH value of the solution is determined by excess OH^-.

   (D) Point D is the second equivalence point at which the pH value equals to $(K_{a2}+K_{a3})/2$

   (E) Between point B and point D, major species in the solution are H_2A^-, HA^{2-} and H_2O.

6. What of the following statement about buffer solutions is/are correct?

   (A) Buffered solutions are much more resistant to change in pH during dilution compared to unbuffered solutions.

   (B) The buffer capacity of a solution is defined as the number of moles of a strong acid or a strong base that causes 1.00 L of the buffer to undergo a 1.00 unit change in pH.

   (C) The buffer capacity is determined by the ratio instead of the amount of the conjugated acid/base pair used to prepare the buffer solution.

   (D) Optimal buffering occurs when the concentrations of acid and its conjugated base are the same.

   (E) The pK_a of an acid used to prepare a buffer should lie within ± 1 unit of the desired pH to have a reasonable buffer capacity.

7. Which of the following statement about ion-selective electrode (ISE) is/are not correct?

   (A) The ISE is composed of an internal reference electrode, internal electrolyte solution and an ion-selective membrane.

   (B) The internal electrolyte of ISE is typically designed to contain ions that match the selectivity of ISE.

   (C) The selectivity coefficient of a sensing membrane for the interferent over the analyte, K_{AI}, should

be significantly less than 1.00 to display good selectivity to the analyte.

(D) For an ISE that responses to the anion, X^{z-}, the potential measured with ISE is proportional to the anion concentration in logarithm scale with a slope of 0.05916/z.

(E) pH meter is the most commonly used cation ISE and typically displays a positive error (i.e., measured pH is larger than the true value) when measuring highly basic solutions.

8. Which of the following statement about sample atomization processes in atomic spectroscopy is/are correct?

(A) In flame atomizer, the alayte solution needs to be nebulized before being carried into a flame where atomization occurs.

(B) During atomization, desolvation involves solvent evaporation to form gaseous molecules.

(C) The atomic gas generated from gaseous molecules through the dissociation process is excited by the application of thermal energy in flame atomizer.

(D) The interzonal region of a flame where free atoms are prevalent is the most widely used part of the flame for spectroscopy.

(E) The region with the maximum temperature of a flame is located in the primary combustion zone and is focused on the entrance slit for spectrometric measurement.

9. The van Deemter equation shown below is applied to estimate the column efficiency. Which of the following statements about this equation is/are correct?

$$H = A + B/u + C_S u + C_M u$$

(A) The parameter A, which describes the effect of eddy diffusion on the band broadening, can be reduced by using a column packed with smaller particles.

(B) The magnitude of parameter B is largely determined by the diffusion coefficient of the analyte in the mobile phase and is much less pronounced in GC than in LC.

(C) With liquid stationary phases, the thickness of the adsorbed liquid layer should be minimized to reduce C_S and thus reduce band broadening.

(D) When operating at low mobile-phase velocities, higher temperature is preferred to enhance mass transfer between stationary and mobile phase, resulting in reduced C_S term to give smaller plate heights.

(E) Most chromatography is done with mobile-phase velocities higher than the optimal velocity so that mass-transfer terms (C_S and C_M terms) control column efficiency.

10. Which of the following attributes is/are not true about using Fourier transfer instrument for spectroscopic measurement?

(A) With the Fourier transfer instrument, the radiant power that reaches the detector is much greater than that in the dispersive instrument.

(B) A Fourier transfer instrument typically provides high resolving power to enable analysis of complex spectra.

(C) In the Fourier transfer instrument, all elements of the light source reach the detector simultaneously.

   (D) The Fourier transfer instrument provides measurement with enhanced signal-to-noise ratios by extending acquisition time.

   (E) The wavelength scale in Fourier transfer instruments is much more reproducible and accurate than that in dispersive instruments.

11. What is the equivalence point's potential when titrating 0.1 M, 5 mL Sn^{2+} with 0.04 MnO_4^- in a buffered solution with pH = 1? $E_{Sn^{4+}/Sn^{2+}} = 0.154\,V$, $E_{MnO_4^-/Mn^{2+}} = 1.51\,V$

   (A) 1.36 V

   (B) 1.12 V

   (C) 1.05 V

   (D) 0.832 V

   (E) 0.764 V

12. Which of the following characteristics is/are indispensable for an ideal detector for both GC and HPLC?

   (A) Minimal internal volume.

   (B) Response time independent of flow rate

   (C) Nondestructive detection

   (D) Responsive great over a temperature range

   (E) Compatible with liquid flow

13. Operational amplifiers (OPA) are widely used in modern chemical instrumentations to enable precise measurement of voltage, current and resistance. What is true about the characteristics of an "ideal" OPA?

   (A) Infinite open-loop gain

   (B) Zero input impedance

   (C) Infinite output impedance

   (D) Zero output voltage for zero input

   (E) The range of output voltage is determined by the applied power supply values.

14. What of the following statements is/are true for the hardware devices used to improve signal-to-noise ratios?

   (A) Modulator can convert low-frequency or dc signal to a higher frequency, where shot noise is less troublesome for signal amplification.

   (B) Lock-in amplifier has very narrow bandwidth, and thus can lock and amplify the signal of specific frequency and phase.

   (C) Low-pass analog filter can effectively remove high-frequency components of the signal, including thermal and shot noise.

   (D) Grounding and shielding the instrument from its surroundings can effectively remove most environmental noise.

   (E) Difference amplifiers are useful to reduce noise generated in the transducer circuit which is usually appears in an amplified form in the instrument readout.

15. Which of the following statement is/are true about IR measurement?
    (A) IR signal is due to the scattering of light by the vibrating molecules.
    (B) Vibration of analyte is IR active if there is change in molecular polarisability.
    (C) It is not necessary for IR active molecules to possess a permanent dipole moment.
    (D) Water and alcohols are difficult to use as solvent in IR measurement due to their broad and variable absorption peaks of $-OH$ group.
    (E) IR measurement can be used to evaluate the ionic character of a molecule.

16. Which of the following statement is/are not true about molecular luminescence?
    (A) Substitution of heavy-atoms decreases the fluorescence of luminescent molecules via enhancing internal conversion in their deactivation processes.
    (B) For most fluorescent compounds, radiation is produced by $\pi^* \to n$ or $\pi^* \to \pi$ process rather than $\sigma^* \to \sigma$ transition.
    (C) The presence of dissolved oxygen reduces the fluorescent intensity by enhancing intersystem crossing that involves crossover between molecular electronic states with the same multiplicity.
    (D) Molecules that lack of structural rigidity might enhance the probability of radiationless deactivation processes and thus display less fluorescence intensity.
    (E) Paramagnetic species tend to quench fluorescence via promoting the conversion of excited molecules to the triplet state.

Part II. Problem-solving and short answer questions. Please show all work, steps, units and explanation if applicable. (20%, 5 points for each question.)

1. In capillary electrochromatography, the sensitivity of absorption detection performed on-column is typically restricted by the limited light path length. To overcome this problem, what modifications can be down in the detector cell to improve the sensitivity of absorption measurement?

2. Photomultiplier tubes (PMTs) are significant radiation transducers especially useful for the measurement of low radiation powers. Draw a schematic to illustrate the construction of this device and explain how a PMT works to transduce radiation energy.

3. The composition of a colored complex can be determined by measuring absorbance with the method of continuous variation. Assuming there is no other reactions occur except the formation of the complex ML_4, draw the continuous-variation plot of the complex. Note: The absorptivity of the cation (ε_m), the ligand (ε_l) and the complex (ε_c) have the following relationship: $\varepsilon_c > \varepsilon_m = \varepsilon_l = 0$.

4. Explain how Doppler shift results in broadening of the line width of atomic spectrums.