科目：物理化學的部份

總分：50 分 （每題 2 分）
請務必依照題目順序答題。

1. What is the expression for the Langmuir isotherm?
   (A)$\theta = KP/(1+KP)$ (B)$\theta = 1/(1+KP)$ (C)$\theta = (1/K)+(1/KP)$ (D)$\theta = 1+(1/KP)$

2. What is the rate of consumption of a reactant R?
   (A)$d[R]/dt$ 　　(B)$d[R]$ 　　(C)$-d[R]/dt$ 　　(D)$-d[R]$

3. The canonical partition function of distinguishable independent molecules:
   (N is the total number of molecules and q is the molecular partition function)
   (A)$Q = q^N/N!$ 　(B)$Q = \Sigma_j e^{-\epsilon j/kT}$ 　(C)$Q = q^N/(N-1)!$ 　(D)$Q = q^N$

4. The time-independent Schrödinger equation for a linear harmonic oscillator can be expressed by
   (A) $-(\hbar^2/2m)(d^2\psi/dx^2) - kx\psi = E\psi$
   (B) $(\hbar^2/2m)(d^2\psi/dx^2) + (kx^2/2)\psi = E\psi$
   (C) $-(h/i)(d\psi/dx) + (kx^2/2)\psi = E\psi$
   (D) $-(h^2/2m)(d^2\psi/dx^2) + (kx^2/2)\psi = E\psi$

5. The relation between fractional coverage and partial pressure of a substance stands for the
   (A) monolayer adsorption
   (B) adsorption isotherm
   (C) partial molar pressure
   (D) equilibrium constant in pressure

6. Adsorption by van der Waals interaction between the adsorbate and the substrate is the definition of
   (A) chemisorption
   (B) cohesion
   (C) catalytic adsorption
   (D) physisorption

7. The highest point on a potential energy surface encountered along the reaction coordinate is
   (A) intermediate state
   (B) saddle point
   (C) energy barrier point
   (D) curve-crossing point

8. What is the possible time duration of a femtosecond pulsed laser?
   (A)1000 fs 　　(B)1×10^4 fs 　　(C)1×10^{-3} ns 　　(D)1×10^{-2} ps

9. Michaelis-Menten mechanism, a mechanism for enzyme-catalyzed reactions, can be written as
   (A) $E + S \longrightarrow ES \rightleftharpoons P$
   (B) $E + S \longrightarrow ES \longrightarrow P$
   (C) $E + S \rightleftharpoons ES \longrightarrow P$
   (D) $E + S \rightleftharpoons ES \rightleftharpoons P$

10. Which of the following describes the temperature dependence of reaction rates
    (A) Clapeyron equation

(B) Langmuir isotherm
(C) Transition-state theory
(D) Arrhenius equation

11. Consider the equilibrium A $\rightleftharpoons$ B, what is the correct relation of $\Delta_r G$ to the chemical potentials of the species?
   (A)$\mu_B \times \mu_A$　　　　(B)μ_B / μ_A　　　　(C)$\mu_B - \mu_A$　　　　(D)$\mu_B + \mu_A$

12. A saturated solution of Na_2SO_4, with excess of the solid, is present at equilibrium with its vapor in a closed vessel. What is the varience (independent variable(s) in phase equilibrium) of the system?
   (A)0　　　　(B)1　　　　(C)3　　　　(D)2

13. What is the Lindemann-Hinshelwood mechanism describing the unimolecular reaction?
   (A) A + A $\rightleftharpoons$ A + A*;　A* $\longrightarrow$ P
   (B) A + $h\nu$ $\longrightarrow$ A* $\longrightarrow$ P
   (C) A + A $\longrightarrow$ A* $\longrightarrow$ P
   (D) A + A $\longrightarrow$ A + A* $\longrightarrow$ P

14. A dispersion of small particles (< 500 nm) of one material in another is called
   (A) nanoparticle
   (B) colloid
   (C) fullerene
   (D) glassy carbon

15. The equation for the origin of the lifetime broadening in spectroscopy is
   (A) $\Delta t = \lambda^2/(2\Delta\lambda)$
   (B) $\delta\nu = (2\nu/c)[2kT\ln2/m]^{1/2}$
   (C) $\delta E = (1/2)h\nu$
   (D) $\delta E \approx h/\tau$

16. How many vibrational degrees of freedom does the molecule CO_2 have?
   (A)4　　　　(B)3　　　　(C)2　　　　(D)9

17. Which of the following scientific laws gives the statement: "The pressure exerted by a mixture of gases is the sum of the partial pressures of the gases"
   (A) Boyle's law
   (B) Charles's law
   (C) Dalton's law
   (D) Avogadro's principle

18. (For questions 18-21) A sample consisting of 1.00 mol of monatomic perfect gas, initially at p_1 =1.00 atm and T_1 = 300 K, is heated reversibly to 400 K at constant volume. Calculate the final pressure.
   (A)1.5　　　　(B)100　　　　(C)2　　　　(D)1.33

19. (continue) Calculate ΔU (in kJ)
   (A)1.25　　　　(B)5　　　　(C)–1.5　　　　(D)0

20. (continue) Calculate w (in kJ)
   (A)–1.25　　　　(B)–1.5　　　　(C)1.5　　　　(D)0

21. (continue) Calculate q (in kJ)
   (A)5　　　　(B)1.25　　　　(C)–1.5　　　　(D)0

22. The interaction energy of the induced-dipole-induced-dipole (dispersion) interactions is given by the London formula,
    (A) $V = C/r^4$
    (B) $V = -(C/r^6)$
    (C) $V = -C/r^4$
    (D) $V = -C/r^{12}$

23. Which of the following molecules does not have a pure rotational microwave absorption spectrum:
    (A) N_2　　　　(B) HCl　　　　(C) CH_4　　　　(D) NH_3

24. Which of the following molecules does not have an vibrational infrared spectrum:
    (A) CO_2　　　　(B) HCl　　　　(C) CH_4　　　　(D) N_2

25. The rate law for the reaction: $2A + 2B \rightarrow 3C + D$ was found to be $\upsilon = k[A]^2[B]^2$. What is the unit of k?
    (A) $L^2\ mol^{-2}\ s^{-1}$　　(B) s^{-1}　　　　(C) $L^3\ mol^{-3}\ s^{-1}$　　(D) $mol\ L^{-1}\ s^{-1}$

化學暨生物化學所碩士班 "分析化學" 試題
選擇題 (單選題) 每題2分

1. Sequentially indicate how many significant figures for the following numbers (If the arithmetic operation is required, please indicated the significant figure of the result):
    0.09030, 1.40×10^4, (4.318×3.6), $\log(5.405 \times 10^{-8})$, $10^{6.142}$.
    (a) 3, 3, 3, 3, 4　　　(b) 4, 3, 2, 3, 4　　　(c) 4, 3, 2, 4, 3,　　　(d) 4, 3, 2, 3, 3
    (e) 4, 3, 2, 4, 4

2. Which of the following method is the most widely used technique for finding a line (or curve) through a set of data points?
    (a) Standard addition method,　(b) Internal standard method,
    (c) Matrix match method,　(d) Area normalization method,　　(e) Least squares method.

3. You are testing a new developed method and evaluating the accuracy of the method with a Reference Standard Material. Which of the following tests should be applied?
    (a) F-test,　　　(b) t-test, (c) Q-test,　　(d) paired t-test,　　(e) chi-square test.

4. A series of sequential flame emission analysis of a blank solution are performed. The readings of the measurement are 0.002, 0.001, 0.008, 0.006, and 0.003 (where average is 0.004, standard deviation is 0.0030). A standard 10 ppb lead solution gives an average emission reading of 0.0060. What is the detection limit of lead for flame emission?
    (a) 45 ppb, (b) 15 ppb,　　　(c) 20 ppb,　　　(d) 6.7 ppb,　　　(e) 20 ppm

5. K_b for methylamine is 1.0×10^{-4}. What is the pH for a 0.010 M methylammonium chloride solution?
    (a) 10,　　　(b) 5.0,　　　(c) 4.0,　　　(d) 6.0　　　(e) 3.0

6. For the reaction　　　aA + bB $\rightleftharpoons$　cC + dD, we write the equilibrium constant, K, in the form of $K = \dfrac{[C]^c[D]^d}{[A]^a[B]^b}$, where the small superscript letters denote stoichiometry coefficients and each capital letter stands for a chemical species.
    Which statement is **not** true about equilibrium constant?
    (a) The concentrations of solutes should be expressed as mole per liter.
    (b) The concentrations of gases should be expressed in atmospheres.
    (c) The equilibrium constant is temperature dependent.
    (d) Le Châterlier's principle predicts the effect on equilibrium constant when reactants or products are added.
    (e) The equilibrium constant is dimensionless.

7. Why are microporous ODS bonded silica stationary phases generally limited to operating in the pH range 2-8?
    (a) Basic compounds are not retained at pH above 8.0.
    (b) Siloxane (Si-O-SiR) bonded hydrolyzes below pH 2.0.
    (c) Silica dissolves in water with pH below 2.0.
    (d) Strong surface absorption occurs at pH below 2.0.
    (e) Strong charge interaction at pH above 8.0.

8. In the isocratic elution of a reversed-phase HPLC, the polarity of each solvent is indicated in parenthesis after each solvent: water (10.2), dimethylsulfoxide (7.2), acetonitrile (5.8), methanol (5.1), dioxane (4.8), and tetrahydrofuran (4.0). Which of the following mobile phase gives the strongest elution strength?
   A:30% water/70% dimethylsulfoxide, B: 50% water/50% acetonitrile, C:70% water/30% tetrahrofuran, D: 60% water/40% dioxane, and E: 50% water/50% methanol. (P.S.: the ratio is based on volume to volume)
   (a) A,　　　(b) B,　　　(c) C,　　　(d) D,　　　(e) E.

9. Which of the following statement is **not** true?
   (a) An internal standard is a known amount of a compound, different from analyte, that is added to the unknown.
   (b) Standard addition is especially appropriate when the sample matrix in the unknown affects the analytical signal.
   (c) Internal standard are especially useful for analyses in which the quantity of sample analyzed varies slightly from run to run for reason are difficult to control.
   (d) Standard addition method is desirable when sample loss can occur during sample preparation steps prior to analysis.
   (e) To use an internal standard, a known mixture of standard and analyte is prepared to measure the relative response of the detector to the two species.

10. Which of the following statement is **not** true in theoretical aspect of chromatography?
   (a) The plate height is depending on the linear flow rate.
   (b) The column with smaller plate height gives higher column efficiency.
   (c) The longitudinal diffusion is a more serious problem in gas chromatography than in liquid chromatography.
   (d) The optimal flow rate is greater for a chromatographic column packed with larger particles.
   (e) Nonlinear partition isotherms lead to non-Gaussian peaks.

11. Which of the following statement is **not** true in voltammetry?
   (a) Charging current arise from charging/discharging at the electrode/solution interface.
   (b) Limit of diffusion process can be achieved by placing the working electrode in a high concentration of high supporting electrolyte without stirring the solution.
   (c) Differential pulse polarography measures the faradaic current when the charging current has decay to near zero.
   (d) Square wave polarography is more sensitive than differential pulse polarography.
   (e) Stripping method is the most sensitive polarographic technique, because the current is measured at low background charging current.

12. Which of the following statement is **not** true in gas chromatography?
   (a) Open tubular columns provide greater resolution than packed columns.
   (b) N_2 allows more rapid linear flow rate than H_2 does, without loss of column efficiency.
   (c) It is illogical to use a thin stationary phase (0.2 μm) in a wide-bore (0.53-mm.53 mm) open tubular column.
   (d) Pressure programming has the advantages of reducing the retention time of late-eluting peak with relative low temperature to decompose thermal sensitive compounds.
   (e) The retention of GC is dependent on boiling point of solute and molecular interaction between stationary phase and solute.

13. If the K_a of barbituric acid is about 1.0×10^{-4} at $25^{\circ}C$, at what pH is the ratio of the unprotonated to protonated for of barbituric acid 50:1.
   (a) 3.3,　　　(b) 3.7,　　　(c) 4.3,　　　(d) 4.7,　　　(e) 5.7

14. Which of the following statement is **not** true for ions in electrolyte solutions?
   (a) Mg^{2+} has a smaller ionic radius than Ba^{2+}, so Mg^{2+} binds water molecules more strongly than Ba^{2+}.
   (b) The solubility of an ionic compound decrease as the ionic strength of the solution increases (at least up to ~0.5M).
   (c) In the ionic strength range 0 - 0.1M, activity coefficients decrease with an increase of ionic charge.
   (d) Hydrated radii decreases in the order $Sn^{4+} > In^{3+} > Cd^{2+} > Rb^{+}$.
   (e) In the ionic strength range 0 - 0.1M, activity coefficients decrease with decreasing hydrated radius.

15. Which of the following statement is **not** true about complexation titration?
   (a) A displacement titration is necessary if the analyte react too slowly with EDTA
   (b) The chelate effect results from those multidentate ligands form more stable metal complexes than do similar, monodentate ligands.
   (c) A back titration is employed when the analyte precipitates in the absence of EDTA.
   (d) For a metal indicator to be useful in EDTA titration, it must bind metal less strongly than EDTA does.
   (e) Fraction of free EDTA in the form of Y is pH dependent, so complexation titration of metal ion with EDTA has to be buffered.

16. Which of the following is **not** the source of error associated with pH measurement with glass electrode?
   (a) Overpotential,　　　(b) Equilibrium time,　　　(c) Junction potential,
   (d) Uncertainty in pH of standard buffer,　　　(e) Sodium error at extreme pH value.

17. If a 0.00100 M solution in a 1.000-cm cuvet exhibits 40% T at 254 nm, what would be the transmittance for a 0.00300 M solution in a 0.500-cm cuvet (estimate the result with simple logarithm).
   (a) 6%,　　　(b) 36%,　　　(c) 25%,　　　(d) 48%,　　　(e) 60%

18. Which statement is **not** true for atomic spectroscopy?
   (a) Spectral interference is much severe in atomic absorption than atomic emission with plasma source.
   (b) Temperature control is more critical for atomic emission.
   (c) Higher temperature decreases the chemical interference.
   (d) Increasing temperature leads to broader linewidth, due to Doppler broadening.
   (e) Deuterium lamp can be used for background correction in atomic absorption.

19. Sensitivity in atomic absorption has been defined as the concentration of analyte that absorbs 1% of the light (corresponding to an absorbance of $-\log (0.99) = 0.0045$). A sample containing 1.00 ppm Cu gave an absorbance of 0.055. Estimate the sensitivity for Cu?
   (a) 0.018 ppm,　　　(b) 0.080 ppm,　　　(c) 8.2 ppm,　　　(d) 0.18 ppm,　　　(e) 1.8 ppm.

20. Which statement is **not** true for atomic absorption spectroscopy?
   (a) Graphite furnace atomizer generally offers better sensitivity than flame atomizer does.
   (b) A magnet is necessary for the instrument with Zeeman background correction.
   (c) Matrix modifiers are used in flame atomic absorption to correct ionization interference.
   (d) Linewidth of a hollow-cathode lamp is narrower than that of absorption line.
   (e) Releasing agents are the chemical that can be added to the sample to decrease chemical interference.

21. Which or the following statement is **not** true for ion chromatography (IC)?
    (a) The elution mechanism is based on the displacement of ionic equilibrium.
    (b) The higher the charge density, the longer the compound will be retained on the stationary phase.
    (c) A suppressor column is employed with conductivity detector to enhance the detection sensitivity.
    (d) The mobile phase is an aqueous solution containing electrolytes and organic modifiers.
    (e) The stationary phase of IC is made by copolymers of polystyrene and divinylbenzene.

22. Which of the following statement is **not** true for a buffer solution?
    (a) The buffer capacity increases as a solution become very acidic or very basic.
    (b) The pH of a buffer nearly independent of concentration.
    (c) The buffer capacity increases as the concentration of buffer increases.
    (d) The maximum buffer capacity is at $pH = pK_a \pm 1$.
    (e) The pH of a buffer solution does not change very much when a limited amount of strong acid or base is added

23. Which of the following statement is **not** true for luminescence?
    (a) Molecules in $\pi \rightarrow \pi^*$ excited states are more likely to undergoes inter-system crossing than those in $n \rightarrow \pi^*$ states.
    (b) Molecular fluorescence competes with two radiationless processes: internal conversion and inter-system crossing.
    (c) Transitions from T to S0 are forbidden because they involve a change in the electron spin of the molecule.
    (d) Xenon arc is more satisfactory as a source for fluorescence work than tungsten filament lamp.
    (e) Fluorescence is quenched when a molecule in an excited electronic state is deactivated without emission of a photon.

24. Radiation of wavelength 400 nm is less likely to cause photodecompositon of an organic molecule that radiation of wavelength 300 nm because
    (a) its photon energy is lower.
    (b) it is visible radiation.
    (c) its intensity is higher.
    (d) it is more ready absorbed
    (e) it is more likely to excite the organic molecule to excited state.

25. Which of the following HPLC detectors can not be used in gradient elution?
    (a) Ultraviolet,　　　(b) Mass spectrometry,　　　(c) Fluorescence,
    (d) Evaporative light-scattering,　　　(e) Refractive index.

Log 2 = 0.301, Log 3 = 0.477, Log 5 = 0.699, Log 7 = 0.845.
Log (a b)= Log a + Log b,　Log (a/b)=Log a – Log b,　Log (a^b) = b Log a,　Log 10^a = a