一。分析化學的部份　　『不可使用計算機』

1. 名辭辭意對照(每小題各 1 分) 將(Ⅱ)中與(Ⅰ)相關名詞標示出來,有可能是多選，答錯不扣分。

		Ⅰ	Ⅱ
例題	a	Hollow cathode lamp	a: AAS
1.1	___	Split injection	b: High performance liquid chromatogra
1.2	___	Titration	c: t-test
1.3	___	Stoichiometry of the complex	d: Isoelectric point
1.4	___	Suppressor column	e: Gas chromatography
1.5	___	Amino acid	f: Potentiometry
1.6	___	Gradient elution	g: Polyprotic acid
1.7	___	Ion-selective electrode	h: Calibration method
1.8	___	Faradaic current	i: Capillary electrophoresis
1.9	___	Electric mobility	j: Gaussian distribution
1.10	___	Experimental errors	k: Mole-ratio method
			l: Indicator
			m: Ion chromatography
			n: Votammetry

2. (10%) 層析分離的 Resolution (R_s)可以用下列方程式表示:

$$R_S = \frac{2(t_{R,2} - t_{R,1})}{W_1 + W_2} \quad (1) \qquad R_S = \frac{\sqrt{N}}{4}\left(\frac{\alpha - 1}{\alpha}\right)\left(\frac{k_2'}{1 + k_{av}'}\right) \quad (2)$$

其中 $k_{av}' = \frac{k_1' + k_2'}{2}$; $t_{R,2}$ and $t_{R,1}$ are the retention of the 2nd and first peak; W_1 and W_2 are the bandwidth of and 2nd peak; α is the selectivity.

(a) 利用(1)推導出(2)式。

(b) 依據(2)式，說明為何在層析分離簡單混合物之最佳化時，capacity factor(k')通常保持在 $1 \leq k'$

(c) 假使 $\alpha = 1.01$, $k_2' = 10.0$, 要得到 $R_s = 1.0$ 之分離所需理論板數(N)?

3. (5%)

Acid	pKa
Cyanoacetic acid	2.44
Formic acid	3.74
Acetic acid	4.76
Imidazole hydrochloride	6.99

(a) Which acid is most suitable for preparing a buffer of pH 5.00?

(b) Write the procedure to prepare 1.00 M, 500 mL of pH 5.00 buffer.

4. (5%) In differential pulse polarography (DPP), small pulses are superimposed on linear voltage ra height of a pulse is called its modulation.

(a) What should the plot of 'current' as the function of 'voltage' (i vs. V) of DPP look like?

(b) Describe and explain the effect of modulation amplitude on voltammogram.

5. (6%) The base B has pK_b =4.00
   (a) What is the value of pK_a for the acid of BH^+?
   (b) At what pH is $[BH^+] = [B]$?
   (c) What is the quotient $[B]/[BH^+]$ at pH 11.0?

6. (4%) Consider the half-reaction

$$As(s) + 3H^+ + 3e^- \rightleftarrows AsH_3(g) \qquad E^o = -0.238\ V$$

   (a) Write the Nernst equation for the half-reaction.
   (b) Find E (not E^o) when pH=1.00 and P_{AsH3} = 760 torr.(1 atm= 760 torr).

7. (5%) From the equations

$$HOCl \rightleftarrows H^+ + OCl^- \qquad K = 3.0 \times 10^{-8}$$

$$HOCl + OBr^- \rightleftarrows HOBr + OCl^- \qquad K = 15$$

   (a) Calculate the numerical value of the equilibrium constant for the reaction:

$$HOBr \rightleftarrows H^+ + OBr^- \qquad K = ?$$

   (b) Calculate the concentration of H^+ and the pH of 0.100 M HOBr solution.

8. (5%) In atomic absorption spectrometry, the sensitivity is defined as the concentration of analyte that has absorbance reading of 0.00436 (i.e. absorbs 1% of light from the lamp and is corresponding to 99% transmittance). A 0.1 ppm Cu sample gave an absorbance of 0.044. Estimate the sensitivity of Cu.

二、物理化學的部份

『不可使用計算機』

總分：50 分 （1~10 題，每題 3 分；11~15 題，每題 4 分）

$h = 6.6\times10^{-34}$ J s; 1 J = 5×10^{22} (cm^{-1}); $R = 8.315$ J K^{-1} mol^{-1} = 0.082 atm L K^{-1} mol^{-1}

1. The fraction of molecules in a one-dimensional gas having kinetic energies between ε_x and $\varepsilon_x + d\varepsilon_x$ can be expressed by dN_x/N, where N is the total number of the molecules. What is the expression for the average energy $\bar{\varepsilon}_x = ?$

(A) $\sum_{N_i} \varepsilon_{x,i}(dN_{x,i}/N)$ (B) $\sum_{N_i} \varepsilon_{x,i}(dN_x/N)$ (C) $\int_0^\infty \varepsilon_x \frac{dN_x}{N}$ (D) $\int_0^\infty \varepsilon_x \frac{dN_x}{N} d\varepsilon_x$

Question 2 to *Question* 4:

The kinetics of the Langmuir isotherm in adsorption with dissociation follows that the process of adsorption is accompanied by the dissociation of the molecule when it becomes attached to the surface:

$$A_2 + \begin{matrix}|&|\\ -S-S-\end{matrix} \rightleftharpoons \begin{matrix}A&A\\ |&|\\ -S-S-\end{matrix}$$

Please follow three steps to deduce an expression for such kinetics in terms of θ, which is the surface coverage.

2. The rate of adsorption, υ_a, is

(A) $k_a[A_2](1-\theta)$ (B) $k_a[A_2]^2\theta$ (C) $k_a[A_2]\cdot\theta^2$ (D) $k_a[A_2](1-\theta)^2$

3. The rate of desorption, υ_d, is

(A) $k_d[A]^2(1-\theta)$ (B) $k_d\theta^2$ (C) $k_d[A]^2\cdot\theta^2$ (D) $k_d(1-\theta)^2$

4. The surface coverage can be expressed in terms of K ($K=k_a/k_d$): $\theta = ?$

(A) $\frac{K^{1/2}[A_2]^{1/2}}{1+K^{1/2}[A_2]^{1/2}}$ (B) $\frac{K^{1/2}[A_2]^{1/2}}{1+K[A_2][A]}$ (C) $\frac{K^{1/2}[A]^{1/2}}{1+K^{1/2}[A]^{1/2}}$ (D) $\frac{K^{1/2}[A]^{1/2}}{1+K[A][A_2]}$

Question 5 to *Question* 7:

The hydrolysis reaction of adenosine triphosphate can be represented by

$$ATP \rightleftharpoons ADP + P$$

The following values have been obtained for the reaction at 37°C (standard state: 1 M):

$\Delta G^\circ = -31.0$ kJ mol^{-1}

$\Delta H^\circ = -20.1$ kJ mol^{-1}

5. ΔS° (at 37°C) = ? (in J K^{-1} mol^{-1})

(A) 10.9 (B) −35.1 (C) 35.1 (D) −51.9

6. K_c (at 37°C) = ? (in M)

(A) $e^{12.02}$ (B) 12.02 (C) $e^{-12.02}$ (D) −12.02

7. On the assumption that ΔH° and ΔS° are temperature independent, calculate K_c (at 37°C) = ? (in M)

(A) −12.33 (B) $e^{12.33}$ (C) $e^{-12.33}$ (D) 12.33

8. After an electronically excited molecule or radical has been produced by absorption of radiation, a number of relaxation processes can happen. Which one of the following processes is brought about by collision?
(A) Fluorescence
(B) Vibrational relaxation
(C) Intersystem crossing
(D) Phosphorescence

9. The function Ae^{-ax} is an eigenfuction of the operator d^2/dx^2. What is the eigenvalue?
(A) $-a$ (B) $1/a$ (C) A (D) a^2

10. Assume that the real functions ψ_1 and ψ_2 are normalized and orthogonal. Find the normalized wave function for $\psi_1+\psi_2$.
(A) $\frac{1}{2}(\psi_1+\psi_2)$ (B) $\frac{1}{\sqrt{2}}(\psi_1+\psi_2)$ (C) $\psi_1+\psi_2$ (D) $\frac{1}{2}(\psi_1-\psi_2)$

11. Estimate the lifetime of a state that, because of lifetime broadening, gives rise to a line of width 1 cm^{-1}.
(A) 1.6×10^{-11} s (B) 3.3×10^{-34} s (C) 2.5×10^{-12} s (D) 5.2×10^{-35} s

Question 12 to *Question* 13:
A particle is moving in one dimension between $x = a$ and $x = b$. The potential energy is such that the particle cannot be outside these limits and that the wave function in between is $\psi = A/x$.

12. Determine the normalization constant $A = ?$
(A) $\sqrt{\frac{ab}{b-a}}$ (B) a/b (C) $\frac{ab}{a-b}$ (D) $\sqrt{\frac{b-a}{ab}}$

13. Calculate the average value of $x = ?$
(A) $\frac{ab}{b-a}\ln\frac{b}{a}$ (B) $\frac{ab}{b-a}$ (C) $\frac{b-a}{ab}\ln a$ (D) $\sqrt{\frac{b-a}{ab}}\ln\frac{b}{a}$

Question 14 to *Question* 15:
For an irreversible reaction of stoichiometry $2A + B \rightarrow Z$, the rate is proportional to $[A]^2[B]$ and the reactants present in stoichiometric proportions; take the initial concentration of A as $2a_0$ and that of B as a_0.

14. Derive the integrated rate equation for the above reaction kinetics using the extent of reaction x.
(A) $\frac{a_0x-x^2}{a_0^2(a_0-2x)^2}=4kt$ (B) $\frac{2a_0x}{a_0^2(a_0-2x)^2}=8kt$ (C) $\frac{2a_0x-x^2}{a_0^2(a_0-x)^2}=4kt$ (D) $\frac{2a_0x-x^2}{a_0^2(a_0-x)^2}=8kt$

15. Obtain an expression for the half-life of the reaction: $t_{1/2} = ?$
(A) $\frac{3}{8a_0^2k}$ (B) $\frac{2}{8a_0k}$ (C) $\frac{1}{4a_0^2k}$ (D) $\frac{3k}{8a_0^2}$