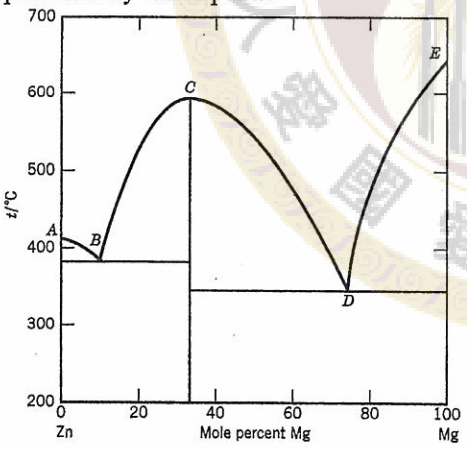
Part I. 物理化學

Section I (14 分): 選擇題 (每題至少一個正確答案)

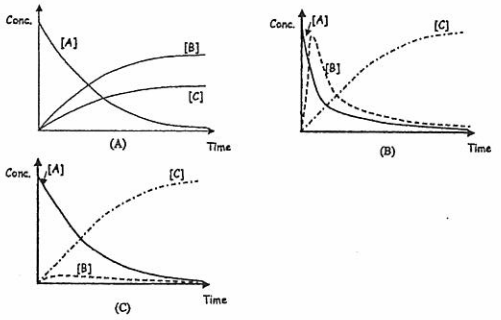
(1). A process can NEVER occur spontaneously at constant temperature and pressure, if
(A) ΔS >0, and ΔH >0
(B) ΔS >0, and ΔH <0
(C) ΔS <0, and ΔH >0
(D) ΔS <0, and ΔH <0

(2). When gaseous HCl in the ground electronic state absorbs infrared radiation, which of the following changes in the vibrational quantum number, v, and the rotational quantum number, J, are allowed?
(A) $\Delta v = 2$, $\Delta J = 0$
(B) $\Delta v = 1$, $\Delta J = 0$
(C) $\Delta v = 1$, $\Delta J = \pm 1$
(D) $\Delta v = 1$, $\Delta J = \pm 2$

(3). The phase diagram for the zinc-magnesium system is shown below. A eutectic point is represented by which point?



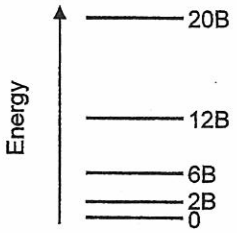
(4). For a reaction of $A \xrightarrow{k_1} B \xrightarrow{k_2} C$: If $k_2 << k_1$, which of the following graph best describes the time-courses of the concentration profiles?



(5). At what temperature will the average kinetic energy of $SO_2(g)$ molecules (M.W.=64 g/mol) be the same as that of $O_2(g)$ molecules (M.W.=32 g/mol) at 300 K?
(A) 300 K
(B) 212 K
(C) 424 K
(D) 150 K
(E) 600 K

(6). Which of the following statement is false?
(A) For a system containing 0.01 M KCl solution, the process of liquid water freezing into ice at 0°C will occur spontaneously.
(B) In the case of 1 moles of Ar and 4 moles of N_2 mixing together at constant T and P, the sign of ΔS_{mix}, ΔH_{mix}, and ΔG_{mix} is (+, 0, −).
(C) For a spontaneous process at constant T and P, ΔG^o is always negative.
(D) The equilibrium constant can be calculated from ΔG^o.

(7). The energy-level diagram shown in the figure below offers information on:



(A) energies of a particle in a one-dimensional box
(B) electronic energies of the hydrogen atom
(C) electronic energies of the hydrogen molecule
(D) bond length of a diatomic molecule
(E) vibrational energies of a diatomic molecule

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Section II (36 分): 敘述題

(16 pts) **(A).** Consider a one-dimensional particle-in-a-box system, where $V(x) = 0$ for $0<x<L$, but $V(x) = \infty$ for $x \geq L$, $x \leq 0$

It has a normalized solution of $\varphi_n(x) = \sqrt{\frac{2}{L}} \sin\left(\frac{n\pi x}{L}\right)$, with $E_n = \frac{n^2h^2}{8mL^2}$, where n = 1, 2, 3…

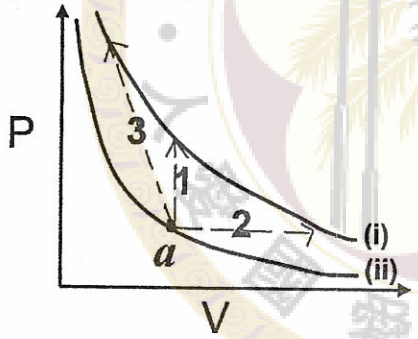
(A1). Given $\hat{p}_x = -i\hbar\frac{\partial}{\partial x}$, calculate $< p_x >$

(A2). Draw the probability density function for the lowest three energy levels for this system.

(A3). Now, consider the box is with finite depth, i.e. $V(x) = 0$ for $0<x<L$, but $V(x) = V_o$ for $x \geq L$, $x \leq 0$, roughly sketch the probability density function for the lowest three energy levels for this finite system.

(A4). Give a chemical example or application for this finite system, and explain how it is related to the particle-in-a-box system.

(12 pts) **(B).** Curves (i) and (ii) are two isothermal curves. Now, heat an ideal gas from state ***a*** through three different paths: ***path 1*** through constant volume, ***path 2*** through constant pressure, and ***path 3*** through an adiabatic process. Given the sign convention is that *work* done on the system is positive, and *heat* adding to the system is positive.



(B1). Which process(es) returns with a positive q?

(B2). Which process(es) returns with a positive w?

(B3). Based on these processes, compare and explain the relative size of C_v and C_p.

(8 pts) **(C).** A two-state system consisting of N distinguishable particles. The energy of the ground state is 0, and that of the excited state is ε_o (with $\varepsilon_o > 0$).

(C1). Write the molecular partition function q.

(C2). Determine the total energy U.

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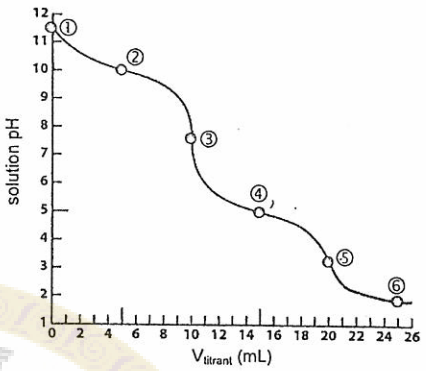
Part II. Analytical Chemistry (50%)

A. 單選題(共 10 題，每題 2 分，選最恰當的選項，答錯倒扣 0.5 分)

(1) Which points in the titration curve (for a diprotic species shown in the left) should *the hydrolysis of weak acid* be taken into consideration to calculate the solution pH?
(a) ①③ (b) ②④ (c) ③ (d) ⑤ (e) ⑥

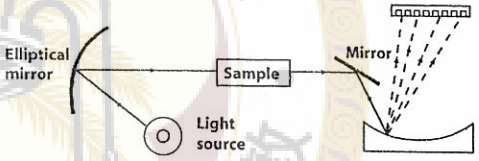


(2) The isoelectric point for glycine (pK_1 2.350, pK_2 9.778) in a solution of 5.0 mM glycine ($C_{glycine}$) dissolved in pure water is
(a) pK_1 (b) pK_2
(c) $p[(K_1 + K_2)/2]$ (d) $-log(\sqrt{K_1 + K_2})$
(e) $-log\left(\sqrt{\frac{K_1K_2C_{glycine} + K_1K_w}{K_1 + C_{glycine}}}\right)$

(3) Which of the following aqueous solutions has the largest ionic strength?
(a) 0.100 M glucose (b) 0.050 M sodium nitrate (c) 0.050 M sodium sulfate
(d) 0.050 M sodium bromide (e) 0.050 M sodium hydroxide and 0.050 M hydrogen chloride

(4) Which of the following is applied to reduce the problem caused by the sample matrix?
(a) internal standards (b) standard hydrogen electrode
(c) standard curves (d) standardization
(e) standard deviation

(5) The wavelength selector in the scheme is a
(a) polychromator. (b) monochromator.
(c) interference filter. (d) interferometer.
(e) photodiode array.



(6) Which of the following ionization methods are suitable for analytes with large molecular weights such as proteins? ① EI, ② CI, ③ ESI, ④ APCI, ⑤ MALDI
(a) ①③ (b) ②④ (c) ③⑤ (d) ② (e) ④⑤

(7~10 單選題) Find the most appropriate answer from a~o.
(a) Arrhenius equation (b) Beer's law (c) blackbody radiation
(d) Boltzmann distribution (e) Brownian motion (f) Debye-Huckel equation
(g) Franck-Condon principle (h) Gaussian distribution (i) Hammett acidity function
(j) intersystem crossing (k) law of mass action (l) Henderson-Hasselbalch equation
(m) Nernst equation (n) Stokes equation (o) van Deemter equation

(7) The central concept for the preparation of buffer solutions.

(8) An important concept that explains the difference in the effect of temperature on the signal intensity of AAS (Atomic Absorption Spectroscopy) and AES (Atomic Emission Spectroscopy).

(9) A concept that explains the relation between the absorption and emission spectra of a fluorophore (namely, $\lambda_{ex} < \lambda_{em}$).

(10) A concept that helps to derive the mobility of analytes in capillary electrophoresis.

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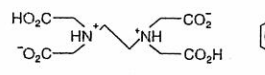
B. 簡答題與計算題(共 30 分)

1. ***Write the equations*** for the propagation of uncertainty. (每小題 2 分；以所列之式子評分，不評計算結果)
   (a) [10.5 (± 0.5) + 15.50 (± 0.95)] = 26 (± ?)
   (b) *log*[8.50 (± 0.07)] = 0.92942 (± ?)

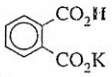
2. Give (i) the full name in English, (ii) the role of use (in the scope of chemical analysis), and (iii) the analytical method for each of the substances, apparatus, and instrument components shown below. The answers for (x) and (y) are given as examples. (六小題，每題 2 分，共 12 分)

(x)

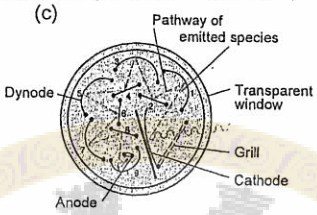


(i) ethylenediaminetetraacetic acid
(ii) a complexing reagent
(iii) complexiometric titration

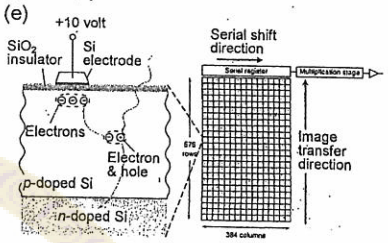
(a)



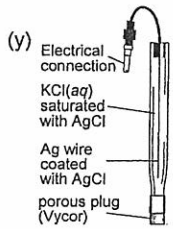
(c)



(e)

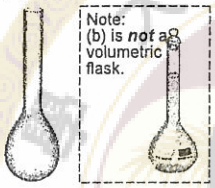


(y)

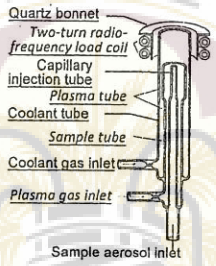


(i) silver/silver choride electrode
(ii) a reference electrode
(iii) voltammetry (or amperometry, electrochemistry, etc.)

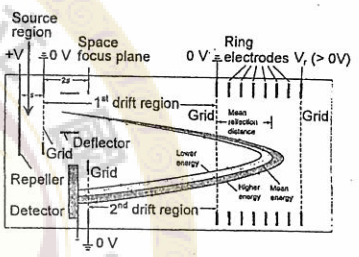
(b)



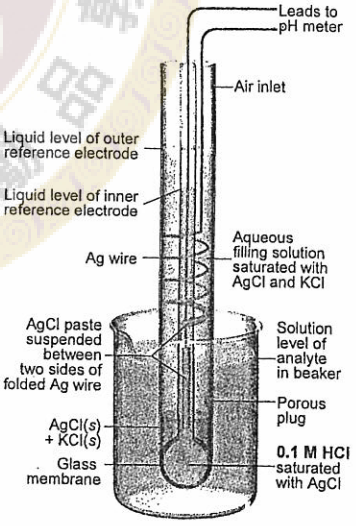
(d)



(f)



3. The diagram shows the measurement of the solution pH by a glass *combination electrode* with a silver/silver chloride reference electrode. The obtained result was $\bar{x}_1 \pm s_1$ (n = 4). Another home-made pH electrode was prepared and used to measure the acidity of the same sample. The pH was found $\bar{x}_2 \pm s_2$ (n = 5). According to *null hypothesis* at the 95% confidence level, $\bar{x}_1$ (± s_1, n = 4) and $\bar{x}_2$ (± s_2, n = 5) are not significantly different.



   (a) (2%) Define *combination electrode*.
   (b) (3%) Define *null hypothesis*.
   (c) (2%) From the concept of *significant figure*, comment on the meaning of the concentration, **0.1** M HCl, shown at the lower right corner of the diagram.
   (d) (2%) If you become a teaching assistant and teach college students using a pH electrode, you will give students instructions on how to protect the electrode from being damaged. Write down two important instructions.
   (e) (5%) Write equations to show the meaning of "According to *null hypothesis* at the 95% confidence level, $\bar{x}_1$ (± s_1, n = 4) and $\bar{x}_2$ (± s_2, n = 5) are not significantly different."

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Table 3-1 Summary of rules for propagation of uncertainty

Function	Uncertainty	Function[a]	Uncertainty[b]
$y = x_1 + x_2$ $y = x_1 - x_2$	$e_y = \sqrt{e_{x_1}^2 + e_{x_2}^2}$	$y = x^a$	$\%e_y = a\%e_x$
		$y = \log x$	$e_y = \frac{1}{\ln 10}\frac{e_x}{x} \approx 0.434\,29\frac{e_x}{x}$
$y = x_1 \cdot x_2$ $y = \frac{x_1}{x_2}$	$\%e_y = \sqrt{\%e_{x_1}^2 + \%e_{x_2}^2}$	$y = \ln x$	$e_y = \frac{e_x}{x}$
		$y = 10^x$	$\frac{e_y}{y} = (\ln 10)e_x \approx 2.302\,6\,e_x$
		$y = e^x$	$\frac{e_y}{y} = e_x$

a. x represents a variable and a represents a constant that has no uncertainty.

b. e_x/x is the relative error in x and $\%e_x$ is $100 \times e_x/x$.

$$x = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}}$$

$$y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2} \qquad \mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

$$t_{calculated} = \frac{|\bar{x}_1 - \bar{x}_2|}{s_{pooled}}\sqrt{\frac{n_1 n_2}{n_1 + n_2}}$$

$$s_{pooled} = \sqrt{\frac{\sum_{set1}(x_i - \bar{x}_1)^2 + \sum_{set2}(x_j - \bar{x}_1)^2}{n_1 + n_2 - 2}} = \sqrt{\frac{s_1^2(n_1 - 1) + s_2^2(n_2 - 1)}{n_1 + n_2 - 2}}$$

TABLE 4-2 Values of Student's t

	Confidence level (%)						
Degrees of freedom	50	90	95	98	99	99.5	99.9
1	1.000	6.314	12.706	31.821	63.657	127.32	636.619
2	0.816	2.920	4.303	6.965	9.925	14.089	31.598
3	0.765	2.353	3.182	4.541	5.841	7.453	12.924
4	0.741	2.132	2.776	3.747	4.604	5.598	8.610
5	0.727	2.015	2.571	3.365	4.032	4.773	6.869
6	0.718	1.943	2.447	3.143	3.707	4.317	5.959
7	0.711	1.895	2.365	2.998	3.500	4.029	5.408
8	0.706	1.860	2.306	2.896	3.355	3.832	5.041
9	0.703	1.833	2.262	2.821	3.250	3.690	4.781
10	0.700	1.812	2.228	2.764	3.169	3.581	4.587
15	0.691	1.753	2.131	2.602	2.947	3.252	4.073
20	0.687	1.725	2.086	2.528	2.845	3.153	3.850
25	0.684	1.708	2.060	2.485	2.787	3.078	3.725
30	0.683	1.697	2.042	2.457	2.750	3.030	3.646
40	0.681	1.684	2.021	2.423	2.704	2.971	3.551
60	0.679	1.671	2.000	2.390	2.660	2.915	3.460
120	0.677	1.658	1.980	2.358	2.617	2.860	3.373
∞	0.674	1.645	1.960	2.326	2.576	2.807	3.291

In calculating confidence intervals, σ may be substituted for s in Equation 4-3 if you have a great deal of experience with a particular method and have therefore determined its "true" population standard deviation. If σ is used instead of s, the value of t to use in Equation 4-3 comes from the bottom row of this table.

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