※ 注意：請於試卷上「非選擇題作答區」內依序作答，並應註明作答之部份及其題號。

Section A. (38%)

(Please write down your answer in detail)

1. The sulfate ion concentration in natural water can be determined by measuring the turbidity that results when an excess of $BaCl_2$ is added to a measured quantity of the sample. A turbidimeter, the instrument used for this analysis, was calibrated with a series of standard Na_2SO_4 solutions. The following data were obtained in the calibration for sulfate concentrations, C_x:

C_x, mg SO_4^{2-}/L	Turbidimeter Reading, R
0.00	0.06
5.00	1.33
10.0	2.51
15.0	4.02
20.0	5.31

(a) What are the two assumption of the least-squares method? (4%)
(b) Compute the least-squares slope and intercept for the best straight line among the points. (4%)
(c) Students found that the unknown concentration of samples were measured with less uncertainty near 10 mg SO_4^{2-}/L from the constructed calibration curve than those made at the extremes. Explain the reason from the following equation: (3%)

$$s_c = \frac{s_r}{m}\sqrt{\frac{1}{M} + \frac{1}{N} + \frac{(\bar{y}_c - \bar{y})^2}{m^2 S_{xx}}}$$

(d) Given that s_m and s_b are 3.321×10^{-5} and 1.992×10^{-5} respectively, find the detection limit for the k value corresponding to 98.3% confidence level? (2%) What is the probability of type I error occurring in a two-tail mode? (2%)

2. Please plot the titration curve for the titration of 10 mL 0.1 M H_3PO_4 with 0.1 M NaOH. Denote the location of the first and second equivalence points in terms of pH value and the amount of NaOH required. In addition, calculate the α_1 value at pH = 6.0. (10%)

H_3PO_4 $K_{a1} = 7.11 \times 10^{-3}$ $K_{a2} = 6.31 \times 10^{-8}$ $K_{a3} = 4.50 \times 10^{-13}$

$$\alpha_0 = \frac{[H_3O^+]^3}{[H_3O^+]^3 + K_{a1}[H_3O^+]^2 + K_{a1}K_{a2}[H_3O^+] + K_{a1}K_{a2}K_{a3}}$$

3. One $CaSO_4$ particle exists in the 10 μM $Ca(NO_3)_2$ aqueous solution. Describe the dielectrical double layer formation mechanism in detail. (5%)

4. Define the following electrochemisty terms as clear as possible. (8%)
(a) Concentration polarization
(b) Faradaic and nonfaradaic current
(c) Polarography
(d) Junction potential

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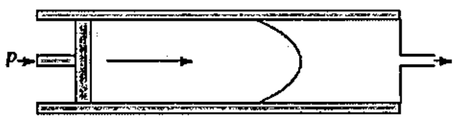
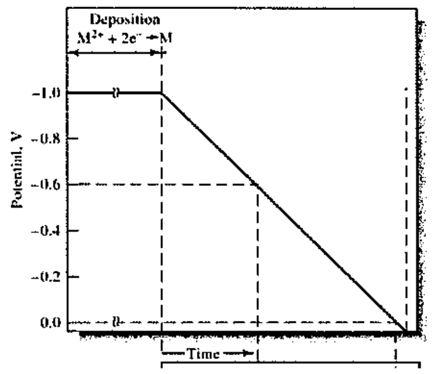
Section B.(12%)

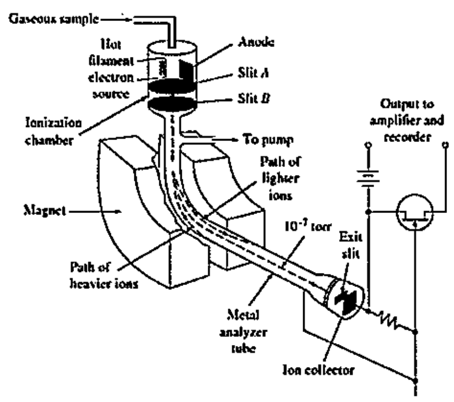
5. Several analytical techniques and figures or equations are shown below. Please assign the appropriate items to the corresponding techniques. (Tick all that apply)
   4-1. Capillary electrophoresis (2%, no partial credit.)
   4-2. Fluorescence spectroscopy (2%, no partial credit.)
   4-3. Liquid chromatography (2%, no partial credit.)
   4-4. Gas chromatography (2%, no partial credit.)
   4-5. Mass spectrometry (2%, no partial credit.)
   4-6. Voltammetry (2%, no partial credit.)



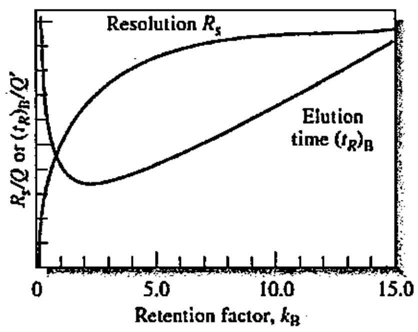
(A)



(B)



(C)



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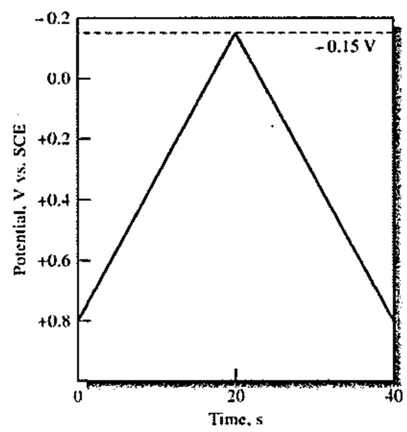

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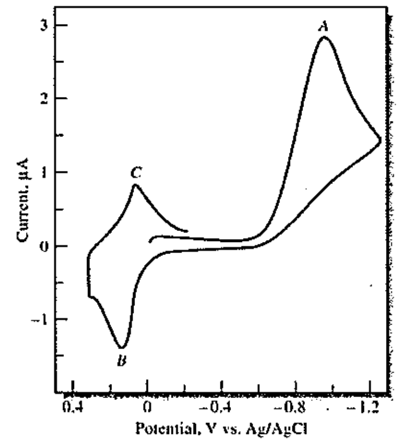
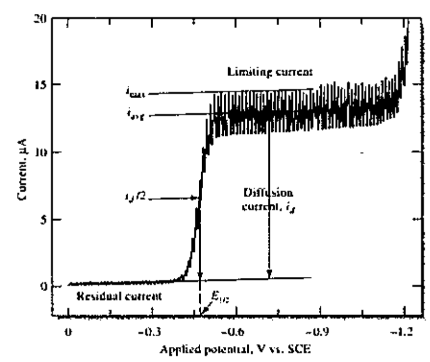


(F)

$$\phi_F = \frac{k_F}{k_F + k_{nr}}$$

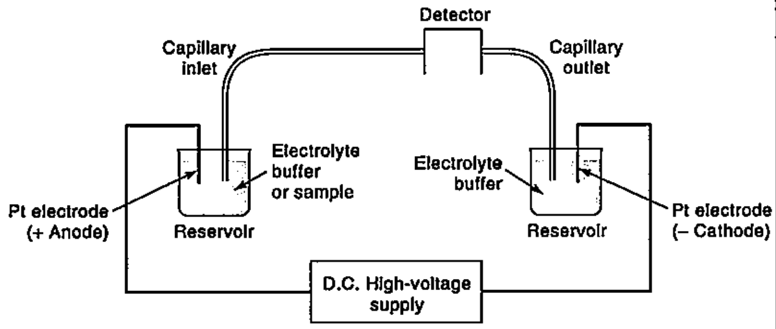
(G)



(H)

$$H = A + \frac{B}{u} + C_S u$$

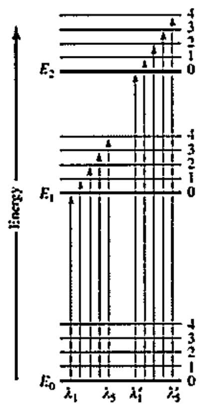
(I)



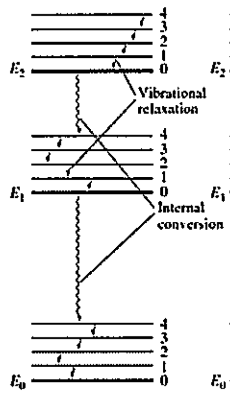
(J)

$$R_s = \frac{\Delta Z}{\frac{W_A}{2} + \frac{W_B}{2}} = \frac{2\Delta Z}{W_A + W_B} = \frac{2[(t_R)_B - (t_R)_A]}{W_A + W_B}$$

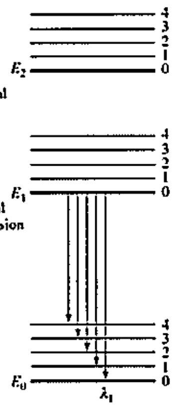
(K)



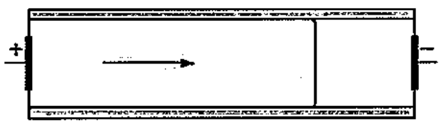
(L)



(M)



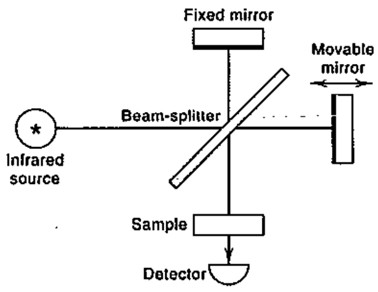
(N)



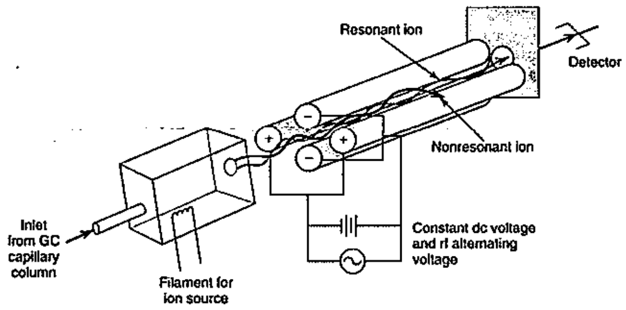
(O)

$$(i_d)_{\max} = 708nD^{1/2}m^{2/3}t^{1/6}c$$

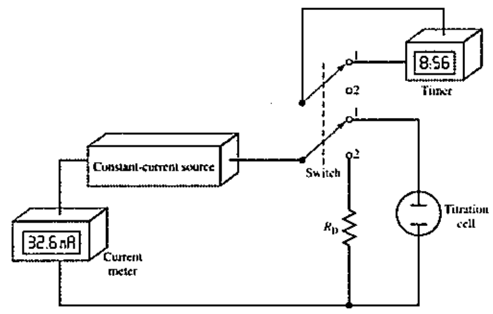
(P)



(Q)



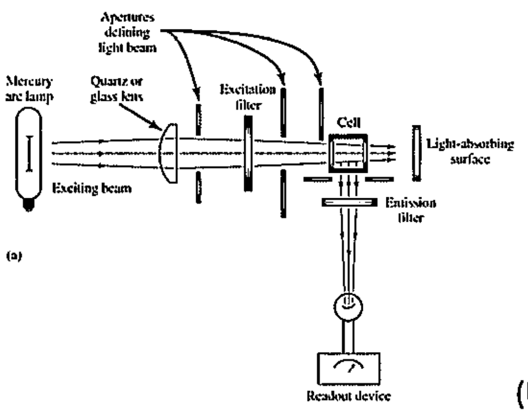
(R)



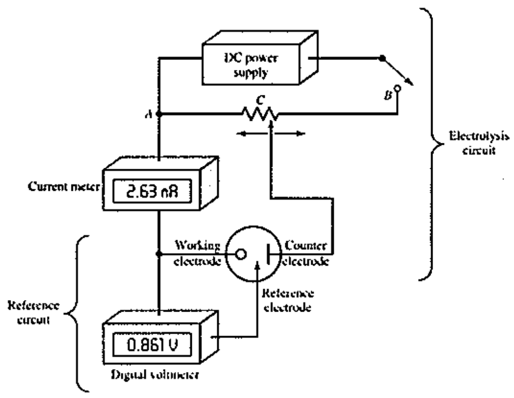
(S)

$$N = \frac{\mu_e V}{2D}$$

(T)



(U)



(V)

Section C. (50%)

1. (8 pts) The mechanism of NO_2Cl decomposition is suggested as follows:

$$NO_2Cl \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + Cl$$

$$NO_2Cl + Cl \xrightarrow{k_2} NO_2 + Cl_2$$

(1A). Use a steady-state approximation to express the Cl_2 production rate in terms of NO_2Cl and NO_2.

(1B). Under what condition, the Cl_2 production rate is second-order to NO_2Cl.

2. (18 pts) The initiate state of 1 mole of an ideal gas is 3.0 L at 300 K.

(2A). The system is now expanded from 3.0 L to 6.0 L isothermally and reversibly (step 1). Calculate ***q, w, ΔS, and ΔG*** of this process.

(2B). The expanded state is then carried out with three additional, sequential steps to return to its initial state: constant volume heating, adiabatic compression, and constant pressure compression. Qualitatively sketch the ***H*** (y-axis) vs. ***S*** (x-axis) curve of all 4 steps and label each step.

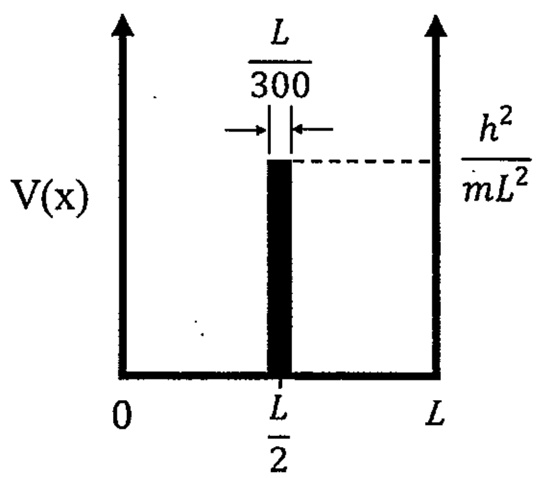
(2C). How to verify if a thermodynamic parameter is a state function.

3. (18 pts) The absorption spectrum of a conjugated molecule of length L can be approximated as an electron trapped in a one-dimensional 1D "particle in a box", where $V(x) = 0$ for $0<x<L$, but $V(x) = \infty$ otherwise. 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…

(3A). Given the dipole operator for the electron is $\hat{\mu} = e\hat{r}$, what are the selection rules for the electronic transitions in this model? Explain why.

(3B). Assume the electron starts in the ground state of the 1D box potential, sketch the absorption spectrum of the molecule.

(3C). Now, if in the middle of the 1D box, there exists a small, thin barrier with barrier height specified as drawn here. Sketch $\varphi_1(x)$ and $\varphi_2(x)$.



4. (6 pts) A three-state system consisting of ***N*** particles. The energy of the ground state is ***0***, and that of the first and second excited states are ε_0 and $(2\varepsilon_0)$, with $\varepsilon_0 > 0$. Determine the total energy ***E*** of this ensemble, starting from the molecular partition function ***q***.