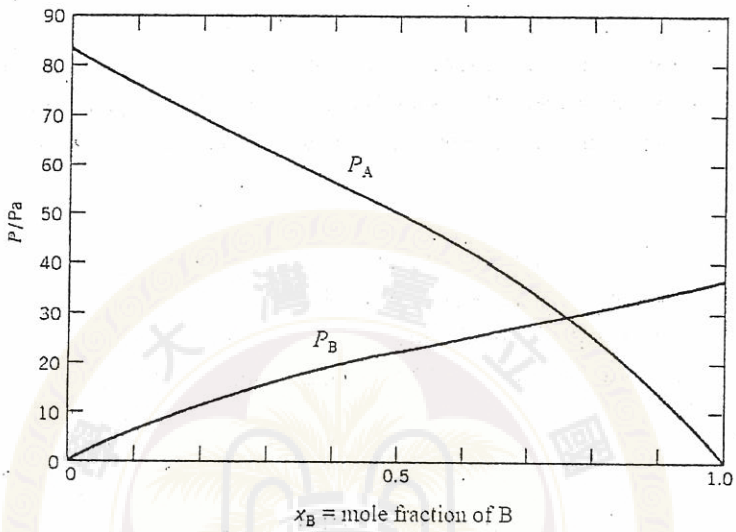
※ 請依序作答，並標明作答之部份及其題號。

Physical Chemistry (50%)

1. (20%) Consider a mixture of two liquids, A and B. The following diagram shows the experimental partial pressure of A and B, denoted as P_A and P_B, respectively.



(a) Explain the relative order (largest, medium, smallest) for the intermolecular interactions of A–B, A–A, and B–B.
(b) Write down the Raoult's law and explain the physical meanings of all the symbols you used.
(c) Write down the Henry's law and explain the physical meanings of all the symbols you used.
(d) Referring to the figure shown above, explain whether there is a region at which both the Henry's law and the Raoult's law are obeyed.
(e) Estimate the Henry's constant of B. Give your answer in the unit of Pa.

2. (10%) For the problem of particle-on-a-line, where

$$V(x)=\begin{cases}0 & for \quad 0\le x\le a\\ \infty & for \quad x>a\\ \infty & for \quad x<0\end{cases},$$

the Hamiltonian of the system is usually written as $-\dfrac{\hbar^2}{2m}\dfrac{\partial^2}{\partial x^2}$. A student argues that because the above Hamiltonian operator commutes with the momentum operator, $\hat{p}_x=-i\hbar\dfrac{\partial}{\partial x}$, therefore the wave function $\Psi(x)=\sqrt{\dfrac{2}{a}}\sin\left(\dfrac{n\pi}{a}x\right)$ must also be the eigenfunction of $\hat{p}_x$. Do you agree with this argument? Explain your answer in two or three sentences.

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3. (10%) The Helmholtz energy is defined as $A = U - TS$. Prove that

$$S = -\left(\frac{\partial A}{\partial T}\right)_V$$

4. (10%) Consider a system of supercooled water at 263 K. If the system is **isolated**, predict what would happen after a spontaneous change. Explain your prediction with or without calculations. [Hints: you still get marks if you can eliminate some impossible results]

You may or may not need the following data:

Heat capacity of ice = 36.8 $JK^{-1}mol^{-1}$

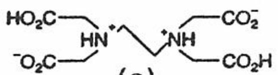
Heat capacity of liquid water = 75.3 $JK^{-1}mol^{-1}$

Latent heat of fusion at 273 K = –6004 $Jmol^{-1}$

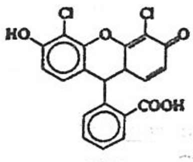
Part II. Analytical Chemistry (50%)

1.(7%) (a) Sketch the appearance of the following analytical apparatus: (i) transfer pipet, (ii) volumetric flask, (iii) Kjeldahl flask, (iv) Buchner funnel. (b) Describe (including all the related chemical equations to show the relationship between the unknown quantity and the final measurement) the procedure used in the indirect Kjeldahl method.

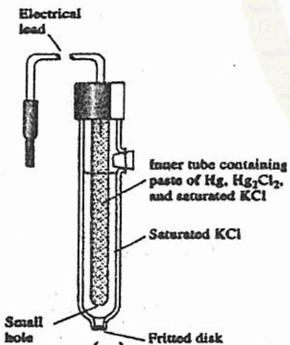
2.(9%) Give (i) the full name, (ii) the role of use (in the scope of chemical analysis), and (iii) the analytical method for each of the substances, apparatus, and instrument components shown below. The answers for (a) are given here as an example: (a) (i) ethylenediaminetetraacetic acid, (ii) a complexing reagent, and (iii) complexiometric titration.



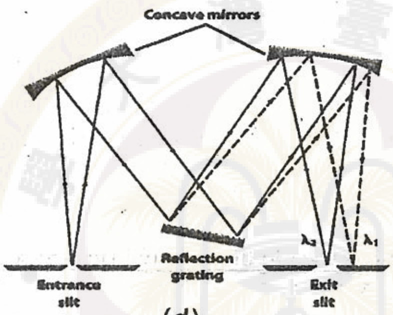
(a)



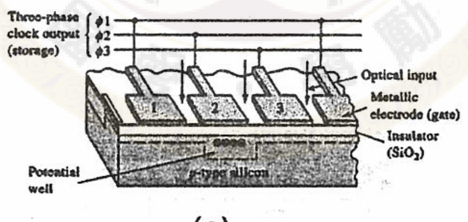
(b)



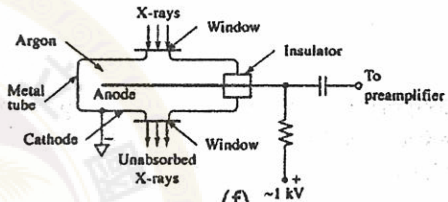
(c)



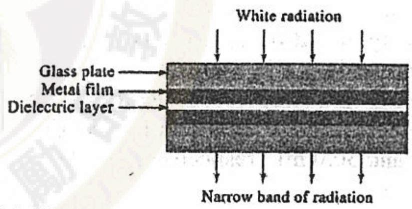
(d)



(e)



(f)



(g)

3.(4%) Define (a) Scatchard plot, (b) standard addition

4.(6%) Distinguish (a) among shot noise, flicker noise, and Johnson noise; (b) among Mie scattering, Rayleigh scattering, and Raman scattering

5.(8%) Zinc ions in aqueous solution are colorless. (a) Suggest an analytical method (including the reagent used and the analytical procedure) with which zinc ions in aqueous solution can be quantitatively determined using a light source which has frequency in the visible region. (b) The accuracy of your suggested method can be checked by analyzing zinc ions in a sample solution and comparing the results with those obtained using a known, established method. Assume that the results (in ppm) are as follows. At a confidence level of 95%, show your calculation to decide if a significant difference exists in analyzing the content of zinc in the sample between the two methods?

Suggested Method	Established Method
21.70	21.00
22.40	21.30
21.60	21.10
22.00	21.70
20.10	21.40
21.80	

6.(6%) (a) Draw a voltage integrator operational amplifier circuit. (b) Write down the general equation of integration for the circuit. (c) Give an example of the use of the voltage integrator circuit in chemical analysis.

7.(10%) A solution of 0.100 M cerium(IV) sulfate is used to titrate a sulfuric acid solution that contains both iron(II) and iron (III) salts. (a) Describe the procedure (including the appropriate apparatus and the chemicals used) one has to take before the titration so as to determine the total amount of iron in the solution by one titration. (b) Before the titration is performed, the above-stated procedure is done on a mixture solution of 100.0 mL sulfuric acid that contains 2.00 mmol of an iron(II) salt and 3.00 mmol of an iron(III) salt. Assume that the formal potential of the Fe^{2+}-Fe^{3+} system in sulfuric acid is 0.68 V and that of the Ce^{3+}-Ce^{4+} system is 1.44 V. Calculate the potentials of a platinum electrode after the addition of 10.0 and 50.0 mL, respectively, of the cerium(IV) titrant.

Critical Values of *F* at the 95% confidence level

Degrees of Freedom (Denominator)	Degrees of Freedom (Numerator) 2	3	4	5	6	10	12	20	∞
2	19.00	19.16	19.25	19.30	19.33	19.40	19.41	19.45	19.50
3	9.55	9.28	9.12	9.01	8.94	8.79	8.74	8.66	8.53
4	6.94	6.59	6.39	6.26	6.16	5.96	5.91	5.80	5.63
5	5.79	5.41	5.19	5.05	4.95	4.74	4.68	4.56	4.36
6	5.14	4.76	4.53	4.39	4.28	4.06	4.00	3.87	3.67
10	4.10	3.71	3.48	3.33	3.22	2.98	2.91	2.77	2.54
12	3.89	3.49	3.26	3.11	3.00	2.75	2.69	2.54	2.30
20	3.49	3.10	2.87	2.71	2.60	2.35	2.28	2.12	1.84
∞	3.00	2.60	2.37	2.21	2.10	1.83	1.75	1.57	1.00

Values of Student's *t*

Degrees of freedom	Confidence level (%) 50	90	95	98	99
1	1.000	6.314	12.706	31.821	63.657
2	0.816	2.920	4.303	6.965	9.925
3	0.765	2.353	3.182	4.541	5.841
4	0.741	2.132	2.776	3.747	4.604
5	0.727	2.015	2.571	3.365	4.032
6	0.718	1.943	2.447	3.143	3.707
7	0.711	1.895	2.365	2.998	3.500
8	0.706	1.860	2.306	2.896	3.355
9	0.703	1.833	2.262	2.821	3.250

Table - Critical Values for T_n

Number of Observations	T_n Confidence Level 95%	97.5%	99%
3	1.15	1.15	1.15
4	1.46	1.48	1.49
5	1.67	1.71	1.75
6	1.82	1.89	1.94
7	1.94	2.02	2.10
8	2.03	2.13	2.22
9	2.11	2.21	2.32
10	2.18	2.29	2.41