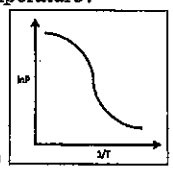
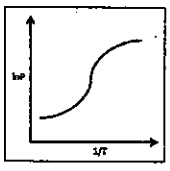
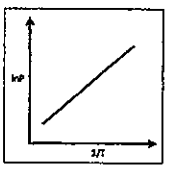
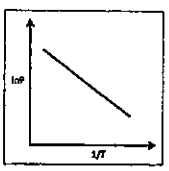
(I). 單選題 (選出一個最適當的答案): 每題 2.5 分. (答案直接填入 "選擇題作答區" 內)

1. Given $\hat{p}_x = -i\hbar\frac{d}{dx}$, what is the commutator $[\hat{p}_x, \hat{x}]$?
   (A) $i\hbar$ (B) $-i\hbar$ (C) $i\hbar\hat{p}_x$ (D) $-i\hbar\hat{p}_x$ (E) None of the above
2. The normalized wave function for a particle in a one-dimensional box is $\psi_n(x) = \sqrt{2/L}\sin(n\pi x/L)$, where L is the length of the box. What is the probability that the particle will lie between $x = 0$ and $x = L/4$ if the particle is in the $n = 2$ excited state?
   (A) $\sqrt{\frac{2}{L}}$ (B) $\frac{\sqrt{2L}}{2\pi}$ (C) $\frac{\pi-2}{4\pi}$ (D) $\frac{1}{4}$ (E) None of the above
3. How many IR active modes are there in the carbon dioxide (CO_2) molecule?
   (A) 0 (B) 1 (C) 2 (D) 3 (E) 4
4. Which one of the following statements is incorrect?
   (A) The zero point energy is lower for a He atom in a box than for an electron. (B) The wave function of a system must satisfy the time-independent Schrödinger equation. (C) Molecules with a longer π-conjugated system tend to absorb photons with higher energies. (D) If we measure the observable $\hat{A}$ when the system's wavefunction is not an eigenfunction of $\hat{A}$, we still get an outcome that is an eigenvalue of $\hat{A}$. (E) The $\hat{L}^2$ eigenfunctions are degenerate except for $l = 0$.
5. Consider carbon atom in the configuration $[He]2s^22p^2$. This carbon configuration contains three terms: ^3P, ^1D, ^1S. The number of states that belong to the ^3P term is?
   (A) 15 (B) 9 (C) 5 (D) 3 (E) None of the above
6. The O-H stretching frequency of an alcohol is 3400 cm^{-1}. What would be the frequency of the same mode when the hydrogen is changed to deuterium?
   (A) 1700 cm^{-1} (B) 2400 cm^{-1} (C) 3400 cm^{-1} (D) 4800 cm^{-1} (E) None of the above
7. 2.00 mol of a monatomic ideal gas is expanded adiabatically and reversibly from a volume of 20.0 L to a volume of 60.0 L. Suppose the system is initially at a temperature of T=310 K, what is the final temperature of the gas?
   (A) 50K (B) 100K (C) 150K (D) 200K (E) 250K
8. Ethanol' s enthalpy of vaporization is 38.7 kJ mol^{-1} at its normal boiling point, 78°C. Assume that the vapor is an ideal gas and neglect the volume of liquid relative to that of the vapor. What is ΔS_{sys} when 1.00 mol ethanol is vaporized reversibly at 78°C and 1 atm? (The gas constant R=8.314 $JK^{-1}mol^{-1}$).
   (A) 110 JK^{-1} (B) 11 JK^{-1} (C) 496 JK^{-1} (D) 49.6 JK^{-1} (E) None of the above
9. The van der Waals equation of state is $\left(P + a\frac{n^2}{V^2}\right)(V - nb) = nRT$. What is the coefficient b related to?
   (A) Strength of intermolecular interactions (B) Density of gas (C) Temperature (D) Excluded volume of the molecule (E) None of the above
10. A thermodynamic engine operates reversibly between two temperature reservoirs, absorbing heat from the high-temperature bath at 500 K and discharging heat to the low-temperature bath at 300 K. What is the thermodynamic efficiency of the engine?
    (A) 50% (B) 40% (C) 30% (D) 20% (E) 10%
11. The Joule – Thomson coefficient of an ideal gas system is?
    (A) V/C_p (B) V/C_V (C) 0 (D) V/nR (E) None of the above
12. Which of the following is a plot of the natural logarithm of the vapor pressure of water versus inverse temperature?
    (A)  (B)  (C)  (D) 
    (E) None of the above

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(II). 敘述與計算題 (共 20 分):

13. Consider a particle with mass m in a one-dimensional harmonic potential, $V(x)=\frac{1}{2}kx^2$.
(A) (2 marks) Give the time-independent Schrödinger equation for this system
(B) (2 marks) Show that the wave function $\psi(x)=Ne^{-\alpha x^2}$ is a solution to the Schrödinger equation (α and N are constants).
(C) (3 marks) Calculate the constant α and the energy of the quantum state represented by this wave function.

14. Heat capacities at constant pressure (C_p) and constant volume (C_v) are related to each other by the thermodynamic identity:

$$C_P - C_V = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]\left(\frac{\partial V}{\partial T}\right)_P$$

(A) (5 marks) Give a proof of this equation
(B) (2 marks) Calculate $C_p - C_v$ for a system containing 1 mol of ideal gas.

15. (6 marks) The kinetics of enzyme catalysis can be summarized by the following scheme:

$$\mathrm{E} + \mathrm{S} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{ES}$$

$$\mathrm{ES} \xrightarrow{k_2} \mathrm{E} + \mathrm{P}$$

where E denotes the enzyme, S is the substrate, and P is the product. Use the steady-state approximation to derive the rate law for the product generation (this is the famous Michaelis – Menten equation).

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Analytical Chemistry (50%)

1. Write down the English full names of the following abbreviations used in Analytical Chemistry: (i) SCE, (ii) EDTA, (iii) ICP, (iv) CCD, (v) HPLC, (vi) ESCA, (vii) AAS, (viii) WDXRF (8%)

2. (a) Discuss the purpose of use of the (i) auxiliary complexing agent and (ii) auxiliary reducing agent in chemical analysis. (b) Name two chemicals for each of the agents stated in (a). (6%)

3. Describe the spectroscopic process involved in (a) uv/vis spectrometry, (b) atomic fluorescence spectrometry, (c) Auger electron spectroscopy. (6%)

4. *Show your calculation* to obtain the equivalence point in (i) E_{Pt} for the titration of 50.0 mL, 0.0100 M Fe^{2+} ($E°_{Fe^{3+}/Fe^{2+}}$(1 M H_2SO_4) = 0.68 V) with 0.0100 M Ce^{4+} ($E°_{Ce^{4+}/Ce^{3+}}$(1 M H_2SO_4) = 1.44 V), both dissolved in 1 M sulfuric acid solution; (ii) pCa for the complexiometric titration of 50.0 mL, 0.0500 M $Ca(NO_3)_2$ with 0.100 M EDTA ($K_{f,\,Ca\text{-}EDTA}$ = 5.0 x 10^{10}), both buffered at pH10 ($\alpha_{4,\,pH10}$ = 0.35). (7%)

5. The air sample collected from an industrial city was analyzed based on a well-developed analysis method to contain 41.13 μg/m³ *p*-dichlorobenzene (*p*DCB). Analysis of the *p*DCB concentration (c_{pDCB}) in the sample using a newly developed molecular absorption spectrometry (with the pathlength of the sample cell of 10.0 cm and the *p*DCB molar absorptivity of 2.30 x 10^4 L/mol-cm) gave the following data: c_{pDCB} (in μg/m³) = 41.02, 40.80, 42.02, 41.11, 41.07. By pooling data from several analyses, it was established that $s \rightarrow \sigma$ = 0.15 μg/m³. (a) Treat the data statistically to show if the data indicate the presence of a systematic error at the 90% confidence level? (b) Quantitative molecular absorption spectrometry is based on Beer's law. Calculate the transmittance of the sample that corresponds to the mean value of the data. (8%)

Table - Critical Values for *Q*

Number of Observations	*Q* Confidence Level 90%	96%	99%
3	0.94	0.98	0.99
4	0.76	0.85	0.93
5	0.64	0.73	0.82
6	0.56	0.64	0.74
7	0.51	0.59	0.68
8	0.47	0.54	0.63
9	0.44	0.51	0.60
10	0.41	0.48	0.57

Confidence Levels for Various Values of *z*

Confidence Level, %	*z*
50	0.67
68	1.00
80	1.28
90	1.64
95	1.96
95.4	2.00
99	2.58
99.7	3.00
99.9	3.29

Values of *t*

Degrees of Freedom	80%	90%	95%	99%	99.9%
1	3.08	6.31	12.7	63.7	637
2	1.89	2.92	4.30	9.92	31.6
3	1.64	2.35	3.18	5.84	12.9
4	1.53	2.13	2.78	4.60	8.61
5	1.48	2.02	2.57	4.03	6.87
6	1.44	1.94	2.45	3.71	5.96
7	1.42	1.90	2.36	3.50	5.41
8	1.40	1.86	2.31	3.36	5.04
9	1.38	1.83	2.26	3.25	4.78
10	1.37	1.81	2.23	3.17	4.59

6. (a) Explain how one can estimate the pH of microscopic vesicles in living cells by infusing an indicator (HIn) into the vesicles and measuring the quotient [In^-]/[HIn] from the spectrum of the indicator inside the vesicles. (b) List at least two main experimental factors that will affect the accuracy of the pH value estimated above. **Explain.** (4%)

7. (a) Describe the molecular property (in less than 5 words each) which change associated with a molecular vibration gives (i) infrared absorption and (ii) Raman scattering, respectively. (b) Discuss in detail why Raman spectroscopy is superior to IR spectroscopy for (i) analyzing organosulfur compounds, (ii) in-vivo study of biomolecules/biomaterials. (c) Suggest one approach with which a peak detected in a spectrometer using a laser as the excitation source can be distinguished as due to Raman scattering or fluorescence. (d) Among three sources (cases) of uncertainties in transmittance measurements (shown on the right), which source limits the Raman spectroscopy resolution most but has the minimum effect on the IR spectroscopy resolution? Explain. (11%)

Category	Characterized by	Typical Sources
Case I	$s_T = k_1$	Limited readout resolution
		Heat detector Johnson noise
		Dark current and amplifier noise
Case II	$s_T = k_2\sqrt{T^2 + T}$	Photon detector shot noise
Case III	$s_T = k_3 T$	Cell positioning uncertainties
		Source flicker

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