You may find the following approximate values and equations useful:

	$X = 2$	3	4	5	6	7	8	9
$\log_{10} X$	0.301	0.477	0.602	0.699	0.788	0.845	0.902	0.954
$10^{X/10}$	1.584	1.995	2.512	3.162	3.981	5.012	0.310	7.943

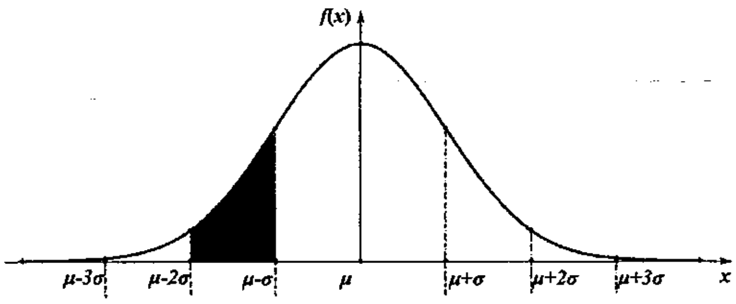
N_A (Avogadro number) ~ 6.02×10^{23} mol^{-1}, h (Planck constant) ~ 6.63×10^{-34} m^2 kg s^{-1}, π ~ 3.14159, e ~ 2.71828
Molar mass (g/mol): $Al(OH)_3$ 78.0, CdS 144.5, CaF_2 78.1, $CaCO_3$ 100.1

Gaussian / normal distribution: $f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2}$ Nernst equation: $E_{red} = E^0_{red} - \frac{RT}{zF} lnQ$

第一大題單選題 考生應作答於答案卡 (1 – 4, 每題 3 分共 12 分)

1. Given the following dataset: 7, 5, 9, 15, 11, 8, 10. Which of the following is correct? (3%)
   A) Mean = 9
   B) Median = 9.3
   C) Variance (σ^2) = 8.78
   D) Sample size (n) = 6
   E) Standard deviation (σ) = 4.11

2. The shaded area accounts for approximately what percentage of the total area under the curve? (3%)



   A) 5.5% B) 10.7% C) 13.5% D) 25.4% E) 68.2%

3. A research group at NTU had studied the effect of a potential anticancer drug **X**. In their randomized trial, one group of mice was given **X** and another group was given sugar pills (placebo). Tumor size in many mice had reduced, and they reported the p-value to be $p = 0.02$. Which of the following interpretation is correct? (3%)
   A) There is a 98% chance drug **X** is an effective anticancer drug.
   B) There is a 98% chance that this experiment can be reproduced by other scientists.
   C) There is a 2% chance drug **X** is an ineffective anticancer drug.
   D) There is a 2% chance to observe the tumor reduction results seen in this study even if drug **X** has no effect at all.
   E) All of the above.

4. Which of the following statements about UV-Vis spectrometry is correct? (3%)
   A) Absorbance (A) is defined as $A = log\left(\frac{P}{P_0}\right)$, where P_0 and P represent the power of the light beam that has passed through the solvent and the analyte-containing solution, respectively.
   B) Absorbance (A) is the reciprocal of transmittance (T); in other words, A = 1/T.
   C) The molar extinction coefficient in Beer's law in SI units is m^2/mol.
   D) The molar extinction coefficient is characteristic of a molecular species and independent of the solvent.
   E) Beer's law accurately describes the absorption behavior of all solutions regardless of their analyte concentration.

第二大題單選題 考生應作答於答案卡 (5 – 10, 每題 4 分共 24 分)

5. Which of the following statements about a Fourier transform IR spectrometer is correct? (4%)
   A) It accurately measures the spectroscopic response one wavelength at a time.

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B) It needs more time to acquire a spectrum than a scanning IR spectrometer.
C) It is usually equipped with a monochromator.
D) The absorbance at all wavelengths are measured simultaneously.
E) This type of instrument was named after the American physicist Daniel J. Fourier.

6. Which of the following description about atomic X-ray spectrometry is *NOT* correct? (4%)
   A) X-rays are electromagnetic radiation with very short wavelengths (≤ 10 nm).
   B) X-ray line spectra involves electronic transitions of the innermost atomic orbitals.
   C) The K series refers to X-radiation as a result of electrons moving from outer orbitals of an atom into a vacant orbital of the K shell.
   D) The K_α line is the result of a vacant K orbital filled by an electron falling from the M shell.
   E) The wavelength (energy) of the K_α lines for molybdenum is independent of its oxidation state.

7. Which of the following description about various forms of light emission is *NOT* correct? (4%)
   A) Fluorescence and phosphorescence signals are typically measured at a 90° angle to the excitation beam.
   B) In fluorescence spectra, the emitted radiation usually has a longer wavelength than the excitation radiation; this difference is called the Stokes shift.
   C) The average lifetime of an excited triplet state is orders of magnitude shorter than that of an excited singlet state.
   D) Chemiluminescence occurs when a chemical reaction generates an electronically excited species; this excited molecular species then emits light as it relaxes to the ground state.
   E) Chemiluminescence is usually measured without selecting a specific wavelength for detection.

8. All of the following are spontaneous reactions that proceed to the right. Standard reduction potentials at 25°C are provided for some half-cell reactions. Based on this information, rank the relative strengths of H^+, Ag^+, Cd^{2+}, Cu^{2+}, and Zn^{2+} as electron acceptors (oxidizing agents) at 25°C. (4%)

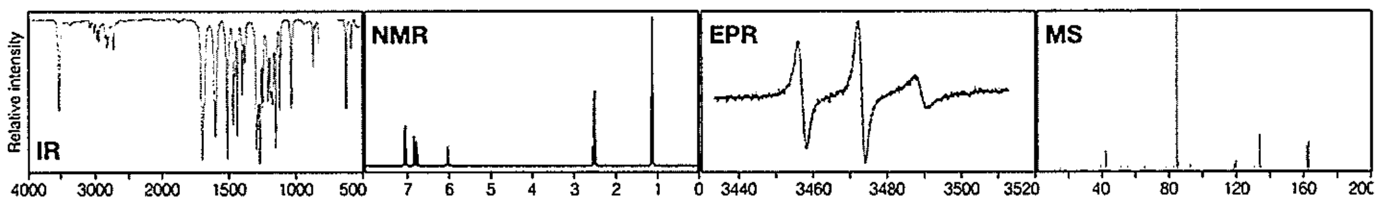
   $2H^+ + Cd_{(s)} \rightleftharpoons H_2 + Cd^{2+}$ $\qquad Ag^+ + e^- \rightleftharpoons Ag_{(s)} \quad E^0_{red} = +0.799\ V$

   $2Ag^+ + H_{2(g)} \rightleftharpoons 2Ag_{(s)} + 2H^+$ $\qquad Cu^{2+} + 2e^- \rightleftharpoons Cu_{(s)}\, E^0_{red} = +0.337\ V$

   $Cd^{2+} + Zn_{(s)} \rightleftharpoons Cd_{(s)} + Zn^{2+}$

   A) $Cu^{2+} > H^+ > Ag^+ > Cd^{2+} > Zn^{2+}$
   B) $Ag^+ > Cu^{2+} > H^+ > Cd^{2+} > Zn^{2+}$
   C) $Zn^{2+} > Cd^+ > Ag^+ > Cu^{2+} > H^+$
   D) $Zn^{2+} > Cd^+ > H^+ > Ag^+ > Cu^{2+}$
   E) There is not enough information to deduce their relative oxidative strengths.

9. Graphs shown below are data obtained by the following analytical methods (from left to right): IR, NMR, EPR, and MS. What are the correct x-axis labels and units? (4%)



   A) Micrometer (μm) – magnetic field (MHz) – magnetic field (G) – atomic mass unit (Da)
   B) Wavenumber (1/cm) – magnetic field (MHz) – magnetic field (G) – atomic mass unit to charge ratio (Da/z)
   C) Wavenumber (1/cm) – chemical shift (ppm) – magnetic field (G) – atomic mass unit to charge ratio (Da/z)
   D) Micrometer (μm) – chemical shift (ppm) – Coulomb (C) – atomic mass unit (Da)
   E) Wavenumber (1/cm) – chemical shift (ppm) – resistance (Ω) – atomic mass unit (Da)

10. Which of the following description is correct? (4%)
   A) The solubility product constant (Ksp) of aluminum hydroxide (Al(OH)3) is 3 × 10–34; the Ksp of cadmium sulfide (CdS) is 1 × 10–27. Based on this information, we know that Al(OH)3 is less soluble than CdS in pure water.

B) A glass of aqueous solution (100 mL) contains $[Ca^{2+}] = 2.13 \times 10^{-4}$ M, $[F^-] = 4.26 \times 10^{-4}$ M, and 0.781 g of insoluble CaF_2 solid. Based on this information, we can estimate the K_{sp} of CaF_2 to be ~3.9×10^{-11}.

C) Even through the same chemical can sometimes exist in more than one crystalline form, *e.g.*, $CaCO_3$ can be both calcite and aragonite, they are always equally soluble.

D) The pK_{a1} and pK_{a2} of methionine are 2.28 and 9.21. Based on this information, we know that methionine has the best buffering power (capacity) at pH 5.75 (the mid-point between the two pK_a values).

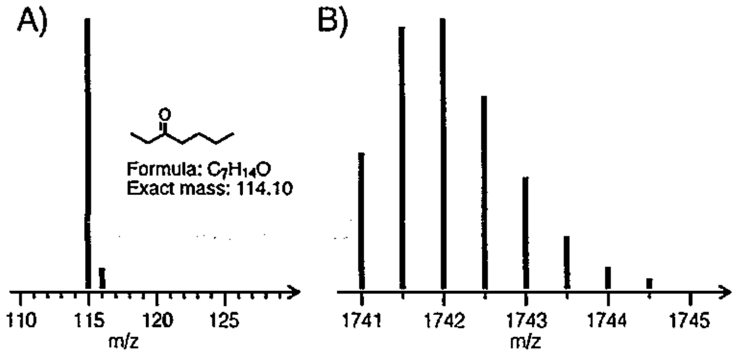
E) The hydrogen cation concentration ($[H^+]$) of a pH 6.5 solution is 5.0×10^{-7} M.

第三大題 考生應作答於答案卷 (11-12, 每題 7 分共 14 分)

11. Mass spectrometry questions.

A) A) is the mass spectrum of a 3-heptanone sample obtained under positive ion mode showing the protonated molecular species $[MH]^+$ with a major peak at 114 + 1 ~ 115 (m/z). This 3-hetpanone sample is chromatographically pure with only a single peak on HPLC. Why does it have a small peak at 116 (m/z) on the mass spectrum? (4%)

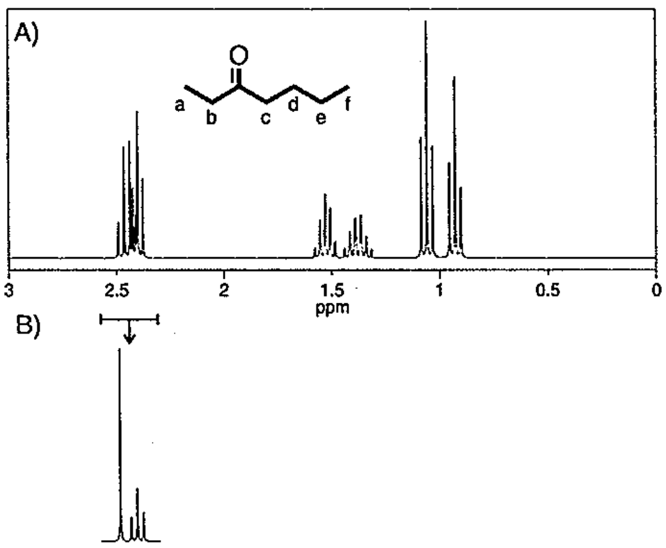
B) B) is the mass spectrum of an unknown organic molecule obtained under positive ion mode. Estimate the number of protons associated with this ion and the mono-isotopic mass of this molecule. Show your work. (3%)



12. Nuclear magnetic resonance (NMR) questions.

A) A) is the [1]H NMR spectrum of 3-hetanone. Hydrogens associated with each carbon are labeled in the molecular structure shown below. Assigned each group of peaks from left to right on the NMR spectrum with lower-case letters (a-f). (4%)

B) Homonuclear decoupling is a technique where the sample to be analyzed is irradiated at a select frequency to eliminate the effect of coupling due to certain nuclei. In other words, the signal of a select nucleus can be selectively saturated, such that this nucleus can no longer couple to neighboring nuclei. This technique helps to simplify complicated peak splitting. Irradiation at which group of protons (a-f) would result in spectral simplification in the 2.3 – 2.6 ppm range as shown in **B)**? Use the same lower-case letter(s) notation in **A)**. (3%)



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13. (20 pts) A system of n mole ideal gas is characterized by (a) $U = nCT$ where U is the internal energy, T the absolute temperature, and C a constant, (b) $PV = nRT$ where R is the gas constant, (c) $\mu = RT\ln(n/V) + CT\ln(n/U)$ where μ is the chemical potential.
   (a) (8 pts) Integrate the first and the second laws $TdS = dU + PdV - \mu dn$, together with the above conditions (a)(b)(c), to obtain the entropy formula $S(U, V, n)$, which is a function of U, V and n (and T, P, μ are all eliminated).
   (b) (4 pts) Suppose that a slightly different gas system satisfies (a') $U = nCT^\delta$ but not (a), where the constant $\delta \neq 1$. Show that the conditions (a')(b)(c) imply that the entropy change dS is not an exact differential.
   (c) (8 pts) Modify the above chemical potential expression (c) into your (c'), so that (a')(b)(c') make dS an exact differential. Obtain the entropy expression $S(U, V, n)$ from (a')(b)(c').

14. (10 pts) Given the reaction mechanism in which the two steps are both the first order reactions.

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

   (a) (2 pts) Write down the rate laws for $d[A(t)]/dt$ and $d[B(t)]/dt$.
   (b) (3 pts) Initially $[A(t=0)] = A_0$, and $[B(t=0)] = [C(t=0)] = 0$. Apply the steady state approximation on the intermediate B, to solve the product concentration $[C(t)]$.
   (c) (5 pts) Without using the steady state approximation, solve the concentration $[C(t)]$ exactly from the rate laws. What is the condition under which the steady state approximation applies?

15. (20 pts) Consider the spin state of a proton. Recall that the spin operators are

$$\hat{I}_x = \frac{\hbar}{2}\begin{pmatrix} 0, & 1 \\ 1, & 0 \end{pmatrix} \qquad \hat{I}_y = \frac{\hbar}{2}\begin{pmatrix} 0, & -i \\ i, & 0 \end{pmatrix} \qquad \hat{I}_z = \frac{\hbar}{2}\begin{pmatrix} 1, & 0 \\ 0, & -1 \end{pmatrix}$$

where $i = \sqrt{-1}$. Suppose that a static external magnetic field is applied along the y direction, so that the hamiltonian is

$$\hat{H} = -\gamma_p B \hat{I}_y$$

where B is the magnetic field strength, and γ_p is a real constant. Denote the spin up state α and the spin down state β as

$$\alpha = \begin{pmatrix} 1 \\ 0 \end{pmatrix} \qquad \beta = \begin{pmatrix} 0 \\ 1 \end{pmatrix}$$

   (a) (2 pts) Show that the hamiltonian is hermitian.
   (b) (4 pts) Solve the energy eigenvalues and their eigenvectors.
   (c) (2 pts) Suppose that at $t = 0$ the proton is at the state

$$\psi(t=0) = N(2\alpha + i\beta) = N\begin{pmatrix} 2 \\ i \end{pmatrix}$$

   Calculate the normalization constant N.
   (d) (6 pts) The time evolution of the spin state $\psi(t)$ obeys the time-dependent Schrodinger equation

$$i\hbar\frac{\partial}{\partial t}\psi(t) = \hat{H}\psi$$

   Together with the initial condition $\psi(t=0)$ given above, solve $\psi(t)$.
   (e) (6 pts) Calculate the vector $(\langle\hat{I}_x(t)\rangle, \langle\hat{I}_y(t)\rangle, \langle\hat{I}_z(t)\rangle)$ where $\langle\hat{I}_j(t)\rangle$ $(j = x, y, z)$ represents the expectation value of the operator $\hat{I}_j$ at the time t. Plot the three components of this vector as functions of time.

試題隨卷繳回