國立中正大學
114 學年度碩士班招生考試

試 題

［第 3 節］

科目名稱	物理分析化學

－作答注意事項－

※作答前請先核對「試題」、「試卷」與「准考證」之系所組別、科目名稱是否相符。

1.預備鈴響時即可入場，但至考試開始鈴響前，不得翻閱試題，並不得書寫、畫記、作答。

2.考試開始鈴響時，即可開始作答；考試結束鈴響畢，應即停止作答。

3.入場後於考試開始 40 分鐘內不得離場。

4.全部答題均須在試卷（答案卷）作答區內完成。

5.試卷作答限用藍色或黑色筆（含鉛筆）書寫。

6.試題須隨試卷繳還。

物理化學

單選題（每題 2.5 分，務必依考題順序填答，否則不予以計分！）

Answer questions 1-6 for a gas expands isothermally and irreversibly.

1. *w* is
   (A) less than zero.　(B) equal to zero.
   (C) greater than zero.　(D) More information is needed.

2. *q* is
   (A) less than zero.　(B) equal to zero.
   (C) greater than zero.　(D) More information is needed.

3. ΔH is
   (A) less than zero.　(B) equal to zero.
   (C) greater than zero.　(D) More information is needed.

4. ΔE is
   (A) less than zero.　(B) equal to zero.
   (C) greater than zero.　(D) More information is needed.

5. ΔS is
   (A) less than zero.　(B) equal to zero.
   (C) greater than zero.　(D) More information is needed.

6. ΔG is
   (A) less than zero.　(B) equal to zero.
   (C) greater than zero.　(D) More information is needed.

7. The average rate of disappearance of ozone in the reaction $2O_3(g) \rightarrow 3O_2(g)$ is found to be 8.8×10^{-3} atm over a certain interval of time. What is the rate of appearance of O_2 during this interval?
   (A) 5.9×10^{-3} atm/time　(B) 2.6×10^{-2} atm/time
   (C) 1.8×10^{-2} atm/time　(D) 1.3×10^{-2} atm/time

Answer questions 8-11 for the reaction $2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$. The following data were collected:

time (minutes)	$[N_2O_5]$ (mol/L)
0	1.24×10^{-2}
10	0.92×10^{-2}
20	0.68×10^{-2}
30	0.50×10^{-2}
40	0.37×10^{-2}
50	0.28×10^{-2}
70	0.15×10^{-2}

8. The half-life of this reaction is approximately

(A) 18 min (B) 36 min (C) 15 min (D) 23 min (E) 45 min

9. The order of this reaction in N_2O_5 is

(A) 0 (B) 1 (C) 2 (D) 3 (E) none of these

10. The concentration of O_2 at $t = 10$ min is

(A) 0.32×10^{-2} mol/L (B) 2.0×10^{-4} mol/L (C) 0.64×10^{-2} mol/L
(D) 0.16×10^{-2} mol/L (E) none of these

11. The concentration N_2O_5 at 100 min will be approximately

(A) 0.10×10^{-2} mol/L (B) 0.01×10^{-2} mol/L (C) 0.06×10^{-2} mol/L
(D) 0.03×10^{-2} mol/L (E) none of these

12. What is the degeneracy of the $n = 2$ energy level of the hydrogen atom?

(A) 1 (B) 2 (C) 3 (D) 4

13. Which approximation is used in the Hückel molecular orbital theory?

(A) Overlap integrals are set to zero.
(B) Electron correlation is explicitly considered.
(C) Nuclear repulsion is ignored.
(D) Only π-electrons are considered.

14. What is the correct expression for the commutator of position ($\hat{x}$) and momentum ($\hat{p}$) operators in quantum mechanics?

(A) $[\hat{x}, \hat{p}] = 0$ (B) $[\hat{x}, \hat{p}] = i\hbar$ (C) $[\hat{x}, \hat{p}] = -i\hbar$ (D) $[\hat{x}, \hat{p}] = \hbar^2$

15. The Born-Oppenheimer approximation simplifies molecular calculations by:

(A) Ignoring electron-electron interactions
(B) Treating nuclei as stationary relative to electrons
(C) Assuming spherical symmetry of atomic orbitals
(D) Treating electrons as independent particles

16. What is the physical significance of the wavefunction (ψ) in quantum mechanics?
    (A) It represents the probability of finding the particle at a certain position.
    (B) It is directly measurable in experiments.
    (C) Its square ($|\psi|^2$) gives the probability density.
    (D) It describes the particle's momentum distribution.

17. In Raman spectroscopy, the Stokes shift occurs when:
    (A) The scattered photon has a higher energy than the incident photon
    (B) The scattered photon has the same energy as the incident photon
    (C) The scattered photon has a lower energy than the incident photon
    (D) The scattered photon has energy unrelated to the incident photon

18. The Raman effect is more intense for:
    (A) Molecules with a permanent dipole moment
    (B) Molecules with highly polarizable electron clouds
    (C) Molecules in a symmetric environment
    (D) Molecules with high rotational constants

19. Which of the following factors influences the linewidth in electronic spectroscopy?
    (A) The lifetime of the excited state
    (B) The energy of the absorbed photons
    (C) The isotopic composition of the molecule
    (D) The strength of the applied electric field

20. The Franck-Condon principle explains:
    (A) The coupling of electronic and vibrational transitions in molecular spectroscopy
    (B) The intensity distribution in rotational spectra
    (C) The origin of spin-orbit coupling in atomic spectroscopy
    (D) The selection rules in Raman spectroscopy

分析化學

單選題（每題 3 分，務必依考題順序填答，否則不予以計分！）

Answer questions 21-23. A clinical chemist obtained the following data for the alcohol content of a sample of blood: % C_2H_5OH: 0.084, 0.089, and 0.079. At a 95% confidence level, the Student's *t*-values for degrees of freedom of 2, 3, and 4 are 4.30, 3.18, and 2.78, respectively.

21. Determine the mean value $[x]$) of the above data.
(A) 0.079 (B) 0.084 (C) 0.089 (D) 0.095

22. If the standard deviation of the data is 0.005%, determine the confidence interval of the mean using the formula $[x] \pm ts/\sqrt{N}$, where t is Student's *t*-value, s is the standard deviation, and s is the number of replicates.
(A) [0.072, 0.096] (B) [0.080, 0.088] (C) [0.067, 0.097] (D) [0.070, 0.094]

23. Which Student's *t*-value should be used to calculate the confidence interval mentioned above?
(A) 4.30 (B) 3.18 (C) 2.78 (D) None of the above

24. For a weak acid HA with a dissociation constant (Ka) of 10^{-5} M, calculate the pH of a solution where 10 mL of 0.1 M is mixed with 5 mL of 0.1 M NaOH.
(A) 4.0 (B) 5.0 (C) 6.0 (D) 7.0

25. For a diprotic acid H_2A with dissociation constants Ka1 = 10^{-5} M and Ka2 = 10^{-9} M, calculate the pH of a solution formed by mixing 10 mL of 0.1 M H_2A with 10 mL of 0.1 M NaOH.
(A) 5.0 (B) 6.0 (C) 7.0 (D) 8.0

26. Calculate the potential at the equivalent point when titrating Fe^{2+} with Ce^{4+}. The reaction in this case is
$Fe^{2+}_{(aq)} + Ce^{4+}_{(aq)} \rightleftharpoons Ce^{3+}_{(aq)} + Fe^{3+}_{(aq)}$
The formal potential for the reduction of Fe^{3+} to Fe^{2+} is +0.767 V, and the formal potential for the reduction of Ce^{4+} to Ce^{3+} is +1.70 V.
(A) 0.993 V (B) 0.467 V (C) 2.467 V (D) 1.234 V

27. Select the appropriate formula to calculate the potential (in volts) at the equivalence point during the titration of Fe^{2+} with MnO_4^-. The reaction in this case is
$5Fe^{2+}_{(aq)} + MnO_4^-{}_{(aq)} + 8H^+_{(aq)} \rightarrow 5Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 4H_2O_{(l)}$,
the formal potential for the reduction of Fe^{3+} to Fe^{2+} is +0.767 V, and the formal potential for the reduction of MnO_4^- to Mn^{2+} is +1.51 V.
(A) 0.767 + 5 × 1.51 (B) 5 × 0.767 + 1.51
(C) (0.767 + 5 × 1.51) ÷ 6 (D) (5 × 0.767 + 1.51) ÷ 6

28. Which electroanalytical method does NOT require the use of an auxiliary electrode?
(A) Cyclic voltammetry (B) Hydrodynamic voltammetry
(C) Polarography (D) Potentiometric titration

29. The atomizer temperatures for an ethylene-air flame, a nitrous oxide flame, and an inductively coupled plasma (ICP) torch are 2300°C, 2700°C, and 4500°C, respectively. Which atomizer offers the highest sensitivity for atomic emission spectroscopy?
(A) Ethylene-air flame (B) Nitrous oxide flame
(C) ICP torch (D) The above atomizers offer the same sensitivity

30. Which statement about photomultiplier tube (PMT) and photodiode (PD) is correct.
(A) PMT provides higher photon counting sensitivity because the photon electrons are multiplied through dynodes.
(B) PMT provides higher photon counting sensitivity because the photon electrons are multiplied through avalanche effect.
(C) PD provides higher photon counting sensitivity because the photon electrons are multiplied through dynodes.
(D) PD provides higher photon counting sensitivity because the photon electrons are multiplied through avalanche effect.

31. Which detector used in gas chromatography (GC) is non-destructive.
(A) Flame ion detector (B) Thermal conductivity detector
(C) Electron ionization mass spectrometer (D) Refraction index detector

32. Which carrier gas can effectively minimize mass transfer resistance between the stationary and mobile phases, thereby enhancing separation resolution in gas chromatography?
(A) Argon (B) Air (C) Nitrogen (D) Helium

33. In reverse-phase HPLC, which of the following shows the correct elution order for a highly polar compound, such as dopamine, when using a cyano, C2, or C8 column?
(A) C2 (fastest) < C8 < cyano (slowest)
(B) C8 (fastest) < C2 < cyano (slowest)
(C) C8 (fastest) < cyano < C2 (slowest)
(D) cyano (fastest) < C8 < C2 (slowest)

34. Which of the following represents the correct elution order for a highly polar compound, such as dopamine, when eluted using a cyano column with a mobile phase consisting of water, methanol, or acetonitrile?
(A) Methanol (longest retention) > Water > Acetonitrile (shortest retention)
(B) Water (longest retention) > Methanol > Acetonitrile (shortest retention)
(C) Acetonitrile (longest retention) > Water > Methanol (shortest retention)
(D) Acetonitrile (longest retention) > Methanol > Water (shortest retention)

計算題（每題 4 分）

1. An echelle grating is illuminated with a polychromatic beam at an incident angle of 45° (angle i) relative to the grating normal. Determine the wavelength of the radiation that appears at the first-order reflection ($n = 1$) at an angle of +30° (angle r), given that the grating has 2000 lines per millimeter.
[Hint: The relationship between the angle of reflection r and the wavelength of the incoming radiation λ is given by the grating equation: $n\lambda = d(\sin i + \sin r)$, where d is the grating spacing (the distance between adjacent lines).]

2. Van Deemter equation describes the relationship between plate height (H) and carrier gas velocity μ: $H = A + B/\mu + C\mu$, where A, B, and C are constant. Prove the optimum H is achieved when $\mu = (B/C)^{1/2}$.