淡江大學八十八學年度碩士班招生考試試題

系別：化學學系　　科目：物理化學　　本試題共 4 頁

一、填充題 （每題 2 分，第 9、10、13 除外）共計 31 分

1. A well-behaved wave function must obey three conditions: (1) _____, (2) _____, and (3) quadratically integrable, or the first derivative of the wave function is continuous.
2. Quantum mechanical operator of $\hat{p}_y$ = _____.
3. Define the probability density for any state in quantum mechanics: _____.
4. If Ψ (q, t) is a normalized state function of a system at time t, then the average value of a physical observable B at time t is $<\hat{B}>$ = _____.
5. If $\{ \psi_n \}$ is an orthonormal set, then $<\psi_i | \psi_j>$ = _____ when i = j, and $<\psi_i | \psi_j>$ = _____ when $i \neq j$.
6. If $\hat{H} = \hat{H}_1 (x_1, y_1, z_1) + \hat{H}_2 (x_2, y_2, z_2)$, where particles 1 and 2 are not interact with each other, $\hat{H}_1 \psi_n (1) = E_n (1) \psi_n (1)$ and $\hat{H}_2 \psi_n (2) = E_n (2) \psi_n (2)$, then the eigenfunction ψ_n = _____ and eigenvalue = _____ for $\hat{H}$.
7. What is the zero-point energy? _____
8. $\int \phi^* \hat{H} \phi d\tau \geq$ _____, if ϕ is a normalized, well-behaved trial function in the variation method.
9. In the perturbation method, $\hat{H} = \hat{H}^\circ + \hat{H}'$, how do you determine $\hat{H}^\circ$? _____, $E_n^{(1)}$ = _____, $E_n \approx$ _____ + $E_n^{(1)}$. (4 %)
10. ψ_{211}, ψ_{210} and ψ_{211} are three states of a hydrogenlike atom, $\psi = \psi_{211} + 2\psi_{210} + 3\psi_{211}$. Is ψ an eigenfunction of $\hat{H}$, $\hat{L}$, $\hat{L}^2$, $\hat{L}_x$, $\hat{L}_y$ and $\hat{L}_z$? **Answer:** ψ is an eigenfunction of the following operators: _____, and ψ is not an eigenfunction of the following operators: _____ (3 %).
11. The length of the spin angular momentum for an electron = _____, the z-component of spin angular momentum = _____.
12. Schrodinger equation of He atom can not be solved exactly because _____
13. Write down the 4 proper two electron spin functions: _____. (4 %)

二、選擇題(每題 3 分，答錯倒扣 0.6 分)，共計 69 分

1. Which of the following is an intensive property? (a) weight, (b) resistance, (c) heat capacity, (d) molecular weight, (e) work.
2. Which of the following is NOT a state function? (a) enthalpy, (b) entropy, (c) heat, (d) Gibbs free energy, (e) Helmholtz free energy.
3. The entropy change in a process from state 1 to state 2 is $\Delta S = \int dq / T$, where the intergral

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must be evaluated following a (a) reaction path, (b) reversible path, (c) constant pressure (d) constant volume, (e) adiabatic path.

4. Which of the following equations is NOT true in a closed system with reversible process? (a) $dG = -SdT + VdP$, (b) $dA = -SdT - PdV$, (c) $dH = -TdS + VdP$, (d) $G = H - TS$, (e) $A = U - TS$.

5. Which of the following statements is NOT true? (a) The unattainability of absolute zero cannot be derived from the second law of thermodynamics. (b) The kinetic energy of a perfect crystal is zero at 0 K. (c) The third law entropy of a perfect diamond crystal is zero at 0 K. (d) The third law entropy of a perfect graphite crystal is zero at 0 K. (e) The unattainability of absolute zero is best regarded as a consequence of the law of thermodynamics.

6. In a closed system, which of the following equations is NOT true? (a) $dw = PdV$ (w is the work done on the system), (b) $\Delta U = q + w$, (c) $dq_P = c_P dT$, (d) $C_V = (\partial U / \partial T)_V$, (e) $\Delta H = q_P$.

7. The Clapeyron equation $dP / dT = \Delta H / (T\Delta V)$ gives the slopes of the lines on a one-component P-T phase diagram. Which of the following statements is NOT true? (a) It tells how the vapor pressure of a solid varies with T. (b) It tells how the vapor pressure of a liquid varies with T. (c) It tells how the boiling point of a liquid varies with P. (d) It tells how the melting point of a solid varies with P. (e) None of the above.

8. The van der Waals equation of real gas is $(P + a / \overline{V}^2)(\overline{V} - b) = RT$. Which of the following statements is TRUE? (a) The term $a / \overline{V}^2$ is meant to correct the effect of the intermolecular repulsive forces on the gas pressure. (b) The term b is meant to correct for the volume available for the molecules to move. (c) b is the volume of the molecules. (d) The value of a is the same for different gases. (e) a is a negative constant.

9. Which of the following statements is TRUE for a standard state? (a) A gas is pure ideal gas at 1 bar and 0 °C. (b) A liquid is pure substance at 1 bar and 0 °C. (c) A solid is pure substance at 1 bar and 0 °C. (d) A solvent A is pure A at T and P of solvent. (e) A solute B is pure B at T and P of solution.

10. Which of the following statements is NOT true for an ideal solution? (a) The chemical potential of each species is given by $\mu_i = \mu_i^*(T, P) + RT \ln x_i$ for all components. (b) $\Delta H_{mix} = 0$ at constant T, P. (c) $\Delta V_{mix} = 0$ at constant T, P. (d) $\Delta S_{mix} = 0$ at constant T, P. (e) The partial pressure in the vapor in equilibrium with an ideal solution are given by Raoult's law $P_i = x_i P_i^*$, where P_i^* is the vapor pressure of pure liquid i at temperature T.

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11. Which of the following statements can NOT determine the molecular weight of a solute? (a) melting point depression, (b) boiling point elevation, (c) heat capacity, (d) osmotic pressure, (e) vapor pressure lowering.
12. A two-component phase diagram is shown *in Figure 1* at constant pressure. Which of the following statements is TRUE? (a) A_2B melts congruently at T_2. (b) The lowest melting point of B + A_2B is T_1. (c) Point D is a peritectic point. (d) Region 1 contains solid solution of B and A_2B. (e) CD line is a saturation solubility curve of solute A in solvent B.
13. From a three-component phase diagram shown *in Figure 2* at constant T and P. The mole ratio of point P with respect to A, B and C is (a) 3:2:1, (b) 1:2:3, (c) 3:1:2, (d) 2:1:3, (e) 1:3:2.
14. Which of the following statements is NOT true for a gas? (a) If a fixed amount of gas is left undistrubed at constant volume and temperature, the pressure of the gas may be changed depending on the container. (b) Gas expands rapidly into an evacuated container. (c) All gases diffuse into one another. (d) A gas expands to fill all available space in its container. (e) Gases are highly compressible compared to liquids.
15. Which of the following compounds is NOT appropriate for making a salt bridge? (a) KNO_3, (b) KCl, (c) KBr, (d) NH_4Cl, (e) $MgSO_4$.
16. Which of the following statements is NOT true? (a) A catalyst can alter the equilibrium constant of a reaction. (b) The decay of radioactive isotope follows first-order kinetics. (c) Enzymes catalyze most of the reactions that occur in living organisms. (d) A catalyst is a substance that increases both the rate of a forward reaction and the reversed reaction. (e) A heterogeneous catalysis, the reaction occurs at the interface between two phases.
17. Which of the following statements is TRUE? (a) Endothermic reactions have higher activation energies than exothermic reactions. (b) The specific rate constant for a reaction is independent of the concentrations of the reacting species. (c) In all reaction mechanisms, there is a single rate-determining step. (d) The rate of a catalyzed reaction is independent of the concentration of the reactants. (e) None of the above.
18. If the reaction's activation energies for the froward and reversed directions are equal in value, (a) the stoichiometry is the mechanism, (b) $\Delta S = 0$, (c) $\Delta H = 0$, (d) the reaction order is 0, (e) there is no catalyst.
19. Which of the following statements is TRUE? (a) The conductivity of a NaCl aqueous

solution can be measured by using a dc current with Pt electrodes. (b) A galvanic cell is a reversible cell. (c) $\Delta H = nFE$ (d) The emf ε of a reversible cell can be determined by the Nernst equation. (e) The equilibrium constant, K, of a cell reaction can be determined by the ΔH at constant T and P.

20. The mechanism proposed for the gas phase reaction $H_2 + Br_2 \longrightarrow 2\ HBr$ is as follows:

step 1		$Br_2 \longrightarrow$	$Br\cdot + Br\cdot$
step 2	$Br\cdot + H_2 \longrightarrow$		$HBr + H\cdot$
step 3	$H\cdot + Br_2 \longrightarrow$		$HBr + Br\cdot$
step 4	$H\cdot + HBr \longrightarrow$		$H_2 + Br\cdot$
step 5	$Br\cdot + Br\cdot \longrightarrow$		Br_2'

Which step is a chain inhibition? (a) 1, (b) 2, (c) 3, (d) 4, (e) 5.

21. Which of the following statements is TRUE? (a) The vibrational degree of freedom of a linear polyatomic molecule with N atoms is 3N – 5. (b) The overtone band is a transition from v = 0 to v = 1, where v is the vibrational quantum number. (c) For CO_2, the symmetric stretchng is IR active. (d) The selection rule for vibration is $\Delta v = 0, \pm 1$. (e) None of the above.

22. The entropy of a thermodynamic system is (a) k log W, (b) R log W, (c) k log N, (d) R log N, (e) k ln N. (W is the total numbers of system quantum states that have a significant probability of being occupied. N = Avogadro's number, k = Boltzmann constant, R = gas constant.)

23. An ionic compound contains three types of atoms, A, B and X. It crystallizes in a cubic unit-cell with A atoms at the body center, B atoms at the corners and X atoms at the center of all the edges. The simplest formula of this compound is (a) ABX, (b) ABX_3, (c) AB_2X_3, (d) AB_8X_{12}, (e) none of above.

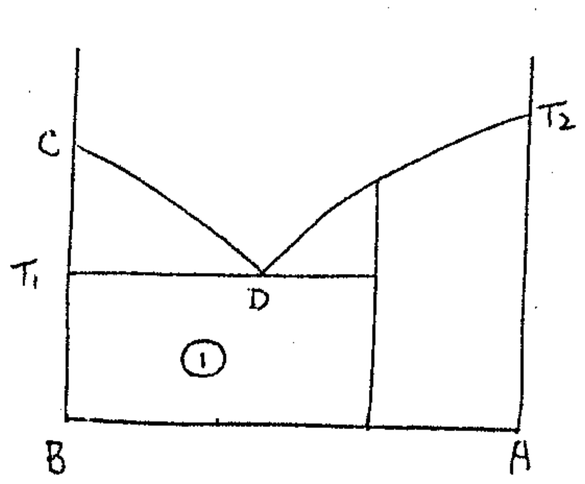

Figure 1

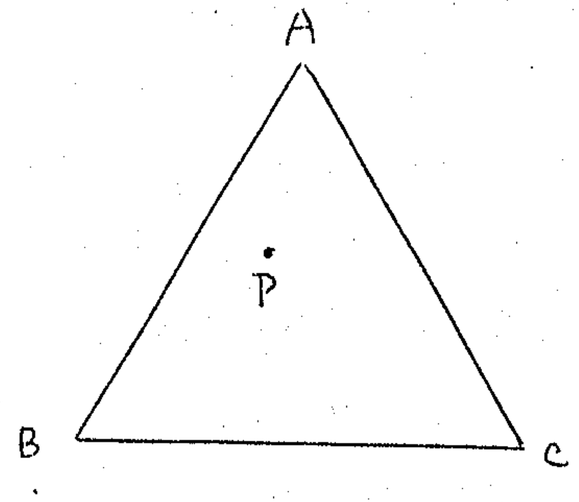

Figure 2.