**第一大題選擇題考生應作答於「答案卡」**

第一大題：選擇題 (每題 2 分,總共 30 分)

Part I: Each question may have one or more than one answer. (2 points each, total 30 points)

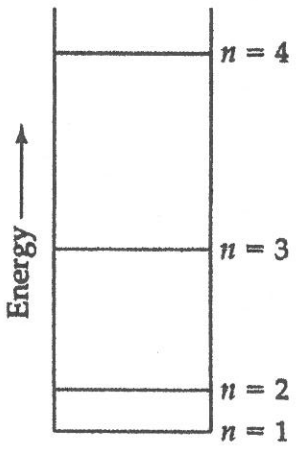
1. The oxidation number of carbon in $CH_3OH$, $CH_2O$, $HCO_3^-$ are respectively
   (a) +2, 0, -2; (b) +2, +1, 0; (c) -2, 0 +2; (d) 0, -1, -2; (e) none of the above

2. A voltaic cell with one electrode half-cell consists of a silver strip placed in a solution of $AgNO_3$, and the other has an iron strip placed in a solution of $FeCl_2$. The overall cell reaction is $Fe(s) + 2\ Ag^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + 2\ Ag_{(s)}$
   (a) Ag(*s*) is the anode, Electrons flow from the Fe electrode toward the Ag electrode
   (b) Fe(*s*) is the anode, Electrons flow from the Ag electrode toward the Fe electrode
   (c) Fe(*s*) is the cathode, Electrons flow from the Ag electrode toward the Fe electrode
   (d) Ag(*s*) is the cathode, Electrons flow from the Ag electrode toward the Fe electrode
   (e) Ag(*s*) is the cathode, Electrons flow from the Fe electrode toward the Ag electrode

3. Consider a cell: $Ni(s)/Ni^{2+}(aq)$ 0.1 M || $Ni^{2+}(aq)$ 0.1 M/Ni(*s*). What is the cell potential?
   (a) -0.1V (b) -0.03V (c) 0V (d) 0.03V (e) 0.1V

4. Consider a mixture of two gases, A and B, confined in a closed vessel. A quantity of a third gas, C, is added to the same vessel at the same temperature. How does the addition of gas C affect the following: (1) the partial pressure of gas A, (2) the total pressure in the vessel, (3) the mole fraction of gas B?
   (a) no change, no change, decrease
   (b) increase, no change, decrease
   (c) increase, decrease, increase
   (d) no change, increase, decrease
   (e) increase, increase, increase

5. A certain quantum mechanical system has the energy levels shown in the following diagram. The energy levels are indexed by a single quantum number *n* that is an integer. Based on the drawing, put the following in order of increasing wavelength of the light absorbed or emitted during the transition:
   (i) n = 1 to n = 2; (ii) n = 3 to n = 2; (iii) n = 2 to n = 4; (iv) n = 3 to n = 1.
   (a) iii < i < iv < ii
   (b) i < ii < iii < iv
   (c) iii < iv < ii < i
   (d) ii < i < iii < iv
   (e) iv < ii < iii < i




6. Consider a voltaic cell whose overall reaction is $Pb^{2+}_{(aq)} + Zn_{(s)} \rightarrow Pb_{(s)} + Zn^{2+}_{(aq)}$. What is the emf generated by this voltaic cell when the ion concentrations are $[Pb^{2+}] = 1.5 \times 10^{-3}$ M and $[Zn^{2+}] = 0.55$ M?
   (a) 0.71 V (b) 0.54 V (c) 0.49 V (d) 0.79 V (e) 0.64 V

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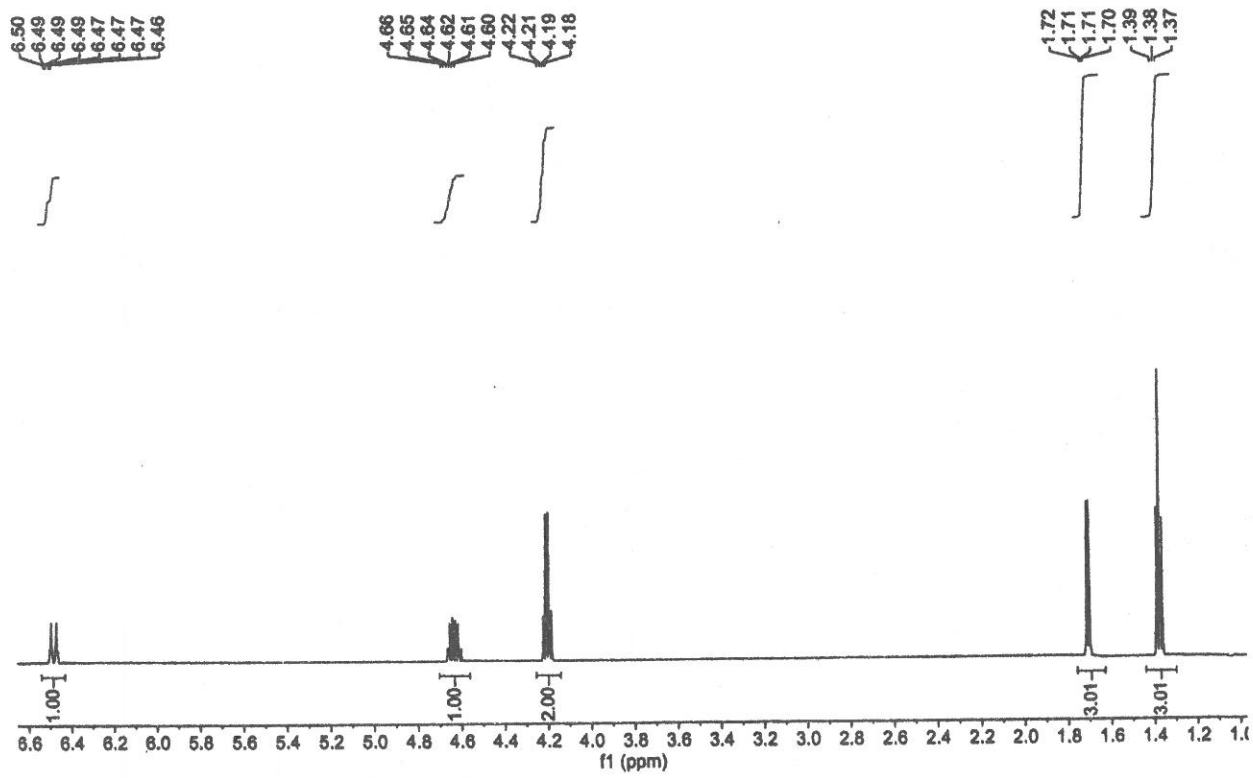
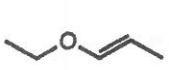
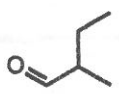
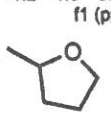
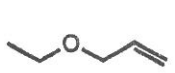
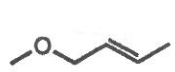
7. The proton NMR spectrum of an organic molecule with formula as $C_5H_{10}O$ is shown below. Which is the correct structure of this molecule.




(a)  (b)  (c)  (d)  (e) 

8. Which one of these statements about formal charge is/are true?
   (a)Formal charge is the same as oxidation number.
   (b)To draw the best Lewis structure, you should minimize formal charge.
   (c)Formal charge takes into account the different electronegativities of the atoms in a molecule.
   (d)Formal charge is most useful for ionic compounds.
   (e)Formal charge is used in calculating the dipole moment of a diatomic molecule.

9. Consider a redox reaction for which $E^0$ is a positive number.
   i. What is the sign of $\Delta G^0$ for the reaction?
   ii. Is this reaction spontaneous?
   iii. Will the equilibrium constant for the reaction be larger or smaller than 1?
   iv. Can an electrochemical cell based on this reaction accomplish work on its surroundings?

   Which of the following statement is correct?
   (a) Positive; No; larger than 1; Yes (b) Negative; Yes; larger than 1; Yes (c) Positive; No; smaller than 1; Yes
   (d) Negative; No; larger than 1; Yes (e) Negative; Yes; smaller than 1; No

10. In 1913, Michaelis and Menten proposed the following mechanism for the biomolecular reaction between enzyme ***E*** and substrate ***S***:

$$E + S \underset{k_2}{\overset{k_1}{\rightleftarrows}} ES \xrightarrow{k_3} E + P$$

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Suppose there is a molecule ***I*** that may occupy the catalytic site of ***E***, but the product ***EI*** will not produce any product ***P***:

$$E + I \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} EI$$

Under the steady-state condition, which of the following statements is/are INCORRECT

(a) The more the amount of ***I***, the less the amount of ***P*** will be formed at the end of the reaction.

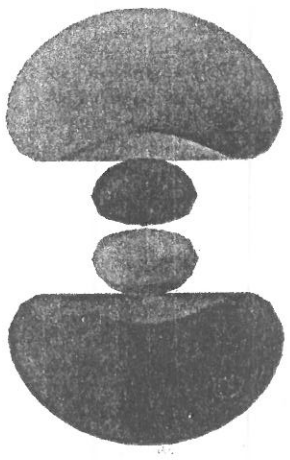
(b) In the general mathematical expression of the rate of change of ***ES***, we do not need to include the concentration of ***I***.

(c) The rate of the formation of ***P*** is reduced in the presence of ***I***.

(d) The amount of enzyme is usually less than the amount of substrate.

(e) All the reaction steps are elementary reactions.

11. For the following p orbital, which of the following statements is/are INCORRECT?



(a) Any two adjacent lobes must have opposite signs.

(b) The electrons in this orbital must obey the Pauli exclusion principle.

(c) This orbital must have lower energy than the 3d orbital of the same atom.

(d) The magnetic quantum number of this orbital must be 1, 0, and –1.

(e) This orbital must be filled up by electrons for an unexcited bromine atom.

12. According to the kinetic data of the reaction:

$$A + B + C \rightarrow E + F$$

| | $[A]_0$ | $[B]_0$ | $[C]_0$ | Rate = - Δ [A]/ Δ t |
|---|---|---|---|---|
| I | 0.100 *M* | $5.0 \times 10^{-4}$ *M* | $1.0 \times 10^{-2}$ *M* | 0.137 *M*/sec |
| II. | 0.100 *M* | $1.0 \times 10^{-3}$ *M* | $1.0 \times 10^{-2}$ *M* | 0.274 *M*/sec |
| III. | 0.200 *M* | $1.0 \times 10^{-3}$ *M* | $1.0 \times 10^{-2}$ *M* | 0.548 *M*/sec |
| IV. | 0.400 *M* | $1.0 \times 10^{-3}$ *M* | $2.0 \times 10^{-2}$ *M* | 1.096 *M*/sec |

Which of the following statements is correct?

(a) The reaction is 1st order to A, B, and C.

(b) Reactants A and B must be involved in the rate determine step.

(c) The rate constant is $2.74 \times 10^4$ M $s^{-1}$

(d) The equilibrium constant is $2.74 \times 10^3$

(e) None of the above.

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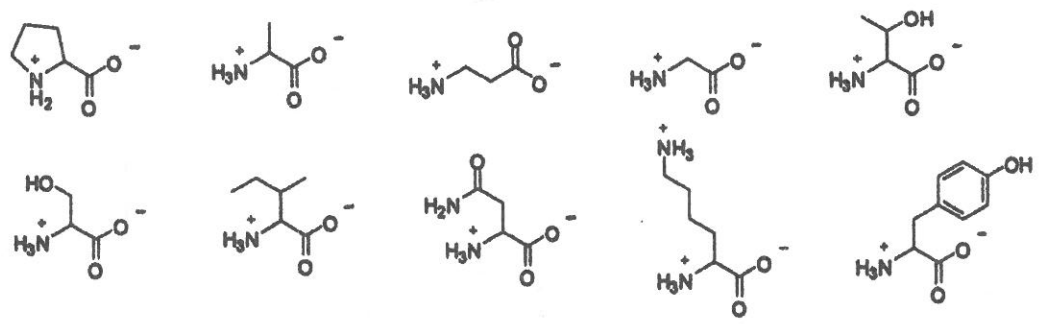
13. Amino acids are important biomolecules and/or building blocks for proteins. Ten of them are shown below. In these ten molecules, which of the following statement(s) is or are correct?

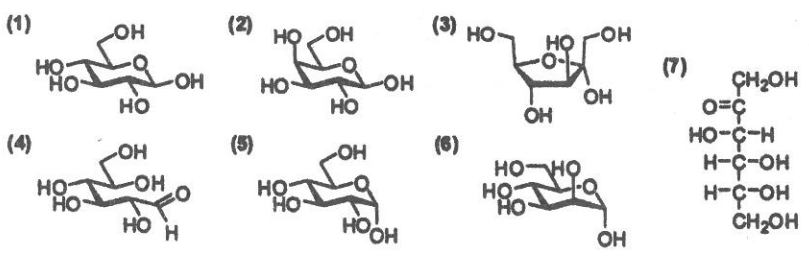


a. There are six amino acids containing only one stereo carbon center
b. There are two amino acids containing primary alcohol
c. There is only one amino acid containing aromatic ring
d. Eight amino acids are not "superimposable" on their mirror images (superimposable means "identical")
e. All ten amino acids are commonly used in proteins

(a) abd
(b) cde
(c) abc
(d) acd
(e) abcde

14. Which of the following statements about the equilibrium of reactions is/are correct?
(a) Activities of a species are concentration independent.
(b) Solutions are homogeneous mixtures of two or more pure substances, and the formation of a solution is favored by the decrease in entropy.
(c) A buffer solution is most effective when the desired pH of the buffer is very close to pKa of the weak acid of the buffer solution.
(d) "Equivalence point" is the point at which the indicator changes color in the titration of an acid-base reaction.
(e) Usage of catalysts in a reaction can increase the rate of the forward reaction, and the equilibrium will favor the product side.

15. Seven different structures of carbohydrate $C_6H_{12}O_6$ are shown below. Which of the following statement(s) is or are correct?



a. (1) and (2) are stereoisomers
b. (5) and (6) are enatiomers
c. (1) and (5) are diastereomers
d. (3) and (7) are constitutional (structural) isomers

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e. **(5)** is the cyclic form of **(7)**
f. In aqueous solution, **(1)** and **(5)** can be interchangeable through **(4)**

(a) abce
(b) acdf
(c) bcde
(d) abcde
(e) acdef

**第二大題問答題考生應依題號順序於「非選擇題作答區」內作答，並應註明作答之部分及題號。**

第二大題：問答題 (共 70 分)

Part II: Please provide a short answer for the following questions. (total 70 points)

16. (total 10 points) Consider the simple LCAO-MO model for three diatomic molecules: $CN^+$, CN, $CN^-$.
    (a) (1 point) What does LCAO-MO stand for?
    (b) (2 points) Give the MO energy diagram for CN. Label the molecular orbitals.
    (c) (3 points) What are the electron configurations of $CN^+$, CN and $CN^-$?
    (d) (2 points) Give the bond order of each molecule. On the basis of bond orders, place the species in order of increasing bond length.
    (e) (2 points) Which, if any, of these three species is paramagnetic? Explain your reasoning.

17. (total 4 points) For the reaction

$$2\,NO_{(g)} + O_{2(g)} \longrightarrow 2\,NO_{2(g)}$$

the currently accepted mechanism is

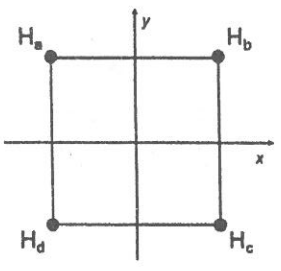
$$\text{step 1} \qquad 2\,NO_{(g)} \longrightarrow N_2O_{2(g)}$$

$$\text{step 2} \qquad N_2O_{2(g)} + O_{2(g)} \longrightarrow 2\,NO_{2(g)}$$

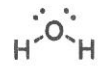
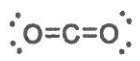
    (a) (1 points) Determine which step is the slow step.
    (b) (3 points) Explain clearly why you chose the reaction you did for the slow step. You may use Lewis structures to help in your explanation.

18. (total 4 points) The first-order rate constant is $1.87 \times 10^{-3}$ $min^{-1}$ at 37 °C (body temperature) for reaction of cisplatin, a cancer chemotherapy agent, with water.
    (a) (2 points) Suppose that the concentration of cisplatin in the bloodstream of a cancer patient is $4.73 \times 10^{-4}$ mol/L. What will the concentration be 24 hours later?
    (b) (2 points) Calculate the half-life of cisplatin in the bloodstream at 37 °C.

19. The four hydrogen atoms are located at the corners of a square lying in the x-y plane (see below). Construct the MOs of square-planar $H_4$ via the interaction of two fragments of your choice. Give the form and relative energies of these MOs. (8 pt)



20. Draw the molecular structure and complete the following table in *English*. (1 pt. each, 12 pt in total)

| Compound | Wedge and dash Lewis structure | Central atom hybridization | Central atom electron pair orientation | Molecular Geometry |
|---|---|---|---|---|
| Water |  | $sp^3$ | tetrahedral | bent |
| |  | | linear | linear |
| Sulfur tetrafluoride | | | | |
| Phosphorus tribromide | | $sp^3$ | | |
| Boron trifluoride | | $sp^2$ | | |

21. (total 6 points) The overall reaction and equilibrium constant value for a hydrogen-oxygen fuel cell at 298 K is

$$2\,H_{2(g)} + O_{2(g)} \longrightarrow 2\,H_2O_{(l)} \quad K = 1.28 \times 10^{83}$$

(a) (2 points) Calculate $E^\circ$ and $\Delta G^\circ$ at 298 K for the fuel-cell reaction.

(b) (2 points) Predict the signs of $\Delta H^\circ$ and $\Delta S^\circ$ for the fuel-cell reaction.

(c) (2 points) As temperature increases, does the maximum amount of work obtained from the fuel-cell reaction increase, decrease or remain the same? Explain.

22. (total 6 points) Consider the van der Waals equation:

$$\left[P + a\left(\frac{n}{V}\right)^2\right] \times (V - nb) = nRT$$

(a) (2 points) Give the units of the van der Waals constants $a$ and $b$, and explain their physical origins.

(b) (1 point) Sort the following gases from smallest $a$ to largest $a$: Ar, Kr, $H_2$, $CO_2$, $H_2O$.

(c) (1 point) Sort the following gases from smallest $b$ to largest $b$: $H_2$, $CO_2$, $H_2O$, $C_3H_8$.

(d) (2 points) The ideal gas law tends to hold best at low pressure and high temperatures. Show how the van der Waals equation simplified to the ideal gas law under these conditions.

23. (total 8 points) If a pentafluoride compound ($XF_5$) moving with a speed of 455 m/s has a de Broglie wavelength of 5.00 pm.

(a) (2 points) What is the molar mass of $XF_5$?

(b) (2 points) What is the identity of atom X?

(c) (2 points) What are the geometry and polarity of $XF_5$?

(d) (2 points) Does X obey the octet rule? Explain why.

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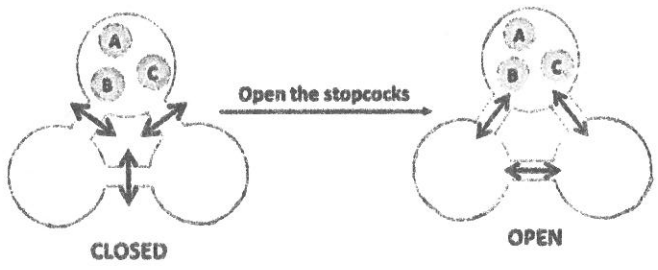
24. (total 9 points) The time-independent Schrödinger equation is given by $\hat{H}\Psi = E\Psi$, where the Hamiltonian operator for a one-dimensional system is defined as $\hat{H} = -\frac{\hbar^2}{2m}\frac{\partial^2}{\partial x^2} + V(x)$.

(a) (2 points) Give the time-independent Schrödinger equation for the quantum harmonic oscillator model. You need to clearly define all the variables in the equation you give.

(b) (4 points) Show that the function $e^{-\alpha x^2}$ satisfied the Schrödinger equation for the quantum harmonic oscillator. Determine $\alpha$. Explain why this wave function (un-normalized) represents the ground state of the quantum harmonic oscillator.

(c) (3 points) What is the zero-point energy of the quantum harmonic oscillator? Explain why a harmonic oscillator state with zero total energy must violate the uncertainty principle, and therefore, does not exist.

25. (total 3 points) The container consists of three identical flasks connected by three stopcocks. With the stopcocks closed, 3 neon atoms, A, B and C, occupy one flask, and the others are evacuated. When the stopcocks are opened the neon gas can expand to the other flasks.




(a) (1 point) How many microstates are possible for this system when the stopcocks are opened?

(b) (2 points) Calculate the statistical entropy for the system.

Periodic table:

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 H 1.00794 | | | | | | | | | | | | | | | | | 2 He 4.002602 |
| 3 Li 6.941 | 4 Be 9.012182 | | | | | | | | | | | 5 B 10.811 | 6 C 12.0107 | 7 N 14.00674 | 8 O 15.9994 | 9 F 18.9984032 | 10 Ne 20.1797 |
| 11 Na 22.989770 | 12 Mg 24.3050 | | | | | | | | | | | 13 Al 26.981538 | 14 Si 28.0855 | 15 P 30.973761 | 16 S 32.066 | 17 Cl 35.4527 | 18 Ar 39.948 |
| 19 K 39.0983 | 20 Ca 40.078 | 21 Sc 44.955910 | 22 Ti 47.867 | 23 V 50.9415 | 24 Cr 51.9961 | 25 Mn 54.938049 | 26 Fe 55.845 | 27 Co 58.933200 | 28 Ni 58.6534 | 29 Cu 63.545 | 30 Zn 65.39 | 31 Ga 69.723 | 32 Ge 72.61 | 33 As 74.92160 | 34 Se 78.96 | 35 Br 79.504 | 36 Kr 83.80 |
| 37 Rb 85.4678 | 38 Sr 87.62 | 39 Y 88.90585 | 40 Zr 91.224 | 41 Nb 92.90638 | 42 Mo 95.94 | 43 Tc (98) | 44 Ru 101.07 | 45 Rh 102.90550 | 46 Pd 106.42 | 47 Ag 196.56655 | 48 Cd 112.411 | 49 In 114.818 | 50 Sn 118.710 | 51 Sb 121.760 | 52 Te 127.60 | 53 I 126.90447 | 54 Xe 131.29 |
| 55 Cs 132.90545 | 56 Ba 137.327 | 57 La 138.9055 | 72 Hf 178.49 | 73 Ta 180.94.79 | 74 W 183.84 | 75 Re 186.207 | 76 Os 190.23 | 77 Ir 192.217 | 78 Pt 195.078 | 79 Au 196.56655 | 80 Hg 200.59 | 81 Tl 204.3833 | 82 Pb 207.2 | 83 Bi 208.58038 | 84 Po (209) | 85 At (210) | 86 Rn (222) |
| 87 Fr (223) | 88 Ra (226) | 89 Ac (227) | 104 Rf (261) | 105 Db (262) | 106 Sg (263) | 107 Bh (262) | 108 Hs (265) | 109 Mt (266) | 110 (269) | 111 (272) | 112 (277) | | 114 (289) (287) | | 116 (289) | | 118 (293) |

Physical constants:

$c=3.0\times10^{8}$ m/s, $m_e=9.1\times10^{-31}$ kg, $h=6.626\times10^{-34}$ Js, $1eV=1.60\times10^{-19}$ J, $R=-13.6$ eV, $N_A=6.02\times10^{23}$, $k = 1.38\times10^{-23}$ J/K.

Standard Reduction Potentials:

$Ni^{2+}_{(aq)} + 2\ e^- \rightarrow Ni_{(s)}$ $E_{red} = -0.23$ V

$Zn^{2+}_{(aq)} + 2\ e^- \rightarrow Zn_{(s)}$ $E_{red} = -0.76$ V

$Pb^{2+}_{(aq)} + 2\ e^- \rightarrow Pb_{(s)}$ $E_{red} = -0.13$ V