1. (15%) 考慮以下之函數極值問題：
$$\min\ z = x^2 + 2xy + w^2.$$
其中限制條件如下
$$2x + y + 3w = 24 \quad 及 \quad x + w = 8.$$
試以拉格朗日乘子法 (Lagrange multipliers) 解之.

2. (15%) 給定曲面
$$z = \cos(x + y).$$
求在點 $(x_0, y_0, z_0) = (\dfrac{\pi}{4}, \dfrac{\pi}{4}, 0)$ 處, 曲面的切平面和法線的方程式.

3. 計算二重積分
$$I = \iint_D x^2 + y^2\, d\sigma.$$
其中
(10%) (a) $D = \{(x, y) \in \mathbb{R}^2 : x^2 + y^2 \le 1\}$ 為圓盤.
(10%) (b) $D = \{(x, y) \in \mathbb{R}^2 : 1 \le x^2 + y^2 \le 9\}$ 為圓環.

4. (20%) 計算迴路積分
$$I = \oint_L (x + y)\, ds.$$
其中 L 為三角形 $\triangle OAB$ 的三條有向邊 $\overrightarrow{OA}$, $\overrightarrow{AB}$ 和 $\overrightarrow{BO}$. 這裡, 三個角點分別是
$$O = (0, 0),\ A = (1, 0) \text{ 和 } B = (0, 1).$$

5. (10%) (a) 證明 $\lim\limits_{n \to \infty} \sqrt[n]{n!} = +\infty$.

(5%) (b) 對於冪級數 $\displaystyle\sum_{k=0}^{\infty} \frac{(-1)^k x^{2k}}{(2k)!}$, 證明其收斂半徑為 $+\infty$.

6. (10%) (a) 證明連續函數 f 會將閉區間 [a,b] 映成為閉區間 [c,d].
(5%) (b) 證明一對一的連續函數 f 會將開區間 (a,b) 映成為開區間 (c,d).

Part I. Multiple Choices (40%)

1. Which statements about bonding molecular orbitals are correct?
   (a) Electrons in bonding orbitals tend to stabilize the molecule.
   (b) Only σ bonds can result from bonding molecular orbitals.
   (c) In a bonding molecular orbital, the electron density is high between the two atoms.
   . (d) Bonding molecular orbitals result from *in phase* overlap of the wave functions of the atomic orbitals.
   (e) The relative numbers of electrons in bonding versus antibonding orbitals determine the overall stability of the molecule.

2. The first ionization energy of sulfur (1005 kJ/mol) is less than that of phosphorus (1060 kJ/mol). Reasonable explanations for this fact involve:
   (a) the stability of the half-filled subshell in atomic sulfur.
   (b) pairing of two electrons in one $3p$ orbital in sulfur atoms.
   (c) the smaller size of sulfur atoms relative to phosphorus atoms.
   (d) the electron-electron repulsion cause the fourth $3p$ electron in sulfur to be easily removed.
   (e) the larger effective nuclear charge Z_{eff} of sulfur atoms

3. Consider CH_4 and CF_4. Electronegativities: C = 2.5, H = 2.1, F = 4.0. Which statement is true?
   (a) Both are sp^3 hybridized at carbon.
   (b) The bond angles in CF_4 are smaller than those in CH_4.
   (c) The C-F bonds are more polar than the C-H bonds.
   (d) Both molecules are nonpolar.
   (e) The bond dipoles in CF_4 are directed toward the fluorine, but those in CH_4 are directed toward the carbon atom.

4. A catalyst
   (a) increases the amount of products present at equilibrium.
   (b) increases the rate at which equilibrium is reached but decreases the equilibrium constant.
   (c) increases the rate at which equilibrium is reached without changing the equilibrium constant.
   (d) increases $\triangle H$ for the process.
   (e) lowers the activation energy by changing the reaction pathways.

5. The gas phase reaction A + B ⟶ C has a reaction rate which is experimentally observed to follow the relationship rate = $k[A]^2[B]$. Which one of the following would affect the value of the specific rate constant, k?
   (a) increasing the temperature　　　　　(b) changing the concentration of A
   (c) changing the concentration of B　　　(d) adding a catalyst
   (e) all of the above

6. For real gas, it follows $(P + \dfrac{n^2 a}{V^2})(V - nb) = nRT$. Which one of the statements is true?
   (a) A real gas behaves more nearly as an ideal gas at high temperatures and low pressures.
   (b) In the van der Waals equation, the "a" factor corrects for attractive forces, and one would expect a larger value of "a" for HF than for He.
   (c) The "b" factor in the van der Waals equation should be larger for He than for Cl_2.
   (d) Gases approach their liquefaction points as temperature decreases and as pressure increases.
   (e) Both "a" and "b" of the van der Waals equation have values of zero for an ideal gas.

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7. About the surface tension, which statements are true?
   (a) The intermolecular interactions among the liquid molecules are responsible for the phenomenon of surface tension.
   (b) The molecules at the surface do not have other molecules on all sides of them and therefore are pulled inwards, which creates internal pressure and forces liquid surfaces to contract to the minimal area.
   (c) Surface tension can also be thought of as the amount of energy required to increase the surface area of a liquid.
   (d) Surface tension is not related to the capillary action.
   (e) From the energy point of view, molecules in the surface area are in the lower energy state than molecules in the interior of a liquid.

8. About proteins, which statements are true?
   (a) The primary structure is the order of the amino acids, which is crucial to the protein's biological function.
   (b) Factors that might affect the tertiary structure of a protein include hydrogen bonds, electrostatic interactions, and hydrophobicity.
   (c) α- helix and β- sheet are common secondary structures of proteins.
   (d) Heat and pH change can lead to denatured proteins.
   (e) The biological functions of proteins are not affected by their tertiary structure.

9. Consider the following reaction occurring at constant pressure and temperature, for which the value of ΔE is negative. Which statements are true ?
$$CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$$

   (a) Work is done by the surroundings on the system.
   (b) Work is positive.
   (c) Heat is released by the system.
   (d) The volume must increase at constant pressure.
   (e) The reaction is non-spontaneous..

10. Which of the following statements regarding a 1 M sucrose solution is correct?
    (a) The boiling point is greater than 100 °C.
    (b) The freezing point is lower than that of a 1 M NaCl solution.
    (c) The freezing point is less than 0.0 °C.
    (d) The boiling point is lower than that of a 1 M NaCl solution.
    (e) The vapor pressure at 100 °C is less than 760 torr.

11. About the color of a coordination compound, which statements are true?
    (a) The color of the complex is the sum of the light absorbed by the complex
    (b) Besides the types of ligands, the color of a complex also depends on the central metal ion and its oxidation state
    (c) It is the energy level of the coordination compound that determines at which wavelength the light can be absorbed
    (d) For complexes with more than one d-electron, there could be several absorption bands
    (e) Higher oxidation state tends to have larger splitting, therefore altering the color of the complex

12. Which statement regarding the photoelectric effect is correct?
    (a) Electrons can be ejected only if the light is of sufficiently short wavelength.
    (b) The current increases with increasing intensity of the light.
    (c) Electrons can be ejected only if the light is of sufficiently high energy.

(d) The current does not depend on the color of the light as long as the wavelength is short enough.
(e) The wavelength limit sufficient for the ejection of electrons is the same for all metals.

13. Which statement regarding a stable **heteronuclear** diatomic molecule is true?
   (a) The bonding molecular orbitals have more of the character of the more electronegative element than of the less electronegative element.
   (b) The antibonding molecular orbitals have more of the character of the more electropositive element than of the more electronegative element.
   (c) All have bond orders greater than zero.
   (d) Their molecular orbital diagrams are more asymmetrical than those of homonuclear diatomic molecules.
   (e) The greater the difference in energy between two overlapping atomic orbitals, the more polar is the bond resulting from the electrons occupying the bonding molecular orbital.

14. There are two ways that C_4H_{10} can exist. Which of the following statements about these two forms is false?
   (a) The two forms have the same boiling point.
   (b) The two forms are called constitutional isomers.
   (c) The two forms have the same molecular weight.
   (d) All carbons in both of the two forms have four bonds.
   (e) The two forms are both alkanes.

15. Which of the following statements about polyprotic acids is correct?
   (a) Polyprotic acids can furnish two or more hydronium ions per molecule.
   (b) It is generally accepted practice to ignore second or third ionizations when calculating the concentration of H_3O^+.
   (c) The ionizations of polyprotic acids occur simultaneously.
   (d) Successive ionization constants for polyprotic acids generally decrease.
   (e) Phosphoric acid is a typical polyprotic acid

16. Which of the following statements concerning octahedral complexes are correct?
   (a) Strong field ligands produce large crystal field splittings.
   (b) Weak field ligands produce high spin complexes.
   (c) Halide ions are strong field ligands.
   (d) Weak field ligands result in relatively small values for Δ_{oct}.
   (e) A relatively large value for Δ_{oct} causes a complex ion to absorb light with shorter wavelength.

17. Which of the statements regarding energy is correct?
   (a) The total energy content of the universe is constant.
   (b) Energy can be converted from one form to another.
   (c) Energy can be defined as the capacity to do work or to produce heat.
   (d) Energy may be destroyed in chemical reactions.
   (e) Energy is a state function, which is dependent on the pathway.

18. Which of the following statements are correct?
   (a) For an electrolysis cell, $W_{electrical} < 0$
   (b) For a spontaneous process, $\triangle G < 0$
   (c) For an adiabatic expansion process, $q = 0$
   (d) For an isothermal compression process, $q = -w$
   (e) For an exothermic process, $\triangle H > 0$

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19. Which of the following statements about the reaction quotient, Q are true?
    (a) The value of Q can be used to predict equilibrium concentrations.
    (b) It has the same expression as the equilibrium constant, K_c.
    (c) Its value is calculated using non-equilibrium concentrations.
    (d) If $Q > K_c$, the reaction must move to equilibrium by forming more reactants.
    (e) For $Q < K_c$, the free energy change is negative.

20. Which one of the following parameters increases as the strength of the attractive intermolecular forces increases?
    (a) the heat of vaporization
    (b) the normal boiling temperature
    (c) the extent of deviations from the ideal gas law
    (d) the sublimation temperature of a solid
    (e) the vapor pressure of a liquid

Part II. Single Choices (40%)

21. Consider the following reaction

    $$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$$

    which would be the appropriate equilibrium constant expression: (single choice)

    (a) $\dfrac{[H_2O]^4}{[H_2]^4}$　　(b) $\dfrac{[H_2]^4}{[H_2O]^4}$　　(c) $\dfrac{[Fe_3O_4][H_2]}{[Fe][H_2O]}$

    (d) $\dfrac{[Fe_3O_4][H_2]^4}{[Fe]^3[H_2O]^4}$　　(e) $\dfrac{[Fe]^3[H_2O]^4}{[Fe_3O_4][H_2]^4}$

22. Nitrogen (atomic mass = 14.0067 amu) has two naturally occurring isotopes. The masses of ^{14}N and ^{15}N are 14.003074 and 15.000108 amu, respectively. What is the percent abundance of ^{15}N?

    (a) 15.0001%　　(b) 14.0031%　　(c) 99.635%　　(d) 0.365%　　(e) 0.0104%

23. What are the number of protons, neutrons, and electrons in the $^{34}_{16}S^{2-}$ ion.
    (a) 16 p, 18 n, 16 e　　(b) 16 p, 18 n, 14e　　(c) 16 p, 16 n, 19 e
    (d) 16 p, 18 n, 18 e　　(e) 34 p, 16 n, 18 e

24. The second law of thermodynamics states:
    (a) The entropy increase for all exothermic processes.
    (b) The enthalpy of the universe always increases in spontaneous processes.
    (c) A spontaneous process always increases entropy.
    (d) $\triangle H < 0$ and $\triangle S > 0$ for all spontaneous processes
    (e) The entropy of the universe always increases in spontaneous processes.

25. What is the bond order for each of the following species: N_2, N_2^-, N_2^+ and which one would be predicted to have the shortest bond length?

	$\underline{N_2}$	$\underline{N_2^-}$	$\underline{N_2^+}$	
	bond order			shortest bond length
(a)	3	3.5	2.5	N_2^+
(b)	3	2.5	2.5	N_2
(c)	3	4	2	N_2^-
(d)	2	3	1	N_2^-
(e)	3	4	2	N_2^-

26. A reaction has an activation energy of 40 kJ and an overall energy change of reaction of –100 kJ. In each of the following potential energy diagrams, the horizontal axis is the reaction coordinate and the vertical axis is potential energy in kJ. Which potential energy diagram best describes this reaction?
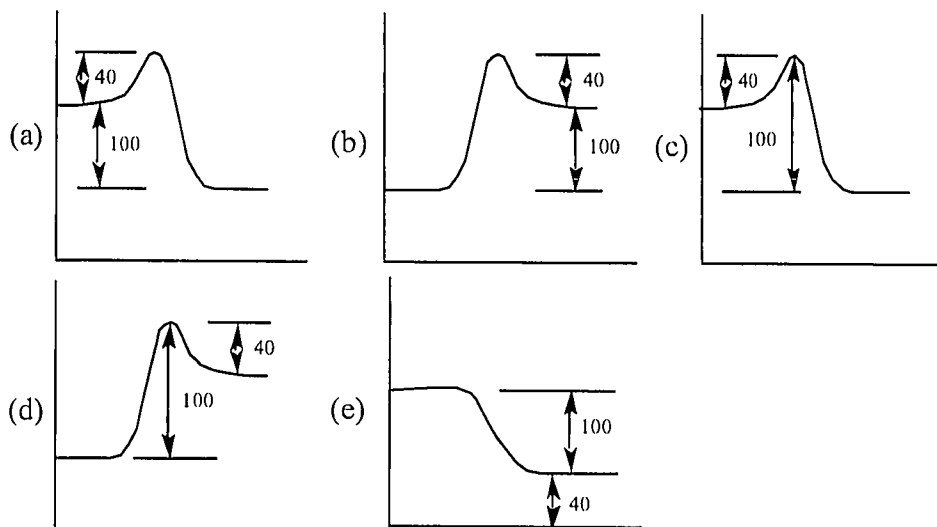
27. What volume of 0.1125 M $K_2Cr_2O_7$ would be required to oxidize 48.16 mL of 0.1006 M Na_2SO_3 in acidic solution? The products include Cr^{3+} and SO_4^{2-} ions.

(a) 14.36 mL　　　(b) 28.75 mL　　　(c) 43.12 mL
(d) 56.12 mL　　　(e) 32.15 mL

28. The dissolution process is exothermic if the amount of energy released in bringing about __a__ interactions exceeds the sum of the amounts of energy absorbed in overcoming __b__ and __c__ interactions.

	a	b	c
(a)	solute-solute	solvent-solvent	solvent-solute
(b)	solvent-solvent	solute-solute	solvent-solute
(c)	solvent-solute	solute-solute	crystal lattice
(d)	solute-solute	crystal lattice	solvent-solvent
(e)	solvent-solute	solute-solute	solvent-solvent

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29. If the concentration of CO_2 is 2.90 g of CO_2 per 1.00 L of soft drink when bottled under 2.0 atm of CO_2 pressure, what will be the concentration of the CO_2 in the drink after it has been opened and left to come to equilibrium with the atmosphere which has a CO_2 partial pressure of 3.0×10^{-4} atm?

(a) 2.2×10^{-3} g CO_2/L　　(b) 2.0×10^{-4} g CO_2/L　　(c) 1.0×10^{-4} g CO_2/L
(d) 4.4×10^{-4} g CO_2/L　　(e) 4.6×10^{-2} g CO_2/L

30. What is the mass % solute of a 2.00 molal (※ note: not molar) H_2SO_4 solution in water?

(a) 1.1 % (b) 9.8 % (c) 19.6 % (d) 2.0 % (e) 16.4 %

31. Sucrose is a nonvolatile, nonionizing solute in water. Determine the vapor pressure lowering, at 27°C, of a solution of 75.0 grams of sucrose, $C_{12}H_{22}O_{11}$, dissolved in 180.0 g of water. The vapor pressure of pure water at 27°C is 26.7 torr. Assume the solution is ideal.

(a) 0.585 torr (b) 0.058 torr (c) 0.571 torr (d) 5.62 torr (e) 0.548 torr

32. If the van't Hoff factor for NaCl is 1.88, what is the freezing point of a 0.50 molal NaCl solution in water? K_f = 1.86°C/m for water.

(a) −0.93 °C　(b) 1.86 °C　(c) −1.75 °C　(d) 1.75 °C　(e) −1.86 °C

33. The following reaction is partially responsible for acid rain:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Rate data have been determined at a particular temperature for the reaction in which all reactants and products are gases.

Trial Run	Initial [SO₃]	Initial [H₂O]	Initial Rate ($M \cdot s^{-1}$)
1	0.35 M	0.35 M	0.150
2	0.70 M	0.35 M	0.600
3	0.35 M	0.70 M	0.300
4	0.70 M	0.70 M	1.20

The rate-law expression is _____.

(a) rate = $k[SO_3]^2[H_2O]^2$　(b) rate = $k[SO_3]^2[H_2O]$　(c) rate = $k[SO_3][H_2O]^2$
(d) rate = $k[SO_3]^2$　　　　　(e) rate = $k[SO_3][H_2O]$

34. At 25°C, the following heats of reaction are known:

	$\triangle H$ (kJ/mol)
$2ClF + O_2 \rightarrow Cl_2O + F_2O$	167.4
$2ClF_3 + 2O_2 \rightarrow Cl_2O + 3F_2O$	341.4
$2F_2 + O_2 \rightarrow 2F_2O$	−43.4

At the same temperature, calculate $\triangle H$ for the reaction:
$$ClF + F_2 \rightarrow ClF_3$$
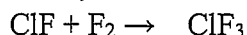
(a) -217.5 kJ/mol　(b) -130.2 kJ/mol　(c) +217.5 kJ/mol (d) -108.7 kJ/mol (e) +108.7 kJ/mol

35. Which of the following is the correct structure for 3-cyclopropyl-2-methylpentane?

(a)

CH_3
|
CH_3——CH_2-CH-CH-CH_3

(b)

(c)

CH_3——CH_2-CH-CH-CH_3
| |
CH_2 CH_3
|
CH_2
|
CH_3

(d)

(e)

CH_3
|
CH_3-CH-CH-CH_2-CH_3
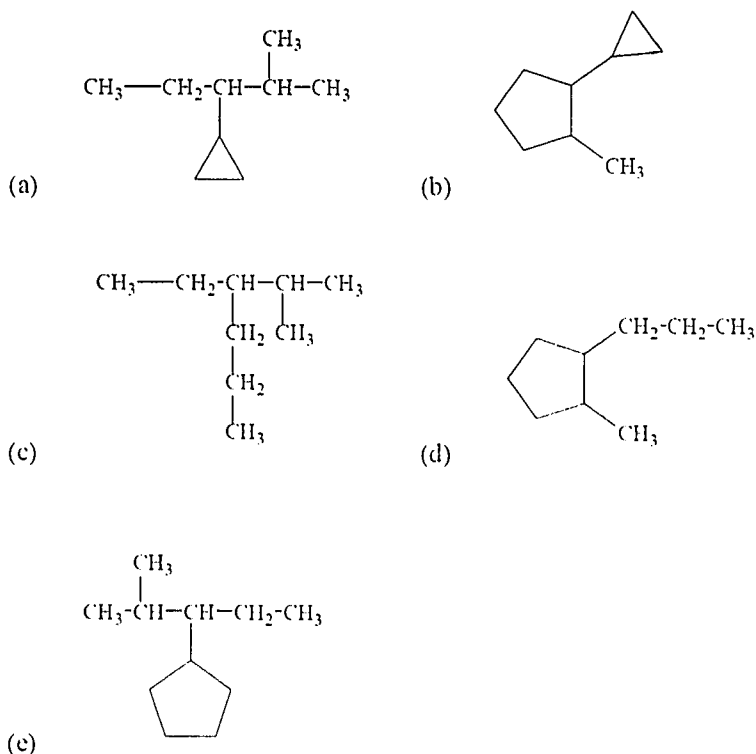
36. A sample of ammonia has a mass of 45.5 g. How many hydrogen atoms are in this sample?
   a) 2.67×10^{22} b) 1.61×10^{24} c) 2.25×10^{23} d) 4.83×10^{24} e) 9.02×10^{-16}

37. The hybridization of the nitrogen atom in the cation NH_2^+ is:
   a) sp^2 b) sp^3 c) dsp^3 d) sp e) $sp^3 d^2$

38. Calculate the enthalpy of formation of LiF(s) given the following:

sublimation energy for Li(s)	$+161$ kJ/mol
$1/2\ F_2(g)$ → F(g)	$+77$ kJ/mol
first ionization energy of Li(g)	$+520$ kJ/mol
electron affinity of F(g)	-328 kJ/mol
lattice energy for LiF(s)	-1047 kJ/mol

   a) -177 kJ/mol   b) -617 kJ/mol   c) -804 kJ/mol   d) -1047 kJ/mol   e) -1234 kJ/mol

39. The fact that O_2 is paramagnetic can be explained by
   a)   the Lewis structure of O_2 b) resonance   c)   a violation of the octet rule
   d)   the molecular orbital diagram for O_2 e) hybridization of atomic orbitals in O_2

40. Iron is biologically important in the transport of oxygen by red blood cells from the lungs to the various organs of the body. In the blood of an adult human, there are approximately 2.69×10^{13} red blood cells with a total of 5.80 g of iron. On the average, how many iron atoms are present in each red blood cell? (molar mass Fe = 55.85 g/mol)

   a) 8.60×10^{-10} b) 2.32×10^9 c) 3.13×10^{22} d) 2.69×10^{13} e) 6.02×10^{-2}

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Part III. Non-choice (20%)

1. (6 %) For the following graphs, determine their corresponding reaction order:

(a)

slope = ak

$1/[A]$

$1/[A]_0$

Time

(b)

$\ln [A]_0$

slope = $-ak$

$\ln [A]$
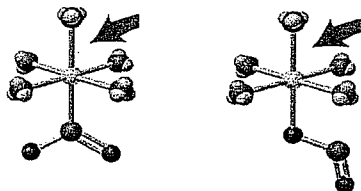
Time

(c)

$[A]_0$

slope = $-ak$

$\ln [A]$

Time
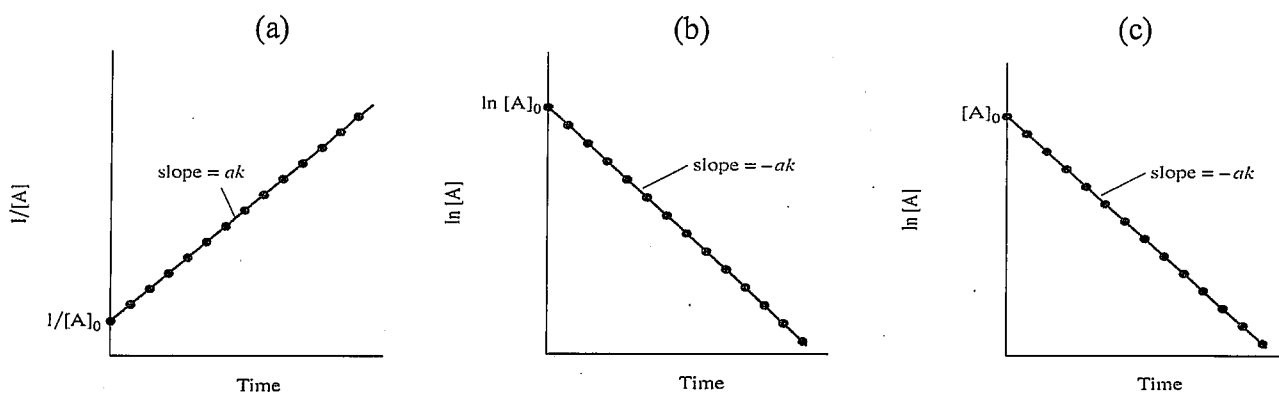
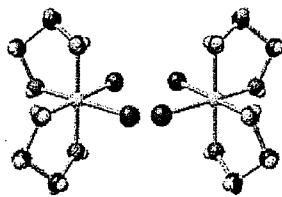2. (6%) Identify the type of isomers for the following sets of isomer

A.
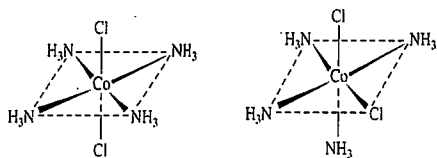
B

C

(a) which set belongs to the optical isomer?

(b) which set belongs to the constitutional isomer?

(c) which set belongs to the linkage isomer?

3. (8 %) Crystal field theory treats the ligands as point charges and considers the effect of these point charges on the relative energies of the d orbitals.

　Consider the five d orbitals in an octahedral coordination configuration

d_{yz}

d_{x2-y2}

d_{xz}

d_{xy}

d_{z2}
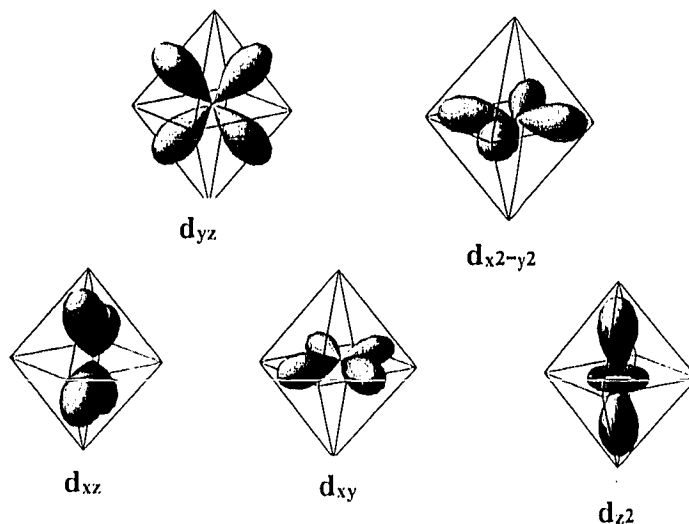
(a) Which orbitals point their lobes *directly* at the point-charge ligands, and are classified as e_g orbitals? (2%)

(b) Which orbitals point their lobes *between* at the point-charge ligands, and are classified as t_{2g} orbitals? (3%)

(c) Which set of orbitals are higher in energy (e_g or t_{2g})? (1%) Please explain why? (2%)