Preparatory Problems

Solutions to the tasks



"Bonding the World with Chemistry"

**49th INTERNATIONAL CHEMISTRY OLYMPIAD   
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**Solution to the Tasks**

***Task 1. Dimerization of Acetic Acid***

1.1) The reaction can be represented as 2CH3COOH ⇌ (CH3COOH)2.

If we begin with, say, 100.0 mol CH3COOH and 92.0% dimerizes, then 8.0 mol will be present at equilibrium. The 92.0 mol that react give rise to 46.0 mol dimers. The total number of moles present is therefore 54.0. Hence using the data at 298 K, the equilibrium constant, *Kp*, is given by



From equation Δ*Go* = -*RT* ln *Kp*,

At 298 K, Δ*Go* = -*RT* ln *Kp*

= -(8.314 J K-1mol-1)(298 K) ln (194)

= -13.0 kJ mol-1

At 318 K, Δ*Go* = -*RT* ln *Kp*

= -(8.314 J K-1mol-1)(318 K) ln (37.3)

= -9.57 kJ mol-1

Applying the equation Δ*Go* = Δ*Ho*-*T*Δ*So*:

The method for the calculation is to write the two equations

Δ*Go*(298 K)= -13.0 kJ mol-1 = Δ*Ho*- (298) Δ*So*

Δ*Go*(318 K)= -9.57 kJ mol-1 = Δ*Ho*- (318) Δ*So*

and solve the equations simultaneously.

Then Δ*Ho*= -64.1 kJ mol-1 and Δ*So* = -170 J K-1 mol-1.

1.2) Applying the Le Chatelier’s principle, an increase of pressure should

✓ favor the dimerization.

⃝ not favor the dimerization.

1.3) The extent of dimerization

✓ decreases with increasing the temperature.

⃝ increases with increasing the temperature.

***Task 2. Solubility of Calcite***

According to Δ*Gosol*= -*RT* ln *Ksp* = Δ*Hosol*-*T*Δ*Sosol*,

we have ln *Ksp* = -Δ*Hosol*/(*RT*) + Δ*Sosol*/*R*.

Assuming that Δ*Hosol* and Δ*Sosol* are temperature-independent,

ln (*Ksp1*/*Ksp2*) = -Δ*Hosol*/*R* (1/*T1*-1/*T2*)

ln (9.50/2.30) = -Δ*Hosol*/*R* (1/273 – 1/323)

Solving this equation to get Δ*Hosol* = -21 kJ mol-1.

***Task 3. Expansion of Ideal Gas and Thermodynamics of Liquid Mixing***

3.1) Δ*U* = 0, *q* = -*w*

*w* = -(1.00 atm)(2.42-0.200 dm3)(101.325 J dm-3 atm-1)

= -225 J

*q* = 225 J

Δ*Ssurr* = -225 J/295.4 K = -0.762 J K-1

Δ*Ssys* =[(0.100 mol)(8.3145 J mol-1 K-1) (295.4 K) ln(2.42 dm3/0.200 dm3)]/(295.4 K) = 2.07 J K-1

Δ*Suniv* = 2.07 + (-0.762) = 1.31 J K-1

3.2) Δ*Hmix* = Δ*Vmix* = 0

The other functions are given by these equations:

 and .

The mole fraction of **A** is 3.00/(3.00+5.00) = 0.375.

The mole fraction of **B** is 1.000-0.375 = 0.625.

= (8.314 J mol-1 K-1)(298.0 K){0.375ln(0.375)+0.625ln(0.625)} = -1639 J mol-1

= -(8.314 J mol-1 K-1){0.375ln(0.375)+0.625ln(0.625)} = 5.50 J K-1 mol-1

***Task 4. Vibrational Frequency of a Diatomic Molecule***

4.1) To find the reduced mass of CX, *μ*CX:







; 













4.2) To find mass of the atom X, mx:











=16.03

Thus, atom X should be oxygen.

***Task 5. Water-gas-shift Reaction***

5.1) The mole fraction of H2 in the reactor,  = = 0.475.

Thus,  = (0.475)(1.00 atm) = 0.475 atm.

And likewise, = 0.475 atm and = = 0.025 atm

**=** 3.6 × 102

Therefore, Δ*Go* = -*RT* ln *K* = -(8.314 J K-1 mol-1)(273 K) ln(3.6 × 102) = -13.4 kJ mol-1.

5.2) The kinetics data given reflects the forward rate of the WGS reaction. The only rate law that is consistent with the given data is , and *kf*= 4.4 × 10-3 atm-1 s-1.

Thus, X = (4.4 × 10-3 atm-1 s-1)(0.28 atm)(0.72 atm) = 8.9 × 10-4 atm s-1.

5.3) *kb* = *kf* /K = (4.4 × 10-3 atm-1 s-1)/(3.6 × 102) = 1.2 × 10-5 atm-1 s-1.

So during the normal course of the reaction,

= (4.4 × 10-3 atm-1 s-1)(0.14 atm)(0.14 atm)–(1.2 × 10-5 atm-1 s-1)  
(0.36 atm)(0.36 atm) = 8.44 × 10-5 atm s-1.

5.4) Δ*G*= Δ*Go* + *RT* ln *Q* = (-13.4 kJ mol-1) + (8.314 J mol-1 K-1)(273 K)= -9.1 kJ mol-1

5.5) The reaction CO2H(ads) → CO2(ads) + H(ads) is first-order, whose rate can be expressed as rate = k[CO2H] = kS0 = k′, where S0 denotes the maximum number of adsorbed intermediates for this surface.

Thus, *θ*= rate/k′ = (1.0 × 1011 molecules s-1 cm-2)/(2.0 × 1012 molecules s-1 cm-2) = 0.050.

***Task 6. Camphor in Benzene***

*X*ben = nben/(nben + ncam)

nben = (100 cm3)(0.877 g cm-3)(1 mol/78.1 g) = 1.12 mol

ncam = (24.6 g)(1 mol/152.2 g) = 0.162 mol

*X*ben = (1.12 mol)/(1.12 mol + 0.162 mol) = 0.874

*P*ben = (*X*ben)(*P*oben ) = (0.874)(100 torr) = 87.4 torr

massben = (100 cm3)(0.877 g cm-3)(1 kg/1000 g) = 0.0877 kg

molality of camphor in solution = 0.162 mol camphor/0.0877 kg benzene = 1.85 mol kg-1

Δ*T* = *Kf* m = (5.12 oC kg mol-1)(1.85 mol kg-1) = 9.46 oC

Since pure benzene freezes at 5.50 oC, the solution will freeze at -3.96 oC.

***Task 7. Gas and Liquid***

7.1) According to the graph, the volume becomes zero at *T* = -100 oC. This means that the absolute temperature should be calculated as *T* (K) = oC + 100 (not *T* (K) = oC + 273.15).

If *V1* = 15 cm3, *T1* = -50 oC + 100 = 50 K, and *T2* = 100 oC + 100 = 200 K, then we have

(15 cm3/50 K) = (*V2*/200 K).

Therefore, *V2* = (15 cm3)(200 K)/(50 K) = 60 cm3.

7.2) From Dalton’s law, the total vapor pressure is the sum of the individual vapor pressures:

*Ptotal* = *PB* + *PC* (1)

Using the Raoult’s law, the total pressure may be obtained by substituting each *P* term with   
*Pi° × Xi*, where *Pi°*  is vapor pressure above pure liquid *i* and *Xi* is mole fraction of liquid *i*:

*Ptotal* = ( × *XB*) + (× *XC*) (2)

We know from the question that there are 7 mol of liquid. We obtain the respective mole fractions *X*: the mole fraction of **B** is 3/7 and the mole fraction of **C** is 4/7.

Substituting values of *Xi* and *Pi°* into equation (2) yields the total pressure *Ptotal* as follows

*Ptotal* = (100.1 kPa × 3/7) + (60.4 kPa × 4/7)

= (42.9 kPa) + (34.5 kPa)

So *Ptotal* = 77.4 kPa

7.3) From the definition of mole fraction *X*, we say



The number of moles *ni* are directly proportional to the partial pressure *Pi*if we assume that each vapor behaves as an ideal gas (we assume here that *T* and *V* are constant). Accordingly, we say



Substituting numbers from question 7.2:



The mole fraction of **B** in the vapor is 0.554, so it contains 55.4% **B**. The remainder of the vapor must be **C**, so the vapor also contains (100-55.4)% = 44.6% of **C**.

Note that the liquid phase comprises 43% **B** and 57% **C**, but the vapor contains proportionately more of the volatile **B**. We should expect the vapor to be richer in the more volatile component.

***Task 8. Decomposition of Nitrous Oxide***

8.1) Because the reaction is second order, therefore

- = (1.10 × 10-3 dm3 mol-1 s-1) (1250 s)

[N2O]t = 0.0940 mol dm-3

8.2) Using Arrhenius equation,

ln = -  

*k*2 = 4.23 × 10-3 dm3 mol-1 s-1

***Task 9. Avogadro’s Number***

9.1)Let v = α3, the volume of the unit cell

The number of unit cell in volume V of the silicon sphere = (V/v)

If n is the number of silicon atoms in the unit cell, the number of silicon atoms in silicon

sphere = n(V/v)

The number of moles of Si in the sphere = (W/A)

The number of silicon atoms in sphere = moles x NA.

*i.e.* (W/A).NA = n(V/v)

NA = n(V/v).(A/W)

9.2) For a face-centered unit cell, the number of atoms at the 8 corners of cell = 8; the number at the 6 faces = 6. Each corner has (1/8) of atom in unit cell and each face has (1/2) of atom. Thus total number of Si atoms in unit cell = 8x(1/8) + 6x(1/2) + 4 = 1 + 3 + 4 = 8.

n = 8

9.3) The volume v of the unit cell must be in unit of cm3.

1 pm = 10-12 m = 10-10 cm

NA = 6.022 141 x 1023

***Task 10. Buffer from Biological Acid: Lysine***

Acid Dissociation Constants

10.1)

*No, the correct form is shown:* 

10.2)



10.3)  *Given that H3L2+ : the most acidic form*

*H2L+ : the first intermediate form*

*HL : the second intermediate form*

*L-: the most basic form*

= [H3L2+] + [H2L+] + [HL] + [L-] = 0.1 mol dm-3

total mol of H3L2+ = *(0.100* mol dm-3*)(0.1* dm3*) = 0.01 mol*

total mol of H3L2+ = (mol H3L2+) + (mol H2L+) + (mol HL) + (mol L-) = 0.01 mol

At pH = 9.5, [H+] = 10-9.5 mol dm-3

At pH = 9.5, the equilibrium moles of all forms can be calculated as follow;

mol H3L2+ = ) =  *mol (negligible)*

mol H2L+ = ) = 2.497 x 10-3 mol

mol HL = ) = 6.88 x 10-3 mol

mol L- = ) = 6.27 x 10-4 mol

Titration reaction to convert H3L2+ to the desired forms;

H3L2+ + OH- 🡪 H2O + H2L+

H2L+ + OH- 🡪 H2O + HL

HL + OH- 🡪 H2O + L-

mol of KOH required = (2.497 x 10-3) + 2(6.88 x 10-3) + 3(6.27 x 10-4)

= 1.814 x 10-2 mol

cm3 of KOH required = *= (* cm3

10.4) In this case, Ka1 is carboxylic acid Ka, Ka2 is ammonium Ka, and Ka3 is substituent Ka.

HL is the second intermediate form

*[H+] =*

Since *Ka2* and *Ka3* are small;

[HL] = = 0.342 mol dm-3

[H+] = = mol dm-3

pH = 9.80

The alternative calculation is pH = (pKa2 + pKa3)/ 2 = (9.06 + 10.54)/2 = 9.80.

10.5) *Ka3* = 10-10.54

*Kb2* = =

From question 10.4; [H+] = mol dm-3

[OH-] = mol dm-3

At equilibrium;

[HL] = )

Where; CHL=0.342 M

[HL] = 0.250 M

*Ka3* =

🡪 [L-] = mol dm-3

*Kb2* =

🡪 [H2L+] = = mol dm-3

*Kb3* = =

*Kb3* =

🡪 [H3L2+] = = mol dm-3

***Task 11. Amperometric Titration: Titration of Pb2+ with Cr2O72-***

11.1) By extrapolating the two straight lines, the titration end-point is located.



11.2) Pb2+(aq) + Cr2O72-(aq)  PbCr2O7(s)

11.3) mol Pb = mol dichromate

0.0020 mol dm-3 x 8.0 cm3 = 20.0 cm3 x Clead

Therefore, [lead] = 0.0020 x 8.0 / 20.0 = 8.0x10-4 mol dm-3

***Task 12. Conductometric Titration***

12.1) The conductivity value before turning point comes from the mobility of H+ and Cl- from HCl. After NaOH was added to the titration vessel, the H+ reacted with OH- and the solution conductivity due to H+ decreases. After the turning point, NaOH becomes excess in solution. The conductivity value increases with amount of added NaOH. The ion mobility of H+ is higher than that of OH-, hence the slope of titration curve before and after turning point is different.

12.2) From titration curve, the turning point is the end point, and is at 108 seconds.

Flow rate of NaOH = 3 drops / sec.

Therefore, the volume of NaOH is 108 x 3 = 324 drops = 324 x 0.029 cm3 = 9.39 cm3

The concentration of HCl = 9.39 x 0.100/ 25 = 0.037 mol dm-3.

***Task 13. Titration of Cu and Zn in Metal Alloy***

13.1) Cu(s) + 4HNO3(aq)  Cu2+ + 2NO3-(aq) + 2NO2(g) + 2H2O(l)

Zn + 2HCl  Zn2+ + H2(g) + 2Cl-

13.2) Total metal by EDTA titration = mol EDTA used = 33.4 x 0.1/1000 = 3.34x10-3 mol

Mol Cu by redox titration

2Cu2+ + 4I-  CuI(s) + I2

I2 + 2S2O32-  2I- + S4O62-

mol Cu = mol thiosulfate used = 29.35x0.1/1000 = 2.935x10-3 mol

grams Cu = 2.935x10-3 mol x 63.5 = 0.1864 grams in 25.00 mL aliquot

Therefore, a 250 cm3 sample solution will contain = 0.1864 x250/25 = 1.864 gram

Thus %w/w Cu = 1.864/2.300 x 100 = 81.0 %

mol Zn = total metal – Cu = 3.34x10-3 – 2.935x10-3 = 4.05x10-4 mol

grams Zn = 4.05x10-4 mol x 65.4 = 2.649x10-2 grams in 25.00 aliquot

Therefore, 250 cm3 sample solution will contain = 2.649x10-2 x250/25 = 0.2649 gram

Thus %w/w Zn = 0.2649/2.300 x 100 = 11.5 %

***Task 14. Spectrophotometric Determination of Iron***

14.1)

a) At CL = 2.20 x 10-2 mol dm-3, [ML3] = 6.25 x 10-5

A = ƐbC, therefore Ɛ = A/bC = 0.750/6.25 x 10-5 = 12,000 L mol-1 cm-1

b) M + 3L  ML3

Kf = [ML3] / [M] [L]3 (1)

at CL = 9.25 x 10-5 M, [ML3] = 0.360 / 12000

[ML3] = 3.0x 10-5 mol dm-3 (2)

therefore, [M] = (3.25 x 10-5) – (3.0x 10-5)

[M] = 0.25 x 10-5 mol dm-3 (3)

[L] = (9.25 x 10-5) – 3 x (3.0x 10-5)

[L] = 0.25 x 10-5 mol dm-3 (4)

Hence Kf = (3.0x 10-5) / (0.25 x 10-5) (0.25 x 10-5)3

Kf = 7.68 x 1017 dm3 mol-3

14.2)mole of C : mole of H : mole of N = 80/12 : 4.44/1 : 15.56/14

= 6.67 : 4.44 : 1.11

= 6 : 4 : 1

therefore, the empirical formula of L is C6H4N

The empirical molar mass = (6 x 12) + (4 x 1) + (1 x 14) = 90

molar mass/ empirical molar mass = 180 / 2

Therefore, the molecular formula of L is C12H8N2.

14.3) d-orbital splitting diagram for ML3



**Possible isomers of Fe2+ complexes**

ML :



ML2 :



ML3 :



Δo of ML < ML2 < ML3 H2O is a weaker field ligand as compared with bipyridine.

14.4)

A = ƐbC, therefore C = A/Ɛb = 0.550/12000 = 4.58 x 10-5 mol dm-3

The concentration of dialyzable iron is

4.58 x 10-5 mol dm-3 x 50.00/5.00 = 4.58 x 10-4 mol dm-3

4.58 x 10-4 mol dm-3 x 55.845 g mol-1 x 1000 mg g-1 = 25.58 mg dm-3

14.5)

From 14.4), the concentration of dialyzable iron is 25.58 mg dm-3 which is also equal to the concentration of iron inside the dialysis bag.

The total volume is 12.50 cm3 (inside the dialysis bag) + 20.00 cm3 (outside the bag)

= 32.50 cm3.

Therefore, the total amount of digestible iron is

(25.58 mg dm-3 x 32.50 cm3) / (1000 cm3 dm-3) = 0.8314 mg

For the supplement of 0.4215 g, the iron content is 0.8314 mg

For the supplement of 1.0000 g, the iron content is 0.8314 mg x 1.0000 g / 0.4215 g

= 1.972 mg

***Task 15. Basic Electrochemistry***

15.1)

*Anode: Mn2+ + 4H2O*  *MnO4- + 8H+ + 5e-*

*Cathode: : 5Ce4+ + 5e-*  *5Ce3+*

*Net : Mn2+ + 4H2O + 5Ce4+*  *MnO4- + 8H+ + 5Ce3+*

*Eocell = Eocathode*- *Eoanode*

*Eocell = 1.70-1.507 = 0.193V*

*Eocell = log K*

*0.193= log K*

*K = 2.05×1016*

15.2)

*5 mg Ce4+ = 3.44 C*

*15.3*)

*Ecell = Eocell – logQ*

*Where Q is a reaction quotient.*

*Ecell = Eocell – log]*

*Ecell = 0.193 – log*

*Ecell = 0.481V*

***Task 16. Calculation of Concentration***

16.1) mol Cu in CuCl2 1.345 g = 1.345 g/ (63.55 + 2(35.45) g mol-1) = 0.0100 mol Cu

mol Cu in 50.00 cm3 of CuSO4 31.9 g dm-3

= (50 cm3 /1000 cm3 dm-3) x (31.9 g dm-3 /159.62 g mol-1) = 0.00999 mol Cu

Therefore, the total mol Cu is 0.0100 + 0.00999 = 0.01999 = 0.02 mol

500 cm3 contains 0.02 mol Cu, therefore the concentration is 0.04 mol dm-3.

16.2) The concentration of Cu in 100.0 cm3

= (25.00 cm3 / 100.0 cm3)x 0.04 mol dm-3 = 0.01 mol dm-3 or 10-2 mol dm-3

pH = 8.0, implying that [OH-] = 10-6 mol dm-3

[Cu2+][OH-]2 = (10-2) (10-6)2 = 10-14 which is greater than the KSP(Cu(OH)2), i.e., 4.8 x 10-20

Therefore, the precipitate of Cu(OH)2 is formed.

***Task 17. Small Molecule Activation by Frustrated Lewis Pairs***

17.1)



17.2)



17.3)



17.4)



17.5)



17.6)



17.7)



17.8)



***Task 18. Silver Iodide***

18.1) 0

The reduction of Ag+ to Ag0 causes the change of color.

18.2) AgF > AgCl > AgBr > AgI

The stronger interaction between Ag+ and I– as well as the low hydration energy of I– result in the poor solubility of AgI. The smaller size of other halide ions led to poorer interaction with Ag+; hence, higher solubility.

18.3) – 0.028 V

Δ*G*o = – *nFE*o

For (a), Δ*G*oa  = – (– 1)(96,500)(0.80) = – 77,200 J (mol Ag)–1

Δ*G*o = – *RT* ln*K*

For (c), Δ*G*oc = – (8.314)(298)(ln1014) = – 79,867 J mol–1

The reduction half reaction of [AgI3]2– :

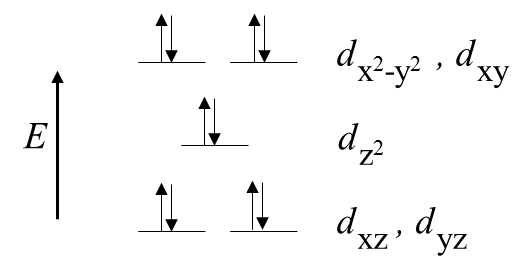
(d) [AgI3]2– (*aq*) + *e*–  Ag (*s*) + 3 I– (*aq*)

Eqn (d) = (a) – (c)

Therefore, Δ*G*od = Δ*G*oa − Δ*G*oc = – 77,200 – (– 79,867) = 2,667 J mol–1

*E*o = −Δ*G*od/(*nF*) = – (2,667)/(96,500) = – 0.028 V

18.4) For trigonal planar,



The ligands lie in the xy plane, then the and orbitals that have their electron density concentrated in this plane will have the highest energy. The and orbitals have their electron density out of this xy plane, so their energies are the lowest. The orbital has its electron density mostly out of the xy plane, but there is a ring of electron density in the xy plane, so the orbital will have energy higher than the and orbitals but still lower than the and orbitals. In addition, the number of *d*-electrons for silver in [AgI3] 2– is 10. Therefore, all *d*-orbitals should be filled.

***Task 19. Perovskite Structure***

19.1) Number of Ca2+ ions: 8 corners x 1/8 ion Ca2+/corner = 1

Number of O2- ions: 6 cube faces x 1/2 O2- ion/cube face = 3

Number of Ti4+ ions: one Ti4+ ion in the cube center = 1

Therefore, the empirical formula is CaTiO3.

19.2) (1) octahedral hole (4 per unit cell), (2) tetrahedral hole (8 per unit cell)

19.3) Octahedral hole

***Task 20. Quantum Numbers and Atomic Orbitals***

20.1) (i) *l* = *n* is not allowed. For a certain value of *n*, *l* can be any value from 0 to *n*-1 (i.e., less than *n*).

(ii) *ml* = -2 is not possible for *l* =1, because the magnitude of the *ml* must not be greater than *l*. (For a certain value of *l*, *ml* = *l*, *l*-1,…,- *l*.)

(iii) *l* = -1 is not possible. *l* cannot have a negative value.

20.2) (i) 6*d*

(ii) 4*f*

(iii) 6*p*

20.3) (i) five

(ii) seven

(iii) one

***Task 21. Radioactivitiy of Iodine and Nuclear Equations***

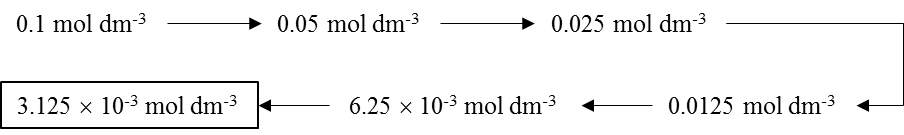
21.1)

(i) After 2 half-lives, the remaining concentration of I-131 will be as follows:

|  |  |
| --- | --- |
| [I-131] |  |

(ii) After 40 days which is equal to 5 half-lives, the remaining concentration of I-131 will be as follows:

[I-131]



21.2) (i) (ii) or β+ (iii) (iv)

(v) (vi) (vii) (viii) or α

***Task 22. Structure and Chemistry of Sodium Chloride***

22.1) (i) 6 and 6

(ii) 4

(iii) 2.21 g cm-3

Density = *m*/*V*

*V* = *a*3 = (560 pm)3 = 1.76 x 10-22 cm3

*mass* = (4 x 58.5 g)/(6.022 x 1023) = 3.89 x 10-22 g

Density = 3.89 x 10-22 g / 1.76 x 10-22 cm3 = 2.21 g cm-3

22.2) (i) *n* = 3, *l* = 0

(ii) Na is larger than Cl, but Cl- is larger than Na+.

(iii) 

(iv) -787 kJ mol-1

Δ*H*overall = -411 kJ mol-1 = Δ*H*sublimation for Na + *IE*1 for Na + ½(Cl-Cl dissociation) +

Electron affinity of Cl + lattice energy

-411 kJ mol-1 = 107 kJ mol-1 + ½ (224) kJ mol-1 + 496 kJ mol-1 – 349 kJ mol-1 + lattice energy

lattice energy = -787 kJ mol-1

22.3) (i) Br2(*l*) + Cl-(*aq*) → no reaction

(ii) Cl-(*aq*) + Ag+(*aq*) → AgCl(*s*)

(iii) Yellow

***Task 23. Natural Chelator from Shrimp Shell***

23.1) The preferred binding sites are indicated in the circles as follows:



23.2)



Pb2+ is a soft metal ion so it prefers to form bond with sulfur. This helps PMCS adsorb Pb2+ better.

23.3) *meso*-tetra(*p*-carboxyphenyl)porphyrin can form ester bond with chitosan as shown in the proposed structure below:



Or amide bonds are formed as below:

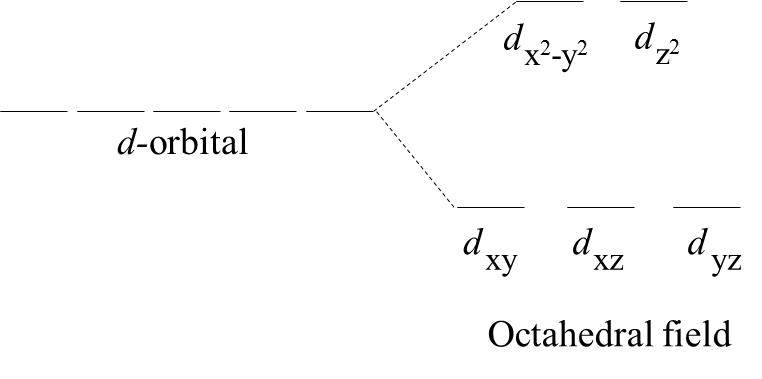


23.4) One of the structures in question 23.3 was chosen to bond with Fe2+ as the proposed structure below.



The two vacant axial sites are bonding with water molecules.

Assuming that the crystal fields are equivalent along the x, y, and z axes, the splitting diagram of Fe2+ *d* orbitals is shown below:



***Task 24. Compound Identification and Related Chemistry***

24.1) **M**Cl3 and **M** = Al

Theoretically, the maximum amount of the product is obtained when the mole fraction of **M** and Cl2 are in the correct stoichiometric ratio. Based on the experiments, **M**:Cl2 = 0.4:0.6 or 2/3 is the stoichiometric ratio needed to form **M**xCly. Thus, the equation is as follows:

2 **M** + 3 Cl2 → 2 **M**Cl3.

∴ the chemical formula of **M**xCly = **M**Cl3

Since 0.4 mole of M generates 0.4 mole of **M**Cl3, the molar mass of **M**Cl3 and atomic mass of M can be derived:

Molar mass of **M**Cl3 = 53.3 g/0.40 mol = 133 g mol-1

Atomic mass of **M** = 133 – (3 × atomic mass Cl) = 133.3 – (3 × 35.45) = 26.9 g mol-1

∴ **M** = Al

24.2) (i) AlCl3 + 3 H2O → Al(OH)3 + 3 HCl

(ii) 2 AlCl3 + 3 H2SO4 → Al2(SO4)3 + 6 HCl

24.3)

***Task 25. Isomerism of Octahedral Fe(II) Complexes***

25.1)

25.2) isomers **A**, **A\***, **B**, **B\***, **E**, and **E\***

***Task 26. Stoichiometry and Structure Determination***

26.1) C9H10O3

*Solution:* % by weight C : H : O = 65.0 : 6.10 : 28.9

% by mol C : H : O = : :

= 5.42 : 6.04 : 1.81

∴ empirical formula C : H : O = 9 : 10 : 3

26.2)



26.3)

|  |  |  |  |
| --- | --- | --- | --- |
| **X =** |  | **Y =** |  |
| **Z =** |  |  |  |

***Task 27. Atropine***

27.1)



27.2)



27.3)



27.4)



***Task 28. Synthesis of Building Blocks for Fluorescent Markers***

Compounds **A**-**I** are shown below:



***Task 29. Synthesis towards Anatoxin-a***



***Task 30. Total Synthesis of Illudin C***

The structures of **A**, **B**, **C** and **D**:



***Task 31. Total Synthesis of μ-Opioid Receptor (MOR) Agonists***



***Task 32. Pericyclic Reaction***

32.1)



32.2)

(i) Structures of compounds **C**-**G**

|  |  |  |
| --- | --- | --- |
| **C** | **D** | **E** |
| **F** | **G** |  |

(ii)



Either position on compound **1** is correct.

(iii) Two.

Reaction between **1** and **2** will give a pair of enantiomers which are inseparable.

*(Note: the two enantiomers can be resolved but this process is not mentioned in the context.)* The subsequent processes, although generated a few new chiral centers, employed achiral reagent and the newly formed stereocenters were controlled by the existing stereochemistry. Therefore, stereochemical information was carried over from compound **C** to compound **3**.

32.3)

(i)



(ii) Racemic mixture of **H** will give product **I** which has a plane of symmetry. Therefore, reduction of **I** (only a stereoisomer) will give only 1 possible product **J**.



***Note:*** *Compound I has a plane of symmetry, thus its mirror image (compound I’) is identical (meso-compound).*

***Task 33. Stereoisomers without Stereocenter***

*Hint: Student is encouraged to use chemistry model to figure out the plane of symmetry and the C2–symmetry in each molecule.*

33.1) (i) From the possible enantiomeric pair,



The molecule has a plane of symmetry, therefore, the structure is achiral.

(ii) From the possible enantiomeric pair,



There is no plane of symmetry in these two molecules. Therefore, these two mirror image structures are non-superimposable. The structure is chiral.

(iii) From the structure of cumulene,



This molecule is flat. As a result, there is a plane of symmetry in this molecule. Consequently, its mirror image is achiral.

(iv) From the possible enantiomeric pair,



There is no plane of symmetry in these two molecules. Therefore, these two mirror image structures are non-superimposable. The structure is chiral.

33.2 (i)



Enantiomers of *trans*-cyclooctene and *trans*-cyclononene are shown above. The two different structures are mirror images of each other and they are non-superimposable.

(ii) The enantiomers of both cycloalkanes are configurational isomers. The enantiomers can be interconverted *via* the ring flipping, similar to that of the chair cyclohexane. The *trans* double bond adds a considerable degree of rigidity to the ring. Since the *trans*-cyclononene has more carbon atoms so it is more flexible and can undergo the configuration inter-conversion more readily.