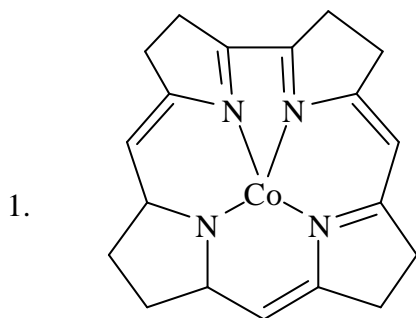


## MAJOR TEST - 4

**IIT-JAM - 2017**

**Solution (31.12.16)**



Number of six membered ring = 3

Number of five membered ring = 5

2. For a molecule to microwave active must have dipole moment.

$\text{CH}_2\text{CH}_2$  has not permanent dipole moment, So microwave inactive.

IR

3.  $\text{C} \equiv \text{CH}$  group  $3300 \text{ cm}^{-1}$

$\text{C} \equiv \text{C}$  group  $2150 \text{ cm}^{-1}$

hence 1-butyne is correct answer.

4. Ionic strength is the measurement of electrical intensity of a solution

Mathematically

$$I = \frac{1}{2} \sum m_i z_i^2$$

$m \rightarrow$  molality

$z \rightarrow$  valency

Note: For aq. solution density of  $\text{H}_2\text{O}$  is consider to be equal  $\therefore$  molality  $\approx$  molarity

0.008 M  $\text{AlCl}_3$  and 0.005 M  $\text{KCl}$


$$I = \frac{1}{2} \left( \overbrace{0.008 \times (3)^2}^{\text{Al}^{3+}} + \overbrace{0.005 \times (1)^2}^{\text{K}^+} + \underbrace{(0.008 \times 3 + 0.005) \times (1)^2}_{\text{Cl}^-} \right)$$

$$= \frac{1}{2} (0.072 + 0.005 + 0.029) = 0.53\text{M}$$

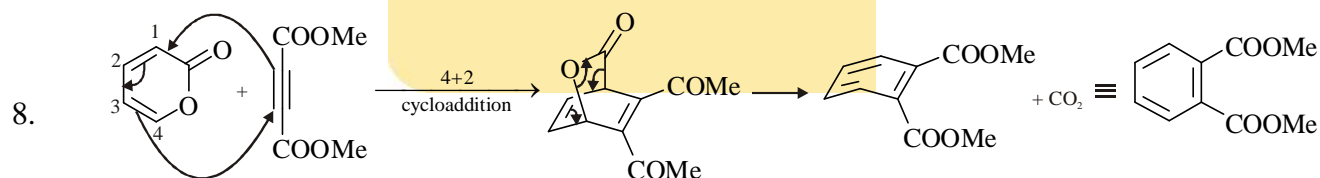
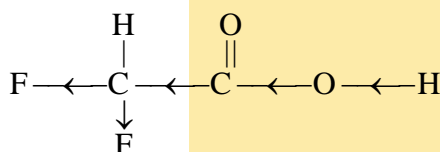


$$\begin{aligned}
 5. \quad \Delta S^\circ &= nF \left( \frac{\partial E^\circ}{\partial T} \right)_P \\
 &= 2 \times 96487 \times (-1.20 \times 10^{-3}) \quad \text{C} \times \text{V} = \text{J} \\
 &\quad \text{mol} \quad \text{C mol}^{-1} \quad \text{V K}^{-1} \\
 &= -231568.8 \times 10^{-3} \text{ JK}^{-1} \\
 &= -2.3 \times 10^2 \text{ JK}^{-1}
 \end{aligned}$$

6.  $\text{NaHCO}_3$  test (sodium bicarbonate test) is given by compounds which having  $-\text{COOH}$  or  $-\text{SO}_3\text{H}$  groups.

Hence (d) carboic acid (phenol)  doesn't give this test.

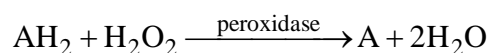
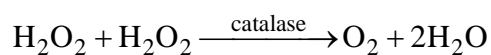
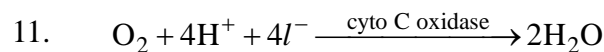
7. Fluoro group causes negative inductive effect increasing ionisation, thus 0.1 M difluoroacetic acid has highest electrical conductivity.

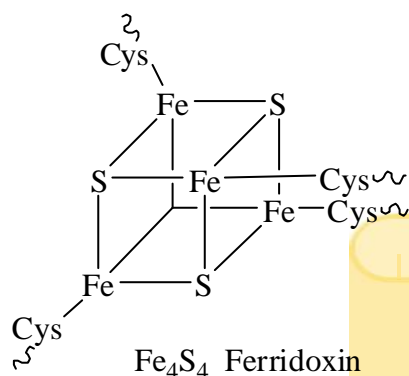
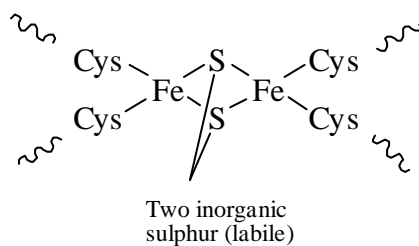
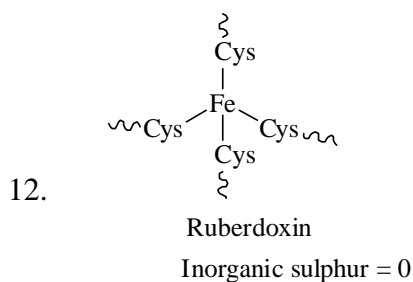


9. Correct Answer is b

10. In potentiometric titration, emf vs volume of titrant added is studied.

Option b is correct





Number of Inorganic sulphur = 4

13.  $J = 0 \rightarrow J = 1$

$$\Delta E = E_1 - E_0 = 2B - 0 = 2B$$

$$2B = 20.68 \text{ cm}^{-1};$$

$$B = 10.34 \text{ cm}^{-1}$$

$$J = 14 \text{ to } J = 15$$

$$\Delta E = 2B(J + 1) = 2 \times 10.34 (14 + 1) = 310.2 \text{ cm}^{-1}$$

14. For  $\text{CO}_2$  molecule

$\vec{\text{O}}=\text{C}=\vec{\text{O}}$  Antisymmetric stretching is IR active.

15. Prussian blue complex  $\rightarrow \text{Fe}_4[\text{Fe}(\text{CN})_6]_3 \rightarrow$  confirms C & N

Purple colouration  $\rightarrow \text{Na}_4[\text{Fe}(\text{CN})_5\text{NOS}] \rightarrow$  Confirms S

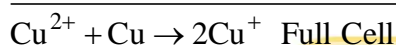
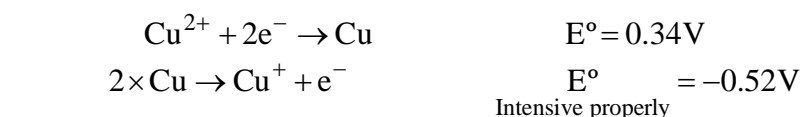
White precipitate  $\rightarrow \text{BaSO}_4$  &  $\text{Mg}_2\text{P}_2\text{O}_7 \rightarrow$  confirms S & P

Hence option (c) is correct answer.

16.  $\begin{array}{c} \text{O} \\ || \\ -\text{C}- \end{array}$  bond has more dipole moment hence it shows more absorption intensity.  
[Adsorption intensity  $\propto$  Polarity of bond]



$$\begin{array}{rcl}
 E_{\text{Fe}^{3+}, \text{Fe}^{2+}}^0 & = & 0.77\text{V} \quad 1 \times 0.77 = 0.77 \\
 E_{\text{Fe}^{2+}, \text{Fe}}^0 & = & -0.44\text{V} \quad 2 \times -0.44 = -0.88\text{V} \\
 \hline
 E_{\text{Fe}^{3+}, \text{Fe}}^0 & = & \frac{-0.11}{3} = -0.04\text{V}
 \end{array}$$



$$\therefore E^\circ = 0.34 - 0.52 = -0.18\text{V}$$

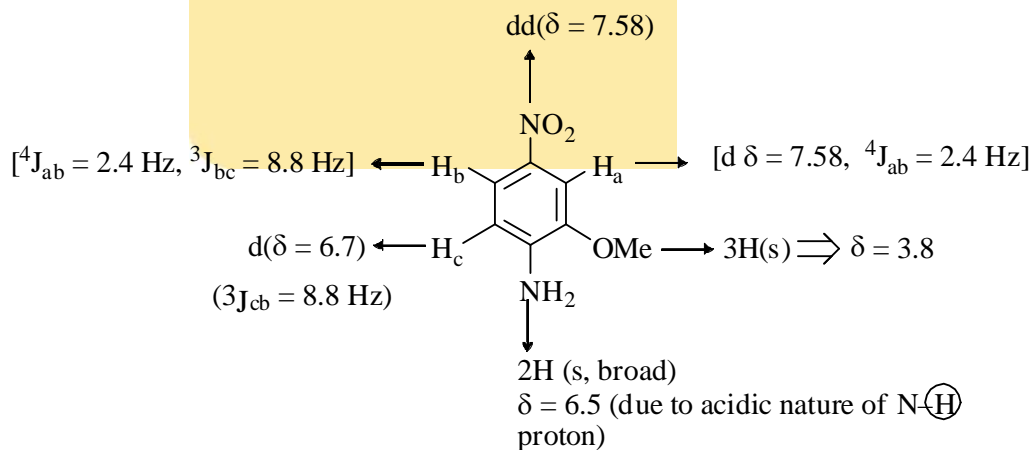
$$E_{\text{Cr}^{3+}, \text{Cr}}^0 = -0.74\text{V} \quad 3 \times -0.74 = 2.22$$

$$E_{\text{Cr}, \text{Cr}^{2+}}^0 = +0.91\text{V} \quad 2 \times 0.91 = 1.82$$

$$E_{\text{Cr}^{3+}, \text{Cr}^{2+}}^0 = -0.40\text{V}$$

Option d is correct

18. Compound matching given data should be



Proton  $\text{H}_b$  shows  $4J$  and  $3J$  coupling with  $\text{H}_a$  and  $\text{H}_c$  proton

Proton  $\text{H}_c$  shows  $3J$  coupling with  $\text{H}_b$  proton

Proton  $\text{H}_a$  shows  $4J$  coupling with  $\text{H}_b$  proton

$$19. J = (\delta_2 - \delta_1) \times B_0(\text{MHz}) \times 10^{-6}$$

$$= (\delta_2 - \delta_1) \times B_0(\text{Hz})$$

$$\text{coupling constant (J)} = (\Delta S) \times B_0(\text{MHz}) \times 10^{-6}$$

$$= (2.142 - 2.202) \times 300\text{Hz}$$

$$J = 19.8 \text{ Hz}$$



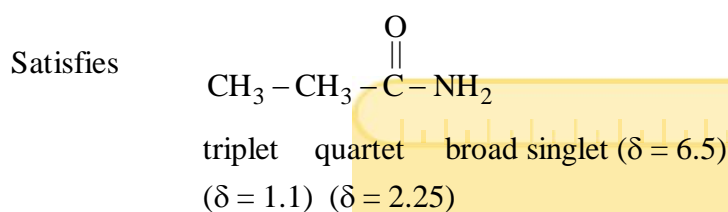
20. Formula  $C_3H_7NO$

$$\text{DBE} = C_n - \frac{\text{number of monovalent atoms}}{2} + \frac{\text{number of trivalent atoms}}{2} + 1$$
$$= 3 - \frac{7}{2} + \frac{1}{2} + 1$$

$$\text{DBE} = 4 - 3 = 1$$

Means there should be one  $\pi$  bond according to options.

$^1\text{H}$  NMR data given



$-\text{NH}_2$  group  $\rightarrow$  gives broad singlet

21. Correct answer is c

22. Correct answer is b

23.  $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$

$$w = zQ$$

where,  $w$  = amount of metal

$$= 5.12 \text{ kg} = 5.12 \times 10^3 \text{ g}$$

$z$  = electrochemical equivalent

$$= \frac{\text{equivalent weight}}{96500} = \frac{\text{atomic mass}}{\text{electrons} \times 96500}$$

$$= \frac{27}{3 \times 96500}$$

$$5.12 \times 10^3 = \frac{27}{3 \times 96500} \times Q$$

$$Q = \frac{5.12 \times 10^3 \times 3 \times 96500}{27} \text{ C} = 5.49 \times 10^7 \text{ C}$$

24. Conductivity due to  $\text{CaF}_2$  alone

$$= K_{\text{solution}} - K_{\text{H}_2\text{O}}$$

$$= (4.2 \times 10^{-5} - 2 \times 10^{-6}) \text{ S cm}^{-1}$$

$$= 4 \times 10^{-5} \text{ S cm}^{-1}$$

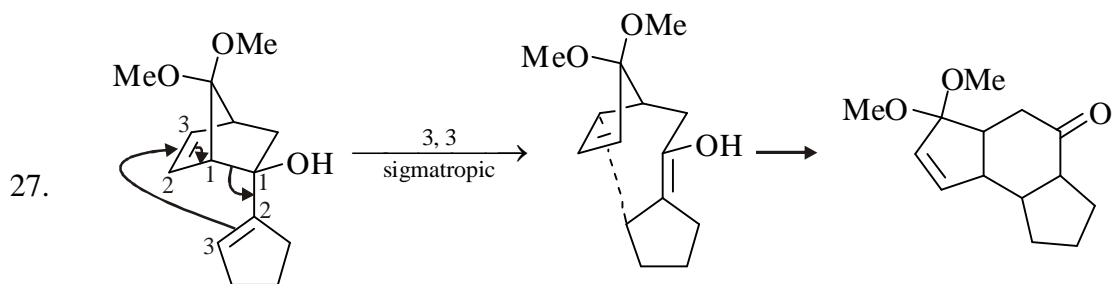
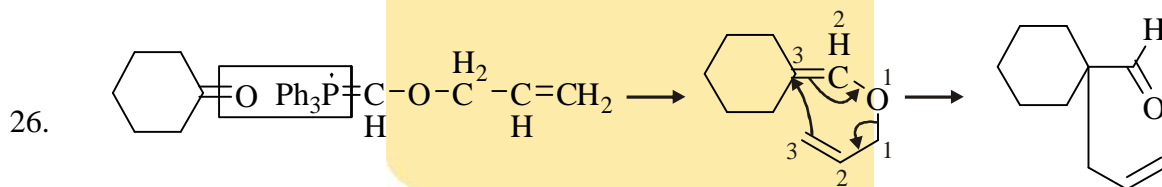
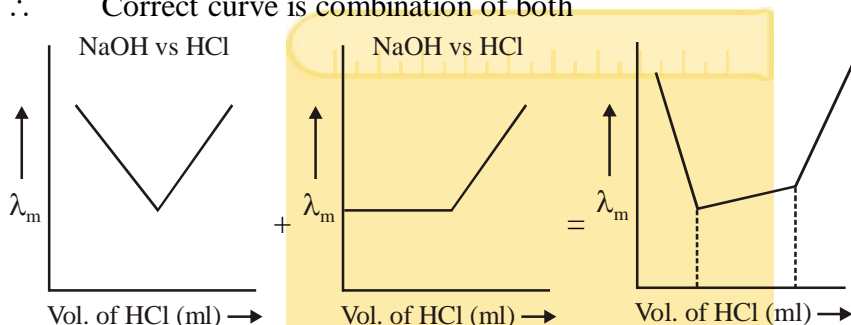
$$\begin{aligned} \text{(S) concentration of CaF}_2 \text{ in solution} &= \frac{K}{\lambda_m} = \frac{K}{\lambda_{\text{Ca}^{2+}} + 2\lambda_{\text{F}}} \\ &= \frac{4.0 \times 10^{-5}}{104 + 2 \times 48} = 2 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

$$\text{For CaF}_2, K_{\text{sp}} = 4S^3 = 3.2 \times 10^{-11} \text{ M}^3$$

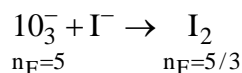
25. Due to presence of strong base NaOH, the weak base is remain undissociated

∴ strong base is titrated first when strong base is neutralised then only weak base is titrated

∴ Correct curve is combination of both



28. From reaction I



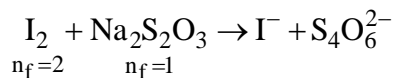
Gram equation of  $\text{KIO}_3 = \text{Gram Eq. of I}_2$

$$M_1 \times V_1 \times n_{\text{F}(1)} = n_{\text{I}_2} \times n_{\text{F}(2)}$$

$$\frac{0.2 \times V_1 \times 5}{5/3} = n_{\text{I}_2} \quad \dots\text{(i)}$$



From Equation II



Gram equation of  $\text{I}_2$  = Gram Equation of  $\text{Na}_2\text{S}_2\text{O}_3$

$$n_{\text{I}_2} \times n_f = M_3 \times V_3 \times n_{f(\text{Na}_2\text{S}_2\text{O}_3)}$$

Substituting the  $n_{\text{I}_2}$  from equation (1)

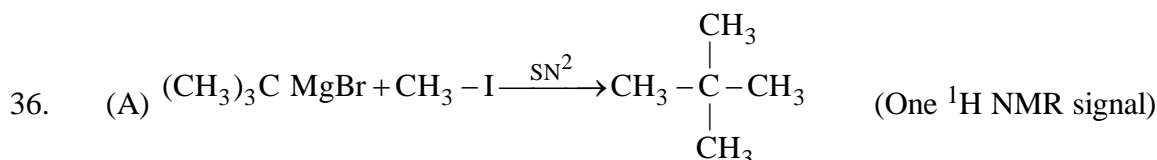
$$\frac{0.2 \times V_1 \times 5 \times 3 \times 2}{5} = 0.2 \times 50 \times 1$$

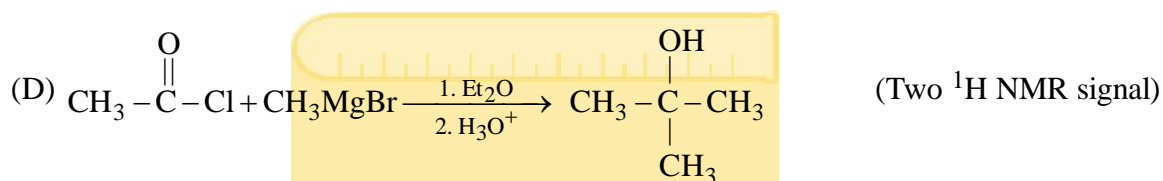
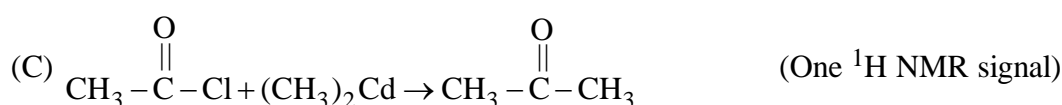
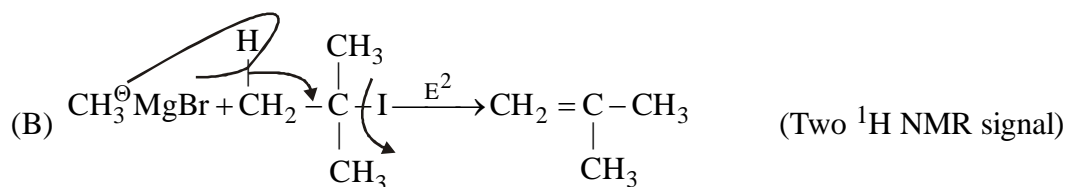
$$V_1 = 50/6$$

29. Correct answer is a
30. Correct answer is b
31. In oxystate of hemerythrin both Fe atom are hexa coordinated and also both the oxy and deoxy form are diamagnetic.
32. Both blue Cu protein and Iron sulphur protein are involved in the transportation of electron. Rubredoxin and Ferridoxin are Iron sulphur protein and plastocyanin and Acurin are Blue-Cu protein.
33. Mobile phone work in the microwave region and spherical rotar are microwave inactive.  
For prolate  $I_A - I_B > I_C$   
The spacins between consecutive rotational line is constant (2B) in rigid rotator.
34. Compound(s) which gives positive test with tollen's reagent [basic ammonium silver nitrate results formation of  $[\text{Ag}(\text{NH}_3)_2]^+$  complex] are  
(1) terminal alkynes (2) Aldehydes (3) formic acid (4) Reducing sugars  
Hence a, b,c,d all are correct answers

$\therefore$  formic  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$  acid gives this test due to presence of  $\text{H}-\overset{\text{O}}{\parallel}{\text{C}}-$  group

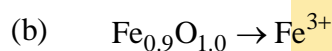
35. Statement (a) is correct  
Rest b, c & d are incorrect





Hence Option A & C are correct.

37. (a) In any solvent the conductivity of its ion is greater than other ions.



$$\begin{aligned}\text{Charge required (Q)} &= (n + n_{\text{F}})F \\ &= (5 \times n_{\text{F}})F\end{aligned}$$

$n_{\text{F}} = \text{change in } 0.5 \times \text{No. of atoms}$

$$\begin{aligned}\text{Fe}_{0.9}\text{O}_{1.0} \\ 0.9x - 2 = 0\end{aligned}$$

$$x = \frac{20}{9}$$

$$\text{Change} = 3 - \frac{20}{9} = \frac{7}{9}$$

$$n_{\text{F}} = \frac{7}{9} \times 0.9 = 0.7$$

$$Q = (5 \times 0.7) F$$

$$Q = 3.5 F$$

(c) Electrophoretic constant depend on solute-solvent interaction which in turns depend on hydration on ion.

As, hydrated size of  $\text{Li}^+ >$  hydrated size of  $\text{Na}^+$

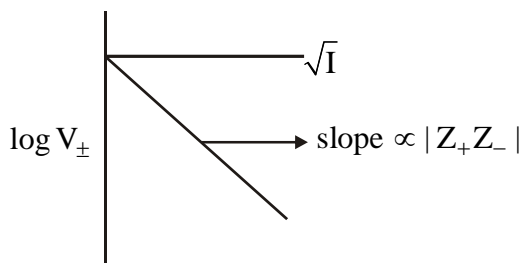
$\therefore$  B is greater for LiCl





(d) From Debye-Huckel limiting law

$$\log V_{\pm} = -0.059 |Z_+ Z_-| \sqrt{I}$$



For  $\text{CaCl}_2$

$$Z_+ = 2$$

$$Z_- = 1$$

$$|Z_+ Z_-| = 1$$

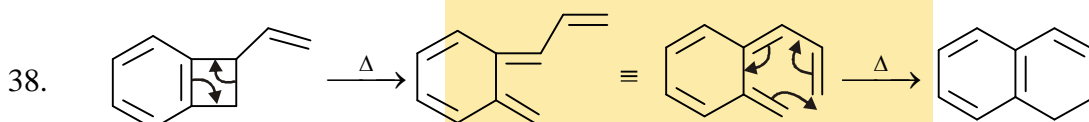
For  $\text{ZnSO}_4$

$$Z_+ = +2$$

$$Z_- = -2$$

$$|Z_+ Z_-| = 4$$

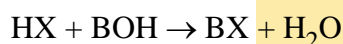
$\therefore$  Slope is more negative for  $\text{ZnSO}_4$



(b)  $4\pi$ -ring opening reaction electrocyclic

(d) followed by  $6\pi$  disrotatory electrocyclic.

39. Initially strong acid will be neutralize



as  $\text{H}^+$  are being replaced by slow moving  $\text{B}^+$

$\therefore$  conductance decrease.

$\therefore V_1$  is volume of base required to neutralize  $\text{HX}$ . After that weak acid will be titrated.

40. Correct answer is a,b

41. Each hemerythin molecule transport 8 molecules of  $\text{O}_2$ .

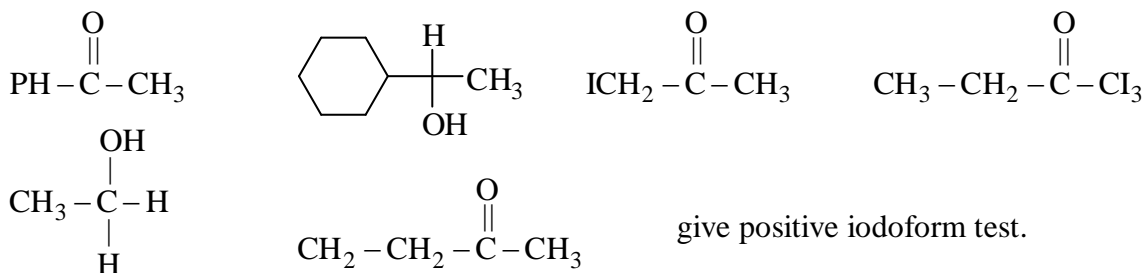
42. 
$$J_{\max} = \sqrt{\frac{kT}{2B\hbar c}} - \frac{1}{2}$$

$$B = 8.5 \text{ cm}^{-1}$$

$$= \sqrt{\frac{1.38 \times 10^{-23} \times 300}{2 \times 8.5 \times 6.63 \times 10^{-34} \times 3 \times 10^{10}}} - \frac{1}{2}$$

43. Iodoform ( $\text{I}_2/\text{OH}^-$ ) is given by compounds having  $\text{CH}_3 - \underset{\text{H}}{\overset{\text{OH}}{\text{C}}} -$  or  $\text{CH}_3 - \overset{\text{O}}{\parallel}{\text{C}} -$  or  $\text{I}_3\text{C} - \overset{\text{O}}{\parallel}{\text{C}} -$  groups

and do not have acidic hydrogen so compounds



Hence correct answer is 6.

44.  $M_{\text{NH}_4^+} = 6 \times 10^{-4} \text{ V}^{-1} \text{ S}^{-1}$

$M_{\text{HCO}_3^-} = 5 \times 10^{-4} \text{ V}^{-1} \text{ S}^{-1}$

( $t_+$ ) transport no. =  $\frac{\text{mobility of cation}}{\text{mobility of cation} + \text{mobility of anion}}$

$t_{\text{NH}_4^+} = \frac{6 \times 10^{-4}}{6 \times 10^{-4} + 5 \times 10^{-4}} = 0.545$

45.  $\text{SAR} = \frac{[\text{Na}^+]}{\sqrt{[\text{Ca}^{2+}] + [\text{Mg}^{2+}]}}$

where concentration in mmol L

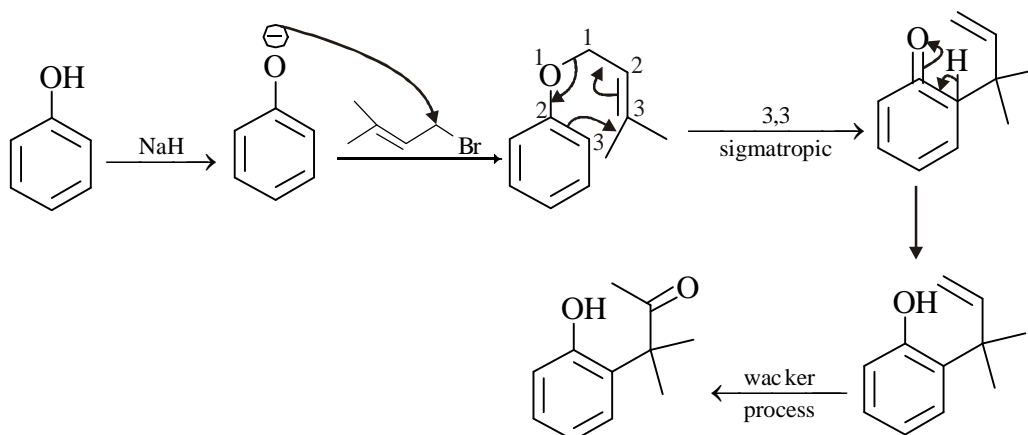
$(\text{Na}^+) = 0.1 \times 60 = 6 \text{ mmol L}^{-1}$

$[\text{Ca}^{2+}] = 0.1 \times 50 = 5 \text{ mmol L}^{-1}$

$[\text{Mg}^{2+}] = 0.1 \times 40 = 4 \text{ mmol L}^{-1}$

$\text{SAR} = \frac{6}{\sqrt{5+4}} = \frac{6}{\sqrt{9}} = \frac{6}{3} = 2$

46.

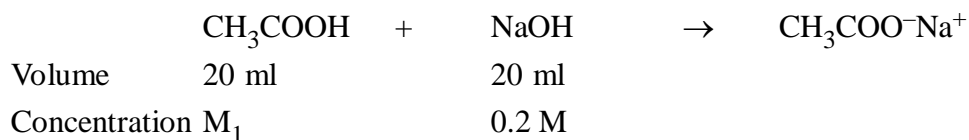


Total number of  $\pi$  bonds are 4.



47. Correct answer is 358

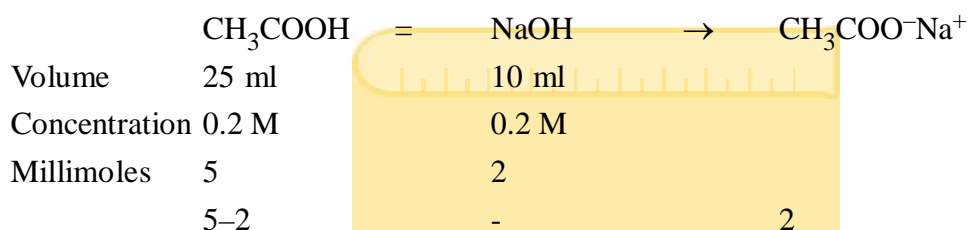
48. Case I



Millimoles for complete titration would be equal

$$\begin{aligned} n_{\text{CH}_3\text{COOH}} &= n_{\text{NaOH}} \\ 20 \times M_1 &= 20 \times 0.2 \\ M_1 &= 0.2 \text{ M} \end{aligned}$$

Case II



$$\text{pH of acidic buffer} = \text{pKa} + 10 \log \frac{[\text{common ion}]}{[\text{Weak acid}]}$$

$$5.8 = \text{pKa} + 10 \log \frac{2/35}{3/35} \quad \text{pKa} = 5.98$$

49.  $\text{CaOCl}_2$

Actually present as  $\text{Ca}(\text{OCl})\text{Cl}$

$\text{OCl}^- \rightarrow \text{Cl}$  is present in +1

$\text{Cl}^- \rightarrow \text{Cl}$  is present in -1

sum of oxidation state (+1) + (-1) = 0

50.  $\overset{+7}{\text{Mn}}\text{O}_4^- \rightarrow \text{Mn}^{2+}$  change 5 = x

$\rightarrow \overset{+6}{\text{Mn}}\text{O}_4^{2-}$  change 1 = y

$\rightarrow \overset{+4}{\text{Mn}}\text{O}_2$  change 3 = p

$\rightarrow \overset{+3}{\text{Mn}_2}\text{O}_3$  change 3 = q

$$x + y + p + q = 12$$



51. The oxidation state of Fe atom in H-peroxodimer is +3.  
52. The maximum population of levels gives maximum intensity of the transition. The value of J at which this occur is

$$J_{\max} = \sqrt{\frac{kT}{2hcB}} - \frac{1}{2}$$

For P branch  $\Delta J = -1$

$$\bar{V}_P = \bar{V}_0 - 2BJ$$

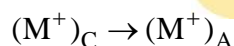
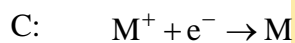
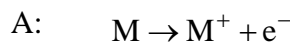
$$\text{Now } \bar{V}_P = \bar{V}_0 - 2B \left( \sqrt{\frac{kT}{2hcB}} - \frac{1}{2} \right)$$

$$\text{Given } \bar{V}_0 = 2143 \text{ cm}^{-1}$$

$$2B = 3.83 \text{ cm}^{-1}; B = 1.915 \text{ cm}^{-1}$$

$$\begin{aligned} \bar{V}_P &= 2143 - 3.83 \left( \sqrt{\frac{1.38 \times 10^{-23} \times 300}{6.63 \times 10^{-34} \times 3 \times 10^{10} \times 3.83}} - \frac{1}{2} \right) \\ &= 2143 - 26.32 = 2116.7 \text{ cm}^{-1}. \end{aligned}$$

53. It is a concentration cell.



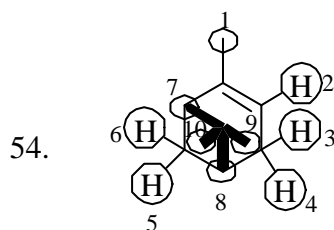
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{2.303RT}{(1)F} \log \frac{(M^+)_{\text{A}}}{(M^+)_{\text{C}}}$$

$$70 \times 10^{-3} = - \frac{2.303RT}{F} \log 0.05$$

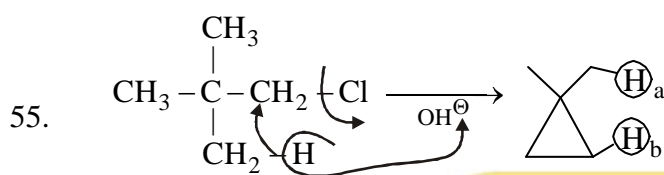
$$70 \times 10^{-3} = + \frac{2.303RT}{F} \times (+1.301)$$

$$\frac{2.303RT}{F} = 53.805 \times 10^{-3}$$

$$\begin{aligned} \therefore E_{\text{cell}} &= -53.805 \times 10^{-3} \log 0.0025 \\ &= -53.805 \times 10^{-3} (-2.602) \\ &= 140 \times 10^{-3} \text{ V} \\ &= 140 \text{ mV} \end{aligned}$$



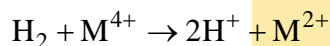
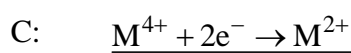
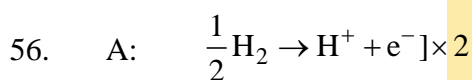
Total number of  $^1\text{H}$  NMR signals equal to 10 due to presence of group above the plane proton (3, 4) and (5, 6) gives different  $^1\text{H}$  NMR signals. There is no POS hence 9 and 10 gives different NMR signals.



Proton (b) are more deshielded protons and attached to  $\text{sp}^3$  carbon hence its shift lies between range (1–2)

hence  $p = 1$  and  $q = 2$

$p + q = 3$



$$E_{\text{cell}}^{\circ} = E_{\text{H}_2/\text{H}^+}^{\circ} + E_{\text{M}^{4+}/\text{M}^{2+}}^{\circ}$$

$$= 0 + 0.151 = 0.151 \text{ V}$$

$$E_{\text{cell}} = E^{\circ} - \frac{2.303RT}{(2)F} \log \frac{[\text{M}^{2+}][\text{H}^+]^2}{[\text{M}^{4+}]}$$

$$0.092 = 0.151 - \frac{0.059}{2} \log(10^x)$$

$$0.092 - 0.151 = -\frac{0.059}{2} \log 10^x$$

$$-0.059 = -\frac{0.0591}{2} \times x \quad \Rightarrow x = 2$$

57. 
$$t_+ = \frac{v_+ \lambda^+}{\lambda^{\circ}}$$



$v_+$  → Number of ions present in formula

$\lambda^+$  → Molar conductivity of cation

$\lambda^\circ$  → Limiting molar conductivity of electrolyte

$$\Rightarrow t_{\text{Na}^+} = \frac{1 \times \lambda_{\text{Na}^+}}{\lambda_{\text{NaCl}}^\circ}$$

$$\Rightarrow \lambda_{\text{Na}^+} = 0.463 \times 96.9 = 44.86 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\lambda_{\text{NaCl}}^{\circ} = \lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}$$

$$96.9 = 44.86 + \lambda_{\text{Cl}^-}^{\circ}$$

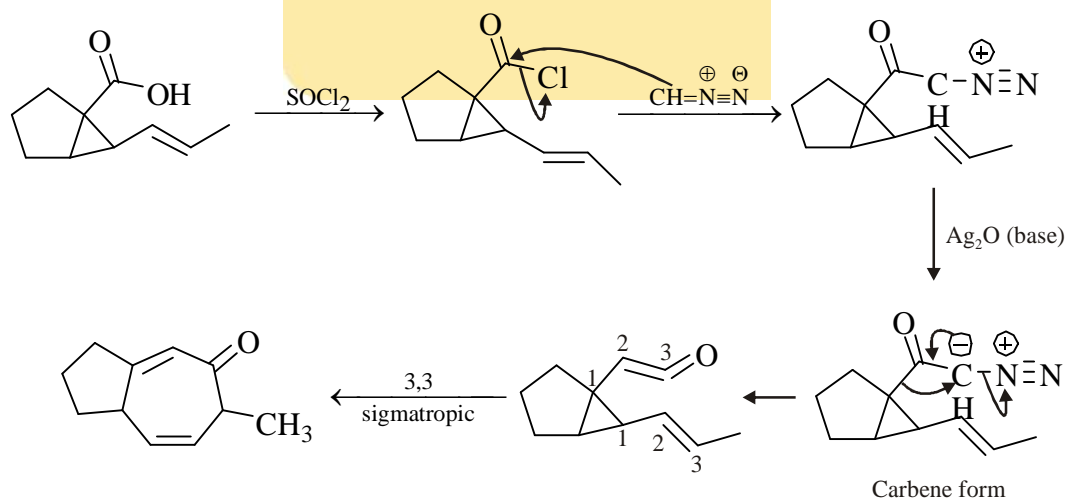
$$\lambda_{\text{Cl}^-}^{\circ} = 51.14 \text{ S cm}^2 \text{ mol}^{-1}$$

$$\Rightarrow \lambda_{\text{HCl}}^{\circ} = \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}$$

$$\lambda_{\text{H}^+}^{\circ} = 192 - 51.14 = 140.86 \text{ S cm}^2 \text{ mol}^{-1}$$

$$t_{\text{H}^+} = \frac{1 \times 140.86}{192} = 0.733$$

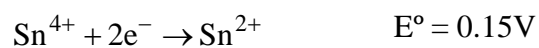
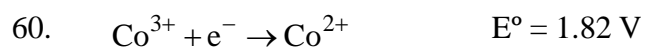
58.



59.  $A = \epsilon \times b \times c$

$$1.5 = \epsilon \times 1 \text{ cm} \times (1 \text{ mmol dm}^{-3})$$

$$\epsilon = \frac{1.5}{10^{-3} \text{ mol dm}^{-3} \times 1 \text{ cm}} = 1500 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$$



$\therefore$  At equivalence point

$$E^{\circ} = \frac{1}{3} [2 \times E^{\circ}_{\text{Sn}^{4+}/\text{Sn}^{2+}} + E^{\circ}_{\text{Co}^{3+}/\text{Co}^{2+}}]$$

$$= \frac{1}{3} [2 \times 0.15 + 1.82]$$

$$= \frac{1}{3} [0.30 + 1.82]$$

$$= \frac{2.12}{3} = 0.71 \text{ V}$$

