SAMPLE PAPER 3

CHEMISTRY PAPER 1
(THEORY)

Maximum Marks: 70

Time Allowed: Three Hours

*(Candidates are allowed **additional 15 minutes** for **only** reading the paper.*

*They must **NOT** start writing during this time.)*

This paper is divided into four sections – A, B, C and D.
*Answer **all** questions.*
***Section – A** consists of **one** question **having sub-parts** of **one** mark each.*
***Section – B** consists of **ten** questions of **two** marks each.*
***Section – C** consists of **seven** questions of **three** marks each, and*
***Section – D** consists of **three** questions of **five** marks each.*
Internal choices have been provided in one question each in Section B,
Section C and Section D.
All working, including rough work, should be done on the same sheet as, and adjacent to the
rest of the answer.
The intended marks for questions or parts of questions are given in brackets [ ].
Balanced equations must be given wherever possible and diagrams where they are helpful.
When solving numerical problems, all essential working must be shown.
In working out problems, use the following data:
Gas constant R = 1.987 cal deg^{-1} mol^{-1} = 8.314 JK^{-1} mol^{-1} = 0.0821 dm^3 atm K^{-1}mol^{-1}
1 L atm = 1 dm^3 atm = 101.3 J, 1 Faraday = 96500 coulombs,   Avogadro's number = 6.023 x 10^{23}

SECTION A – 14 MARKS

Question 1

(A)

(i)
Ans.: mol^{-1} L s^{-1}, L mol^{-1} s^{-1}

(ii)
Ans.: 6, 2

(iii)
Ans.: electrophilic, nucleophilic

(iv)
Ans.: yellow, iodoform

(B)

(i)

Ans.: (c) 3

Explanation: $A + B \rightarrow C$

On doubling the concentration of A, rate of reaction increases by 4 times.

$\therefore$ rate $\propto [A]^2$ (w.r.t. A)

However, on doubling the concentration of B rate of reaction increases two times.

$\therefore$ rate $\propto [B]^2$ (w. r. t. B)

Thus, overall order of reaction $=2+1=3$

(ii)

Ans.: (a) $\Delta_o < P$

Explanation: Water is a weak filed ligand. The crystal field splitting caused by water is small. Hence, $\Delta_o < P$.

(iii)

Ans.: (d) Sc (III), Ti (IV) are diamagnetic and Pd(II), Cu(II) are paramagnetic

Explanation: Sc^{3+} $(3d^0)$, $Ti^{4+} (3d^0)$ are diamagnetic due to absence of unpaired electrons. While $Pd^{2+}(4d^8)$, $Cu^{2+}(3d^9)$ contain two, and one unpaired electron respectively. Hence, these are paramagnetic.

(iv)

Ans.: (c) CH_3NH_2 on reaction with nitrous acid releases NO_2 gas.

Explanation: The gas evolved when methylamine reacts with nitrous acid is nitrogen.

(v)

Ans.: (b) 87%

Explanation: $Ba(NO_3)_2 \rightleftharpoons Ba^{2+} + 2NO_3^-$

1 mole   0   0   initial

$1 - \alpha$ α 2α after dissociation

Total moles $= 1 + 2\alpha$

$i = 1 + 2\alpha$

$\alpha = \dfrac{i - 1}{2} = \dfrac{2.74 - 1}{2} = 0.87 = 87\%$

(vi)

Ans.: (c) Assertion is true but Reason is false.

(vii)

Ans.: (b) Both Assertion and Reason are true but Reason is not the correct explanation for Assertion

(C)

Ans.: **(i)** Moles of $C_6H_6 = \frac{7.8}{78} = 0.1$

Moles of $C_6H_5CH_3 = \frac{9.2}{92} = 0.1$

Mole fraction of $C_6H_6 = \frac{0.1}{0.1+0.1} = 0.5$

$\Rightarrow$ Mole fraction of $C_6H_5CH_3 = 0.5$

Vapour pressure of toluene $=$ Vapour pressure of pure toluene $\times$ mole fraction of toluene

$= 0.0925 \times 0.5 = 0.04625$

Vapour pressure of benzene $= 0.256 \times 0.5 = 0.128$

Total vapour pressure of solution $= 0.17425$

(ii) Mole fraction of benzene in vapour phase in solution I

$$y_{benzene} = \frac{p_{benzene}}{P_{total}} = \frac{0.128}{0.17425} = 0.734$$

(iii) True.

Mole fraction of benzene in vapour phase in solution $-I = 0.734$

Mole fraction of benzene in vapour phase in solution-II $= \frac{0.0128}{0.026675} = 0.479$

Thus, mole fraction of benzene in vapour phase is less in solution-II.

SECTION B – 20 MARKS

Question 2

Ans.: **(i)** Phenol $<$ 4-nitrophenol $<$ 2,4,6-trinitrophenol

(ii) In phenol, conjugation with the aromatic ring imparts partial double bond character to the carbon-oxygen bond. The oxygen is attached to an sp^2 hybridized carbon, leading to a more stable and shorter bond compared to methanol, where oxygen is attached to an sp^3 hybridized carbon.
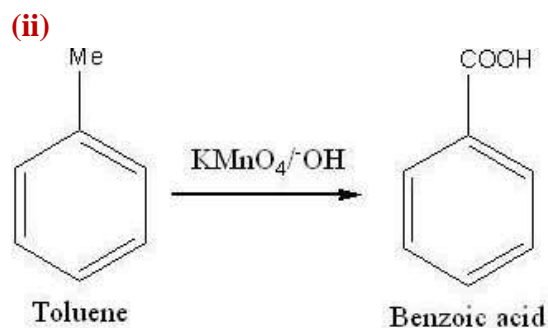
Question 3

Ans.: **(i)** La^{3+}

(ii) Cu^{2+} is paramagnetic because it contains unpaired electrons in d-orbital, Cu+ is diamagnetic as no unpaired electron is present.

Question 4

Ans.: **(i)** $NO_2CH_2COOH > FCH_2COOH > C_6H_5COOH$

Electron withdrawing groups increase the acidity of carboxylic acids by stabilizing the conjugate base through delocalization of the negative charge by inductive and/or resonance effects.

(ii)

Question 5

Ans.:

(i) Transition elements have variable oxidation state giving unstable intermediates, thus act as catalysts.

(ii) Transition elements have high effective nuclear charge and a large number of valence electrons. Therefore, they form very strong metallic bonds or metal-metal bonding which arises due to unpaired electrons in the (n-1)d subshell. As a result, the enthalpies of atomization transition metals are high.
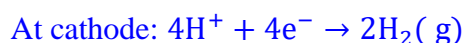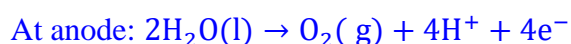
Question 6

Ans.: (i) Due to +I and +H effect groups, the 2° carbonium ion $CH_3 - \overset{+}{C}H - CH_2 - CH_3$ derived from sec. butyl chloride is more stable than the 1° carbonium ion $CH_3 - CH_2 - \overset{+}{C}H_2$ derived from n-propyl chloride. Therefore sec. butyl chloride hydrolysed more easily than n-propyl chloride under S_N1 conditions.

(ii) CH_3I as I^- ion is better leaving group than Br^- ion.

Question 7

Ans.: (i) pH of the solution remains constant as $[H^+]$ remains same during the whole reaction.

At anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+ + 4e^-$

At cathode: $4H^+ + 4e^- \rightarrow 2H_2(g)$

(ii) At equilibrium $\Delta_r G = 0 E_{cell} = 0$

Question 8

Ans.: (i)

(ii) CH_3CH_2Cl + KOH (alc.) → $CH_2=CH_2$ + KCl + H_2O

Question 9

Ans.: M_2 (ethylene glycol) = 62 g mol^{-1}

W_1 = 5.50 kg = 5500 g,

$\Delta T_f^o = T_f = 0°C - (-10) = 10°C$

and K_f = 1.86 K kg mol^{-1}

$$\Delta T_f = \frac{K_f \times W_2 \times 1000}{M_2 \times W_1}$$

$$W_2 = \frac{\Delta T_f \times M_2 \times W_1}{K_f \times 1000}$$

$$= \frac{10 \times 62 \times 5500}{1.86 \times 1000}$$

$$= 1833.33 \text{ g}$$

$$= 1.833 \text{ kg}$$

Question 10

Ans.: (i) Phenyl ring of benzaldehyde undergoes electrophilic substitution reactions such as nitration, sulphonation, etc. Since the -CHO group is an electron withdrawing group, it is a meta-directing group.

(ii) (a) Due to much stronger I-effect of F over Cl, the FCH_2COO- ion is much more stable than $ClCH_2COO-$ ion and hence FCH_2COOH is a stronger acid than$ClCH_2COOH$.

(b) Ethanoic acid is stronger acid than phenol due to less pKa than that of phenol and the carboxylate ion is much more resonance stabilized than phenoxide ion.

Question 11

Ans.:

(i) Copper exhibits +1 oxidation state more frequently, i/e., Cu+ because of its electronic configuration

(ii) Zinc, cadmium and Mercury have completely filled d-orbitals in their atomic as well as in their common oxidation states. They do not exhibit characteristic properties of transition elements; hence they are not considered as transition elements.

SECTION C – 21 MARKS

Question 12

Ans.:
(a) For the reaction of first order,

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

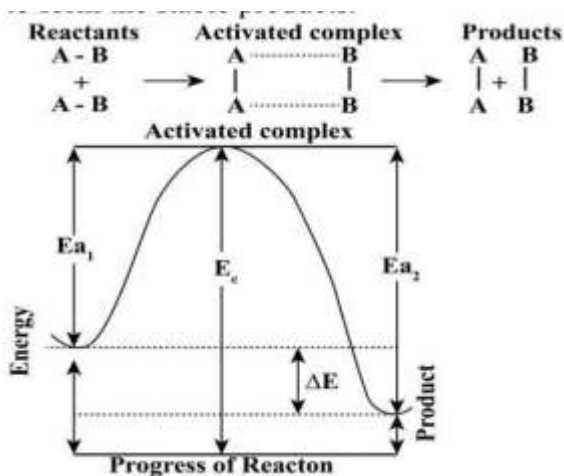$$\Rightarrow k = \frac{2.303}{100} \log \frac{100}{40} - 0.00916$$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$\Rightarrow 0.00916 = \frac{2.303}{t} \log \frac{100}{10}$$

$$\Rightarrow t = \frac{2.303}{0.00916} \log 10$$

$$= 251.4 \text{ minutes}$$

(b) It is believed that when the reactant molecules absorb energy, their bonds are loosened and new loose bonds are formed between them both). The intermediate thus formed is called an activated complex. It is unstable and immediately dissociated to form the stable products.

Question 13

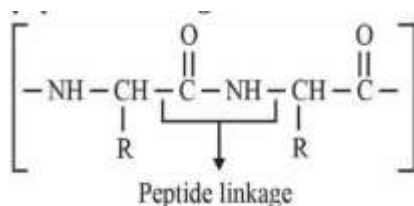**Ans.: (i)** $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

(ii) *p*-nitroaniline < aniline < *p*-toluidine

Question 14

Ans.:

(i) Uracil is found in nucleotide of RNA only.

(ii) Proteins are the polymers of α-amino acids linked by amide formation between carboxyl and amino group. This is called peptide linkage or peptide bond e.g.,

Peptide linkage

(iii) Starch is polymer of α-D glucose units whereas cellulose is linear polymer of β-D glucose units.
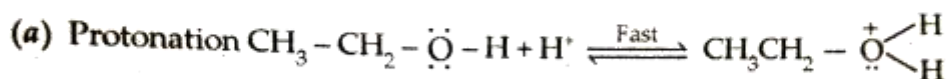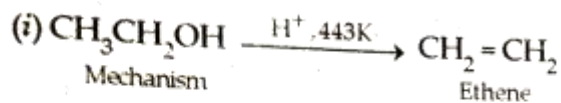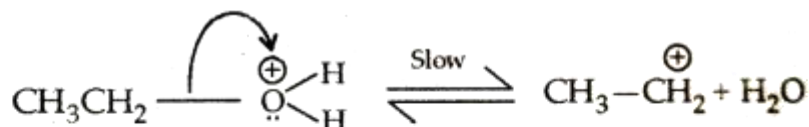
Question 15

Ans.: (i) Reverse osmosis

(ii) To fresh water container

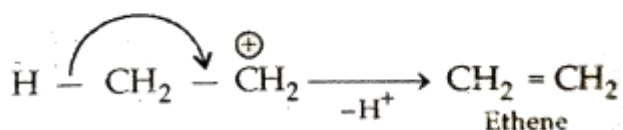**(iii)** This can be used as desalination plants to meet potable water requirements.

Question 16

Ans.:

(i)

$$\underset{[A]}{\overset{CN}{\bigcirc}} \quad \underset{\text{CuCN/ KCN}}{\xrightarrow{\hspace{1cm}}} \quad \underset{[A]}{\overset{CN}{\bigcirc}} \quad \underset{\text{H}_2\text{O/ H}^+}{\xrightarrow{\hspace{1cm}}} \quad \underset{[B]}{\overset{COOH}{\bigcirc}} \quad \underset{\triangle}{\overset{\text{NH}_3}{\xrightarrow{\hspace{1cm}}}} \quad \underset{[C]}{\overset{CONH_2}{\bigcirc}}$$

Starting material: $\overset{+}{N_2}\overset{-}{Cl}$ on benzene ring.

(ii)

$$\underset{[A]}{\overset{NO_2}{\bigcirc}} \quad \underset{\text{Fe/HCl}}{\xrightarrow{\hspace{1cm}}} \quad \underset{[A]}{\overset{NH_2}{\bigcirc}} \quad \underset{\substack{\text{NaNO}_2 + \text{HCl} \\ \text{273 K}}}{\xrightarrow{\hspace{1cm}}} \quad \underset{[B]}{\overset{\overset{+}{N_2}\overset{-}{Cl}}{\bigcirc}} \quad \underset{\text{C}_2\text{H}_5\text{OH}}{\xrightarrow{\hspace{1cm}}} \quad \underset{[C]}{\bigcirc}$$

Question 17

Ans.:

(a)

$$\underset{}{\overset{OH}{\bigcirc}} \quad + \quad 3\ \text{Conc. HNO}_3 \quad \underset{}{\overset{\text{Conc. H}_2\text{SO}_4}{\xrightarrow{\hspace{1.5cm}}}} \quad \underset{\text{NO}_2}{\overset{\overset{OH}{\underset{O_2N}{\bigcirc}}NO_2}{}} \quad + \quad 3\text{H}_2\text{O}$$

(b)

$$\underset{\text{Propene}}{\text{CH}_3 - \text{CH} = \text{CH}_2} \quad \xrightarrow{\text{dil. H}_2\text{SO}_4} \quad \underset{\text{Propane-2-ol}}{\text{CH}_3 - \overset{\overset{\displaystyle OH}{|}}{\text{CH}} - \text{CH}_3}$$

(c)

$$\underset{\text{Ethyl magnesium chloride}}{\text{C}_2\text{H}_5\text{Mg}Cl} \quad \xrightarrow[\text{(ii) H}^+]{\text{(i) HCHO}} \quad \underset{\text{Propan-1-ol}}{\text{CH}_3 - \text{CH}_2 - \text{CH}_2\text{OH}}$$

OR

(ii)

Ans.:

(i) $CH_3CH_2OH \xrightarrow{\text{H}^+,443K} CH_2 = CH_2$
Mechanism   Ethene

(a) Protonation $CH_3 - CH_2 - \overset{\cdot\cdot}{\underset{\cdot\cdot}{O}} - H + H^+ \underset{}{\overset{\text{Fast}}{\rightleftharpoons}} CH_3CH_2 - \overset{+}{\underset{\cdot\cdot}{O}}{\overset{H}{\underset{H}{\diagdown}}}$

(b) Formation of Carbocation

$CH_3CH_2 \longrightarrow \overset{\oplus}{\underset{\cdot\cdot}{O}}{\overset{H}{\underset{H}{\diagup}}} \overset{\text{Slow}}{\rightleftharpoons} CH_3 - \overset{\oplus}{C}H_2 + H_2O$

(c) Loss of proton

$\overset{\cdot}{H} - CH_2 - \overset{\oplus}{C}H_2 \xrightarrow{-H^+} CH_2 = CH_2$
                                     Ethene

Question 18

Ans.: (a)

$$k = \frac{2.303}{t} \log \frac{a}{a - x}$$

$$\Rightarrow 2 \times 10^{-4} = \frac{2.303}{900} \log \frac{100}{100 - x}$$

$$\log \frac{100}{100 - x} = \frac{9}{115.15} = 0.0781$$

$$\Rightarrow \frac{100}{100-x} = \text{Anti log } (0.0781)$$

$$\Rightarrow 100 = 1.197[100 - x]$$

$$\Rightarrow 100 = 119.7 - 1.197x$$

$$\Rightarrow 1.197x = 19.7$$

$$\therefore x = \frac{19.7}{1.197} = 16.45\%$$

    (b) (i) No effect

       (ii) Decreases

SECTION D – 15 MARKS

Question 19

Ans.: (i)

(a) Aromatic carboxylic acids do not undergo Friedel Crafts reaction because - COOH group is deactivating and the catalyst aluminium chloride (Lewis acid) gets bonded to the carboxyl group.

(b) The methyl group due to +ve I effect reduces the positive charge on carbonyl atom. Moreover it also hinders the approach of the nuclephilic. Since in ethanal there is one methyl group while in methanal there is no methyl group on carbonyl carbon atom therefore methanal is more reactive towards nucleophilic addition reaction than ethanal.

(c) Due to the presence of a strong electron withdrawing $(-NO_2)$ group in 4-nitrobenzoic acid, it stabilizes the carboxylate anion and hence strengthens the acid. Therefore, 4-nitrobenzoic acid is more acidic than benzoic acid and its pKa value is lower.

Ans.: (ii) Since, A gives haloform test, it must contain —$COCH_3$ group. Thus, its possible formula is $C_2H_5COCH_3$. On reduction, it gives 2-butanol, i.e., compound B which on dehydration with sulphuric acid gives 2-butene (C). Ozonolysis of 2-butene gives only acetaldehyde (E).
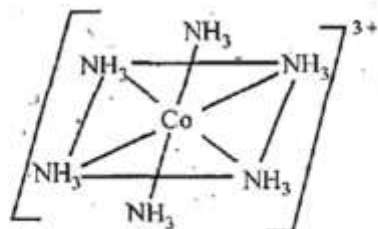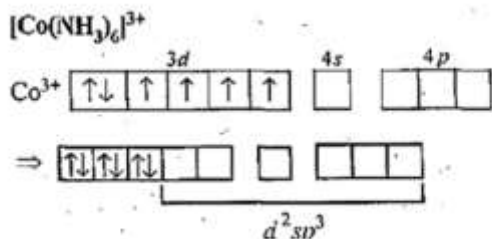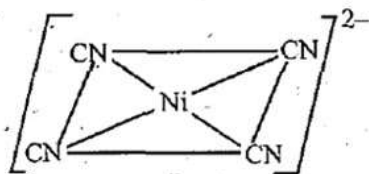
The equations involved are

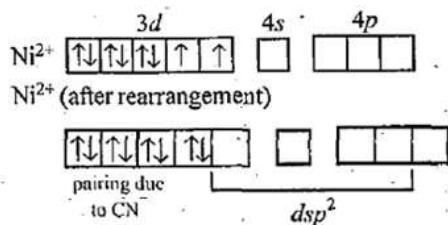$CH_3COCH_2CH_3 \xrightarrow[LiAlH_4]{[H]} CH_3-CH-CH_2CH_3$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad |$
$\qquad\qquad\qquad\qquad\qquad\qquad\quad OH$
$\qquad\qquad\qquad\qquad\qquad\quad$ 2-butanol
$\qquad\qquad\qquad\qquad\qquad\qquad\quad$ (B)

Butan-2-one

(A)

$\xrightarrow[-H_2O]{Conc.\ H_2SO_4} CH_3-CH=CH-CH_3 \xrightarrow[Ozonolysis]{O_3}$

$\qquad\qquad$ 2-butene

$\qquad\qquad\qquad$ (C)

$CH_3-CH \underset{O-O}{\overset{O}{\diagdown\diagup}} CH-CH_3 \xrightarrow{Zn/H_2O} 2CH_3CHO$

Mono-ozonide   Acetaldehyde
(D)

$\qquad\qquad\qquad\qquad\qquad$ (E)
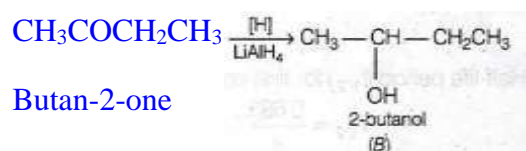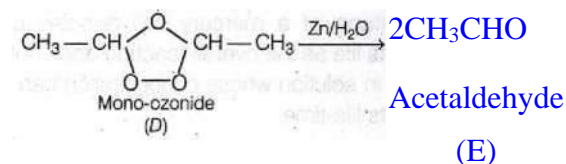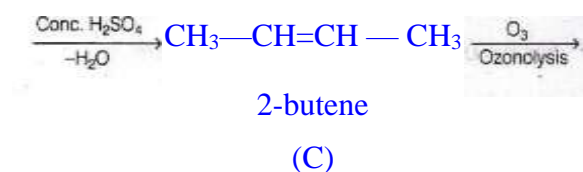
Question 20

Ans.: (i)
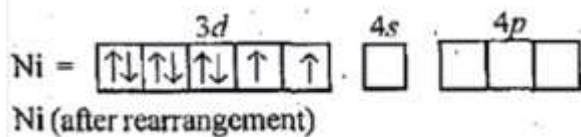
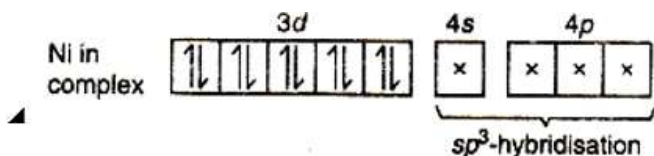In $[Co(NH_3)_6]^{3+}$ cobalt is present as Co3+ and its coordination number is six.

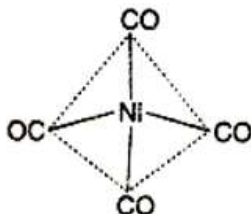Octahedral complex, d^2sp^3 hybridisation

Square planar dsp^2 hybridisation

So, structure of $Ni(CO)_4$ is tetrahedral,

which is represented as shown :

(ii) The IUPAC name of the complex ion is Hexaminecobalt(III) ion. The oxidation state of Co in $[Co(NH_3)_6]^{3+}$ is :

$x + 6(0) = +3$

$x = +3$

Question 21

Ans.: (i) (a) $\Delta G° = -nFE^0_{cell}$

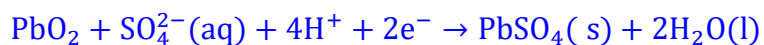$= -2 \times 96500 Cmol^{-1} \times 1.1 \text{ V}$

$= -212300 \text{ J mol}^{-1}$

or $= -212.3 \text{ kJ mol}^{-1}$

(b)

Lead storage battery

Anode: $Pb(s) + SO_4^{2-}(aq) \rightarrow PbSO_4(s) + 2e^-$

Cathode:

$PbO_2 + SO_4^{2-}(aq) + 4H^+ + 2e^- \rightarrow PbSO_4(s) + 2H_2O(l)$
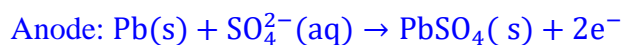
(c) $\Lambda_m = \frac{1000k}{C}$

$\Lambda_m = \frac{1.65 \times 10^{-4} \text{ S cm}^{-1} \times 1000 \text{ cm}^3 \text{ L}^{-1}}{0.01 \text{ mol L}^{-1}}$

$= 16.5 \text{ S cm}^2 \text{ mol}^{-1}$

OR

Ans.: (ii) (a) $\Lambda_m = \frac{1000 \times K}{M} Scm^2\ mol^{-1}$

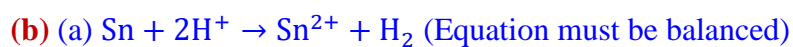$\Lambda_m = \frac{1000 \times 5.25 \times 10^{-5}}{2.5 \times 10^{-4}}\ S\ cm^2\ mol^{-1}$

$\Lambda_m^\circ HCOOH = \lambda^\circ HCOO^- + \lambda^\circ H^+$

$R = (50.5 + 349.5) Scm^2\ mol^{-1}$
$= 400\ S\ cm^2\ mol^{-1}$
$\alpha = \Lambda_m / \Lambda_m^\circ$
$\alpha = 210/400 = 0.525$

(b) (a) $Sn + 2H^+ \rightarrow Sn^{2+} + H_2$ (Equation must be balanced)

$E = E^\circ - \frac{0.059}{2} \log \frac{[Sn^{2+}]}{[H^+]}$

$= [0.(-0.14)] - 0.295 \log \frac{(0.004)}{(0.02)^2}$

$= 0.14 - 0.0295 \log 10$

$= 0.11\ V / 0.1105\ V$

(c) Because the number of ions per unit volume decreases.