AMINES

Detailed Solutions

- 1. 2, 4, 6-Tribromoaniline
- 2. CH₃CH₂NHCH₃(*N*-methylethanamine)

- 4. But-3-en-1-amine
- 5. CH₃N-C₂H₅ (N, N-ethylmethylamine)
- **6.** (a) But-3-en-2-amine
 - (b) N-phenylethanamide
- 7. R—CONH₂ + Br₂ + 4NaOH \longrightarrow Acid amide

$$R$$
— $NH_2 + Na_2CO_3 + 2 NaBr + 2H_2O$
1° amine

8.
$$CH_3CN + 4[H] \xrightarrow{Na + C_2H_5OH} CH_3CH_2NH$$

Ethanenitrile Ethanamine

9. Gabriel phthalimide synthesis: In this reaction phthalimide is converted into its potassium salt by treating it with alcoholic potassium hydroxide. Then potassium phthalimide is heated with an alkyl halide to yield an *N*-alkylpthalimide which is hydrolysed to phthalic acid and primary amine by alkaline hydrolysis.

CO NH
$$\xrightarrow{\text{KOH (alc.)}}$$
 CO $\xrightarrow{\text{NK}^+}$ CO $\xrightarrow{\text{NK}^+}$ CO $\xrightarrow{\text{NK}^+}$ CO NC₂H₅I $\xrightarrow{\text{NaOH}_{(aq)}}$ CO NC₂H₅ COOH + C₂H₅NH₂ COOH Ethylamine Phthalic acid

10.
$$CH_2-CI CH_2-CN CH_2-CH_2-NH_2$$

Benzyl $CH_2-CH_2-CH_2-NH_2$
 $CH_2-CH_2-CH_2-NH_2$
 $CH_2-CH_2-CH_2-NH_2$
 $CH_2-CH_2-CH_2-NH_2$
 $CH_2-CH_2-CH_2-NH_2$

chloride

- 11. Aromatic amines cannot be prepared by Gabriel phthalimide synthesis because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.
- **12.** Alkyl halides when treated with ethanolic solution of ammonia give a mixture of primary, secondary, tertiary amines and quaternary ammonium salt.

$$R = NH_{3} \xrightarrow{373 \text{ K}} R - NH_{2} \xrightarrow{RX} R_{2}NH \xrightarrow{RX} R_{3}NH$$
Primary amine Secondary amine $R_{4} \stackrel{\dagger}{N} \overline{X} \xleftarrow{RX} R_{3}N$
Quaternary Tertiary amponium salt amine $R_{4} \stackrel{\dagger}{N} \overline{X} \xrightarrow{RX} R_{3}N$

13. (i)
$$NO_2$$
 NH_2

Nitrobenzene Aniline

(ii)
$$CH_3COOH \xrightarrow{PCl_5} CH_3 \xrightarrow{C} CI \xrightarrow{NH_3} NH_3$$

Ethanoic acid
(Acetic acid) $CH_3 = NH_2 \xleftarrow{Br_2/KOH} CH_3 = C = NH_2$

14. (i)
$$CH_3CH_2CI \xrightarrow{NaCN} CH_3CH_2C \equiv N$$
Chloroethane Propane nitrile
$$CH_3CH_2CH_2NH_2 \xleftarrow{Reduction}_{Ni/H_2}$$
1-Propanamine

(ii)
$$\underbrace{\begin{array}{c} NO_2 \\ Nitration \\ Nitrobenzene \end{array}}_{Nitrobenzene} \underbrace{\begin{array}{c} NH_2 \\ NH_2 \\ Aniline \\ Aniline \\ \end{array}}_{Nitrobenzene}$$

- 15. (i) Refer to answer 9.
- (ii) Refer to answer 7.
- **16.** (i) Refer to answer 13(i).
- (ii) Refer to answer 12.

17. Primary amines $(R - NH_2)$ have two hydrogen atoms on nitrogen which can undergo intermolecular hydrogen bonding whereas no such hydrogen bonding is present in tertiary amines (R_3N) . So, primary amines boil at a higher temperature than tertiary amines.

18. Increasing order of boiling points : $(CH_3)_3N < C_2H_5NH_2 < C_2H_5OH$

Tertiary amine does not have hydrogen to form hydrogen bonding and hydrogen bonding in alcohol is stronger than that of amines because oxygen is more electronegative than nitrogen.

- 19. Refer to answer 17.
- 20. Refer to answer 17.
- 21. Ethylamine is soluble in water due to formation of intermolecular hydrogen bonds with water molecules. However, in aniline due to large hydrophobic aryl group the extent of hydrogen bonding decreases considerably and hence aniline is insoluble in water.
- **22.** The nitro compounds are highly polar molecules. Due to this polarity they have strong intermolecular dipole dipole interactions which causes them to have higher boiling points in comparison to the hydrocarbons having almost same molecular mass.
- 23. (i) Refer to answer 21.
- (ii) Refer to answer 17.
- **24.** When treated with benzenesulphonyl chloride (Hinsberg's reagent), $(CH_3)_2NH$ forms insoluble N, N-dialkylbenzene sulphonamide which is insoluble in KOH whereas tertiary amine does not react at all.

25.
$$\bigvee_{\text{NO}_2}^{\text{NH}_2} < \bigvee_{\text{Aniline}}^{\text{NH}_2} < \bigvee_{\text{CH}_3}^{\text{NH}_2}$$

Electron withdrawing group (-NO₂) on benzene ring decreases the basicity and electron donating group (-CH₃) on benzene ring increases the basicity of compound.

26. $C_6H_5NH_2 < (C_2H_5)_2NH < C_2H_5NH_2$ 1° amines are more soluble in water than 2° amines. Aniline due to large hydrophobic benzene ring is least soluble.

27.
$$(CH_3CO)_2O$$
Aniline

N-Phenylethanamide
(Acetanilide)

28. $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5CH_2NH_2$ $C_6H_5NH_2$ and $C_6H_5NHCH_3$ are less basic than aliphatic amine $C_6H_5CH_2NH_2$ due to lone pair of nitrogen is in conjugation with benzene ring. But due to +*I* effect of —CH₃ group in $C_6H_5NHCH_3$, it is more basic than $C_6H_5NH_2$.

29. Increasing order of basic strength in gaseous state is as follows:

 $C_6H_5NH_2 < C_6H_5NHCH_3 < C_6H_5N(CH_3)_2$

As the number of $-CH_3$ groups (+I effect) attached to nitrogen increases, its basicity its basicity will increases.

- **30.** Methyl amine is more basic than ammonia because of the presence of electron donating methyl group (+I effect), which increases the electron density on nitrogen atom.
- **31.** $CH_3(C_6H_4)NH_2$ is more basic than $C_6H_5NH_2$ due to electron releasing nature of methyl group which pushes electrons towards nitrogen.
- **32.** CH₃NH₂ is more basic than C₆H₅NH₂ because in aniline the lone pair of electrons on nitrogen are involved in resonance.
- **33.** In case of small alkyl groups like CH₃ the order of basicity is secondary amine > primary amine > tertiary amine due to solvation effect and +*I* effect of —CH₃ group.

$$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N$$

p $K_b = 3.27 = 3.38 = 4.22$

- **34.** $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
- **35.** Carbylamine reaction is the reaction in which 1° amines produce a bad smelling compound when treated with chloroform in the presence of alkali. $RNH_2 + CHCl_3 + 3KOH \longrightarrow R N \Longrightarrow C + 3KCl + 3H_2O$

It is the test for primary amines.

36.
$$C_6H_5NH_2 + Br_{2(aq)} \longrightarrow Br + 3HBr_{2(aq)}$$

37.
$$(C_6H_5)_2NH < C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_3NH_2$$

- **38.** In aniline, the lone pair of electrons on N-atom is delocalised over benzene ring due to resonance. As a result, electron density on the nitrogen atom decreases. In contrast, in methylamine, +I-effect of CH₃ group increases electron density on the nitrogen atom. Therefore, aniline is a weaker base than methylamine hence, its p K_b value is more than that for methylamine.
- **39.** Aniline being an aromatic primary amine on treatment with $\text{HNO}_2[\text{NaNO}_2 + \text{HCl (dil.})]}$ at 273–278 K followed by treatment with an alkaline solution of β -naphthol gives an orange coloured azo dye. Ethylamine does not give this test.
- **40.** Electron density of N-atom increases due to the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.

$$\ddot{N}H_3$$
, $R \rightarrow \ddot{N}H_2$

41.
$$CH_3CH_2NH_2 \xrightarrow{\text{(i) NaNO}_2/HCl} CH_3CH_2OH \xrightarrow{\text{K}_2Cr}_2O_7/\text{H}^+ CH_3CH_2OH$$

42. In aniline, the lone pair of electrons of N-atom are delocalised over the benzene ring. As a result, electron density on the nitrogen decreases. In contrast, in CH_3 — NH_2 , +I effect of — CH_3 group increases the electron density on the N-atom.

Therefore, aniline is a weaker base than methylamine and hence, its pK_b value is higher than that of methylamine.

- **43.** Because the electron pair of nitrogen can coordinate with the electron deficient electrophiles.
- **44.** In CH₃CONH₂, the lone pair of electrons on nitrogen atom is involved in resonance with the carbonyl group. So, the electron pair of nitrogen is not easily available for protonation. Hence, CH₃CONH₂ is a weaker base than CH₃CH₂NH₂.

$$\mathsf{CH_3} \overset{\mathsf{CO}}{-} \overset{\mathsf{CH}_3}{\overset{\mathsf{CH}_2}{\longleftrightarrow}} \mathsf{CH_3} \overset{\mathsf{O}^-}{-} \overset{\mathsf{O}^-}{\mathsf{N}} \mathsf{H_2} ; \mathsf{CH_3} \mathsf{CH_2} \overset{\mathsf{\bullet}^-}{\to} \overset{\mathsf{N}}{\mathsf{N}} \mathsf{H_2}$$

45. (i) In Friedel - Crafts reaction, $AlCl_3$ is added as a catalyst which is a Lewis acid. It forms a salt with aniline due to which the nitrogen of aniline acquires positive charge. This positively charged nitrogen acts as a strong deactivating group, hence aniline does not undergo Friedel - Crafts reaction.

- (ii) In aqueous solution 2° amine is more basic than 3° amine due to the combination of inductive effect, solvation effect and steric reasons.
- **46.** (i) Refer to answer 28.
- (ii) Refer to answer 25.

47. (i) Benzamide
$$R_2 + KOH$$
 Aniline $R_2 + KOH$

NH₂

NH₂

NaNO₂

Aniline $R_2 + KOH$

OH

Aniline $R_2 + KOH$

Phenol

- **48**. (i) Refer to answer 12.
- (ii) Acetylation of amines: The process of

introducing an acetyl group (CH₃—C—) into a molecule is called acetylation.

$$CH_{3}CH_{2}NH_{2} + CH_{3} - C - Cl \xrightarrow{Base}$$

$$CH_{3} - C - NHC_{2}H_{5} + HCl$$

$$N-\text{ethyl acetamide}$$

49. (i)
$$C_6H_5NO_2 \xrightarrow{Sn + HCl} C_6H_5NH_2 \xrightarrow{A}$$

$$C_6H_5OH \xleftarrow{H_2O} C_6H_5N_2^+Cl^- \xleftarrow{NaNO_2 + HCl} C_6H_5N_2^+Cl^- \xrightarrow{B} C_6H_5N_2^+Cl^- \xrightarrow{B} C_6H_5N_2^+Cl^- \xrightarrow{C} C_6H_5N_2^- C_6H_5N_2^+Cl^- C_6H_5N_2^- C_6H_5N_2^- C_6H_5N_2^- C_6H_5N_2^- C_6H_5N_2^- C_6H_5N_2^- C_6H_5N_2^- C_6H_5N_2^- C_6H_5N_2^- C_$$

(ii)
$$CH_3CN \xrightarrow{H_2O/H^1} CH_3COOH \xrightarrow{NH_3} CH_3CONH_2$$

----er 45(i).

- **50.** (i) Refer to answer 45(i).
- (ii) Refer to answer 42.
- **51.** (i) Increasing order of basic strength is $C_6H_5NH_2 < C_6H_5N(CH_3)_2 < CH_5NH_2 < (C_2H_5)_2NH$
- (ii) Stronger the base lower will be its pK_b value hence, the decreasing order of pK_b values:
- $C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

52. (i)
$$CH_3-CH_2-NH_2+CHCl_3+3KOH \longrightarrow CH_3-CH_2-NC+3KCl+3H_2O$$

(ii)
$$\sim$$
 NH₂ + HCl $\xrightarrow{\text{H}_2\text{O}}$ \sim NH₃Cl

53. (i) Refer to answer 36.

(ii) CH₃—NH₂ Methanamine

54. (i) Aniline gives white or brown precipitate with bromine water.

Ethylamine does not react with bromine water.

(ii) When heated with an alcoholic solution of KOH and CHCl₃, ethylamine gives foul smelling ethyl isocyanide. Dimethylamine does not give this test.

55. (i) Aniline is weaker base than cyclohexylamine because of resonance. Due to electromeric effect, the lone pair on nitrogen is attracted by benzene ring. Hence, donor tendency of $-\mathring{N}H_2$ group decreases.

There is no resonance in cyclohexylamine. Electron repelling nature of cyclohexyl group further increases the donor property of NH₂ group. So, cyclohexylamine is a stronger base.

(ii) The ammonolysis of alkyl halides with ammonia is a nucleophilic substitution reaction in which ammonia acts as a nucleophile by donating the electron pair on nitrogen atom to form primary amine as the initial product. Now, the primary amine can act as a nucleophile and combine with alkyl halide (if available) to give secondary amine and the reaction continues in the same way to form tertiary amine and finally quaternary ammonium salt. Thus, a mixture of products is formed and it is not possible to separate individual amines from the mixture.

$$R - X \xrightarrow{\text{NH}_2} R - \text{NH}_2 \xrightarrow{R-X} R_2 \text{NH} \xrightarrow{R-X} R_4 \text{N}^+ X^-$$

56. (i) Benzene ring in aromatic amines is highly activated. Due to the displacement of lone pair of nitrogen towards the ring. It results, increase in

the electron density on the ring. This facilitates the electrophilic attack on the ring.

(ii) Refer to answer 44.

57. (i) Refer to answer 55(i).

(ii) Methylamine forms hydroxide ions when dissolved in water due to the following acid - base equilibrium.

$$CH_3$$
- NH_2 + H_2O \rightleftharpoons CH_3 - NH_3 + OH^-
These OH^- ions react with Fe^{3+} ions to form ferric hydroxide.

$$2\text{Fe} + 6\text{OH}^{-} \longrightarrow 2\text{Fe}(\text{OH})_{3}$$

58. (i) Refer to answer 54 (i).

(ii) **Aniline and benzylamine :** Benzylamine reacts with nitrous acid to form a diazonium salt which is unstable at low temperature and decomposes with evolution of N₂ gas.

$$C_{6}H_{5}CH_{2}NH_{2} \xrightarrow{\text{NaNO}_{2}} [C_{6}H_{5}CH_{2} - N^{+} \equiv NCl^{-}]$$
Benzylamine
$$C_{6}H_{5}CH_{2}OH + N_{2}\uparrow + HCl \xleftarrow{H_{2}O}$$
Benzyl alcohol

Aniline reacts with $\mathrm{HNO_2}$ to form benzene diazonium chloride which is stable at 273 - 278 K and hence does not evolve $\mathrm{N_2}$ gas. It forms orange dye with 2-naphthol.

$$NH_{2} \xrightarrow{NaNO_{2}, HCl} NH_{2} \xrightarrow{NaNO_{2}, HCl} N \equiv NCl^{-1}$$
Aniline

Benzenediazonium chloride

- **59.** (i) Methyl amine gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform, followed by heating it gives offensive odour of methyl isocyanide. Dimethyl amine does not give this test.
- (ii) Aniline gives carbylamine test, *i.e.*, on treatment with alc. KOH and chloroform followed by heating it gives offensive odour of phenylisocyanide but *N*-methylaniline being secondary amine, does not show this test.

60. (i) Refer to answer 35.

(ii) Refer to answer 48(ii).

61. (i) Refer to answer 42(ii).

(ii) Refer to answer 45(i).

- **62.** (i) Refer to answer 54(i).
- (ii) Refer to answer 59(i).
- **63.** (i) Loss of proton from amines gives *R*NHion whereas loss of proton from alcohol forms alkoxide ion. Since, O is more electronegative than N therefore, *RO*⁻ can accommodate the negative charge more easily than *RN*⁻H. Further, O—H bond is more polar than N—H bond. Hence, amines are less acidic than alcohols.
- (ii) In aromatic amines, the lone pair of electrons present on nitrogen takes part in resonance and hence, not available for donation. However, in aliphatic amines, the lone pair is available for donation. That's why aliphatic amines are more basic than aromatic amines.
- **64.** (i) The increasing order of basic strength in water of the given amines and ammonia follows the following order:

$$C_6H_5NH_2 < NH_3 < (C_2H_5)_3N < (C_2H_5)_2NH$$

$$CH_3NH_2 < C_2H_5NH_2 < (C_2H_5)_2NH < (C_2H_5)_3N$$

- **65.** (i) Refer to answer 45(i).
- (ii) Refer to answer 63(ii).
- **66.** (i) Refer to answer 54(i).
- (ii) Refer to answer 59(ii).

67. (i)
$$\begin{array}{c|c}
Br_2 & 0-5^{\circ}C \\
\hline
 & aq. \text{ KOH}
\end{array}$$

$$\begin{array}{c|c}
 & (A) & 0-5^{\circ}C \\
\hline
 & NaNO_2 + HCl
\end{array}$$
(ii) $CH_3 - Cl \xrightarrow{KCN} CH_3CN \xrightarrow{LiAlH_4} CH_3CH_2NH_2$
(A)
$$\begin{array}{c|c}
 & (B) \\
\hline
 & (CH_3CH_2NC) \xrightarrow{CHCl_3 + alc. \text{ KOH}}
\end{array}$$

$$\begin{array}{c|c}
 & (CH_3CH_2NC) \xrightarrow{CHCl_3 + alc. \text{ KOH}}
\end{array}$$

68. (i)
$$\xrightarrow{NH_2}$$
 $\xrightarrow{3Br_2 \text{ water}}$ \xrightarrow{Br} $\xrightarrow{NH_2}$ \xrightarrow{Br} \xrightarrow{Br}

2,4,6-Tribromoaniline

Acetanilide

$$(ii) \begin{array}{c} NH_2 \\ \\ \\ \end{array} + HCl \longrightarrow \begin{array}{c} \\ \\ \\ \end{array}$$

Anilinium chloride $NH_{2} \qquad \qquad NHCOCH_{3}$ $(CH_{3}CO)_{2}O/Pyridine \longrightarrow OH_{3}$ $CH_{3}COOH \longrightarrow OH_{3}$

69. (i) Refer to answer 68(i).

(ii)
$$NH_2$$

+ CHCl₃ + 3KOH NC
+ 3KCl + 3H₂O

- (iii) Refer to answer 68(ii).
- **70**. (i) Refer to answer 49(i).

(ii) CH₃Cl
$$\xrightarrow{\text{KCN}}$$
 CH₃CN $\xrightarrow{\text{LiAlH}_4}$ CH₃CH₂NH₂

$$A \qquad \qquad B \qquad \qquad C\text{H}_3\text{CH}_2\text{OH} \xleftarrow{\text{HNO}_2}$$

71. Formula of the compound 'C' indicates it to be an amine. Since it is obtained by the reaction of Br_2 and KOH with the compound 'B' so compound 'B' can be an amide. As 'B' is obtained from compound 'A' by reaction with ammonia followed by heating so, compound 'A' could be an aromatic acid. Formula of compound 'C' shows it to be aniline, then 'B' is benzamide and compound 'A' is benzoic acid. The sequence of reactions can be written as follows:

(ii)
$$\text{CH}_3\text{COOH} \xrightarrow{\text{NH}_3} \text{CH}_3\text{CONH}_2 \xrightarrow{\text{Br}_2 + \text{KOH}}$$

$$\text{CH}_3\text{NC} \xleftarrow{\text{CHCl}_3 + \text{NaOH}} \text{CH}_3\text{NH}_2$$

$$\text{(C)} \qquad \text{(B)}$$

73. (i)
$$A = CH_3CH_2CN$$

 $B = CH_3CH_2CH_2NH_2$
 $C = CH_3CH_2CH_2OH$

- (ii) Refer to answer 72(ii).
- 74. (i) Refer to answer 42.
- (ii) Refer to answer 57(ii).
- (iii) Refer to answer 45(i).

75.
$$C_6H_5N_2Cl + H_3PO_2 + H_2O \longrightarrow C_6H_6 + N_2 + H_3PO_3 + HCl$$

76. Diazotisation reaction.

78. Diazonium salts react with aromatic amines in weakly acidic medium and phenols in weakly alkaline medium to form coloured compounds called azo dyes by coupling at *p*-position of amines or phenols.

80.
$$NO_2$$

$$+ 6[H] \xrightarrow{Fe + HCl} NaNO_2 + HCl$$

$$273 - 278 K$$

$$OH \qquad N_2 Cl$$

$$+ H_2O \qquad Benzenediazonium chloride$$

81.
$$\underbrace{\bigcap_{\text{NaNO}_2 + \text{HCl}}^{\text{N4NO}_2 + \text{HCl}}}_{\text{Aniline}} \xrightarrow{\underbrace{\bigcap_{\text{Diazonium}}^{\text{CuCl/HCl}}}_{\text{Calt}}}_{\text{Calt}} \xrightarrow{\text{Chlorobenzene}}$$

82.
$$\underbrace{\bigcap_{\text{NaNO}_2 + \text{HCl}}^{\text{NaNO}_2 + \text{HCl}}}_{\text{Aniline}} \xrightarrow{\underbrace{\bigcap_{\text{CuCN/Pyridine}}^{\text{CuCN/Pyridine}}_{\text{KCN}}}_{\text{CN}}$$

84.
$$NH_2$$
 $N_2^+Cl^ C \equiv N$

NaNO₂/HCl

O - 5°C

Aniline

Benzonitrile

85. (i)
$$NO_2$$
 NH_2 $N_2^+Cl^-$
Nitrobenzene NO_2 NH_2 $N_2^+Cl^ NaNO_2/HCl$ $Ouch$
 $Nitrobenzene$ $Ouch$
 $Nitrobenzene$
 $Ouch$
 Ouc

(ii)
$$NH_2$$

$$NaNO_2/HCl$$

$$Z73 - 278 \text{ K}$$

$$CuCN$$

$$LiAlH_4$$

$$CH_2-OH$$

$$CH_2-NH_2$$

$$NaNO_2/HCl$$

$$Z73 - 278 \text{ K}$$

$$N_2^+Cl^-$$

$$CuCN$$

$$CuCN$$

$$CH_2-NH_2$$

$$RaNO_2/HCl$$

$$Z73 - 278 \text{ K}$$

$$RanO_2/HCl$$

$$Z73 - 278 \text{ K}$$

86. (i) **Sandmeyer reaction :** By this reaction nulceophiles like Cl⁻, Br⁻, CN⁻ etc. can easily be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of Cu(I) ion.

$$\begin{array}{c|c}
\hline
& N_2^+Cl^- \xrightarrow{Cu_2Cl_2/HCl} \\
\hline
& Chlorobenzene \\
& chloride
\end{array}$$

(ii) Refer to answer 78.

87. (i)
$$C_6H_5N_2^+Cl^-\frac{CuCN}{}$$
 C_6H_5CN

Benzonitrile
(A)

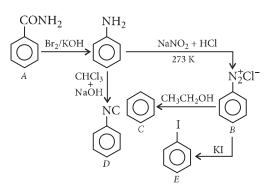
 $C_6H_5CONH_2 \stackrel{NH_3}{\longleftarrow} C_6H_5COOH$

Benzamide
(C)

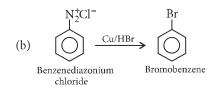
Benzoic acid
(B)

(ii) Refer to answer 49(i).

88.



89. (i) (a)
$$\xrightarrow{N_2^+Cl^-} \xrightarrow{HBF_4/\Delta} \xrightarrow{Fluorobenzene}$$
 chloride



- (ii) (a) Refer to answer 49(i).
- (b) Refer to answer 70(ii).

