1. The lowest boiling point amide in the table is methanamide (formamide), b.p. = 210°C.

\[ \text{NH}_2\text{HC}=\text{NH}_2 \]

The highest boiling point amide is \( N \)-phenylethanamide (acetanilide), b.p. = 304°C.

\[ \text{CH}_3\text{C}--\text{N}--\text{HC}=\text{NH}_2 \]

The larger size of \( N \)-phenylethanamide contributes significantly to its higher boiling point.

2. Procaine contains an amine. When the amine reacts with HCl it forms a salt that is much more soluble in water.

3. (a) With reference to Section 25.6, acetylcholine contains a quaternary (4°) amine.
(b) With reference to Section 25.8, cocaine contains a tertiary (3°) amine.
(c) With reference to Section 25.7, serotonin contains a primary (1°) and a secondary (2°) amine.
(d) With reference to Section 25.8, methamphetamine contains a secondary (2°) amine.

4. Amides: Unsubstituted amides (except formamide) are solids at room temperature. Many are odorless and colorless. Low molar-mass amides are water soluble. Solubility in water decreases as the molar mass increases. Amides are neutral compounds. The \( \text{NH}_2 \) group is capable of hydrogen bonding.

Amines: Low molar-mass amines are flammable gases with an ammonia-like odor. Aliphatic amines up to six carbon atoms are water soluble. Many amines have a “fishy” odor and many have very foul odors. Aromatic amines occur as liquids and solids. Soluble aliphatic amines give basic solutions. Aromatic amines are less soluble in water and less basic than aliphatic amines. The \( \text{NH}_2 \) group is capable of hydrogen bonding.

5. Unlike esters, unsubstituted amides can hydrogen bond to each other. Thus, they have a higher melting point than esters of similar molar mass.

6. (a) Heterocyclic compounds are those in which all the atoms in the ring are not alike.
(b) The number of heterocyclic rings in each of the compounds is:
   (i) purine, 2 (ii) histamine, 1 (iii) methadone, 0 (iv) nicotine, 2

7. Ammonia is a toxic, basic, water-soluble compound which can increase the pH of the blood and the urine and would be painful to pass through bodily tissues. However, ammonia is converted in the liver to the neutral diamide, urea, which is water soluble and is excreted in the urine.
8. A “condensation polymer” is made when monomers connect together with the loss of a small molecule, most often, water.

\[
\text{HOOC} - (\text{CH}_2)_4 - \text{COOH} + \text{H}_2\text{N} - (\text{CH}_2)_6 - \text{NH}_2 \rightarrow \]

\[
\begin{array}{c}
\text{O} \\
\downarrow \\
\text{C} - (\text{CH}_2)_4 - \text{C} - \text{NH} - (\text{CH}_2)_6 - \text{NH}
\end{array}
\]

\[\] + \text{H}_2\text{O}

9. The nitrogen in a compound that has four groups bonded to it is positively charged and is called a quaternary ammonium nitrogen. The compound is called a quaternary ammonium salt.

10. An amine must have at least one hydrogen atom bonded to the nitrogen atom to react with an acid chloride. A tertiary amine does not meet this requirement.

11. The nitrogen in cocaine is an amine nitrogen. If it was an amide nitrogen it would be bonded to a carbonyl group.

12. The name of the compound is \(\text{N}\)-methyl-2-methylbutanamine. Methyl (a) is included in the name butanamine; methyl (b) is part of 2-methyl; methyl (c) is included in \(\text{N}\)-methyl.
- Chapter 25 -

SOLUTIONS TO EXERCISES

1. (a) \[ \begin{array}{c}
\text{O} \\
\text{C} \quad \text{NH}_2
\end{array} \]  
(b) \[ \begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{C} \quad \text{NH}_2
\end{array} \]  
(c) \[ \begin{array}{c}
\text{O} \\
\text{C} \quad \text{NHCH}_3
\end{array} \]  
(d) \[ \begin{array}{c}
\text{CH}_3 \\
\text{O} \\
\text{C} \quad \text{NH}_2
\end{array} \]

2. (a) \[ \begin{array}{c}
\text{CH}_3 \text{CH}_2 \text{CH}_2 \text{CH}_2 \\
\text{O} \\
\text{C} \quad \text{N} \quad \text{CH}_3
\end{array} \]  
(b) \[ \begin{array}{c}
\text{O} \\
\text{C} \quad \text{NH}_2
\end{array} \]  
(c) \[ \begin{array}{c}
\text{CH}_3 \text{CH}_2 \\
\text{CH} \quad \text{CH} \quad \text{C} \\
\text{O}
\end{array} \]  
(d) \[ \begin{array}{c}
\text{O} \\
\text{C} \quad \text{NH} \quad \text{CH}_2 \text{CH}_3
\end{array} \]

3. (a) common, formamide; IUPAC, methanamide  
(b) IUPAC, $N,N$-dimethyl-3,3-dimethylbutanamide  
(c) IUPAC, $N$-butylethanamide

4. (a) IUPAC, benzamide  
(b) IUPAC, $N,N$-dibutylethanamide  
(c) common, $N$-methylacetamide, IUPAC, $N$-methylethanamide

- 369 -
5. The larger amides are less water soluble. Thus, the largest amide, \(N,N\)-diethyl-3-methylhexanamide is the least water soluble. The intermediate sized amide, 3-methylhexanamide will be of intermediate solubility and the smallest amide, acetamide, will be the most water soluble.

6. The larger amides are less water soluble. Thus, the largest amide, benzamide, is the least water soluble. The intermediate sized amide, propanamide, will be of intermediate solubility and the smallest amide, formamide, will be the most water soluble.

7. 

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{N} & \text{H} \\
\text{O} & \\
\text{CH}_3\text{CH}_2\text{N} & \text{H} \\
\text{H} & \\
\text{O} & \\
\text{CH}_3\text{CH}_2\text{N} & \text{H} \\
\text{H} & \\
\end{align*}
\]

8. 

\[
\begin{align*}
\text{CH}_3\text{N} & \text{H} \\
\text{O} & \\
\text{CH}_3\text{N} & \text{H} \\
\text{H} & \\
\text{O} & \\
\text{CH}_3\text{N} & \text{H} \\
\text{H} & \\
\end{align*}
\]

9. Organic products

(a) \(\text{CH}_3\text{C}—\text{OH} + \text{CH}_3\text{NH}_3^+\)

(b) \(\text{CH}_3\text{C}—\text{NHCH(CH}_3)\text{_2}\)

(c) \(\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COONa}\)
10. Organic products

(a) \( \text{O} \quad \text{CH}_3\text{C} - \text{N(CH}_2\text{CH}_3)_2 \) 

(b) \( \text{CH}_2\text{COOH} + \text{CH}_3\text{NH}_2\text{CH}_3 \)

(c) \( \text{O} \quad \text{CH}_3\text{CHCH}_2\text{C} - \text{NHCH}_3 \) 

\( \text{CH}_3 \)

11. (a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{C} - \text{OH} + \text{NH}_2\text{CH}_3 \)

(b) \( \text{CH}_3\text{CH}_2\text{C} - \text{OH} + \text{NH}_2\text{CH}_2\text{CH}_3 \)

(c) \( \text{O} \quad \text{HC} - \text{NH} \quad + \quad \text{HCl} + \text{H}_2\text{O} \)

12. (a) \( \text{CH}_3\text{C} - \text{NHCH}_2\text{CH}_3 + \text{NaOH} \)

(b) \( \text{CH}_3\text{CH}_2\text{C} - \text{OH} + \text{CH}_3\text{NHCH}_3 \)

(c) \( \text{CH}_3\text{C} - \text{NH}_2 + \text{HCl} + \text{H}_2\text{O} \)

13. Structures of amines with formula \( \text{C}_4\text{H}_{11}\text{N} \).

\( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \quad \text{CH}_3\text{CHCH}_2\text{NH}_2 \quad \text{CH}_3\text{CH}_2\text{CHCH}_3 \)

\( \text{CH}_3 \quad 1^\circ \quad \text{CH}_3 \quad 1^\circ \quad \text{NH}_2 \quad 1^\circ \)

\( \text{CH}_3\text{CNH}_2 \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_3 \quad (\text{CH}_3)_2\text{CHNHCH}_3 \)

\( \text{CH}_3 \quad 1^\circ \quad 2^\circ \quad 2^\circ \)

\( \text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3 \quad \text{CH}_3\text{CH}_2\text{NCH}_3 \)

\( 2^\circ \quad 3^\circ \)
14. Structures of amines with formula C₃H₉N.

\[
\begin{array}{c|c|c|c}
\text{CH₃CH₂CH₂NH₂} & \text{CH₃CHCH₃} & \text{CH₃CH₂NHCH₃} & \text{CH₃NCH₃} \\
1° & 1° & 2° & 3° \\
\end{array}
\]

15. Classification of amines
(a) primary (b) tertiary (c) primary (d) both primary

16. Classification of amines
(a) secondary (b) tertiary (c) secondary (d) tertiary

17. The triethylamine solution in 1.0 M NaOH would have the more objectionable odor because it would be in the form of the free amine, while in the acid solution the amine would form a salt that will have little or no odor.

18. The isopropylamine solution in 1.0 M KOH would have the more objectionable odor because it would be in the form of the free amine, while in the acid solution the amine would form a salt that will have little or no odor.

19. Names
(a) CH₃NHCH₃ dimethylamine
(b) o-ethylaniline
(c) cyclohexanamine
(d) tetraethylammonium iodide
(e) m-nitroaniline
(f) cyclohexyldiethylamine

20. Names
(a) N-ethylaniline
21. Structural formulas
(a) \( \text{CH}_3\text{CH}_2\text{NHCH}_3 \)
(b) \( \text{CH}_3\text{CH}_2\text{NH}_2 \)
(c) \( \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \)
(d) \( \text{CH}_3\text{CH}_2\text{NCH(CH}_3_2 \)
(e) \( \text{O} \)
(f) \( \text{CH}_3\text{C-NHCH}_2\text{CH}_3 \) 

22. Structural formulas
(a) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \)
(b) \( \text{CH}_3\text{C-NH}_2\text{Cl}^- \)
(c) \( \text{CH}_3\text{CH}_2\text{NH}_3\text{Cl}^- \)

(d) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \)

\[ \text{NH}_2 \]

\[ \text{CH}_3 \]

(e) \( \text{CH}_3\text{CH}_2\text{CH}_2\text{C} = \text{CH} - \text{NH} - \text{CH} \)

\[ \text{CH}_3 \]

\[ \text{CH}_3 \]

(f) \( \text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \)

23. (a) Butylamine has the following structure:
\( \text{CH}_3\text{CH}_2\text{CH}_2\text{NH}_2 \)
Its IUPAC name is 1-butanamine.

(b) \textit{tert}-butylamine has the following structure:
\[ \text{CH}_3 \]
\[ \text{CH}_3 \]
\[ \text{C} - \text{NH}_2 \]
\[ \text{CH}_3 \]
Its IUPAC name is 2-methyl-2-propanamine.

(c) Formamide has the following structure:
\[ \text{O} \]
\[ \text{HC} - \text{NH}_2 \]
Its IUPAC name is methanamide.

24. (a) Isopropylamine has the following structure:
\[ \text{CH}_3 \]
\[ \text{CH}_3\text{CHNH}_2 \]
Its IUPAC name is 2-propanamine.

(b) Diethylamine has the following structure:
\( \text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3 \)
Its IUPAC name is N-ethylethanamine.

(c) Acetamide has the following structure:
\[ \text{O} \]
\[ \text{CH}_3\text{C} - \text{NH}_2 \]
Its IUPAC name is ethanamide.
25. (a) This reaction adds methyl groups to a primary amine to form a tertiary amine.

\[
\text{CH}_3 \text{CH}_3 \\
\text{CH}_3 - \text{C} - \text{N} - \text{CH}_3 \\
\text{CH}_3
\]

\(N,N\text{-dimethyl-2-methyl-2-propanamine}\)

(b) This reaction reduces the nitrile to form an amine.

\[
\text{CH}_3\text{NH}_2
\]

menthanamine (methylamine)

(c) This reaction reduces the amide to form an amine.

\[
\text{CH}_3\text{CH}_2\text{NHCH}_2\text{CH}_3
\]

\(N\text{-ethylethanamine} \ (\text{diethylamine})\)

26. (a) This reaction reduces an amide to form an amine.

\[
(\text{CH}_3)_3\text{N}
\]

\(N,N\text{-dimethylmethanamine} \ (\text{trimethylamine})\)

(b) This reaction reduces a nitro group to form a substituted aniline.

\[
\text{CH}_3
\]

\[
\text{CH}_3
\]

\(3,4\text{-dimethylaniline}\)

(c) This reaction adds a methyl group to a primary amine to form a secondary amine.

\[
\text{CH}_3\text{CH}_2\text{NHCH}_3
\]

\(N\text{-methylethanamine} \ (\text{methylethylamine})\)

27. Organic molecule A

\[
\text{CH}_3
\]

\(o\text{-methylaniline}\)

Organic molecule B

\[
\text{CH}_3
\]

\(o\text{-methylanilinium bromide}\)
28. Organic molecule A

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}_3\text{C} - \text{CH} - \text{CH}_2 - \text{NH}_2 \\
2\text{-methylpropanamine}
\end{array}
\]

Organic molecule B

\[
\begin{array}{c}
\text{CH}_3 \\
\text{H}_3\text{C} - \text{CH} - \text{CH}_2 - \text{NH}_2 \text{OH} \\
2\text{-methylpropanammonium hydroxide}
\end{array}
\]

29. Amines are bases while carboxylic acids and phenols are acids. Alcohols and amides are neither acids nor bases.

(a) amine, base (b) amide, neither (c) amide, neither
(d) carboxylic acid, acid (e) alcohol, neither (f) alcohol, neither

30. Amines are bases while carboxylic acids and phenols are acids. Alcohols and amides are neither acids nor bases.

(a) alcohol, neither (b) carboxylic acid, acid (c) amide, neither
(d) amine, base (e) amine, base (f) phenol, acid

31. The main reason why trimethylamine has a lower boiling point than propylamine and ethylmethylamine is that trimethylamine cannot hydrogen bond because it has no hydrogen atoms bonded to the nitrogen atom. The other two amines do have hydrogen atom(s) bonded to the nitrogen atom and their molecules can hydrogen bond, which results in higher boiling points.

32. Biogenic amines are derived from amino acids and act as neurotransmitters and hormones in animals. In contrast, alkaloids are basic compounds derived from plants that show physiological activity.

33. This calculation requires Avogadro’s number, \(6.02 \times 10^{23}\) dopamine molecules/mole.

\[
(5 \times 10^{-18} \text{ moles}) \times (6.02 \times 10^{23} \text{ dopamine molecules/mole}) = 3 \times 10^6 \text{ dopamine molecules}
\]

About three million dopamine molecules are sent from one neuron to the next.

34. (a) \[
\begin{array}{c}
\text{O} \\
\text{CH}_3\text{C} - \text{Cl} + 2\text{CH}_2\text{NH}_2 \rightarrow \text{O} \\
\text{CH}_3\text{C} - \text{NHCH}_3 + \text{CH}_3\text{NH}_3^+ \text{Cl}^{-}
\end{array}
\]

(b) \[
\begin{array}{c}
\text{O} \\
\text{CH}_3\text{C} - \text{NHCH}_3 \rightarrow \text{LiAlH}_4 \rightarrow \text{CH}_3\text{CH}_2\text{NHCH}_3
\end{array}
\]

(c) \[
\begin{array}{c}
\text{O} \\
\text{CH}_3\text{CH}_2\text{NHCH}_3 + \text{CH}_3\text{Br} (1 \text{ mole}) \rightarrow \text{CH}_3\text{CH}_2\text{N(CH}_3)_2
\end{array}
\]
35. There is one amine and two amides in ampicillin.

36. Lemon juice, being acidic, will react with the basic amines forming salts, which are soluble and can be washed away with water.

37. \[
\text{amine} + \text{HCl} \rightarrow \text{amine}^+\text{Cl}^-
\]

38. \(\text{H}_2\text{N}--\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2--\text{NH}_2\)

Putrescine has two primary amines.

39. Drugs are given as ammonium salts because the salts are soluble in water.

40. Aspartame

41. Kevlar polymer

42. (a) \(\text{HO}--\text{C}--\text{(CH}_2\text{)}_6\text{C}--\text{OH}\) and \(\text{H}_2\text{N}--\text{(CH}_2\text{)}_6\text{NH}_2\)

(b) \(\text{HO}--\text{C}--\text{(CH}_2\text{)}_6\text{C}--\text{OH}\) and \(\text{H}_2\text{N}--\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2--\text{NH}_2\)
43. (a) \( \text{CH}_3\text{CH}_2\text{OH} \xrightarrow{\text{H}_2\text{SO}_4/140^\circ \text{C}} \text{CH}_2=\text{CH}_2 \xrightarrow{\text{Br}_2} \text{BrCH}_2\text{CH}_2\text{Br} \)
\( \xrightarrow{\text{KCN}} \text{NCCH}_2\text{CH}_2\text{CN} \xrightarrow{\text{H}_2/\text{Ni}} \text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \)
1, 4-butenediamine

(b) \( \text{CH}_3\text{C}—\text{Cl} + \text{NH}_3 \rightarrow \text{CH}_3\text{C}—\text{NH}_2 \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{CH}_2\text{NH}_2 \)
\( \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{C}—\text{NHCH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{NHCH}_3 \)
\( \xrightarrow{\text{LiAlH}_4} \text{CH}_3\text{C}—\text{N(CH}_3)_2 \rightarrow \text{CH}_3\text{CH}_2\text{N(CH}_3)_2 \)