AMINES

ethyamine ($1^\circ$)  diethylamine ($2^\circ$)  triethylamine ($3^\circ$)

\[
\text{RNH}_2 + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_3^+ + \text{OH}^- \quad K_b (pK_b)
\]

\[
\text{RNH}_3^+ + \text{H}_2\text{O} \rightleftharpoons \text{RNH}_2 + \text{H}_3\text{O}^+ \quad K_a (pK_a = 14 - pK_b)
\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>$pK_a$</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{NH}_3$</td>
<td>9.26</td>
<td>5.34</td>
</tr>
<tr>
<td>$\text{CH}_3\text{NH}_2$</td>
<td>10.66</td>
<td></td>
</tr>
<tr>
<td>$(\text{CH}_3)_2\text{NH}$</td>
<td>10.73</td>
<td>4.63</td>
</tr>
<tr>
<td>$\text{NH}_2\text{CH}_3\text{O}$</td>
<td>5.25</td>
<td>1.0</td>
</tr>
<tr>
<td>$\text{NH}_2\text{O}_2\text{N}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
SYNTHESIS OF AMINES

1. From alkyl halides
   a) ammonia or amines as nucleophiles

   \[ RX + R'NH_2 \rightarrow RNHR' \]

   b) azide as the nucleophile, followed by reduction

   \[ RX + NaN_3 \rightarrow RN_3 \rightarrow RNH_2 \]

   c) imide anion as the nucleophile, followed by hydrolysis (Gabriel synthesis)

   \[ RX + KN \rightarrow RN \rightarrow RNH_2 \]

2. Reduction of nitriles ([H] = LiAlH₄)

   \[ RCN \rightarrow RCH₂NH₂ \]

3. Reductive amination ([H] = NaCNBH₃)

   \[ R_2C=O + R'NH_2 \rightarrow R_2CH-NHR' \]

4. Hofmann and Curtius Rearrangements

   \[ RCONH₂ \rightarrow RNH₂ \text{ or } RCON₃ \rightarrow RNH₂ \]

5. Reduction of aromatic nitro compounds to aromatic amines ([H] = H₂/Pd)

   \[ ArNO₂ \rightarrow ArNH₂ \]
REACTIONS OF AMINES

1. Alkylation (see synthesis)

\[ RX + R'NH_2 \rightarrow RNHR' \]

2. Acylation (see carbonyl derivatives)

\[ RCOX + R'NH_2 \rightarrow RCONHR' \]

3. Hofmann elimination (to less highly substituted alkene)

\[ \text{amine} \rightarrow \text{alkene} \]

4. Diazonium salts (Sandmeyer Reaction)

\[ \text{amine} \rightarrow \text{azo compound} \rightarrow \text{substituted aromatic} \]

\[ X: \]

- Cl
- Br
- I
- CN
- OH
- H