22.4
Measures of Amine Basicity
The basicity of amines may be measured by:

1) $K_b$
2) $pK_b$
3) $K_a$ of conjugate acid
4) $pK_a$ of conjugate acid
Basicity Constant \((K_b)\) and \(pK_b\)

\(K_b\) is the equilibrium constant for the reaction:

\[
R_3N^+ + HOH \rightleftharpoons R_3NH+ + HO^- \]

\[
K_b = \frac{[R_3NH^+][HO^-]}{[R_3N]} \]

and \(pK_b = - \log K_b\)
$K_a$ and $pK_a$ of Conjugate Acid

$K_a$ is the equilibrium constant for the dissociation of the conjugate acid of the amine:

$$R_3N + H^+ \rightleftharpoons R_3NH^+ + H_2O$$

$$K_a = \frac{[R_3N][H^+]}{[R_3NH^+]}$$

and

$$pK_a = -\log K_a$$
Relationships between acidity and basicity constants

\[ K_a \ K_b = 10^{-14} \]

\[ pK_a + pK_b = 14 \]
22.5
Basicity of Amines
Effect of Structure on Basicity

1. Alkylamines are slightly stronger bases than ammonia.
<table>
<thead>
<tr>
<th>Amine</th>
<th>Conj. Acid</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>NH&lt;sub&gt;4&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>9.3</td>
</tr>
<tr>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NH&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>10.8</td>
</tr>
</tbody>
</table>

*Table 22.1 (page 866)*

**Basicity of Amines in Aqueous Solution**
### Table 22.1 (page 866)

**Basicity of Amines in Aqueous Solution**

<table>
<thead>
<tr>
<th>Amine</th>
<th>Conj. Acid</th>
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<tbody>
<tr>
<td>NH\textsubscript{3}</td>
<td>NH\textsubscript{4}^{+}</td>
<td>9.3</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}NH\textsubscript{2}</td>
<td>CH\textsubscript{3}CH\textsubscript{2}NH\textsubscript{3}^{+}</td>
<td>10.8</td>
</tr>
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</table>

CH\textsubscript{3}CH\textsubscript{2}NH\textsubscript{3}^{+} is a weaker acid than NH\textsubscript{4}^{+}; therefore, CH\textsubscript{3}CH\textsubscript{2}NH\textsubscript{2} is a stronger base than NH\textsubscript{3}. 
Effect of Structure on Basicity

1. Alkylamines are slightly stronger bases than ammonia.

2. Alkylamines differ very little in basicity.
### Table 22.1 (page 866) 
**Basicity of Amines in Aqueous Solution**

<table>
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<th>Amine</th>
<th>Conj. Acid</th>
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<td>NH₃</td>
<td>NH₄⁺</td>
<td>9.3</td>
</tr>
<tr>
<td>CH₃CH₂NH₂</td>
<td>CH₃CH₂NH₃⁺</td>
<td>10.8</td>
</tr>
<tr>
<td>(CH₃CH₂)₂NH</td>
<td>(CH₃CH₂)₂NH₂⁺</td>
<td>11.1</td>
</tr>
<tr>
<td>(CH₃CH₂)₃N</td>
<td>(CH₃CH₂)₃NH⁺</td>
<td>10.8</td>
</tr>
</tbody>
</table>

Notice that the difference separating a primary, secondary, and tertiary amine is only 0.3 pK units.
Effect of Structure on Basicity

1. Alkylamines are slightly stronger bases than ammonia.

2. Alkylamines differ very little in basicity.

3. Arylamines are much weaker bases than ammonia.
### Table 22.1 (page 866)

**Basicity of Amines in Aqueous Solution**

<table>
<thead>
<tr>
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<th>Conj. Acid</th>
<th>pK&lt;sub&gt;a&lt;/sub&gt;</th>
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<td>CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;NH&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>10.8</td>
</tr>
<tr>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;NH</td>
<td>(CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;2&lt;/sub&gt;NH&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>11.1</td>
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<td>(CH&lt;sub&gt;3&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;)&lt;sub&gt;3&lt;/sub&gt;N</td>
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<td>10.8</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;NH&lt;sub&gt;2&lt;/sub&gt;</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;5&lt;/sub&gt;NH&lt;sub&gt;3&lt;/sub&gt;&lt;sup&gt;+&lt;/sup&gt;</td>
<td>4.6</td>
</tr>
</tbody>
</table>
Decreased basicity of arylamines

\[
\text{PhNH}_2 + \text{H}_2\text{OH} \rightleftharpoons \text{PhNH}_3^+ + \text{OH}^- 
\]
Aniline (reactant) is stabilized by conjugation of nitrogen lone pair with ring $\pi$ system. This stabilization is lost on protonation.

Decreased basicity of arylamines
Decreased basicity of arylamines

Increasing delocalization makes diphenylamine a weaker base than aniline, and triphenylamine a weaker base than diphenylamine.

\[
\begin{array}{ccc}
C_6H_5NH_2 & (C_6H_5)_2NH & (C_6H_5)_3N \\
K_b & 3.8 \times 10^{-10} & 6 \times 10^{-14} & \sim 10^{-19}
\end{array}
\]
Effect of Substituents on Basicity of Arylamines

1. Alkyl groups on the ring increase basicity, but only slightly (less than 1 pK unit).
Basicity of Arylamines

Basicity of Arylamines

\[ \text{Basicity of Arylamines} \]

\[ X - \text{NH}_2 \quad \text{pK}_b \]

\[ X - \text{NH}_3^+ \quad \text{pK}_a \]

<table>
<thead>
<tr>
<th>X</th>
<th>(\text{pK}_b)</th>
<th>(\text{pK}_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>9.4</td>
<td>4.6</td>
</tr>
<tr>
<td>(\text{CH}_3)</td>
<td>8.7</td>
<td>5.3</td>
</tr>
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Effect of Substituents on Basicity of Arylamines

1. Alkyl groups on the ring increase basicity, but only slightly (less than 1 $pK$ unit).

2. Electron withdrawing groups, especially ortho and/or para to amine group, decrease basicity and can have a large effect.
## Basicity of Arylamines

<table>
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<td>5.3</td>
</tr>
<tr>
<td>CF₃</td>
<td>11.5</td>
<td>2.5</td>
</tr>
<tr>
<td>O₂N</td>
<td>13.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>
Lone pair on amine nitrogen is conjugated with $p$-nitro group—more delocalized than in aniline itself. Delocalization lost on protonation.
Effect is Cumulative

Aniline is 3800 times more basic than \textit{p}-nitroaniline.
Aniline is \(~1,000,000,000\) times more basic than \textit{2,4-}dinitroaniline.
Heterocyclic Amines

piperidine

\[ K_b = 1.6 \times 10^{-3} \]

(an alkylamine)

pyridine

\[ K_b = 1.4 \times 10^{-9} \]

( resembles an arylamine in basicity)
Heterocyclic Amines

imidazole is more basic than pyridine

\[ K_b = 1 \times 10^{-7} \]  

\[ K_b = 1.4 \times 10^{-9} \]
Which nitrogen is protonated in imidazole?
Which nitrogen is protonated in imidazole?
Imidazole

Protonation in the direction shown gives a stabilized ion.
22.6
Tetraalkylammonium Salts
as Phase-Transfer Catalysts
Phase-transfer agents promote the solubility of ionic substances in nonpolar solvents. They transfer the ionic substance from an aqueous phase to a non-aqueous one.

Phase-transfer agents increase the rates of reactions involving anions. The anion is relatively unsolvated and very reactive in nonpolar media compared to water or alcohols.
Phase-Transfer Catalysis

Quaternary ammonium salts are phase-transfer catalysts. They are soluble in nonpolar solvents.

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

\[
\text{H}_3\text{C}^+\text{N}^+\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \quad \text{Cl}^-
\]

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

Methyltrioctylammonium chloride
Quaternary ammonium salts are phase-transfer catalysts. They are soluble in nonpolar solvents.

Benzyltriethylammonium chloride
Example

The $S_N2$ reaction of sodium cyanide with butyl bromide occurs much faster when benzyl-triethylammonium chloride is present than when it is not.

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{NaCN} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CN} + \text{NaBr}$$
Mechanism

\[
\text{N}^+\text{CH}_2\text{CH}_3 \quad \text{Cl}^- \quad + \quad \text{CN}^- \quad (\text{aqueous})
\]
Mechanism

\[
\text{N}^+\text{CH}_2\text{CH}_3 \quad \text{Cl}^- + \quad \text{CN}^- \\
\text{CH}_2\text{CH}_3 \quad \text{N}^+\text{CH}_2\text{CH}_3 \quad \text{CN}^- + \quad \text{Cl}^- \\
\text{CH}_2\text{CH}_3 \quad \text{N}^+\text{CH}_2\text{CH}_3 \quad \text{CN}^- + \quad \text{Cl}^- \quad \text{(aqueous)}
\]

(aqueous)
Mechanism

\[
\text{NNCHCH22CHCH332CHCH332CHCH32CHCH33CHCH2CHCH3N}^+ \text{CH}_2\text{CH}_3 \text{CN}^- \text{CH}_2\text{CH}_3
\]

(aqueous)
(in butyl bromide)

Mechanism

(aqueous)
Mechanism

\[
\text{NCH}_{2}\text{CH}_{3}^{+}\text{CH}_{2}\text{CH}_{3}\text{CN}^{-} + \text{CH}_{3}\text{CH}_{2}\text{CH}_{2}\text{CH}_{2}\text{Br} \]

(in butyl bromide)
Mechanism

\[
\begin{align*}
\text{CH}_2\text{CH}_3 & \quad \text{N}^+ \quad \text{CH}_2\text{CH}_3 \quad \text{CN}^- + \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} \\
\text{CH}_2\text{CH}_3 & \quad \text{CH}_2\text{CH}_3 \quad \text{CH}_2\text{CH}_3 \\
\text{(in butyl bromide)} & \quad \text{(in butyl bromide)}
\end{align*}
\]