Chapter 4 covers acid-base chemistry. That should help you get going.

1 Use curved arrows to illustrate the transfer of a proton (i.e. an $\text{H}^+$) from benzoic acid to phenoxide, and draw the products. It might be a good idea to add the lone pairs first.

\[
\text{\begin{tikzpicture}
\node (a) at (0,0) {$\text{O}^-$};
\node (b) at (1,0) {$\text{H-O-C}$};
\node (c) at (2,0) {$\text{H}^+$};
\node (d) at (3,0) {$\text{O}$};
\end{tikzpicture}}\]

2 Which way this equilibrium lies depends on the relative stabilities (i.e. energies) of the two products as compared to the two reactants. Although we could determine this from acidity constants, let's instead try to make a prediction based on structures.

All 4 structures you drew have several additional resonance structures, but we don't need to draw them all to answer this question! Our time is valuable, so let's skip the busy-work. We're looking for resonance that has a significant impact on stabilities and that changes in going from one side of the equation to the other. Notice that we can shuffle electrons around the aromatic ring in each structure. Fine. Everything's aromatic. That doesn't change, so skip it. We can also move electrons around in the neutral structures and draw minor contributors. Because these are minor, so is their effect on the energies. We'll worry about minor contributors in these reactions only when nothing else is changing. In two of the structures, there's a heap of extra electrons (neg charge) that would desperately like to spread out. This would have a huge impact on stability. Can you help those molecules out by spreading their charges around? They'd sure appreciate it.

3 Now for the tough part — give it your best shot... Which anion do you think is stabilized more by resonance? Is it the raw number of resonance structures, or does the quality matter? Does disrupting an aromatic cycle affect the relative importance? Hmmm... (this is unavoidably an apples vs oranges comparison, but use your chemical intuition... if you dare...)
Lecture outline

Acids and Bases

Bronsted-Lowry definition —

*Acids are proton (H\(^+\)) donors — i.e., an acid can give up an H\(^+\)*

*Bases are proton (H\(^+\)) acceptors — i.e., an H\(^+\) can attach to a base*

Of course, some acids give up an H\(^+\) more readily than others. The greater the tendency to give up an H\(^+\), the stronger the acid. The things we generally think of as "acids" — H\(_2\)SO\(_4\), HCl, etc — are compounds that dissociate completely (in water), but there are also weak acids—some so weak that they don't give up an H\(^+\) except when an extremely strong base is present to "rip" it off.

It's important to be able to rank compounds according to their relative tendencies to give up an H\(^+\) to form their *conjugate bases*. The extent of the dissociation is given by the equilibrium constant for the following reaction. (This is a simplified version of the more correct equation in the text that shows the H\(^+\) being transferred to water; however the concentration of water is not included in the equilibrium that defines the acidity constant, so let's leave it out.)

\[
\begin{align*}
&H^- A \\ &\xrightleftharpoons{K_a} H^+ + A^- \\
K_a &= \frac{[H^+][A^-]}{[HA]} 
\end{align*}
\]

The larger the \(K_a\), the greater the tendency for the acid, HA, to dissociate. Because the \(K_a\)s are so large or so small, it's usually more convenient to talk about \(pK_a\)s —

\[
pK_a = -\log(K_a)
\]

For example, if \(K_a = 10^{-38}\), \(pK_a =

and if \(K_a = 10^{+5}\), \(pK_a =

We could do the same thing to define a scale of basicities that would quantify the tendency of each compound to *accept* an H\(^+\) and form its *conjugate acid*, but instead of creating a second series of numbers, we can just express basicity in terms of the \(pK_a\) of the conjugate acid. This is easier. In other words, looking at the equilibrium above, the basicity of A\(^-\) is related to the acidity of its conjugate acid, HA as follows...
The stronger the acid, \( HA \), (i.e., the more "willing" \( HA \) is to lose \( H^+ \) and form \( A^- \)), the weaker the conjugate base, \( A^- \) (i.e., the less "willing" \( A^- \) is to accept \( H^+ \) and form \( HA \)).

Here's a summary of how the various quantities are related — be sure you understand this — it's important.

- **low** \( pK_a \) \( \Rightarrow \) **large** \( K_a \) \( \Rightarrow \) HA is a stronger acid; A\(^-\) is a weaker base
- **high** \( pK_a \) \( \Rightarrow \) **small** \( K_a \) \( \Rightarrow \) HA is a weaker acid; A\(^-\) is a stronger base

(note that "strong" and "weak" in this context are comparative terms and imply nothing about extent of dissociation in water)

**Acidity and basicity depend on relative stabilities of conjugate acid and base**  
(*not rates* of \( H^+ \) gain or loss, i.e. thermodynamics, not kinetics)

Structural features that stabilize \( A^- \) and/or destabilize HA
make HA more "willing" to give up \( H^+ \) and A\(^-\) less "willing" to accept \( H^+ \)
i.e., increasing the acidity of HA and decreasing the basicity of A\(^-\).

and vice versa

Let's draw a diagram to illustrate this idea. Consider two structurally related acids, HA and HA'.
Let's say HA' is destabilized relative to HA, but its conjugate base, A'\(^-\), is stabilized relative to A\(^-\). Which of these is the stronger acid? Which is the stronger base?

Now let's consider a different situation. Acid HA' is stabilized by a large amount relative to HA and its conjugate base, A'\(^-\), is also stabilized relative to A\(^-\), but not as much. Now which is the stronger acid and which is the stronger base?
**Trends and factors affecting acidity and basicity** —

1. **Electronegativity.** *Across a row* of the periodic table, increasing *electronegativity* makes $A^-$ better able to accommodate negative charge (and $HA^+$ less able to accommodate a positive charge), $\therefore$ increasing acidity of $HA$ (or $HA^+$)

   (variation in bond strength works in opposite direction and is less important)

<table>
<thead>
<tr>
<th>Acid</th>
<th>$pK_a$</th>
<th>Conj Base</th>
</tr>
</thead>
<tbody>
<tr>
<td>$NH_4^+$</td>
<td>$pK_a = 9$</td>
<td>$NH_3$</td>
</tr>
<tr>
<td>$H_3O^+$</td>
<td>$pK_a = -2$</td>
<td>$H_2O$</td>
</tr>
<tr>
<td>$H_2CO_3$</td>
<td>$pK_a = 6.3$</td>
<td>$HCO_3^-$</td>
</tr>
</tbody>
</table>

2. **Bond strength.** *Down a column* of the periodic table, decreasing *bond strength* makes the $H-A$ bond break more easily, $\therefore$ increasing acidity of $HA$

   (variation in electronegativity works in opposite direction and is less important)

3. **Charge.** + charge on acid increases acidity; – charge on acid decreases acidity
4. **Resonance.** Resonance stabilization of conjugate base increases acidity of conjugate acid; resonance stabilization of conj acid decreases its acidity.

Now, you can make this difficult by memorizing these statements, or make it easy by simply thinking about what is stabilized and how that affects the energy change in the reaction! There's no new concept to learn here!

For example, let's look at methanol vs acetic acid...

And, as is our custom, let's draw an energy diagram.

Q: Can't we just simplify this and say "resonance increases acidity"? A: NO!!! That's not true! Resonance stabilization of the conjugate acid will decrease its acidity. And moreover, that's not ever the way we treat factors that affect the stability of a molecule in a reaction — the question is always what is stabilized or destabilized and how does that affect the energy change in the process. This could go either way.
5. **Inductive effects.** Electronegative atoms and groups "pull" (withdraw) e⁻-density through σ-bonds. Electropositive atoms and groups "push" (donate) e⁻-density through σ-bonds. Not surprisingly, the stability of ions is affected much more than neutral molecules. This is analogous to what we saw with resonance — spreading charge around is always better than having it "piled up" in one place. Same principle in this case, but now we're talking about σ-electrons. Anything that pulls e⁻'s away from a – or pushes them toward a + decreases the charge at that point (spreads it around), which is good. Pushing e⁻'s toward a – or pulling them away from a + increases the charge at that point, which is bad.

Examples:

As you might expect, inductive effects decrease with increasing distance.

6. **Hybridization.** Greater s-character of the lone pair orbital of the conjugate base stabilizes it. How does this explain the following acidity trend?

\[
\begin{align*}
\text{C—H} & \quad \text{pK}_a \approx 50 \\
\text{≡C—H} & \quad \text{pK}_a \approx 43 \\
\end{align*}
\]

\[
\begin{align*}
\text{≡C—H} & \quad \text{pK}_a \approx 25
\end{align*}
\]
7. **Hydrogen bonding.** (and anything else that affects stability of an acid or base) some pKₐ comparisons clearly indicate slight stabilization due to intramolecular (internal) hydrogen bonding.

Examples: