Loudon Ch. 3 Review: Acids/Bases/Curved Arrows

Jacquie Richardson, CU Boulder – Last updated 2/5/2016

There are two different definitions of acids and bases that show up in this chapter:

1. Lewis acids accept an electron pair; Lewis bases donate an electron pair
2. Brønsted -Lowry acids donate a proton (H^+ ion); Brønsted -Lowry bases accept a proton

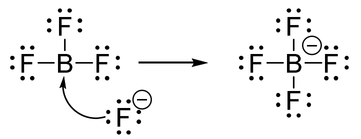
Brønsted -Lowry acids/bases are a subset of Lewis acids/bases. If something is a Brønsted-Lowry base it must also be a Lewis base but the reverse is not true.

Lewis Acids and Bases

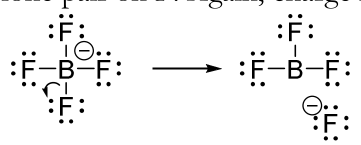
We can show the flow of electrons to a Lewis acid by using curved arrows. These are used to show the movement of **electrons only**, not anything else! Two electrons moving as a pair (like in a reaction between a Lewis acid and base) are shown as a full-headed arrow. (One electron moving by itself is shown as a half-headed or fishhook arrow – we'll cover these later.) The Lewis base "attacks" the Lewis acid by pushing electrons towards it.

Lewis base	Lewis acid	2 electrons move: full-headed arrow	single e^- donor	single e^- acceptor	1 electron moves: half-headed (fishhook) arrow

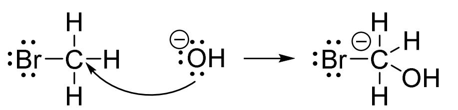
Lewis acids accept electron pairs, so a common category of Lewis acids is atoms with less than a full octet (electron-deficient compounds), such as BF_3. We can show this reacting with an electron-rich compound like F^-, a Lewis base. One of the lone pairs on F^- is sent towards B, creating a new F-B bond afterwards. Note that the total charge is conserved: there's an overall -1 charge before the reaction, so there has to be an overall -1 charge after the reaction.



You can also show this reaction happening in reverse: here, the electrons come out of the F-B bond and recreate the fourth lone pair on F. Again, charge is conserved.

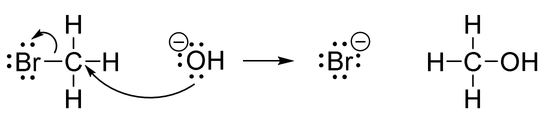


Not all Lewis acids are electron-deficient – some already have a full octet but have a δ^+ charge due to polar bonds. It's tempting to show the same kind of reaction as above, but if we only add new electrons to carbon then we'll violate the octet rule.



Octet violation = bad!

Instead, something else needs to leave the carbon to free up some space. This makes the reaction an **electron pair displacement**. In this case the lone pairs on O are attacking the C and displacing the electrons out of the C-Br bond.



It is also possible to use electrons from a bond to perform the attack, rather than using a lone pair. In this example, even though B has a negative charge, it does not have a lone pair. Instead, it attacks with the electrons out of the B-H bond.

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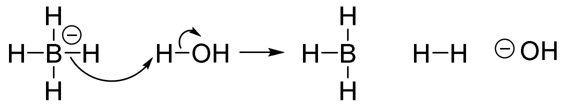
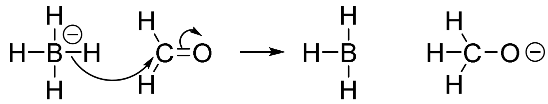
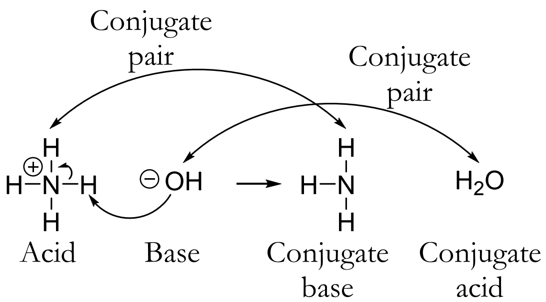


In the displacement reactions we've shown so far, the bond that got broken was a σ bond. It's also possible to break a π bond by attacking it.

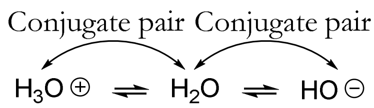


Brønsted-Lowry Acids and Bases

These can be shown with the same curved arrows as before, but now we're specifically looking at attacking a proton. When an acid loses a proton, it becomes a conjugate base. When a base gains a proton, it becomes a conjugate acid. Whether a structure is gaining or losing a proton, the two forms are called a conjugate pair. The stronger an acid is, the weaker its conjugate base is, and vice versa.

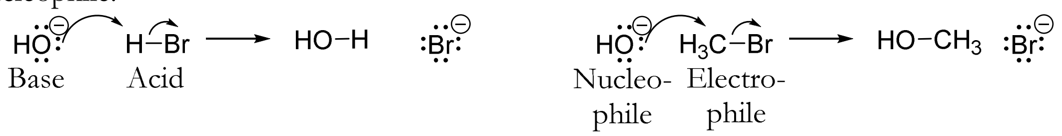


Compounds that can act as either an acid or base are called **amphoteric**. Water is the most common example. This means it's part of two conjugate pairs at once.



Names for Roles of Reactants

When an organic chemist says "acid" or "base", what they normally mean is **Brønsted-Lowry** acid or base. If something acts as a Lewis base without acting as a B-L base (in other words, if it attacks any atom other than a proton), it is called a **nucleophile** (Nu or Nu^-). If something acts as a Lewis acid without acting as a B-L acid (in other words, if it is attacked on any of its atoms other than a proton), it is called an **electrophile** (E or E^+). The only difference between the two reactions below is what group is being attacked by the HO^- - if it's a proton, the HO^- is acting as a base, and if it's a methyl group, the HO^- is acting as a nucleophile.



Another role to consider is the group that gets displaced – the **leaving group** (LG). This group takes the electrons from its former bond with it when it leaves. This means that if you showed the same reaction in reverse, the leaving group would become the base/nucleophile and vice versa.

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Measuring Acid and Base Strength

This is determined by the equilibrium position for an acid-base reaction with water. The equilibrium constant, K_{eq}, is determined the way it normally is: all of the product concentrations, divided by all of the reactant concentrations. However, since H_2O is a reactant and its concentration is assumed to be constant, this term can be multiplied out to give K_a, the acidity constant.

$$HA + H_2O \rightleftharpoons A^{\ominus} + H_3O^{\oplus} \qquad K_{eq} = \frac{[A^{\ominus}][H_3O^{\oplus}]}{[HA][H_2O]} \qquad K_a = K_{eq}[H_2O] = \frac{[A^{\ominus}][H_3O^{\oplus}]}{[HA]} \qquad pK_a = -\log(K_a)$$

Stronger acids have an equilibrium that favors the products more, so the equilibrium will lie farther to the right. This means that **stronger acids have higher K_a values**. However, the possible range of K_a values covers so many orders of magnitude that we usually put it into more manageable terms. We can do this by converting K_a to pK_a. The "p" of something is the negative base-ten log of it (this is the same as with pH, the negative log of $[H^+]$). Since a large K_a means a small pK_a, this means that **stronger acids have lower pK_a values**. Since stronger acids have weaker conjugate bases, this also means that **weaker bases have lower pK_a values**. You can think of pK_a as a rating of how badly a compound wants to hang on to its proton or get its proton back – a large number means it really wants to keep its proton, which makes it a very weak acid and (if it does get deprotonated) a very strong base. Reactions will always favor making the weaker acid and base over the stronger acid and base. The textbook has a table of pK_a values – you do not need to memorize these, but it will be helpful in future to get a feel for where compounds rank relative to each other. (The exact numbers will also vary from book to book.) Here are some examples:

pKa	Acid	Conj. Base
-10	HI	I^-
-1.7	H_3O^+	H_2O
9.3	NH_4^+	NH_3
15.7	H_2O	HO^-

pK_a tables normally only show the acid form explicitly, but it's important to remember that they're describing the balance between the acid and its conjugate base. In many reactions, the strength of the conjugate base is the determining factor in outcome, so you need to mentally convert the compounds in the table to their conjugate bases before comparing them to your compound.

The only pK_a values that can be directly measured in comparison to water are the ones that lie between the pK_a values for water acting as an acid or base (-1.7 to 15.7). Anything outside of this range is harder to measure directly, but it can be measured in relation to an acid with a known pK_a in a solvent other than water. pK_a values can shift by several units depending on conditions such as solvent, but the relative rankings tend to stay the same.

pK_a values can be used to predict the equilibrium in acid-base reactions. The general way to do this is with this equation:

$$AH + B^{\ominus} \rightleftharpoons A^{\ominus} + BH \qquad K_{eq} = 10^{(pKa_{AH} - pKa_{BH})}$$

For example, we can calculate that in a reaction between CH_3^- and H_2O, the equilibrium will massively favor the products.

$$\underset{\text{pK}_a=15.7}{H_3C^{\ominus} + \underset{\text{AH}}{H_2O}} \rightleftharpoons \underset{\text{pK}_a=60}{\underset{\text{BH}}{H_4C} + HO^{\ominus}}$$

$K_{eq} = 10^{(60 - 15.7)} = 10^{44.3}$ = huge!
Equilibrium favors products exclusively

In the reaction between I$^-$ and HCl, the reactants are favored instead.

$$\underset{\text{pK}_a=-6}{I^{\ominus} + \underset{\text{AH}}{HCl}} \rightleftharpoons \underset{\text{pK}_a=-10}{\underset{\text{BH}}{HI} + Cl^{\ominus}}$$

$K_{eq} = 10^{(-10 - -6)} = 10^{-4}$ = small
Equilibrium favors reactants

For a reaction to be considered "quantitative" or ~100% complete, the K_{eq} has to be at least 10^2. This means that less than 1% of the reactants are left.

The K_{eq} for a reaction can also be used to find the energy change for the reaction. This is given in terms of Gibbs free energy, or ΔG°. Since it's an exponential equation, a small change in ΔG° makes a very large change to the K_{eq} for the reaction.

$$K_{eq} = 10^{-\Delta G/(2.3RT)}$$

Relationships between Structure and Acidity

Even if we do not know the pK_a for a compound, we can estimate it based on several trends.

1. Element effect: if you look at the atom that is losing a proton and its place in the periodic table, it will be more acidic as you move left to right and top to bottom in the table.

increasing acidity →

H–CH$_3$ 60	H–NH$_2$ 35	H–OH 15.7	H–F 3.2	increasing acidity ↓
		H–SH 7	H–Cl -3	
			H–Br -5	
			H–I -9	

If we assumed base strength was determined solely by electronegativity, then the left-to-right trend makes sense (F is more stable with a negative charge than C, so it's more willing to act like an acid by giving up a proton). But the top-to-bottom trend does not make sense – F is more electronegative than I, but HI is more acidic. This is because the process of an acid dissociating from its proton can be broken into three theoretical steps. These don't happen in real life acid-base reactions but they can be measured under other conditions.

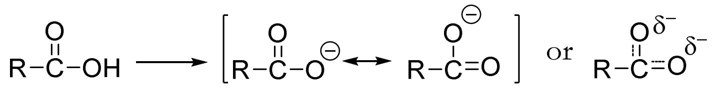
1) $H\text{-}A \longrightarrow H^{\cdot} + A^{\cdot}$ Energy depends on H-A bond strength

2) $H^{\cdot} \longrightarrow H^{\oplus} + e^{\ominus}$ (constant for all acids)

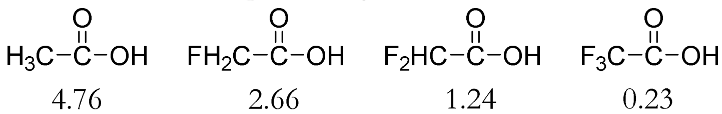
3) $A^{\cdot} + e^{\ominus} \longrightarrow A^{\ominus}$ Energy depends on electronegativity of A

The reason HI is such a strong acid is because even though I is not that electronegative, the H-I bond is so weak that breaking it costs very little energy. This effect is larger than the effect caused by the difference in electronegativities. So vertical differences within the periodic table are caused mostly by different costs in step 1, while horizontal differences are caused mostly by differences in step 3.

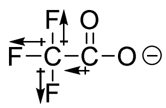
2. Charge effect: Positive charge on something makes it more acidic and negative charge makes it less acidic. This is because they will become more negative after they lose a proton, so the more positive they are to begin with, the more stabilization they will gain. As an example, H_3O^+ has a pK_a of -1.7, while H_2O has a pK_a of 15.7.
3. Polar or inductive effect: This is caused by atoms further away from the acidic site (the atom that loses a proton). We'll use carboxylic acids as examples. When these lose a proton, they take on a negative charge that can be distributed out through resonance. This makes the charge more stable, which means that they're more acidic than most other organic molecules.



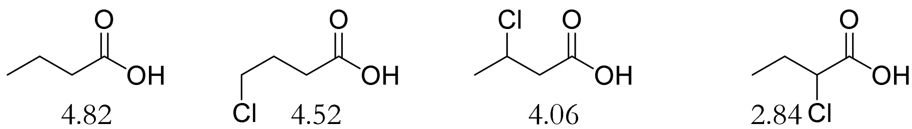
We can look at how different R groups will change the pK_a of the carboxylic acid. We'll start with acetic acid, where R is just a CH_3 group, and replace more and more of its Hs with Fs to see how the pK_a changes.



As it turns out, having more F atoms drops the pK_a by several units. This effect is due to the F-C polar bonds pulling some electron density down the chain away from the carboxylic group, which reduces and stabilizes the negative charge it has when it is in its conjugate base form.



As another example, we can look at the change in pK_a values when the same group is move closer to the acidic site.



Again, this is because the dipole is being pulled along the chain towards the Cl, but the effect gets weaker the further the Cl gets from the carboxylic acid. F and Cl are two examples of groups that are inductively electron-withdrawing. It is also possible to have groups that are inductively electron-donating, so they destabilize the negative charge and make the compound less acidic instead of more.

Showing Resonance with Curved Arrows

We've already seen how to draw resonance structures for simple molecules in Ch. 1, but for more complicated molecules it can sometimes be difficult to figure out multiple Lewis dot structures just by placing electrons. For this reason, curved arrows are helpful to more electrons around and generate a new resonance form from a structure you already know. Some rules to follow are:

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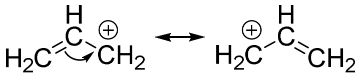
1. The number of total electrons must stay the same. If there's an overall negative charge on one form, there must be an overall negative charge on all forms.
2. Electrons typically only move over by one atom at a time. They don't hop long distances around the molecule.
3. Nuclei don't move around, only electrons. So you can't change the connectivity of a structure by moving an atom to somewhere else. This means that π bonds and charges tend to be the parts that move around most often.
4. The same rules we saw above for curved arrows still apply. If you're trying to add electrons to an atom with a full octet, then that atom has to relinquish electrons to somewhere else.

With this in mind, we can look at an example. For clarity, this is shown two different ways: with the atoms explicitly written, and as skeletal structures. Here, the positive carbon on the right end of the molecule is electron-deficient, so the π bond donates some electron density to it. This leaves the leftmost carbon electron-deficient afterwards.



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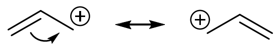
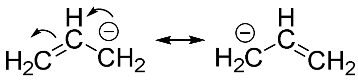


As another example, we can look at an electron-rich molecule. In this case the negative carbon is sending its electrons to create a new π bond with the central carbon, but this means the central carbon has to drop it existing π bond, which becomes a new lone pair elsewhere.



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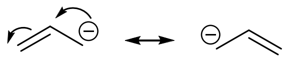

One more example: something with no charges, only π bonds. This shows that all the C-C bonds in benzene are equivalent.