Chapter 3 – Acids & Bases. Curved-Arrow Notation

Introduction

This chapter combines two new challenges: a new way to draw electron patterns and a new way to talk about some chemical reactions. Probably the best way to appreciate these challenges is to look at some end-of-chapter problems:

- Loudon 3.25: Give the *curved-arrow notation* for, and *predict the* immediate *product of* each of the following reactions.
- Loudon 3.34: *Predict the products* of each of the following reactions. Use the *curved-arrow notation* to help you.
- Loudon 3.44: Which of the following two reactions would have an *equilibrium constant more favorable to the right*?

The italics are mine. Notice what they highlight in the first problem: using a new drawing tool (curved arrows) and making a new kind of prediction (the outcome of a chemical reaction). Predictions might really throw you the first time you try your hand at it because Loudon won't tell you what type of reaction to expect. He will simply draw the reactants and wait for you to do the rest.

Notice that the second problem calls upon the same skills as the first. This is particularly interesting when you realize that these problems are separated by *two pages* worth of material. Loudon is like a terrier. He's got something in his teeth ("draw", "predict") and he isn't going to let go. In fact, these two tasks are going to permeate the entire book.

The third problem, at first glance, looks substantially different from the other two, but it really isn't. You are shown a pair of reactions (reactants and products for each) and asked to compare them. This calls for some very high order thinking too. To solve this problem, you must:

- identify the class of reaction in each equation
- determine the roles of the reactants *and* products
- decide which reactant pair is more likely to turn into its companion products

That's a lot to handle. But the first two steps are also needed (and practiced) when you do the first two problems. So work hard, but be patient. The pieces will fall into place.

Checklist

When you have finished studying Chapter 3, you should be able to:

1. Perform the *mental* calculations[1] needed to describe acid-base reactions
   a. calculate pK_a from K_a and *vice versa*
   b. calculate K_{eq} for acid-base reaction from K_a of reactant and product acids
   c. calculate pH from $[H_3O^+]$ and *vice versa*
   d. calculate $[A^-]/[HA]$ from K_a and pH and *vice versa*
2. identify and describe a Bronsted-Lowry acid-base reaction
   a. identify an acid, draw its conjugate base
   b. identify a base, draw its conjugate acid
   c. decide whether a reaction is un/favorable
   d. draw curved arrows to show electronic changes
3. identify and describe both a Lewis acid-base association and dissociation reaction
   a. identify/draw the Lewis acid, Lewis base, and the complex they form (or are derived from)
   b. draw curved arrows to show electronic changes
4. draw curved arrows to show important changes in electron patterns associated with:
   a. resonance
   b. chemical reactions
   c. use curved arrows to assign general reaction role labels:
      i) nucleophile
      ii) electrophile
      iii) leaving group
5. describe how a given molecule would be transformed if it acted as a Bronsted-Lowry acid, Bronsted-Lowry base, Lewis acid, Lewis base
   a. identify its most reactive sites
   b. describe its reactivity, e.g., Bronsted-Lowry acid strength, Bronsted-Lowry base strength
   c. rationalize its reactivity
6. know the pK_a of the OH and NH functional groups in the chart on the last page of this handout

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[1] Calculators will not be allowed on exams so "calculate" means working with numbers that have been rounded to the closest power of 10 and, when necessary, taking logs and antilogs. Recall $\log_{10}(10^x) = x$. Recall $\text{antilog}_{10}(x) = 10^x$. Recall $10^x/10^y = 10^{x-y}$.

7. predict/rationalize the relative reactivity of a series of Bronsted-Lowry acids and bases by considering:
    a. element effects
    b. charge effects
    c. "field/inductive" effects:
8. describe the bonding and antibonding molecular orbitals associated with *polar* covalent bonds
    a. draw an orbital interaction diagram
    b. draw orbital cartoons and describe the relative contributions made by each atomic orbital

Top 14 Problems for Chapter 3

All of these problems are drawn from the *Additional Problems* located at the end of the chapter 3. Except for #45, all have solutions in the Solutions Manual.

The top 14 for chapter 3 are **25ac, 29a, 31c, 32cd, 33ac, 34ac, 35a, 39ac, 40ab, 42a, 43abc, 44, 45, 49**

Additional Readings

Two ROCO readings that might prove helpful:

- *Acid-Base*
- *Arrows*

Supplement

Calculations

You will not have a calculator to use on exams, so I am not going to ask you to perform mental calculations of any complexity. Typical calculation questions might include:

- Use pK_a values to estimate K_{eq}
- Use pK_a and pH values to estimating $[A^-]/[HA]$ ratio
- interconvert pH and $[H_3O^+]$

That's pretty much the limit *for exam calculations*. The pK_a values that you need to know (or might be given) will be *integer* powers of 10 only. This greatly simplifies things. You might have to take the log of 10^5 (or the antilog of 5), but you won't have to take the log of 4×10^5.

Your book shows you how to interconvert free energy and pK_a (and also K_{eq}). The fact that free energy and pK_a are proportional is extremely handy in chemical calculations, and I will almost certainly use these formulas in the future. Please familiarize yourselves with eqs. 3.28, 3.29, 3.30, 3.31ab, but don't expect to do any *exam calculations* with them, *except* for the material in the next paragraph.

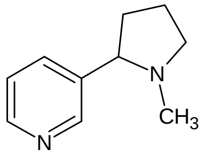
Your book (p. 107, Table 3.2) points out two useful number facts:

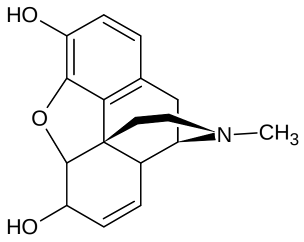
- $K_{eq} = 1$ corresponds to $\Delta G^o = 0$.
- A 10-fold increase (or decrease) in K_{eq} corresponds to subtracting (or adding) 5.7 kJ/mol to ΔG^o (only for a system at 298 K, but don't worry about other temperatures).

Working with Bronsted-Lowry acid-base reactions

These are proton transfer reactions. Most of the reactions that will interest us at this point will involve proton transfer between various combinations of O and N atoms, (O to O, O to N, N to O, N to N). Proton transfers involving halogen acids, HX (X = F, Cl, Br, I) will also be important.

It will take practice to learn the O and N functional groups (see last page of study guide; remember that this chart will not be available during the exam – you must memorize the information it contains). It will take additional practice to recognize functional groups when they are "camouflaged" by typical molecular surroundings. For example, can you see that both nicotine (left) and morphine (right) contain amine groups and will, to a first approximation, be equally basic? (What other acid/base groups can you spot?)[2]





Remember, it's only *after* you cross the hurdle of functional group identification that the real fun will begin: predicting the most reactive spot in each molecule, predicting the ionization state as a function of pH, and estimating K_{eq}

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[2] Nicotine contains a *pyridine* ring (conjugate acid pKa ~5) and an amine (conjugate acid pKa ~10). Morphine contains an amine, a *phenol* (pKa ~10), an *alcohol* (pKa ~18), and an *ether* (conjugate acid pKa ~-2).

for a reaction involving one of these species and some other acid or base.

One of the most complicated tasks in this chapter is to predict the outcome of a reaction given just the starting materials, HX and HY. One logical way to do this is:

1. Identify the most acidic site in HX and the most basic site in HY
2. Write a chemical equation assuming the sites identified in step 1 behave as expected
3. Use pK_a values to determine whether this equilibrium is favorable
4. Repeat steps 1-3, but reverse the roles of HX (treat it as a base) and HY (treat it as an acid)
5. One possibility will always have a much more favorable K_{eq} than the other. This will be the only outcome worth considering.

Here's a sample that you can practice on: the reaction of NaOH and CH_3CO_2H might yield H_2O and CH_3CO_2Na (correct) or it might yield NaO^- and $CH_3CO_2H_2^+$ (incorrect). Try using the five-step procedure described above to show why only the first outcome is reasonable.

Lewis acid-base reactions

At this point you will not be expected to predict whether a Lewis acid-base association (or dissociation) is favorable or not, but here is a general observation: *carbocations* (R_3C^+) are very strong Lewis acids. Therefore, the reaction of a carbocation with almost any Lewis base will be favorable.

Molecular reactivity patterns

Any molecule that contains H can act as a Bronsted-Lowry acid and practically any molecule can act as a Bronsted-Lowry base. This makes acid-base behavior incredibly open-ended and leads to considerable confusion when you try to decide what an unfamiliar molecule will do next.

The way to get out of this bind is to identify and focus on the most reactive sites in the molecule. In other words, first find the most acidic H (it might help to "remove" different protons and draw the corresponding conjugate bases) and then find the most basic site (again, it might help to "add" a proton to different atoms and draw the corresponding acids).

The most acidic H can be identified in various ways.

- If you have a potential map, look for one "blue" H.
- Use the "element" effect: OH groups are generally more acidic than NH, so find all OH sites. If there aren't any, find all NH sites.
- Use the "charge" effect: N^+H acids are generally more acidic than NH acids. Unfortunately, they are also more acidic than certain OH acids too, so always consider the "charge" effect even when relying on other effects, e.g., the "element" effect.
- If the element and charge effects leave you with ambiguities, try using the resonance and field/inductive effects.
- If you can identify all of the acidic functional groups in your molecule, compare their pK_a's. The site with the lowest pK_a is the most acidic one.

Similar lines of reasoning can be used to identify the most basic site. It may prove helpful to draw the conjugate acids of the bases that are trying to compare. Give it a try. Organic chemistry is learned and practiced through the fingertips.

Predict / rationalize reactivity trends

This applies only to Bronsted-Lowry acids and bases.

It is helpful to remember that acid strength and base strength are defined by the position of a chemical equilibrium. To put it another way, acid or base "strength" reflects a free energy *change*. We need to look at *two* molecules, a reacting molecule and its conjugate, before settling on an answer or explanation.

At this point, to rationalize a reactivity trend simply means to invoke the right effect: Element? Charge? Resonance? Field/Inductive? Be prepared to elaborate on these labels with additional information and/or drawings.

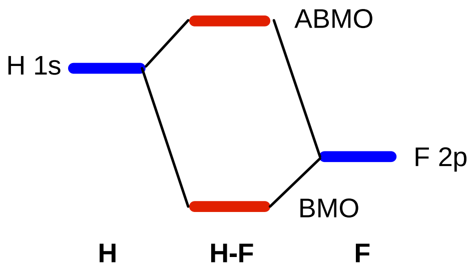
- Element effect – could be due to bond energy differences or electronegativity differences
- Charge effect – make sure you correctly identify the formal charge on the atom bonded to H

- Resonance effect – draw important (high weight) resonance structures
- Field/Inductive effect – draw partial charges on influential atoms, draw structural formula that shows the location of charged atoms relative to the reaction site

Describe MO Models for Polar Covalent Bonds

The basic MO model of covalent bonds requires only a few tweaks in order to work with polar covalent bonds.

First, the orbital interaction diagram should be drawn with the valence AO of the *more electronegative* atom at lower energy. For example, for HF, we would draw:



Electrons get added to this diagram in the same way as before, and the number of electrons has the expected effect: 2 electrons provides maximum bonding, 4 electrons makes the atoms more favorable than the molecule.

The second tweak is to adjust the shapes of the BMO and ABMO. The *nodal* structure is exactly the same as before. The only thing that changes is the amount that each AO contributes to each MO. The rules for the latter are simple:

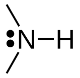
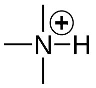
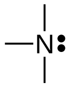
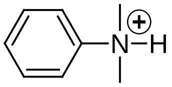
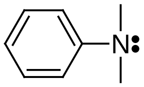
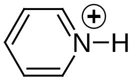
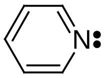
- the BMO is dominated by the lower energy AO (F 2p in the case of HF)
- the ABMO is dominated by the higher energy AO (H 1s in the case of HF).

These tweaks are consistent with our expectations regarding bond polarity. If the BMO is biased towards the more electronegative atom, the bonding electrons will spend more time near this atom and the bond will be polar. At the same time, the less electronegative atom will become electron-poor and will attract nucleophiles.

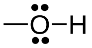
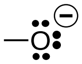
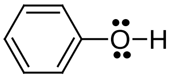
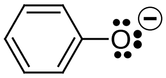
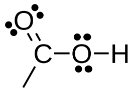
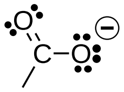
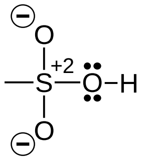
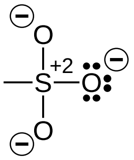
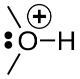
Common Acidic Functional Groups

An “empty” bond indicates that an alkyl group (R) or hydrogen can occupy this position.

NH acids

HA	A^-	pK_a	Factors that enhance NH acidity
		36	—
	 “amine”	10	Formal charge
	 “aniline”	5	Formal charge + lone pair delocalization in conj. base
	 “pyridine”	5	Formal charge + hybridization

OH acids

HA	A^-	pK_a	Factors that enhance OH acidity
		18	—
 “phenol”		10	Lone pair/charge delocalization in conj. base
		5	Lone pair/charge delocalization in conj. base (+ field/inductive effect of C=O)
		0	Inductive effect + field effect of SO_2 dipole in conj. base
 “oxonium ion”		–2	Formal charge

Only a few factors are needed to explain the reactivity of these acids and these factors can also be applied to many other functional groups too.