

Chapter 6 Worksheets

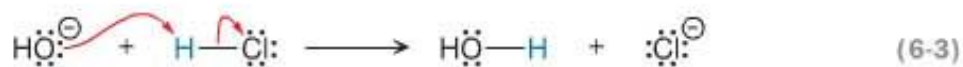
Organic Chemistry

In Equation 6-3, circle all of the electrons that are involved in the chemical reaction. Label each curved arrow as either “bond breaking” or “bond formation.”

Answers to Your Turns are in the back of the book.

6.1 YOUR TURN

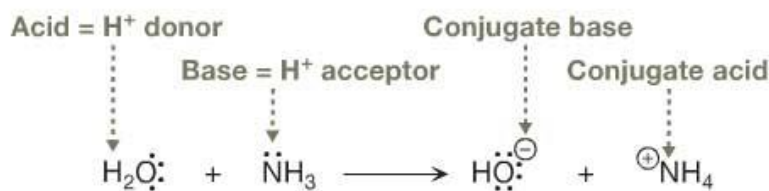
The curved arrow notation for the reaction in Equation 6-1 is illustrated in Equation 6-3.



SOLVED problem 6.1 Draw the curved arrow notation for the proton transfer between ammonia (NH_3) and water, where water acts as the acid and ammonia acts as the base.

Think What does it mean to be an acid? A base? What are the important electrons to keep track of during the course of the reaction? What bonds are broken? What bonds are formed?

Solve Because water acts as an acid (a proton donor) and ammonia acts as a base (a proton acceptor), we may write the reaction as follows:

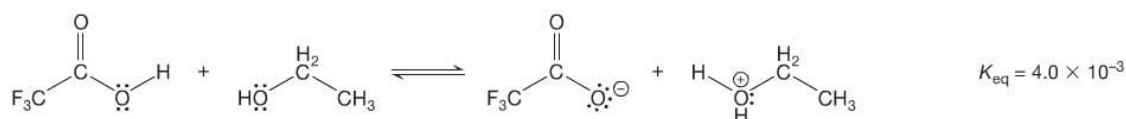
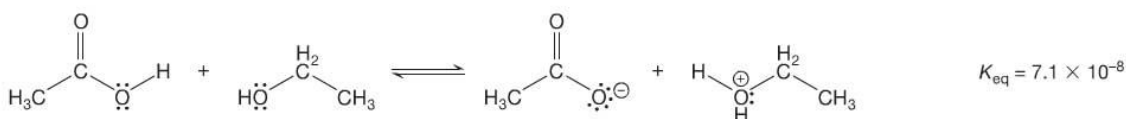


problem 6.2 Draw the curved arrow notation for the reverse of the reaction in Solved Problem 6.1.

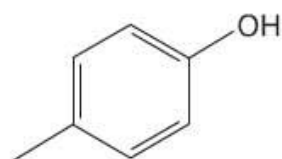
problem 6.3 Draw the curved arrow notation for the proton transfer reaction between NH_3 and H_2O , in which NH_3 acts as the acid and H_2O acts as the base.

6.2 YOUR TURN

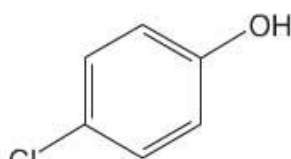
Add the curved arrow notation to each of the following reactions. Based on the K_{eq} values, which reaction tends to form more products at equilibrium?



SOLVED problem 6.4 Which of the following is a stronger acid? By what factor?



4-Methylphenol
 $\text{p}K_{\text{a}} = 10.26$

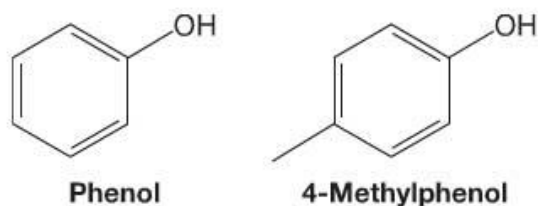


4-Chlorophenol
 $\text{p}K_{\text{a}} = 9.43$

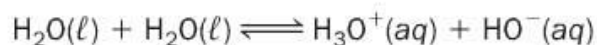
Think Is the stronger acid the one with the more positive $\text{p}K_{\text{a}}$ or the less positive $\text{p}K_{\text{a}}$? What is the difference in their $\text{p}K_{\text{a}}$ values and how can that difference be used to calculate the difference in their acid strengths?

Solve The compound with the less positive $\text{p}K_{\text{a}}$ value, 4-chlorophenol, is the stronger acid. The difference in $\text{p}K_{\text{a}}$ values is $10.26 - 9.43 = 0.83$, which corresponds to a difference in acid strength of $10^{0.83} = 6.8$. Thus, 4-chlorophenol is 6.8 times stronger an acid than 4-methylphenol.

problem 6.5 Which is a stronger acid, phenol or 4-methylphenol? By what factor?
(Hint: Consult Table 6-1 and Solved Problem 6.4.)



problem 6.6 Recall from general chemistry that water undergoes *autoionization*, a reaction in which water acts as both an acid and a base:



The expression for the autoionization constant for water, K_w , is the product $K_w = [\text{H}_3\text{O}^+(\text{aq})]_{\text{eq}}[\text{HO}^-(\text{aq})]_{\text{eq}}$. Using water's $\text{p}K_a$ value, calculate K_w .

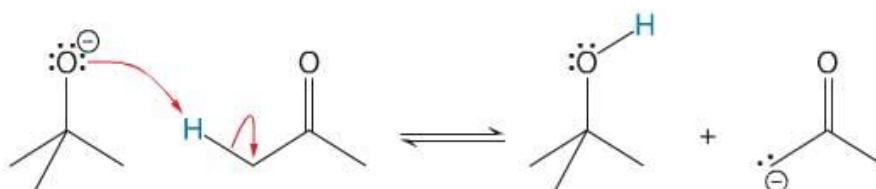
problem 6.7 In the following proton transfer reaction, the hydronium ion (H_3O^+) acts as the acid and water acts as the base.



- (a) Write the expression for the equilibrium constant, K_{eq} , according to Equation 6-6 and evaluate it.
- (b) Next, evaluate K_a according to Equation 6-7. Convert this value of K_a to $\text{p}K_a$ and compare your answer to the value in Table 6-1.
-

problem 6.8 Which is a stronger base, Cl^- or the phenoxide anion ($\text{C}_6\text{H}_5\text{O}^-$)? By what factor? Explain. (*Hint*: Consult Table 6-1.)

SOLVED problem 6.9 Predict which side of the following reaction is favored. To what extent is that side favored?



Think What acid is present on each side of the reaction? Which one is stronger? What is the difference in their $\text{p}K_a$ values?

Solve The acid on the left is propanone (acetone), $(\text{CH}_3)_2\text{C}=\text{O}$, whose $\text{p}K_a$ value is 20. The conjugate acid on the right is methylpropan-2-ol (*tert*-butyl alcohol), $(\text{CH}_3)_3\text{COH}$, whose $\text{p}K_a$ is 19. Therefore, the acid on the right is stronger (lower $\text{p}K_a$), making the left side of the equilibrium favored. Using Equation 6-11, $K_{\text{eq}} = 10^{(19 - 20)} = 10^{-1} = 0.1$. Thus, the left side of the equation is favored over the right by a factor of 10.

problem 6.10 Repeat Solved Problem 6.9 using $(\text{CH}_3)_2\text{N}^-$ as the base.

problem 6.11 Derive the result in Equation 6-11. (*Hint*: The expression for K_{eq} is obtained from the reaction in Equation 6-9. You will need to use Equation 6-8 to substitute for $\text{p}K_a$. You will also need to use the following two properties: $10^{\log x} = x$ and $\log x + \log y = \log xy$.)

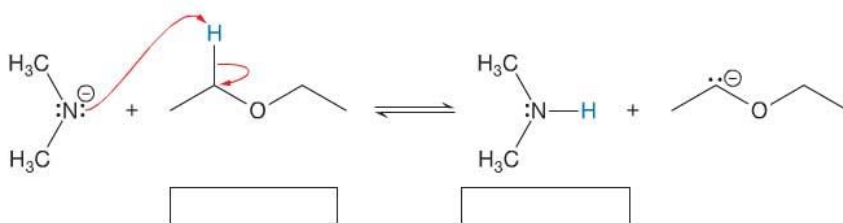
YOUR TURN 6.3

What are the pK_a values of HCl and H_3O^+ in Equation 6-12, and do they verify that HCl is a stronger acid than H_3O^+ ?

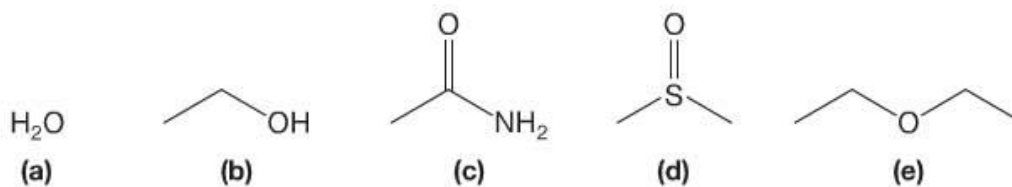
YOUR TURN 6.4

What are the pK_a values of H_2O and $(CH_3)_2NH$ in Equation 6-13, and do they verify that H_2O is a stronger acid than $(CH_3)_2NH$?

Verify the preceding statement that diethyl ether would be a suitable solvent for $(CH_3)_2N^-$. To do so, use Table 6-1 to fill in the boxes below with the appropriate pK_a values and label which one is the stronger acid. Indicate which side of the reaction is favored at equilibrium. Is this the same side that is favored in Equation 6-13?

**6.5 YOUR TURN**

problem 6.12 With respect to the leveling effect, determine whether each of the following solvents would be suitable for a reaction involving $HC\equiv C:^-$ as a reactant? (*Hint: Is it desirable for HCC^- to react with the solvent?*)



6.6 YOUR TURN

In Figure 6-1, how many pH units above the acid's pK_a must the solution be to cause the acid to dissociate nearly 100%? _____
How many pH units below the acid's pK_a must the solution be for the acid to be nearly 100% associated? _____

YOUR TURN 6.7

In Figure 6-1, sketch a plot of the percent dissociation of an acid with $pK_a = 9$ as a function of pH.

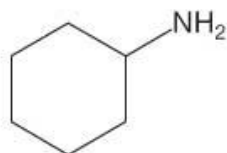
YOUR TURN 6.8

In Figure 6-2b, as the reaction coordinate increases, does the distance between Cl and H increase or does it decrease? _____ Does the distance between the O and H increase or decrease? _____

YOUR TURN 6.9

Indicate ΔG_{rxn}° and ΔG^{\ddagger} in Figure 6-2b the way it is done in Figure 6-2a. Which reaction has a greater ΔG^{\ddagger} , the one in Figure 6-2a or the one in Figure 6-2b? _____

SOLVED problem 6.13 Using Table 6-1, estimate the pK_a for the NH_2 protons in cyclohexylamine.

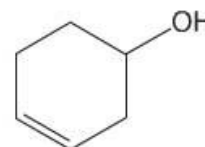
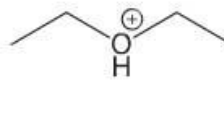
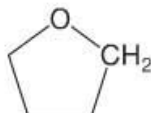
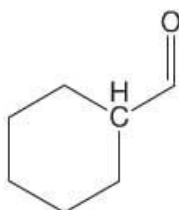
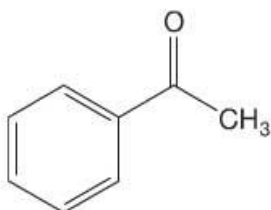


Cyclohexylamine

Think On what functional group do the H atoms appear? What molecule(s) in Table 6-1 have the same functional group? Are there any nearby electronegative atoms or adjacent double bonds?

Solve The H atom in question is part of an amine functional group. According to Table 6-1, the pK_a of $(CH_3)_2NH$, another amine, is 38. Because cyclohexylamine does not have any nearby electronegative atoms or adjacent double bonds, we estimate its pK_a to be ~ 38 , too.

problem 6.14 Using Table 6-1 and/or Appendix A, estimate the pK_a for the proton explicitly shown on each of the following compounds.



(a)

(b)

(c)

(d)

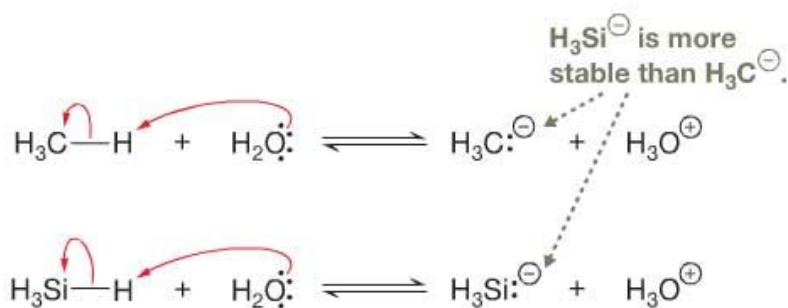
(e)

problem 6.15 Draw an energy diagram similar to Figure 6-6, using H_3O^+ and H_2O as the acids. Based on the energy diagram, which acid is predicted to be stronger? Is this consistent with their relative $\text{p}K_{\text{a}}$ values?

SOLVED problem 6.16 Predict which has a lower $\text{p}K_{\text{a}}$: CH_4 or SiH_4 .

Think Which is more stable, H_3C^- or H_3Si^- ? Based on their relative stabilities, which anion's conjugate acid is deprotonated more favorably? How does that correspond to the relative $\text{p}K_{\text{a}}$ values of the uncharged acids?

Solve The negative charges in H_3C^- and H_3Si^- appear on C and Si, respectively, which are different atoms in the same column of the periodic table. Because Si is significantly larger than C, H_3Si^- is more stable than H_3C^- . Thus, the products of the second reaction below are more stable than the products of the first.



Consequently, SiH_4 is deprotonated more favorably than CH_4 , making SiH_4 the stronger acid. SiH_4 has a lower $\text{p}K_{\text{a}}$ than CH_4 .

Verify that HCl is a stronger acid than H_2S by looking up their $\text{p}K_{\text{a}}$ values in Table 6-1. HCl _____ H_2S _____

6.10 YOUR TURN

YOUR TURN 6.11

Verify that H_3O^+ is a stronger acid than H_4N^+ by looking up their $\text{p}K_a$ values in Table 6-1. H_3O^+ _____ H_4N^+ _____

problem 6.17 Which is a stronger acid, HBr or HI? Explain.

problem 6.18 Which is a stronger acid, CH_4 or PH_3 ? Explain.

YOUR TURN 6.12

Verify the relative acidities of ethane, ethene, and ethyne by looking up their $\text{p}K_a$ values in Table 6-1.

$\text{p}K_a$: $\text{H}_3\text{C}-\text{CH}_3$ _____ $\text{H}_2\text{C}=\text{CH}_2$ _____ $\text{HC}\equiv\text{CH}$ _____

SOLVED problem 6.19 Predict which acid is stronger: $(\text{CH}_3)_2\text{C}=\text{OH}^+$ or $(\text{CH}_3)_2\text{CH}-\text{OH}_2^+$.

Think Which atom bears the positive charge in each acid? What is the hybridization of each of those atoms, and which atom has a greater effective electronegativity? How do their relative effective electronegativities correspond to the relative stabilities of the positively charged species? Based on those stabilities, which acid undergoes deprotonation more favorably?

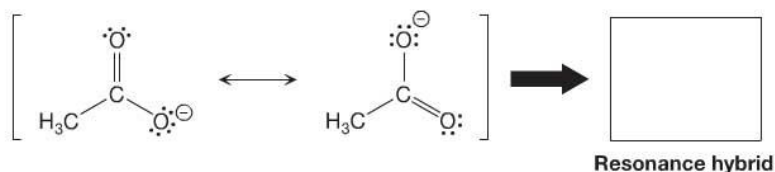
YOUR TURN 6.13

Use Table 6-1 to look up the $\text{p}K_a$ values of ethanoic acid and ethanol.

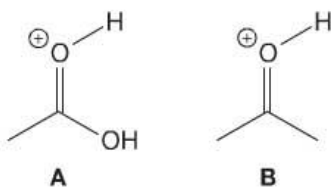
$\text{p}K_a$: Ethanoic acid _____ Ethanol _____

problem 6.20 Which is a stronger acid: $\text{CH}_3-\text{NH}_3^+$ or $\text{HC}\equiv\text{NH}^+$?

In the space provided here, draw the curved arrow notation for the conversion of one of the ethanoate anion's resonance structures into the other and draw the resonance hybrid. (You may want to review Section 1.10.)

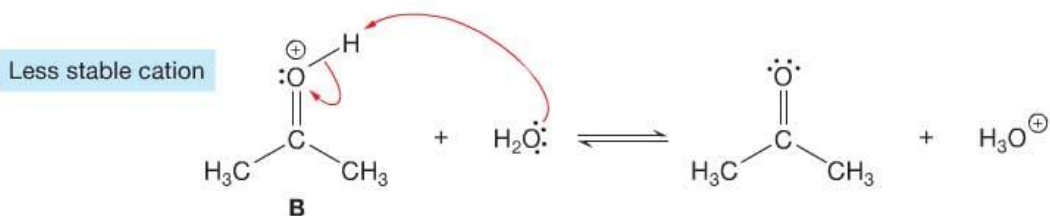
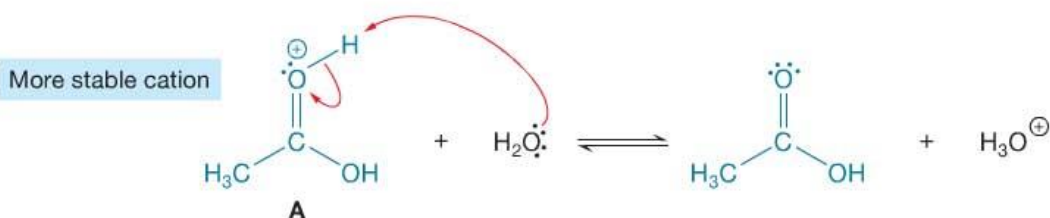


SOLVED problem 6.21 Predict which of the following species is a stronger acid:

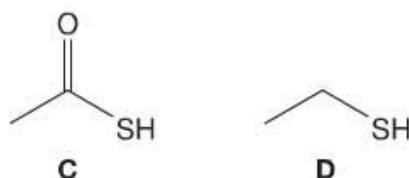


Think Write reactions that depict each acid being deprotonated by a base. Do you expect a significant difference in energy between the reactants of one and the reactants of the other? Between the products of one and the products of the other? Are the charge-bearing atoms different in these two acids? Do they have different effective electronegativities? Do the ions differ in resonance delocalization of the charge?

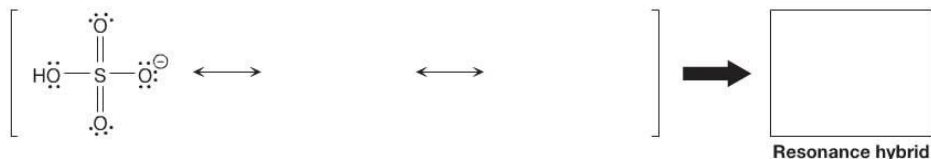
Solve The acids can be deprotonated by water according to the following reactions:



problem 6.22 Which of the following compounds is a stronger acid? Explain.



In the space provided, draw the two remaining resonance structures of HSO_4^- that illustrate the sharing of its negative charge. Be sure to include the appropriate curved arrows. Then, draw the corresponding resonance hybrid.

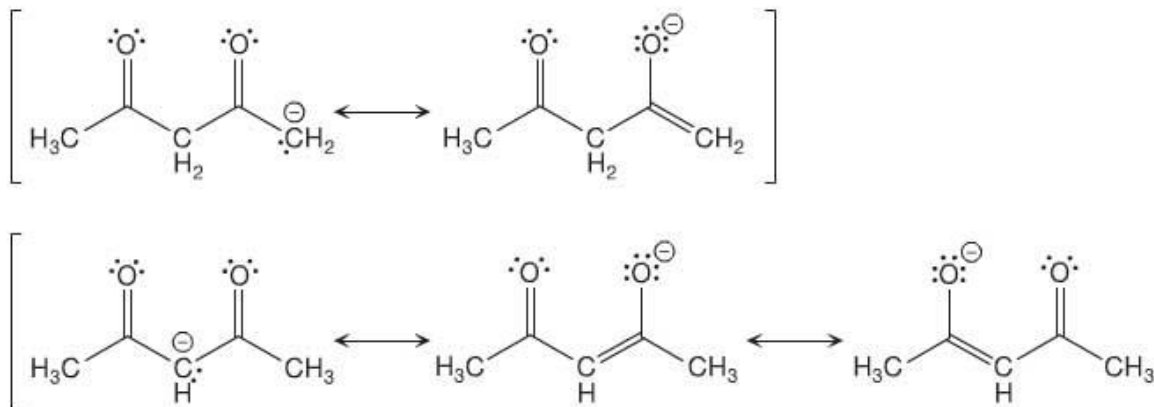


SOLVED problem 6.23 Deprotonation in pentane-2,4-dione may occur at a terminal C atom or at the central C atom. Which site is more acidic? Explain.



Think Does charge stability play a role in the acid or in the conjugate bases? What, specifically, leads to differences in charge stability? The type of atom? Effective electronegativity? Resonance delocalization of the charge? How are the answers to these questions related to the relative strengths of the acids?

Solve The acid is uncharged, so we must look for differences in charge stability in the possible conjugate bases. Since both acidic protons are attached to sp^3 -hybridized C atoms, neither the type of atom nor effective electronegativity should play a role. We do find, however, that there is a difference in resonance stabilization of the resulting charge.



If deprotonation occurs at a terminal C, then the resulting negative charge in the conjugate base is delocalized over the C atom and an O atom via resonance. On the other hand, if deprotonation occurs at the central C, then the negative charge is delocalized over the C atom and two O atoms. As a result, the negative charge that develops is less concentrated, so the conjugate base is more stable. This makes the central C atom more acidic than a terminal C atom.

Add the appropriate curved arrows to the resonance structures in Solved Problem 6.23 to show how each is transformed into the one on its right.

6.16 YOUR TURN

problem 6.24 Based on differences in resonance delocalization, predict whether HNO_3 or $\text{CH}_3\text{CO}_2\text{H}$ is the stronger acid. Explain. (*Hint*: In this case, you can ignore the fact that the O atoms are bonded to different atoms [i.e., N vs. C].)

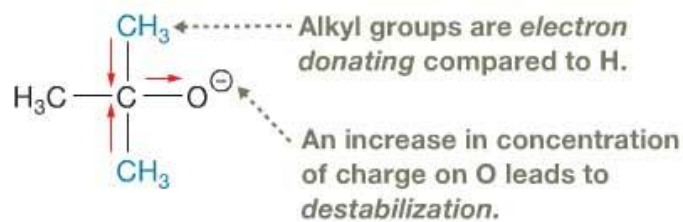
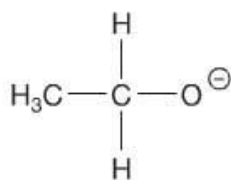
problem 6.25 Predict which of the following protonated alcohols is the stronger acid.



Most substituents, like chlorine, are inductively electron-withdrawing groups because most atoms common in organic compounds are more electronegative than hydrogen. However, there are a handful of substituents that are inductively **electron donating**. A silicon atom, for example, is electron donating relative to hydrogen because silicon is less electronegative than hydrogen.

The most common electron-donating groups in organic chemistry are *alkyl groups*. $(\text{CH}_3)_3\text{COH}$ ($\text{p}K_a = 19$), for example, is about three $\text{p}K_a$ units *less acidic* than $\text{CH}_3\text{CH}_2\text{OH}$ ($\text{p}K_a = 16$), suggesting that $(\text{CH}_3)_3\text{CO}^-$ is less stable than $\text{CH}_3\text{CH}_2\text{O}^-$. $(\text{CH}_3)_3\text{CO}^-$ is less stable because the electron-donating ability of the CH_3 groups compared to H atoms increases the concentration of negative charge on O.

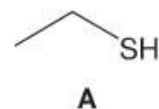
Less stable anion



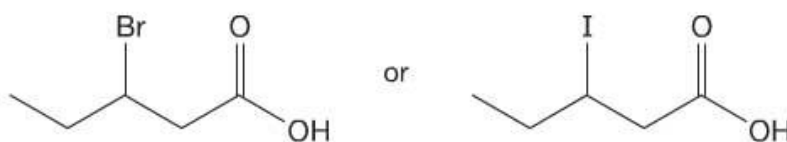
YOUR TURN 6.17

Draw the arrow in CH_3NH_3^+ in the previous graphic to represent the inductive effect of the CH_3 group.

problem 6.26 Predict which of these compounds is a stronger acid. Explain.



SOLVED problem 6.27 Predict which of the following carboxylic acids is more acidic.

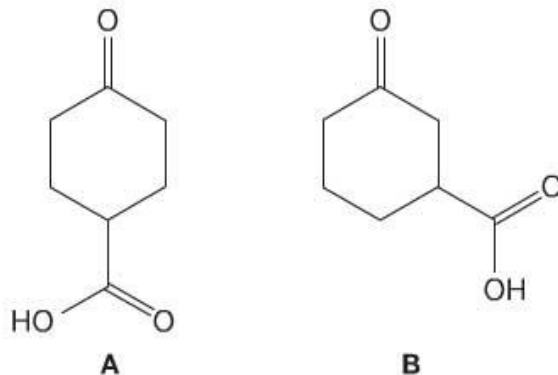


Think For each acid, does the stability of the acid or the stability of the conjugate base dictate $\text{p}K_a$? Do electron-donating or electron-withdrawing effects stabilize those species? Are the Br and I substituents electron donating or electron withdrawing? Which substituent invokes stronger inductive effects?

Solve These are uncharged acids, so their $\text{p}K_a$ values are dictated by the stability of their negatively charged conjugate bases. Both Br and I are electron-withdrawing substituents, so they stabilize negatively charged species. Br is more electronegative than I, so Br better stabilizes the conjugate base, in which case the acid on the left is stronger.

problem 6.28 Which acid is stronger, $\text{O}_2\text{NCH}_2\text{CH}_2\text{OH}$ or $\text{H}_2\text{NCH}_2\text{CH}_2\text{OH}$? Explain. (*Hint*: Draw out the complete Lewis structure for each.)

problem 6.29 Which carboxylic acid functional group has the more acidic proton? Explain.



YOUR TURN 6.18

Verify the differences in pK_a between the protonated and uncharged amines and alcohols just mentioned by estimating the pK_a values of the generic species shown below based on actual compounds in Table 6-1. Write them in the spaces provided here.

pK_a : $R-NH_3^+$ _____ $R-NH_2$ _____ $R-OH_2^+$ _____ $R-OH$ _____

YOUR TURN 6.19

Verify the preceding statements by estimating the pK_a values of the generic alcohol, amine, alkane, and terminal alkyne species shown below based on actual compounds in Table 6-1. Write them in the spaces provided here.

pK_a : $R-OH$ _____ $R-NH_2$ _____ $R-CH_3$ _____ $RC\equiv CH$ _____

In the preceding graphic, draw the curved arrows needed to show how each resonance structure of $C_6H_5NH^-$ is converted to the one on its right. Then, draw the resonance hybrid to the right of the resonance structures.

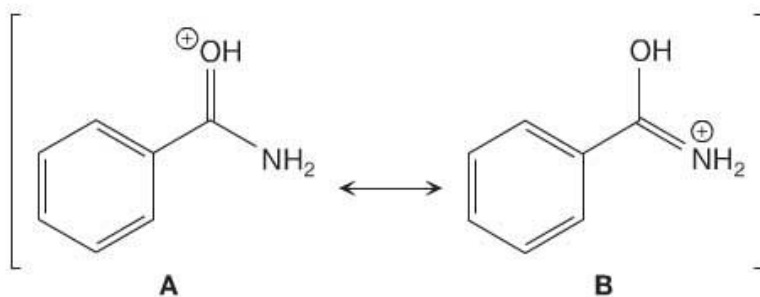
6.20 YOUR TURN

problem 6.30

- (a) Draw the curved arrows necessary to convert the resonance structure on the left into the one on the right.
- (b) Which resonance contributes more to the hybrid? Explain.



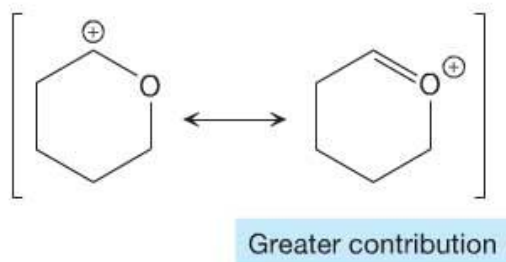
problem 6.31 Which resonance structure contributes more to the hybrid? Explain.



problem 6.32 Of the following two resonance structures, the greater contribution is on the right.

(a) Explain why this is counterintuitive based on charge stability.

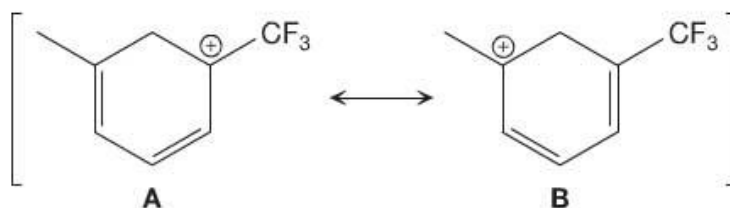
(b) Why does the structure on the right contribute more?



(a)

(b)

problem 6.33 Predict which of the following is the more important resonance contributor. Explain.



problem 6.34 Draw the dominant form of alanine in solutions whose pH values are 1, 4, 8, and 11.

problem 6.35 Draw the structure of the most abundant form of glutamic acid in solutions whose pH values are 1, 3, 5, and 11. Do the same for cysteine in solutions whose pH values are 1, 4, 6, 9, and 11.

problem 6.36 Draw the structure of the most abundant form of arginine in solutions whose pH values are 1, 4, 8, 10, and 14. Do the same for histidine in solutions whose pH values are 1, 3, 5, 7, and 11.

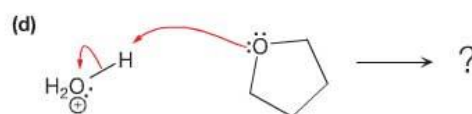
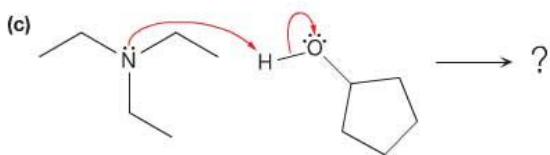
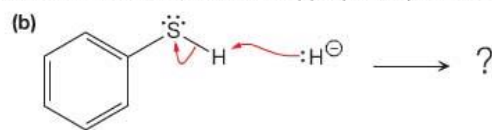
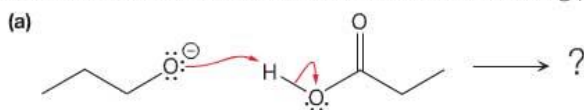
problem 6.37 In an electrophoresis experiment where the pH of the gel is 7, will glycine migrate toward the anode or the cathode? Explain.

problem 6.38 Calculate the pI of alanine. In an electrophoresis experiment where the pH of the gel is 4, will alanine migrate toward the anode or the cathode? Explain.

problem 6.39 Compute the pI values of glutamic acid and tyrosine. If the gel in an electrophoresis experiment is at pH 7, in which direction will each of these amino acids migrate, toward the cathode or toward the anode? Explain.

problem 6.40 The pI for lysine is 9.74. In an isoelectric focusing experiment, toward which terminal will lysine migrate if it is placed on the gel at a pH of 12? If it is placed on the gel at a pH of 1? If it is placed on the gel at a pH of 7? At what pH will lysine remain stationary?

6.41 Given the curved arrow notation for each of the following proton transfer reactions, draw the appropriate products.



(a)

(b)

(c)

(d)