Chapter 3
Acids and Bases.
The Curved-Arrow Notation

Solutions to In-Text Problems

3.1 (b) The nitrogen of ammonia donates an electron pair to electron-deficient boron of BF$_3$. (The electron pairs on the fluorine are not shown because they have no direct part in the reaction.)

\[
\text{electron donor} \
\begin{array}{c}
\text{F} \\
\text{B} \\
\text{F}
\end{array} 
\rightarrow 
\begin{array}{c}
\text{NH}_3 \\
\text{F}
\end{array} 
\rightarrow 
\begin{array}{c}
\text{F} \\
\text{B} \\
\text{F}
\end{array} 
\text{Lewis base} 
\begin{array}{c}
\text{NH}_3 \\
\text{F}
\end{array}
\]

3.2 (b) (d)

3.3 (b)

\[
\text{H}_3\text{N} : \overset{\text{Br}}{\text{H}} : \overset{\text{Br}}{\text{H}} : \overset{\text{Br}}{\text{H}} 
\rightarrow 
\text{H}_3\text{N}^+ \overset{\text{Br}}{\text{CH}} : \overset{\text{Br}}{\text{H}}
\]

3.4 (b)

\[
\text{H}_2\text{C} : \overset{\text{CH}}{\text{CH}} = \overset{\text{CH}}{\text{CH}} \leftrightarrow \text{H}_2\text{C} = \overset{\text{CH}}{\text{CH}} = \overset{\text{CH}}{\text{CH}}
\]

3.6 Let H$_2$O be the acid on the left. Then CH$_3$OH is the acid on the right. (If you chose CH$_3$OH as the acid on the left, then switch reactants and products in the reaction below.)

\[
\begin{array}{c}
\text{conjugate base–acid pair} \\
\text{H}_2\text{O}^+ \\
\text{H}_2\text{O} \\
\text{CH}_3\text{OH}
\end{array} 
\rightarrow 
\begin{array}{c}
\text{conjugate acid–base pair} \\
\text{H}_2\text{O}^- \\
\text{H}_3\text{O}^+ \\
\text{CH}_3\text{OH}
\end{array}
\]

3.7 (a) The reverse of reaction 3.18a is a Lewis acid–base association reaction; there is no leaving group.
(b) The reverse of reaction 3.18b is a Lewis acid–base dissociation reaction. There is no nucleophile.

(c) Like the forward reaction, the reverse of reaction 3.18c is a Brønsted acid–base reaction.

3.8 (b) This is a Lewis acid–base association reaction.

The reverse reaction is a Lewis acid–base dissociation reaction:

3.9 (b) The curved-arrow notation:

The analogous Brønsted acid–base reaction replaces the ethyl group with H:
3.12 Find the $K_a$ by changing the sign of the $pK_a$ and taking the antilog.

(a) $K_a = 10^{-4}$

(b) $K_a = 10^{-7.8} = 1.58 \times 10^{-8}$

(c) $K_a = 10^2 = 100$

3.13 (b) The strongest acid in Problem 3.12 is the one with the largest $K_a$—that is, (c).

3.14 (b) The acid–base reaction is

$$H\text{--CN} + \text{F}^- \rightleftharpoons CN^- + H\text{--F}$$

The acid on the right side of the equation is $H\text{--F}$ ($pK_a = 3.2$), and the acid on the left side is $H\text{--CN}$ ($pK_a = 9.4$). Using the procedure in part (a), we find that $\log K_{eq} = 3.2 - 9.4 = -6.2$, and $K_{eq} = 10^{-6.2} = 6.3 \times 10^{-7}$.

3.16 (b) For this calculation use Eq. 3.30 on text p. 106.

$$\Delta G^\circ = -2.30RT \log K_{eq} = -5.71 \log(305) \text{ kJ mol}^{-1} = -5.71(2.48) \text{ kJ mol}^{-1} = -14.2 \text{ kJ mol}^{-1}$$

In these solutions and in the Study Guide and Solutions Manual, kJ mol$^{-1}$ is used as the unit of energy. If you wish to convert kJ mol$^{-1}$ to kcal mol$^{-1}$, simply divide by 4.184 kJ kcal$^{-1}$. Also, it is helpful to remember that $2.30RT$ at 298 K (25 °C) is 5.71 kJ mol$^{-1}$.

3.17 (b) If the $\Delta G^\circ$ is positive, the equilibrium constant is less than unity and the reaction is less favorable; consequently, there should be much less $C$ and more $A$ and $B$ at equilibrium.

An actual calculation shows that $[C] = 0.0061$. Then $[A] = 0.1 - x = 0.0939 \, M$, and $[B] = 0.2 - x = 0.1939$. The concentration of $C$ is 10% of that in part (a), a result consistent with the statement in part (b).

3.18 (a) 5.71

3.19 (b) The more acidic species is $\text{CH}_3\text{--}^+\text{SH}_2$.

3.20 (b) Compound $A$ is much more basic than compound $B$ (charge effect). By the element effect, $C$ is much more basic than $A$; this follows from the fact that if we rank their conjugate acids, the conjugate acid of $C$, ammonia, is less acidic than the conjugate acid of $A$, $\text{CH}_3\text{OH}$. Note that a comparison of $A$ and $B$ brings into play the amphoterism of methanol: like water, it can act as both an acid and a base in different reactions.

A negatively charged atom is more basic than the same neutral atom. This can be understood on the basis of the charge effect for positively charged atoms by taking into account the relationships of conjugate acids and bases. By the charge effect, an acidic proton on a positively charged atom is more acidic than an acidic proton on the same neutral atom. It follows, then, that the neutral conjugate base of the positively charged acid is less basic than the negatively charged conjugate base of the neutral acid.

3.21 In each set, label the compounds from left to right as $A$, $B$, and $C$.

(b) The order of $pK_a$ values is $B$ (least acidic) $> A > C$ (most acidic). The acidity of compound $A$, relative to compound $B$, is increased by the polar effect of one methoxy ($\text{--OCH}_3$) group. The acidity of compound $C$ is increased by the polar effect of two methoxy groups.

3.22 (b) $\Delta G^\circ = 2.3RT(pK_a) = (5.71)(4.76) = 27.2 \text{ kJ mol}^{-1}$. More energy is required to ionize the less acidic compound.
Solutions to Additional Problems

3.24  (b) Every atom has an octet; therefore, this is not an electron-deficient compound.
      (d) The boron is electron-deficient because it has a sextet of electrons.

3.25  (b)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{H}_3\text{C}-\text{C}-\text{CH}_3 & \quad \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\
& \quad \text{Cl}^-
\end{align*}
\]

(d)

\[
\begin{align*}
\text{(CH}_3\text{)_B} & \quad \text{C}=\hat{\text{O}} \\
& \quad \text{(CH}_3\text{)_B} \quad \text{C}=\hat{\text{O}}
\end{align*}
\]

3.26  (b)

(a)

As in Problem 3.27, every reaction that involves the donation or acceptance of electron pairs, and therefore every reaction in this problem, is (1)—a Lewis acid–base reaction.

(b) In general, if a reaction in one direction is a Bronsted acid–base reaction, it is also a Bronsted acid–base reaction in the reverse direction. Therefore, Steps 1 and 3 are (5)—Bronsted acid–base reactions—and (4)—electron-pair displacement reactions.

(b) The conjugate acid–base relationship is unchanged by the direction of the reaction. The answer is the same as for Problem 3.27(b).

(c) See the equations in part (d).

(d) The curved-arrow notation and the labeling of the various species:
Step 1:

3.29 (b) Interconversion of the resonance structures of carbon monoxide with the curved-arrow notation:

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\text{C} & \quad \text{O}
\end{align*}
\]

Because the carbon in the structure on the left has a sextet of electrons, it can accept another electron pair.

Step 2:

3.31 (b) The resonance structures of the carbonate ion are shown in Problem 1.34, text p. 44. The solution to that problem discusses the significance of these structures. The hybrid structure:

\[
\begin{align*}
\text{C} & \quad \text{O} \\
\text{O} & \quad \text{O}
\end{align*}
\]

hybrid structure of the carbonate ion

3.32 (b) (d)

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{C}^+ \quad + \quad \text{N} \equiv \text{N} \\
\text{CH}_3 & \quad \text{H}_3\text{C} & \quad \text{C} \equiv \text{NH}_2 + \quad \text{O}: \quad \text{OC}_2\text{H}_5
\end{align*}
\]
3.33 Remember that an arrow must originate at a source of electrons—a bond or an electron pair.

(b) 

\[ \begin{align*} \text{Br} & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{C} \quad \begin{array}{c} \text{O} \end{array} & \quad \rightarrow & \quad \begin{array}{c} \text{Br}^- \end{array} \quad + \quad \text{H}_2\text{C} \quad \text{CH}_2 \quad + \quad \begin{array}{c} \text{O} \end{array} \quad \text{C} \quad \begin{array}{c} \text{O} \end{array} \end{align*} \]

(d) 

\[ \begin{align*} \text{H}_2\text{C} \quad \begin{array}{c} \text{O} \end{array} \quad \text{CH}_2 \quad \text{CN} & \quad \rightarrow & \quad \text{CH}_2 \quad \text{CH}_2 \quad \text{CN} \end{align*} \]

3.34 (b) The reaction is a Lewis acid–base association.

\[ \begin{align*} \text{H}_3\text{O} \quad \begin{array}{c} \text{O} \end{array} \quad \begin{array}{c} \text{AlCl}_3 \end{array} & \quad \rightarrow & \quad \text{H}_3\text{C} \quad \begin{array}{c} \text{C} \end{array} \quad \text{CH}_3 \end{align*} \]

(d) The reaction is a Brønsted acid–base reaction with a proton:

\[ \begin{align*} \text{H}_2\text{O} \quad \begin{array}{c} \text{H} \end{array} \quad \text{NH}_2 \quad \text{CH}_2\text{CH}_3 & \quad \rightarrow & \quad \text{H}_2\text{O} \quad \begin{array}{c} \text{H} \end{array} \quad + \quad \text{NH}_2 \quad \text{CH}_2\text{CH}_3 \end{align*} \]

3.35 (b) Species \( A \) is a Lewis base and a nucleophile. Carbon \( B \) is an electrophile. Carbon \( C \) is a leaving group towards carbon \( B \) but also a nucleophile towards carbon \( D \). Carbon \( D \) is an electrophile. Oxygen \( E \) serves as a leaving group (and also a Lewis acid). When atoms in double or triple bonds serve as leaving groups, one bond remains intact, so that the leaving group doesn’t actually “leave,” but remains tethered within the same molecule. This is the case with atoms \( C \) and \( E \).

\[ \begin{align*} \text{CH}_3\text{Si} & \quad \begin{array}{c} \text{O} \end{array} \quad \text{H}_2\text{C} \quad \begin{array}{c} \text{C} \end{array} \quad \text{CH}_3 \quad \text{C} \quad \text{CH}_3 \quad \text{C} \quad \text{CH}_3 & \quad \rightarrow & \quad \text{CH}_3\text{Si} \quad \text{H}_2\text{C} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{C} \quad \text{CH}_3 \quad \text{CH}_3 \end{align*} \]

3.36 (b) The one curved arrow is shown correctly, but a second one is needed. Otherwise, carbon would have five bonds in the product, and this situation would violate the octet rule.

\[ \begin{align*} \text{H}_3\text{C} \quad \begin{array}{c} \text{O} \end{array} \quad \text{H}_3\text{C} \quad \text{Br} \quad \rightarrow & \quad \text{H}_3\text{C} \quad \begin{array}{c} \text{O} \end{array} \quad \text{CH}_3 \quad + \quad \text{Br}^- \end{align*} \]

3.37 (b) The resonance structures of anthracene:

\[ \text{anthracene} \]

3.38 (b) Let \( K_{eq} \) be the ratio \([\text{anti}] / [\text{gauche}]\); then \( \Delta G^\circ \) for gauche \( \leftrightarrow \text{anti} \) is \(-2.8 \text{ kJ mol}^{-1}\). (Because gauche has higher energy than anti, \( \Delta G^\circ \) is negative.) Then use Eq. 3.31b in the text.

\[ K_{eq} = 10^{-\Delta G^\circ/2.3RT} = 10^{(-2.8)/5.71} = 10^{0.49} = 3.1 \]
This is the ratio of the anti conformation to any one gauche conformation. Taking the total fraction of butane as 1.0, and noting from above that [anti] = 3.1[gauche],

$$1.0 = [\text{anti}] + 2[\text{gauche}] = 3.1[\text{gauche}] + 2[\text{gauche}] = 5.1[\text{gauche}]$$

or

$$[\text{gauche}] = 1.0/5.1 = 0.20$$

Consequently, the total fraction of gauche conformations is $2 \times 0.20 = 0.40$ (that is, about 40% gauche conformations); and the total fraction of anti conformation is $1.0 - 0.40 = 0.60$ (that is, about 60% anti conformation) in a sample of butane.

3.39
(b) Because of the element effect, both thiols (the compounds with —SH groups) are more acidic than ethanol (CH$_3$CH$_2$OH). The compound ClCH$_2$CH$_2$SH is the more acidic of the two thiols because of the polar effect of the chlorine substituent.

(d) CH$_3$CH$_2$OH is less acidic than (CH$_3$)$_2$NCH$_2$CH$_2$OH because of the polar effect of the electronegative nitrogen substituent. In the last compound, not only is the polar effect of the nitrogen present, but also a positive charge, which can stabilize the conjugate-base anion (charge effect). Furthermore, the positively-charged nitrogen is closer to the —OH group. Consequently, (CH$_3$)$_3$N$^+$—OH is the most acidic of the three compounds and it is thus the strongest acid of all.

3.40
In each part, we apply Eq. 3.25b on text p. 104 and the procedure used in Study Problem 3.6.

(b) We apply text Eq. 3.25b with $pK_a = 15.7$ for H$_2$O.

$$K_{eq} = 10^{15.7-10.5} = 10^{5.2} = 1.58 \times 10^5$$

Don’t confuse equilibrium constants for the reactions of acids and bases with dissociation constants $K_a$. These equilibrium constants use dissociation constants in their calculation, but are not themselves dissociation constants. Similarly, log $K_{eq}$ is related to the $pK_a$ values of the two acid–base systems involved, but is not itself a $pK_a$.

3.41
(b) Use the same procedure as in part (a) in the Study Guide and Solutions Manual.

$$\Delta G^o = -2.3RT \log K_{eq} = (-5.71)(5.2) = -29.7 \text{ kJ mol}^{-1}$$

3.42
(b) The problem is asking for the standard free energy of dissociation $\Delta G_a^o$. Use Eq. 3.37 in the text. (Assume 25 °C or 298 K.)

$$\Delta G_a^o = 2.3RT(pK_a) = 5.71(4.31) = 24.6 \text{ kJ mol}^{-1}$$

3.45
According to text Fig. 3.2 (text p. 113), selective destabilization of the conjugate acid form of an acid-base pair raises the energy of the acidic form relative to its conjugate base and reduces its $pK_a$.

Now let’s apply this reasoning to the specific example in the problem. This analysis is similar to the one used in the solution to Problem 3.44. First, assume that the chlorine affects the stability of the charged species, which in this case is the conjugate acid:

![bond dipole of the C—Cl bond interacts repulsively with the positive charge](image)

The repulsive interaction between the positive charge and the positive end of the C—Cl bond dipole selectively raises the energy of the conjugate acid. This should reduce the $pK_a$ of the conjugate acid of $A$ relative to the $pK_a$ of the conjugate acid of $B$. This is shown diagrammatically in Fig. IS3.1. This means that $B$ is the more basic of the
two conjugate bases. The actual data bear out this prediction: chlorine substitution reduces the $pK_a$ of ethylammonium ion by almost two units:

$$
\begin{align*}
\text{Cl—CH}_2\text{CH}_2—\text{NH}_3 & \quad \text{2-chloroethylammonium ion} \\
\text{CH}_3\text{CH}_2—\text{NH}_3 & \quad \text{ethylammonium ion}
\end{align*}
$$

3.47 The $\Delta G^\circ$ for the reaction is found by taking the logarithm of the equilibrium constant and multiplying it by $-2.3R$. 

$$
\Delta G^\circ_{\text{eq}} = -2.3RT \log K_{\text{eq}} = -2.3RT(pK_{A}^\circ - pK_{A}^\circ) = \Delta G^\circ_{A, AH} - \Delta G^\circ_{A, BH}
$$

3.48 (b) The amide ion is strong enough to react completely with water, and this reaction results in a $10^{-3} M$ solution of hydroxide ion—that is, a solution pH = 11. This is identical to the solution made from $10^{-3} M$ hydroxide itself, except for the ammonia by-product, which reacts only slightly with water.

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**Figure IS3.1.** The effect of chlorine substitution on the energy and $pK_a$ of the conjugate acid of ethylamine to accompany the solution to Problem 3.46. Note that by raising the energy of the conjugate acid, chlorine substitution reduces the $pK_a$. (The two conjugate bases, which are uncharged, are arbitrarily placed at the same energy for comparison purposes.)