

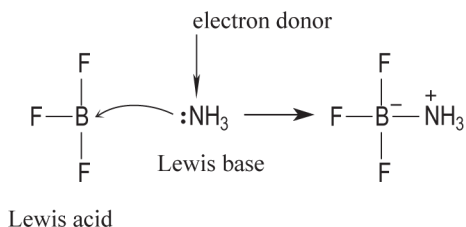
Chapter 3

Acids and Bases.

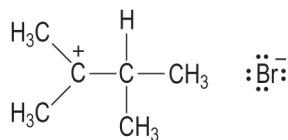
The Curved-Arrow Notation

Solutions to In-Text Problems

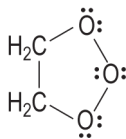
- 3.1 (b) The nitrogen of ammonia donates an electron pair to electron-deficient boron of BF_3 . (The electron pairs on the fluorine are not shown because they have no direct part in the reaction.)



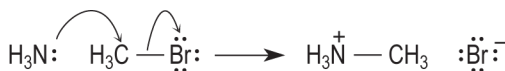
- 3.2 (b)



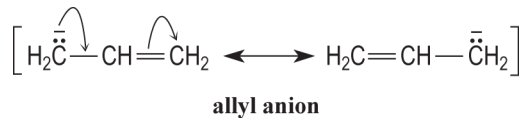
- (d)



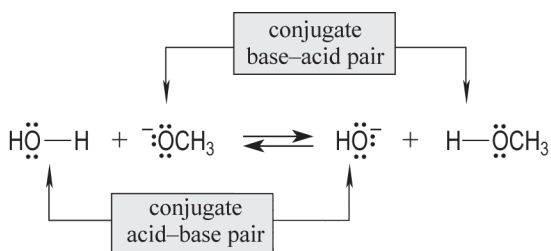
- 3.3 (b)



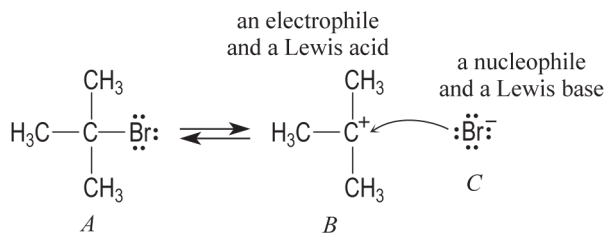
- 3.4 (b)



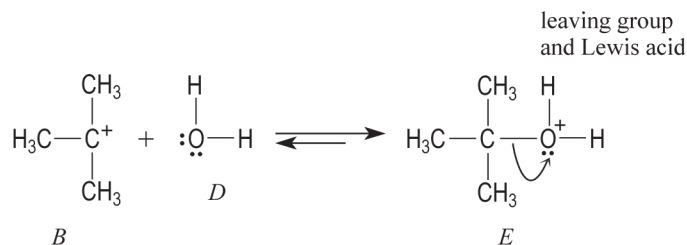
- 3.6 Let H_2O be the acid on the left. Then CH_3OH is the acid on the right. (If you chose CH_3OH as the acid on the left, then switch reactants and products in the reaction below.)



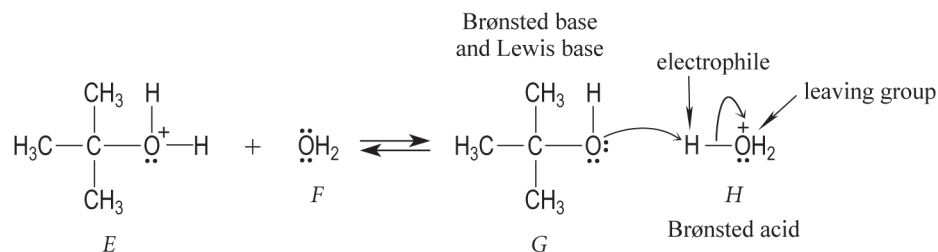
- 3.7 (a) The reverse of reaction 3.18a is a Lewis acid-base association reaction; there is no leaving group.



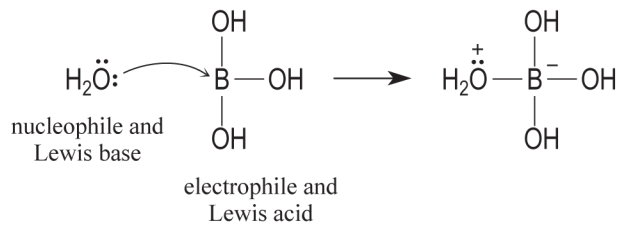
- (b) The reverse of reaction 3.18b is a Lewis acid–base dissociation reaction. There is no nucleophile.



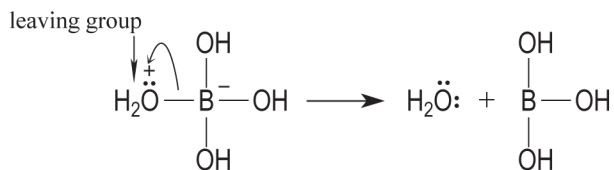
- (c) Like the forward reaction, the reverse of reaction 3.18c is a Brønsted acid–base reaction.



- 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).

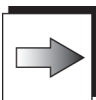
3.14 (b) The acid–base reaction is



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

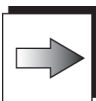
3.16 (b) For this calculation use Eq. 3.30 on text p. 106.

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



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 ΔG° 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.

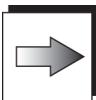


An actual calculation shows that $[C] = 0.0061$. Then $[A] = 0.1 - x = 0.0939 \text{ M}$, and $[B] = 0.2 - x = 0.1939$. The concentration of *C* is 10% of that in part (a), a result consistent with the statement in part (b).

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*, CH_3OH . Note that a comparison of *A* and *B* brings into play the amphotericism 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*.

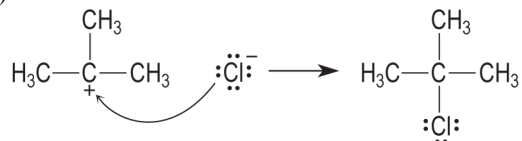
(b) The order of pK_a values is *B* (least acidic) $>$ *A* $>$ *C* (most acidic). The acidity of compound *A*, relative to compound *B*, is increased by the polar effect of one methoxy (—OCH_3) group. The acidity of compound *C* is increased by the polar effect of two methoxy groups.

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

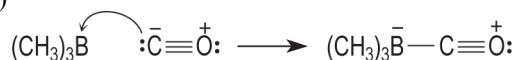
Solutions to Additional Problems

- 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.

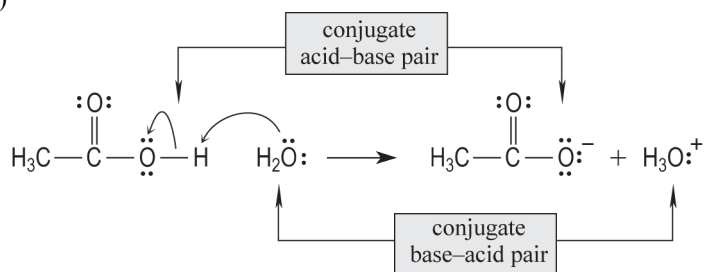
3.25 (b)



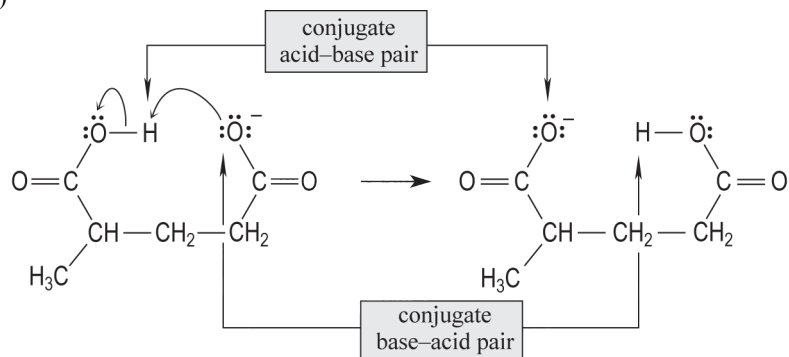
(d)



3.26 (b)



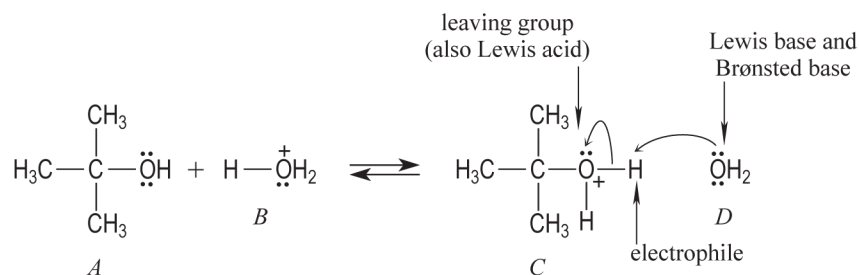
(d)



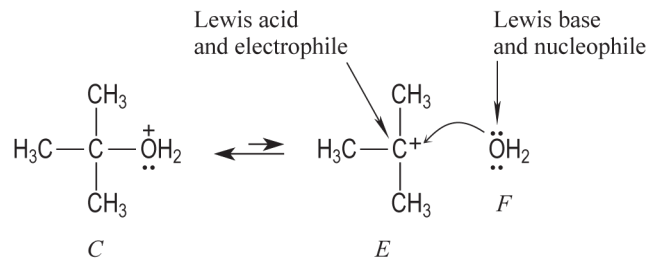
3.28 As in Problem 3.27, every reaction that involves the donation or acceptance of electron pairs, and therefore every reaction in this problem, is (1)—a Lewis acid–base reaction.

- (a) In general, if a reaction in one direction is a Brønsted acid–base reaction, it is also a Brønsted acid–base reaction in the reverse direction. Therefore, *Steps 1* and *3* are (5)—Brønsted 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:

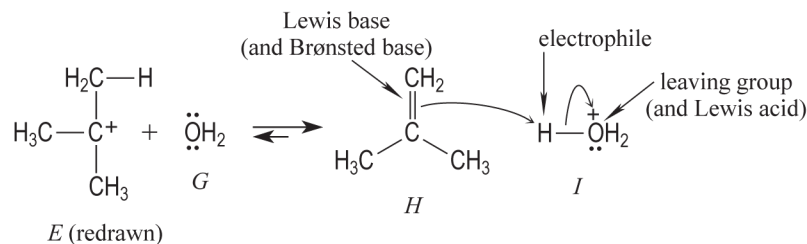
Step 1:



Step 2:



Step 3:

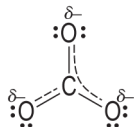


- 3.29 (b) Interconversion of the resonance structures of carbon monoxide with the curved-arrow notation:



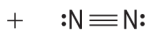
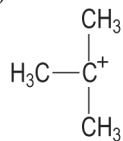
Because the carbon in the structure on the left has a sextet of electrons, it can accept another electron pair.

- 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:

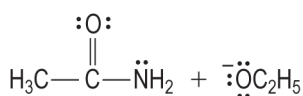


hybrid structure of the carbonate ion

- 3.32 (b)

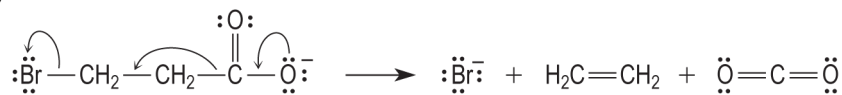


- (d)

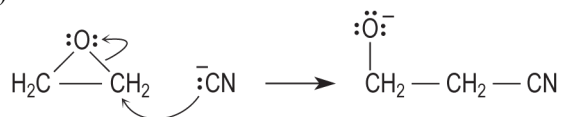


3.33 Remember that an arrow must originate at a *source* of electrons—a bond or an electron pair.

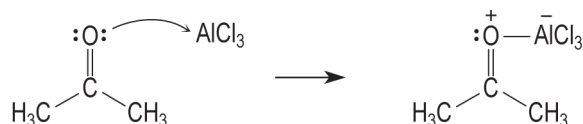
(b)



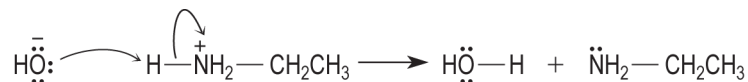
(d)



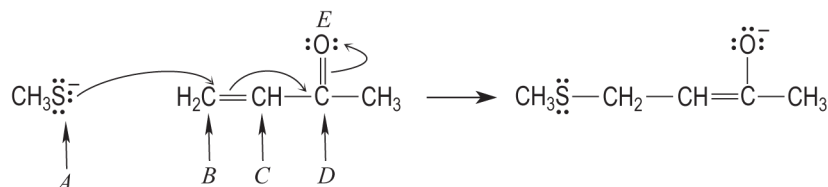
3.34 (b) The reaction is a Lewis acid–base association.



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



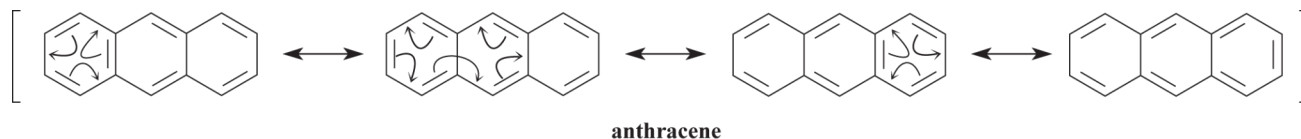
3.35 (b) Species *A* is a Lewis base and a nucleophile. Carbon *B* is an electrophile. Carbon *C* is a leaving group towards carbon *B* but also a nucleophile towards carbon *D*. Carbon *D* is an electrophile. Oxygen *E* serves as a leaving group (and also a Lewis acid). When atoms in double or triple 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*.



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.



3.37 (b) The resonance structures of anthracene:



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

$$K_{\text{eq}} = 10^{-\Delta G^\circ/2.3RT} = 10^{-(-2.8)/5.71} = 10^{0.49} = 3.1$$

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 $[\text{anti}] = 3.1[\text{gauche}]$,

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

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 ($\text{CH}_3\text{CH}_2\text{OH}$). The compound $\text{ClCH}_2\text{CH}_2\text{SH}$ is the more acidic of the two thiols because of the polar effect of the chlorine substituent.
- (d) $\text{CH}_3\text{CH}_2\text{OH}$ is less acidic than $(\text{CH}_3)_2\text{NCH}_2\text{CH}_2\text{OH}$ 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, $(\text{CH}_3)_3\text{N}^+\text{—OH}$ 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 $\text{p}K_a = 15.7$ for H_2O .

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



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, $\log K_{\text{eq}}$ is related to the $\text{p}K_a$ values of the two acid–base systems involved, but is not itself a $\text{p}K_a$.

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

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

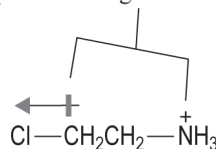
- 3.42 (b) The problem is asking for the standard free energy of dissociation ΔG_a° . Use Eq. 3.37 in the text. (Assume 25 °C or 298 K.)

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

- 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 $\text{p}K_a$.

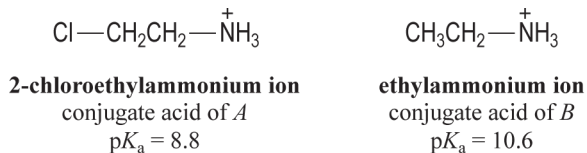
Now let's apply this reasoning to the specific example in the problem. This analysis is similar to the one used in the solution to Problem 3.44. First, assume that the chlorine affects the stability of the *charged species*, which in this case is the conjugate *acid*:

bond dipole of the C—Cl bond
interacts repulsively with the
positive charge



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 $\text{p}K_a$ of the *conjugate acid* of *A* relative to the $\text{p}K_a$ 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:



- 3.47 The ΔG° for the reaction is found by taking the logarithm of the equilibrium constant and multiplying it by $-2.3RT$.

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

- 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 $\text{pH} = 11$. 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.

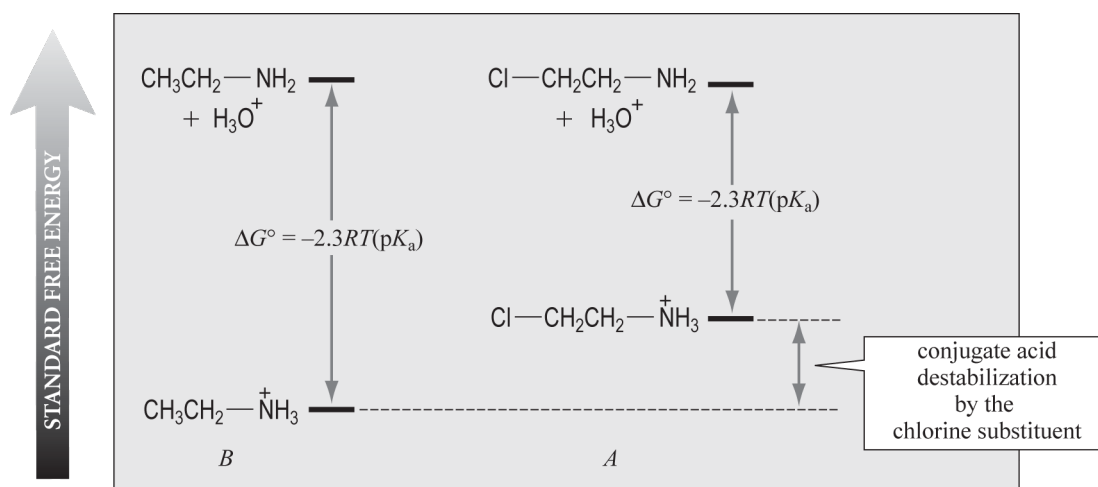


Figure IS3.1. The effect of chlorine substitution on the energy and pK_a of the conjugate acid of ethylamine to accompany the solution to Problem 3.46. Note that by raising the energy of the conjugate acid, chlorine substitution reduces the pK_a . (The two conjugate bases, which are uncharged, are arbitrarily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