

## 14.20: Solutions to Selected Problems

With contributions from Nicholas Jones and Kate Graham, College of Saint Benedict / Saint John's University

### Exercise 14.2.1:

A Lewis base must have lone pairs or non-bonding electron pairs so that it can donate them to a Lewis acid.

Alternatively, in some cases the electrons in a  $\pi$ -bond can be donated instead, so sometimes compounds with  $\pi$ -bonds can be Lewis basic.

### Exercise 14.2.2:

- a. not a Lewis base
- b. not a Lewis base
- c. Lewis base
- d. Lewis base
- e. Lewis base

### Exercise 14.3.1:

A Lewis acid atom attracts electrons from a Lewis base.

The most common feature of a Lewis acid is an atom that is not "electronically saturated" or has not filled its octet. For example, an aluminum with only six electrons rather than eight is Lewis acidic.

Other atoms, like transition metals, have "octets" of eighteen electrons, so having fewer than eighteen electrons in their valence shell can make these atoms Lewis acidic.

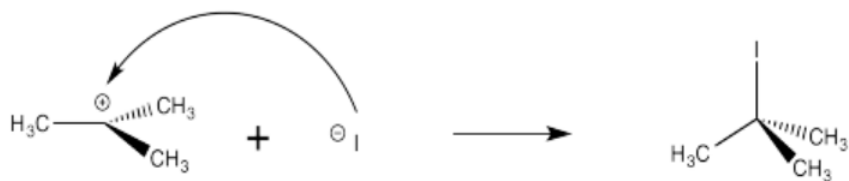
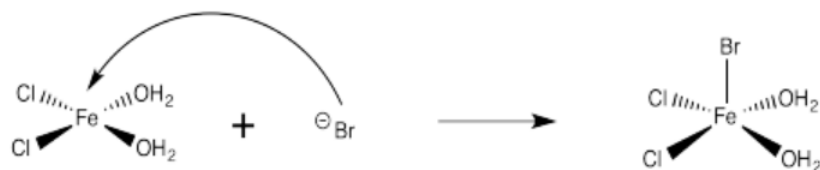
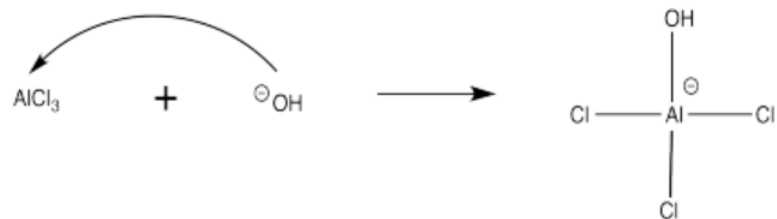
### Exercise 14.3.2:

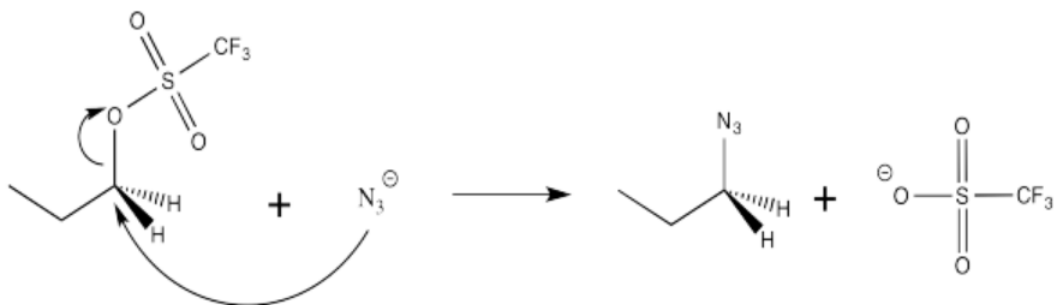
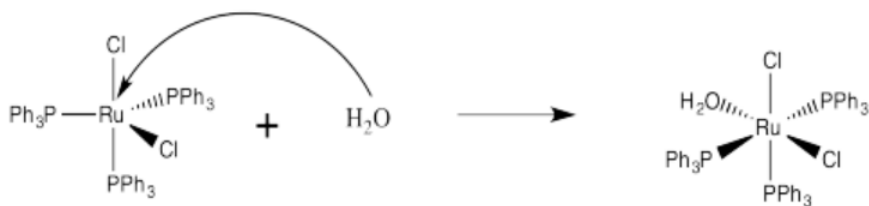
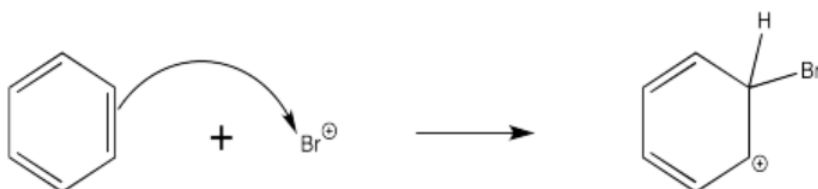
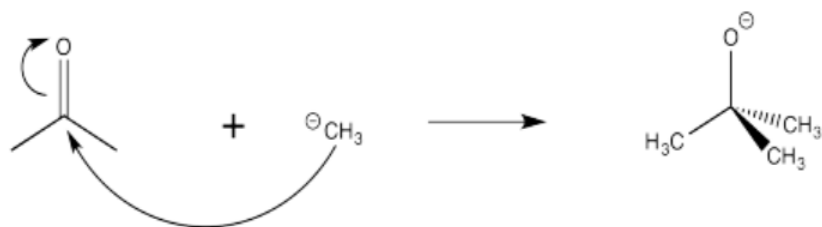
- a. Lewis acid
- b. Lewis acid
- c. not a Lewis acid
- d. Lewis acid
- e. not a Lewis acid

### Exercise 14.3.3:

- a)
- b) cations
- c) possibly ion-dipole forces; alternatively, the oxygen atoms could act as Lewis bases, donating lone pairs to a cation.
- d)
- e) anions
- f)
- g)
- h) When the chloride ion binds to the sensor molecule it gives the overall complex a negative charge and addition of the potassium ion cancels out this charge.

### Exercise 14.4.1:





Exercise 14.4.2:

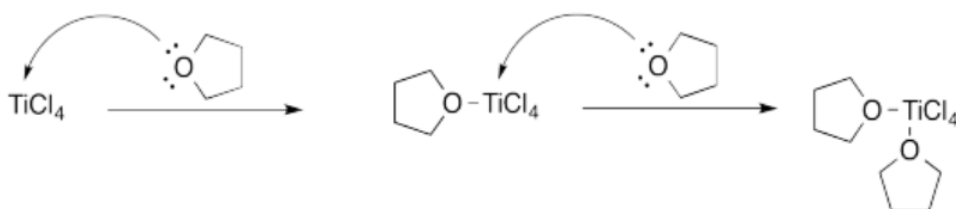
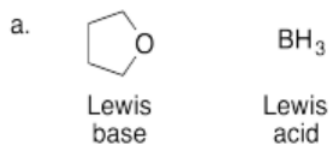


Figure 14.20.1:

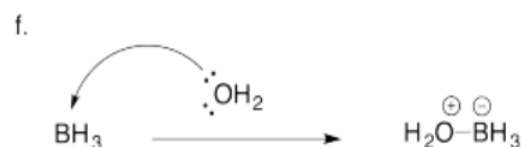
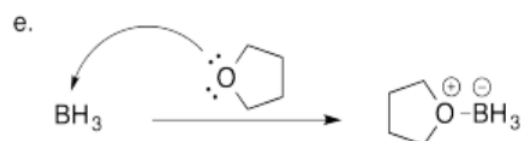
Exercise 14.4.3:



b. boron's empty p-orbital

c. non-bonding electrons on oxygen

d. one pair of electrons



g. borane is already complexed with THF and will be slower to react with water in the atmosphere

Figure 14.20.1:

Exercise 14.4.5:

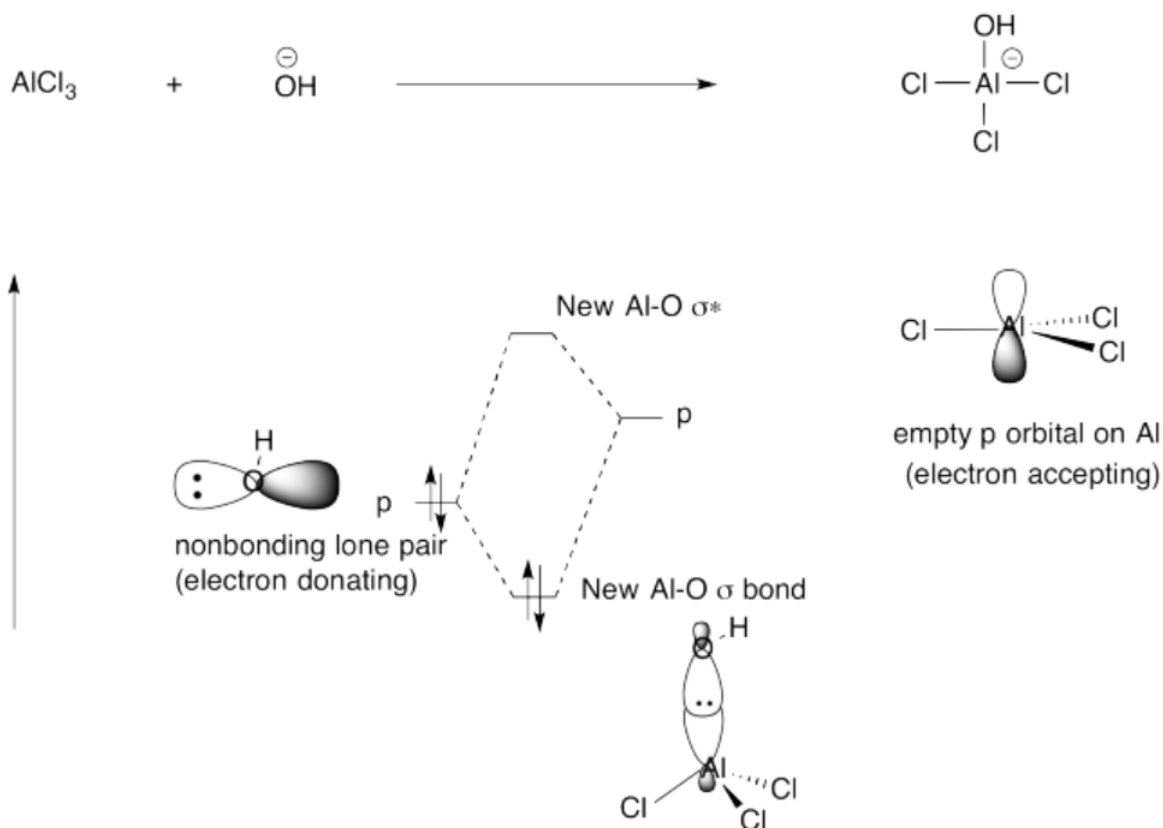


Figure 14.20.1:

Exercise 14.4.6:

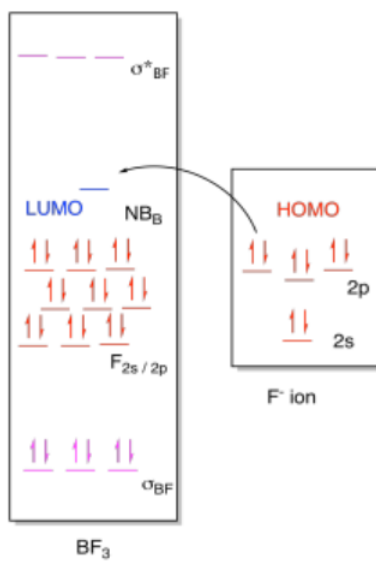
- 
- The benzene rings take up more space than a fluorine atom; they may get in the way, making it harder for the water molecule to approach.

Also, the aromatic rings may be able to form a conjugated system with the empty p orbital; if that p orbital is partially filled, the boron atom becomes less Lewis acidic.

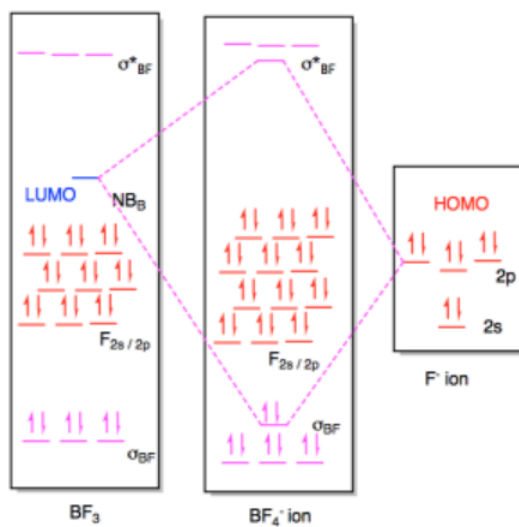
- A larger group than fluorine may cause more steric hindrance. Replacing the two fluorines closest to the boron on each arene (aromatic ring) with a  $\text{CH}_3$  or  $\text{CF}_3$  group would slow down the formation of an adduct. Alternatively, a less electronegative group than fluorine would also make the boron seem less positive; a  $\text{CH}_3$  or  $\text{OCH}_3$  are two possibilities.
- An even more electron-withdrawing group than fluorine would make the Lewis acid more reactive. Examples include nitro ( $\text{NO}_2$ ) and carbonyl groups (such as  $\text{CH}_3\text{C}=\text{O}$ ); these groups are resonance-withdrawing. Alternatively, a smaller group such as a hydrogen would lower steric resistance, but would also lead to lower electrophilicity at boron, owing to the lower electronegativity of hydrogen compared to fluorine.

Exercise 14.4.7:

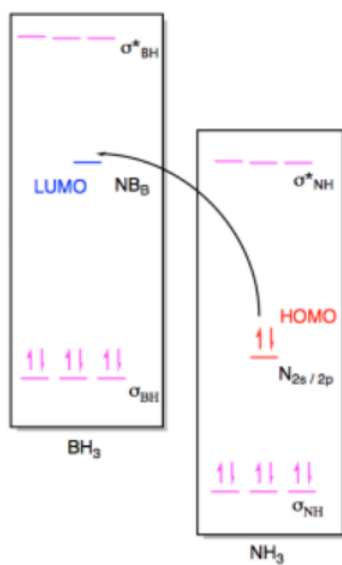
- (i)



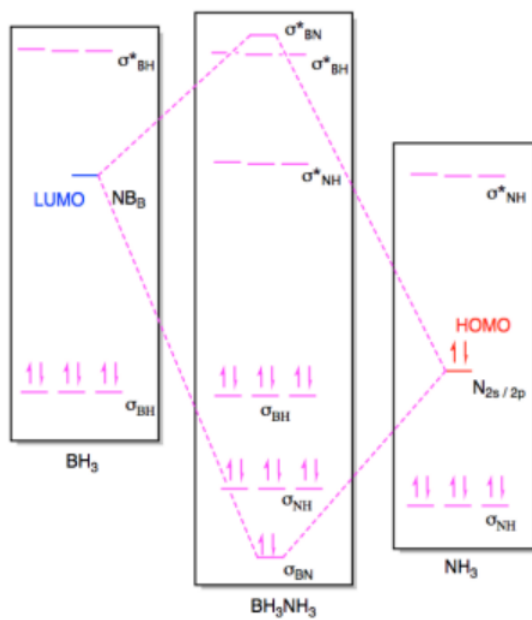
(ii)



b) (i)



(ii)



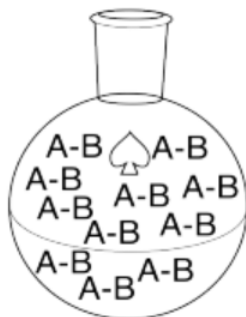
Exercise 14.5.1:



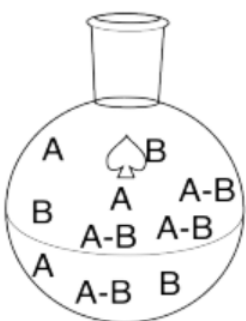


Exercise 14.5.2:

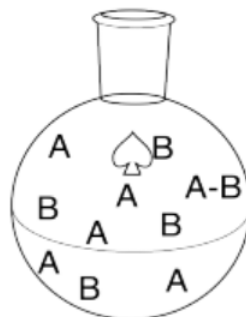
a.



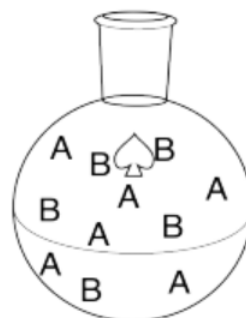
b.



c.



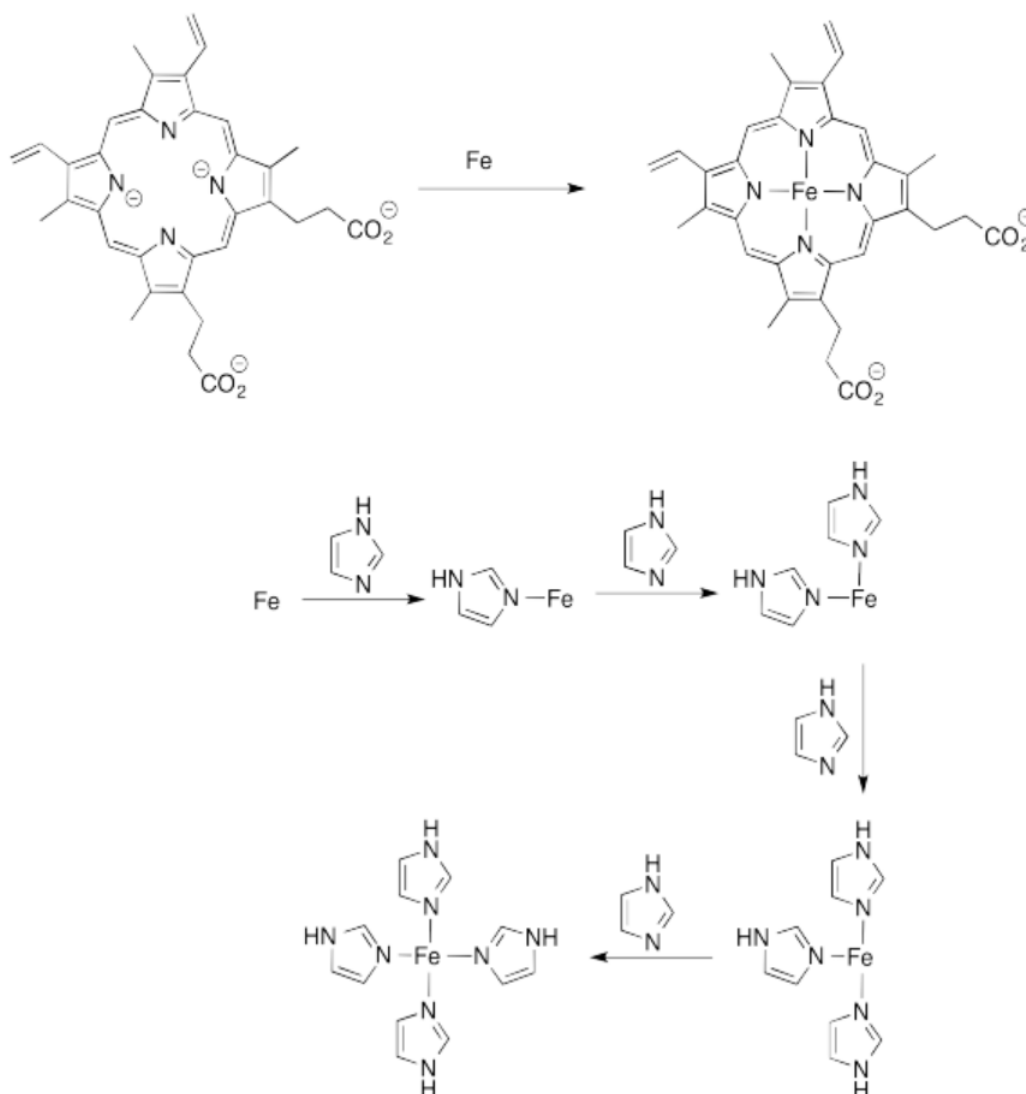
d.





Exercise 14.5.3:

The heme subunit is tetradentate and forms 4 iron-ligand bonds. Four independent monodentate nitrogen ligands would be required to form a similar complex. Thus Iron binding to a heme does not produce the same loss of degrees of freedom as iron binding four independent nitrogen ligands.

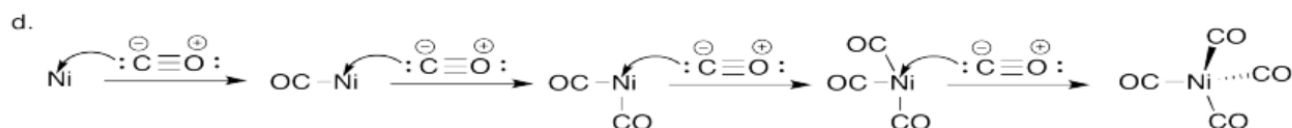


Exercise 14.6.1:

a. Lewis acid

b.  $\text{:C}\equiv\text{O:}^{\ominus}$

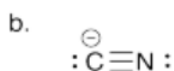
c. carbon will be nucleophilic due to the lone pair electrons and the negative charge



e. Ni<sup>0</sup> is d<sup>10</sup> and with 4 CO ligands the nickel tetracarbonyl complex has 18 electrons

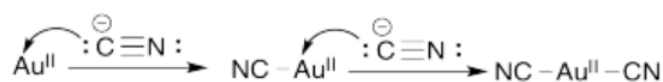
Exercise 14.6.2

a. Lewis acid



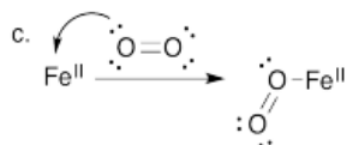
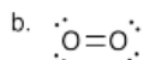
c. carbon will be nucleophilic due to the lone pair electrons and the negative charge

d.



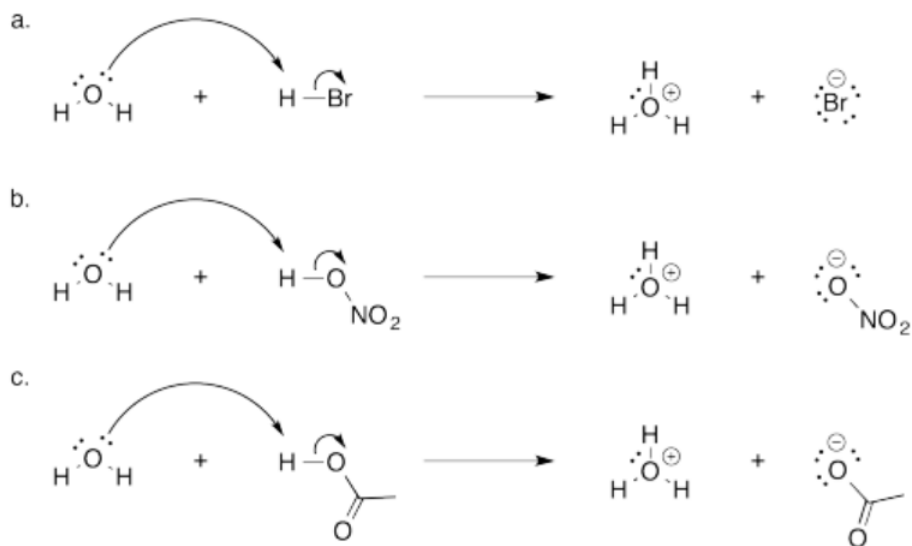
Exercise 14.6.3:

a. Lewis acid

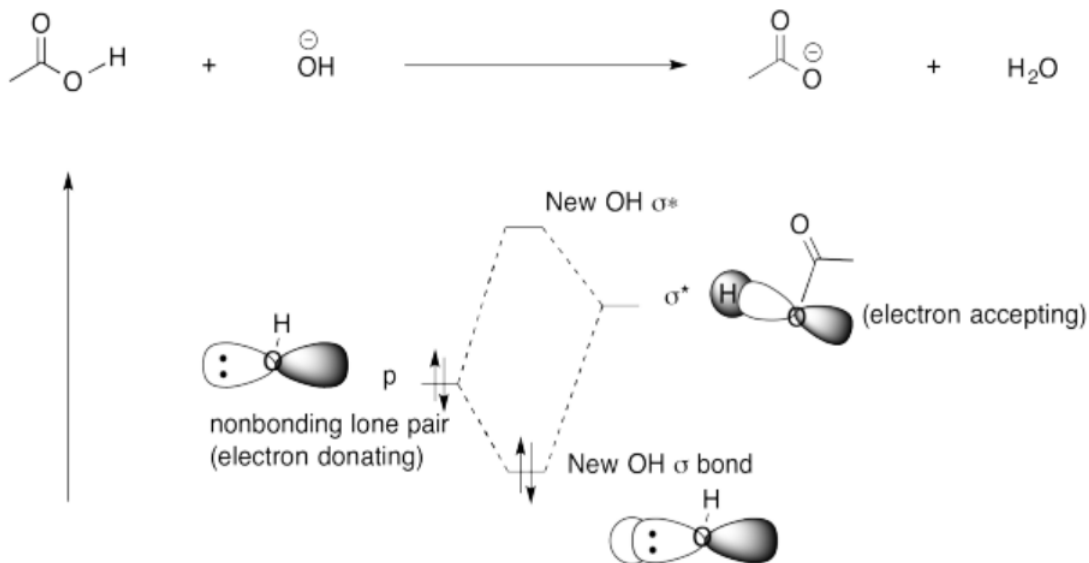


d. the bound oxygen would be predicted to have a trigonal planar electronic (bend molecular) geometry based on the Lewis structure.

Exercise 14.7.1:

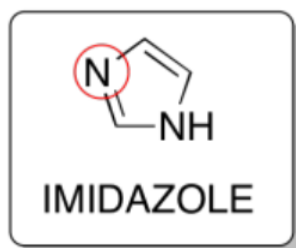


Exercise 14.7.2:

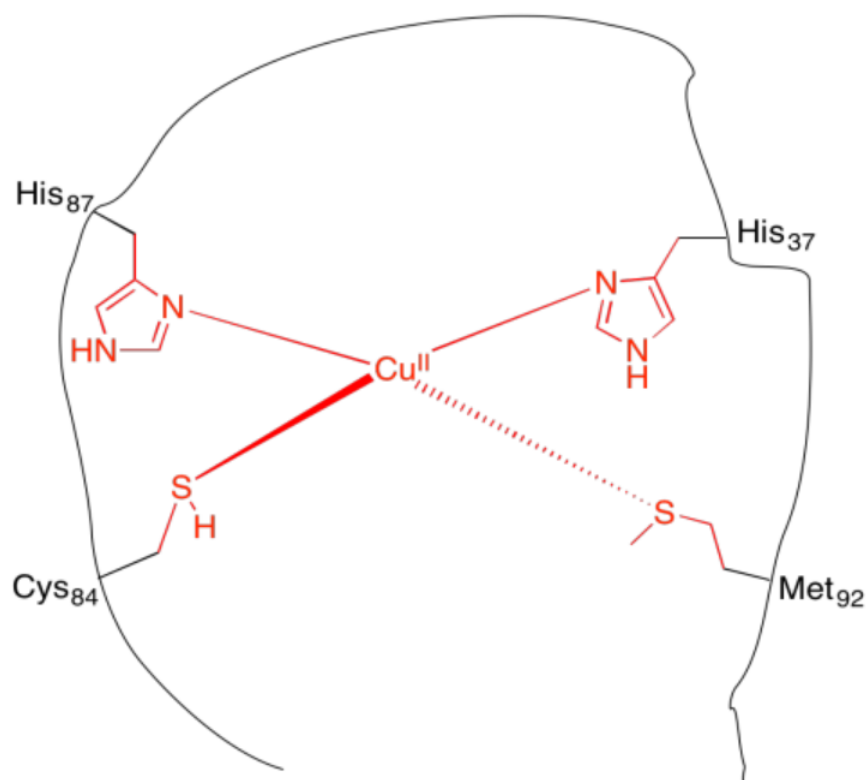


Exercise 14.7.3:

- 
- 
- 
- 
- aromatic
- 
- 



- This nitrogen atom can donate a lone pair of electrons without disturbing the aromatic character of the molecule.
- 
- 
- Each side chain has a Lewis base with a lone pair of electrons to donate the copper ion.
-



m)  $CN = 4$

n) tetrahedral

o) Cu:  $11 e^-$

Cu(II):  $9 e^-$

$$4 \times 2e^- = 8e^-$$

$$8e^- + 9e^- = 17e^-$$

p) If the imidazole becomes occupied by a proton, then the imidazole no longer has the lone pair to donate to the copper ion.

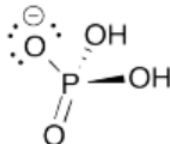
q) trigonal

Exercise 14.8.1:

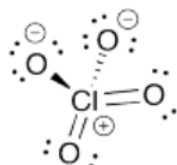
a.



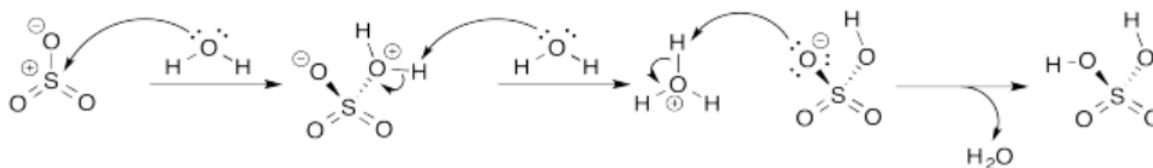
b.



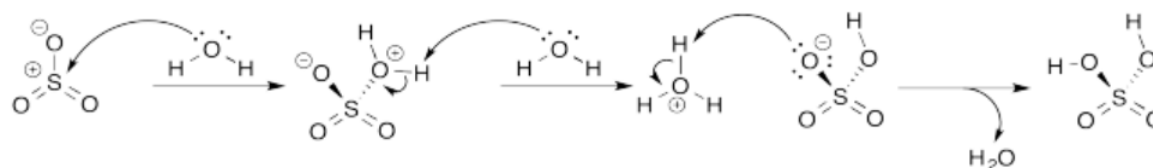
c.



Exercise 14.8.2:



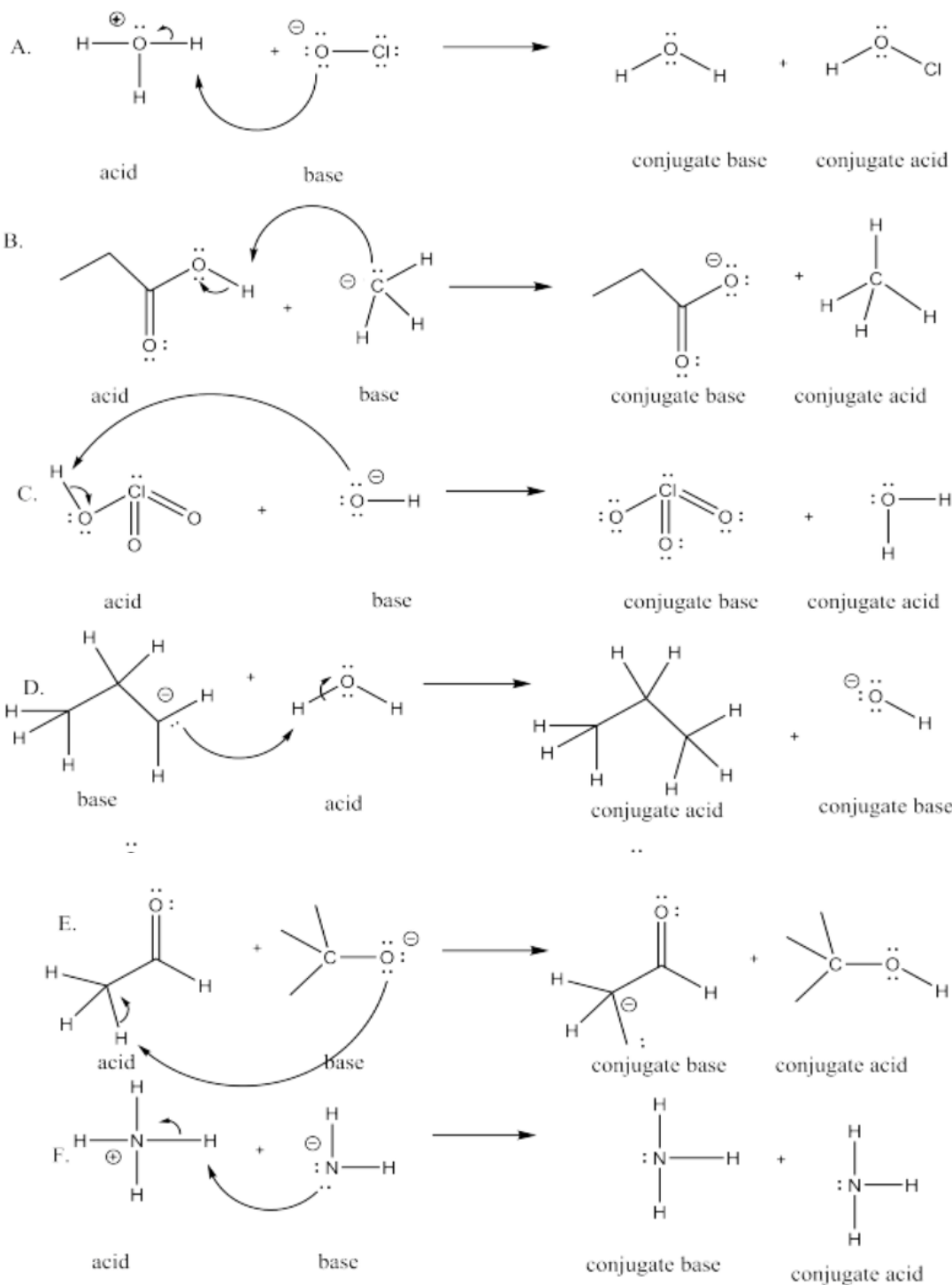
Exercise 14.8.3:



Exercise 14.8.4:

- The O-H bond is polar covalent. The oxygen is much more electronegative than the hydrogen, so the bond is easily ionized to give  $\text{H}^+$ .
- In a case like NaOH, the electronegativity difference between the sodium and oxygen is much greater than the electronegativity difference between the oxygen and the hydrogen. The Na-O bond is ionic. The removal of a proton from hydroxide ion is harder than the removal from a proton from hydroxide. It would make an oxide anion,  $\text{O}^{2-}$ ; that buildup of negative charge is more difficult than the formation of  $\text{OH}^-$ .

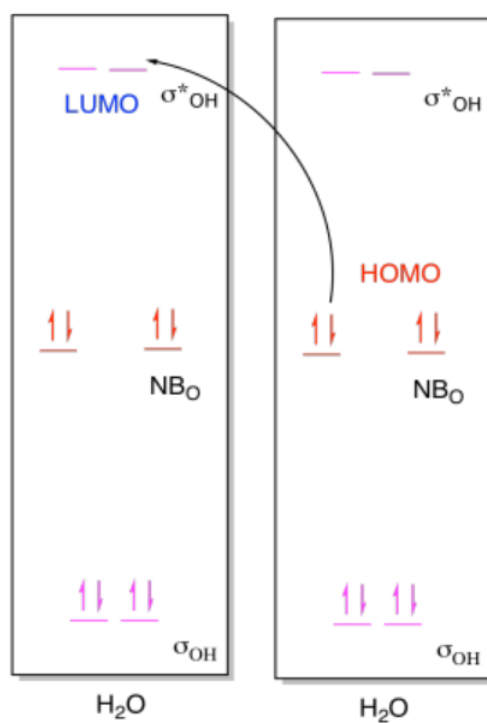
Exercise 14.8.5:



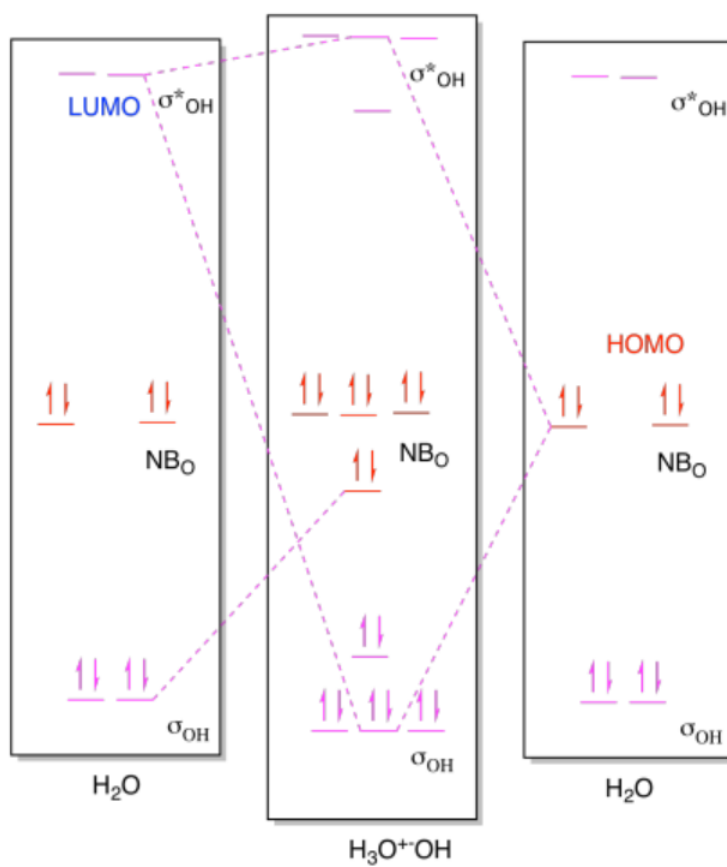
Exercise 14.8.6:

a) i)

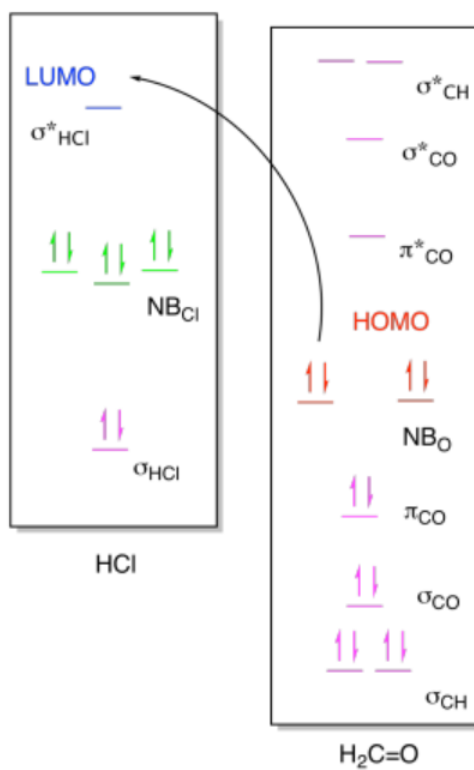




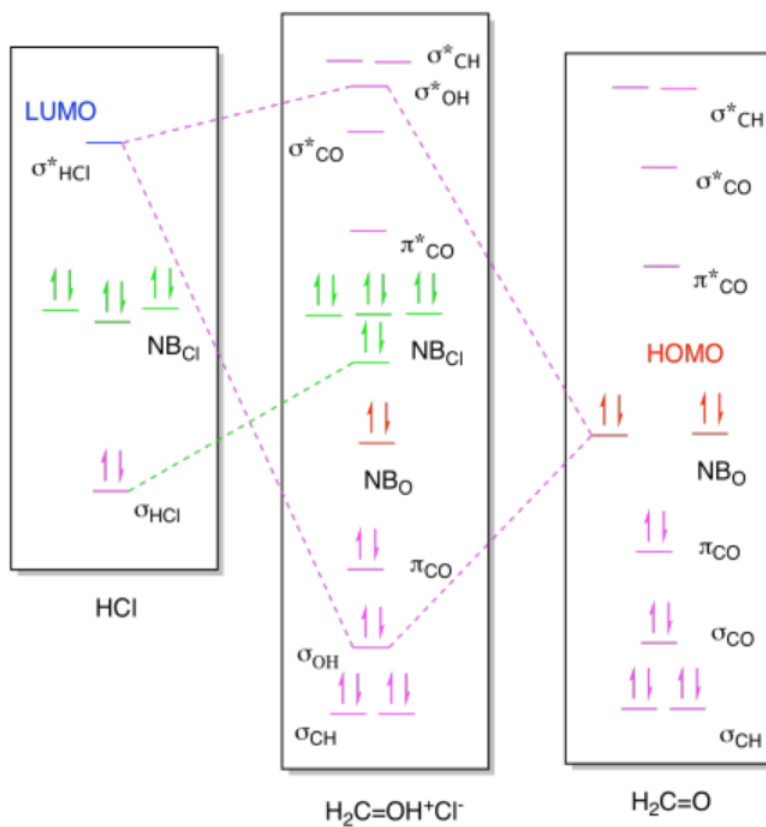
ii)



b) i)



ii)



Exercise 14.9.1

a)  $\text{HNO}_3$  ( $\text{pK}_a = -1.3$ );  $\text{HNO}_2$  ( $\text{pK}_a = 3.3$ )

$\text{HNO}_3$  is a stronger Brønsted acid compared to  $\text{HNO}_2$

b)  $\text{H}_2\text{Se}$  ( $\text{pK}_a = 3.9$ );  $\text{H}_2\text{O}$  ( $\text{pK}_a = 14$ )

$\text{H}_2\text{Se}$  is a stronger Brønsted acid compared to  $\text{H}_2\text{O}$

c)  $\text{HCl}$  ( $\text{pK}_a = -8$ );  $\text{H}_2\text{SO}_4$  ( $\text{pK}_a = -3$ )

$\text{HCl}$  is a stronger acid compared to  $\text{H}_2\text{SO}_4$

d)  $\text{Ba}(\text{OH})_2$  ( $\text{pK}_a > 50$ );  $\text{HSeO}_3$  ( $\text{pK}_a = 6.6$ )

$\text{HSeO}_3^-$  is a stronger Brønsted acid compared to  $\text{Ba}(\text{OH})_2$

#### Exercise 14.9.2:

a)  $\text{NH}_4^+$  ( $\text{pK}_a = 9.2$ );  $\text{HN}_3$  ( $\text{pK}_a = 4.7$ )

$\text{NH}_3$  is a stronger Brønsted base compared to  $\text{N}_3^-$

b)  $\text{HCN}$  ( $\text{pK}_a = 9.4$ );  $\text{HSCN}$  ( $\text{pK}_a = 4$ )

$^-\text{CN}$  is a stronger Brønsted base compared to  $^-\text{SCN}$

c)  $\text{NH}_3$  ( $\text{pK}_a = 35$ );  $\text{H}_2\text{O}$  ( $\text{pK}_a = 14$ )

$^-\text{NH}_2$  is a stronger Brønsted base compared to  $\text{HO}^-$

#### Exercise 14.10.1

a.  $\text{HClO}_4$

b.  $\text{H}_3\text{PO}_4$

#### Exercise 14.11.1:

a)  $\text{H}_2\text{S}$  or  $\text{SiH}_4$  b)  $\text{GaH}_3$  or  $\text{AsH}_3$

c)  $\text{PH}_3$  or  $\text{AlH}_3$  d)  $\text{H}_2\text{Se}$  or  $\text{HBr}$

#### Exercise 14.11.2:

a)  $^+\text{NH}_4$  or  $\text{NH}_3$  b)  $^-\text{PH}_2$  or  $\text{PH}_3$

c)  $\text{H}_2\text{O}$  or  $^+\text{NH}_4$  d)  $^+\text{H}_3\text{O}$  or  $\text{CH}_4$

#### Exercise 14.11.3:

a)  $\text{H}_2\text{S}$  or  $\text{H}_2\text{Te}$  b)  $\text{GeH}_4$  or  $\text{SnH}_4$

c)  $\text{HCl}$  or  $\text{HBr}$  d)  $\text{NH}_3$  or  $\text{AsH}_3$

#### Exercise 14.11.4:

a.  $\text{AsH}_3 > \text{PH}_3 > \text{NH}_3$

b.  $\text{HCl} > \text{H}_2\text{S} > \text{PH}_3 > \text{SiH}_4$

c.  $\text{HI} > \text{SeH}_2 > \text{SiH}_4 > \text{BH}_3$

#### Exercise 14.11.5:

a. Polarizability would not be useful as the atom that will be anionic in the conjugate base is the same (oxygen).

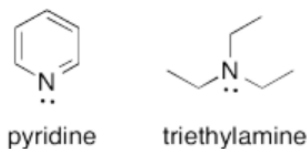
b. Se is larger and therefore more polarizable leading to  $\text{H}_2\text{Se}$  being more acidic compared to  $\text{H}_2\text{S}$ .

c. Ge is larger and therefore more polarizable leading to  $\text{GeH}_4$  being more acidic compared to  $\text{SiH}_4$ .

d. Polarizability would not be useful as the atoms are next to one another in the same row and therefore likely to have the same polarizability.

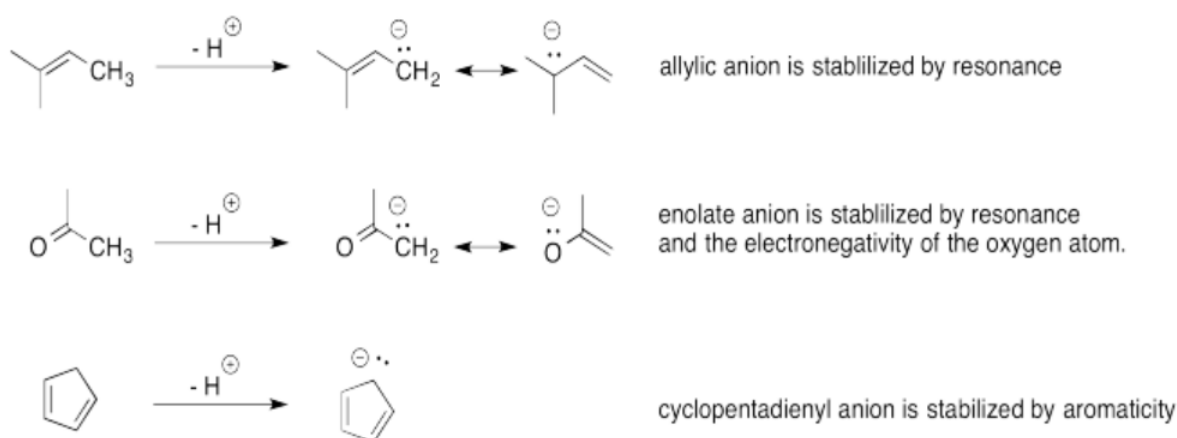
#### Exercise 14.11.3:

Triethylamine will be more basic than pyridine due to the hybridization effect. The nitrogen in triethylamine is  $sp^3$  while the pyridine nitrogen is  $sp^2$ .



#### Exercise 14.12.1:

Alkanes typically have a  $pK_a > 50$ , however CH's adjacent to  $\pi$  systems lead to anions that are stabilized by conjugation or aromaticity. Examples of these are shown below:



#### Exercise 14.12.2:

a. Vinyl alcohol would be more acidic as its anion is stabilized by resonance while the anionic charge on ethoxide would be localized on the oxygen atom.

b. Nitromethane would be more acidic as its anion is stabilized by resonance while the anionic charge of the trimethylamine anion would be localized on the carbon atom.

c. Acetonitrile would be more acidic as its anion is stabilized by resonance while the anionic charge of the trimethylamine would be localized on the carbon atom.

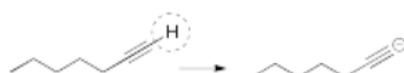
#### Exercise 14.12.3:



#### Exercise 14.12.4:



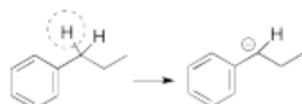
most electronegative atom



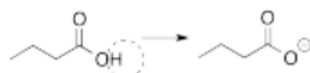
hybridization



decreases net charge of molecule



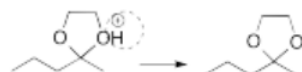
extends the conjugation



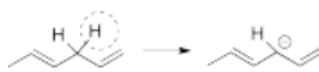
most electronegative atom  
extends the conjugation



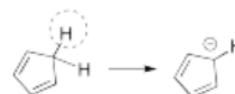
most electronegative atom



decreases net charge of molecule



extends the conjugation



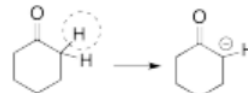
makes the molecule aromatic



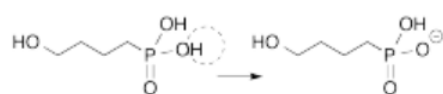
most polarizable atom



decreases net charge of molecule



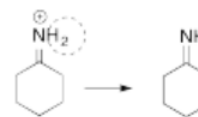
extends the conjugation



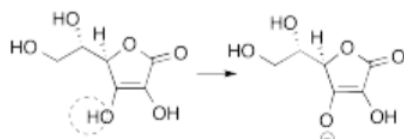
most electronegative atom  
extends the conjugation



makes the molecule aromatic

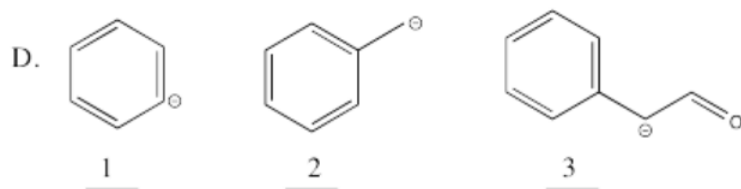
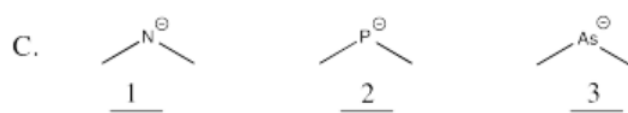
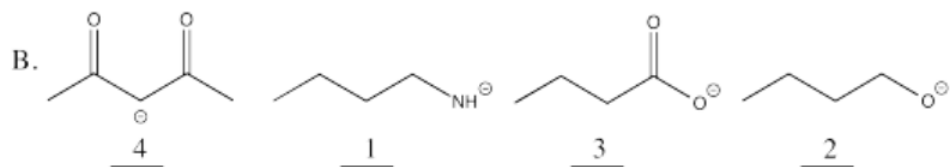
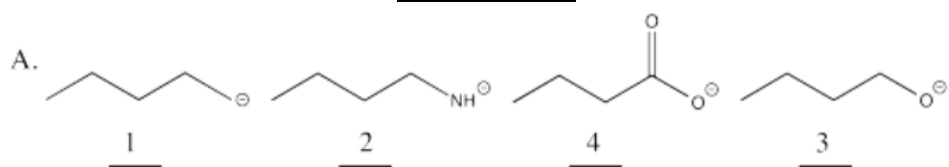


decreases net charge of molecule



most electronegative atom  
extends the conjugation

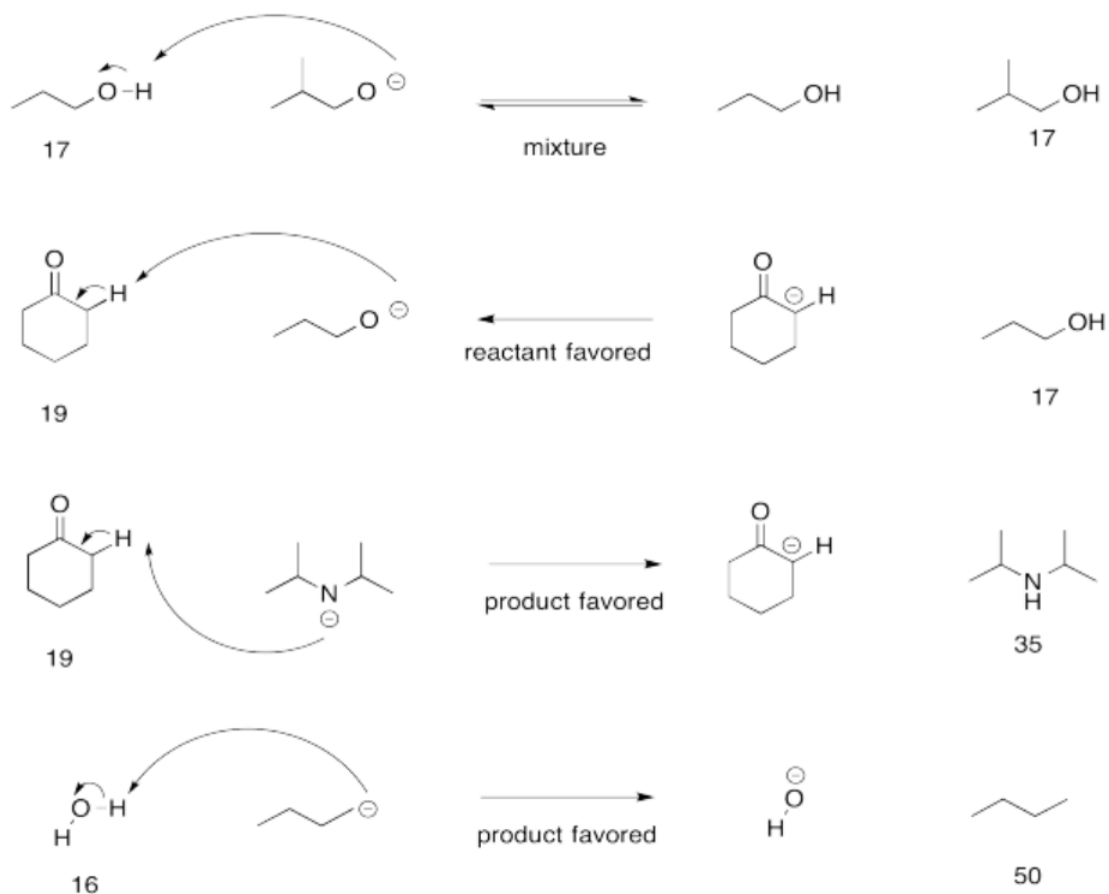
Exercise 14.13.1:

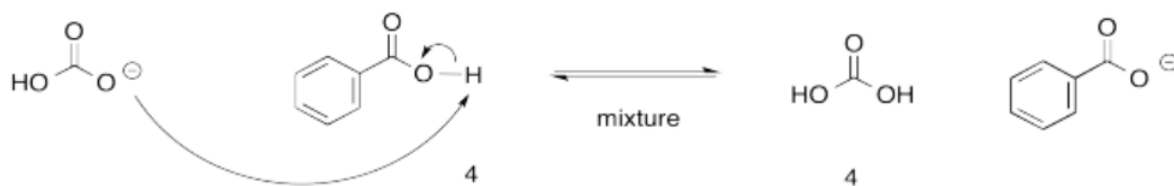
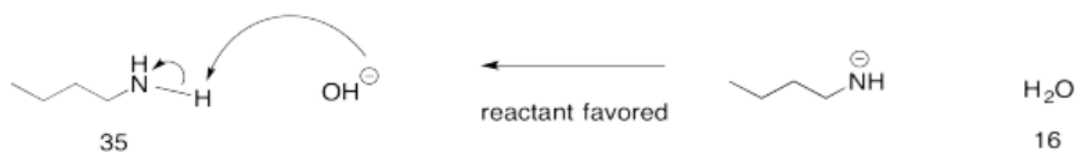
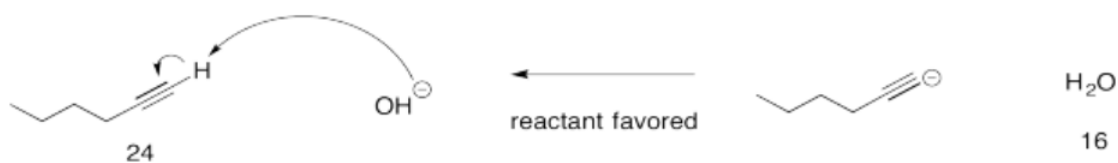


Exercise 14.14.1:

- a.  $\text{HF} + \text{H}_2\text{O} \rightleftharpoons \text{F}^- + \text{H}_3\text{O}^+$  At equilibrium the reactants will be favored  
 $\text{HF } \text{pK}_a = 3$   $\text{H}_3\text{O}^+ \text{pK}_a = -2$
- b.  $\text{CH}_3\text{CO}_2\text{H} + \text{NH}_3 \rightleftharpoons \text{CH}_3\text{CO}_2^- + \text{NH}_4^+$  At equilibrium the products will be favored  
 $\text{CH}_3\text{CO}_2\text{H } \text{pK}_a = 5$   $\text{NH}_4^+ \text{pK}_a = 9$
- c.  $\text{PhOH} + \text{CO}_3^{2-} \rightleftharpoons \text{PhO}^- + \text{HCO}_3^-$  At equilibrium reactants and products will be present in equal amounts  
 $\text{PhOH } \text{pK}_a = 10$   $\text{HCO}_3^- \text{pK}_a = 10$
- d.  $\text{HCN} + \text{CH}_3\text{CN} \rightleftharpoons \text{CN}^- + \text{CH}_3\text{CNH}^+$  At equilibrium the reactants will be favored  
 $\text{HCN } \text{pK}_a = 9$   $\text{CH}_3\text{CNH}^+ \text{pK}_a = -10$

Exercise 14.14.2:





Exercise 14.15.1:

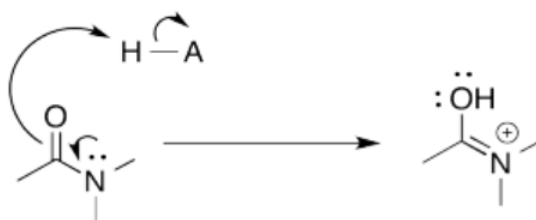
the nitrogen lone pair electrons in an amide are delocalized making them less basic





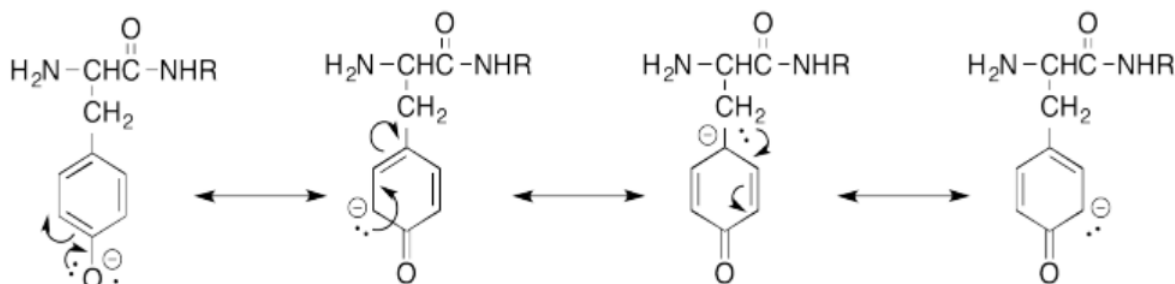
Exercise 14.15.2:

protonation of the oxygen leads to a conjugate acid that is conjugated



Exercise 14.15.3:

The alcohol proton on tyrosine is more acidic due the resonance stabilization of the conjugate base. The conjugate base of serine possesses a localized anionic charge and is relatively less stable.



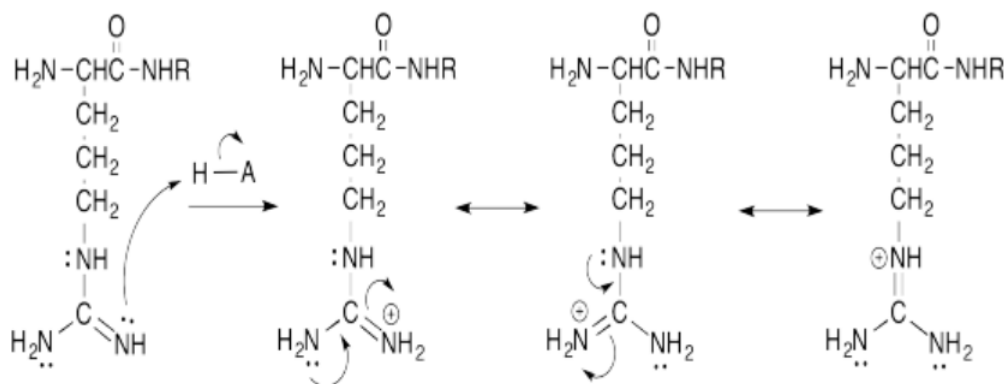
*resonance structures for the tyrosine anion*

Exercise 14.15.4:

The thiol proton on cystine is more acidic due to the polarizability of the sulfur anion stabilizing the conjugate base's anionic charge. The oxygen anion is less polarizable and therefore less stable rendering the alcohol proton less acidic.

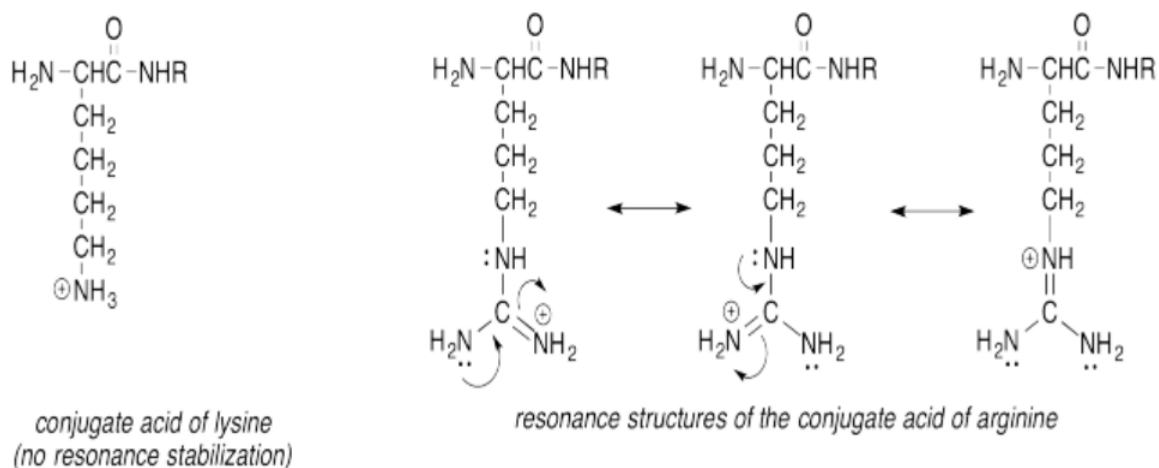
Exercise 14.15.5:

Protonation of the indicated nitrogen leads to a conjugate acid that still benefits from resonance stabilization, while protonation of the other two nitrogen atoms would decrease conjugation.



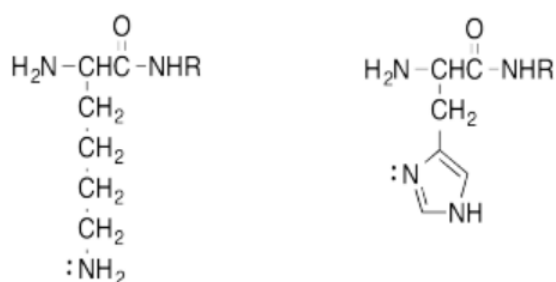
*resonance structures of the conjugate acid of arginine*

The  $pK_a$  of protonated arginine is higher than protonated lysine due to the resonance stabilization of the cationic charge



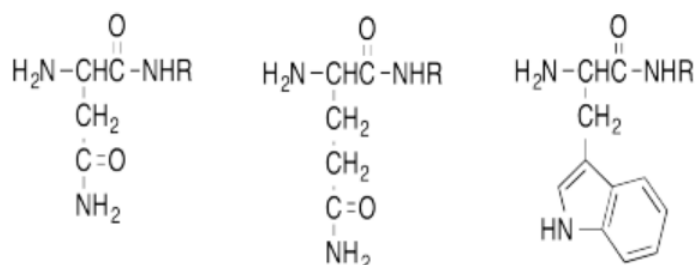
#### Exercise 14.15.6:

Lysine is a stronger amine base than histidine due to the difference in hybridization ( $sp^3$  vs.  $sp^2$ )



#### Exercise 14.15.7

The lone pair electrons on the un-basic are resonance delocalized and not available for protonation. The side chain nitrogens on asparagine and glutamine are found in amide groups and the nitrogen on tryptophan is part of an aromatic ring. Protonation of any of these nitrogens would break up a conjugated system.



#### Exercise 14.16.1:

Ammonium bromide is more soluble because in water it can participate in both ion-dipole and hydrogen-bonding, while sodium bromide only benefits from ion-dipole interactions.

#### Exercise 14.16.2:

Hydrogen cyanide will have a lower  $pK_a$  in water as the resulting cyanide anion will be stabilized by both ion-dipole and hydrogen-bonding interactions. Hydrogen cyanide would have a higher  $pK_a$  in pentanes as the resulting cyanide anion would only experience ion-induced dipole interactions which are relatively weak.

Exercise 14.17.1:

a.  $K_a = \frac{[NC^-][H_3O^+]}{[HCN]}$

b.  $K_a = \frac{[HS^-][H_3O^+]}{[H_2S]}$

c.  $K_a = \frac{[H_2N^-][(CH_3)_2SOH^+]}{[HCN]}$

Exercise 14.17.2:

a.  $pK_a = -6$

b.  $pK_a = 9$

c.  $pK_a = 24$

d.  $pK_a = 16$

Exercise 14.17.3:

a.  $K_a = 10^{3.5}$

b.  $K_a = 10^{-4.3}$

c.  $K_a = 10^{-25}$

d.  $K_a = 10^{-9}$

Exercise 14.17.4:

At equilibrium formation of the Lewis acid-base complex is slightly favored.

Exercise 14.17.5:

At equilibrium formation of the Lewis acid-base complex of dimethylether and  $BF_3$  is more favored than the corresponding diethylether  $BF_3$  complex. This is likely due to the decreased steric bulk of the methy groups compared to the ethyl groups.

Exercise 14.17.6:

a.  $K_{eq} = \frac{[(NH_3)_2PtCl_2]}{[(NH_3)PtCl_2][NH_3]}$

b.  $K_{eq} = \frac{[Mo(CO)_6]}{[Mo(CO)_5][CO]}$

c.  $K_{eq} = \frac{[FeCl_4^-]}{[FeCl_3][Cl^-]}$

Exercise 14.18.1:

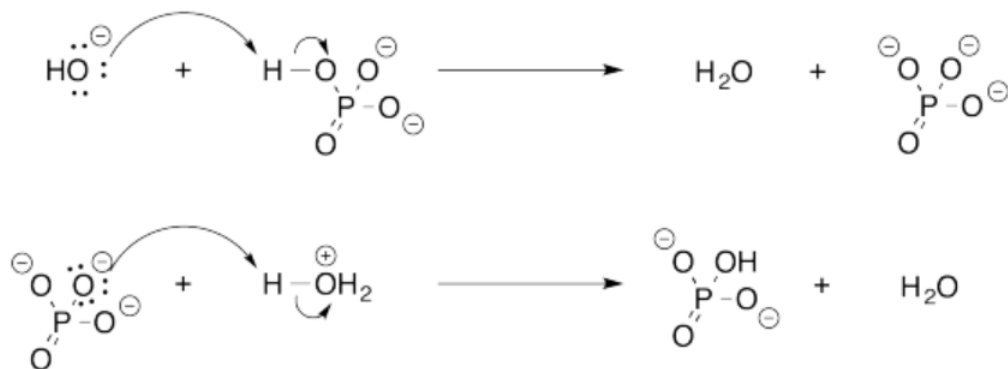
a.



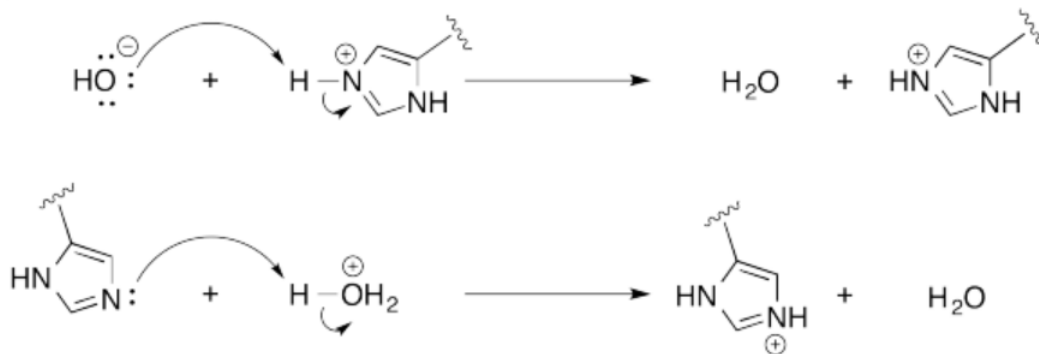
b.



c.



d.



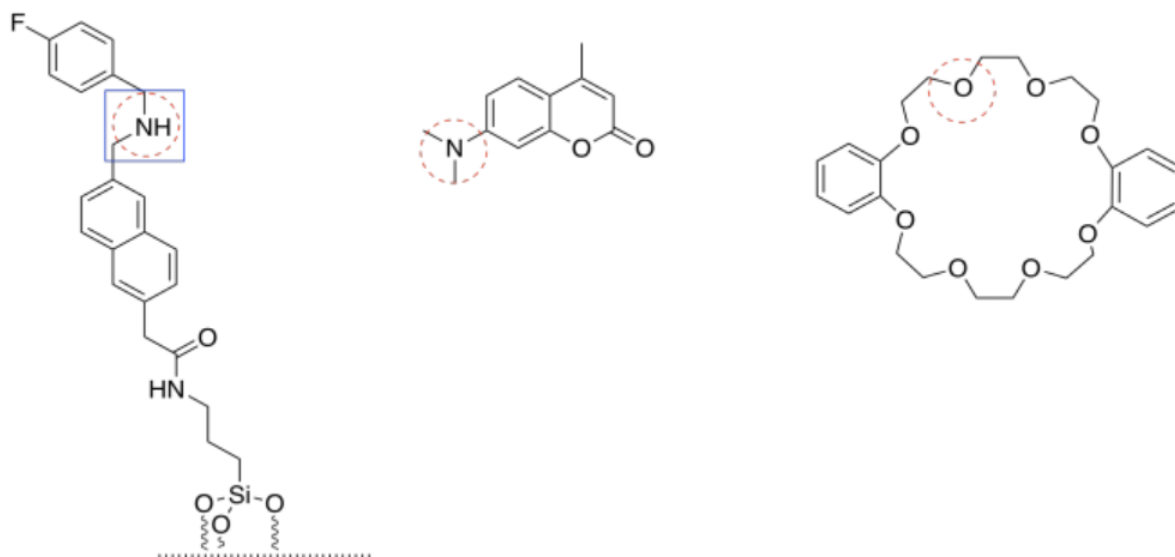
#### Exercise 14.19.1:

- all bases have lone pairs.
- F, N, and O have lone pairs. They can be bases.

Their order of basicity would be  $N > O > F$ .

These three elements come from the same row of the periodic table and so they are of similar sizes. However, N is the least electronegative and F is the most electronegative. N is most able to donate electrons and most able to support a positive charge, compared to the other two.

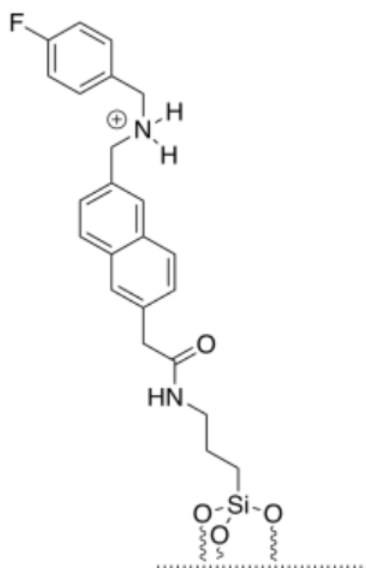
c)



If possible, a nitrogen is circled in each molecule. The cap has only basic oxygen atoms. If there is a choice between two nitrogens (in the tether) or two oxygens (in the cap), the non-conjugated lone pair would be most basic. Conjugated lone pairs are held in place by their stable interaction with their neighbors.

The most basic of all is the amine (non-conjugated) nitrogen in the tether.

d)

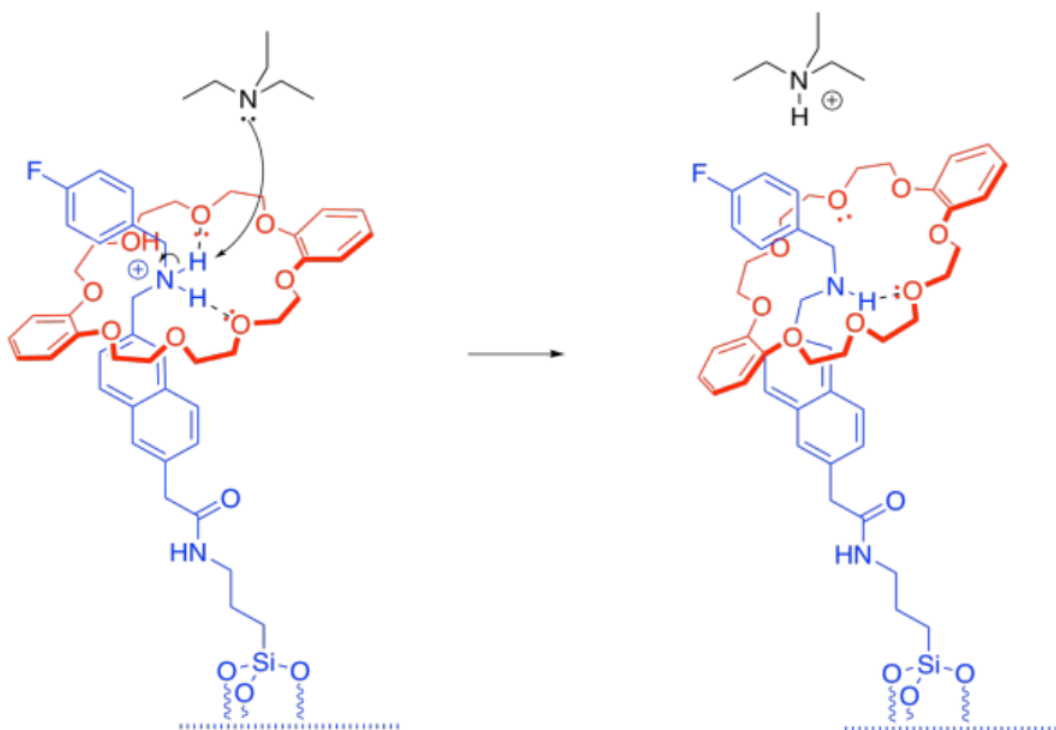


e) The cap and tether would be bound by hydrogen bonding. However, hydrogen bonding becomes much stronger if there is an ionic component. It is not a full ionic bond because the cap does not contain an anion, but its strength is between that of a normal hydrogen bond and an ionic bond.

f) Steric crowding traps the dye between the cap above and the silica surface below. The dye is too big to squeeze past the cap.

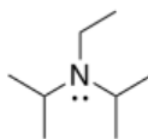
g) The dye has been released, and is now in the water.

h) There is an equilibrium between the protonated tether and the protonated triethylamine.



i) Once the tether has been deprotonated, the tether-cap interaction is just a normal hydrogen bond. It's still strong, but not as strong as the ion-boosted hydrogen bonding that we had before.

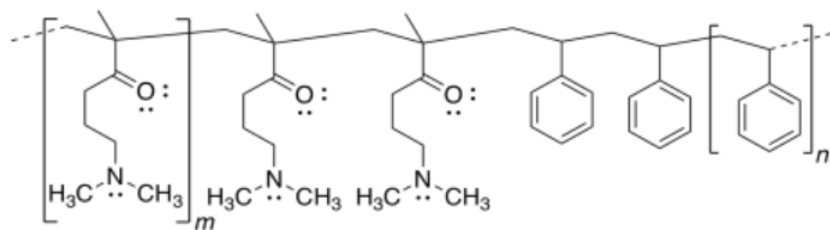
j) N,N-Diisopropylethylamine or Hunig's base:



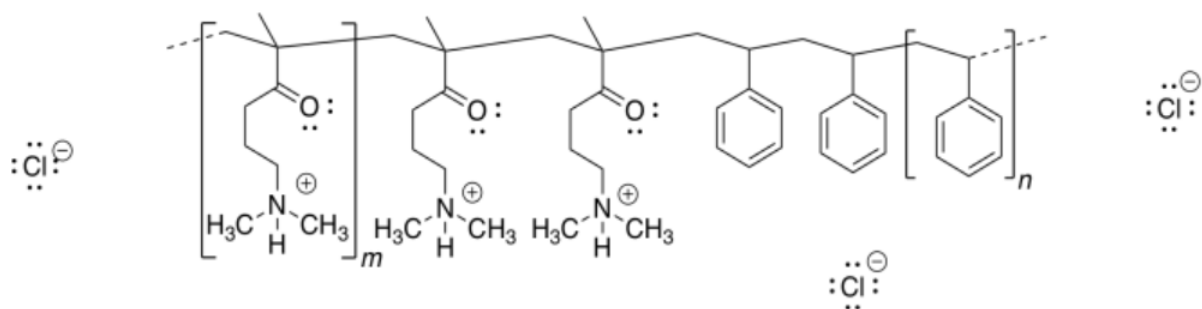
k) The lone pair in Hunig's base is much more crowded than the one in triethylamine, so it cannot remove the proton as quickly.

#### Exercise 14.19.2:

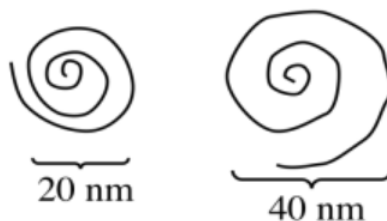
a)



b)

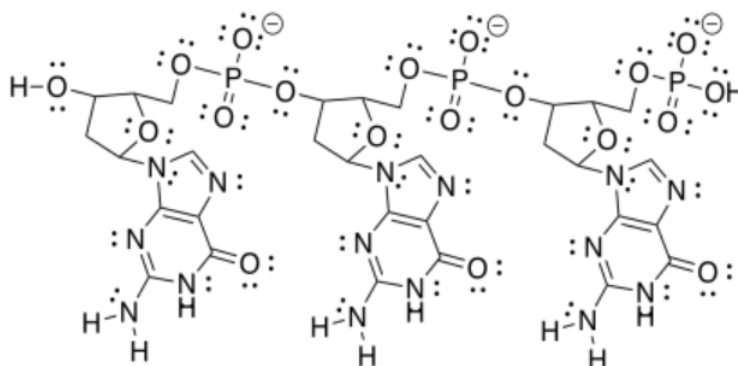


c)

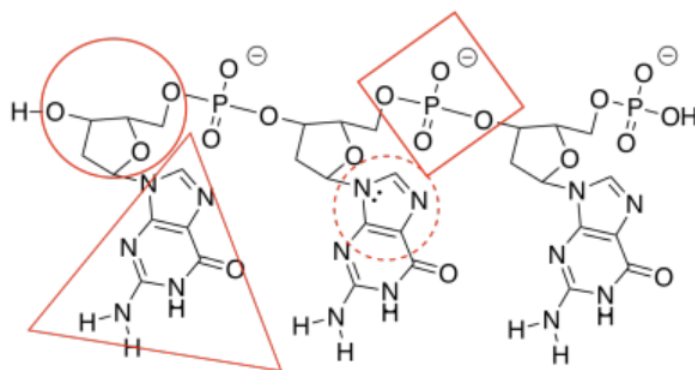


d) Repulsion between the positively-charged quaternary ammonium groups ( $\text{poly-CH}_2\text{-N(H)(CH}_3)_2^+$ ) would cause the nanoparticle to uncoil.

e)

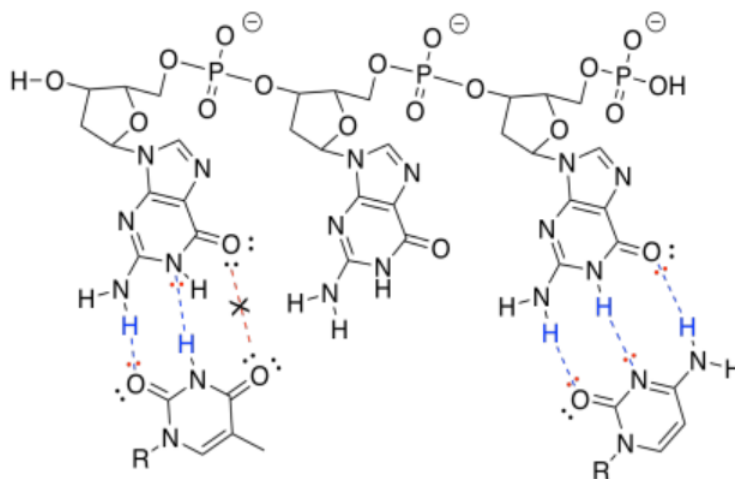


f)



g)





h) The one on the right forms three hydrogen bonds with the DNA and binds more tightly than the one on the left, which forms only two hydrogen bonds with the DNA.

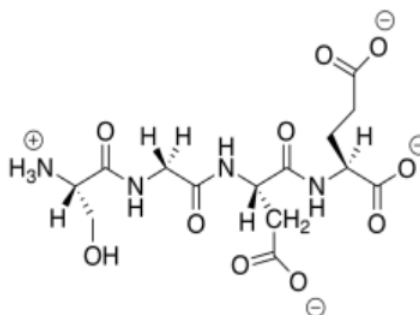
i) The polymer is positively charged after acid treatment. It binds the negatively charged DNA via ion-ion interactions.

j) If there are enough of them, the chloride anions could "wash out" the anionic DNA. These individual anions would replace the DNA anion previously bound to the nanoparticle.

k) The triethylamine could remove the proton from the polymer chain. If the polymer chain were no longer charged, it would no longer bind the anionic DNA.

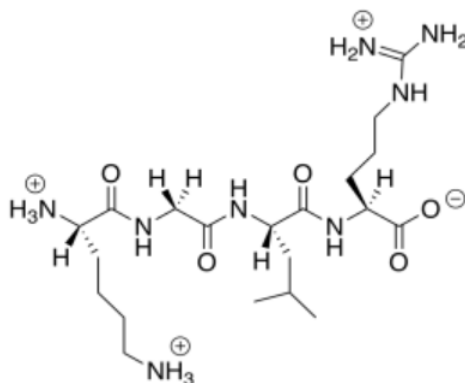
l) Also, because the nanoparticles would no longer be charged, there would no longer be repulsive forces causing the polymer to uncoil.

m)



n) This anionic (overall) peptide would bind to the cationic nanoparticles, replacing the DNA.

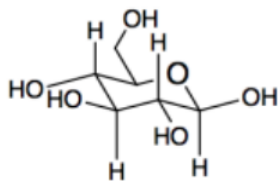
o)



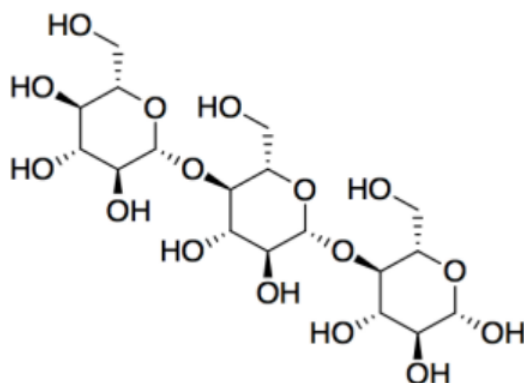
This cationic (overall) peptide would not bind to the cationic nanoparticles, so it would not displace the DNA.

Exercise 14.19.4:

a)



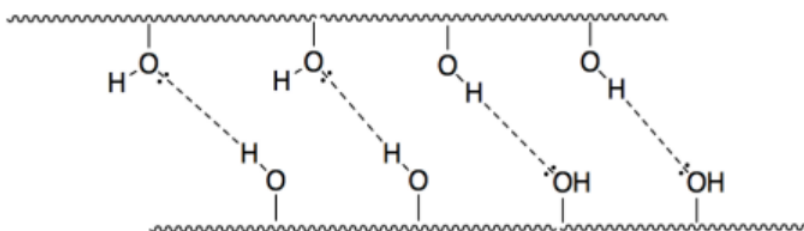
b)



c) carbohydrates

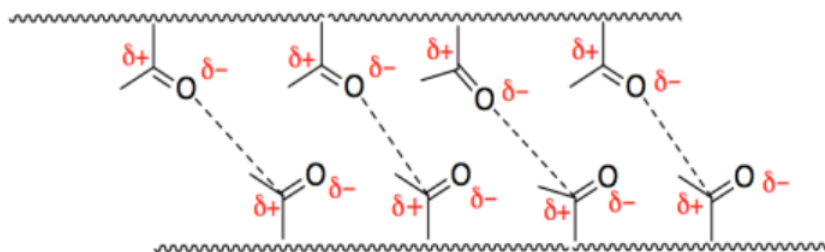
d) Cellulose is the major component of cotton (textiles and money) and paper.

e)



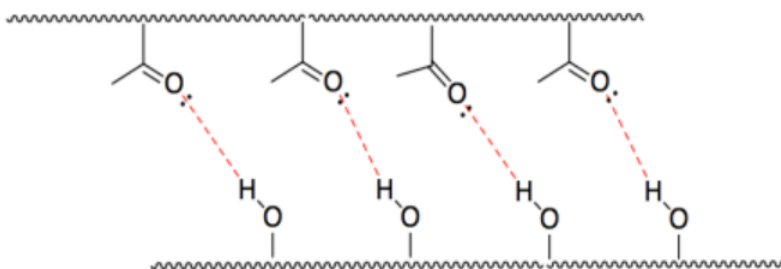
f) ester

g)

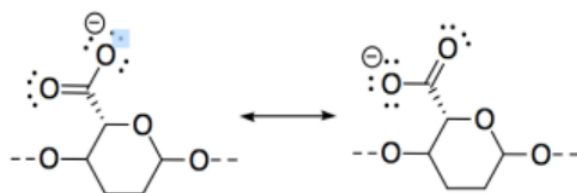


h) Body temperature is closer to 40°C, so the hip would be soft and rubbery. That would make walking a little unpredictable.

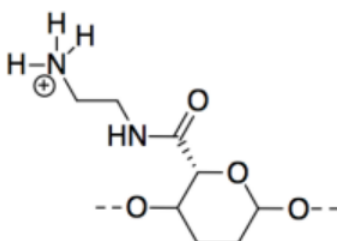
i)



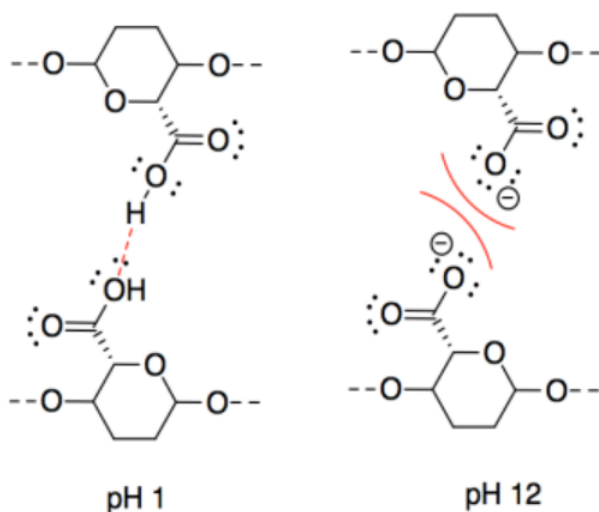
- j) HCl is acidic because the H-Cl bond is polarized with electrons closer to Cl.
- k) NaOH is basic because the Na-O bond is more polarized, with electrons closer to O.
- l) CNC-CO<sub>2</sub>H is most acidic because of the resonance stabilized anion in the conjugate base.



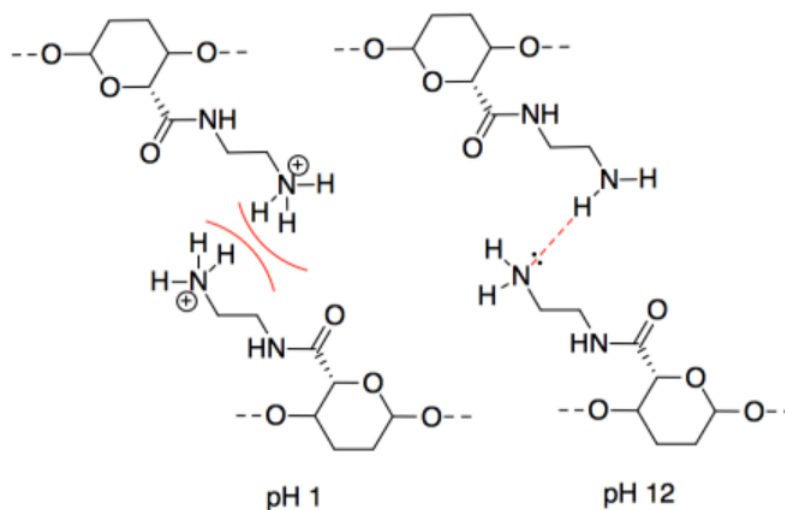
- m) CNC-NH<sub>2</sub> is most basic because, although all three compounds possess lone pairs, the lone pair on the nitrogen is on a less electronegative atom than the lone pairs on oxygens, so it is more readily donated to a proton.



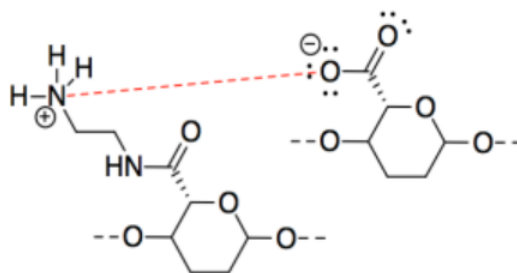
- n) This one may seem counterintuitive. The intermolecular forces at pH 11 are ionic, which should be stronger than hydrogen bonding. However, interactions between two anionic chains are repulsive, which would decrease the attraction between neighbouring CNC chains.



o) The intermolecular forces at pH 3 are ionic, which should be stronger than hydrogen bonding. However, interactions between two cationic chains are repulsive, which would decrease the attraction between neighbouring CNC chains.



p) A proton would be transferred from the acidic site to the basic site. The oppositely charged CNC chains would attract each other strongly.



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