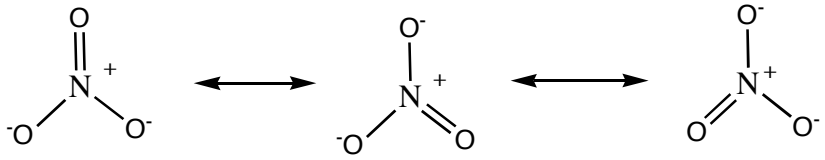
Additional Problems for practice

1. Rank each of the following compounds from the most to the least acidic:
In all cases, consider the stability of conjugate base form of the acid:

$$HA + H_2O \Leftrightarrow H_3O^+ + A^-$$

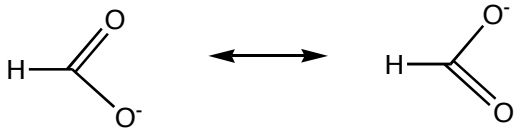
a. HCO_2H, HNO_3, NH_3

$HNO_3 + H_2O \Leftrightarrow H_3O^+ + NO_3^-$



three resonance forms of conjugate base

$HCOOH + H_2O \Leftrightarrow H_3O^+ + HCOO^-$



two resonance forms of conjugate base

$NH_3 + H_2O \Leftrightarrow H_3O^+ + H_3N^-$

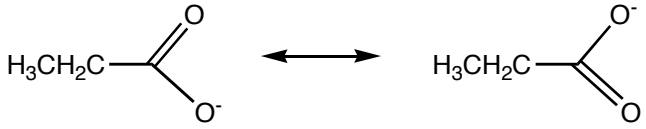
thus, HNO_3(3 resonance forms of conjugate base)> HCO_2H(two resonance forms of conjugate base)> NH_3 (no resonance forms. Negative charge on nitrogen, not oxygen)

b. CH_3CH_2OH, $CH_3CH_2CO_2H$, $CH_3CH_2NH_2$

$CH_3CH_2OH + H_2O \Leftrightarrow H_3O^+ + CH_3CH_2O^-$

(No resonance forms of conjugate base)

$CH_3CH_2CO_2H + H_2O \Leftrightarrow H_3O^+ + CH_3CH_2CO_2^-$



two resonance forms of conjugate base

$CH_3CH_2NH_2 + H_2O \Leftrightarrow H_3O^+ + CH_3CH_2HN^-$

No resonance forms of conjugate base; negative charge on less electronegative nitrogen)

Thus, $CH_3CH_2CO_2H$(two resonance forms of conjugate base)>CH_3CH_2OH (negative charge on oxygen)> $CH_3CH_2NH_2$ (negative charge on nitrogen)

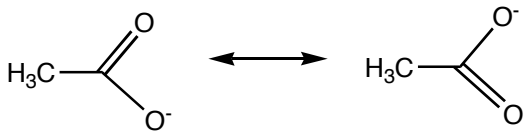
c. CH_4, HCN, H_2O, CH_3CO_2H

$CH_4 + H_2O \Leftrightarrow H_3O^+ + H_3C^-$
No resonance forms of conjugate base; negative charge on carbon, which is a relatively electropositive element

$HCN + H_2O \Leftrightarrow H_3O^+ + NC^-$
No resonance forms of conjugate base; negative charge on carbon, which is attached to electronegative nitrogen atom

$H_2O + H_2O \Leftrightarrow H_3O^+ + HO^-$
No resonance forms of conjugate base; negative charge localized on oxygen atom

$CH_3CO_2H + H_2O \Leftrightarrow H_3O^+ + CH_3CO_2^-$



two resonance forms of conjugate base

CH_3CO_2H (two resonance forms of conjugate base)> HCN (negative charge on C, but negative charge in an sp orbital, which places electron density closer to nucleus)> H_2O (negative charge on O)> CH_4 (negative charge in an sp^3 orbital on C)

2. Classify the following reagents as Lewis acids or Lewis bases
   (a) $AlBr_3$ Lewis acid, electron-deficient aluminum atom (Aluminum lacks an octet); Br, though it has three lone pairs, is a very electronegative element and thus should not be considered a Lewis base

   (b)HF Lewis acid, dissociates to H^+ (a lewis acid) and F^- (very electronegative, so should not be considered a lewis base despite having three lone pairs).

   (c)BH_3 Lewis acid (Boron lacks an octet and is thus electron-deficient)

   (d)$TiCl_4$ (Ti in +4 oxidation state attached to four electronegative chlorine atoms is electron-deficient, thus this is a Lewis acid)

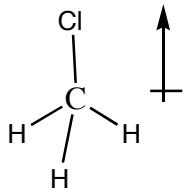
   (e) CH_3SCH_3 (Lewis base, lone pairs on S available for donation)

   (f)$CH_3CH_2NH_2$ (a lewis base, lone pairs on N available for donation)

   Remember, although the halogens have lone pairs, they are not considered Lewis bases because they are not likely to share these electrons because of their electronegativity.

3. Which of the following compounds have polar bonds, and which have dipole moments?

(a) CH_3Cl Polar C-Cl bond, net dipole moment

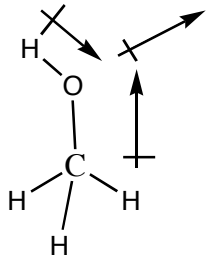


net dipole moment

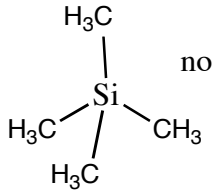
(b) Cl_2 Non-polar Cl-Cl bond, no dipole moment

(c)CH_3OH polar C-O and O-H bond, dipole moment

net dipole moment

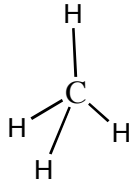


(d)$(CH_3)_4Si$ non-polar Si-C bond, no dipole moment



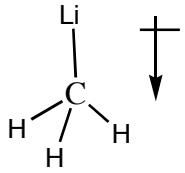
no polar bonds; nonet dipole moment

(e)CH_4 non-polar C-H bonds, no dipole moment



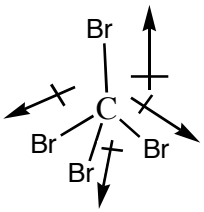
no polar bonds; no net dipole moment

(f) CH_3Li polar C-Li bond, dipole moment



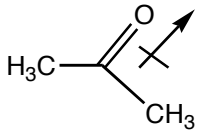
very polar C-Li bond; net dipole moment

(g) CBr_4 polar C-Br bonds, no dipole moment



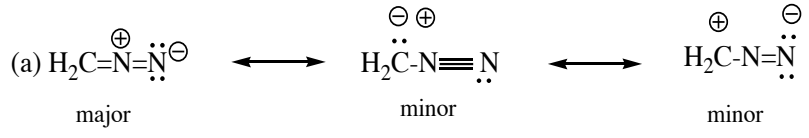
Polar C-Br bonds; no net dipole moment because all dipoles cancel each other

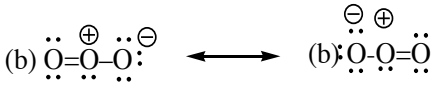
(h) CH_3COCH_3 polar C-O bond, dipole moment

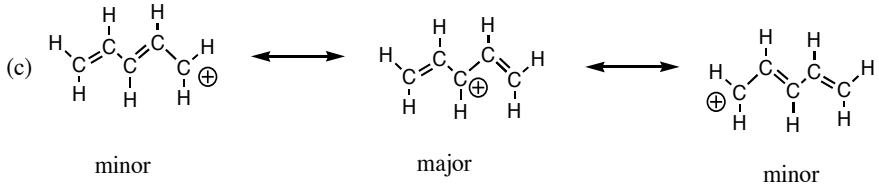


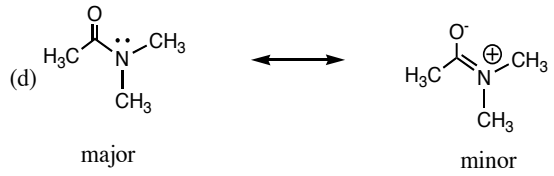
net dipole moment

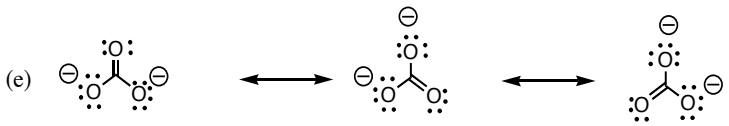
4. Draw all important resonance structure for the following species. If applicable, indicate major and minor resonance contributors





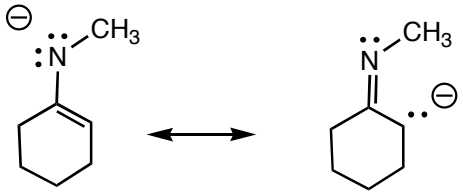






5. Predict the major and minor resonance contributors in each case.
Place the negative charge on the more electronegative element:

(a)



major minor

(b) $H_3C-C\equiv N-O$ $\longleftrightarrow$ $H_3C-C=N-O$

major minor

maximize the number of bonds