ORGANIC CHEMISTRY I

PRACTICE PROBLEMS FOR BRONSTED-LOWRY ACID-BASE CHEMISTRY

1. For each of the species below, identify the most acidic proton and provide the structure of the corresponding conjugate base. You might want to draw detailed Lewis formulas in some cases.



2. For each of the species below, identify the basic atom and provide the structure of the corresponding conjugate acid. You might want to draw detailed Lewis formulas in some cases.



3. Fill in the reactants or products for the following acid-base reactions. Keep in mind that in line-angle formulas hydrogens are not shown. When in doubt, write complete Lewis structures. Abbreviations used: Ph=phenyl (a benzene ring attached to a carbon chain)



4. Arrange the substances by order of acidity or basicity as indicated. You may use pKa tables, periodic tables, or any other tools available to you (except for your cell phone).

H ₂ Se H ₂ O H ₂ S		
	weakest acid	strongest acid
	strongest base	weakest base
CH ₄ HI PH ₃ H ₂ Se		
	strongest acid	weakest acid
FOH NH2 CH3CH	2CH ₂ CH ₂ CH ₂	
	weakest basse	strongest base
CH ₃ CH ₂ OH CH ₃ COC	DH HF Benzene	
	weakest acid	strongest acid

5. Circle the side favored by equilibrium in the following acid-base reactions.

$$CN^{-} + NH_{3} \implies HCN + N\overline{H}_{2}$$

$$+OH + H_{3C} \stackrel{\circ}{\xrightarrow{}}_{CH_{2}} \implies +O^{-} + H_{3C} \stackrel{\circ}{\xrightarrow{}}_{CH_{3}}$$

$$H_{2}O + \stackrel{\circ}{\underbrace{}}_{-NH_{3}} \implies H_{3}O^{+} + \stackrel{\circ}{\underbrace{}}_{-NH_{2}}$$

$$H_{2}CO_{3} + H_{2}O \implies HC\overline{O}_{3} + H_{3}O^{+}$$

$$CH_{3}CH_{2}CH_{2}CH_{3} + \stackrel{\circ}{\underbrace{}}_{-CH_{2}} \implies CH_{3}CH_{2}CH_{2}CH_{2} + \stackrel{\circ}{\underbrace{}}_{-CH_{3}}$$

6. The conjugate acid of ammonia, NH₃, is:

A) NH_4^+ B) NH_2OH C) NH_2^- D) none of the above

7. Methanesulfonic acid, CH_3SO_3H , has a pK_a of -7 while ethanol, CH_3CH_2OH , has a pK_a of 15.9. Which is the stronger acid and what accounts for this large difference in relative acidity?

8. Would you predict trifluoromethanesulfonic acid, CF_3SO_3H , to be a stronger or weaker acid than methanesulfonic acid, CH_3SO_3H ? Explain your reasoning.

9. Consider the species CH_3O^- , NH_2^- , and CH_3COO^- . Rank these ions in order of increasing basicity, and explain your rationale.

10. The K_a of formic acid is 1.7 x 10⁻⁴. The pK_a of formic acid is _____.

A) 1.7 B) 10.3 C) 4.0 D) 3.8 E) -2.3

11. Provide the structure of the conjugate base of phenol (shown below) and all its resonance forms.



12. Rank the following in order of increasing acidity: CH₃OH, HCl, NH₃, and CH₄.

13. Rank the following in order of increasing basicity: CH_3O^- , H_2N^- , H_2O , and NH_3 .

14. When methanol (CH₃OH) acts as a base, its conjugate acid is ______.

A) CH_4OH B) $CH_3OH_2^+$ C) CH_4O^+ D) CH_3O^- E) $-CH_2OH$

15. Which of the following pairs of bases lists the stronger base first?

A) $H_2O > HO^-$ B) $H_2N^- > CH_3COO^-$ C) $CH_3COO^- > HO^-$ D) $I^- > CI^-$ E) $HO^- > H_2N^-$

16. Draw the structure of the conjugate acid of acetone (CH_3COCH_3) .

ANSWERS



HF	FΘ	CH ₃ CH ₃	Ө СН ₃ СН ₂
CH₃CH₃OH	б CH ₃ CH ₃ O	CH₂CN	⊖ CH₂CN
+ H ₃ O	H ₂ O	нс≡сн	Θ HC≡C:
ů L	ө	H ₂	.н ^ө
+ RNH ₃	RNH ₂	+ CH ₃ OH ₂	СН₃ОН

2.



$$HNO_{3} + H_{2}O \implies H_{3}O^{+} + NO_{3}^{-}$$

$$HF + H_{2}O \implies F^{-} + H_{3}O^{+}$$

$$HF + H_{2}O \implies F^{-} + H_{3}O^{+}$$

$$H_{3}C \stackrel{\frown}{\longleftarrow} CH_{3} + \stackrel{\frown}{O}H \implies H_{3}C \stackrel{\frown}{\longleftarrow} CH_{2} + H_{2}O$$

$$PhCOOH + CI^{-} \implies PhCOO^{-} + HCI$$

$$H_{2}CO_{3} + \stackrel{\frown}{O}H \implies HCO_{3}^{-} + H_{2}O$$

$$\stackrel{\frown}{\bigoplus} : \stackrel{\frown}{=} + H_{2}O \implies \stackrel{\frown}{\bigoplus} \stackrel{\frown}{\bigoplus} + OH^{-}$$

$$INH_{2} + HC \equiv CH \implies NH_{3} + HC \equiv C.^{-}$$

$$\stackrel{\frown}{\longrightarrow} H_{2} + HC \equiv CH \implies NH_{3} + HC \equiv C.^{-}$$

$$\stackrel{\frown}{\longrightarrow} H_{2} + HC \equiv CH \implies H_{3} + HC \equiv C.^{-}$$

$$\stackrel{\frown}{\longrightarrow} H_{2} + HC \equiv CH \implies H_{3} + HC \equiv C.^{-}$$

$$Periodic trend \qquad \frac{H_{2}O < H_{5}S < H_{2}Se}{\text{weakest acid}}$$

$$Periodic trend \qquad \frac{F^{-} > CI^{-} > Br^{-} > I^{-}}{\text{strongest base}}$$

$$Periodic trend \qquad \frac{HI > H_{2}Se > PH_{3} > CH_{4}}{\text{strongest acid}}$$

$$Periodic trend \qquad \frac{F^{-} < OH^{-} < NH_{2}^{-} < CH_{3}CH_{2}CH$$

 $pK_{a} \text{ trend} \quad \frac{\text{Benzene} < \text{CH}_{3}\text{CH}_{2}\text{OH} < \text{CH}_{3}\text{COOH} < \text{HF}}{\text{weakest acid}}$

3.

4.

5. The numbers represent approximate pK_a values for the substances acting as acids.



6. A

7. Methanesulfonic acid is the stronger acid. The lower the pKa, the stronger the acid. A lower pKa is associated with a larger Ka which signifies greater dissociation. The large relative difference in acidity in this case can be most easily seen by gauging the relative basicities of the conjugate bases. The weaker the base, the stronger the corresponding conjugate acid. Methanesulfonate, $CH_3SO_3^-$, is considerably stabilized by resonance delocalization which is not found in ethoxide, $CH_3CH_2O^-$. This effect greatly reduces the basicity of methanesulfonate relative to ethoxide. Draw the Lewis formula for methanesulfonate and the resonance forms for practice.

8. Trifluoromethanesulfonic acid is a stronger acid. Compare the strengths of the conjugate bases and remember that the weaker the base, the stronger the conjugate acid. Both bases are stabilized by resonance, but in the case of the trifluoro derivative, the presence of the highly electronegative fluorine atoms serves to delocalize the negative charge to an even greater extent by the inductive effect of fluorine. This additional delocalization makes trifluoromethanesulfonate a weaker base.

9. $CH_3COO^- < CH_3O^- < NH_2^-$

first factor to consider is the nature of the atom which bears the negative charge. The more electronegative the atom that bears the negative charge, the more stable the

anion. Stable anions are less reactive and are hence weaker bases. Since O is more electronegative than N, the NH_2^- is the strongest base in the set. In the remaining two species, the negative charge is on the O, but in the case of CH_3COO^- , the negative charge is also delocalized by resonance.

10. D

11. See class notes, or p. 417 of the Wade textbook, for all the resonance structures of the phenoxide ion shown below.



12. $CH_4 < NH_3 < CH_3OH < HCl$ (periodic trend)

13. $H_2O < NH_3 < CH_3O^- < H_2N^-$ Negatively charged ions are stronger bases than neutral counterparts. A table of pK_a values will further aid in deciding the final order of basicity.

14. B

15. B

16.

