Organic Chemistry, 8e (Bruice)
Chapter 2  Acids and Bases: Central to Understanding Organic Chemistry

1) Which of the following is not a conjugate acid-base pair?
   A) H2O, HO-
   B) H2O, H3O+
   C) HSO4-, H2SO4
   D) -OH, O2-
   E) NO3-, NO2-
   Answer: E
   Section: 2-1
   MCAT: 1.4

2) What is the product formed from the following acid-base reaction when ammonia functions as a base? The equilibrium lies far to the reactants.
   \[ \text{CH}_3\text{OH} + \text{NH}_3 \rightleftharpoons \]
   A) CH3O- + NH4
   B) CH2OH + NH3
   C) CH3OH2+ + NH2
   D) CH3NH2 + H2O
   E) CH4 + NH2OH
   Answer: A
   Section: 2-1
   MCAT: 1.4

3) The conjugate acid of H2O is
   A) H3O-
   B) H3O
   C) H3O+.
   D) HO-
   E) H2O+.
   Answer: C
   Section: 2-1
   MCAT: 1.4
4) Which of the following ions is the strongest acid?
A) H-
B) HO-
C) HSO4-
D) H2O
E) H3O+
Answer: E
Section: 2-1
MCAT: 1.4

5) Which species act as bases in the following reaction?
\[ H_2SO_4 + HNO_3 \rightarrow H_2NO_3 + HSO_4^- \]
A) 1 and 2
B) 3 and 4
C) 2 and 4
D) 1 and 3
E) 2 and 3
Answer: C
Section: 2-1
MCAT: 1.4

6) What is the conjugate acid of NH3?
A) +NH3
B) -NH
C) +NH4
D) -NH2
E) +NH2
Answer: C
Section: 2-1
MCAT: 1.4

7) What is the conjugate acid of CH3NH2?
A) CH3NH3+
B) CH3NH-
C) NH4+
D) NH2-
Answer: A
Section: 2-1
MCAT: 1.4
8) What is the conjugate base of CH₃NH₂?
A) CH₃NH₃⁺
B) CH₃NH⁻
C) NH₄⁺
D) NH₂⁻
Answer: B
Section: 2-1

9) Give the conjugate acid and the conjugate base for HSO₄⁻:
Answer: conjugate acid: H₂SO₄
conjugate base: SO₄²⁻
Section: 2-1
MCAT: 1.4

10) Write a completed equation for the acid-base pair shown below.
HCO₂H + -NH₂ →
Answer: HCO₂H + -NH₂ → HCO₂⁻ + NH₃
Section: 2-1
MCAT: 1.4

11) What is the pH of a 0.1 M solution of HCl? (Note: pKₐ for HCl is -6.)
A) 6
B) -6
C) 1
D) -8
E) -1
Answer: C
Section: 2-2
MCAT: 1.4
GLO: G2, G4

12) If H₂O has a pKₐ value of 15.7 and HF has a pKₐ value of 3.2, which is a stronger base, HO⁻ or F⁻? Explain.
Answer: HO⁻ is a stronger base than F⁻ because HF is a stronger acid than H₂O, and the stronger the acid the weaker its conjugate base.
Section: 2-2
MCAT: 1.4
GLO: G2
13) 2-Propanol is shown below. Draw the structure of its conjugate base.

(\text{CH}_3)_2\text{CHOH}

Answer:

\[ \begin{array}{c}
\text{H}_3\text{C} \quad \text{C} \quad \text{C} \\
\text{H} \\
\end{array} \]

Section: 2-3

14) Which of the following is the strongest acid?

A) \text{CH}_3\text{OH} \\
B) \text{CH}_3\text{OH}_2^+ \\
C) \text{H}_2\text{N}^- \\
D) \text{CH}_3\text{NH}_2 \\
E) \text{CH}_3\text{NH}_3^+ \\

Answer: B

Section: 2-6

GLO: G2

15) The pKa of \text{CH}_3\text{COOH} is 4.8 and the pKa of \text{HCOOH} is 3.8. Given this information, one knows that

A) \text{CH}_3\text{COOH} completely ionizes in water. \\
B) \text{HCOOH} is a weaker acid than \text{CH}_3\text{COOH}. \\
C) \text{HCOO}^- is a weaker base than \text{CH}_3\text{COO}^- . \\
D) \text{CH}_3\text{COOH} reacts with \text{HO}^- while \text{HCOOH} does not. \\
E) \text{HCOOH} reacts with \text{HO}^- while \text{CH}_3\text{COOH} does not. \\

Answer: C

Section: 2-6

MCAT: 20.2

16) Which of the following is the strongest acid?

A) \text{HF} \\
B) \text{H}_2\text{O} \\
C) :\text{NH}_3 \\
D) \text{CH}_4 \\
E) \text{CH}_3\text{OH} \\

Answer: A

Section: 2-6

MCAT: 1.4
17) Which of the following is the strongest acid?
A) CH₃CH₂OH
B) CH₃OCH₃
C) CH₃—NH—CH₃
D) CH₃—C≡CH
E) CH₃—CH=CH₂
Answer: A
Section: 2-6
MCAT: 1.4

18) Consider the set of compounds, NH₃, HF, and H₂O. Rank these compounds in order of increasing acidity and discuss your rationale.
Answer: NH₃ < H₂O < HF
When determining relative acidity, it is often useful to look at the relative basicity of the conjugate bases. The stronger the acid, the weaker (more stable, less reactive) the conjugate base. In this case, one would look at the relative basicity of F⁻, OH⁻, and NH₂⁻. The relative strengths of these species can be gauged based on the electronegativity of the charged atom in each base. Since fluorine is the most electronegative, F⁻ is the most stable, least reactive base in the group. This means that its conjugate acid, HF, is the strongest.
Section: 2-6
MCAT: 1.4
GLO: G2

19) Identify the compound with the highest pKₐ.
A) CH₃NH₂
B) CH₃OH
C) CH₃COOH
D) H₂O
E) CH₃NH₃⁺
Answer: A
Section: 2-6
MCAT: 1.4
GLO: G2

20) Identify the compound with the highest pKₐ.
A) CH₃CH₃
B) HCCCH
C) CH₂CH₂
D) CH₃OH
E) CH₃NH₂
Answer: A
Section: 2-6
MCAT: 1.4
21) Identify the most acidic carboxylic acid.
A) ICH₂COOH
B) BrCH₂COOH
C) CH₃COOH
D) FCH₂COOH
E) ClCH₂COOH
Answer: D
Section: 2-7
MCAT: 1.4, 20.2

22) Which of the following is the strongest acid?

\[
\begin{align*}
\text{I.} & \quad \begin{array}{c}
\text{C} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \\
\text{\text{COOH}} \\
\text{II.} & \quad \begin{array}{c}
\text{C} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \\
\text{\text{COOH}} \\
\text{III.} & \quad \begin{array}{c}
\text{C} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \\
\text{\text{COOH}} \\
\text{IV.} & \quad \begin{array}{c}
\text{C} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \\
\text{\text{COOH}} \\
\text{V.} & \quad \begin{array}{c}
\text{C} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H}
\end{array} \\
\text{\text{COOH}}
\end{align*}
\]

A) I
B) II
C) III
D) IV
E) V
Answer: E
Section: 2-7
MCAT: 1.4, 20.2

23) Explain why : NF₃ is a weaker base than : NH₃.
Answer: Fluorine has an electron withdrawing effect that reduces the availability of the pair of electrons on nitrogen. Thus the basicity of : NF₃ is less than that of : NH₃.
Section: 2-7
MCAT: 1.4
GLO: G2
24) Would you predict trifluoromethanesulfonic acid, CF$_3$SO$_3$H, to be a stronger or weaker acid than methanesulfonic acid, CH$_3$SO$_3$H? Explain your reasoning.

Answer: 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. In the case of the trifluoro derivative, the presence of the highly electronegative fluorine atoms serves to delocalize the negative charge to a greater extent. This additional delocalization makes trifluoromethanesulfonate a weaker base.

Section: 2-7
MCAT: 1.4

25) Which of the following anions, CH$_3$CHBrCO$_2$- or CH$_3$CHFCO$_2$- is the stronger base? Explain your choice.

Answer: CH$_3$CHBrCO$_2$- is the stronger base. The more electronegative F atom can more effectively delocalize the negative charge via induction. This greater delocalization stabilizes CH$_3$CHFCO$_2$- relative to CH$_3$CHBrCO$_2$- and makes it a weaker base.

Section: 2-7
MCAT: 1.4, 20.2
GLO: G2

26) Draw a resonance contributor and the resonance hybrid for HOCO$_2$-.

Answer: resonance contributor: resonance hybrid:

27) The pKa of CH$_3$COOH is 4.8. If the pH of an aqueous solution of CH$_3$COOH and CH$_3$COO$^-$ is 4.8, then one knows

A) CH$_3$COOH is completely ionized.
B) [CH$_3$COOH] > [CH$_3$COO$^-$].
C) [CH$_3$COOH] = [CH$_3$COO$^-$].
D) [CH$_3$COOH] < [CH$_3$COO$^-$].
E) CH$_3$COOH is completely unionized.

Answer: C
Section: 2-10
GLO: G2, G4
28) When a small amount of hexanoic acid \([\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}, \text{pKa} \sim 4.8]\), is added to a separatory funnel which contains the organic solvent diethyl ether and water with a pH of 2.0, it is found mainly in the ________ phase as ________.
A) ether; \text{CH}_3(\text{CH}_2)_4\text{CO}_2^-
B) water; \text{CH}_3(\text{CH}_2)_4\text{CO}_2^-
C) ether; \text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}
D) water; \text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}
E) none of the above

Answer: C
Section: 2-10
GLO: G2, G4

29) When a small amount of hexanoic acid \([\text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}, \text{pK}_a \sim 4.8]\), is added to a separatory funnel which contains the organic solvent diethyl ether and water with a pH of 12.0, it is found mainly in the ________ phase as ________.
A) ether; \text{CH}_3(\text{CH}_2)_4\text{CO}_2^-
B) water; \text{CH}_3(\text{CH}_2)_4\text{CO}_2^-
C) ether; \text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}
D) water; \text{CH}_3(\text{CH}_2)_4\text{CO}_2\text{H}
E) none of the above

Answer: B
Section: 2-10
GLO: G2, G4

30) At what pH will 25% of a compound with a pKa of 5.3 be in its basic form?
Answer: 4.8
Section: 2-10
GLO: G2, G4

31) The amino acid glycine (\(\text{H}_3\text{N}^+\text{CH}_2\text{CO}_2\text{H}\)) has two acidic Hs, one with pKa = 2.34 and the other with pKa=9.60. Draw the structure of the form of glycine that predominates at a pH of 12.
Answer:

![Glycine Structure]

Section: 2-10
MCAT: 24.3
GLO: G2, G4
32) H-A is an acid with a pKa of 4.5. Which of the following statements about an aqueous solution of H-A is true?
A) At pH = 4.5, the solution contains much more H-A than A-.
B) At pH = 4.5, the solution contains much more A- than H-A.
C) At pH = 3.5, the solution contains about 90% A- and 10% H-A.
D) At pH = 6.5, the solution contains about 80% A- and 20% H-A.
E) At pH = 5.5, the solution contains about 90% A- and 10% H-A.
Answer: E
Section: 2-10
GLO: G2, G4

33) At what pH will the concentration of a compound with a pKa of 5.7 be 100 times greater in its acidic form than in its basic form?
Answer: 3.7
Section: 2-10
GLO: G2, G4

34) HCN has a pKa = 9.1. What form of the compound, HCN or CN-, will predominate in a solution of pH = 7.0
Answer: HCN
Section: 2-10
GLO: G2, G4

35) Propanoic acid, CH₃CH₂COOH, has a pKa = 4.9. Draw the structure of the conjugate base of propanoic acid and give the pH above which 90% of the compound will be in this conjugate base form.
Answer: CH₃CH₂COO⁻; 5.9
Section: 2-10
GLO: G2, G4

36) Buffering is used to maintain the pH of human blood in the relatively narrow 7.3 - 7.4 range. What acid/base pair serves to buffer the blood?
A) H₂O / HO⁻
B) H₃O⁺ / H₂O
C) H₂CO₃ / HCO₃⁻
D) NH₄⁺ / NH₃
E) HCl / Cl⁻
Answer: C
Section: 2-11
GLO: G2, G7
37) Explain why AlCl₃ is a Lewis acid.
Answer: A Lewis acid is an electron pair acceptor. Aluminum in AlCl₃ has an empty p orbital that can accommodate the pair of electrons provided by a Lewis base.
Section: 2-12
MCAT: 1.4

38) Structure of Lorazepam, a widely known drug for short-term anxiety is shown below. Is the indicated lone pair localized or delocalized?

Answer: Delocalized
Section: 2-8
MCAT: 2.3

39) Predict the direction of equilibrium in the following reaction. Explain your answer.

Answer: Right
Conjugate base on the right is more stable due to resonance that puts negative charge on the oxygen atom.
Section: 2-9
MCAT: 1.3
GLO: G2

40) What would be the conjugate base in the following acid base reaction?

A) CH₂O
B) CH₃OH
C) CH₃SH₂+
D) CH₃S⁻
E) H₂O

Answer: D
Section: 2-3
MCAT: 1.4
41) What would be the conjugate acid in the following acid base reaction?

\[
\text{CH}_3\text{O}^- + \text{CH}_3\text{SH} \xrightleftharpoons{} \text{CH}_3\text{OH} + \text{CH}_3\text{S}^-
\]

A) CH₂O  
B) CH₃OH  
C) CH₃SH₂⁺  
D) CH₃S⁻  
E) H₂O  
Answer: B  
Section: 2-3  
MCAT: 1.4

42) What is the product of the following Lewis acid-base reaction?

\[
\text{Cl}^-\text{Fe}^\text{III}\text{Cl}_3 + \text{Cl}^- \rightarrow \text{Cl}^-\text{Fe}^-\text{Cl}_2\text{Cl}^\text{II}\text{Cl}^-\text{Cl}^\text{I}
\]

Answer:  
Section: 2-2  
MCAT: 1.4

43) Which of the following species cannot function as a Lewis acid?

A) H⁺  
B) TiCl₄  
C) AlCl₃  
D) NH₄⁺  
E) H₂O  
Answer: E  
Section: 2-12  
MCAT: 1.4