Chapter 12 Exercises

1. Distinguish between an Arrhenius, a Brønsted, and a Lewis acid.

2. Define a Lewis acid and a Lewis base.

3. What is a salt?

4. What is a conjugate acid-base pair?

5. Use curved arrows to show the mechanisms of the following Lewis acid-base reactions. Identify the Lewis acid and the Lewis base. What is the hybridization of the boron before and after reaction (a)? What is the hybridization of the carbons before and after reaction b? Note that reaction (b) is a two-step reaction like that shown in Figure 12.4.

a) $BF_3 + NH_3 \rightarrow F_3B\text{-}NH_3$ **b)** $CO_2 + H_2O \rightarrow H_2CO_3$

6. Use curved arrows to show the mechanisms of the following Lewis acid-base reactions. Identify the Lewis acid and the Lewis base. What is the hybridization of the boron before and after reaction (a)? What is the hybridization of the sulfurs before and after reaction b? Note that reaction (b) is a two-step reaction like that shown in Figure 12.4.

a) $B(OH)_3 + OH^{1-} \rightarrow B(OH)_4^{1-}$ **b)** $SO_2 + H_2O \rightarrow H_2SO_3$

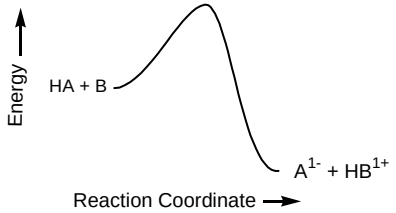
7. The potential energy diagram below is for following the acid-base reaction: $HA(aq) + B(aq) \rightarrow A^{1-}(aq) + HB^{1+}(aq)$

a) Which is the stronger acid?

b) Which is the stronger base?

c) What is the magnitude of the equilibrium constant for the reaction (K > 1 or K < 1)?

d) Draw a probable transition state (Section 9.7).



8. What is the conjugate acid of each of the following?

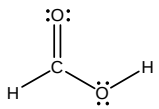
a) F^{1-} **b)** OH^{1-} **c)** HSO_3^{1-} **d)** S^{2-}

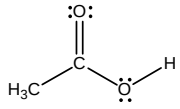
9. What is the conjugate base of each of the following?

a) HClO **b)** NH_4^{1+} **c)** H_3PO_4 **d)** HSO_3^{1-}

10. CH_3 and CH_2 groups are said to be *electron donating* groups because they place electron density on the atoms to which they are attached. Which is a stronger base CH_3NH_2 or NH_3? Explain.

11. Which is the stronger acid, formic acid or acetic acid? Which acid has the greater pK_a? Explain your answers. Refer to Exercise 10 for information about CH_3 groups.


formic acid


acetic acid

12. Which is the stronger base, NH_3 or NF_3? Explain.

13. List the following compounds in order of increasing acidity. (Recall that from Exercise 10 that CH_3 groups are electron donating.)

H-O-H H-O-Cl $H\text{-}O\text{-}CH_3$ H-O-I

14. Indicate the stronger acid in each of the following pairs and explain your choice:

a) H_3AsO_4 or H_3AsO_3

b) H_2SeO_4 or H_2SO_4

c) CH_4 or NH_3 (see Table 9.1 on page 176)

15. Indicate the stronger acid in each of the following pairs and explain your choice:

a) H_2SeO_3 or $HSeO_3^{1-}$

b) HIO_4 or HIO_2

c) CH_3COOH or CF_3COOH

16. Use curved arrows and Lewis structures to indicate the mechanisms of the following acid-base reactions:

a) $HClO_2 + H_2O$ **b)** $PO_4^{3-} + HCN$ **c)** $HC_2H_3O_2 + OH^{1-}$

17. Use curved arrows and Lewis structures to indicate the mechanisms of the following acid-base reactions.

a) $HF + S^{2-}$ **b)** $NH_3 + HNO_2$ **c)** $H_2SO_3 + C_2H_3O_2^{1-}$

18. Equal amounts of benzoic acid and sodium acetate are mixed. At equilibrium, the concentration of the benzoate ion is just slightly greater than that of the acetate ion. What can be concluded about the relative acid strengths of acetic acid and benzoic acid?

19. Consider the reaction, $HBrO + CN^{1-} \rightleftharpoons BrO^{1-} + HCN$ K = 5

a) Which is the weaker of the two acids in the above reaction?

b) Which is the weaker of the two bases in the above reaction?

c) Given that K = 0.08 for $HBrO + ClO^{1-} \rightleftharpoons BrO^{1-} + HClO$ predict where on the acid-base table should HBrO be placed, above HClO, between HClO and HCN, or below HCN?

20. Consider the following reaction: $H_2C_2O_4 + F^{1-} \rightleftharpoons HC_2O_4^{1-} + HF \quad K \sim 100$

a) Which of the two bases is stronger?

b) Which of the two acids is stronger?

c) What is the approximate value of K_a for $H_2C_2O_4$?

21. The K_a of nitrous acid (HNO_2) is 4.0×10^{-4}.

a) Write the reaction to which this equilibrium constant applies.

b) Express the K_a of nitrous acid in terms of concentrations.

For Exercises 22 and 23, use Equation 12.1 and Table 12.3 to determine the value of the equilibrium constant and write the equilibrium constant expression for each reaction.

22. a) $H_2CO_3 + SO_4^{2-} \rightleftharpoons HCO_3^{1-} + HSO_4^{1-}$

b) $H_2S + NH_3 \rightleftharpoons HS^{1-} + NH_4^{1+}$

c) $S^{2-} + H_2O \rightleftharpoons HS^{1-} + OH^{1-}$

23. a) $NO_2^{1-} + H_2O \rightleftharpoons HNO_2 + OH^{1-}$

b) $HSO_3^{1-} + HCO_3^{1-} \rightleftharpoons SO_3^{2-} + H_2CO_3$

c) $H_3PO_4 + OH^{1-} \rightleftharpoons H_2PO_4^{1-} + H_2O$

For Exercises 24 and 25, write net equations for the acid-base reactions that occur when the given <u>aqueous</u> solutions are mixed. Determine the value of the equilibrium constant. Use single arrows for extensive reactions (K>1000) but double arrows otherwise.

24. a) $HNO_2 + NaOH$ **b)** $NH_4Cl + Na_2SO_3$

c) $NaClO + NaH_2PO_4$ **d)** $HBr + NH_3$

e) $HF + NaCN$ **f)** $H_3PO_4 + NaC_2H_3O_2$

g) $HClO_4 + NaH_2PO_4$

25. a) $NaC_2H_3O_2 + HCN$ **b)** $KOH + HI$

c) $H_2S + K_2HPO_4$ **d)** $NaOH + HClO$

e) $NaNO_2 + H_2CO_3$ **f)** $NH_4Cl + KOH$

g) $HNO_3 + KF$

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26. Indicate whether each of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte:

a) HF **b)** NaF **c)** HCl **d)** CH_3Cl

27. Indicate whether each of the following is a strong electrolyte, a weak electrolyte, or a nonelectrolyte:

a) NH_3 **b)** C_6H_6 **c)** HClO **d)** NH_4Cl

28. What is meant by a neutral solution?

29. Which of the following compounds could be used to lower the pH of a solution?

a) K_2S **b)** NH_4Cl **c)** KCl **d)** $KHSO_4$ **e)** HF

30. Indicate whether each of the following solutions is acidic, basic, or neutral:

a) 0.1 M KNO_2

b) a solution with a pH of 3

c) a solution in which $[OH^{1-}] = 10^{-4}$ M

e) a solution in which $[OH^{1-}] = 10^{-8}$ M

31. Indicate whether each of the following solutions is acidic, basic, or neutral:

a) 0.10 M CH_3COOH

b) 0.10 M NaCN

c) 0.10 M KBr

d) a solution in which $[H_3O^{1+}] = 10^{-5}$ M

32. Indicate which solution in each pair has the **lower** pH:

a) 0.1 M $HClO_2$ or 0.2 M $HClO_2$

b) 0.1 M K_3PO_4 or 0.2 M K_3PO_4

c) 0.1 M $HC_2H_3O_2$ or 0.1 M HNO_2

d) 0.1 M NaOH or water

33. Calculate the pH of each of the following strong acid solutions:

a) 0.0032 M HCl **b)** 0.016 M HCl **c)** 1.5 M HNO_3

34. Calculate the pH of each of the following strong acid solutions:

a) 0.80 M HCl

b) 2.1×10^{-5} M $HClO_4$

c) 2.1×10^{-3} M HCl

35. Calculate the pH of the following basic solutions:

a) 0.0032 M NaOH

b) 0.016 M KOH

c) 0.040 M $Ba(OH)_2$

36. Write the expression for K_a for each of the following acids and the chemical equation to which it applies.

a) NH_4^{1+} **b)** H_3PO_4 **c)** HSO_3^{1-} **d)** CH_3COOH

37. Determine the pK_a of each of the following weak acids:

a) HF **b)** HClO **c)** HS^{1-}

38. Determine the pK_a of each of the following weak acids:

a) $H_2PO_4^{1-}$ **b)** H_2O **c)** H_2S

39. The pK_a of acid HA is greater than that of acid HB.

a) Which is the stronger acid?

b) Which is the stronger base, B^{1-} or A^{1-}?

40. The pK_a of acid HA is greater than that of acid HB.

a) Which has the higher pH, 0.1 M HA or 0.1 M HB?

b) Which has the higher pH, 0.1 M KA or 0.1 M KB?

41. What is the K_a of an acid with a pK_a of 4.87?

42. Formic acid (HCOOH) is a weak acid. Write the K_a reaction and determine the value of K_a if [HCOOH] = 0.10 M and $[HCOO^{1-}] = [H_3O^{1+}]$ = 0.0042 M. Above which acid in Table 12.3 would formic acid be placed?

43. Phenol (C_6H_5OH) is a weak acid with $K_a = 1.0 \times 10^{-10}$.

a) Write the reaction to which this number applies.

b) What is the pK_a of phenol?

c) What is the concentration of phenol in a solution in which $[C_6H_5O^{1-}] = 3.2 \times 10^{-6}$ M and pH = 6.00?

44. Determine the hydronium ion concentration in a solution in which the concentrations of acetic acid and acetate ion are equal. What is the pH of this solution? The K_a of acetic acid is 1.8×10^{-5}.