Chapter 12

Acid-Base Chemistry

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

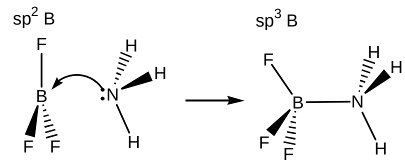
An Arrhenius acid is any compound that contains an H and produces H^{1+} ions in solution. A Brønsted acid is a proton donor, and a Lewis acid is a substance that can share electrons with a Lewis base to form a covalent bond.

3. What is a salt?

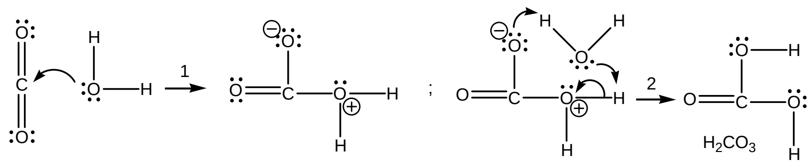
A salt is a product of an acid-base reaction. It consists of a cation derived from the base and the anion derived from the acid. KCl is a salt that is formed from the reaction of KOH and HCl.

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?

a) $BF_3 + NH_3 \rightarrow F_3B\text{-}NH_3$



b) $CO_2 + H_2O \rightarrow H_2CO_3$



1. The Lewis base (H_2O) attacks the Lewis acid (CO_2).
2. A proton transfer from the oxygen with positive formal charge to the oxygen with negative formal charge is mediated by the solvent (H_2O) in the second step to produce carbonic acid, H_2CO_3.

7. Use potential energy diagram in the text for the following the acid-base reaction: $HA + B \rightleftharpoons A^{1-} + HB^{1+}$

a) Which is the stronger acid, HA or HB^{1+}?

The reaction is exothermic, so the formed bond is stronger than the broken bond. Thus, HA has the weaker bond and is the stronger acid.

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

HB is the stronger bond, which makes B the stronger base.

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

The reaction is exothermic which means that K > 1 so long as entropy effects can be ignored.

d) Draw a probable transition state (see Section 9.7 for a review of transition states).

The transition state must have an H-A bond and an H-B bond if it can be reached from either side. The transition state: A-H-B

9. What is the conjugate base of each of the following: Remove one proton to form conjugate base.

a) HClO $\rightarrow ClO^{1-} + H^{1+}$ **b) NH_4^{1+}** $\rightarrow NH_3 + H^{1+}$

c) H_3PO_4 $\rightarrow H_2PO_4^{1-} + H^{1+}$ **d) HSO_3^{1-}** $\rightarrow SO_3^{2-} + H^{1+}$

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

The CH_3 group increases the electron density, which strengthens of the O-H bond making acetic acid a weaker acid. Thus, the pK_a of acetic acid is a higher than that of formic acid.

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-O-CH_3** **H-O-I**

The acidity increases as electron density is removed from the O-H bond. CH_3 groups increase the electron density and therefore H-O-CH_3 is the weakest acid. The electronegativity order of the other elements bound to the O-H is H < I < Cl, *i.e.*, Cl is the best electron withdrawing element, which makes HClO the strongest acid. Thus, the order of acid strengths is:

H-O-CH_3 < H-O-H < H-O-I < H-O-Cl.

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

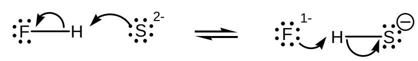
a) **H_2SeO_3 or $HSeO_3^{1-}$** — H_2SeO_3 because the negative charge on the anion increases electron density in the O-H bond, which weakens the acid.

b) **HIO_4 or HIO_2** — HIO_4 due to its higher oxidation state.

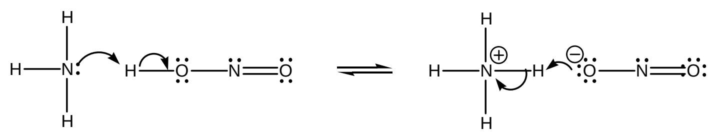
c) **CH_3COOH or CF_3COOH** — CF_3COOH because F withdraws electron density from the O-H bond.

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

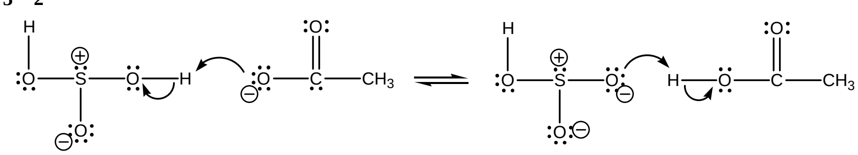
a) **HF + S^{2-}**



b) **NH_3 + HNO_2**



c) **H_2SO_3 + $C_2H_3O_2^{1-}$**



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?**

K > 1 means that the produced acid and base are the weaker acid and base. Therefore, the reacting acid (HBrO) is the stronger acid.

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

BrO^{1-} is the weaker base because it is the produced base in a reaction in which K > 1 or because it is the conjugate base of the stronger acid.

c) **HBrO reacts with ClO^{1-}, $HBrO + ClO^{1-} \rightleftharpoons BrO^{1-} + HClO$ K = 0.08 . Where on the acid-base table should HBrO be placed, above HClO, between HClO and HCN, or below HCN?**

K < 1 means that HBrO is a weaker acid than HClO. However, HBrO is stronger than HCN from part a. Therefore, HBrO should be placed between HClO and HCN.

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

a) **Write the reaction to which this equilibrium constant applies.** $HNO_2(aq) + H_2O(l) \rightleftharpoons H_3O^{1+}(aq) + NO_2^{1-}(aq)$

b) **Express the K_a of nitrous acid in terms of concentrations.** $K_a = \dfrac{[H_3O^{1+}][NO_2^{1-}]}{[HNO_2]}$

23. Determine the equilibrium constant for each of the following.

Use Equation 12.1 {K_a = K_a(reacting acid)/K_a(produced acid)}. The equilibrium expression is the product of the concentrations of the products divided by the product of the concentrations of the reactants

a) $\mathbf{NO_2^{1-} + H_2O \rightleftharpoons HNO_2 + OH^{1-}}$ Reacting acid: H_2O Produced acid: HNO_2

$$K = \frac{K_a(H_2O)}{K_a(HNO_2)} = \frac{1.0\times10^{-14}}{4.0\times10^{-4}} = 2.5\times10^{-11} = \frac{[HNO_2][OH^{1-}]}{[NO_2^{1-}]}$$

Water is the solvent and is treated as a pure liquid, so it enters the expression as '1'.

b) $\mathbf{HSO_3^{1-} + HCO_3^{1-} \rightleftharpoons SO_3^{2-} + H_2CO_3}$ Reacting acid: HSO_3^{1-} Produced acid: H_2CO_3

$$K = \frac{K_a(HSO_3^{1-})}{K_a(H_2CO_3)} = \frac{1.0\times10^{-7}}{4.3\times10^{-7}} = 0.23 = \frac{[SO_3^{2-}][H_2CO_3]}{[HSO_3^{1-}][HCO_3^{1-}]}$$

c) $\mathbf{H_3PO_4 + OH^{1-} \rightleftharpoons H_2PO_4^{1-} + H_2O}$ Reacting acid: H_3PO_4 Produced acid: H_2O

$$K = \frac{K_a(H_3PO_4)}{K_a(H_2O)} = \frac{7.5\times10^{-3}}{1.0\times10^{-14}} = 7.5\times10^{11} = \frac{[H_2PO_4^{1-}]}{[H_3PO_4][OH^{1-}]}$$

25. Write net equations for the Brønsted acid-base reactions that occur when the following solutions are mixed. Determine the value of the equilibrium constant. Use single arrows for extensive and double arrows otherwise.

Equilibrium constants are determined as in Exercises 22 and 23. Single arrows are used when K > 1000.

a) $\mathbf{NaC_2H_3O_2 + HCN}$ $C_2H_3O_2^{1-} + HCN \rightleftharpoons HC_2H_3O_2 + CN^{1-}$ $K = \frac{4.0\times10^{-10}}{1.8\times10^{-5}} = 2.2\times10^{-5}$

b) $\mathbf{KOH + HI}$ $OH^{1-} + H_3O^{1+} \rightarrow H_2O + H_2O$ $K = \frac{1.0}{1.0\times10^{-14}} = 1.0\times10^{14}$

c) $\mathbf{H_2S + K_2HPO_4}$ $H_2S + HPO_4^{2-} \rightleftharpoons HS^{1-} + H_2PO_4^{1-}$ $K = \frac{1.0\times10^{-7}}{6.2\times10^{-8}} = 1.6$

d) $\mathbf{NaOH + HClO}$ $OH^{1-} + HClO \rightarrow H_2O + ClO^{1-}$ $K = \frac{3.5\times10^{-8}}{1.0\times10^{-14}} = 3.5\times10^{6}$

e) $\mathbf{NaNO_2 + H_2CO_3}$ $NO_2^{1-} + H_2CO_3 \rightleftharpoons HNO_2 + HCO_3^{1-}$ $K = \frac{4.3\times10^{-7}}{4.0\times10^{-4}} = 1.1\times10^{-3}$

f) $\mathbf{NH_4Cl + KOH}$ $NH_4^{1+} + OH^{1-} \rightarrow NH_3 + H_2O$ $K = \frac{5.6\times10^{-10}}{1.0\times10^{-14}} = 5.6\times10^{4}$

g) $\mathbf{HNO_3 + KF}$ $H_3O^{1+} + F^{1-} \rightarrow HF + H_2O$ $K = \frac{1.0}{7.2\times10^{-4}} = 1.4\times10^{3}$

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

a) $\mathbf{NH_3}$ (weak) **b)** $\mathbf{C_6H_6}$ (non) **c) HClO** (weak) **d)** $\mathbf{NH_4Cl}$ (strong)

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

a) $\mathbf{K_2S}$ Anions are basic, so S^{2-} is a base, which would raise the pH.

b) $\mathbf{NH_4Cl}$ NH_4^{1+} is an acid, so it would lower the pH.

c) KCl KCl is a salt that would not affect the pH.

d) $\mathbf{KHSO_4}$ HSO_4^{1-} is an acid, so it would lower the pH.

e) HF HF is an acid, so it would lower the pH.

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

a) 0.10 M CH_3COOH Acidic because CH_3COOH is a weak acid

b) 0.10 M NaCN Basic because CN^{1-} ion is a weak base

c) 0.10 M KBr Neutral because there is no acid or base

d) a solution in which $[H_3O^{1+}] = 10^{-5}$ M Acidic because $[H_3O^{1+}] > 10^{-7}$ M

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

a) 0.0032 M HCl pH = - log$[H_3O^{1+}]$ = - log(0.0032) = 2.95

b) 0.016 M HCl pH = - log$[H_3O^{1+}]$ = - log(0.016) = 1.80

c) 1.5 M HNO_3 pH = - log$[H_3O^{1+}]$ = - log(1.5) = - 0.18

35. Calculate the pH of the following basic solutions:

a) 0.0032 M NaOH pH = 14.00 + log$[OH^{1-}]$ = 14.00 + log (0.0032) = 11.51

b) 0.016 M KOH pH = 14.00 + log$[OH^{1-}]$ = 14.00 + log (0.016) = 12.20

c) 0.040 M $Ba(OH)_2$ pH = 14.00 + log$[OH^{1-}]$ = 14.00 + log (0.080) = 12.90. Note that $[OH^{1}] = 2(0.040)$

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

a) HF $pK_a = -\log(K_a) = -\log(7.2 \times 10^{-4}) = 3.14$

b) HClO $pK_a = -\log(K_a) = -\log(3.5 \times 10^{-8}) = 7.46$

c) HS^{1-} $pK_a = -\log(K_a) = -\log(1.3 \times 10^{-13}) = 12.89$

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

a) Which is the stronger acid?

A high pK_a implies a weak acid. Thus, HB is the stronger acid.

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

The stronger base is conjugate base of the weaker acid. Consequently, A^{1-} is the stronger base.

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

$K_a = 10^{-pKa} = 10^{-4.87} = 1.3x10^{-5}$

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.

The H attached to the O must be the acidic proton, so the K_a reaction is

$C_6H_5OH + H_2O \rightleftharpoons C_6H_5O^{1-} + H_3O^{1+}$

b) What is the pK_a of phenol? $pK_a = -\log K_a = -\log(1.0 \times 10^{-10}) = 10.00$

c) What is the concentration of phenol in a solution in which $[C_6H_5O^{1-}] = 3.2x10^{-6}$ M and pH = 6.00?

$[H_3O^{1+}] = 10^{-pH} = 1.0 \times 10^{-6}$ M, $[C_6H_5O^{1-}] = 3.2 \times 10^{-6}$, and $K_a = 1.0 \times 10^{-10}$

$$K_a = \frac{[H_3O^{1+}][C_6H_5O^{1-}]}{[HC_6H_5O]} = 1.0 \times 10^{-10}$$

$$[HC_6H_5O] = \frac{[H_3O^{1+}][C_6H_5O^{1-}]}{K_a} = \frac{(1.0 \times 10^{-6})(3.2 \times 10^{-6})}{1.0 \times 10^{-10}} = 0.032 \text{ M}$$