

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.

2. Define a Lewis acid and a Lewis base.

A Lewis acid is a substance with an empty orbital that can be used to share a pair of electrons in a covalent bond. A Lewis base is a substance that has a lone pair of electrons that it can share in a covalent bond.

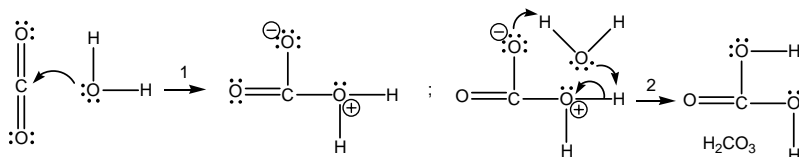
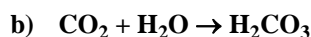
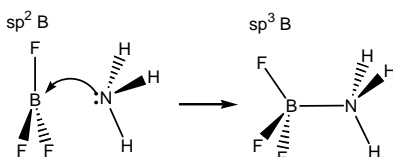
3. What is a salt?

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.

4. What is a conjugate acid-base pair?

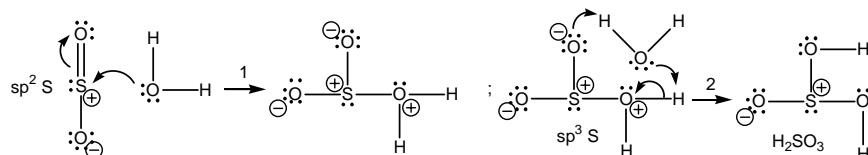
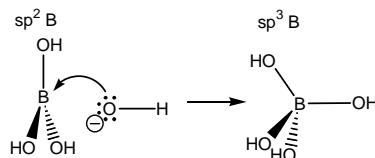
A conjugate acid-base pair consists of an acid and a base that differ by a single proton.

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)?



- The Lewis base (H_2O) attacks the Lewis acid (CO_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 .

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 carbons before and after reaction b)?



- The Lewis base (H_2O) attacks the Lewis acid (SO_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 sulfurous acid, H_2SO_3 .

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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

8. What is the conjugate acid of each of the following: Add one proton to form conjugate acid.



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



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.

The CH_3 group increases the electron density on the nitrogen, which makes it a better base. CH_3NH_2 is therefore the better base.

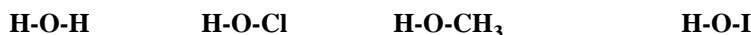
11. Which is the stronger acid, formic acid or acetic acid (see structures in text)? Which acid has the greater pK_a ? Explain your answers. Refer to Exercise 10 for information about CH_3 groups.

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.

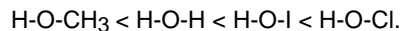
12. Which is the stronger base, NH_3 or NF_3 ? Explain.

The highly electronegative fluorine atoms withdraw electron density from the nitrogen, which makes NF_3 the weaker base. NH_3 is a stronger base than NF_3 .

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



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:



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

a) H_3AsO_4 or H_3AsO_3 H_3AsO_4 because the As atom is in a higher oxidation state

b) H_2SeO_4 or H_2SO_4 H_2SO_4 because sulfur is more electronegative than selenium

c) CH_4 or NH_3 NH_3 because an N-H bond is weaker and more polar than a C-H bond

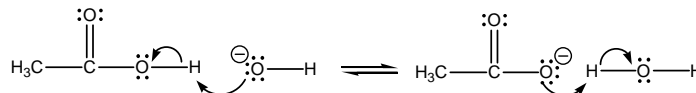
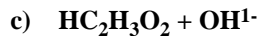
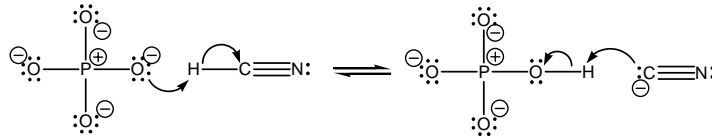
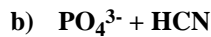
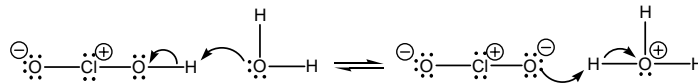
15. Indicate the stronger acid in each of the following pairs and explain your choice:

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.

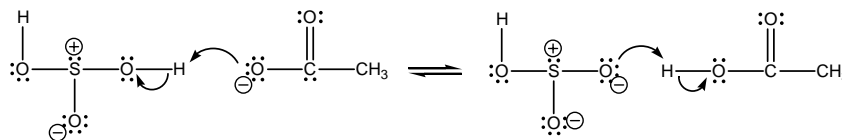
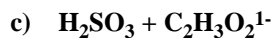
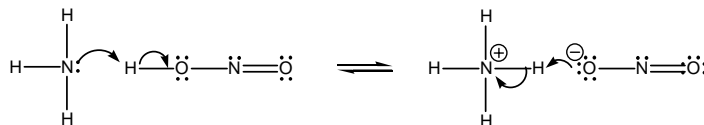
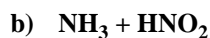
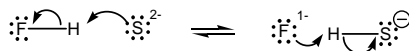
b) HIO_4 or HIO_2 HIO_4 due to its higher oxidation state.

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

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



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



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?

Benzoic acid is slightly stronger than acetic acid because the concentration of benzoate ion is slightly greater than that of acetate ion. The greater the relative strength of an acid, the greater is the concentration of its conjugate base.

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

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-} , $\text{HBrO} + \text{ClO}^{1-} \rightleftharpoons \text{BrO}^{1-} + \text{HClO}$ $K = 0.08$. 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.

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20. The equilibrium constant is ~100 for the reaction: $\text{H}_2\text{C}_2\text{O}_4 + \text{F}^{1-} \rightleftharpoons \text{HC}_2\text{O}_4^{1-} + \text{HF}$

a) Which of the two bases is stronger?

$K > 1$ means that the reacting acid and base are the stronger acid and base. Therefore, F^{1-} is a stronger base than $\text{HC}_2\text{O}_4^{1-}$.

b) Which of the two acids is stronger?

$K > 1$ means that the reacting acid is the stronger acid. Consequently, $\text{H}_2\text{C}_2\text{O}_4$ is a stronger acid than HF.

c) What is the approximate value of K_a for oxalic acid, $\text{H}_2\text{C}_2\text{O}_4$? Refer to Table 12.3 for the K_a of HF.

Solve Equation 12.1 for the unknown K_a .

$$K = \frac{K_a(\text{reacting acid})}{K_a(\text{produced acid})} = \frac{K_a(\text{H}_2\text{C}_2\text{O}_4)}{K_a(\text{HF})} \sim 100$$

$$K_a(\text{H}_2\text{C}_2\text{O}_4) \sim 100 \times K_a(\text{HF}) = (100)(7.2 \times 10^{-4}) = 0.072$$

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

a) Write the reaction to which this equilibrium constant applies. $\text{HNO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_3\text{O}^{1+}(\text{aq}) + \text{NO}_2^{1-}(\text{aq})$

b) Express the K_a of nitrous acid in terms of concentrations. $K_a = \frac{[\text{H}_3\text{O}^{1+}][\text{NO}_2^{1-}]}{[\text{HNO}_2]}$

22. Write the expression for the equilibrium constant and determine its value.

Equation 12.1 states that the value of the equilibrium constant for an acid-base reaction equals the K_a of the reacting acid divided by the K_a of the 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) $\text{H}_2\text{CO}_3 + \text{SO}_4^{2-} \rightleftharpoons \text{HCO}_3^{1-} + \text{HSO}_4^{1-}$ Reacting acid: H_2CO_3 Produced acid: HSO_4^{1-}

$$K = \frac{K_a(\text{H}_2\text{CO}_3)}{K_a(\text{HSO}_4^{1-})} = \frac{4.3 \times 10^{-7}}{1.2 \times 10^{-2}} = 3.6 \times 10^{-5} = \frac{[\text{HCO}_3^{1-}][\text{HSO}_4^{1-}]}{[\text{H}_2\text{CO}_3][\text{SO}_4^{2-}]}$$

b) $\text{H}_2\text{S} + \text{NH}_3 \rightleftharpoons \text{HS}^{1-} + \text{NH}_4^{1+}$ Reacting acid: H_2S Produced acid: NH_4^{1+}

$$K = \frac{K_a(\text{H}_2\text{S})}{K_a(\text{NH}_4^{1+})} = \frac{1.0 \times 10^{-7}}{5.6 \times 10^{-10}} = 1.8 \times 10^{+2} = \frac{[\text{HS}^{1-}][\text{NH}_4^{1+}]}{[\text{H}_2\text{S}][\text{NH}_3]}$$

c) $\text{S}^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{HS}^{1-} + \text{OH}^{1-}$ Reacting acid: H_2O Produced acid: HNO_2

$$K = \frac{K_a(\text{H}_2\text{O})}{K_a(\text{HS}^{1-})} = \frac{1.0 \times 10^{-14}}{1.3 \times 10^{-13}} = 7.7 \times 10^{-2} = \frac{[\text{HS}^{1-}][\text{OH}^{1-}]}{[\text{S}^{2-}]}$$

Remember that water is a liquid, so it enters the expression as '1', which is not normally shown.

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

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

a) $\text{NO}_2^{1-} + \text{H}_2\text{O} \rightleftharpoons \text{HNO}_2 + \text{OH}^{1-}$ Reacting acid: H_2O Produced acid: HNO_2

$$K = \frac{K_a(\text{H}_2\text{O})}{K_a(\text{HNO}_2)} = \frac{1.0 \times 10^{-14}}{4.0 \times 10^{-4}} = 2.5 \times 10^{-11} = \frac{[\text{HNO}_2][\text{OH}^{1-}]}{[\text{NO}_2^{1-}]}$$

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



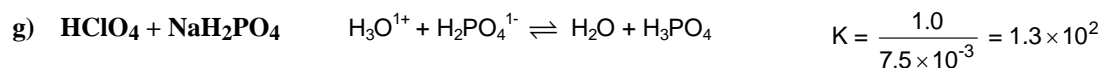
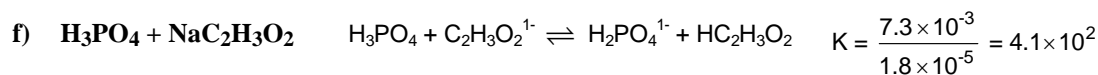
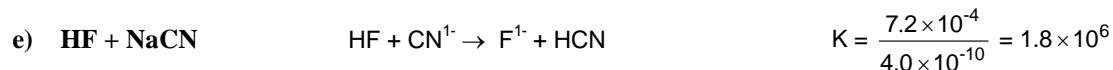
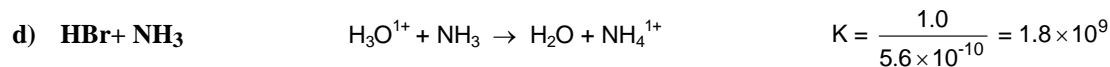
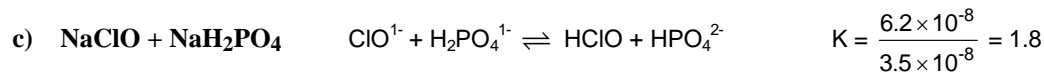
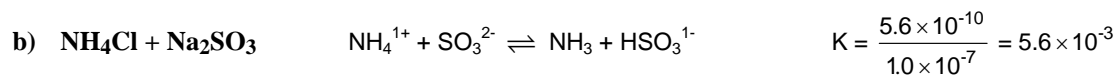
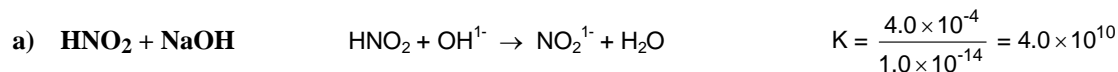
$$K = \frac{K_a(\text{HSO}_3^{1-})}{K_a(\text{H}_2\text{CO}_3)} = \frac{1.0 \times 10^{-7}}{4.3 \times 10^{-7}} = 0.23 = \frac{[\text{SO}_3^{2-}][\text{H}_2\text{CO}_3]}{[\text{HSO}_3^{1-}][\text{HCO}_3^{1-}]}$$



$$K = \frac{K_a(\text{H}_3\text{PO}_4)}{K_a(\text{H}_2\text{O})} = \frac{7.5 \times 10^{-3}}{1.0 \times 10^{-14}} = 7.5 \times 10^{11} = \frac{[\text{H}_2\text{PO}_4^{1-}]}{[\text{H}_3\text{PO}_4][\text{OH}^{1-}]}$$

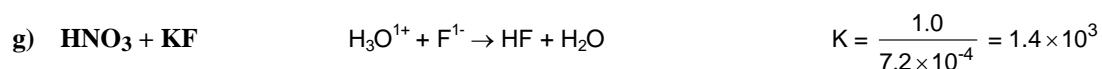
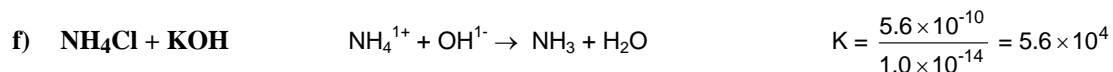
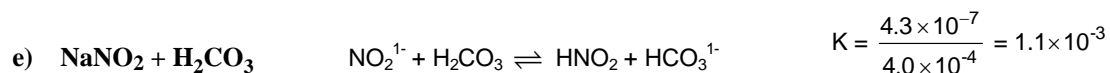
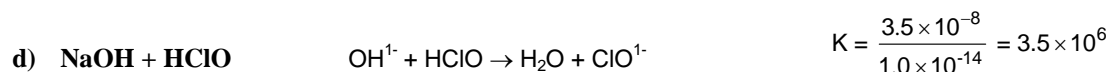
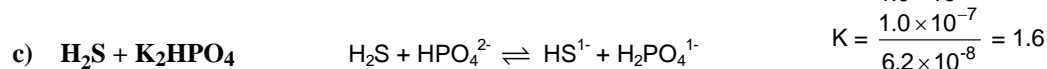
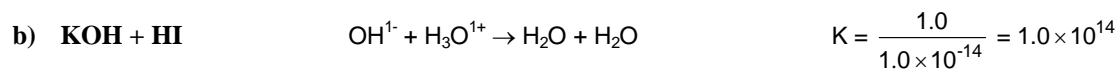
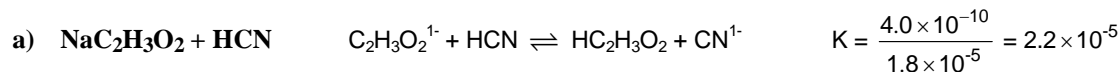
- 24. Write net equations for the Brønsted acid-base reactions that occur when the following solutions are mixed. Determine the value of the equilibrium constant. Use single arrows for extensive and double arrows otherwise.**

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



- 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 $K > 1000$.



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



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

- a) NH_3 (weak) b) C_6H_6 (non) c) HClO (weak) d) NH_4Cl (strong)

28. What is meant by a neutral solution?

A neutral solution is one in which $[\text{H}_3\text{O}^{1+}] = [\text{OH}^{1-}]$.

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

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

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

- a) 0.1 M KNO_2 Basic because NO_2^{1-} is a weak base
b) a solution with a pH of 3 Acidic because $\text{pH} < 7$
c) a solution in which $[\text{OH}^{1-}] = 10^{-4}$ M Basic because $[\text{OH}^{1-}] > 10^{-7}$ M
d) a solution in which $[\text{OH}^{1-}] = 10^{-8}$ M Acidic because $[\text{OH}^{1-}] < 10^{-7}$ M, which means that $[\text{H}_3\text{O}^{1+}] > 10^{-7}$ M

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 $[\text{H}_3\text{O}^{1+}] = 10^{-5}$ M Acidic because $[\text{H}_3\text{O}^{1+}] > 10^{-7}$ M

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

- a) 0.1 M HClO_2 or 0.2 M HClO_2 0.2 M HClO_2 because it has the higher concentration of H_3O^{1+}
b) 0.1 M K_3PO_4 or 0.2 M K_3PO_4 0.1 M K_3PO_4 because it has the lower concentration of base
c) 0.1 M $\text{HC}_2\text{H}_3\text{O}_2$ or 0.1 M HNO_2 0.1 M HNO_2 because it is the stronger acid
d) 0.1 M NaOH or water Water has less base and therefore is more acidic

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

- a) 0.0032 M HCl $\text{pH} = -\log[\text{H}_3\text{O}^{1+}] = -\log(0.0032) = 2.95$
b) 0.016 M HCl $\text{pH} = -\log[\text{H}_3\text{O}^{1+}] = -\log(0.016) = 1.80$
c) 1.5 M HNO_3 $\text{pH} = -\log[\text{H}_3\text{O}^{1+}] = -\log(1.5) = -0.18$

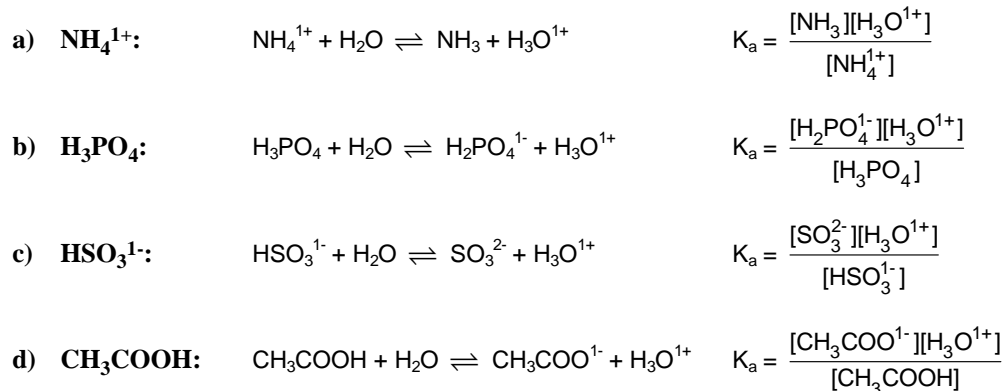
34. Calculate the pH of each of the following strong acid solutions:

- a) 0.80 M HCl $\text{pH} = -\log[\text{H}_3\text{O}^{1+}] = -\log(0.80) = 0.097$
b) 2.1×10^{-5} M HClO_4 $\text{pH} = -\log[\text{H}_3\text{O}^{1+}] = -\log(2.1 \times 10^{-5}) = 4.68$
c) 2.1×10^{-3} M HCl $\text{pH} = -\log[\text{H}_3\text{O}^{1+}] = -\log(2.1 \times 10^{-3}) = 2.68$

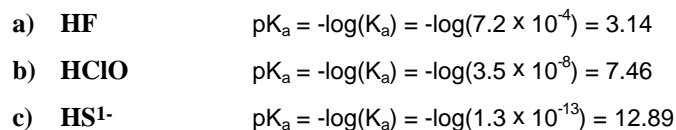
35. Calculate the pH of the following basic solutions:

- a) 0.0032 M NaOH $\text{pH} = 14.00 + \log[\text{OH}^{1-}] = 14.00 + \log(0.0032) = 11.51$
b) 0.016 M KOH $\text{pH} = 14.00 + \log[\text{OH}^{1-}] = 14.00 + \log(0.016) = 12.20$
c) 0.040 M $\text{Ba}(\text{OH})_2$ $\text{pH} = 14.00 + \log[\text{OH}^{1-}] = 14.00 + \log(0.080) = 12.90$. Note that $[\text{OH}^{1-}] = 2(0.040)$

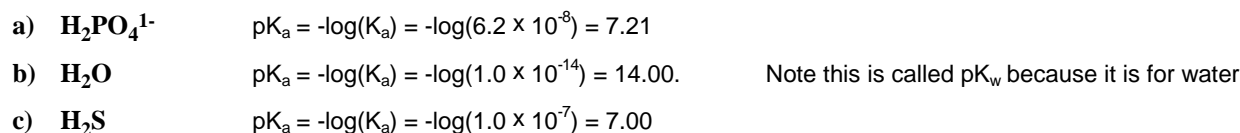
36. Write the expression for K_a for each of the following acids and the chemical equation to which it applies.



37. Determine the $\text{p}K_a$ of each of the following weak acids:



38. Determine the $\text{p}K_a$ of each of the following weak acids:



39. The $\text{p}K_a$ of acid HA is greater than that of acid HB.

- a) Which is the stronger acid?
A high $\text{p}K_a$ 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.

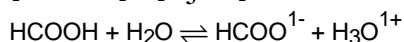
40. The $\text{p}K_a$ of acid HA is greater than that of acid HB.

- a) Which has the higher pH, 0.1 M HA or 0.1 M HB?
The weaker acid will have the higher pH. Therefore a 0.1-M solution of HA has the higher pH.
- b) Which has the higher pH, 0.1 M KA or 0.1 M KB?
The solution of the stronger base has the higher pH. Consequently, a 0.1-M solution of KA has the higher pH.

41. What is the K_a of an acid with a $\text{p}K_a$ of 4.87?

$$K_a = 10^{-\text{p}K_a} = 10^{-4.87} = 1.3 \times 10^{-5}$$

42. Formic acid (HCOOH) is a weak acid. Write the K_a reaction and determine the value of K_a if $[\text{HCOOH}] = 0.10 \text{ M}$ and $[\text{HCOO}^{1-}] = [\text{H}_3\text{O}^{1+}] = 0.0042 \text{ M}$. Above which acid in Table 12.3 would formic acid be placed?



$$K_a = \frac{[\text{HCOO}^{1-}][\text{H}_3\text{O}^{1+}]}{[\text{HCOOH}]} = \frac{(0.0042)(0.0042)}{0.10} = 1.8 \times 10^{-4}$$

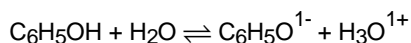
Formic acid would be located above acetic acid in Table 12.3.

Acid-Base Chemistry

43. Phenol ($\text{C}_6\text{H}_5\text{OH}$) 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



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

c) What is the concentration of phenol in a solution in which $[\text{C}_6\text{H}_5\text{O}^{1-}] = 3.2 \times 10^{-6} \text{ M}$ and $\text{pH} = 6.00$?

$$[\text{H}_3\text{O}^{1+}] = 10^{-\text{pH}} = 1.0 \times 10^{-6} \text{ M}, [\text{C}_6\text{H}_5\text{O}^{1-}] = 3.2 \times 10^{-6}, \text{ and } K_a = 1.0 \times 10^{-10}$$

$$K_a = \frac{[\text{H}_3\text{O}^{1+}][\text{C}_6\text{H}_5\text{O}^{1-}]}{[\text{C}_6\text{H}_5\text{O}]} = 1.0 \times 10^{-10}$$

$$[\text{C}_6\text{H}_5\text{O}] = \frac{[\text{H}_3\text{O}^{1+}][\text{C}_6\text{H}_5\text{O}^{1-}]}{K_a} = \frac{(1.0 \times 10^{-6})(3.2 \times 10^{-6})}{1.0 \times 10^{-10}} = 0.032 \text{ M}$$

44. What is the pH of a solution in which the concentrations of acetic acid and acetate ion are equal?

Use the K_a of acetic acid in Table 12.3

$$K_a = \frac{[\text{H}_3\text{O}^{1+}][\text{C}_2\text{H}_3\text{O}_2^{1-}]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 1.8 \times 10^{-5}$$

but $[\text{C}_2\text{H}_3\text{O}_2^{1-}] = [\text{HC}_2\text{H}_3\text{O}_2]$, so they cancel in the above to yield $[\text{H}_3\text{O}^{1+}] = 1.8 \times 10^{-5} \text{ M}$

$$\text{pH} = -\log [\text{H}_3\text{O}^{1+}] = -\log (1.8 \times 10^{-5}) = 4.74$$