Problems Chapter 16 – Acids and Bases

1. Oxalic acid, HOOCCOOH, a weak diprotic acid, has $pK_{a1} = 1.25$ and $pK_{a2} = 3.81$. A related diprotic acid, suberic acid, $HOOC(CH_2)_8COOH$ has $pK_{a1} = 4.21$ and $pK_{a2} = 5.40$. Offer a plausible reason as to why the *difference* between pK_{a1} and pK_{a2} is so much greater for oxalic acid than for suberic acid.

2. The following four equilibria lie to the right
   $N_2H_5^+ + CH_3NH_2 \rightarrow N_2H_4 + CH_3NH_3^+$
   $H_2SO_3 + F^- \rightarrow HSO_3^- + HF$
   $CH_3NH_3^+ + OH^- \rightarrow CH_3NH_2 + H_2O$
   $HF + N_2H_4 \rightarrow F^- + N_2H_5^+$
   a. Rank all the acids involved in order of decreasing acid strength.
   b. Rank all the bases involved in order of decreasing base strength.
   c. State whether each of the following two equilibria lies primarily to the right or to the left:
      i. $HF + OH^- \Leftrightarrow F^- + H_2O$
      ii. $CH_3NH_3^+ + HSO_3^- \Leftrightarrow CH_3NH_2 + H_2SO_3$

3. Hemoglobin plays a part in a series of equilibria involving protonation-deprotonation and oxygenation-deoxygenation. The overall reaction is approximately as follows:

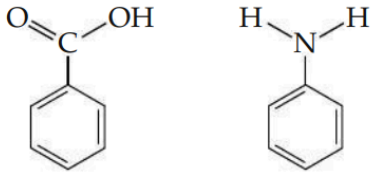
   $HbH^+ (aq) + O_2 (aq) \Leftrightarrow HbO_2 (aq) + H^+ (aq)$

   where Hb stands for hemoglobin and HbO_2 for oxyhemoglobin.

   a. The concentration of O_2 is higher in the lungs and lower in the tissues. What effect does high $[O_2]$ have on the position of this equilibrium?
   b. The normal pH of blood is 7.4 Is the blood acidic, basic or neutral?
   c. If the blood pH is lowered by the presence of large amounts of acidic metabolism products, a condition known as acidosis results. What effect does lowering blood pH have on the ability of hemoglobin to transport O_2?

4. Succinic acid ($H_2C_4H_6O_4$), which we will denote H_2Suc, is a biologically relevant diprotic acid. At 25 ˚C, the acid dissociation constants for succinic acid are $K_{a1} = 5.9 \times 10^{-5}$ and $K_{a2} = 2.5 \times 10^{-6}$.
   a. Determine the pH of a 0.32 M solution of H_2Suc at 25 ˚C, assuming that only the first dissociation is relevant.
   b. Determine the molar concentration of Suc^{2-} in the solution in part (a).
   c. Is the assumption you made in part (a) justified by the result from part (b)?
   d. Will a solution of the salt NaHSuc be acidic, basic or neutral?

5. Benzoic acid (C_6H_5COOH) and aniline ($C_6H_5NH_2$) are both derivatives of benzene. Benzoic acid is an acid with $K_a = 6.3 \times 10^{-5}$ and aniline is a base with $K_b = 4.3 \times 10^{-10}$.



Benzoic acid Aniline

   a. What are the conjugate base of benzoic acid and the conjugate acid of aniline?
   b. Anilinium chloride ($C_6H_5NH_3Cl$) is a strong electrolyte that dissociates into anilinium ions ($C_6H_5NH_3^+$) and chloride ions. Which will be more acidic, a 0.10 M solution of benzoic acid or a 0.10 M solution of anilinium chloride?
   c. What is the value of the equilibrium constant for the following equilibrium?

$$C_6H_5COOH\ (aq) + C_6H_5NH_2\ (aq) \Leftrightarrow C_6H_5COO^-\ (aq) + C_6H_5NH_3^+\ (aq)$$

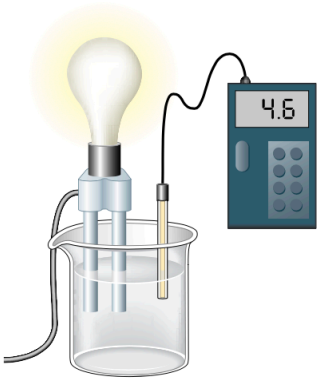
6. Arrange the following 0.10 M solutions in order of increasing acidity (decreasing pH):
   a. NH_4NO_3
   b. $NaNO_3$
   c. CH_3COONH_4
   d. NaF
   e. CH_3COONa

7. The following observations are made about a diprotic acid H_2A.
   a. A 0.10 M solution of H_2A has pH = 3.30.
   b. A 0.10 M solution of the salt NaHA is acidic.

   Which of the following could be the value of pK_{a2}?
   a. 3.22
   b. 5.30
   c. 7.47
   d. 9.82

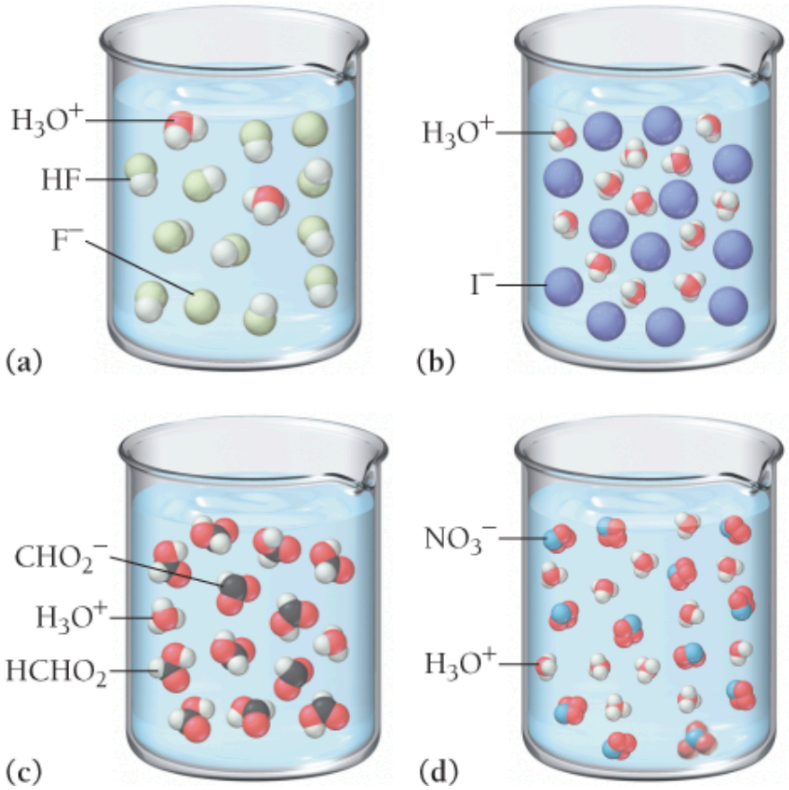
8. Write net ionic equations for the reactions that take place when aqueous solutions of the following substances are mixed:
   a. NaCN and HNO_3
   b. NH_4Cl and NaOH
   c. NaCN and NH_4Br
   d. $KHSO_4$ and $LiCH_3COO$
   e. NaClO and NH_3

9. A solution is tested for pH and conductivity as pictured below:



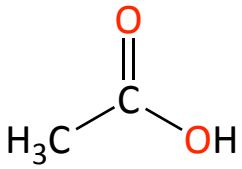
The solution contains one of the following substances: HCl, NaOH, NH_4Cl, HCN, NH_3, HF or NaCN. If the solute concentration is about 1.0 M, what is the identity of the solute?

10. Based on these molecular views, determine whether each pictured acid is weak or strong.



11. Indicate whether each of the following statements is correct or incorrect.
    a. Every Brønsted-Lowry acid is also a Lewis acid.
    b. Every Lewis acid is also a Brønsted-Lowry acid.
    c. Conjugate acids of weak bases produce more acidic solutions that conjugate acids of strong bases.
    d. K^+ ion is acidic in water because it causes hydrating water molecules to become more acidic.

12. The structural formula for acetic acid is shown below. Replacing hydrogen atoms on the carbon with chlorine atoms causes an increase in acidity as follows:



Acetic acid

Acid	Formula	K_a(25 °C)
Acetic	CH_3COOH	1.8×10^{-5}
Chloroacetic	$CH_2ClCOOH$	1.4×10^{-3}
Dichloroacetic	$CHCl_2COOH$	3.3×10^{-2}
Trichloroacetic	CCl_3COOH	2×10^{-1}

Using Lewis structures as the basis of your discussion, explain the observed trend in acidities in the series.

13. A 0.20 M sodium chlorobenzoate ($NaC_7H_4ClO_2$) solution has a pH of 8.65. Calculate the pH of a 0.20 M chlorobenzoic acid ($HC_7H_4ClO_2$) solution.

14. Nicotine, $C_{10}H_{14}N_2$, has two basic nitrogen atoms, and both can react with water.

    $Nic\ (aq) + H_2O\ (l) \Leftrightarrow NicH^+\ (aq) + OH^-\ (aq)$
    $NicH^+\ (aq) + H_2O\ (l) \Leftrightarrow NicH_2^{2+}\ (aq) + OH^-\ (aq)$

    K_{b1} is 7.0×10^{-7} and K_{b2} is 1.1×10^{-10}. Calculate the approximate pH of a 0.020 M solution.

15. About this time, you may be wishing you had an aspirin. Aspirin is an organic acid with a K_a of 3.27×10^{-4} for the reaction

    $HC_9H_7O_4\ (aq) + H_2O\ (l) \Leftrightarrow C_9H_7O_4^-\ (aq) + H_3O^+\ (aq)$

If you have two tablets, each containing 0.325 g of aspirin (mixed with a neutral "binder" to hold the tablet together), and you dissolve them in a glass of water to give 225 mL of solution, what is the pH of the solution?

16. A 2.50-g sample of a solid that could be $Ba(OH)_2$ or $Sr(OH)_2$ was dissolved in enough water to make 1.00 L of solution. If the pH of the solution is 12.61, what is the identity of the solid?

17. The base ethylamine ($CH_3CH_2NH_2$) has a K_b of 4.3×10^{-4}. A closely related base, ethanolamine ($HOCH_2CH_2NH_2$), has a K_b of 3.2×10^{-5}.
    a. Which of the two bases is stronger?
    b. Calculate the pH of a 0.10 M solution of the stronger base.

18. Rank the following 0.10 M solutions in order of increasing pH.
    (K_a of $C_6H_5NH_3^+$ is 2.6×10^{-5}. K_a of HOC_6H_5 is 1.3×10^{-10}.)
    a. HI, HF, NaF, NaI
    b. NH_4Br, HBr, KBr, NH_3
    c. $C_6H_5NH_3NO_3$, $NaNO_3$, NaOH, HOC_6H_5, KOC_6H_5, $C_6H_5NH_2$, HNO_3

19. Determine the pH of each two-component solution.
    a. 0.0550 M in HI and 0.00850 M in HF
    b. 0.112 M in NaCl and 0.0953 M in KF
    c. 0.132 M in NH_4Cl and 0.150 M in HNO_3
    d. 0.0887 M in sodium benzoate and 0.225 M in potassium bromide
    e. 0.0450 M in HCl and 0.0225 M in HNO_3

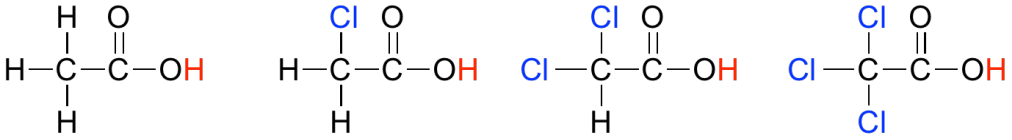
20. The equilibrium constant K_a for the reaction

$$Fe(H_2O)_6^{3+}\,(aq) + H_2O\,(l) \Leftrightarrow Fe(H_2O)_5(OH)^{2+}\,(aq) + H_3O^+\,(aq)$$

    is 6.0×10^{-3}.
    a. Calculate the pH of a 0.10 M solution of $Fe(H_2O)_6^{3+}$.
    b. Will a 1.0 M solution of $Fe(NO_3)_2$ have a higher or lower pH than a 1.0 M solution of $Fe(NO_3)_3$? Explain.

St. Elmo Brady: the carboxylic acid prodigy and pioneer of chemistry education

You learned that the acidity of a substance is determined by various elements of its molecular structure. For example, a straight-chain carboxylic acid becomes more acidic when some of the hydrogen atoms attached to the carbon closest to the –COOH group are replaced with halogen atoms. These electronegative atoms are good at bearing negative charge. As a result, when these carboxylic acids become deprotonated, the halogen atoms withdraw some of the electron density from the negative oxygen atom, thus stabilizing the structure of the conjugate base – and making the carboxylic acid molecules bearing them more acidic (more prone to donate an H^+).



$pK_a = 4.8$ $pK_a = 2.8$ $pK_a = 1.3$ $pK_a = 0.64$

St. Elmo Brady, the first African American to obtain a PhD degree in chemistry in USA (in 1916 from the University of Illinois – Urbana-Champaign), was interested in how the acidity of straight-chain carboxylic acids is affected by replacing a pair of hydrogens with an oxygen double-bonded to the carbon atom (a carbonyl group). He completed his PhD in just two years, during which he published three scholarly abstracts in *Science* and developed new synthesis and purification methods for a range of compounds. He made these amazing accomplishments while facing numerous challenges, including living in a segregated community and struggling to find housing. After finishing his doctoral studies, Brady embarked on a long career as a pioneer in chemistry education. He was a chair of chemistry departments in leading historically black colleges and universities (HBCUs) Howard and Fisk; in both places, he raised funds towards construction of new, modernly equipped chemistry buildings. Particularly at Fisk, he helped

construct the first modern chemistry building at an HBCU, which is now known as the Talley-Brady Hall to honor him (and is on the US National Park Service's National Register of Historic Places).

References:

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