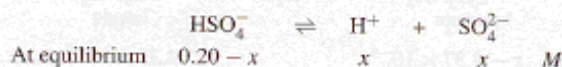


Homework #9 (Apr 3)

- 8.12 What are the concentrations of HSO_4^- , SO_4^{2-} , and H^+ in a 0.20 M KHSO_4 solution? (Hint: H_2SO_4 is a strong acid; K_a for $\text{HSO}_4^- = 1.3 \times 10^{-2}$.)

KHSO_4 is a strong electrolyte and dissociates completely into K^+ and HSO_4^- . K^+ is neither a Brønsted acid nor a Brønsted base, and it does not hydrolyze. HSO_4^- functions as a Brønsted acid and a Brønsted base. As the Brønsted base of a strong acid, H_2SO_4 , HSO_4^- does not hydrolyze to any significant extent to give the acid. As a Brønsted acid, it dissociates and makes the solution acidic. Assume that x M of HSO_4^- dissociates in the solution, then the equilibrium concentrations of various species are



x is determined using the equilibrium expression

$$K_a = 1.3 \times 10^{-2} = \frac{[\text{H}^+][\text{SO}_4^{2-}]}{[\text{HSO}_4^-]} = \frac{x^2}{0.20 - x}$$

$$x^2 + 1.3 \times 10^{-2}x - 2.6 \times 10^{-3} = 0$$

$$x = 4.49 \times 10^{-2}$$

Therefore,

$$[\text{HSO}_4^-] = (0.20 - x) \text{ M} = 0.16 \text{ M}$$

$$[\text{H}^+] = x \text{ M} = 4.5 \times 10^{-2} \text{ M}$$

$$[\text{SO}_4^{2-}] = x \text{ M} = 4.5 \times 10^{-2} \text{ M}$$

- 8.40 A phosphate buffer has a pH equal to 7.30. (a) What is the predominant conjugate pair present in this buffer? (b) If the concentration of this buffer is 0.10 M, what is the new pH after the addition of 5.0 mL of 0.10 M HCl to 20.0 mL of this buffer solution?

(a) The predominant conjugate pair will involve an acid with a $\text{p}K_a$ value similar to the pH of the buffer. Since for H_2PO_4^- , $\text{p}K_a'' = 7.21$, H_2PO_4^- and HPO_4^{2-} are the chief components of this buffer.

(b) First the concentrations of H_2PO_4^- and HPO_4^{2-} need to be calculated. The sum of the concentrations is 0.10 M. In other words,

$$[\text{HPO}_4^{2-}] = 0.10 \text{ M} - [\text{H}_2\text{PO}_4^-]$$

Using the Henderson-Hasselbalch equation,

$$\text{pH} = \text{p}K_a'' + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]}$$

$$7.30 = 7.21 + \log \frac{0.10 \text{ M} - [\text{H}_2\text{PO}_4^-]}{[\text{H}_2\text{PO}_4^-]}$$

$$\frac{0.10 \text{ M} - [\text{H}_2\text{PO}_4^-]}{[\text{H}_2\text{PO}_4^-]} = 10^{0.09} = 1.2$$

$$[\text{H}_2\text{PO}_4^-] = 4.5 \times 10^{-2} \text{ M}$$

$$[\text{HPO}_4^{2-}] = 0.10 \text{ M} - 4.5 \times 10^{-2} \text{ M} = 5.5 \times 10^{-2} \text{ M}$$

Before the addition of HCl,

$$\text{Number of moles of H}_2\text{PO}_4^- = (4.5 \times 10^{-2} M) (20.0 \times 10^{-3} L) = 9.0 \times 10^{-4} \text{ mol}$$

$$\text{Number of moles of HPO}_4^{2-} = (5.5 \times 10^{-2} M) (20.0 \times 10^{-3} L) = 1.1 \times 10^{-3} \text{ mol}$$

When HCl is added, it will react with HPO_4^{2-} :



and the reaction will proceed to near completion.

$$\text{Moles of HCl added} = (0.10 M) (5.0 \times 10^{-3} L) = 5.0 \times 10^{-4} \text{ mol}$$

$$\text{Moles of HPO}_4^{2-} \text{ after reaction with HCl} = 1.1 \times 10^{-3} \text{ mol} - 5.0 \times 10^{-4} \text{ mol} = 6 \times 10^{-4} \text{ mol}$$

$$[\text{HPO}_4^{2-}] \text{ after reaction with HCl} = \frac{6 \times 10^{-4} \text{ mol}}{25.0 \times 10^{-3} L} = 0.02 M$$

$$\text{Moles of H}_2\text{PO}_4^- \text{ after reaction with HCl} = 9.0 \times 10^{-4} \text{ mol} + 5.0 \times 10^{-4} \text{ mol} = 1.40 \times 10^{-3} \text{ mol}$$

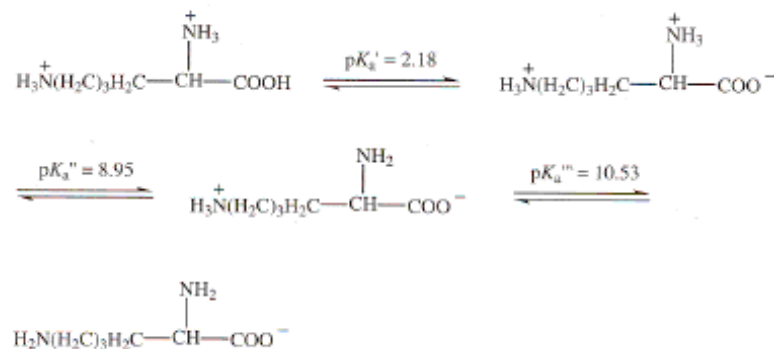
$$[\text{H}_2\text{PO}_4^-] \text{ after reaction with HCl} = \frac{1.40 \times 10^{-3} \text{ mol}}{25.0 \times 10^{-3} L} = 0.056 M$$

The new pH can now be calculated using the Henderson-Hasselbalch equation.

$$\begin{aligned} \text{pH} &= \text{p}K_a'' + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} \\ &= 7.21 + \log \frac{0.02}{0.056} \\ &= 6.76 \end{aligned}$$

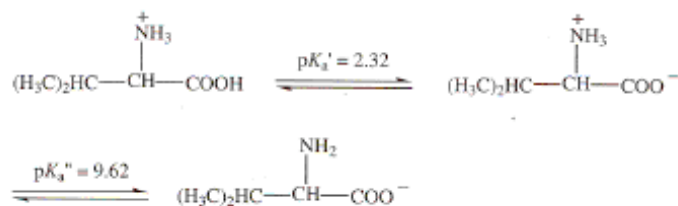
8.54 From the pK_a values listed in Table 8.4, calculate the pI value for amino acids lysine and valine.

Lysine



$$pI = \frac{8.95 + 10.53}{2} = 9.74$$

Valine



$$pI = \frac{2.32 + 9.62}{2} = 5.97$$

8.53 Calculate the ionic strength of a 0.035 M serine buffer at pH 9.15.

The components of the buffer are



Since pH is the same as pK_a'' , the concentration of S^- and S^0 are the same. Of the serine species present in solution, only the net charged S^- contributes to the ionic strength. The buffer can be prepared by titrating isoelectric serine (S^0) at 0.070 M with NaOH to yield

$$[S^0] = 0.035 M$$

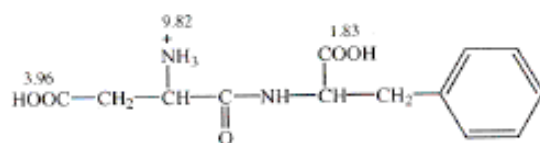
$$[S^-] = 0.035 M$$

$$[\text{Na}^+] = 0.035 M$$

Thus, assuming molarity is equal to molality,

$$I = \frac{1}{2} (m_+ z_+^2 + m_- z_-^2) = \frac{1}{2} [(0.035) (1)^2 + (0.035) (1)^2] = 0.035 m$$

8.81 (a) Use Equation 8.17 to derive an expression showing the fraction of an acid (f) in terms of its pK_a and the pH of the solution. (b) Aspartame is the artificial sweetener containing the dipeptide aspartyl phenylalanine,



where the numbers denote the pK_a values of the acidic groups. Calculate the net charge on the dipeptide at pH = 3.00 and 7.00. Assume the pK_a 's are unaffected by other groups present. Also, calculate the isoelectric point of the dipeptide.

(a) From Equation 8.17,

$$\begin{aligned} \text{pH} &= pK_a + \log \frac{[\text{A}^-]}{[\text{HA}]} \\ \log \frac{[\text{A}^-]}{[\text{HA}]} &= \text{pH} - pK_a \\ \frac{[\text{A}^-]}{[\text{HA}]} &= 10^{\text{pH} - pK_a} \end{aligned} \quad (8.81.1)$$

The fraction of an acid is

$$f = \frac{[\text{HA}]}{[\text{HA}] + [\text{A}^-]}$$

Now relate f and $\frac{[\text{A}^-]}{[\text{HA}]}$. Taking the inverse of f ,

$$\begin{aligned} \frac{1}{f} &= \frac{[\text{HA}] + [\text{A}^-]}{[\text{HA}]} = 1 + \frac{[\text{A}^-]}{[\text{HA}]} \\ \frac{[\text{A}^-]}{[\text{HA}]} &= \frac{1}{f} - 1 \end{aligned} \quad (8.81.2)$$

Substitute Equation (8.81.2) into Equation (8.81.1):

$$\begin{aligned} \frac{1}{f} - 1 &= 10^{\text{pH} - pK_a} \\ \frac{1}{f} &= 1 + 10^{\text{pH} - pK_a} \\ f &= \frac{1}{1 + 10^{\text{pH} - pK_a}} \end{aligned} \quad (8.81.3)$$

(b) Let the fractions of the acidic NH_3^+ group, the α -COOH ($pK_a = 1.83$) group, and the side chain COOH ($pK_a = 3.96$) group be represented by f_1 , f_2 , and f_3 , respectively. The net charge on

the dipeptide results from a combination of the fraction of the NH_3^+ group (f_1), the fraction of the $\alpha\text{-COO}^-$ group ($1 - f_2$), and the fraction of the side chain COO^- group ($1 - f_3$). Remembering that f is the fraction of undissociated acid, and because the last two groups contribute negative charges, the net charge on the dipeptide, Q , can be expressed as

$$Q = f_1 - (1 - f_2) - (1 - f_3)$$

For $\text{pH} = 3.00$,

$$f_1 = \frac{1}{1 + 10^{3.00-9.82}} = 1.00$$

$$f_2 = \frac{1}{1 + 10^{3.00-1.83}} = 0.063$$

$$f_3 = \frac{1}{1 + 10^{3.00-3.96}} = 0.90$$

The NH_3^+ group is fully protonated, the $\alpha\text{-COOH}$ group is nearly fully dissociated, and the side chain carboxyl group is only slightly dissociated. The net charge on the dipeptide is

$$Q = 1.00 - (1 - 0.063) - (1 - 0.90) = -0.037$$

For $\text{pH} = 7.00$,

$$f_1 = \frac{1}{1 + 10^{7.00-9.82}} = 1.00$$

$$f_2 = \frac{1}{1 + 10^{7.00-1.83}} = 6.8 \times 10^{-6} \approx 0.00$$

$$f_3 = \frac{1}{1 + 10^{7.00-3.96}} = 9.1 \times 10^{-4} \approx 0.00$$

The NH_3^+ group is fully protonated whereas the side chain COOH group and the α -carboxyl group are completely dissociated. The net charge on the dipeptide is

$$Q = 1.00 - (1 - 0.00) - (1 - 0.00) = -1.00$$

At the isoelectric point, the dipeptide has no charge; that is,

$$Q = f_1 - (1 - f_2) - (1 - f_3) = 0$$

$$f_1 + f_2 + f_3 = 2$$

As the above calculations above show, even at pH as high as 7.00, the fraction of NH_3^+ is 1.00. (f_1 remains 1.00 for lower pH .) On the other hand, at this pH , both carboxyl groups are completely dissociated. The isoelectric point has to be much less than 7.00 for appreciable fractions of COOH groups to remain associated, but not so acidic to inhibit dissociation completely. Nevertheless, at the isoelectric point, $f_1 = 1.00$, and

$$f_1 + f_2 + f_3 = 1.00 + f_2 + f_3 = 2$$

$$f_2 + f_3 = 1$$

$$\frac{1}{1 + 10^{\text{pH}-1.83}} + \frac{1}{1 + 10^{\text{pH}-3.96}} = 1$$

$$\frac{1 + 10^{\text{pH}-3.96} + 1 + 10^{\text{pH}-1.83}}{(1 + 10^{\text{pH}-1.83})(1 + 10^{\text{pH}-3.96})} = 1$$

$$2 + 10^{\text{pH}-3.96} + 10^{\text{pH}-1.83} = (1 + 10^{\text{pH}-1.83})(1 + 10^{\text{pH}-3.96})$$

$$2 + 10^{\text{pH}-3.96} + 10^{\text{pH}-1.83} = 1 + 10^{\text{pH}-3.96} + 10^{\text{pH}-1.83} + 10^{2\text{pH}-1.83-3.96}$$

$$10^{2\text{pH}-1.83-3.96} = 12\text{pH} - 1.83 - 3.96 = \log 1 = 0$$

$$\text{pI} = \frac{1.83 + 3.96}{2} = 2.90$$

At $\text{pH} = \text{pI}$, the situation is not much different from $\text{pH} = 3.00$ as described above.