
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 $HSO_4^- = 1.3 \times 10^{-2}$.)

$KHSO_4$ 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

$$\begin{array}{lccccccc} & HSO_4^- & \rightleftharpoons & H^+ & + & SO_4^{2-} & \\ \text{At equilibrium} & 0.20 - x & & x & & x & M \end{array}$$

x is determined using the equilibrium expression

$$K_a = 1.3 \times 10^{-2} = \frac{[H^+]\left[SO_4^{2-}\right]}{[HSO_4^-]} = \frac{x^2}{0.2 - x}$$

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

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

Therefore,

$$[HSO_4^-] = (0.20 - x)\ M = 0.16\ M$$

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

$$\left[SO_4^{2-}\right] = x\ M = 4.5 \times 10^{-2}\ M$$

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 pK_a value similar to the pH of the buffer. Since for $H_2PO_4^-$, $pK_a'' = 7.21$, $H_2PO_4^-$ 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,

$$\left[HPO_4^{2-}\right] = 0.10\ M - [H_2PO_4^-]$$

Using the Henderson–Hasselbalch equation,

$$pH = pK_a'' + \log \frac{\left[HPO_4^{2-}\right]}{[H_2PO_4^-]}$$

$$7.30 = 7.21 + \log \frac{0.10\ M - [H_2PO_4^-]}{[H_2PO_4^-]}$$

$$\frac{0.10\ M - [H_2PO_4^-]}{[H_2PO_4^-]} = 10^{0.09} = 1.2$$

$$[H_2PO_4^-] = 4.5 \times 10^{-2}\ M$$

$$\left[HPO_4^{2-}\right] = 0.10\ M - 4.5 \times 10^{-2}\ M = 5.5 \times 10^{-2}\ M$$

Before the addition of HCl,

$$\text{Number of moles of } H_2PO_4^- = \left(4.5 \times 10^{-2}\ M\right)\left(20.0 \times 10^{-3}\ \text{L}\right) = 9.0 \times 10^{-4}\ \text{mol}$$

$$\text{Number of moles of } HPO_4^{2-} = \left(5.5 \times 10^{-2}\ M\right)\left(20.0 \times 10^{-3}\ \text{L}\right) = 1.1 \times 10^{-3}\ \text{mol}$$

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

$$H^+ + HPO_4^{2-} \rightleftharpoons H_2PO_4^-$$

and the reaction will proceed to near completion.

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

$$\text{Moles of } HPO_4^{2-} \text{ after reaction with HCl} = 1.1 \times 10^{-3}\ \text{mol} - 5.0 \times 10^{-4}\ \text{mol} = 6 \times 10^{-4}\ \text{mol}$$

$$\left[HPO_4^{2-}\right] \text{ after reaction with HCl} = \frac{6 \times 10^{-4}\ \text{mol}}{25.0 \times 10^{-3}\ \text{L}} = 0.02\ M$$

$$\text{Moles of } H_2PO_4^- \text{ after reaction with HCl} = 9.0 \times 10^{-4}\ \text{mol} + 5.0 \times 10^{-4}\ \text{mol} = 1.40 \times 10^{-3}\ \text{mol}$$

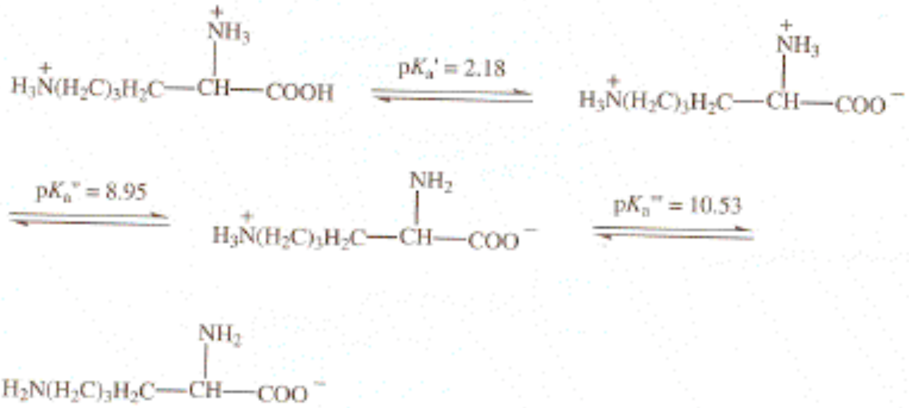
$$\left[H_2PO_4^{2-}\right] \text{ after reaction with HCl} = \frac{1.40 \times 10^{-3}\ \text{mol}}{25.0 \times 10^{-3}\ \text{L}} = 0.056\ M$$

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

$$\begin{aligned} pH &= pK_a'' + \log \frac{\left[HPO_4^{2-}\right]}{\left[H_2PO_4^-\right]} \\ &= 7.21 + \log \frac{0.02}{0.056} \\ &= 6.76 \end{aligned}$$

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

Lysine



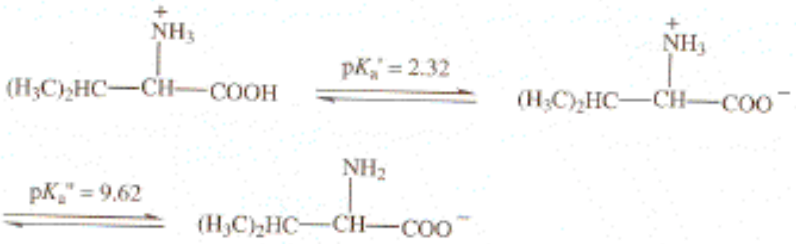
$$H_3\overset{+}{N}(H_2C)_3H_2C-\overset{\overset{+}{N}H_3}{\overset{|}{CH}}-COOH \xrightleftharpoons{pK_a' = 2.18} H_3\overset{+}{N}(H_2C)_3H_2C-\overset{\overset{+}{N}H_3}{\overset{|}{CH}}-COO^-$$

$$\xrightleftharpoons{pK_a'' = 8.95} H_3\overset{+}{N}(H_2C)_3H_2C-\overset{NH_2}{\overset{|}{CH}}-COO^- \xrightleftharpoons{pK_a''' = 10.53}$$

$$H_2N(H_2C)_3H_2C-\overset{NH_2}{\overset{|}{CH}}-COO^-$$

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

Valine

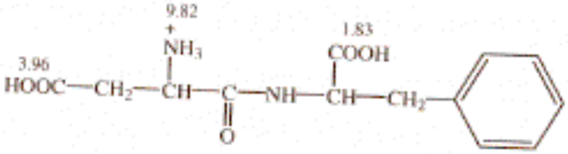


$$(H_3C)_2HC-\overset{\overset{+}{N}H_3}{\overset{|}{CH}}-COOH \xrightleftharpoons{pK_a' = 2.32} (H_3C)_2HC-\overset{\overset{+}{N}H_3}{\overset{|}{CH}}-COO^-$$

$$\xrightleftharpoons{pK_a'' = 9.62} (H_3C)_2HC-\overset{NH_2}{\overset{|}{CH}}-COO^-$$

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

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 phenyalanine,



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,

$$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\log\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = \mathrm{pH} - \mathrm{p}K_a$$

$$\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = 10^{\mathrm{pH}-\mathrm{p}K_a} \tag{8.81.1}$$

The fraction of an acid is

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

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

$$\frac{1}{f} = \frac{[\mathrm{HA}]+[\mathrm{A^-}]}{[\mathrm{HA}]} = 1 + \frac{[\mathrm{A^-}]}{[\mathrm{HA}]}$$

$$\frac{[\mathrm{A^-}]}{[\mathrm{HA}]} = \frac{1}{f} - 1 \tag{8.81.2}$$

Substitute Equation (8.81.2) into Equation (8.81.1):

$$\frac{1}{f} - 1 = 10^{\mathrm{pH}-\mathrm{p}K_a}$$

$$\frac{1}{f} = 1 + 10^{\mathrm{pH}-\mathrm{p}K_a}$$

$$f = \frac{1}{1 + 10^{\mathrm{pH}-\mathrm{p}K_a}} \tag{8.81.3}$$

(b) Let the fractions of the acidic $\mathrm{NH_3^+}$ 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

HW8 Freshly distilled, deionized water has a pH of 7. Left standing in air, however, the water gradually becomes acidic. Calculate the pH of the "solution" at equilibrium. (*Hint*: First calculate the solubility of CO_2 in water according to Example 5.3. Assume the partial pressure of CO_2 is 0.00030 atm.)

The solubility of CO_2 in water can be calculated using Henry's law.

$$m = \frac{P_2}{K'} = \frac{3.0 \times 10^{-4}\ \text{atm}}{29.3\ \text{atm mol}^{-1}\ \text{kg H}_2\text{O}} = 1.02 \times 10^{-5}\ \text{mol (kg H}_2\text{O)}^{-1}$$

The dissolved CO_2 forms carbonic acid with a molarity of 1.02×10^{-5} *M* (for a dilute solution, molarity is very similar to molality), which dissociates according to

	H_2CO_3	$\rightleftharpoons$	H^+	+	HCO_3^-	
Initial	1.02×10^{-5}		0		0	*M*
At equilibrium	$1.02 \times 10^{-5} - x$		x		x	*M*

$$K_a = 4.2 \times 10^{-7} = \frac{x^2}{1.02 \times 10^{-5} - x}$$

$$x^2 + 4.2 \times 10^{-7}x - 4.28 \times 10^{-12} = 0$$

$$x = 1.87 \times 10^{-6}$$

Thus,

$$\text{pH} = -\log\left(1.87 \times 10^{-6}\right) = 5.73$$

2.70 How does the mean free path of a gas depend on **(a)** the temperature at constant volume, **(b)** the density, **(c)** the pressure at constant temperature, **(d)** the volume at constant temperature, and **(e)** the size of molecules?

The mean free path is given by Equation 2.32 in the text

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 \left(\frac{N}{V}\right)}$$

Although it is possible to answer this question solely by reference to the equation, it is useful to have an understanding of the physical basis for the effects observed. The key physical quantity is the density of the gas.

(a) The mean free path is independent of temperature at constant volume. T does not appear in the equation. As the temperature is increased the molecules are moving faster, but the average distance between them is not affected. The mean time between collisions decreases, but the mean distance traveled between collisions remains the same.

(b) As the density increases, the mean free path decreases, since $\frac{N}{V}$ appears in the denominator. In a more dense gas, the molecules are more closely spaced.

(c) As the pressure increases at constant temperature, the mean free path decreases. These conditions lead to a decrease in volume, hence an increase in density. The molecules are being squeezed closer together.

(d) As the volume increases at constant temperature, the mean free path increases. As the molecules move into the expanded volume, they move further apart from each other.

(e) As the size of the molecules increases, the mean free path decreases. The collision diameter, d, appears in the denominator of the equation. Larger molecules do not have to travel as far before they run into each other.

2.72 Calculate the mean free path and the binary number of collisions per liter per second between HI molecules at 300 K and 1.00 atm. The collision diameter of the HI molecules may be taken to be 5.10 Å. Assume ideal-gas behavior.

The ideal gas law is used to calculate $\frac{N}{V}$, which is then used to calculate the mean free path.

$$PV = nRT = \frac{N}{N_A}RT$$

$$\frac{N}{V} = \frac{PN_A}{RT} = \frac{(1.00\ \text{atm})\ (6.022\times 10^{23}\ \text{mol}^{-1})}{(0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K})} = 2.446\times 10^{22}\ \text{L}^{-1}\left(\frac{1000\ \text{L}}{1\ \text{m}^3}\right)$$

$$= 2.446\times 10^{25}\ \text{m}^{-3}$$

$$\lambda = \frac{1}{\sqrt{2}\pi d^2\left(\frac{N}{V}\right)} = \frac{1}{\sqrt{2}\pi\ (5.10\times 10^{-10}\ \text{m})^2\ (2.446\times 10^{25}\ \text{m}^{-3})} = 3.53\times 10^{-8}\ \text{m}$$

The binary number of collisions depends on the average molecular speed, which is

$$\bar{c} = \sqrt{\frac{8RT}{\pi \mathcal{M}}} = \sqrt{\frac{8\ (8.314\ \text{J K}^{-1}\ \text{mol}^{-1})\ (300\ \text{K})}{\pi\ (127.9\times 10^{-3}\ \text{kg mol}^{-1})}} = 222.8\ \text{m s}^{-1}$$

$$Z_{11} = \frac{\sqrt{2}}{2}\pi d^2\bar{c}\left(\frac{N}{V}\right)^2 = \frac{\sqrt{2}}{2}\pi\left(5.10\times 10^{-10}\ \text{m}\right)^2\left(222.8\ \text{m s}^{-1}\right)\left(2.446\times 10^{25}\ \text{m}^{-3}\right)^2$$

$$= \left(7.702\times 10^{34}\ \text{m}^{-3}\ \text{s}^{-1}\right)\left(\frac{1\ \text{m}^3}{1000\ \text{L}}\right) = 7.70\times 10^{31}\ \text{collisions L}^{-1}\ \text{s}^{-1}$$