3

• In a standard acid-base titration, 25.00 mL of 0.1043 M NaOH solution was found to react exactly with 28.45 mL of an HCl solution of unknown concentration. What is the pH of the unknown HCl solution at 25 °C?

The reaction follows the equation $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ so that the number of moles of H^+ that reacts is equal to the number of moles of OH^-.

For OH^-:

number of moles = concentration × volume
= 0.1043 mol L^{-1} × 0.02500 L = 0.002608 mol

This is equal to the number of moles of $H^+(aq)$ in 28.45 mL, so:

concentration of $H^+(aq)$ = number of moles / volume
= 0.002608 mol / 0.02845 L = 0.9165 mol L^{-1}

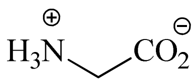
Using $pH = -\log_{10}[H^+(aq)]$:

$pH = -\log_{10}(0.9165) = 1.04$

pH = **1.04**

Marks
7

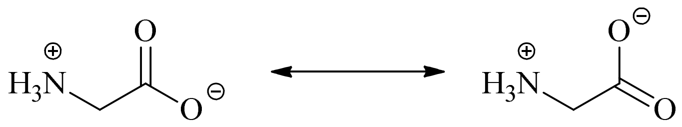
- Glycine, NH_2CH_2COOH, is the simplest of all naturally occurring amino acids. The pK_a of the acid group is 2.35 and the pK_a associated with the amino group is 9.78. Draw a structure that indicates the charges on the molecule at the physiological pH of 7.4.



This pH is much *greater* than the pK_a value of the acid group: it is *deprotonated*.

This pH is much *lower* than the pK_a value of the amino group: it is *protonated*.

Use your structure to illustrate the concept of resonance.



What are the hybridisation states and geometries of the two carbon atoms and the nitrogen atom in glycine?

The carbon on the acid group is sp^2 hybridised and the geometry is trigonal planar.

The carbon on the CH_2 group is sp^3 hybridised and the geometry is tetrahedral.

The nitrogen is sp^3 hybridised and the geometry is tetrahedral.

Propionic acid, CH_3CH_2COOH, has a melting point of –20.7 °C while glycine has a melting point of 292 °C. Suggest a reason why these two molecules have such different melting points.

Propionic acid has strong hydrogen bonds, giving it a relatively high melting point.

However, glycine has very strong ionic bonds between the NH_3^+ and CO_2^- groups giving it *very* high melting point.

Marks
2

- Explain the terms '*weak*' and '*strong*' and the terms '*dilute*' and '*concentrated*' in the context of acids and bases.

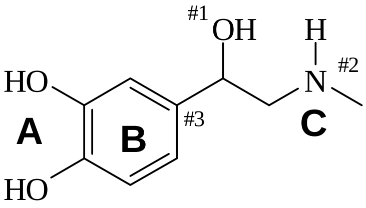
A weak acid or base is one which only partially dissociates in water:
e.g. $\mathbf{CH_3COOH(aq) \rightleftharpoons CH_3CO_2^-(aq) + H^+(aq)}$

A strong acid or base is one which completely dissociates in water:
e.g. $\mathbf{HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)}$

Concentrated and dilute are terms that can be used in reference to any solute, describing the number of moles of solute relative to the volume of solvent. A concentrated solution has a high solute : solvent ratio, whilst a dilute solution has a low solute:solvent ratio.

Marks
4

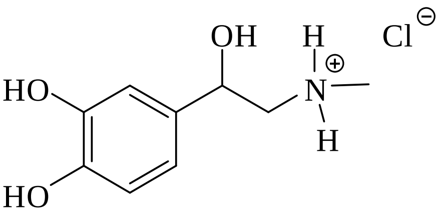
- The molecular structure of adrenaline (epinephrine), a hormone involved in the "fight or flight" response, is shown below.



List the types of intermolecular interactions that each of the following sites on adrenaline would be involved in if dissolved in water.

A	**H-bonding, dipole-dipole, dispersion forces**
B	**dispersion forces**
C	**H-bonding, dipole-dipole, dispersion forces**

Pharmaceuticals with amine groups are frequently supplied as their "hydrochloride salts". Draw the structure that would result if adrenaline were reacted with one equivalent of HCl. What **additional** intermolecular forces would be present if this form of adrenaline were dissolved in water?



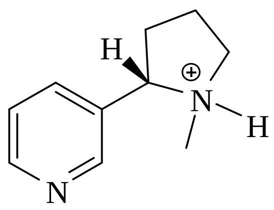
With this form present, ion-dipole interactions would be introduced.

The pK_b of N-1 is 10.88 and the pK_b of N-2 is 5.98. Draw the structure of the predominant form of nicotine that exists in the human body at pH 7.4.

4

For N-1, the *pK*$_a$ of the protonated form (the conjugate acid) is (14.00 – 10.88) = 3.12. As the pH is *higher* than the *pK*$_a$, the conjugate acid is deprotonated: *very* little protonation occurs.

For N=2, the *pK*$_a$ of the protonated form is (14.00 – 5.98) = 8.02. As the pH is *lower* than the *pK*$_a$, the conjugate acid form dominates: protonation occurs.

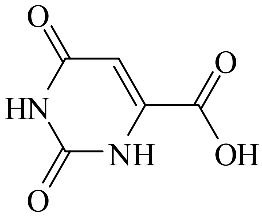


Marks
4

- Lithium salts, especially lithium carbonate, are commonly used in the treatment of bipolar disorder. Write the net ionic equation for the reaction which occurs between lithium carbonate and hydrochloric acid in the stomach.

$Li_2CO_3(s) + 2H^+(aq) \rightarrow 2Li^+(aq) + H_2O(l) + CO_2(g)$

Lithium orotate (as a monohydrate salt, $LiC_5H_3N_2O_4 \cdot H_2O$) is a controversial alternative formulation sold in some health food stores. The orotate ion is the conjugate base of orotic acid, whose structure is shown below.



orotic acid

Like the carbonate, lithium orotate is taken orally. Using an equation, comment on any differences between the form in which lithium is bioavailable from these two lithium salts.

When lithium orotate, $LiC_5H_3N_2O_4$, dissolves in water, it forms $Li^+(aq)$ ions and orotate ions:

$LiC_5H_3N_2O_4(s) \rightarrow Li^+(aq) + C_5H_3N_2O_4^-(aq)$

Both lithium carbonate and lithium orotate thus give rise to the same form of lithium, $Li^+(aq)$, when taken orally.

Marks 5

- Glycine, NH_2CH_2COOH, the simplest of all naturally occurring amino acids, has a melting point of 292 °C. The pK_a of the acid group is 2.35 and the pK_a associated with the amino group is 9.78. Draw a structure that indicates the charges on the molecule at the physiological pH of 7.4.

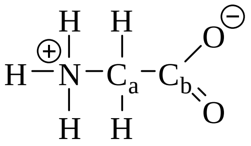
As pH = 7.4 is higher than the pK_a of the acid group, -COOH, it will exist primarily in its deprotonated, conjugate base form, $-COO^-$.

As pH = 7.4 is lower than the pK_a of the amino group, $-NH_2$, it will exist primarility in its protonated form, $-NH_3^+$.

Glycine will exist in the uncharged, zwitterionic form: $H_3\overset{\oplus}{N}-CH_2-COO^{\ominus}$

Describe the hybridisation of the two carbon atoms and the nitrogen atom in glycine and the geometry of the atoms surrounding these three atoms.

The structure is:



N has 4 bonds and no lone pairs: sp^3 with a tetrahedral arrangement.

C_a has 4 bonds and no lone pairs: sp^3 with a tetrahedral arrangement.

C_b has 3 bonds and no lone pairs: sp^2 with a trigonal planar arrangement.

Glycine has an unusually high melting point for a small molecule. Suggest a reason for this.

Glycine with a positively and a negatively charged end. There is therefore ionic bonding between the molecules leading to strong intermolecular forces.

Marks
5

- Consider the following equation.

$$HBrO(aq) + NH_3(aq) \rightleftharpoons BrO^-(aq) + NH_4^+(aq)$$

Name all of the species in this equation.

HBrO	**hypobromous acid**
BrO^-	**hypobromite ion**
NH_3	**ammonia**
NH_4^+	**ammonium ion**

Complete the following table by giving the correct pK_a or pK_b value where it can be calculated. Mark with a cross (✕) those cells for which insufficient data have been given to calculate a value.

Species	HBrO	NH_3	BrO^-	NH_4^+
pK_a of acid	8.64	✕	✕	**9.24**
pK_b of base	✕	4.76	**5.36**	✕

Determine on which side (left or right hand side) the equilibrium for the reaction above will lie. Provide a brief rationale for your answer.

The reaction is the sum of the acid-base equilibra for HBrO and NH_3:

$HBrO(aq) \rightarrow H^+(aq) + BrO^-(aq)$	**$K_a(HBrO) = 10^{-8.64}$**
$H^+(aq) + NH_3(aq) \rightarrow NH_4^+(aq)$	**$K(NH_3) = \dfrac{1}{K_a(NH_4^+)} = 10^{+9.24}$**
$HBrO(aq) + NH_3(aq) \rightarrow BrO^-(aq)$	**$K = K_a(HBrO) \times K(NH_3)$**

Hence, $K = (10^{-8.64}) \times (10^{+9.24}) = 10^{+0.64} = 4.4$. As $K > 1$, the reaction favours products.