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# Acids and bases

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## Answers to worked examples

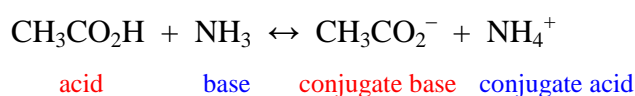
### WE 7.1 Conjugate acids and conjugate bases (on p. 307 in *Chemistry*<sup>3</sup>)

Pure ethanoic acid ( $\text{CH}_3\text{CO}_2\text{H}$ ) reacts with liquid ammonia ( $\text{NH}_3$ ) to form ions in a proton transfer equilibrium. Write an equation for the reaction and identify the conjugate acid-base pairs involved. (Omit state symbols.)

#### Strategy

Write out the equation for the equilibrium by deciding which reactant is most likely to be the proton donor (acid). The product formed by the loss of a proton is its conjugate base.

#### Solution



The conjugate acid–base pairs are  $\text{CH}_3\text{CO}_2\text{H} / \text{CH}_3\text{CO}_2^-$  and  $\text{NH}_4^+ / \text{NH}_3$ .

### WE 7.2 Calculating the pH of a strong acid (on p. 311 in *Chemistry*<sup>3</sup>)

Calculate the pH of 0.245  $\text{mol dm}^{-3}$  nitric acid ( $\text{HNO}_3$ ).

#### Strategy

For a strong acid, the proton transfer reaction to water practically goes to completion, so the amount in moles of  $\text{H}_3\text{O}^+$  in the solution is equal to the amount in moles of acid put into the solution. Equation 7.5,  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+(\text{aq})]$ .

Solution

Using Equation 7.5,  $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+(\text{aq})]$  where the  $[\text{H}_3\text{O}^+] = 0.245 \text{ mol dm}^{-3}$ , so  $\text{pH} = -\log_{10}(0.245) = 0.61$

**WE 7.3 Calculating the pH of a weak acid (on p. 312 in *Chemistry*<sup>3</sup>)**

A solution of ethanoic acid in water has a pH of 3.2. Calculate the concentration of the solution.

Strategy

Ethanoic acid is a weak acid and it is not fully ionized in water. This means that the  $[\text{H}_3\text{O}^+(\text{aq})]$  concentration that can be calculated using Equation 7.5 from the pH is not the same as the acid concentration. The acid concentration has to be calculated using Equation 7.2 for the acidity constant,  $K_a$ . In addition, two assumptions have to be made to complete the calculation; firstly, that the  $[\text{H}_3\text{O}^+(\text{aq})] = [\text{A}^-(\text{aq})]$  which ignores the  $[\text{H}_3\text{O}^+(\text{aq})]$  generated by the self ionization of water; secondly that the  $[\text{HA}(\text{aq})]$  is equal to the concentration of HA at equilibrium.

Solution

Use Equation 7.5 to calculate the  $[\text{H}_3\text{O}^+(\text{aq})]$ ,

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = 3.2$$

$$\text{Therefore } [\text{H}_3\text{O}^+] = 10^{-3.2} = 6.3 \times 10^{-4} \text{ mol dm}^{-3}.$$

Use Equation 7.2 and the assumptions described in the strategy,

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})]^2}{[\text{CH}_3\text{CO}_2\text{H}(\text{aq})]}, \text{ so}$$

$$\begin{aligned} [\text{CH}_3\text{CO}_2\text{H}(\text{aq})] &= \frac{[\text{H}_3\text{O}^+(\text{aq})]^2}{K_a} \\ &= \frac{(6.3 \times 10^{-4} \text{ mol dm}^{-3})^2}{1.7 \times 10^{-5} \text{ mol dm}^{-3}} \\ &= 0.02 \text{ mol dm}^{-3} \end{aligned}$$

**WE 7.4 Strengths of acids and bases (on p. 316 in *Chemistry*<sup>3</sup>)**

Use Table 7.2 to predict which is the stronger base,  $F^-$  ions or  $NO_3^-$  ions.

**Strategy**

The strength of a base can be predicted by considering the  $pK_a$  of its conjugate acid. A stronger acid has the weaker conjugate base.

**Solution**

$pK_a(HF) > pK_a(HNO_3)$ , so  $HNO_3$  is the stronger acid. The stronger acid has the weaker conjugate base, so  $F^-$  is a stronger base than  $NO_3^-$ .

**WE 7.5 Buffer solutions (on p. 320 in *Chemistry*<sup>3</sup>)**

Calculate the pH of a buffer solution made by mixing  $250\text{ cm}^3$  of  $0.250\text{ mol dm}^{-3}$  methanoic acid ( $HCO_2H$ ) and  $500\text{ cm}^3$  of  $0.500\text{ mol dm}^{-3}$  sodium methanoate ( $pK_a$  for methanoic acid is 3.75 at 298 K). *Hint:* In this case the concentrations of acid and conjugate base in the buffer are different from those in the solutions added to make it because they dilute one another when they are mixed. Remember to take this dilution into account.

**Strategy**

Calculate the new concentrations of acid and conjugate base in the buffer based on the new volume of the solution and then use these concentrations in Equation 7.16 (p.320) to calculate the pH.

**Solution**

$$\begin{aligned}\text{Total volume} &= 250\text{ cm}^3 + 500\text{ cm}^3 \\ &= 750\text{ cm}^3\end{aligned}$$

Since the molarity is defined as number of moles in  $1\text{ dm}^{-3}$  ( $1000\text{ cm}^3$ ), number of moles in the aliquots added together can be calculated as follows:

The buffer solution contains  $\frac{0.250}{4} \text{ mol HCO}_2\text{H}$  and  $\frac{0.500}{2} \text{ mol HCO}_2^-$ .

The concentration of these species in the  $0.750 \text{ dm}^3$  solution is

$$[\text{acid}] = \frac{0.250 \text{ mol}}{4 \times 0.750 \text{ dm}^3} = 0.0833 \text{ mol dm}^3$$

$$[\text{conjugate base}] = \frac{0.500 \text{ mol}}{2 \times 0.750 \text{ dm}^3} = 0.333 \text{ mol dm}^3$$

Using Equation 7.16,  $\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{conjugate base}]}{[\text{acid}]}$

$$\begin{aligned} \text{pH} &= 3.75 + \log_{10} \frac{(0.333)}{(0.0833)} \\ &= 3.75 + \log_{10}(4.00) \\ &= 4.35 \end{aligned}$$

### WE 7.6 Calculating the pH in a titration reaction (on p. 324 in *Chemistry*<sup>3</sup>)

What is the pH of the solution in the conical flask when  $11.9 \text{ cm}^3$  of NaOH have been added?

#### Strategy

As the equivalence point has not been reached, the  $[\text{H}_3\text{O}^+]$  has to be calculated using Equation 7.17 before Equation 7.5 can be applied to calculate the pH.

#### Solution

Using Equation 7.17

$$\begin{aligned} [\text{H}_3\text{O}^+(\text{aq})] &= \frac{(0.240 \text{ mol dm}^{-3} \times 0.0200 \text{ dm}^3) - (0.400 \text{ mol dm}^{-3} \times 0.0119 \text{ dm}^3)}{(0.0200 + 0.0119) \text{ dm}^3} \\ &= 1.25 \times 10^{-3} \text{ mol dm}^{-3} \end{aligned}$$

$$\text{pH} = -\log_{10}(1.25 \times 10^{-3}) = 2.90$$

**WE 7.7 Lewis acids and bases (on p. 337 in *Chemistry*<sup>3</sup>)**

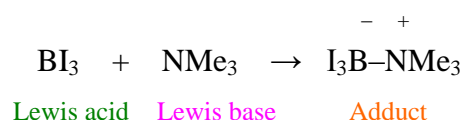
Identify the Lewis acid and the Lewis base in the reaction between boron triiodide, BI<sub>3</sub>, and trimethylamine, Me<sub>3</sub>N. What is the product of the reaction?

Strategy

The Lewis acid is an electron pair acceptor, therefore the Lewis acid will be electron deficient so that it can interact with the electron pair.

Solution

In this reaction, BI<sub>3</sub> has only 6 valence electrons, so is a Lewis acid, accepting two electrons to fill the octet. NMe<sub>3</sub> has a lone pair on the nitrogen atom, so is a Lewis base.



## Answers to boxes

**Box 7.1 Solvation (on p. 305 in *Chemistry*<sup>3</sup>)**

Suggest why sucrose does not dissolve in hexane.

Strategy

Consider the properties that are required from a solvent to solubilise polar molecules such as sucrose.

Solution

Hexane is non-polar, so unable to form strong intermolecular interactions with sucrose. The intermolecular interactions in solid sucrose are stronger than the sucrose-hexane interactions, so sucrose does not dissolve.

**Box 7.2 Acids, alkalis, and human tissue (on p. 307 in *Chemistry*<sup>3</sup>)**

What mass of sulfuric acid is present in 500  $\text{cm}^3$  of a solution with the concentration 2  $\text{mol dm}^{-3}$  of  $\text{SO}_4^{2-}$ ?

Strategy

Since one mole of sulfuric acid generates one mole of sulfate anions, the number of moles of the parent acid is the same as that of the sulfate anions. The mass of acid can then be calculated from the molar mass of sulfuric acid.

Solution

500  $\text{cm}^3$  of a solution with the concentration 2  $\text{mol dm}^{-3}$  of  $\text{SO}_4^{2-}$  contains 1  $\text{mol}$   $\text{SO}_4^{2-}$ . This is generated by 1  $\text{mol}$   $\text{H}_2\text{SO}_4$ .  $M_r(\text{H}_2\text{SO}_4) = 98.1$ , so the solution contains 98.1  $\text{g}$  of  $\text{H}_2\text{SO}_4$ .

**Box 7.3 Acidic water in disused mines (on p. 312 in *Chemistry*<sup>3</sup>)**

What is the concentration of  $\text{H}_3\text{O}^+$  in a solution of pH  $-3.6$ ?

Strategy

The pH can be directly calculated from Equation 7.5.

Solution

From Equation 7.5

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -3.6$$

$$\log_{10}[\text{H}_3\text{O}^+] = 3.6,$$

$$\begin{aligned} \text{Taking the inverse logarithm of both sides gives } [\text{H}_3\text{O}^+] &= 10^{3.6} \\ &= 4000 \text{ mol dm}^{-3} \end{aligned}$$

**Box 7.4 Controlling pH in a swimming pool (on p. 317 in *Chemistry*<sup>3</sup>)**

The  $pK_a$  of HOCl is 7.40. Calculate the pH of a  $0.100 \text{ mol dm}^{-3}$  HOCl solution, explaining any assumptions you make.

Strategy

The HOCl is not fully ionized in water as it is a weak acid and hence the  $[\text{H}_3\text{O}^+(\text{aq})]$  is not the same as the acid concentration.  $[\text{H}_3\text{O}^+(\text{aq})]$  must be calculated using Equation 7.2 for the acidity constant,  $K_a$ . The  $[\text{H}_3\text{O}^+(\text{aq})]$  can then be used in Equation 7.5, to calculate the pH.

Two assumptions have to be made to carry out this calculation. Firstly, that the  $[\text{H}_3\text{O}^+(\text{aq})] = [\text{A}^-(\text{aq})]$  which ignores the  $[\text{H}_3\text{O}^+(\text{aq})]$  generated by the self ionization of water. Secondly, that the  $[\text{HA}(\text{aq})]$  is equal to the concentration of HA at equilibrium.  $[\text{H}_3\text{O}^+(\text{aq})]$  must be calculated using Equation 7.2 for the acidity constant,  $K_a$ .

Solution

If the  $pK_a$  is 7.40,  $K_a = 10^{-7.40} = 4.0 \times 10^{-8} \text{ mol dm}^{-3}$ .

Assuming that  $[\text{H}_3\text{O}^+(\text{aq})] = [\text{OCl}^-(\text{aq})]$ , and that  $[\text{HOCl}(\text{aq})]$  at equilibrium is equal to the concentration of HOCl used to make the solution,

From Equation 7.2,

$$K_a = \frac{[\text{H}_3\text{O}^+]^2}{[\text{HOCl}]}, \text{ so } 4.0 \times 10^{-8} \text{ mol dm}^{-3} = \frac{[\text{H}_3\text{O}^+]^2}{0.100 \text{ mol dm}^{-3}}$$

Multiplying both sides by  $0.100 \text{ mol dm}^{-3}$

$$\begin{aligned} [\text{H}_3\text{O}^+]^2 &= 4.0 \times 10^{-8} \text{ mol dm}^{-3} \times 0.100 \text{ mol dm}^{-3} \\ &= 4.0 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6} \\ [\text{H}_3\text{O}^+] &= (4.0 \times 10^{-9} \text{ mol}^2 \text{ dm}^{-6})^{1/2} \\ &= 6.3 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

Substituting this value into Equation 7.5 gives

$$\begin{aligned} \text{pH} &= -\log_{10}(6.3 \times 10^{-5}) \\ &= 4.2 \end{aligned}$$

**Box 7.5 Buffering in the blood (on p. 321 in *Chemistry*<sup>3</sup>)**

If blood pH rises above 7.45, a potentially life-threatening condition called *alkalosis* can result. This can happen in patients who are hyperventilating from severe anxiety, or in climbers suffering from oxygen deficiency at high altitude. Although no longer recommended first aid, one way to treat alkalosis is to get the patient to breathe into a bag so that the exhaled  $\text{CO}_2$  is re-inhaled. Use the above equilibria to explain how this brings down blood pH.

Strategy

Using Le Chatelier's principle and the carbonate equilibria given in Box 7.5, consider what the effect of increasing the carbon dioxide levels has on the amount of  $[\text{H}_3\text{O}^+(\text{aq})]$  in the blood.

Solution

$[\text{CO}_2(\text{g})]$  in the lungs increases as the exhaled  $\text{CO}_2$  is re-inhaled. This increases  $[\text{CO}_2(\text{aq})]$  in the blood. This pushes the positions of equilibrium in the three equilibria to the right hand side. The overall effect is to increase the concentration of  $[\text{H}_3\text{O}^+(\text{aq})]$  in the blood, thus lowering the pH.

**Box 7.6 Cooking with acids and bases (on p. 334 in *Chemistry*<sup>3</sup>)**

Predict the form of the titration curve for the reaction between malic acid and sodium hydroxide.

Strategy

As shown in Box 7.6 (p.335) malic acid has two carboxylic acid ( $-\text{CO}_2\text{H}$ ) groups. Each carboxylic acid group will have a different  $\text{p}K_{\text{a}}$ . The titration curve will depend on the strength of the acid and the strength of the base.

Solution

Malic acid is a weak dibasic acid and sodium hydroxide is a strong base. The titration curve will be similar in appearance to that in Figure 7.12 (p.333) where there will be two equivalence points corresponding to the two different carboxylic acid groups.



**Box 7.7 Superacids (on p. 337 in *Chemistry*<sup>3</sup>)**

Use VSEPR theory to predict the shapes of the  $\text{SbF}_5$  molecule and the  $\text{SbF}_6^-$  anion. Refer to Chapter 5 for the background to VSEPR theory if you need help.

Strategy

For neutral species, count up the number of electrons around the central atom and determine the number of bond pairs and lone pairs. If relevant, place lone pairs strategically to avoid interactions at  $90^\circ$ . For the anion, remember to add on the electron(s) for the negative charge.

Solution

$\text{SbF}_5$ : 5 electrons from Sb and 5 electrons from 5F. 10 electrons around Sb, so 5 electron pairs. Based on a trigonal bipyramidal with no lone pairs.  $\text{SbF}_5$  is **trigonal bipyramidal**.

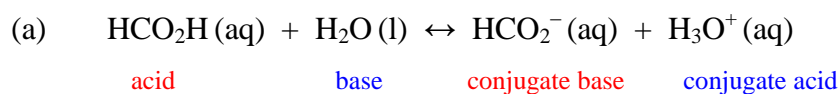
$\text{SbF}_6^-$ : 5 electrons from Sb, 6 electrons from 6F and 1 electron from the negative charge. 12 electrons around Sb, so 6 electron pairs. Based on an octahedron with no lone pairs.  $\text{SbF}_6^-$  is **octahedral**.

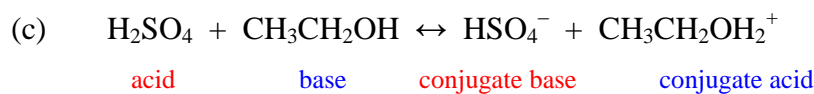
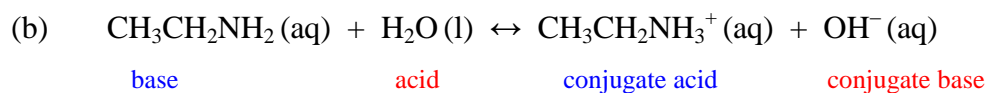
**Answers to end of chapter questions**

1. Identify the acid, base, conjugate acid, and conjugate base in the following equilibria.
- (a)  $\text{HCO}_2\text{H}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{HCO}_2^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq})$
- (b)  $\text{CH}_3\text{CH}_2\text{NH}_2(\text{aq}) + \text{H}_2\text{O}(\text{l}) \leftrightarrow \text{CH}_3\text{CH}_2\text{NH}_3^+(\text{aq}) + \text{OH}^-(\text{aq})$
- (c)  $\text{H}_2\text{SO}_4 + \text{CH}_3\text{CH}_2\text{OH} \leftrightarrow \text{HSO}_4^- + \text{CH}_3\text{CH}_2\text{OH}_2^+$

Strategy

Write out the equation for the equilibrium by deciding which reactant is most likely to be the proton donor (acid). The product formed by the loss of a proton is its conjugate base.

Solution



2. Aspirin is acetylsalicylic acid, which has a  $pK_a$  of 3.49

(a) Calculate the pH of a  $0.10 \text{ mol dm}^{-3}$  solution of this acid.

### Strategy

Acetylsalicylic acid is a weak acid and it is not fully ionized in water. This means that  $[\text{H}_3\text{O}^+(\text{aq})]$  concentration that can be calculated using Equation 7.5 from the pH is not the same as the acid concentration. The acid concentration has to be calculated using Equation 7.2 for the acidity constant,  $K_a$ . In addition, two assumptions have to be made to complete the calculation, firstly, that the  $[\text{H}_3\text{O}^+(\text{aq})] = [\text{A}^-(\text{aq})]$  which ignores the  $[\text{H}_3\text{O}^+(\text{aq})]$  generated by the self ionisation of water and, secondly, that the  $[\text{HA}(\text{aq})]$  is equal to the concentration of HA at equilibrium.

### Solution

(a)  $pK_a = -\log_{10}K_a$ , so  $K_a = 10^{-3.49} = 3.24 \times 10^{-4} \text{ mol dm}^{-3}$

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{A}^-(\text{aq})]}{[\text{HA}(\text{aq})]}$$

Assuming  $[\text{H}_3\text{O}^+(\text{aq})] = [\text{A}^-(\text{aq})]$ , and  $[\text{HA}(\text{aq})]$  at equilibrium is equal to the concentration of HA used to make the solution,

$$K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})]^2}{0.1 \text{ mol dm}^{-3}} = 3.24 \times 10^{-4} \text{ mol dm}^{-3}$$

Rearranging:

$$\begin{aligned} [\text{H}_3\text{O}^+(\text{aq})]^2 &= (0.10 \text{ mol dm}^{-3}) \times (3.24 \times 10^{-4} \text{ mol dm}^{-3}) \\ &= 3.24 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6} \\ [\text{H}_3\text{O}^+(\text{aq})] &= (3.24 \times 10^{-5} \text{ mol}^2 \text{ dm}^{-6})^{1/2} \end{aligned}$$

$$= 5.69 \times 10^{-3} \text{ mol dm}^{-3}.$$

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = -\log_{10}(5.69 \times 10^{-3}) = 2.25$$

- (b) Would you expect the sodium salt of acetylsalicylic acid to be acidic, neutral or basic for an aqueous solution at this temperature?

### Strategy

Consider whether the hydrolysis of the alkali metal or the weak acid will have the greatest effect on the pH of the solution.

### Solution

Acetylsalicylic acid is a weak acid, so the sodium salt will be basic in solution because of hydrolysis.

3.  $K_w$  for water at 40°C is  $3.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$ . Is pH 7 neutral, acidic, or basic for an aqueous solution at this temperature?

### Strategy

The equation for the self ionization of water is  $2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$

$[\text{OH}^-]$  is therefore equal to  $[\text{H}_3\text{O}^+]$  meaning that the  $[\text{H}_3\text{O}^+]$  can be calculated from  $K_w$ . The  $[\text{H}_3\text{O}^+ (\text{aq})]$  concentration can then be used with Equation 7.5 to calculate the pH.

### Solution

$$K_w = 3.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6} = [\text{H}_3\text{O}^+ (\text{aq})][\text{OH}^- (\text{aq})]$$

For pure water  $[\text{H}_3\text{O}^+ (\text{aq})] = [\text{OH}^- (\text{aq})]$ ,

$$[\text{H}_3\text{O}^+ (\text{aq})] = (3.0 \times 10^{-14})^{1/2} = 1.7 \times 10^{-7} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}[\text{H}_3\text{O}^+] = 6.8$$

At 40°C, pure water has a pH of 6.8, so this pH corresponds to neutrality. Any pH below this is acidic and any pH above this is basic. This means that pH 7 is basic at 40°C.

4. Calculate the following:
- $[\text{H}_3\text{O}^+(\text{aq})]$  in a solution of HCl at pH 1.5;
  - $[\text{OH}^-(\text{aq})]$  in a solution of KOH at pH 12.8.

Strategy

HCl is a strong acid and KOH is a strong base. Both species will be fully ionized in solution and Equation 7.5 can be used to calculate the pH. Since  $\text{pH} + \text{pOH} = 14$ , pOH can be calculated once the pH has been determined.

Solution

- $\text{pH} = -\log_{10}[\text{H}_3\text{O}^+]$ , so  $[\text{H}_3\text{O}^+] = 10^{-1.5} = 3.2 \times 10^{-2} \text{ mol dm}^{-3}$
- $\text{pH} = 12.8$ . Using Equation 7.8,  $\text{pH} + \text{pOH} = 14.00$ .  
 $\text{pOH} = 14 - 12.8 = 1.2$   
 $\text{pOH} = -\log_{10}[\text{OH}^-]$ , so  $[\text{OH}^-] = 10^{-1.2} = 6.3 \times 10^{-2} \text{ mol dm}^{-3}$

5. Hydroxylamine ( $\text{NH}_2\text{OH}$ ) is a weak base. A  $0.20 \text{ mol dm}^{-3}$  solution of hydroxylamine has a pH of 9.7.
- Calculate  $K_b$  and  $\text{p}K_b$  for hydroxylamine.
  - What is the  $\text{p}K_a$  of  $\text{NH}_3\text{OH}^+$ ?

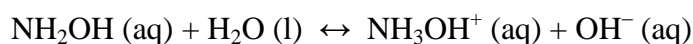
Strategy

By using Equation 7.8,  $\text{pH} + \text{pOH} = 14$ , pOH can be calculated by difference. Using the  $K_b$  equation (7.5) the  $\text{p}K_b$  can be calculated

Solution

- $\text{pH} = 9.7$ . Using Equation 7.8,  $\text{pH} + \text{pOH} = 14.00$ .  
 $\text{pOH} = 14 - 9.7 = 4.3$ .  
 $\text{pOH} = -\log_{10}[\text{OH}^-]$ , so  $[\text{OH}^-] = 10^{-4.3} = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$

For this reaction



$$K_b = \frac{[\text{NH}_3\text{OH}^+(\text{aq})][\text{OH}^-(\text{aq})]}{[\text{NH}_2\text{OH}(\text{aq})]} = \frac{[\text{OH}^-(\text{aq})]^2}{[\text{NH}_2\text{OH}(\text{aq})]} = \frac{(5.0 \times 10^{-5} \text{ mol dm}^{-3})^2}{0.20 \text{ mol dm}^{-3}}$$

$$= 1.3 \times 10^{-8} \text{ mol dm}^{-3}.$$

$$\text{p}K_b = -\log_{10}(1.3 \times 10^{-8}) = 7.9.$$

(b) Using Equation 7.13,  $\text{p}K_a + \text{p}K_b = 14.00$  at 298 K

$$\text{p}K_a = 14.0 - 7.9 = 6.1.$$

6. Methylamine ( $\text{CH}_3\text{NH}_2$ ) is a base with  $\text{p}K_b$  3.34. Identify the conjugate acid of methylamine, and determine the  $\text{p}K_a$  for this at 298 K.

#### Strategy

The conjugate acid of a base has an additional proton. The  $\text{p}K_a$  for this can be obtained from Equation 7.13,  $\text{p}K_a + \text{p}K_b = 14.00$  at 298 K

#### Solution

The conjugate acid is  $\text{CH}_3\text{NH}_3^+$ .

Using Equation 7.13,  $\text{p}K_a + \text{p}K_b = 14.00$  at 298 K

$$\text{p}K_a = 14.0 - 3.34 = 10.66.$$

7. The pH inside most cells is maintained at around 7.4 by a phosphate buffer made up from the  $\text{H}_2\text{PO}_4^-$  (aq) ion and its conjugate base,  $\text{HPO}_4^{2-}$  (aq). The  $\text{p}K_a$  of the acid  $\text{H}_2\text{PO}_4^-$  (aq) is 7.2.
- Write an expression for  $K_a$  for  $\text{H}_2\text{PO}_4^-$  (aq).
  - Calculate the ratio of  $[\text{HPO}_4^{2-}(\text{aq})/\text{H}_2\text{PO}_4^-(\text{aq})]$  needed to give a pH of 7.4 in the cell.
  - A typical value for the total phosphate concentration in a cell,  $[\text{H}_2\text{PO}_4^-(\text{aq})] + [\text{HPO}_4^{2-}(\text{aq})]$  is  $0.020 \text{ mol dm}^{-3}$ . Calculate the typical values of  $[\text{HPO}_4^{2-}(\text{aq})]$  and  $[\text{H}_2\text{PO}_4^-(\text{aq})]$  inside a cell.

#### Strategy

Write an expression for  $K_a$  based on the concentration of species generated via a proton transfer reaction from dihydrogen phosphate to water. Use the Henderson-Hasselbalch equation (Equation 7.16) to calculate the pH.

Solution

$$(a) \quad K_a = \frac{[\text{H}_3\text{O}^+(\text{aq})][\text{HPO}_4^{2-}(\text{aq})]}{[\text{H}_2\text{PO}_4^-(\text{aq})]}$$

(b) Using the Henderson-Hasselbalch equation (Equation 7.16),

$$\text{pH} = \text{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log_{10} \frac{[\text{HPO}_4^{2-}(\text{aq})]}{[\text{H}_2\text{PO}_4^-(\text{aq})]} \\ &= 7.2 + \log_{10} \frac{[\text{HPO}_4^{2-}(\text{aq})]}{[\text{H}_2\text{PO}_4^-(\text{aq})]} = 7.4 \end{aligned}$$

$$\text{So, } \log_{10} \frac{[\text{HPO}_4^{2-}(\text{aq})]}{[\text{H}_2\text{PO}_4^-(\text{aq})]} = 0.2$$

$$\text{And } \frac{[\text{HPO}_4^{2-}(\text{aq})]}{[\text{H}_2\text{PO}_4^-(\text{aq})]} = 1.6$$

$$\begin{aligned} (c) \quad & [\text{H}_2\text{PO}_4^-(\text{aq})] + [\text{HPO}_4^{2-}(\text{aq})] = 0.020 \text{ mol dm}^{-3} \\ & \text{But from (b), } [\text{HPO}_4^{2-}(\text{aq})] = 1.6 \times [\text{H}_2\text{PO}_4^-(\text{aq})] \\ & \text{So, } [\text{H}_2\text{PO}_4^-(\text{aq})] + 1.6 \times [\text{H}_2\text{PO}_4^-(\text{aq})] = 0.020 \text{ mol dm}^{-3} \\ & [\text{H}_2\text{PO}_4^-(\text{aq})] = 7.7 \times 10^{-3} \text{ mol dm}^{-3} \\ & \text{Then, } [\text{HPO}_4^{2-}(\text{aq})] = 1.6 \times (7.7 \times 10^{-3} \text{ mol dm}^{-3}) \\ & \quad = 1.2 \times 10^{-2} \text{ mol dm}^{-3} \end{aligned}$$

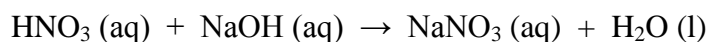
8. In a titration, a solution of  $0.200 \text{ mol dm}^{-3}$  NaOH solution is added from a burette to  $30.0 \text{ cm}^3$  of  $0.100 \text{ mol dm}^{-3}$  HNO<sub>3</sub> solution in a conical flask. Calculate the pH of the solution:

- (a) before any NaOH is added;  
 (b) after addition of 5.0 cm<sup>3</sup> of the NaOH solution;  
 (c) after addition of 10.0 cm<sup>3</sup> of the NaOH solution;  
 (d) at the equivalence point;  
 (e) after addition of 20.0 cm<sup>3</sup> of the NaOH solution.

### Strategy

This reaction involves a strong acid reacting with a strong base. All the acid will be fully dissociated and hence the acid concentration will be equal to the H<sub>3</sub>O<sup>+</sup> concentration and pH can be calculated according to Equation 7.5. It is then necessary for the volume of NaOH required to reach the equivalence point to be calculated to answer the questions relating to calculating the pH.

### Solution



1 mol HNO<sub>3</sub> (aq) reacts with 1 mol NaOH (aq), so the equivalence point occurs when 15.0 cm<sup>3</sup> of 0.200 mol dm<sup>-3</sup> NaOH solution has been added.

- (a)  $\text{pH} = -\log_{10}(0.100) = 1.0$   
 (b) This is before the equivalence point, so use Equation 7.17 or Equation 7.18.  
 Using Equation 7.18

$$[\text{H}_3\text{O}^+] = \frac{(0.100 \text{ mol dm}^{-3} \times 0.0300 \text{ dm}^3) - (0.200 \text{ mol dm}^{-3} \times 0.0050 \text{ dm}^3)}{(0.0300 + 0.0050) \text{ dm}^3}$$

$$= 5.7 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(5.7 \times 10^{-2}) = 1.2$$

- (c) This is also before the equivalence point. Using Equation 7.18

$$[\text{H}_3\text{O}^+] = \frac{(0.100 \text{ mol dm}^{-3} \times 0.0300 \text{ dm}^3) - (0.200 \text{ mol dm}^{-3} \times 0.0100 \text{ dm}^3)}{(0.0300 + 0.0100) \text{ dm}^3}$$

$$= 2.5 \times 10^{-2} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log_{10}(2.5 \times 10^{-2}) = 1.6$$

- (d) Since the titration is between a strong acid and a strong base the equivalence point occurs at pH 7.0.  
 (e) This is after the equivalence point. The solution contains 5.0 cm<sup>3</sup> unreacted NaOH in a total volume of 50.0 cm<sup>3</sup>.

$[\text{OH}^-]$  is given by

$$[\text{OH}^- (\text{aq})] = \frac{(0.200 \text{ mol dm}^{-3} \times 0.0050 \text{ dm}^3)}{0.05000 \text{ dm}^3} = 0.020 \text{ mol dm}^{-3}$$

$$\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}(0.020) = 1.7$$

Using Equation 7.8,  $\text{pH} + \text{pOH} = 14.00$  at 298 K,

$$\text{pH} = 14 - \text{pOH} = 14 - 1.7 = 12.3$$

9. For the following titrations, select which of the two indicators given is more appropriate.
- Propanoic acid titrated against sodium hydroxide using either phenolphthalein ( $\text{p}K_{\text{in}} 9.4$ ) or methyl orange ( $\text{p}K_{\text{in}} 3.4$ ).
  - Hydrochloric acid titrated against methylamine using either thymol blue ( $\text{p}K_{\text{in}} 9.0$ ) or bromophenol blue ( $\text{p}K_{\text{in}} 3.9$ ).

#### Strategy

The choice of indicator depends on the type of reaction. For a strong base with a weak acid the indicator would need to exhibit a colour change at  $\text{pH} > 7$  whereas for a weak base with a strong acid, the indicator would need to exhibit a colour change at  $\text{pH} < 7$ .

#### Solution

- Propanoic acid is a weak acid, whereas NaOH is a strong base. So, the equivalence point will have  $\text{pH} > 7.0$ . Phenolphthalein is the better indicator (see Figure 7.9 on p.328).
  - Methylamine is a weak base, whereas HCl is a strong acid. So, the equivalence point will have  $\text{pH} < 7.0$ . Bromophenol blue is the better indicator.
10. Estimate  $\text{p}K_{\text{a}1}$ , for the following oxoacids (a)  $\text{HBrO}_3$ , (b)  $\text{H}_2\text{SeO}_3$ , (c)  $\text{H}_2\text{CO}_3$ . The actual values of  $\text{p}K_{\text{a}1}$  and  $\text{p}K_{\text{a}2}$  for  $\text{H}_2\text{CO}_3$  are 6.35 and 10.33, respectively. Suggest a reason for the large difference between these and your calculated values.

#### Strategy

By using Table 7.5 and the information given on pp.330-1, the values of  $\text{p}K_{\text{a}1}$  can be estimated for the oxoacids.



Solution

- (a) For  $\text{HBrO}_3$ ,  $n - m = 2$ , so  $\text{p}K_{a1}$  is likely to be between  $-3$  and  $0.8$ .  
 (b) For  $\text{H}_2\text{SeO}_3$ ,  $n - m = 1$ , so  $\text{p}K_{a1}$  is likely to be between  $1.8$  and  $3.3$ .  
 (c) For  $\text{H}_2\text{CO}_3$ ,  $n - m = 1$ , so  $\text{p}K_{a1}$  is likely to be between  $1.8$  and  $3.3$ .

The estimated  $\text{p}K_{a1}$  value suggests that  $\text{H}_2\text{CO}_3$  is much stronger than it is in reality. The difference arises because much of the  $\text{H}_2\text{CO}_3$  in aqueous solution is in the form of dissolved  $\text{CO}_2$ :



- 11.** The structure of diphosphonic acid ( $\text{H}_4\text{P}_2\text{O}_7$ ) is shown below. Its four  $\text{p}K_a$  values are  $1.0$ ,  $1.8$ ,  $6.6$  and  $9.6$ . Suggest reasons for the relative values.

Strategy

The variance in the four  $\text{p}K_a$ 's depends on the arrangement of protons in the oxoacid and how the protons are lost from OH groups.

Solution

There is a relatively small difference between  $\text{p}K_{a1}$  and  $\text{p}K_{a2}$  as the protons are lost from OH groups on different phosphorus atoms. The difference between  $\text{p}K_{a1}$  and  $\text{p}K_{a3}$  is larger as for the third ionization, the proton is removed from a phosphorus atom already bearing an ionized group. There is only a small difference between  $\text{p}K_{a3}$  and  $\text{p}K_{a4}$  as, in a similar way to  $\text{p}K_{a1}$  and  $\text{p}K_{a2}$ , the protons are lost from OH groups on different phosphorus atoms.

- 12.** Citric acid (see Box 7.6, p.334-5) has the speciation curve shown on p.340 in water at  $298 \text{ K}$ . Use this to estimate values for  $\text{p}K_{a1}$ ,  $\text{p}K_{a2}$  and  $\text{p}K_{a3}$ .

Strategy

When the concentrations of the acid and its conjugate base are equal,  $\text{p}K_a = \text{pH}$ . From the speciation curve, this is the point for each equilibrium at which the two relevant lines cross. The three values where this happens can be estimated from the figure.

Solution

From the figure,  $pK_{a1} = 3.1$ ,  $pK_{a2} = 4.8$  and  $pK_{a3} = 6.4$ .

**13.** Identify the Lewis acid and Lewis base in the following reactions.

- (a)  $I_2 + I^- \rightarrow I_3^-$
- (b)  $NH_3 + HBr \rightarrow NH_4Br$
- (c)  $SiF_4 + 2py \rightarrow SiF_4(py)_2$
- (d)  $CO_2 + OH^- \rightarrow HCO_3^-$

Which, if any, of the reactions are also Brønsted-Lowry acid-base reactions.

Strategy

Identify which of the reagents is acting as the electron pair donor and which is acting as the electron pair acceptor. If the reaction involves proton transfer it is also a Brønsted-Lowry acid-base reaction.

Solution

- (a)  $I^-$  is the electron pair donor (Lewis base).  $I_2$  is the electron pair acceptor (Lewis acid).
- (b)  $NH_3$  is the electron pair donor (Lewis base).  $HBr$  is the electron pair acceptor (Lewis acid).
- (c) Pyridine is the electron pair donor (Lewis base).  $SiF_4$  is the electron pair acceptor (Lewis acid).
- (d)  $OH^-$  is the electron pair donor (Lewis base).  $CO_2$  is the electron pair acceptor (Lewis acid).

The reaction between  $NH_3$  and  $HBr$  is also a Brønsted-Lowry acid-base reaction.

**14.** Sulfur dioxide can act as either a Lewis acid or a Lewis base. Suggest how it reacts with (a)  $NMe_3$  and (b)  $SbF_5$ , in each case identifying the product and stating whether  $SO_2$  is acting as a Lewis acid or a Lewis base.

Strategy

Since  $\text{SO}_2$  can act as a Lewis acid or Lewis base, its behaviour must depend on the other reagent. Identify this as a Lewis acid or base, and react with  $\text{SO}_2$  accordingly.

Solution

(a)  $\text{NMe}_3$  has a lone pair of electrons, so can act as a Lewis base. In this reaction,  $\text{SO}_2$  acts as the Lewis acid and the product is the adduct  $\text{O}_2\text{S}\leftarrow\text{NMe}_3$ .

(b)  $\text{SbF}_5$  normally acts as a Lewis acid. In this reaction,  $\text{SO}_2$  acts as a Lewis base, donating a pair of electrons from the oxygen atom to the antimony atom to give the adduct  $\text{F}_5\text{Sb}\leftarrow\text{OSO}$ .