Volumetric calculations

1. A sample of cloudy ammonia is suspected of having been diluted by a unscrupulous supplier. 100.0 mL of the cloudy ammonia is carefully and quickly transferred to a 500.0 mL volumetric fl ask and made up to 500 mL with de-ionised water. A 20.00 mL aliquot of this diluted ammonia solution was placed in a conical fl ask with several drops of methyl orange. The ammonia solution was titrated to the methyl orange end point with 0.0500 mol L_1 HCl and the average of three concordant titres was 18.42 mL.

a Determine the concentration, in mol L_1, of ammonia in the undiluted cloudy ammonia sample.
b When the label on the cloudy ammonia bottle was checked, it claimed that the concentration of ammonia was 10 g of ammonia per 100 g of solution. Was the sample diluted? The density of the cloudy ammonia is 0.9g/mL

(a) $NH_{3(aq)} + H^+_{(aq)} \rightarrow NH_4^+{}_{(aq)}$

$n\,HCl = c\,HCl \times V\,HCl = \cdot 0500 \times \cdot 01842 = 9{\cdot}2 \times 10^{-4}$ mole

$= n(H^+)$

1 mol of H^+ reacts with 1 mol of NH_3

amount of NH_3 in 20 mL aliquot $= 9{\cdot}210 \times 10^{-4}$ mol

amount of NH_3 in 500 mL $= \frac{9{\cdot}210 \times 10^{-4} \times 500}{20}$

$= 0{\cdot}02302$ mol

(you can use $C_1V_1 = C_2V_2$)
(but this is a short cut method)

Concentration of NH_3 in cloudy $NH_3 = \frac{n\,NH_3}{V\,NH_3}$

$= \frac{0{\cdot}02302}{\cdot 1000}$

$= \boxed{\cdot 230 \text{ m/L}}$

The label suggest 100g cloudy NH_3 has 10g of NH_3

(b) Volume of 100g of cloudy $NH_3 = \frac{100}{\cdot 90} = 111$mL or $\cdot 111$L

$\boxed{D = \frac{m}{V}}$

$n(NH_3$ dissolved in this volume$) = \frac{m\,NH_3}{M\,NH_3} = \frac{10}{17{\cdot}034}$

$= \cdot 587$ mol

$c(\text{cloudy } NH_3) = \frac{n(NH_3}{V(\text{cloudy } NH_3)} = \frac{\cdot 587}{0{\cdot}111} = \boxed{5{\cdot}3}$M

$\therefore$ cloudy NH_3 was diluted

2. Aspirin (acetylsalicylic acid) is a weak monoprotic acid. A 300 mg aspirin tablet was crushed and placed in a conical fl ask together with 25.00 mL of 0.1000 mol L_1 sodium hydroxide and the mixture allowed to react completely until the tablet had dissolved. Three drops of phenolphthalein were added to the solution and a pink colour was produced indicating that sodium hydroxide was in excess.

The excess sodium hydroxide in the fl ask was titrated with 0.0500 mol L_1 HCl and the titre required to reach the phenolphthalein end point was 16.90 mL.

Calculate the percentage purity of the aspirin tablet if the formula of acetylsalicyclic acid is C9H8O4.

$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O(L)$

n HCl used in titration = c × V = ·0500 × ·01690

= $8·450 \times 10^{-4}$ mol

n H^+ = n OH^- = $8·450 \times 10^{-4}$ mol

so n(OH^-) in the flask after reaction with aspirin

$\boxed{= 8·450 \times 10^{-4} \text{ mol}}$

n(OH^-) originally added to the aspirin = c(NaOH) × V_{NaOH}

= ·1000 × ·02500

= $2·5 \times 10^{-3}$ mol

n(OH^-) reacted = $2·5 \times 10^{-3} - 8·450 \times 10^{-4}$

$\boxed{= 1·655 \times 10^{-3} \text{ mol}}$

because acetylsalicylic acid in asprin is monoprotic

1 mol of OH^- react with 1 mol of $C_9H_8O_4$)

n($C_9H_8O_4$) in 1 tablet = $1·655 \times 10^{-3}$ mol

m($C_9H_8O_4$) = n × M

m($C_9H_8O_4$) = $1·655 \times 10^{-3} \times 180·154$

$\boxed{= ·2982 g}$

M $C_9H_8O_4$ = 180·154 g/mol

% purity = $\frac{m(C_9H_8O_4)}{m \text{ talet}} \times 100$ = $\frac{·2982}{·300} \times 100$

↑

$\boxed{99·4\%}$

3. Some photographic developing agents contain a base that provides hydroxide ions. A 10.00 mL

sample of developer was diluted to 100.0 mL in a volumetric flask. 20.00 mL of this diluted solution was titrated with 0.0900 mol L_1 sulfuric acid and required 21.40 mL to reach a methyl orange end point. Calculate the concentration, in mol L_1, of the hydroxide ions in the original developer. (Hint: Sulfuric acid is diprotic.)

$n\ H_2SO_4 = c \times V$

$= .0900 \times .02140$

$= .001926$ mol

$\therefore\ H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

$= 2 \times .001926 = \boxed{.003852 \text{ mol}}$

$\cancel{2}H^+ + \cancel{2}OH^- \rightarrow \cancel{2}H_2O$

$n\ H^+ = .003852 = n\ OH^-$ in 20 mL soln

$n\ OH^- = 100$ mL $= 5 \times .003852 = .01926$ mol

[can use $c_1V_1 = c_2V_2$] (however its long)

$c\ OH^-$ in the developer $= \dfrac{n(OH^-)}{V(\text{developer})} = \dfrac{.01926}{.0100}$

$= 1.93$ mol/L

4.A patient suffering from indigestion provides a sample of gastric juices for analysis. A 40.00 mL sample of gastric juice was titrated with 0.1050 mol L_1 sodium hydroxide to a phenolphthalein end point. The volume of sodium hydroxide solution required was 17.25 mL. Calculate the pH of the gastric juice in the patient.

n NaOH = c NaOH x V NaOH

$= \cdot 1050 \times \cdot 01725 = \cdot 001811$ mol

$n(OH^-)$ required to react with H_3O^+ in the gastric juice

$H_3O^+ + OH^- \rightarrow 2H_2O\,(l)$

$n\,H_3O^+ = n\,OH^- = \cdot 001811$ mol

$c\,H_3O^+$ in gastric juice $= \frac{n\,H_3O^+}{V}$

$= \frac{\cdot 001811}{\cdot 04000} = \cdot 04528$ m/L

$\boxed{pH = 1 \cdot 34}$

5 A 4.674 g sample of limestone (impure CaCO3) was treated with 375 mL of 0.261 mol L_1 hydrochloric acid. After the reaction was over, the mixture was filtered and a 25.0 mL sample of the filtrate was titrated with 0.0517 mol L_1 Ba(OH)2 to the phenolphthalein end point. The volume of the barium hydroxide solution required was 17.62 mL.

Calculate the percentage, by mass, of CaCO3 in the limestone sample.

$CaCO_3 + 2H^+ \rightarrow Ca^{2+}_{(aq)} + H_2O_{(l)} + CO_2$

$H^+ + OH^- \rightarrow H_2O$

$n\,Ba(OH)_2 = c \times V$

$= \cdot 0517 \times \cdot 0176$

$= 9 \cdot 11 \times 10^{-4}$ mol

$n(OH^-)$ used in the titration

$= 2 \times 9 \cdot 110 \times 10^{-4} = 1 \cdot 822 \times 10^{-3}$ mol

$n\,H^+ = n\,OH^- = 1 \cdot 822 \times 10^{-3}$ mol in 25 mL soln.

$n\,H^+$ unreacted in the 375 ml original sample $= 1 \cdot 8 \times 10^{-3} \times \frac{375}{25}$

$\boxed{= \cdot 02733 \text{ mol}}$

n HCl originally added $= c \times V$

$= \cdot 261 \times \cdot 375$

$\boxed{= \cdot 09788 \text{ mol}}$

$n\,H^+$ reacted with $CaCO_3 = \cdot 097 - \cdot 027$

$= 0 \cdot 07055$

$n\,CaCO_3 = \frac{1}{2} \times \cdot 0705 = \cdot 03528$

$m\,CaCO_3 = m \times M = 3 \cdot 5$ g

$\%\,CaCO_3 = \frac{3 \cdot 5}{4 \cdot 67} \times 100 = \boxed{75 \cdot 5\%}$

Anskey

1.

→ **Solution**

$n(\text{NaOH}) = c(\text{NaOH}) \times V(\text{NaOH})$

$= 0.1030 \times 0.01478 = 1.5223 \times 10^{-3}$ mol of NaOH

$=$ mol of $\text{OH}^-(aq)$

$$\text{H}^+(aq) + \text{OH}^-(aq) \rightarrow \text{H}_2\text{O}(l)$$

1 mol of $\text{OH}^-(aq)$ reacts with 1 mol of $\text{H}^+(aq)$.

Amount of $\text{H}^+(aq)$ in 25.00 mL aliquot $= 1.522 \times 10^{-3}$ mol

Amount of $\text{H}^+(aq)$ in 100 mL of wine $= 1.522 \times 10^{-3} \times 4$

$= \mathbf{6.09 \times 10^{-3}}$ **mol**

2.

→ **Solution**

The ionic equation for the reaction is:

$$\text{CH}_3\text{COOH}(aq) + \text{OH}^-(aq) \rightarrow \text{CH}_3\text{COO}^-(aq) + \text{H}_2\text{O}(l)$$

$n(\text{NaOH reacting}) = c(\text{NaOH}) \times V(\text{NaOH})$

$= 0.1146 \times 0.02000 = 2.2920 \times 10^{-3}$ mol

$n(\text{OH}^- \text{ reacting}) = 2.2920 \times 10^{-3}$ mol

1 mol of OH^- reacts with 1 mol of CH_3COOH

Amount of acetic acid in 33.45 mL titre $= 2.2920 \times 10^{-3}$ mol

Amount of acetic acid in 250 mL $= 2.2920 \times 10^{-3} \times \dfrac{250.0}{33.45} = 1.7130 \times 10^{-2}$ mol

$m(\text{CH}_3\text{COOH in 250 mL solution}) = n(\text{CH}_3\text{COOH}) \times M(\text{CH}_3\text{COOH})$

$M(\text{CH}_3\text{COOH}) = 60.052 \text{ g mol}^{-1}$

$m(\text{CH}_3\text{COOH in 250 mL solution}) = 1.7130 \times 10^{-2} \times 60.052 = 1.0287$ g

$$\text{Percentage of acetic acid in vinegar} = \frac{m(\text{CH}_3\text{COOH})}{m(\text{vinegar})} \cdot 100 = \frac{1.0287}{22.17} \cdot 100$$

$= \mathbf{4.640\%}$

3.

➔ Solution

The ionic equation for the reaction is (procedures for balancing these equations will be given in the next chapter):

$$5H_2O_2(aq) + 2MnO_4^-(aq) + 6H^+(aq) \rightarrow 2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g)$$

Amount of $KMnO_4$ reacting $= c(KMnO_4) \times V(KMnO_4)$

$= 0.01894 \times 0.02868 = 5.432 \times 10^{-4}$ mol

$= n(MnO_4^-)$ reacted with H_2O_2

From the ionic equation,

2 mol of MnO_4^- reacts with 5 mol of H_2O_2

so 5.432×10^{-4} mol of MnO_4^- reacts with $5.432 \times 10^{-4} \times \frac{5}{2}$

$= 1.358 \times 10^{-3}$ mol of H_2O_2 = mol of H_2O_2 in 25 mL aliquot

Amount of H_2O_2 in 250.0 mL $= 1.358 \times 10^{-3} \times 10 = 0.013\,58$ mol

= mol of H_2O_2 in 10.00 mL of commercial bleach solution

$$c(H_2O_2) \text{ in commercial bleach} = \frac{n(H_2O_2)}{V(H_2O_2)} = \frac{0.013\,58}{0.010\,00}$$

$= \mathbf{1.358\ mol\ L^{-1}}$

Mass of H_2O_2 in 10.00 mL of bleach $= n(H_2O_2) \times M(H_2O_2)$

$M(H_2O_2) = 34.016$ g mol^{-1}

Mass $(H_2O_2) = 0.013\,58 \times 34.016 = 0.4619$ g

$$\text{Percentage of } H_2O_2 \text{ in bleach} = \frac{m(H_2O_2)}{m(\text{bleach})} \cdot 100 = \frac{0.4619}{10.00} \cdot 100$$

$= \mathbf{4.62\%}$

Accuracy

Accuracy is a term used to describe the combination of both the trueness and the precision of the result and is influenced by both systematic and random errors.

5.2. Types of errors

An error is defined as any deviation from the true value and can be classified as systematic, random or gross errors.

Systematic errors

A systematic error is an error that is constant or drifting slightly and is due to a consistent mistake made during the analysis. Typical systematic errors in titration analyses include:

- Differing or incorrect analytical method compared to that used to determine the 'true' value
- Incorrect calculation formulas
- Sampling errors
- Sample size errors e.g. due to a constant weighing error
- Incorrect titrant concentration
- False or missing blank value
- Incorrect or missing sensor adjustment
- Too high titration speed for the chemical reaction
- Too high titration speed for the electrode response

Once the source of a systematic error is identified it is usually easy to correct for these errors.

Random errors

A random error is a component of the overall error that varies in an unpredictable fashion. It is usually difficult to identify these errors. Typical sources of random errors include:

- Poor sample handling
- Inadequate equipment e.g. too low balance resolution, wrong grade of glassware etc.
- Incorrect method parameters e.g. too large increments, insufficient waiting time between increments.
- Bubbles in burette tubes
- Ineffective rinsing between samples
- Lack of operator training
- Inadequate environmental conditions e.g. temperature and humidity fluctuations

If the source of a random error cannot be identified then the only solution is to increase the number of replicates in order to get a more trustworthy mean value. This generally leads to waste of sample, reagents and time.

Gross errors

Gross errors are a form of both systematic and random errors caused by blunders or mistakes and are easily identifiable. Another name for gross errors is avoidable mistakes. Typical gross errors include:

- Notation mistakes
- Calculation errors
- Mix up of samples and/or reagents
- Wrong sample sizes