Chem Factsheet

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Thermometric Titrations

By completing this Factsheet you will be able to:
- understand how to carry out thermometric titrations.
- use data from thermometric titrations to calculate concentrations of unknown substances.
- use data from thermometric titrations to calculate enthalpy changes.
- understand why experimental data from thermometric titrations may underestimate the exothermic nature of enthalpy changes of neutralisation.

To succeed with this Factsheet you should be able to:
- do titration calculations
- do enthalpy calculations.

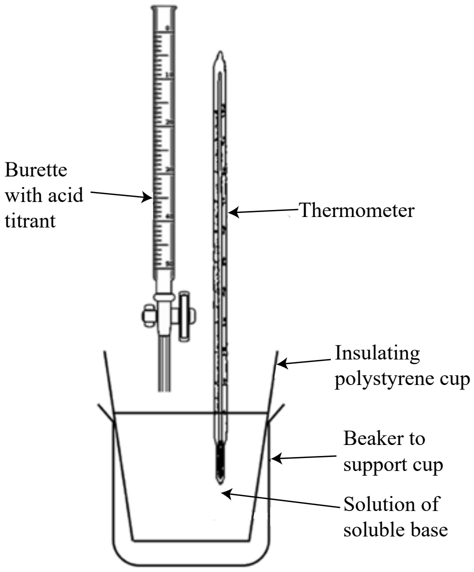
Titrations are a common method of determining the concentration of a substance, for example an acid, by reacting it completely with another substance whose concentration is known, for example an aqueous base. Acid-base titrations often use an indicator to detect the point when the two reactants have precisely reacted with each other, i.e. the equivalence point is shown by the indicator's end-point colour change.

Thermometric titrations are a similar technique but the end-point of a reaction is determined accurately by means of measuring the temperature changes as the reaction proceeds.

In thermometric titrations, one reactant (the titrant) is added at a constant rate to another (the titrand). The temperature of the reaction mixture is recorded, often with an electronic temperature probe.

In the school laboratory, a burette may be used to deliver precise volumes of acid to a known volume of soluble base. The temperature may be recorded after the addition of each volume with a thermometer which can also act as a stirrer.

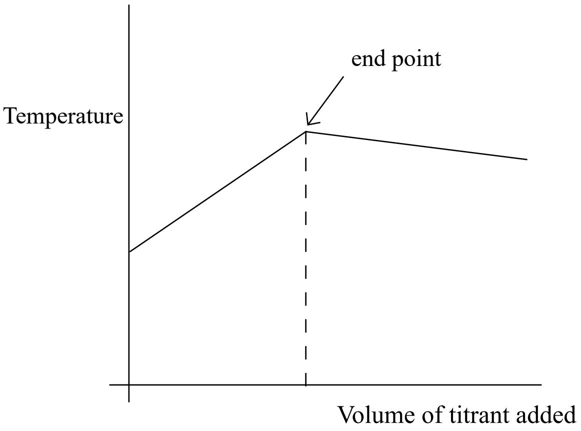
Fig. 1 Equipment for thermometric titration in a school laboratory



The end point of the reaction can be determined by an inflection in the curve of the line (i.e. a change in direction) generated by plotting temperature of reaction mixture against volume of acid added.

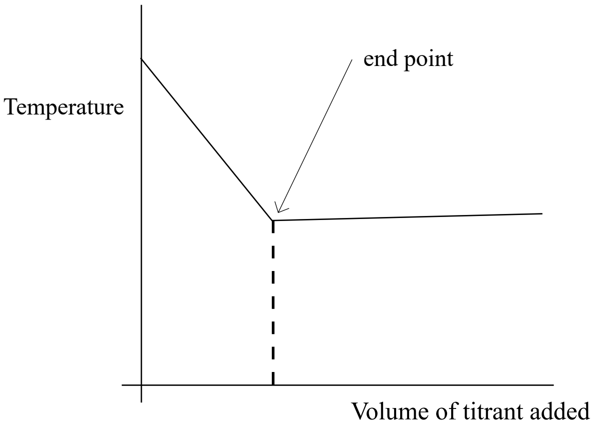
Since the reaction of acid and soluble base is exothermic, an increase in temperature can be expected as the acid and alkali react. Once fully neutralised, the excess acid - added at room temperature - will cause the temperature of the warmer reaction mixture to fall.

Fig. 2 Stylised titration plot for an exothermic reaction



For an endothermic reaction, a decrease in temperature can be expected until the reaction has reached its endpoint.

Fig. 3 Stylised titration plot of an endothermic reaction

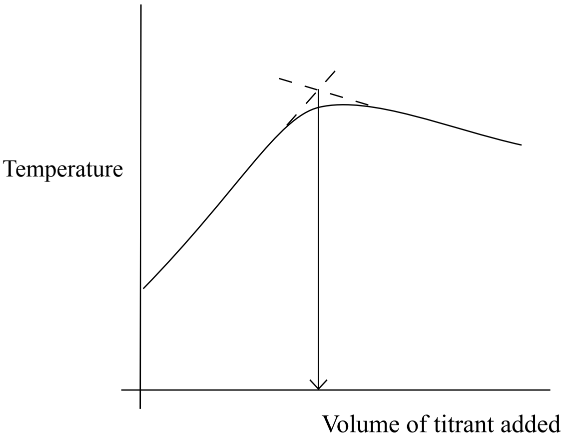


In practice, plots obtained may look a little different. This is due to a number of factors that have to be taken into account:

- heat loss to the surroundings during an exothermic reaction or heat gain from the surroundings during an endothermic reaction
- differences in the temperatures of the reagents
- evaporation from the surface of the reaction mixture
- enthalpy changes of solution when the salt produced dissolves in the solvent
- heat from any stirring device (although this has a very minimal effect).

Consequently, it is possible that a titration plot of temperature and volume of reagent added may show a curve. The precise end point can be determined by extrapolating the increasing and decreasing lines and finding the point at which they intersect. This allows for the fact that the reaction mixture would have reached a higher temperature than was actually recorded had there not been any heat loss.

Fig. 4 Determining the end point by extrapolation



Enthalpy change is a characteristic of all chemical reactions and therefore thermometric titrations can be used to determine the end point of a range of titrations e.g. acid/base, redox and precipitation reactions.

Worked example - calculating the concentration of ethanoic acid by thermometric titration.

25.0 cm^3 of 0.50 mol dm^{-3} NaOH solution is titrated with ethanoic acid.
The temperature of the reaction mixture is recorded at known volumes of ethanoic acid
The results are shown below.

Volume of ethanoic acid / cm^3	0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	20.0
Temperature / ^{o}C	20.0	20.9	21.8	22.7	23.5	23.7	23.6	23.4	23.2	23.0	22.8

Note: Higher concentrations (e.g. 0.50 mol dm^{-3}) are used compared to ordinary titrations using an indicator (e.g. 0.10 mol dm^{-3}) in order to give a significant temperature change and so reduce % error.

Determine the concentration of the ethanoic acid used.

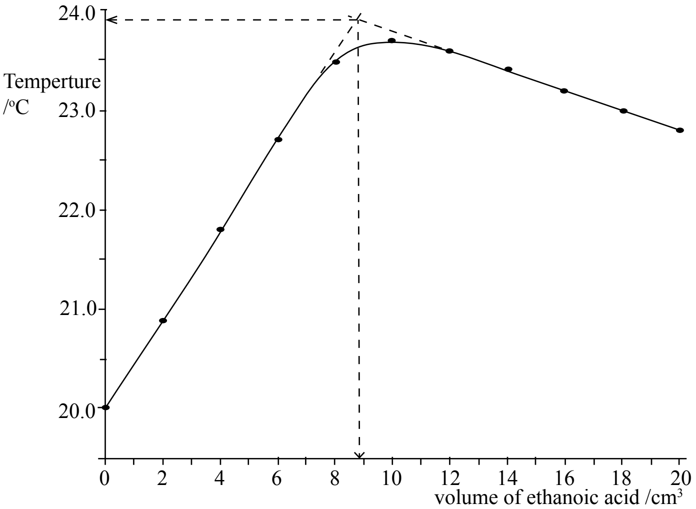
Firstly, the equation for reaction between ethanoic acid and sodium hydroxide must be established.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

From this equation, it can be seen that the stoichiometric ratio between ethanoic acid and sodium hydroxide is 1:1
The moles of sodium hydroxide used in the titration is
0.0125 (i.e. 0.500 × 25/1000)
Therefore the moles of ethanoic needed for neutralisation is also 0.0125

To find the exact volume of acid that was needed for neutralisation, plot a graph of the reaction mixture temperature against volume of acid added and extrapolate the lines. The intersection of the two extrapolated lines marks the end-point of the reaction.

Fig. 5 Graph of results



From the graph, it can be seen that the volume of ethanoic acid needed for neutralisation = 8.8 cm^3
Therefore concentration of ethanoic acid
= 1.42 moldm^{-3} (i.e. 0.0125 / 0.0088)

In addition to working out the concentration of an unknown reactant, thermometric titrations can also be used to determine the enthalpy of neutralisation of an acid.

Worked example - calculating enthalpy of neutralisation of ethanoic acid.

The enthalpy of neutralisation is defined as the energy change that accompanies the neutralisation of an aqueous acid by an aqueous base per mole of water produced.

To calculate this, the maximum temperature must be worked out and the total volume of the reaction mixture at the end point.
The equation $q = mc\Delta T$ can then be used where q is the energy transferred to the surroundings, m is the mass of the solution, c is the specific heat capacity of the reaction mixture and ΔT is the change in temperature of the reaction mixture.

From the graph it can be seen that the starting temperature was 20.0°C and the maximum temperature reached was 23.9°C. Therefore the temperature change (ΔT) = +3.9°C.

The total volume of the reaction mixture at the end point is the volume of NaOH (25.0 cm^3) added to the volume of acid (8.8 cm^3) added. Assuming a density of 1 gcm^{-3}, the mass of solution at end point is therefore 33.8 g

Assuming that the specific heat capacity of the reaction mixture is the same as water, 4.18 $Jg^{-1}K^{-1}$, the energy transferred to the surroundings, $q = 33.8 \times 4.18 \times 3.9 = 551$ J.

In this example, the number of moles of water produced in the reaction is equal to the number of moles of sodium hydroxide used = 0.0125

Therefore $\Delta H_{neut} = -551/0.0125 = -44.080$ $Jmol^{-1}$ (or -44.1 $kJmol^{-1}$)

Redox Titrations

Redox reactions are often exothermic and so can also be followed using thermometric titrations. For example the reaction between Fe^{2+} and acidified MnO_4^- has an enthalpy change much more negative than an acid-base reaction.

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Similarly, the reaction of H_2O_2 and acidified MnO_4^- is even more exothermic.

$$2MnO_4^- + 6H^+ + 5H_2O_2 \rightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

Consequently, the concentrations of Fe^{2+} or H_2O_2 solutions can be determined.

Precipitation Reactions

Precipitation reactions are also exothermic. For example the reaction between aqueous silver ions (Ag^+) and chloride ions (Cl^-) to form the silver chloride has a very negative enthalpy change. Therefore it is also possible to determine the concentration of chloride ions using a standard solution of silver nitrate.

Worked example - calculating the concentration of chloride ions by reaction with silver nitrate

10.00 cm^3 of 0.50M silver nitrate solution was titrated thermometrically with $CaCl_2$ solution of unknown concentration. The temperature was recorded by an electronic temperature probe. Initial temperature was 18.35°C and maximum temperature reached was 20.54°C. Maximum temperature was recorded on addition of 8.95cm^3 of $CaCl_2$.

Calculate the concentration of the calcium chloride solution.

The equation for the precipitation reaction is $Ag^+ (aq) + Cl^- (aq) \rightarrow AgCl (s)$

Firstly, calculate the number of moles of silver nitrate used: $0.50 \times 10.0/1000 = 5 \times 10^{-3}$

From the equation of the reaction, it can be seen that the number of moles of chloride ions is the same as the number of moles of silver nitrate $= 5 \text{ x } 10^{-3}$

Each mole of calcium chloride gives 2 moles of chloride ions. Therefore the number of moles of calcium chloride $= 5 \times 10^{-3}/ 2 = 2.5 \times 10^{-3}$

Finally, the concentration of calcium chloride can be worked out as $2.5 \times 10^{-3} / 0.00895 = 0.28$ $moldm^{-3}$

Questions

1 (a) 25.0 cm^3 of 1.00moldm^{-3} NaOH solution was titrated thermometrically with sulfuric acid.
Use the data below to calculate the concentration of sulfuric acid.

Volume of sulfuric acid added / cm^3	0.0	2.0	4.0	6.0	8.0	10.0	12.0	14.0	16.0	18.0	20.0
Temperature / °C	20.2	21.9	23.5	25.1	26.7	28.1	28.5	28.2	27.8	27.2	26.6

(b) Calculate the enthalpy of neutralisation of sulfuric acid using the data in the previous part of the question.
(specific heat capacity = 4.18 Jg^{-1}K^{-1}).

(c) Suggest why the *standard* enthalpy change of neutralisation sulfuric acid is more exothermic than the value you have calculated in 1b.

Answers

1 (a) From graph of results, max temperature = 29.2°C achieved when 11.1cm^3 H_2SO_4 added
Moles of NaOH = 1.00 × 25.0 / 1000 = 0.025
→ Moles of H_2SO_4 = 0.0125 since $2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$
→ Concentration of H_2SO_4 = 0.0125 × 1000 / 11.1 = 1.13 moldm^{-3}

(b) From graph of results:
$\Delta T = 9.0°C$
m = 25.0 + 11.1 = 36.1g
→ q = 36.1 × 4.18 × 9.0 = 1358 J
Also, moles of water produced = mols of NaOH used = 0.025
→ ΔH_{neut} = -q/moles = -1358/0.025 = -54320 Jmol^{-1} (-54.3 kJmol^{-1})

(c) The experimentally calculated enthalpy change of neutralisation is less negative than the standard enthalpy change of neutralisation due to heat loss to the surroundings.

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