RT · Redox titrations

Completed notes

Goals: Explain titrant, analyte, titre, endpoint and equivalence. Use the mole ratio from a balanced redox equation to find an unknown concentration or mass. Scale an aliquot and predict which way an error moves a result.

Slide 1 of 9 · Two solutions, two jobs

A titration finds an unknown **concentration** by reacting a measured volume of one solution with a solution whose concentration is already known.

The solution in the buret is the **titrant**. The solution in the flask is the **analyte**, the one being analysed.

A good titration needs a reaction that goes **to completion** quickly, a visible change called the **endpoint**, and carefully measured volumes.

Use a **pipette** to deliver the analyte and a **buret** to deliver the titrant. A graduated cylinder is less precise.

Example. A flask holds 25.00 mL of $Fe^{2+}(aq)$ of unknown concentration. A buret holds 0.0200 mol/L $MnO_4^-(aq)$. Which solution is the titrant, which is the analyte, and how does the known solution help find the unknown concentration?

1. The $MnO_4^-(aq)$ in the buret is the titrant. Its concentration is known.

2. The $Fe^{2+}(aq)$ in the flask is the analyte. Its concentration is unknown.

3. The titre of MnO_4^- gives moles of titrant. The balanced equation turns that into moles of Fe^{2+}.

Try it. A buret holds 0.0150 mol/L $MnO_4^-(aq)$. A flask holds 10.00 mL of $Sn^{2+}(aq)$ of unknown concentration. Name the titrant and the analyte, and say which glassware should measure the 10.00 mL.

1. The titrant is $MnO_4^-(aq)$ and the analyte is $Sn^{2+}(aq)$.

2. A pipette measures the 10.00 mL of analyte precisely.

Slide 2 of 9 · Read the buret and use the trials

A buret is numbered from **zero** at the top, so the readings get larger as liquid leaves.

The volume delivered is called the **titre**. It equals the final reading **minus** the initial reading.

Read the curved surface, the **meniscus**, at eye level. For dark purple permanganate, read the **top** edge. Record **two** decimal places.

Repeat the titration and average only the trials that agree within the **limit** the question states. For a limit of 0.20 mL, the largest and smallest trials kept may differ by at most **0.20 mL**.

Example. A buret has an initial reading of 0.40 mL and a final reading of 18.90 mL. Find the titre.

1. Titre = final reading − initial reading

2. Titre = 18.90 mL − 0.40 mL = 18.50 mL

Try it. Three trials give titres of 18.50 mL, 18.60 mL and 19.60 mL. Trials may differ by at most 0.20 mL from largest to smallest. Which trials do you average, and what is the average titre?

1. Keep the first two: 18.60 mL − 18.50 mL = 0.10 mL. That is at most 0.20 mL.

2. The third is 19.60 mL − 18.60 mL = 1.00 mL above the second. That is outside the limit, so leave it out.

3. Average = (18.50 mL + 18.60 mL) ÷ 2 = 18.55 mL.

Slide 3 of 9 · The equation sets the mole ratio

The coefficients in a balanced equation count particles, so they also give the **mole ratio**. In $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$, MnO_4^- to Fe^{2+} is **1 : 5**.

Manganese goes from **+7** to +2, so each MnO_4^- gains **5** electrons. Iron goes from +2 to +3, so each Fe^{2+} loses 1 electron.

Electrons lost must **equal** electrons gained. That is why **five** Fe^{2+} ions are needed for each MnO_4^-, and the ratio is not 1 : 1.

$E°_{reaction} = E°(\text{oxidizing agent}) - E°(\text{reducing agent})$, using values from the Data Booklet table printed on p. **7**. A **positive** result means the written direction is spontaneous. Acidified MnO_4^- or $Cr_2O_7^{2-}$ is usually the strongest oxidizing agent in a titration.

Example. Given in acidic solution: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$. Give the mole ratio of Fe^{2+} to MnO_4^- and explain it with electrons. Then find $E°_{reaction}$ using $E°(MnO_4^-/Mn^{2+}) = +1.51$ V and $E°(Fe^{3+}/Fe^{2+}) = +0.77$ V.

1. The ratio is 5 mol Fe^{2+} to 1 mol MnO_4^-, read from the coefficients.

2. Mn goes from +7 to +2, so each MnO_4^- gains 5 e^-. Fe goes from +2 to +3, so each Fe^{2+} loses 1 e^-.

3. Five Fe^{2+} supply the five electrons that one MnO_4^- takes.

4. MnO_4^-/Mn^{2+} has the higher value, so MnO_4^- is the oxidizing agent.

5. $E°_{reaction} = E°(\text{oxidizing agent}) - E°(\text{reducing agent}) = +1.51\text{ V} - (+0.77\text{ V}) = +0.74$ V

6. The value is positive, so the written direction is spontaneous.

Try it. Given in acidic solution: $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$. Give the mole ratio of $H_2C_2O_4$ to MnO_4^-. Each carbon atom in $H_2C_2O_4$ goes from +3 to +4. How many electrons does one $H_2C_2O_4$ lose?

1. The ratio is 5 mol $H_2C_2O_4$ to 2 mol MnO_4^-.

2. Each $H_2C_2O_4$ has 2 carbon atoms, and each carbon goes from +3 to +4, so it loses 1 e^-.

3. One $H_2C_2O_4$ loses 2 e^-. Five lose 10 e^-, which equals the 10 e^- gained by two MnO_4^- (5 e^- each).

Slide 4 of 9 · Endpoint: a faint pink that stays

MnO_4^- ions are deep **purple**. Mn^{2+} ions at 0.010 mol/L are **colourless**, and pale pink at 1.0 mol/L (Data Booklet, p. 11).

Before the reaction is complete, Fe^{2+} reduces each drop of MnO_4^-, so the purple of the drop **disappears**. The acid in the flask supplies the $\mathbf{H^+}$ in the equation.

When all the Fe^{2+} has reacted, the next drop leaves a faint pink-purple colour that **stays**. This is the **endpoint**, and permanganate needs no extra indicator.

Equivalence is calculated, and the endpoint is **seen**. A deep pink means the titre is too **large**.

Example. A permanganate solution is added from a buret to $Fe^{2+}(aq)$ in a flask. What does the flask look like before the reaction is complete, and what tells you to stop?

1. Before the endpoint, each drop of purple MnO_4^- turns colourless as it reacts with Fe^{2+}, because Mn^{2+} is colourless at 0.010 mol/L.

2. Stop at the first faint pink-purple colour that stays. This is the endpoint.

Try it. A student keeps adding permanganate until the flask is deep pink. Is the titre too large, too small or correct? Explain.

1. The titre is too large.

2. A deep pink means more MnO_4^- was added than the Fe^{2+} needed, so too much titrant was added.

Slide 5 of 9 · The titration calculation

Concentration is moles per litre, so change every volume from mL to L first. Divide by **1000**. For example, 18.50 mL = **0.01850** L.

The plan is moles of titrant, then the **mole ratio**, then moles of analyte, then **concentration**.

Moles of titrant: n = **c × V**, where c is concentration in mol/L and V is volume in **litres**.

Write the ratio fraction with the **wanted** substance on top. Divide the moles of analyte by the **flask** volume, never by the titre.

Example. Given the equation $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$. A 25.00 mL sample of $Fe^{2+}(aq)$ is titrated with 0.0200 mol/L $MnO_4^-(aq)$. The average titre is 18.50 mL. Find $c(Fe^{2+})$ in mol/L.

1. Volumes: titre 18.50 mL = 0.01850 L. Flask 25.00 mL = 0.02500 L.

2. $n(MnO_4^-) = c \times V = 0.0200\ mol/L \times 0.01850\ L = 3.70 \times 10^{-4}\ mol$

3. $n(Fe^{2+}) = 3.70 \times 10^{-4}\ mol\ MnO_4^- \times (5\ mol\ Fe^{2+} \div 1\ mol\ MnO_4^-) = 1.85 \times 10^{-3}\ mol$

4. $c(Fe^{2+}) = n \div V = 1.85 \times 10^{-3}\ mol \div 0.02500\ L = 0.0740\ mol/L$. This has three significant digits, from 0.0200 mol/L.

5. Check: $0.0740\ mol/L \times 0.02500\ L = 1.85 \times 10^{-3}\ mol$

Try it. Given the same equation. A 20.00 mL sample of $Fe^{2+}(aq)$ is titrated with 0.0250 mol/L $MnO_4^-(aq)$. The average titre is 16.80 mL. Find $c(Fe^{2+})$ in mol/L.

1. Volumes: titre 16.80 mL = 0.01680 L. Flask 20.00 mL = 0.02000 L.

2. $n(MnO_4^-) = 0.0250\ mol/L \times 0.01680\ L = 4.20 \times 10^{-4}\ mol$

3. $n(Fe^{2+}) = 4.20 \times 10^{-4}\ mol \times 5 = 2.10 \times 10^{-3}\ mol$

4. $c(Fe^{2+}) = 2.10 \times 10^{-3}\ mol \div 0.02000\ L = 0.105\ mol/L$

Slide 6 of 9 · Method: how to do a redox titration calculation

Step 1. **Average** the trials that agree within the limit.

Step 2. Change **mL** to **L** by dividing by 1000.

Step 3. Find n = **cV** for the solution you know.

Step 4. Use the mole **ratio** from the balanced equation, with the wanted substance on top.

Step 5. Find the unknown with c = n ÷ V. Use the volume of the **sample** in the flask.

Check: multiply back. c × V must give the **moles** you found.

Example. Use the method on 25.00 mL of $Fe^{2+}(aq)$ titrated with 0.0200 mol/L $MnO_4^-(aq)$. The average titre is 18.50 mL. The equation is $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$. Find $c(Fe^{2+})$.

1. Step 2: 18.50 mL = 0.01850 L and 25.00 mL = 0.02500 L.

2. Step 3: $n(MnO_4^-) = 0.0200\ mol/L \times 0.01850\ L = 3.70 \times 10^{-4}\ mol$.

3. Step 4: $n(Fe^{2+}) = 5 \times 3.70 \times 10^{-4}\ mol = 1.85 \times 10^{-3}\ mol$.

4. Step 5: $c(Fe^{2+}) = 1.85 \times 10^{-3}\ mol \div 0.02500\ L = 0.0740\ mol/L$.

Try it. Use the method on 20.00 mL of a Fe^{2+} solution that needs 15.00 mL of 0.0200 mol/L MnO_4^- with the same equation. Find $c(Fe^{2+})$.

1. $n(MnO_4^-) = 0.0200\ mol/L \times 0.01500\ L = 3.00 \times 10^{-4}\ mol$.

2. $n(Fe^{2+}) = 5 \times 3.00 \times 10^{-4}\ mol = 1.50 \times 10^{-3}\ mol$.

3. $c(Fe^{2+}) = 1.50 \times 10^{-3}\ mol \div 0.02000\ L = 0.0750\ mol/L$.

Slide 7 of 9 · Your turn: a different ratio

The steps are the same for every titration, but the ratio comes from the **equation you are given**.

In $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$, $H_2C_2O_4$ to MnO_4^- is **5 : 2**, so we multiply by **5/2**.

The ratio goes from the **known** substance to the **wanted** substance, with the coefficient of the wanted substance on top.

Two common slips are a wrong ratio and an upside-down **fraction**. Check by multiplying the answer by the flask **volume**.

Example. Given $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$. A 20.00 mL sample of $H_2C_2O_4(aq)$ needs 16.30 mL of 0.0150 mol/L $MnO_4^-(aq)$ to reach the endpoint. Find $c(H_2C_2O_4)$ in mol/L.

1. Titre: 16.30 mL = 0.01630 L. Sample: 20.00 mL = 0.02000 L.

2. $n(MnO_4^-) = 0.0150 \text{ mol/L} \times 0.01630 \text{ L} = 2.445 \times 10^{-4} \text{ mol}$

3. $n(H_2C_2O_4) = 2.445 \times 10^{-4} \text{ mol} \times (5 \div 2) = 6.1125 \times 10^{-4} \text{ mol}$

4. $c(H_2C_2O_4) = 6.1125 \times 10^{-4} \text{ mol} \div 0.02000 \text{ L} = 0.03056 \text{ mol/L}$, which rounds to 0.0306 mol/L

5. Check: $0.0306 \text{ mol/L} \times 0.02000 \text{ L} = 6.12 \times 10^{-4} \text{ mol}$, which matches.

Try it. Given the same equation. A 25.00 mL sample of $H_2C_2O_4(aq)$ needs 14.50 mL of 0.0120 mol/L $MnO_4^-(aq)$ to reach the endpoint. Find $c(H_2C_2O_4)$ in mol/L.

1. Titre: 14.50 mL = 0.01450 L. Sample: 25.00 mL = 0.02500 L.

2. $n(MnO_4^-) = 0.0120 \text{ mol/L} \times 0.01450 \text{ L} = 1.74 \times 10^{-4} \text{ mol}$

3. $n(H_2C_2O_4) = 1.74 \times 10^{-4} \text{ mol} \times (5 \div 2) = 4.35 \times 10^{-4} \text{ mol}$

4. $c(H_2C_2O_4) = 4.35 \times 10^{-4} \text{ mol} \div 0.02500 \text{ L} = 0.0174 \text{ mol/L}$

Slide 8 of 9 · An aliquot from a larger solution

A measured part of a larger solution is called an **aliquot**. The moles found by titrating it are the moles in the **aliquot** only.

Whole ÷ part = whole volume ÷ **aliquot volume**. Here 100.0 mL ÷ 20.00 mL = **5.000**.

The whole solution has the **same** concentration, so it holds **5.000** times the moles of the aliquot.

Mass = n × M, where M is molar mass in **g/mol**. Mass percent = mass of iron ÷ **mass of the tablet** × 100.

Example. An iron tablet of mass 0.800 g is dissolved and made up to 100.0 mL of $Fe^{2+}(aq)$. A 20.00 mL aliquot needs 14.10 mL of 0.0200 mol/L $MnO_4^-(aq)$. The equation is $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$. Find the mass of iron in the tablet and the mass percent of iron (Fe: 55.85 g/mol).

1. Titre: 14.10 mL = 0.01410 L.

2. $n(MnO_4^-) = 0.0200\ mol/L \times 0.01410\ L = 2.82 \times 10^{-4}\ mol$

3. $n(Fe^{2+})$ in the aliquot $= 5 \times 2.82 \times 10^{-4}\ mol = 1.41 \times 10^{-3}\ mol$

4. Whole ÷ part = 100.0 mL ÷ 20.00 mL = 5.000

5. $n(Fe^{2+})$ in the whole solution $= 1.41 \times 10^{-3}\ mol \times 5.000 = 7.05 \times 10^{-3}\ mol$

6. $m(Fe) = 7.05 \times 10^{-3}\ mol \times 55.85\ g/mol = 0.3937\ g$, which rounds to 0.394 g

7. Mass percent = 0.3937 g ÷ 0.800 g × 100 = 49.2 %

Try it. Given the same equation. An iron tablet of mass 0.500 g is dissolved and made up to 250.0 mL of $Fe^{2+}(aq)$. A 25.00 mL aliquot needs 13.40 mL of 0.0100 mol/L $MnO_4^-(aq)$. Find the mass of iron in the tablet and the mass percent of iron (Fe: 55.85 g/mol).

1. Titre: 13.40 mL = 0.01340 L.

2. $n(MnO_4^-) = 0.0100\ mol/L \times 0.01340\ L = 1.34 \times 10^{-4}\ mol$

3. $n(Fe^{2+})$ in the aliquot $= 5 \times 1.34 \times 10^{-4}\ mol = 6.70 \times 10^{-4}\ mol$

4. Whole ÷ part = 250.0 mL ÷ 25.00 mL = 10.00

5. $n(Fe^{2+})$ in the whole solution $= 6.70 \times 10^{-4}\ mol \times 10.00 = 6.70 \times 10^{-3}\ mol$

6. $m(Fe) = 6.70 \times 10^{-3}\ mol \times 55.85\ g/mol = 0.3742\ g$, which rounds to 0.374 g

7. Mass percent = 0.3742 g ÷ 0.500 g × 100 = 74.8 %

Slide 9 of 9 · Which way does an error push the answer?

Follow the chain. The titre sets the moles of **titrant**, which set the moles of analyte, which set the **concentration**.

Adding too much titrant makes the titre too **large**, so the calculated c(Fe^{2+}) is too **high**.

A buret rinsed with water makes the titrant weaker, so more volume is needed and the titre is too large. The calculation still uses the **given** concentration, so c is too high.

A wet flask adds no moles of Fe^{2+}, so the result is **unchanged**. For each error, mark every step larger, smaller or unchanged.

Example. A student rinses the buret with water, then fills it with 0.0200 mol/L MnO_4^-(aq) and titrates Fe^{2+}(aq). Is the calculated c(Fe^{2+}) too high, too low or unchanged? Follow the chain.

1. The water film makes the titrant weaker, so each millilitre holds fewer moles of MnO_4^-.

2. More volume is needed to reach the endpoint, so the titre is too large.

3. The calculation still uses 0.0200 mol/L, so n(MnO_4^-) is too large, then n(Fe^{2+}) is too large, so c(Fe^{2+}) is too high.

Try it. A student stops the titration just before the faint pink colour appears. Is the calculated c(Fe^{2+}) too high, too low or unchanged? Follow the chain.

1. The titre is too small.

2. Then n(MnO_4^-) and n(Fe^{2+}) are too small, so c(Fe^{2+}) is too low.

RT · Worked practice

Redox titrations | Questions 1-2 of 7

1. Given buret readings: initial 2.15 mL and final 21.85 mL. Find the titre.

Titre = final − initial = 21.85 − 2.15 = 19.70 mL.

2. Given $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$. A 25.00 mL sample of $Fe^{2+}(aq)$ needs 22.40 mL of 0.0150 mol/L $MnO_4^-(aq)$. Find $c(Fe^{2+})$ in mol/L.

Use Method: how to do a redox titration calculation. $n(MnO_4^-) = 0.0150$ mol/L × 0.02240 L (22.40 mL ÷ 1000) = 3.36×10^{-4} mol. $n(Fe^{2+}) = 5 \times 3.36 \times 10^{-4} = 1.68 \times 10^{-3}$ mol. $c = 1.68 \times 10^{-3} \div 0.02500 = 0.0672$ mol/L.

RT · Worked practice

Redox titrations | Questions 3-4 of 7

3. Given $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$. A 10.00 mL sample of $H_2C_2O_4(aq)$ needs 12.60 mL of 0.0200 mol/L $MnO_4^-(aq)$. Find $c(H_2C_2O_4)$ in mol/L.

Use Method: how to do a redox titration calculation. $n(MnO_4^-) = 0.0200 \text{ mol/L} \times 0.01260 \text{ L}$ (12.60 mL ÷ 1000) $= 2.52 \times 10^{-4}$ mol. $n(H_2C_2O_4) = 2.52 \times 10^{-4} \times 5/2 = 6.30 \times 10^{-4}$ mol. $c = 6.30 \times 10^{-4} \div 0.01000 = 0.0630$ mol/L.

4. Given $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$. A 10.00 mL aliquot from a 250.0 mL flask of $Fe^{2+}(aq)$ needs 15.60 mL of 0.0100 mol/L $MnO_4^-(aq)$. Find the mass of iron in the whole flask (Fe: 55.85 g/mol, Alberta Chemistry 30 Data Booklet).

$n(MnO_4^-) = 0.0100 \text{ mol/L} \times 0.01560 \text{ L}$ (15.60 mL ÷ 1000) $= 1.56 \times 10^{-4}$ mol. $n(Fe^{2+})$ in the aliquot $= 5 \times 1.56 \times 10^{-4} = 7.80 \times 10^{-4}$ mol. Scale by 250.0 ÷ 10.00 = 25.00: 1.95×10^{-2} mol. Mass $= 1.95 \times 10^{-2} \times 55.85 = 1.09$ g.

RT · Worked practice

Redox titrations | Questions 5-6 of 7

5. A student reads the final buret reading 0.50 mL too large in a permanganate titration of Fe^{2+}. Is the calculated $c(Fe^{2+})$ too high, too low or unchanged? Explain with the chain of calculation.

Too high. The titre is final minus initial, so it is 0.50 mL too large. Then $n(MnO_4^-)$, $n(Fe^{2+})$ and $c(Fe^{2+})$ are all too large.

6. Explain why a permanganate titration of iron(II) needs no added indicator, and describe the endpoint colour.

Permanganate is purple and is reduced to colourless Mn^{2+} while iron(II) remains. After the last Fe^{2+} reacts, one extra drop leaves a faint pink-purple that stays, so the titrant is its own indicator.

RT · Worked practice

Redox titrations | Questions 7-7 of 7

7. Challenge: Given $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$. An iron sample is dissolved and made up to 100.0 mL. A 20.00 mL aliquot needs 14.80 mL of 0.0100 mol/L $Cr_2O_7^{2-}(aq)$. Find the mass of iron in the whole sample, in grams, to three significant digits (M(Fe) = 55.85 g/mol, from the Data Booklet).

Titrant: $n(Cr_2O_7^{2-}) = 0.01480\ L \times 0.0100\ mol/L = 1.480 \times 10^{-4}$ mol. Mole ratio 6 Fe^{2+} to 1 $Cr_2O_7^{2-}$: $n(Fe^{2+})$ in the aliquot $= 6 \times 1.480 \times 10^{-4} = 8.880 \times 10^{-4}$ mol. Scale up: the flask is 100.0 ÷ 20.00 = 5 times the aliquot, so $n(Fe^{2+})$ in the sample $= 4.440 \times 10^{-3}$ mol. Mass: $m = 4.440 \times 10^{-3}\ mol \times 55.85\ g/mol = 0.248$ g.