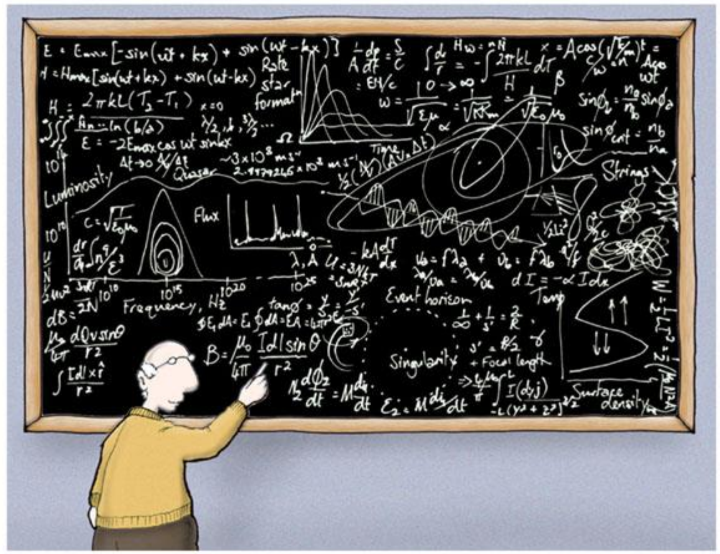
STEPPING UP TO SCHOLARSHIP CHEMISTRY

HUTT WORKSHOP

6 JUNE 2018



Astrophysics made simple

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TE WHARE WĀNANGA O TE ŪPOKO O TE IKA A MĀUI
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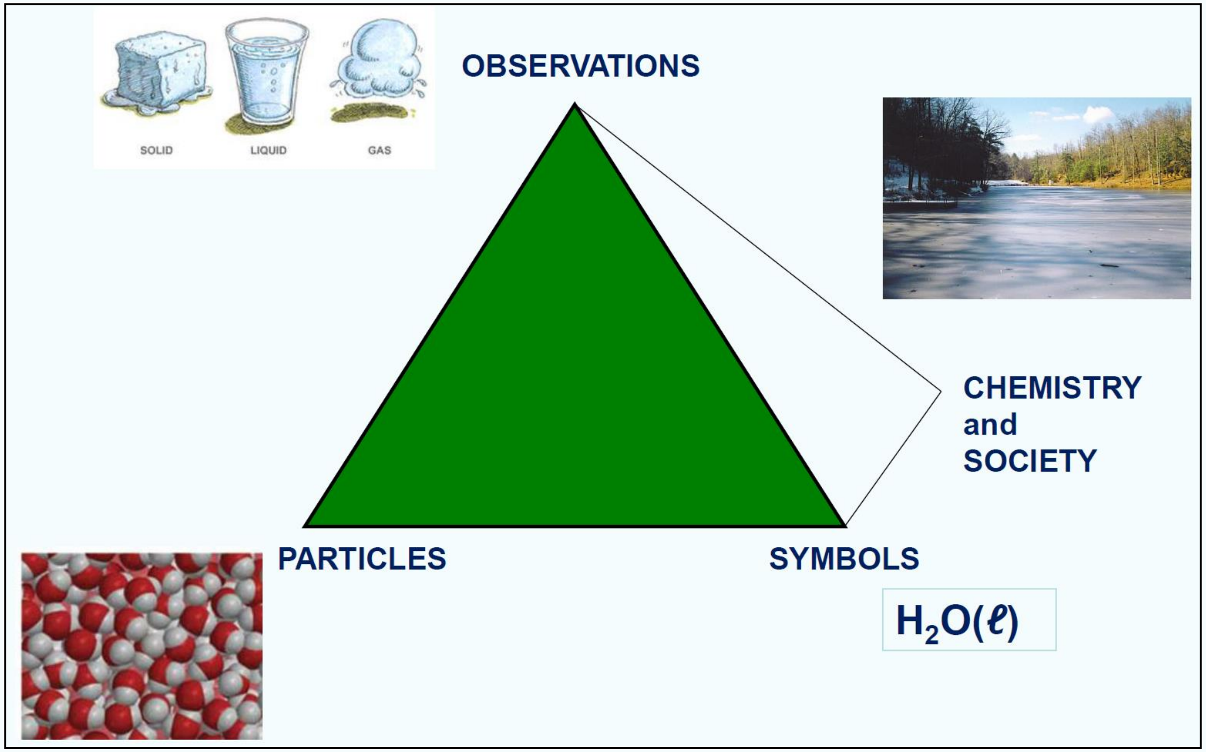
HOW CHEMISTS VIEW THE WORLD

Chemists investigate the ‘molecular’ reasons for the processes that occur in our macroscopic world. They often communicate their understanding using symbols.



Three dimensions to understanding chemistry:

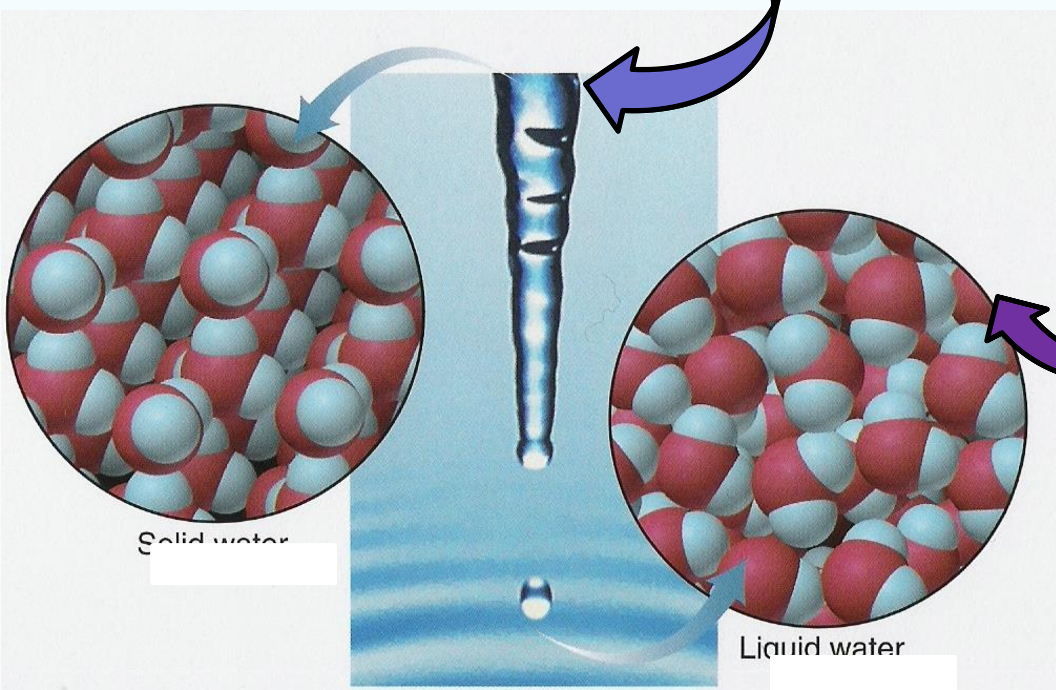
- ***macroscopic world*** – observing chemical reactions
- ***sub–microscopic world*** of atoms, molecules and ions
- ***symbolic world*** formula and equations

MACROSCOPIC / OBSERVATIONS

- chemical and physical properties
- chemical reactions
- physical changes
- quantitative measurements

PARTICLES:

- thinking about atoms/ions/molecules
- nature of particles present – atoms/ions/molecules
- interactions between particles
- changes to particles or numbers of particles
- chemical principles and laws e.g. gas laws



$$H_2O(\ell) \longrightarrow H_2O(s)$$

SYMBOLS: formulae, equations

LOGICAL PLANNED COHERENT ANSWERS

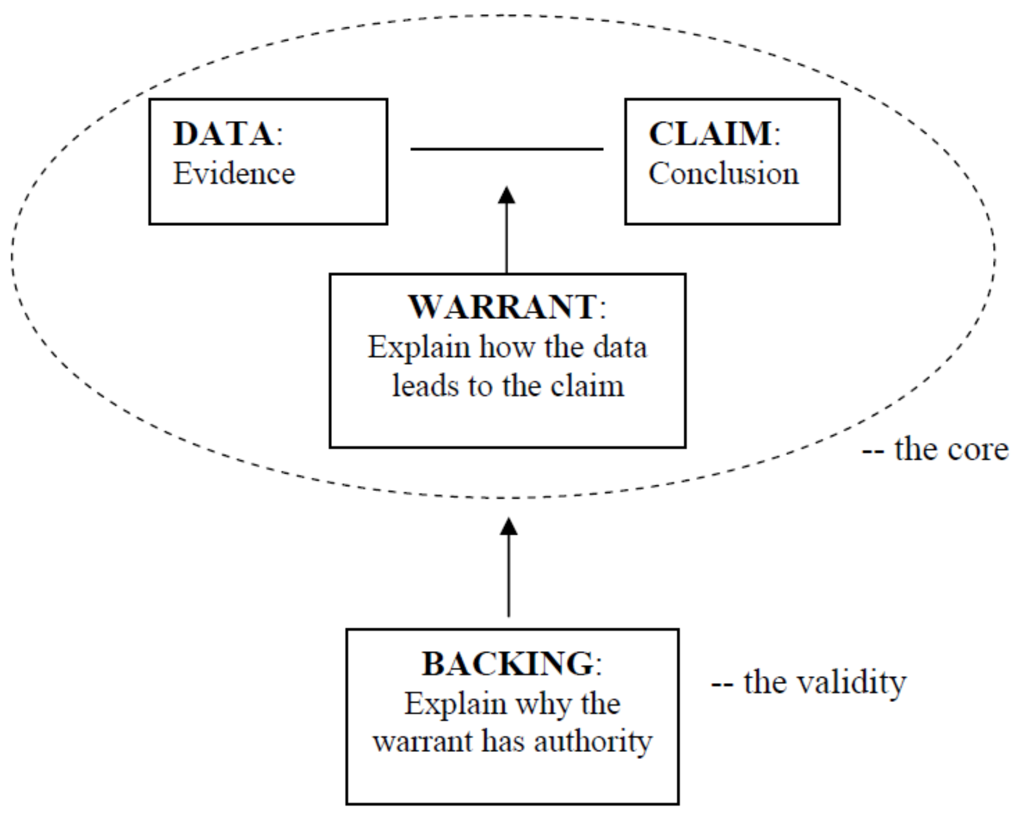


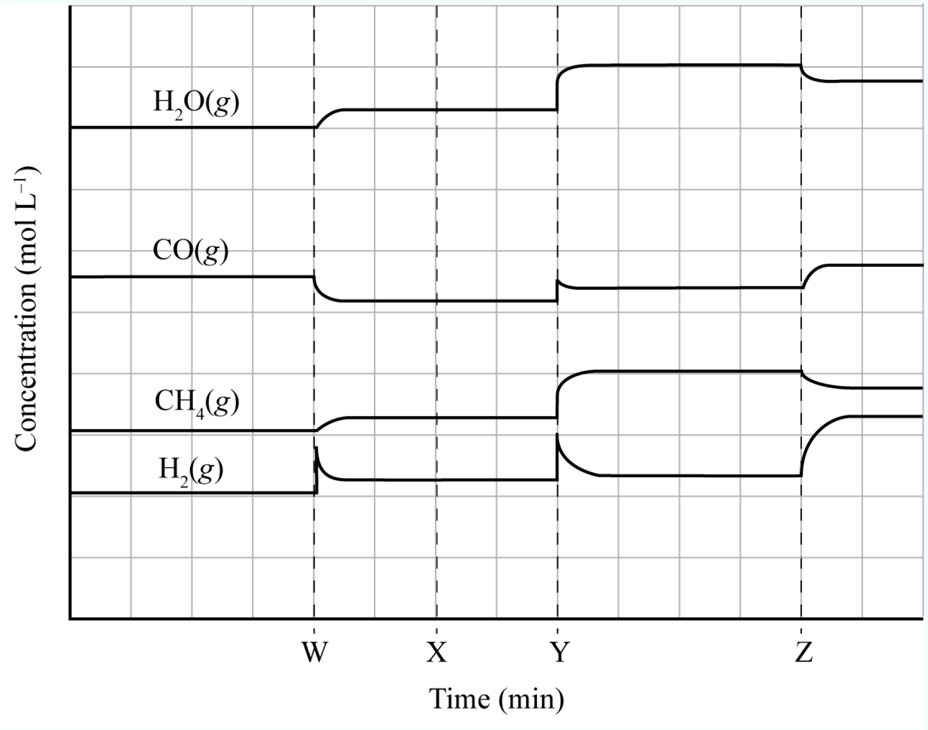
Figure 1. Toulmin's model of argumentation.

Claim
a conclusion derived from the data / focus of the argument
Data
Measurements / observations on which the claim is based / evidence
Warrant
links data to the claim / supports the claim
Backing
additional information or support for the warrant
Qualifier
may indicate the strength of the leap from the data to the claim / limitations of the claim

COMMUNICATION EXERCISE 1 (SCHOLARSHIP 2007)

The graph below shows changes in the concentration of the species present in a system involving the following reaction at equilibrium. The reaction is endothermic in the forward direction.

$$CH_4(g) \quad + \quad H_2O(g) \rightleftharpoons CO(g) \quad + \quad 3H_2(g)$$



Data:

W: H_2 ↑ (lots) CH_4 ↑, H_2O ↑ CO ↓

X: no change

Y: everything goes up

then CO, H_2O ↓

Z: H_2 ↑ CO ↑, H_2O ↓ CH_4 ↓

Discuss the nature of the stresses applied to the system at positions **W, X, Y** and **Z**, and how these stresses result in the changes in the concentrations of the species present in the system.

Claim:

When stress is applied to a system at equilibrium it will shift in the direction to reduce the stress.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H > 0$$

Data:

W: $H_2 \uparrow$ (lots) $CH_4 \uparrow$, $H_2O \uparrow$ $CO \downarrow$ Added product

X: no change Catalyst?

Y: everything goes up then CO, $H_2O \downarrow$ Pressure

Z: $H_2 \uparrow$ $CO \uparrow$, $H_2O \downarrow$ $CH_4 \downarrow$

Temperature – endothermic so added temp favours the products

At position **W** there is a sudden sharp increase in the concentration of H_2 consistent with the addition of H_2 to the system. Since H_2 is a product of the reaction the equilibrium then shifts to the left, decreasing CO and H_2 concentrations while at the same time increasing the concentration of CH_4 and H_2O.

At position **Y** there is a sudden sharp increase in the concentration of all 4 gases. Following this the concentrations of CO and H_2 decrease while the concentrations of the CH_4 and H_2O increase. This is consistent with an increase in pressure causing a shift towards the reactants where there are fewer gas particles than in the products.

At point **Z** the stress applied results in an increase in concentrations of CO_2 and H_2 and a decrease in the concentrations of CH_4 and H_2O. This is consistent with a shift towards the products. Since this reaction is endothermic the increase would have been caused by heating the equilibrium system.

At position **X** there is no change to the concentration of any of the species. This means any change to the system is something which has no effect on the equilibrium – in other words it is the addition of an inert gas such as nitrogen or the addition of a catalyst.

COMMUNICATION PRACTICE 2 (SCHOLARSHIP 2007)

You have 5 bottles labelled A to E. Each bottle contains one of the following liquids:

propanone, water, propan-2-ol, methanol, hexane

Determine the identity of the Compounds A to E using the data below. Relate the data to the structure and bonding in the compounds.

Time for 1 drop of each sample to evaporate at room temperature:

Sample	Time(s)
A	135
B	more than 1200
C	65
D	30
E	20

Solubility of glucose, $C_6H_{12}O_6$, in each liquid (at room temperature)

B dissolved in glucose in the greatest amount
A and C dissolved in a small amount of glucose
E dissolved even less glucose than A and C
D dissolved almost no glucose

Miscibility (ability of two liquids to mix):

B and D were not miscible, forming two distinct layers
A, B, C and E were miscible with one another

PROBLEM SOLVING/CALCULATIONS

"PROBLEM SOLVING is what you do when you don't know what to do"

Suggestions:

1. Read the **whole** problem carefully. Identify what the problem is asking (make sure that you answer this!)
2. Find a way of 'unpacking the question' e.g. identify key pieces of information / extra information given that is not needed – possibly draw a flow chart/write equations
3. Link important information to the processes or species discussed e.g. identify key observations e.g. colour, state or identify key reactions: oxidation – reduction, acid – base, precipitation

For calculations:

- Make a list of the knowns and unknowns and identify a path to get from what is given to what is asked for.
- Check your answer and make sure that it is reasonable.

Remember: Whenever you solve a numerical problem think about what the numbers actually represent on the molecular level i.e. in terms of atoms and molecules.
Include units in your working as this confirms the correct equations

REDOX TITRATIONS

- Titrations can be performed for any reaction that goes to completion provided that the end-point can be observed. Redox reactions are often convenient in analysis because the appearance or disappearance of a colour related to an ion is an ideal criterion for the end-point of the reaction.
  e.g. $6H^+ + 2MnO_4^- + 5(COOH)_2 \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$
- Iodine is widely used as a reagent for the volumetric determination of strong reductants such as thiosulfate ($S_2O_3^{2-}$). A starch indicator will determine the end point as it is blue in the presence of iodine. Neither iodine nor sodium thiosulfate are suitable as primary standards. However, potassium iodate is a powerful oxidising reagent and a 'good' primary standard. Standard 'iodine' solutions can be prepared from potassium iodate via the reaction: $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$
  The liberated iodine is titrated with sodium thiosulfate.

$$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$$

$$S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

$$(6S_2O_3^{2-} + 3I_2 \rightarrow 3S_4O_6^{2-} + 6I^-)$$

Overall: $IO_3^- + 6S_2O_3^{2} + 6H^+ \rightarrow 3S_4O_6^{2-} + 3I_2 + 3H_2O$

TITRATION PROBLEM 1 (SCHOLARSHIP 2014)

A bottle of household bleach contains the following information:

Active ingredients: Sodium hypochlorite 42 g L^{-1} (available chlorine 4.0% m/V), available chlorine by 'use by date' 2.0% m / V, sodium hydroxide 9 g L^{-1}.

The following procedure is carried out to determine the extent of the decomposition of the contents of the bottle of household bleach.

A 20.00 mL sample of the bleach is diluted to 250.00 mL, using a volumetric flask. Excess potassium iodide is added to a 10.00 mL sample of the diluted bleach solution, along with 10 mL of dilute sulfuric acid.

$$H^+ + 2I^- + OCl^- \rightarrow I_2 + Cl^- + OH^-$$

The liberated iodine is titrated with a standard sodium thiosulfate ($Na_2S_2O_3$) solution of concentration 0.04562 mol L^{-1}. The end point is determined by the change of colour of a starch indicator.

$$2S_2O_3^{2-} + I_2 \rightarrow 2I^- + S_4O_6^{2-}$$

The titration data is given below. Determine the extent of the decomposition of the bleach by comparing the available chlorine (% m/V) in the bottle, with that given on the label.

Titre	Final volume /mL	Initial volume /mL
1	16.88	0.16
2	33.56	16.88
3	16.98	0.02
4	33.64	16.98

Step 1: Titration equation

$OCl^{-} + 2S_2O_3^{2-} + H^{+} \rightarrow Cl^{-} + OH^{-} + S_4O_6^{2-}$

Average titre = 16.69 mL (number 3 not concordant so don't use)

Moles of known*:*

$n(S_2O_3^{2-}) = 0.04562 \times 0.016687 = 7.612 \times 10^{-4}$ mol

Moles unknown

$n(OCl^{-}) = 3.8062 \times 10^{-4}$ mol

Concentration unknown $c(OCl^{-}) = \dfrac{3.806 \times 10^{-4}}{0.01000} = 0.03806 \text{ mol L}^{-1}$

Undiluted OCl^{-} = $\dfrac{250}{20} \times 0.03806 = 0.4758 \text{ mol L}^{-1}$

Concentration g L^{-1} $c(NaOCl) = 0.4758 \text{ mol L}^{-1} \times 74.5 \text{ g mol}^{-1} = 35.45 \text{ g L}^{-1}$

% available chlorine: 42 g L^{-1} ≡ 4.0% $\dfrac{35.45}{42} \times 4.0 = 3.38\%$

This value suggests that some of the bleach has decomposed but it is still above the value that should be available by the use by date.

% still available = 3.38/4.0 × 100 = 84.4% so 15.6% decomposed

BACK TITRATION

- Used when reactions are slow OR there are competing reactions OR the is no easy way to detect the end point
- A measured amount of reagent is added all at once (more than is needed to completely react with the sample)
- When reaction is complete the amount of unreacted reagent (excess) is determined using a standard solution

This amount will be known accurately and usually added in the first step

KNOWN AMOUNT OF EXCESS

UNKNOWN TO BE ANALYSED | TITRATION

Subtract titration result from excess. Check stoichiometry.

Look for the titration data and make sure you do this calculation

TITRATION PROBLEM 2

25.00 mL of 0.100 mol L^{-1} NaOH were added to 10.00 mL of a solution of NH_4Cl. The volume was diluted to about 150 mL and then gently boiled till no more ammonia was evolved. The solution was cooled and then the amount of unreacted NaOH was measured by titrating against H_2SO_4. 15.50 mL of 0.0521 mol L^{-1} H_2SO_4 were required for complete reaction.

Calculate the concentration of the NH_4Cl solution

NaOH

NH_4Cl

KNOWN AMOUNT OF EXCESS

UNKNOWN TO BE ANALYSED | TITRATION

NaOH with H_2SO_4

$NH_4Cl + NaOH \rightarrow NH_3 + H_2O + NaCl$

$n(NaOH)_{added} = 0.0250\ L \times 0.100\ mol\ L^{-1} = 2.50 \times 10^{-3}$ mol

titration $2NaOH + H_2SO_4 \rightarrow 2H_2O + Na_2SO_4$

$n(H_2SO_4) = 0.0155 \times 0.0521 = 7.905 \times 10^{-4}$

$n(NaOH)_{left} = 2 \times 0.0155 \times 0.0521 = 1.615 \times 10^{-3}$

$n(NaOH)_{reacted} = 2.50 \times 10^{-3} - 1.62 \times 10^{-3} = 0.88 \times 10^{-3}$ mol $= n(NH_4Cl)$

$n(NH_4Cl) = 0.88 \times 10^{-3}$ mol / 0.0100 L = 0.088 mol L^{-1}

TITRATION PROBLEM 3 (SCHOLARSHIP 2009)

15.35 g of a mixture of sodium nitrate, $NaNO_3$, and magnesium nitrate, $Mg(NO_3)_2$, was heated until no more gases were evolved. The $NaNO_3$ decomposes giving $NaNO_2$ and oxygen gas, while the $Mg(NO_3)_2$ decomposes to give the metal oxide, NO_2 and oxygen. The water soluble part of the residue produced on heating was used to prepare a 1.00 L solution. 10.00 mL of this solution was reacted with 20.00 mL of acidified $KMnO_4$ (which oxidises NO_2^- to NO_3^-). The excess potassium permanganate required 10.25 mL of 0.0500 mol L^{-1} oxalic acid, $H_2C_2O_4$, for complete reaction in which CO_2 is produced.

Write balanced equations for all the reactions and calculate the mass, in grams, of each metal nitrate present in the original mixture.

$$2NaNO_3 \rightarrow 2NaNO_2 + O_2$$

$$2Mg(NO_3)_2 \rightarrow 2MgO + 4NO_2 + O_2$$

$$H_2O + NO_2^- \rightarrow NO_3^- + 2H^+ + 2e^-$$

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

$$6H^+ + 2MnO_4^- + 5NO_2^- \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$$

	KNOWN AMOUNT OF EXCESS		$KMnO_4$
$NaNO_2$	***UNKNOWN TO BE ANALYSED***	TITRATION	$H_2C_2O_4$

The excess potassium permanganate required 10.25 mL of 0.0500 mol L^{-1} oxalic acid, $H_2C_2O_4$, for complete reaction in which CO_2 is produced.

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

$H_2C_2O_4 \rightarrow 2CO_2 + 2H^+ + 2e^-$

$6H^+ + 2MnO_4^- + 5H_2C_2O_4 \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$

$n(H_2C_2O_4) = 0.000513$ mol

$n(MnO_4^-) = 2/5 \times 0.000513$ mol = 0.000205 mol

This is the MnO_4^- left unreacted from the $NaNO_2/MnO_4^-$ mix

Original $n(MnO_4^-)$ added = 0.0200 mol $L^{-1} \times 0.0200$ L = 4.00×10^{-4} mol

$n(MnO_4^-)$ reacted with nitrite = 4.00×10^{-4} mol – 2.05×10^{-4} mol

= 1.95×10^{-4} mol

$6H^+ + 2MnO_4^- + 5NO_2^- \rightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$

$n(NO_2^-)$ in 10.0 mL = $5/2 \times n(MnO_4^-)$ = 4.875×10^{-4} mol

In 1 litre $n(NO_2^-)$ = 0.04875 mol $NaNO_2$ = $n(NaNO_3)$ in the original mixture.

$M(NaNO_3)$ = 85 g mol^{-1} and $m(NaNO_3)$ = 4.14 g

$m(Mg(NO_3)_2)$ = 15.35 – 4.14 = 11.21 g

TITRATION PROBLEM 4 (SCHOLARSHIP 2004)

Alcohol levels in blood samples can be determined by back titration. The alcohol is first removed from
the blood by distillation and then heated with a known excess of acidified potassium dichromate solution. Excess potassium iodide is added and the resulting solution is titrated with standard sodium thiosulfate solution. Starch indicator is added near the end point.

Equations for the reactions are:

$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$

$Cr_2O_7^{2-} + 14H^+ + 6I^– \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^– + S_4O_6^{2-}$

(a) Discuss the method described above, justifying the need for each step involved.

(b) A blood sample has been removed from a suspected adult drunk driver. The alcohol from 10.0 mL samples is added to 10.0 mL of acidified 0.0492 mol $L^{–1}$ $K_2Cr_2O_7$ solution and warmed in a water bath. When oxidation is complete, excess KI is added and the sample is titrated with 0.105 mol $L^{–1}$ $Na_2S_2O_3$ solution. The titre values for four successive 10.0 mL blood samples from the same driver were: 17.94, 17.86, 17.70 and 17.84 mL.

Calculate the concentration of alcohol in the blood and determine if the sample is above the legal limit of 80 mg alcohol per 100 mL of blood.

(c) A student decides to use this analytical method to determine the amount of alcohol present in some home brew. Initial trials of diluted samples of the home brew gave titre values of less than 1 mL.

$Cr_2O_7^{2-} + 14H^+ + 6S_2O_3^{2-} \rightarrow 2Cr^{3+} + 7H_2O + 3S_4O_6^{2-}$

Average value of concordant titres is 17.84 mL

$n(S_2O_3^{2-}) = 0.01784 \times 0.105 = 1.873 \times 10^{-3}$ mol

n(dichromate remaining) =1/6 $\times\ n(S_2O_3^{2-}) = 3.122 \times 10^{-4}$ mol

n(dichromate originally added) = $0.0492 \times 0.010 = 4.92 \times 10^{-4}$ mol

n(dichromate used up) = $(4.92 - 3.12) \times 10^{-4}$ mol $= 1.80 \times 10^{-4}$ mol

$3CH_3CH_2OH + 2Cr_2O_7^{2-} + 16H^+ \rightarrow 3CH_3COOH + 4Cr^{3+} + 11H_2O$

n(alcohol) = 3/2 $\times\ n$(dichromate used up) = 2.70×10^{-4} mol present in 10 mL sample

n(alcohol) in 100 mL = 2.70×10^{-3} mol (> 0.0174 mol L^{-1})

m(alcohol) in 100 mL = 2.70×10^{-3} mol $\times$ 46 g mol^{-1} = 0.124 g or 124 mg

The amount of alcohol present in the blood sample is over the legal limit.

TITRATION PROBLEM 5: (SCHOLARSHIP 2005)

Hydroxylammonium chloride ($^{+}NH_3OHCl^{-}$) reacts with Fe^{3+} ions to produce Fe^{2+} 1.00 g of hydroxylammonium chloride was dissolved in distilled water and diluted to 250.0 mL. 25.00 mL of this solution was added to a solution containing an excess of iron(III) ions and sulfuric acid. The mixture was boiled. After cooling it was then titrated with a solution of 0.0200 mol L^{-1} potassium permanganate. 28.90 mL was needed to reach the equivalence point. Determine which of N_2, NO, N_2O, N_2O_4 or NH_3 is the nitrogen-containing product of the reaction between the hydroxylammonium chloride and iron(III) and hence write a balanced equation for the reaction of iron(III) with hydroxylammonium chloride.

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

$n(MnO_4^{-}) = 0.0200 \times 0.0289 = 5.78 \times 10^{-4}$

$n(Fe^{3+}) = 5 \times 5.78 \times 10^{-4} = 2.89 \times 10^{-3}$

$n(\text{hac}) = {}^{1}/_{65} \times 0.1 = 1.44 \times 10^{-3}$

$n(Fe^{3+}) : n(\text{hac}) = 2.89 \times 10^{-3} : 1.44 \times 10^{-3} = 2:1$

Oxidation Number (N) in hydroxylammonium chloride (hac) is –1.

Oxidation Number increases by 2 ($2e^{-}$ transferred) so product is N_2O

$Fe^{3+} + e^{-} \rightarrow Fe^{2+}$

$2\ {}^{+}NH_3OHCl^{-} \rightarrow N_2O + H_2O + 6H^{+} + 4e^{-} + 2Cl^{-}$

$4Fe^{3+} + 2\ {}^{+}NH_3OHCl^{-} \rightarrow 4Fe^{2+} + N_2O + H_2O + 6H^{+} + 2Cl^{-}$