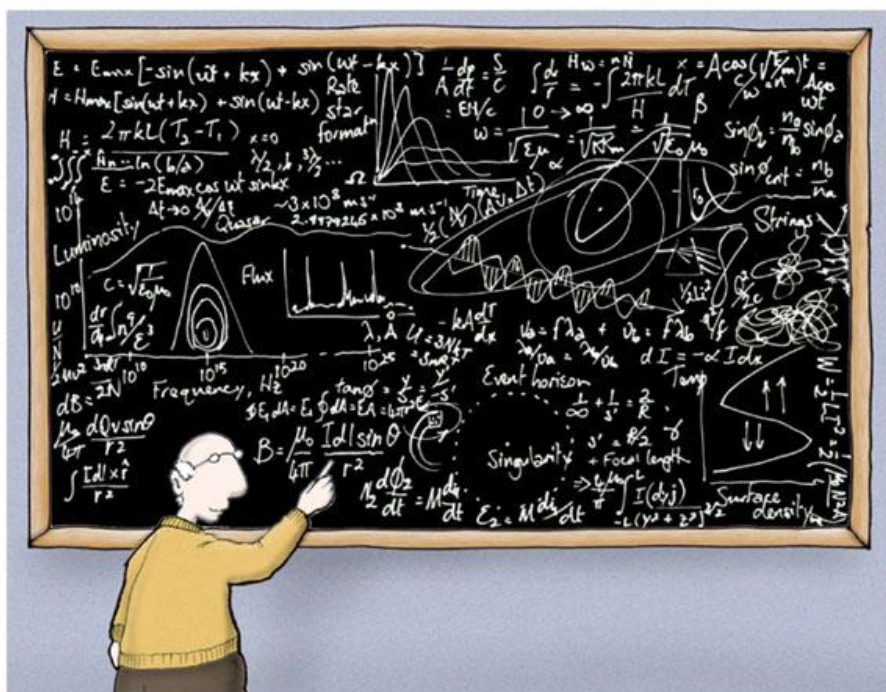


Skills for Stepping Up to Scholarship Chemistry Workshop Dec 2022



Astrophysics made simple

Prepared by
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Cartoon by Nick D Kim, scienceandink.com. Used by permission.

Skills for Stepping Up to Scholarship Chemistry

Introduction

This resource has been prepared for teachers and students to provide guidance to develop three important skills students need in order to step up from Level 3 to Scholarship Chemistry. It is based on observations, made in workshops and tutorials over a number of years, that many Level 3 “Excellence” students struggle to make the transition to the expectations of the Scholarship examination. Each skill is illustrated using examples from the NZIC Scholarship examinations. In particular, for the second two skills, there are suggested processes that students can use as they approach a question and develop their answer. There are worked examples across the range of chemistry topics along with practice exercises and answers. Using questions selected from the NZIC Scholarship examinations expands the range of practice exercises available to Scholarship candidates.

The Scholarship Performance standard

Rather than a list of chemistry knowledge/concepts, the Chemistry Scholarship Performance Standard¹ provides information about the *skills that candidates need to be able to use their chemistry knowledge* (from NCEA Levels 2 and 3) to answer the examination questions.

Three important competencies indicated in the performance standard are:

- **understanding the world from a chemical perspective**
- **communicating** with explanations that are logical, precise, coherent, well reasoned and convincing using the conventions, vocabulary, and principles of chemistry.
- **problem solving that uses chemical principles** and may involve integration, synthesis, perception, insight, abstraction, and extrapolation

From the Chemistry Scholarship Standard:

.. it is expected that answers will involve “planning, processing, linking, and applying chemical principles across all areas of chemistry to solve problems or provide explanations of observations from a chemical perspective”.

It is important that students have a thorough knowledge of the relevant Level 2 and 3 chemistry material before they attempt to answer scholarship questions. However, they often comment that they struggle to “know how to get started” or to “figure out what the question is asking for”. In these situations, having a plan to ‘unpack’ the question can help provide a way into the answer and having a framework for discussions can help set up the logical, concise, well-reasoned answers required at this level.

Examples of comments from examiner’s reports indicate the importance of developing these competencies. The best performing candidates demonstrated the following²:

- *achieved convincing communication by having a clear understanding of the language of chemistry, particularly with respect to attractive forces, enthalpy and entropy changes, molecular shapes, structure and bonding.*
- *could interpret the intent of the questions and use critical thinking skills to develop logical coherent, concise answers that were appropriate to the questions rather than being dependent on learned phrases*
- *had a strong understanding of organic functional groups, properties of organic compounds and could interpret spectroscopic data to determine and justify the identity of an unknown organic compound.*
- *could interpret and use the mathematical data provided in questions to carry out calculations, with detailed and logical working to develop quality answers.*
- *took time to read the questions carefully and provided answers with greater clarity and depth than that expected of answers to NCEA Level 3 examinations.*

¹ <https://www.nzqa.govt.nz/qualifications-standards/awards/new-zealand-scholarship/scholarship-subjects/scholarship-chemistry/>

² Collected from Scholarship Assessment Reports: <https://www.nzqa.govt.nz/qualifications-standards/awards/new-zealand-scholarship/scholarship-subjects/scholarship-chemistry/scholarship-chemistry-report/>

1. Understanding the World from a Chemistry Perspective – How Chemists See the World.

Many chemistry students struggle to define what it is that sets chemistry apart from the other sciences – i.e. how to give a chemistry perspective of the world. Various scholars have proposed a list of ‘big ideas of Chemistry’ and the one idea that always comes out on top is that **matter is made of tiny particles (called atoms)**. So perhaps chemistry could be summarised as:

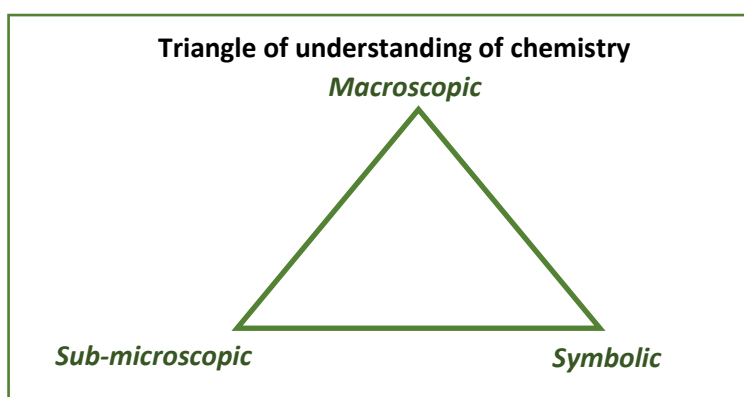
“a way of understanding the world from the perspective of the properties and interactions of the particles (atoms, ions and molecules) of which all matter is made”.

Chemists explain observations in the natural world by exploring the properties and interactions of the very small particles, that cannot be seen, but from which all matter is made. These properties and interactions can explain the physical properties of substances (structure and bonding) and also the chemical properties (reactivity of particles). Chemists use symbols to communicate their ideas.

Chemistry is often portrayed at three different levels of representation – *macroscopic, submicroscopic and symbolic*. Together, these three levels can enrich understanding of chemical concepts.

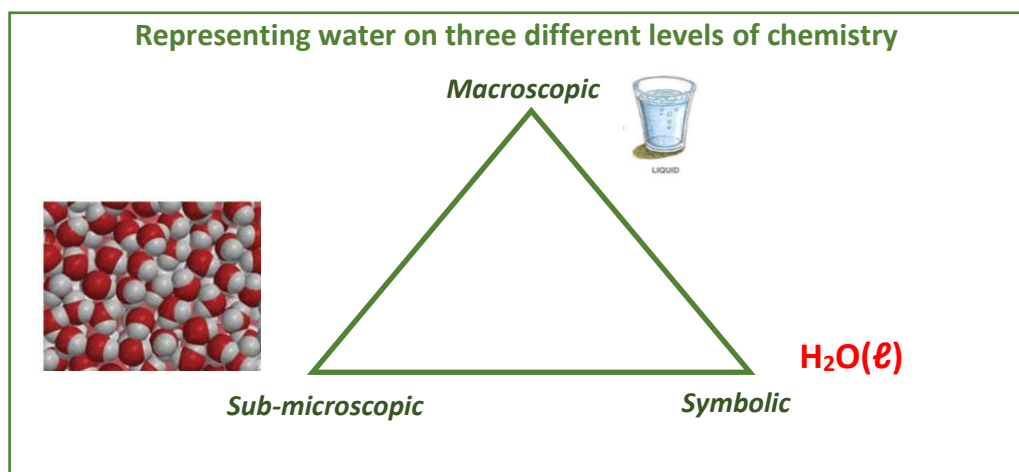
A Triangle of Understanding for Chemistry – Linking the Three Levels of Representations in Chemistry

The observable world/matter – the **macroscopic** level - can be explained by the small particles from which make up all matter the **submicroscopic** level - and these two levels of understanding chemistry can be linked by the **symbolic** level (formulae/equations/calculations/graphs) that chemists use to communicate their ideas. This leads to a **triangle of understanding of chemistry**.



- **Macroscopic** = observations - what can be seen touched and smelt (measured)
- **Sub-microscopic** = particles (atoms, molecules, ions)
- **Symbols** = formulae, equations, calculations and graphs

For example: liquid water can be represented as $\text{H}_2\text{O}(\ell)$ and its properties explained by understanding the interactions of the water particles molecules at the appropriate temperature



Chemical literacy is demonstrated through explanations that accurately link observations to the nature of the particles involved and represent these using chemical symbolism such as equations

2a. Communicating in Chemistry - Using the Three representations of chemistry

Explanations in the chemistry scholarship examination will usually require integration of the three representations of chemistry; macroscopic (observations) explained using an understanding of submicroscopic (particles) linked to the symbolic (formulae and equations). Chemistry literate people are able to easily switch between these ways of thinking with formulae and equations supporting explanations and discussions of chemistry phenomena.

Worked Example 1:

Note: This is not a Scholarship level question but is a good illustration of the 3 levels of understanding required for the discussion.

The following table provides information about 0.100 mol L⁻¹ solutions of ammonia, ammonium nitrate and nitric acid. Account of the variation in the properties.

Compound	Electrical Conductivity	pH
NH ₃	Poor	11.1
NH ₄ NO ₃	Good	5.1
HNO ₃	Good	1.0

Three representations:

Macroscopic	Submicroscopic	Symbols / Equations
Conductivity		
pH		

Note: It is important to take care to differentiate between the *macro* and *sub-micro* levels in chemistry explanations as the **language of chemistry** can be quite confusing.

For example, consider the statement: 'C₆H₁₄ is hexane'

Chemists can interpret this in a number of ways; the term '*hexane*' can be used to mean the colourless liquid (*macro*) or the molecule (*sub-micro*) which has the molecular formula C₆H₁₄ (*symbolic*).

This statement could be more accurately written as: '*Hexane is a colourless liquid. The composition of the molecules of hexane can be represented as C₆H₁₄.*'

Other examples of ambiguous statements which muddle the macro and submicro levels are:

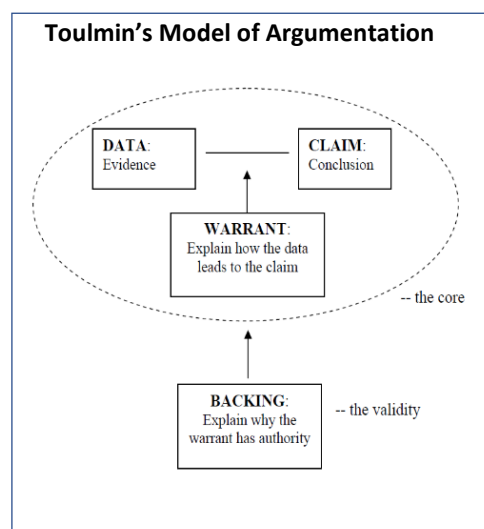
- Nylon is a long molecule (*what does the term 'nylon' mean?*)
- In an oxidation reaction zinc loses electrons (*what is losing electrons?*)
- Helium is the smallest element
- Molecules of methane are non-polar so they have a low boiling point (*can a molecule have a boiling point?*)

2b. Communication - Logical, coherent answers linking chemistry principles to the question.

Logical, coherent answers need to be **planned** to avoid repetitive, long-winded circular arguments AND to ensure they are linked to the context of the question.

A useful framework for a reasoned discussion can be derived from the "Toulmin analysis", a method originally devised to analyse arguments in law students' assignments³.

An answer begins by laying out the *core* ideas: a summary of the measurements/**data**/trends to be explained, the chemical principle that **claims** to explain the data and the **link** (warrant) that connects the data and the claim. Once the core ideas are established the answer is *validated* with **backing/reasoning** that explains the how the chemical principle explain the data, using the language and symbols of chemistry.



The Framework:

- 1. Data = Evidence** - What is the trend/pattern/observation/measurements to be explained?
- 2. Claim = Chemical principle** - What chemistry idea will explain this data = focus of the argument?
- 3. Warrant = Link** - What is the link between the data and the claim?
- 4. Backing = reasoning** - How does the chemical principle explain the data?

While the final written answer will not use the terms data, claim, warrant etc, identifying these ideas will shape the answer and there is a better chance that it will be clear, logical and concise.

Worked Example 2:

Note: This is not a Scholarship level question but illustrates how the core ideas can be developed and validated with extended reasoning.

Account for the trend in the table below:

Data
Table 1: Boiling Points (Bps) of Some Organic Compounds

Compound	Molecular Structure	Bp (°C)
1-pentene		30
1-hexene		63
1-heptene		94
1-octene		121
1-nonene		147
1-decene		171

Core ideas:

Data:

Claim:

Link/Warrant:

Validation:

Backing or Reasoning

³ Toulmin S. E., (1958), *The Uses of Argument*, Cambridge: Cambridge University Press

NOTES:

- Stating the **core ideas** at the beginning streamlines an answer as they can be referred to in the discussion without too much repetition.
- Starting with a summary of the **data** clarifies the focus of the question and stating the **claim** introduces the key idea to be used in the explanation.
- Including the **warrant** means that the discussion is specifically linked to the data and there is less chance of the answer just being a brain dump of the chemistry principles involved
- The discussion (**backing**) should be planned so that it logically addresses the data. This means thinking about how to group similar and different aspects of the data, before beginning to write.

The final answer will begin with a summary of the **observations** to be explained followed by a statement of the **chemical principle** used to explain these observations. Then a **link** between the chemical principles and the observations is provided. The main part of the answer then provides a **reasoned explanation** based on these core ideas.

Worked Example 3: NZIC Scholarship 2019

Note: This example illustrates one way of presenting an explanation using entropy principles. By presenting the core ideas at the beginning of the answer it is less likely that they will be overlooked.

Sulfur forms many cyclic allotropes with different ring sizes. In the solid state, the most stable allotrope of sulfur is S_8 . In the gas phase, all ring sizes from S_3 to S_{12} have been detected as well as S_2 molecules. The following equilibrium is observed in the gas phase.



Account for the observation that S_2 molecules do not exist at room temperature but are more abundant at higher temperatures. You should consider both entropy and enthalpy effects.

Data – to be explained: S_2 molecules do not exist at room temperature but are more abundant (stable) at higher temperatures.

Claim – the reason why S_2 molecules become more stable as temperature increases – is because at higher temperatures the total entropy of the formation reaction, $S_8(g) \rightleftharpoons 4S_2(g)$ is increasing/will be positive. At room temperature the non-spontaneous reaction will have negative entropy (be decreasing).

Warrant – linking the data and the claim: Total entropy depends on entropy of system and surroundings, $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$. At room temperature the positive enthalpy of the reaction means that $\Delta S_{\text{surroundings}}$ and ΔS_{total} are both negative (<0) but at higher temperatures $\Delta S_{\text{surroundings}}$ and hence and ΔS_{total} will increase.

Reasoning – explains the statement given above:

For the reaction, $S_8(g) \rightleftharpoons 4S_2(g)$, $\Delta_r H > 0$ so the reaction is endothermic. This means that the entropy change of the surroundings, $\Delta S_{\text{surroundings}}$, is negative since energy is removed from the surroundings thus reducing the movement/disorder of the particles. The entropy change of the system, ΔS_{system} is positive since there are more product particles, $4S_2(g)$, than there are reactant particles products, $S_8(g)$. Since S_2 molecules do not exist at room temperature, the reaction is not spontaneous, and the overall entropy is negative. Hence the positive entropy change for the system must be small in comparison to the large negative entropy change for the surroundings.

For the endothermic reaction, the equilibrium reaction will shift to favour the products at higher temperatures. This means there will be more S_2 particles and hence an increase in ΔS_{system} . Also, at higher temperatures the particles gain kinetic energy also increasing ΔS_{system} . This results in an overall increase in ΔS_{total} and the spontaneity of the reaction.

Note: There is no 'right answer' for presenting the 'core' ideas and the discussion. This method is to help develop a concise, logical answer. It may be necessary to spend a few minutes deciding how to organise the justification/discussion to ensure it is also logical and well ordered.

Communication Check List – use this to review practice answers.

- Are my answers concise, coherent, relevant to the question?
- Have I correctly integrated chemistry symbols and conventions into my answer?
- Does my answer show “joined up thinking”?
- Was my answer planned to link to the data give or is it just a brain dump?

PRACTICE EXERCISES – COMMUNICATION SKILLS

The exercises below can be used to practice identifying the key components/core ideas of an answer. Once this is done, a plan can be developed to present the backing i.e. the reasoning, explanation or argument.

It is important to **practice writing out complete answers and then get feedback** to take forward into further practice opportunities. Answers are available in **Appendix 3** at the back of this resource.

Q1. Structure and Bonding (NZIC 2019)

Sulfur can form different compounds with fluorine.

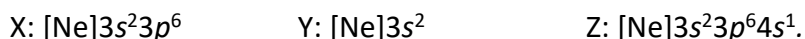
Sulfur tetrafluoride, SF₄, (boiling point: –38°C), has a higher boiling point than sulfur hexafluoride, SF₆, (boiling point: –64°C). SF₄ is also considerably more reactive in water than sulfur hexafluoride, which is regarded as chemically inert as it has virtually no known reaction chemistry.

Account for the difference in boiling point and reactivity in water of sulfur tetrafluoride, SF₄, and sulfur hexafluoride, SF₆ based on your understanding of structure and bonding.

Sulfur fluorides are not part of NCEA Level 3. However, once structures are drawn to give more information about the nature of the molecules, there will be clues about how to respond to the reactivity differences. This question is a good example of how Scholarship questions differ from Level 3 where a list of what needs to be included in the answers is provided. Students need to think about how to develop a logical answer from the formula given to determine intermolecular forces.

Q2. Atomic Structure (NZIC 2017)

The atoms of three elements X, Y and Z have the following electron configurations:



The 1st ionisation energies of the elements (in MJ mol⁻¹) are known to be 0.4188, 0.7377 & 1.520.

The 2nd ionisation energies of the elements (in MJ mol⁻¹) are known to be 1.457, 2.672 & 3.058.

(This is the energy to remove a valence electron from a +1 atomic ion)

Match the ionisation energies to the elements X, Y and Z. Justify your answer with reference to the electron configurations, including a comparison of the differences between first and second ionization energies. You are not required to identify the elements. (NZIC 2017)

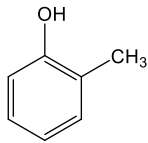
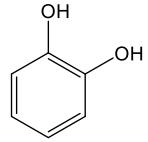
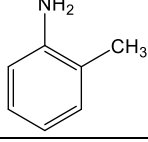
Q3. Entropy (NZIC 2020)

When NaCl(s) is mixed with hexane, C₆H₁₄(ℓ), ΔH_{soln} is large and positive and the salt does not dissolve. However, when octane, C₈H₁₈(ℓ), is mixed with hexane, ΔH_{soln} is small (close to zero) and negative and the octane dissolves. Account for the different solubilities of NaCl(s) and C₈H₁₈(ℓ) in hexane by considering both enthalpy and entropy.

Q4. Intermolecular Forces (also referencing pH) (NZIC 2019)

The melting points and solubilities of three benzene derivatives are given in the table below. Account for the differences in the melting points and solubilities of the three Compounds **R**, **S** and **T** using the data provided in the Table (assume the benzene ring contribution to the intermolecular forces is the same for all three compounds).

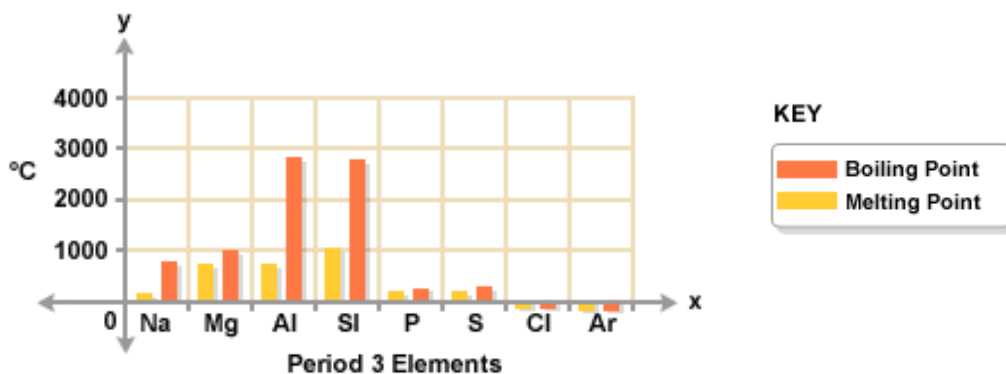
In this question it is probably useful to discuss the melting point trend and the solubility separately.

	Molecular formula	pH of a dilute solution	Molar mass / g mol ⁻¹	Melting point / °C	Solubility / g L ⁻¹
R		weakly acidic	108	31	31
S		weakly acidic	110	105	430
T		≈7	107	-24	1.9

Q5. Periodic Trends (NZIC 2018)

Discuss the similarities, differences, and trends in the melting and boiling points of the elements given in the graph below.

Note: Sulfur occurs naturally as S₈ molecules and phosphorus occurs naturally as P₄ molecules.

**Q6. Shapes of Molecules (NZIC 2018)**

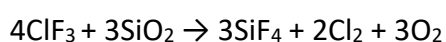
(i) The molecule sulfurchlorotrifluoride, SF₃Cl, is highly reactive. Its shape is based on a trigonal bipyramidal arrangement of electron pairs about the sulfur atom giving, potentially, four different arrangements of the halogen atoms around the central sulfur atom.

Draw each of these arrangements and predict, with reasons, which is likely to be the most stable and which will be the second most stable of the structures.

(ii) Account for the fact that SeF₃Cl and TeF₃Cl could exist while OF₃Cl could not.

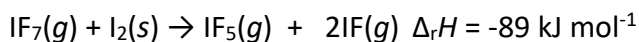
Q7. Intermolecular Forces (NZIC 2021)

Explain why the boiling point of ClF₃ is higher than that of any of the products in the equation below.



Q8. Entropy (NZIC 2021)

Discuss the spontaneity of the reaction producing iodine monofluoride, $\text{IF}(g)$, and iodine pentafluoride, $\text{IF}_5(g)$ in terms of entropy changes accompanying this process.

**Q9. Intermolecular Forces (NZIC 2017)**

Palmitic acid is the most common saturated fatty acid found in both plants and animals. Oleic acid is a monounsaturated fatty acid that occurs naturally in animal and vegetable fats and oils. Linoleic acid is a poly unsaturated acid that is found in vegetable oils. Information about the oils is given in the table below:

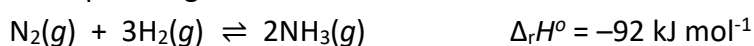
Acid	Molecular Formula	Systematic Name	Molar mass/ g mol ⁻¹	Melting point / °C
palmitic	C ₁₆ H ₃₂ O ₂	hexadecanoic acid	256	63
oleic	C ₁₈ H ₃₄ O ₂	<i>cis</i> , -octadec-9-enoic acid	282	14
linoleic	C ₁₈ H ₃₄ O ₂	<i>cis, cis</i> -octadec-9,12-enoic acid	280	-5

Compare and contrast the structure and bonding in the three acids to account for the melting points differences. Decide, with reasons, whether the melting point of elaidic acid, the *trans* isomer of oleic acid will be higher or lower than that of oleic acid.

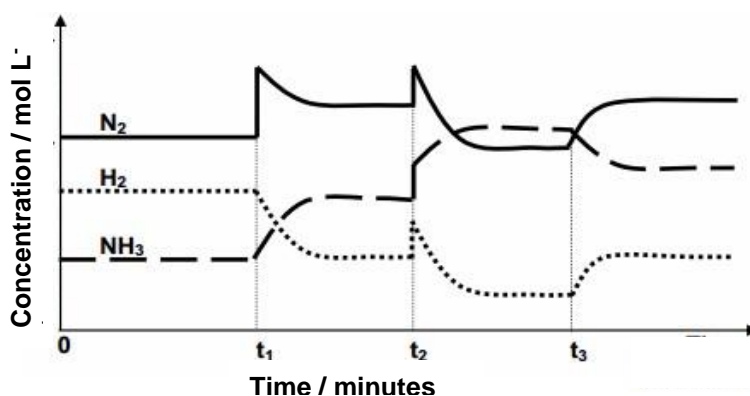
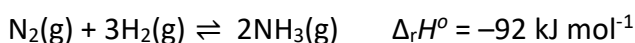
Q10. Equilibria (NZIC 2019)

Le Chatelier's principle states that when a system in equilibrium is stressed the equilibrium will shift in the direction that counteracts the effect of the stress.

The Haber Process combines nitrogen from the air with hydrogen to form ammonia as shown by the equation given below. The reaction is carried out at high pressure and temperature.



(i) The graph below shows changes in the concentration of the species present in a system involving the following nitrogen/hydrogen/ammonia reaction system at equilibrium.



Discuss the nature of the stresses applied to the equilibrium systems at t_1 , t_2 and t_3 and how and why these stresses result in the changes in the concentrations of the reactants and products given in the graph. (Note: the relative values of each species after the stress is applied are not drawn to scale)

(ii) Discuss the validity of the statement that "any change that results in an increase in pressure of this system results in formation of more NH_3 ".

3. Problem Solving in Chemistry

Problem Solving is what you do when you don't know what to do. Key Idea - Have a Plan

Level 3 chemistry students who consistently achieve at Excellence level can sometimes struggle to step up to Scholarship. They often comment that they “don't know how to get started” or “cannot figure out what the question is asking for”. In these situations, having a plan to ‘unpack’ the question can help provide a way into the answer.

The chemistry principles needed to answer a particular scholarship question may not be immediately obvious. Often it is necessary to extrapolate from what is learned in Level 3 to solve problems in unfamiliar contexts. It may be that the format of a question, or the way the data is presented is presented that is unfamiliar. Or it may be that the application of the chemical principle is in an unfamiliar context. In this situation, the challenge is to find a link to access the new context using Level 3 knowledge. For example, questions about atomic structure may use elements beyond Krypton, Kr, in the Periodic Table but applying periodic principles will allow assumptions to be made about such things as electron configuration, periodic properties, and reactivity of other elements.

It is useful to **have a plan** when working with unfamiliar contexts. The following **5 steps** provide a way of interrogating a question to extract relevant information and establish links to relevant chemistry principles. A plan can then be developed to solve the problem and answer the question. Example of problem solving in Scholarship exams include; identifying a set of organic unknowns, analysing the contents of a solution including a titration calculation, calculating pH of a solution that requires a range of different factors to be considered, calculating energy changes that require several reactions to be utilised. These **5 steps** will not always be needed to solve the presented problems. However, having a plan will provide a way to access some of the more difficult challenges presented in the scholarship examination.

A Five Step Plan for Problem Solving⁴

Step 1: Understand – define/deconstruct the problem: What is the question? What chemical principles are involved? What key types of chemical reactions are involved eg oxidation-reduction, acid-base, precipitation? What do the terms used in the question mean?

Step 2: Analyse: What is known (data provided)? What is unknown (what is needed to solve the problem)? What equations, mathematical formulae etc are needed? *This step is a summary of all the information available, in the text of the question, to solve the problem. Sometimes key information needs to be extracted from a large amount of text, some of which is not needed for the answer. In some cases, such as for questions about identifying unknowns, a **flow chart** or a **table** is helpful.* At this step it is sometimes useful to add notes about additional information that can be deduced from the data.

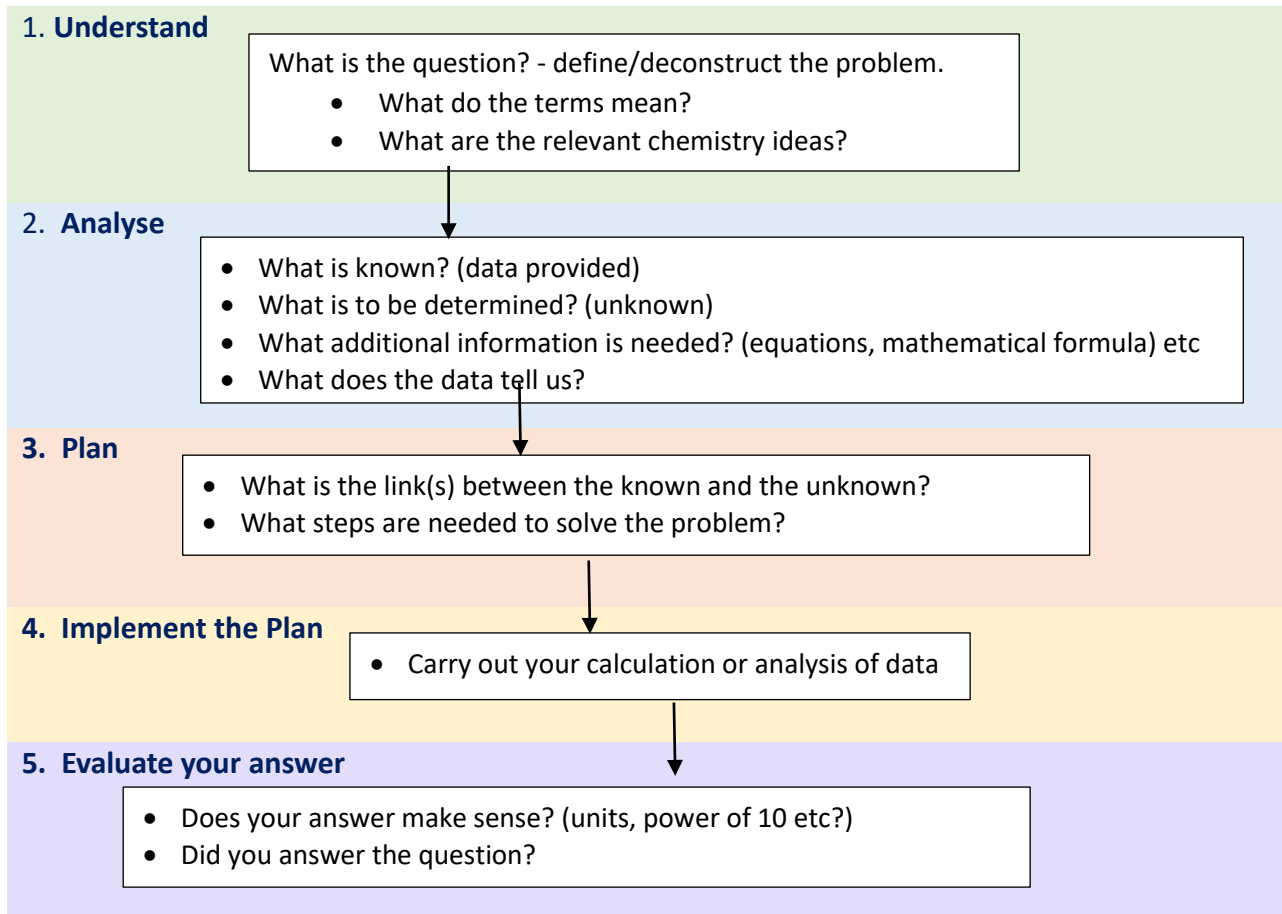
Step 3: Plan: What are the connections between the known and the unknown? What steps are needed to make the connections and reach a conclusion?

Step 4: Implement: Carry out the plan to find the required answer

Step 5: Evaluate: Does the answer make sense - units, order of magnitude etc? Did I answer the question(s)?

⁴ Adapted from: Yuriev, E., Naidu, S., Schembri, L. S. and Short, J. L. (2017) Scaffolding the development of problem-solving skills in chemistry: guiding novice students out of dead ends and false starts. *Chemistry Education Research and Practice*, 18, 486-504

The 5-Step Plan for Problem Solving in Chemistry



Special notes for Calculations

All working should be shown in calculations. Numerical answers should be rounded to an appropriate number of significant figures. Correct units must be included. Explanations and calculations are to be well set out and concise

WORKED EXAMPLES

- *The following worked examples demonstrate the use of the **5-step plan** for solving different types of chemistry problems. Often these steps all not all be necessary as the solution to the problem may be obvious. However, practicing using the 5 step process means that, when 'you don't know what to do' you will have a plan to take you forward.*
- *The emphasis here is 'solving the problem' rather than on the final written answer. There is no 'right' way to set out these planning steps, the aim is to come up with a plan to find a way into difficult problems.*
- *Often, in summarizing all the data, the steps to the solution are revealed.*
- *The final written answer can be crafted at the end of the 'implementation' stage.*

Worked Example 1 (NZIC Scholarship Exam 2019)

This problem probably doesn't need all the steps but it useful to illustrate how they can be used. It is also a useful reminder of the need to understand how to use elemental analysis and molar mass to determine the molecular formula of a compound.

Determine the molar mass and structure of a monoprotic organic acid **X** using the following information.

- The compound contains the elements C, H and O and has the elemental analysis: C, 40.0% and H, 6.70%.
- 1.000 g samples of acid **X** were dissolved in sufficient water to make 50.00 mL of solution. The resulting solution was titrated with 0.3000 mol L⁻¹ NaOH(aq) using phenolphthalein as indicator. The average volume for the titration was 37.00 mL.
- Acid **X** is found to rotate plane-polarised light.

Applying the 5-step process

- 1. Understand:** Determine structure of compound **X**, monoprotic organic acid (RCOOH)
- 2. Analyse:** Given: C, 40.0% and H, 6.70% - implies that O, 53.3%
Titration data: X + NaOH $c(\text{NaOH}) = 0.3000 \text{ mol L}^{-1}$ $V(\text{NaOH}) = 37.00 \text{ mL}$
 $c(\text{X}) = 1.000 \text{ g in } 50.00 \text{ mL}$
Structure: acid implies -COOH, chiral means there is a C with 4 different groups attached
- 3. Plan:** Use % data to find empirical formula
Use titration data to find moles of acid X (in 1 g) and hence molar mass
Use chirality data to decide structure
- 4. Implement:** Assume 100 g of compound
 $n(\text{C}) = 40.0 \text{ g} / 12.0 \text{ g mol}^{-1} = 3.33$;
 $n(\text{H}) = 6.70 \text{ g} / 1.01 \text{ g mol}^{-1} = 6.70$;
 $n(\text{O}) = 53.3 \text{ g} / 16.0 \text{ g mol}^{-1} = 3.33$
Ratio: C:H:O = 1:2:1 Empirical formula (EF): CH₂O
From titration: $n(\text{NaOH}) = 0.03700 \text{ L} \times 0.3000 \text{ mol L}^{-1} = 0.01110 \text{ mol} = n(\text{acid})$
From $m(\text{acid})$: $M = m/n = 1.000 \text{ g} / 0.01110 \text{ mol} = 90.09 \text{ g mol}^{-1}$
 $M(\text{CH}_2\text{O}) = 30.00 \text{ g mol}^{-1} \Rightarrow$ Molecular Formula is $3 \times \text{EF}$: C₃H₆O₃
Structure: acid so -COOH group, 3 C atom chain, another O atom – most likely an -OH group.
Position of -OH determined from chirality
Answer: $\text{CH}_3\text{-CH(OH)-C(=O)-OH}$
- 5. Evaluate:** Structure is an acid and has a chiral C so meets the requirement of the question.

Worked Example 2: Redox potentials (NZIC Scholarship 2019)

There is a lot of information packed into the way this question has been written. By working through the first 2 steps of the problem-solving process (understand and analyse), a starting point for the answer is uncovered.

Uranium, U, is commonly alloyed with other metals such as iron, Fe, cobalt, Co, and niobium, Nb. These metals all undergo the same chemical reactions as uranium and hence the determination of the uranium content in the alloys presents a challenge. One method to determine the uranium content involves the use of zinc metal, Zn. The uranium containing alloy is dissolved in a mixture of hydrofluoric and sulfuric acids to give U^{6+} (in the form of UO_2^{2+}) which is then reacted with Zn to give U^{4+} . Addition of excess Fe^{3+} solution converts the U^{4+} back to U^{6+} and produces Fe^{2+} which can be titrated with a standardised solution of Ce^{4+} resulting in Fe^{3+} and Ce^{3+} . The solution remains acidic throughout the determination. Unfortunately, if niobium is present in the alloy it will also be involved in the reactions used during the analysis. Niobium is present as Nb^{5+} , which reacts with Zn to give Nb^{3+} which also reacts with Fe^{3+} resulting in Nb^{5+} and Fe^{2+} . However, if bismuth metal, Bi, is used instead of Zn, U^{6+} is the only ion present that will convert Bi metal to Bi^{3+} .

Rank the reduction potentials of all the redox couples mentioned above, from highest to lowest, using the information given. Justify your answers.

5-Step Method

1. Understand:

2. Analyse:

3. Plan:

4. Implementation

5. Evaluation:

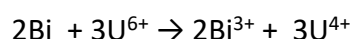
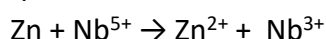
Note: This method is to find a way to solving the problem. The actual answer written should combine aspects of the analysis and the implementation, and link to equations and E° comparisons.

Worked Example 3: Titration (NZIC Scholarship Exam 2019)

The uranium in a 1.000 g sample of a uranium alloy was determined using the following procedure. The U containing alloy is dissolved in a mixture of hydrofluoric and sulfuric acids to give U^{6+} (in the form of UO_2^{2+}) which is then reacted with Zn to give U^{4+} . The resulting solution is reacted with excess Fe^{3+} , and the products titrated with $0.3750 \text{ mol L}^{-1} \text{ Ce}^{4+}(aq)$. In the titration, 20.69 mL of $Ce^{4+}(aq)$ was used. Unfortunately, if niobium is present in the alloy it will also be involved in the reactions used during the analysis. Niobium is present as Nb^{5+} , which reacts with Zn to give Nb^{3+} which also reacts with Fe^{3+} resulting in Nb^{5+} and Fe^{2+} . However, if bismuth metal, Bi, is used instead of Zn, only U^{6+} will convert Bi metal to Bi^{3+} .

Hence a second 1.000 g sample of the same alloy was analysed using bismuth in the place of zinc. This titration required 18.62 mL of the same Ce^{4+} solution.

Equations for the reactions are: $Zn + U^{6+} \rightarrow Zn^{2+} + U^{4+}$



Calculate the percentage by mass of uranium and niobium in the alloy.

$$M(U) = 238 \text{ g mol}^{-1}$$

$$M(Nb) = 92.9 \text{ g mol}^{-1}$$

5-Step Method

1. Understand:

2. Analyse:

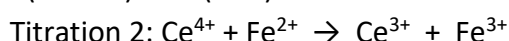
3. Plan:

4. Implement: Titration 1: $Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+}$

$$n(Ce^{4+}) = 0.3750 \text{ mol L}^{-1} \times 0.02069 \text{ L} = 0.007759 \text{ mol} \quad n(Fe^{2+}) = n(Ce^{4+}) = 0.007759 \text{ mol}$$



$$n(U + Nb) = \frac{1}{2}n(Fe^{2+}) = \frac{1}{2} \times 0.007759 = 0.003879 \text{ mol}$$



$$n(Ce^{4+}) = 0.3750 \text{ mol L}^{-1} \times 0.01862 \text{ L} = 0.0069825 \text{ mol} \quad n(Fe^{2+}) = n(Ce^{4+}) = 0.0069825 \text{ mol}$$

$$n(U) = \frac{1}{2}n(Fe^{2+}) = \frac{1}{2} \times 0.006983 = 0.003491 \text{ mol}$$

$$m(U) = n(U) \times M(U) = 0.003491 \text{ mol} \times 238 \text{ g mol}^{-1} = 0.831 \text{ g} \quad \% (U) = 83.1 \%$$

$$n(Nb) = n(U + Nb) - n(U) = 0.003879 \text{ mol} - 0.003491 \text{ mol} = 0.0003881 \text{ mol}$$

$$m(Nb) = 3.881 \times 10^{-4} \text{ mol} \times 92.9 \text{ g mol}^{-1} = 0.0361 \text{ g} \quad \% (Nb) = 3.61 \%$$

5. Evaluate All data used in the calculation (cannot assume that only Nb and U in sample so both values of M used). Calculation carried out using all significant figures given (mostly 4) but M only given to 3 significant figures so this is the number used for the answer.

In Scholarship exams titration questions may include:

- *Oxidation reduction reactions where the unknown is reacted to produce a species that is able to be easily analysed by titration e.g. iodometric titrations*
- *A precipitation reaction or a reaction involving complex ions*
- *A 'back titration' where a known excess of reagent is reacted with the unknown and the 'left over' reagent is then analysed by titration allowing the amount of the unknown present to be calculated.*

See Appendix 1

Worked Examples - Organic Chemistry (NZIC Scholarship Exam 2019)

- *Organic chemistry problems often require the identification of unknowns from a range the data. This may include molecular formulae, functional group reaction, infra-red, ^{13}C NMR or mass spectral data.*
- *Unpacking and summarizing the data is the key to solving the problem. Usually a **flow diagram/scheme** is a good starting point. The scheme can be annotated with chemistry ideas linked to the data provided.*
- *Sometimes a question requires knowledge outside Level 3 NCEA organic chemistry. In this case, extra information will be provided in a box early in the question.*
- *Once the problem has been solved and the structures determined, the final written answer needs to link the structures and the data supplied. The annotations in the flow diagram provide a basis for writing this justification.*

Worked Example 4: Organic Chemistry (NZEST Scholarship)

This problem illustrates the process for constructing & using a flow diagram but lacks spectroscopic data.

Compound A has the molecular formula C_6H_{12} and is optically active. Treatment of A with aqueous sulfuric acid gives the compounds B and C, both of which have the molecular $\text{C}_6\text{H}_{14}\text{O}$. B on treatment with acidic aqueous potassium dichromate gives D, molecular formula $\text{C}_6\text{H}_{12}\text{O}_2$. Compound C, on heating with concentrated sulfuric acid, gives A and E. A and E can be reduced by treatment with hydrogen in the presence of platinum catalyst to give a single compound F, molecular formula C_6H_{14} which does not exhibit optical activity. Draw structures of compounds A to F. Justify your answers.

5-step Process

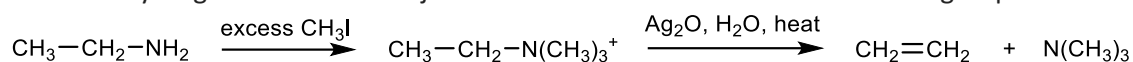
1. **Understand:** Give structural formulae for Compounds A to F
2. **Analyse:** Summarize data in a flow diagram. Identify reaction types and functional groups. Add notes about links to structures

Plan: Draw all possible isomers for A (C_6H_{12} , chiral, alkene with double bond at the end of the chain) then select the best answer based on the rest of the data. (Answer is available in the Appendix at the end of the resource.)

Worked Example 5: Organic Chemistry (NZIC Scholarship 2019)

INFORMATION:

The **Hofmann elimination** reaction involves conversion of an amine to an alkene. This reaction is possible only if there is a hydrogen on a carbon adjacent to the carbon attached to the amine group.



This is a two-step process. The amine is treated with excess iodomethane to form a quaternary ammonium iodide salt. Reaction of this salt with Ag_2O and H_2O gives a tertiary amine and an alkene as the organic products.

Compound **E** is an unknown organic compound. In order to determine its identity, the following reactions were carried out.

Compound **E** was hydrolysed under acidic conditions to give Compounds **F** and **G**. Compounds **F** and **G** are not cyclic and compound **F** is found to have a molecular ion peak, M^+ , at 118.0 m/z.

Compound **F** is chiral and reacts with one mole equivalent of $\text{NaOH}(aq)$ to give compound **H**. Reaction of Compound **F** with concentrated sulfuric acid, H_2SO_4 , gives four isomeric compounds, **I**, **J**, **K** and **L**, of which **J** and **K** are geometric isomers.

Compound **G** reacts with one mole equivalent of $\text{NaOH}(aq)$ to give Compound **M** which has a molecular ion peak, M^+ , at 87 m/z. Compound **M**, treated with an excess of iodomethane, CH_3I , followed by Ag_2O and water, gives Compounds **N** and **O**. Compounds **N** and **O** are reacted with cold potassium permanganate solution, $\text{KMnO}_4(aq)$, followed by acidified potassium dichromate solution, $\text{K}_2\text{CrO}_7/\text{H}^+$ to give Compounds **P** and **Q** respectively.

The ^{13}C NMR spectra are given for Compounds **E**, **F**, **I**, **J** and **K**, **L**, **M**, **P** and **Q** (See Appendix)

Determine the identity of Compounds **E** to **Q** and justify your answers by linking the structural formulae of the compounds to the spectra provided* and the information given above. (Annotated spectra can be used to support your justification).

* Spectra are provided in **Appendix 2** at the end of this resource

5-step Process

- Understand:** Give structural formulae for Compounds **E** to **Q** and justify answers linked to spectra and information given.
- Analyse:** The information given was first summarized in a flow diagram. Links between the information and the structures and functionality *blue*.

E → **F** + **G** (acidic hydrolysis) $M^+(\text{F})$ at 118.0 m/z. $M(\text{F}) = 118.8 \text{ g mol}^{-1}$ **F** is chiral

F + OH^- (1 equivalent) → **H** **F** has 1 acid group, **H** an acid salt

F with conc. H_2SO_4 → **I** + **J** + **K** + **L** (isomers) **J** and **K** are geometric isomers (*cis/trans*)

Elimination reaction products are alkenes - **F** has an -OH group in 2° or 3° position

G + OH^- → **M** $M^+(\text{M})$ at 87 m/z $M(\text{M}) = 87 \text{ g mol}^{-1}$ - odd number so **M** has an N (amine) so **G** is amine salt, **E** is an amide

M with CH_3I and Ag_2O^{**} → **N** and **O** - 2 products **M** is a 2° amine and **N** and **O** are alkenes

(**extra information needed here that is outside Level 3 knowledge - see question introduction)

N and **O** with KMnO_4 followed by $\text{H}^+/\text{Cr}_2\text{O}_7^{2-}$ alkene to alcohol (-OH added to double bond) and then alcohol to either ketone or acid.

From NMR data: **E** – 10 peaks = 10 C environments.

F – 5 peaks, 1 at 180 ppm for acid and 1 at 70 ppm for alcohol

I, **J** and **K** – 5 peaks including at 180 ppm for acid and peaks between 115 and 140 ppm for $\text{C}=\text{C}$

L – 5 peaks including 180 ppm – no peaks between 115 and 140 so not alkene - possibly cyclic ester?

M, **P** and **Q** – 5 peaks. For **P** 2 peaks at 200 ppm suggesting 2 ketone groups and **Q** peaks at 200 and 170 ppm suggesting acid and ketone.

Worked Example 6: Aqueous Chemistry (NZIC Scholarship Exam 2018)

Magnesium hydroxide, $\text{Mg}(\text{OH})_2$, is an insoluble solid. $K_s = 5.60 \times 10^{-12}$.

Calculate the volume of 2.00 mol L^{-1} hydrochloric acid, $\text{HCl}(\text{aq})$ that would need to be added to a 250 mL sample of a solution containing 0.100 mol L^{-1} of $\text{Mg}^{2+}(\text{aq})$ and 0.240 mol L^{-1} ethanolamine, $\text{HOCH}_2\text{CH}_2\text{NH}_2$, in order to prevent the precipitation of $\text{Mg}(\text{OH})_2(\text{s})$.

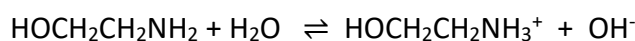
$$K_a(\text{HOCH}_2\text{CH}_2\text{NH}_3^+) = 3.16 \times 10^{-10}$$

5-Step Process

- Understand:** Calculate $V(\text{HCl})$ to prevent precipitation of $\text{Mg}(\text{OH})_2$ from the basic solution of $\text{HOCH}_2\text{CH}_2\text{NH}_2$. Need: $[\text{Mg}^{2+}][\text{OH}^-]^2 < K_s$. Adding H^+ to $\text{HOCH}_2\text{CH}_2\text{NH}_2$ will make a buffer solution.
- Analyse:** $K_s(\text{Mg}(\text{OH})_2) = 5.60 \times 10^{-12}$ $[\text{Mg}^{2+}] = 0.100 \text{ mol L}^{-1}$ $[\text{HOCH}_2\text{CH}_2\text{NH}_2] = 0.240 \text{ mol L}^{-1}$
 $K_a(\text{HOCH}_2\text{CH}_2\text{NH}_3^+) = 3.16 \times 10^{-10}$ $[\text{H}^+] = 2.00 \text{ mol L}^{-1}$ $V(\text{ethanolamine}) = 250 \text{ mL}$
 Need to calculate $[\text{OH}^-]$ needed for precipitation. Then calculate H^+ to be added to $\text{HOCH}_2\text{CH}_2\text{NH}_2$ solution to give this $[\text{OH}^-]$ (this will be a buffer solution)
- Plan:** Use $[\text{Mg}^{2+}][\text{OH}^-]^2 > K_s$ to calculate $[\text{OH}^-]$. Use K_a or K_b to find buffer composition that gives this $[\text{OH}^-]$. Hence find $V(\text{HCl})$ to prepare buffer from $\text{HOCH}_2\text{CH}_2\text{NH}_2$.

$$4. \text{ Implement: } [\text{Mg}^{2+}] = 0.100 \text{ mol L}^{-1} \quad [\text{OH}^-] = \sqrt{\frac{5.6 \times 10^{-12}}{0.100}} = 7.48 \times 10^{-6}$$

To prevent precipitation $[\text{OH}^-] < 7.48 \times 10^{-6}$



$$K_b = 3.16 \times 10^{-5} = \frac{[\text{OH}^-][\text{RNH}_3^+]}{[\text{RNH}_2]} = \frac{[\text{RNH}_3^+]}{[\text{RNH}_2]} = \frac{3.16 \times 10^{-5}}{7.48 \times 10^{-6}} = 4.23$$

In 250 mL 0.240 ethanolamine solution (RNH_2): $n(\text{RNH}_2) = 0.250 \text{ L} \times 0.240 \text{ mol L}^{-1} = 0.600 \text{ mol}$

For buffer: $n(\text{RNH}_2) + n(\text{RNH}_3^+) = 0.600$ and $n(\text{RNH}_3^+) = 4.23 n(\text{RNH}_2)$

$$n(\text{RNH}_2) + 4.23 n(\text{RNH}_2) = 0.600 \text{ so } n(\text{RNH}_2) = \frac{0.600}{5.23} = 0.115 \text{ mol}$$

$$n(\text{RNH}_3^+) = 4.23 n(\text{RNH}_2) = 4.23 \times 0.115 \text{ mol} = 0.485 \text{ mol}$$

$$V(\text{HCl}) = \frac{n}{c} = \frac{0.485 \text{ mol}}{2.00 \text{ mol L}^{-1}} = 0.2425 \text{ L} = 24.3 \text{ mL}$$

- Evaluate:** Volume of HCl calculated. Answer given to 3 significant figures as data provided is a mix of 3 and 4 significant figures.

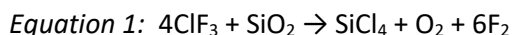
PRACTICE EXERCISES – PROBLEM SOLVING

These exercises are from past NZIC Scholarship Papers. Other practice opportunities are available from past NZQA Scholarship exams that can be accessed from <https://www.nzqa.govt.nz/qualifications-standards/awards/new-zealand-scholarship/scholarship-subjects/scholarship-chemistry/>

Answers are available in **Appendix 3** at the end of this resource.

Q1. Electron Transfer (NZIC 2021)

Chlorine trifluoride, ClF_3 , is one of the most reactive substances known. ClF_3 gas reacts with sand, SiO_2 , to give three products that are gases. Two of the product gases are elements that arise by electron transfer between two atoms in the reactants. The third product is a compound. Three possible equations for the reaction are given below.

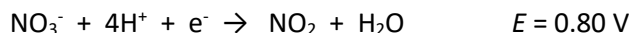
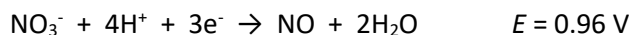


Choose the equation that is consistent with the information given and justify your choice, including descriptions of the electron transfers involved in the reaction.

Q2. Electrode Potentials + Heat of Reaction (NZIC 2017)

50.0 g of gold is dissolved in aqua regia, a mixture of concentrated nitric and hydrochloric acids. The resulting 1.20 L of solution has a pH of -1. This solution is neutralized by adding 1.00 mol L^{-1} sodium hydroxide solutions $\text{NaOH}(\text{aq})$.

- (i) Use the electrode potential data below to explain why aqua regia will dissolve up gold when it is not possible to dissolve it up in only nitric or hydrochloric acids and suggest the likely reaction products.



- (ii) Determine whether cooling is needed, during the neutralization process to prevent the solution from boiling.

$$\Delta H(\text{neutralization}) = -55.90 \text{ kJ mol}^{-1} \quad M(\text{H}_2\text{O}) = 18.02 \text{ g mol}^{-1} \quad d(\text{H}_2\text{O}) = 1.00 \text{ g mL}^{-1}$$

$$\text{Heat capacity of water, } C_m = 74.5 \text{ J mol}^{-1} \text{ } ^\circ\text{C}^{-1}$$

Q3. Thermochemistry (NZIC 2018)

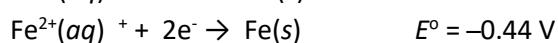
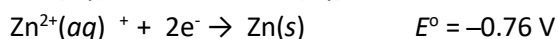
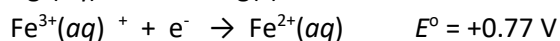
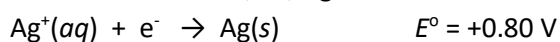
The heads of “strike-anywhere” matches contain a mixture of phosphorus sesquisulfide, P_4S_3 , and potassium chlorate, KClO_3 . When the match is struck across a rough surface the heat of friction is sufficient to ignite the phosphorus sesquisulfide. The products of this reaction are phosphorus(V) oxide, P_4O_{10} , and sulfur dioxide, SO_2 . At the same time the potassium chlorate decomposes to provide sufficient oxygen for the combustion of the P_4S_3 .

Calculate the standard enthalpy change for the combustion reaction described above using the standard enthalpies of formation given below.

$\Delta_f H^\circ$	KCl (s)	KClO ₃ (s)	SO ₂ (g)	P ₄ S ₃ (s)	P ₄ O ₁₀ (s)
kJ mol^{-1}	-436.7	-397.7	-296.8	-154.0	-2948

Q4. Electrode Potentials (NZIC 2018)

A solution containing ferrous ions, $\text{Fe}^{2+}(\text{aq})$, is to be kept as pure as possible and free of ferric ions, $\text{Fe}^{3+}(\text{aq})$. Evaluate the metals, Fe, Ag and Zn for their usefulness in keeping this solution pure.



Q5. Aqueous Chemistry (NZIC 2018)

Ethanolamine, $\text{HOCH}_2\text{CH}_2\text{NH}_2$, is a weak organic base. $K_a(\text{HOCH}_2\text{CH}_2\text{NH}_3^+) = 3.16 \times 10^{-10}$

Sketch a curve to show how the pH changes during the titration of 20.0 mL of 0.240 mol L⁻¹ ethanolamine solution, titrated with 0.120 mol L⁻¹ hydrochloric acid, $\text{HCl}(\text{aq})$.

Include on your graph the pH before the addition of HCl, at the addition of 10 mL of HCl, at the equivalence point of the reaction and at the addition of 10 mL of HCl past the volume needed for the equivalence point. Show your working for all calculations.

Q6. Volumetric Analysis (NZIC 2018)

Chrome plating is a technique of electroplating a thin layer of chromium onto a metal object. It requires a non-ferrous solution of chromium(III) ions (usually in acidic solution) yet the most common source of chromium is the mineral chromite which has the formula, FeCr_2O_4 . To prepare a non-ferrous solution of chromium (III), the chromite is oxidised in air with molten sodium hydroxide to give sodium chromate, Na_2CrO_4 , which is then extracted with water, precipitated and reduced with carbon to give chromium(III) oxide, $\text{Cr}_2\text{O}_3(\text{s})$. The chromium oxide is dissolved in sulfuric acid to generate the desired solution. In order to determine the chromium content of a chromite ore sample the following procedure was carried out.

A 5.000 g sample of a chromite ore was oxidised to sodium chromate, Na_2CrO_4 , as described above. The product, in a sodium hydroxide solution, was quantitatively collected in a 1.000 L volumetric flask and made up to the mark with water. A 25.00 mL sample of this solution was transferred into a conical flask containing a buffer solution and approximately 100-150 mL of distilled water. Approximately 3 g of solid potassium iodide, KI, was added resulting in the formation of iodine and chromium(III) ions. The iodine formed in the reaction was then titrated with 0.1000 mol L⁻¹ potassium thiosulfate solution, $\text{K}_2\text{S}_2\text{O}_3(\text{aq})$ to give iodide ions and tetrathionate ions, $\text{S}_4\text{O}_6^{2-}$. The titration was repeated resulting in the following titre volumes: 23.64, 23.16, 23.20 and 23.02 mL.

Write balanced equations for the reactions involved in the preparation of a chromium(III) solution from chromite, calculate the percentage chromium, by mass, in the ore sample. $M(\text{FeCr}_2\text{O}_4) = 223.8 \text{ g mol}^{-1}$

Q7. Electrode Potentials (NZIC 2020)

Four unlabelled bottles contain 1 mol L⁻¹ solutions of the salts sodium chloride, NaCl, sodium bromide, NaBr, sodium iodide, NaI, and sodium nitrate, NaNO_3 .

Devise a procedure for identifying the solutions using only the solutions and the reagents listed below.

Justify your answer linked to the standard electrode potential data given and include expected observations and relevant equations for any reactions that will occur.

Reagents available: 1 mol L⁻¹ H_2SO_4 , MnO_2 powder

Redox reaction	Standard electrode potentials / V
$\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$	1.36
$\text{Br}_2 + 2\text{e}^- \rightarrow 2\text{Br}^-$	1.07
$\text{I}_2 + 2\text{e}^- \rightarrow 2\text{I}^-$	0.54
$\text{MnO}_2 + 2\text{e}^- + 4\text{H}^+ \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$	1.22
$\text{NO}_3^- + \text{e}^- + 2\text{H}^+ \rightarrow \text{NO}_2 + 2\text{H}_2\text{O}$	0.80

Q8. Thermochemistry (NZIC 2020)

A straight chain organic compound, **Y**, consists of carbon, hydrogen and oxygen. Compound **Y** is stable.

Burning 3.00 g of Compound **Y** releases 46.32 kJ of energy.

Compound **Y** does not contain any O-O single bonds.

The following data is available:

$$\Delta_f H(\text{Compound X}) = -344.2 \text{ kJ mol}^{-1}$$

$$\Delta_c H(\text{Compound X}) = -926.4 \text{ kJ mol}^{-1}$$

$$\Delta_f H(\text{CO}_2(g)) = -393.5 \text{ kJ mol}^{-1}$$

$$\Delta_f H(\text{H}_2\text{O}(\ell)) = -241.8 \text{ kJ mol}^{-1}$$

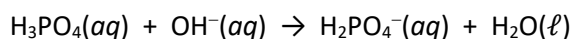
Determine the molecular formula for Compound **Y** and justify your answer linked to the data provided.

Q9. Aqueous (NZIC 2020)

When phosphoric acid solution, $\text{H}_3\text{PO}_4(aq)$, is titrated against sodium hydroxide solution, $\text{NaOH}(aq)$, the neutralisation of each of the acidic protons can be considered independently.

Sodium hydroxide solution, $\text{NaOH}(aq)$, with a concentration of 2.0 mol L^{-1} , is added to 10.0 mL of 2.5 mol L^{-1} phosphoric acid solution, $\text{H}_3\text{PO}_4(aq)$.

(i) Sketch the titration curve for the addition of 0 to 10 mL of $\text{NaOH}(aq)$. The equation for the reaction is:



Show your working for at least three data points that you use for the graph

(ii) Calculate the mass of $\text{NaOH}(s)$ that must be mixed with 3.601 g of phosphoric acid, $\text{H}_3\text{PO}_4(\ell)$, and sufficient water to give 250.0 mL of solution with a pH of 2.3.

$$M(\text{NaOH}) = 40.0 \text{ g mol}^{-1} \quad M(\text{H}_3\text{PO}_4) = 98.0 \text{ g mol}^{-1} \quad \text{p}K_{a1}(\text{H}_3\text{PO}_4) = 2.14$$

Q10. Aqueous Chemistry (NZIC 2021)

A precipitate is observed when sodium sulfide, $\text{Na}_2\text{S}(s)$, is added to a solution that contains $0.0099 \text{ mol L}^{-1}$ silver nitrate, $\text{AgNO}_3(aq)$, and 0.021 mol L^{-1} copper sulfate, $\text{CuSO}_4(aq)$. The concentration of the first ion to precipitate is decreased as its precipitate forms.

$$K_s(\text{Ag}_2\text{S}) = 6.3 \times 10^{-50} \quad K_s(\text{CuS}) = 6.0 \times 10^{-37}$$

(i) Determine which of the sulfides, Ag_2S or CuS , precipitates first.

(ii) Calculate the concentration of the first ion to precipitate when the second ion begins to precipitate.

Q11. Thermochemistry + Redox (NZIC 2021)

Two displacement reactions were carried out to determine the relative reduction potentials of magnesium, copper and silver metal.

In the first experiment, excess magnesium powder was added to 100 mL of 1.00 mol L^{-1} copper(II) nitrate solution. The temperature of the calorimeter and solution rose from $19.5 \text{ }^\circ\text{C}$ to $39.6 \text{ }^\circ\text{C}$.

In the second experiment, excess copper powder was added to 100 mL of 0.500 mol L^{-1} silver nitrate solution. The temperature of the calorimeter and the solution rose from $19.5 \text{ }^\circ\text{C}$ to $20.9 \text{ }^\circ\text{C}$.

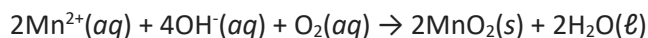
The heat capacity of the calorimeter is $2000 \text{ J }^\circ\text{C}^{-1}$ and the specific heat capacity of the copper(II) nitrate and silver nitrate solutions should be taken as $4.2 \text{ J }^\circ\text{C}^{-1} \text{ mL}^{-1}$

(i) Calculate the enthalpy of reaction, $\Delta_r H_z$ in each experiment and use your answers to determine $\Delta_r H$ for the reaction between magnesium metal and silver nitrate solution.

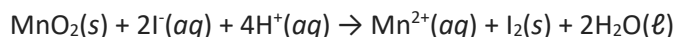
(ii) Identify the strongest reductant and the strongest oxidant in the reactions, and, on the basis of this, which couple, Mg^{2+}/Mg , Cu^{2+}/Cu or Ag^+/Ag , has the most negative electrode potential. Justify your answer.

Q12. Volumetric Analysis (NZIC 2021)

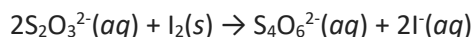
Biological Oxygen Demand (BOD) is the amount of dissolved O_2 needed by aerobic biological organisms to break down organic material present in a water. The BOD value is commonly expressed in milligrams of O_2 consumed per litre of sample during 5 days of incubation at $20^\circ C$. The Winkler method is used to test for dissolved oxygen. In this test an excess of a manganese(II) salt, and iodide, I^- , and hydroxide, OH^- , ions are added to a water sample resulting in the precipitation of white $Mn(OH)_2$.



This precipitate then reacts with the dissolved oxygen to give a brown precipitate of manganese dioxide, MnO_2 , which reacts with the added iodide, in the presence of sulfuric acid:

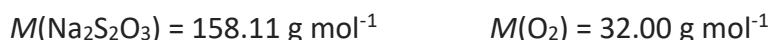


The amount of dissolved oxygen is determined by titrating the resulting iodine against a standardised solution of thiosulfate, $S_2O_3^{2-}$.



To determine the BOD of water from a local stream, two samples were collected from the same location. The first sample was treated at the site to fix the amount of dissolved oxygen by adding aqueous solutions of manganese sulfate, potassium iodide and potassium hydroxide, followed by concentrated sulfuric acid. In the laboratory, 100.0 mL portions of the treated water were titrated against freshly prepared sodium thiosulfate solution, $Na_2S_2O_3(aq)$, and took, on average, 32.43 mL to react with the iodine. The sodium thiosulfate solution was prepared by dissolving 0.4743 g of solid in sufficient water to make 250.0 mL of solution. The second sample of stream water was incubated in the laboratory for 5 days, after which it was treated, as described above, to fix the amount of dissolved oxygen. 100.0 mL portions were then titrated against freshly prepared sodium thiosulfate solution (0.4825 g of solid in sufficient water to make 250.0 mL of solution) and took, on average, 12.70 mL to react with the iodine.

Calculate the BOD for this water at this site in the stream.



Q13. Analysis and Organic (NZIC 2021)

This question is concerned with an organic acid (dicarboxylic acid), H_2X .

(i) Consider the following data collected about acid, H_2X .

- The acid is not branched and is not cyclic.
- Combustion analysis gives the percentage composition: C, 31.98%; H, 4.00%; O, 63.96%.
- In a titration experiment, 250.0 mL of a solution of the acid H_2X was prepared by dissolving 1.85 g in water in a volumetric flask. When 20.00 mL of this solution was titrated against $0.1300 \text{ mol L}^{-1}$ KOH solution, 15.17 mL was required to reach the final equivalence point.

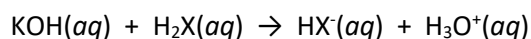
The equation for the titration reaction is:



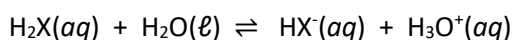
- In a separate experiment, 1.00 g of the acid, H_2X , was dissolved in a suitable solvent and reacted with thionyl chloride, $SOCl_2$, to generate 1.1939 L of the combined gases SO_2 and HCl , produced in a 1:1 ratio. (Assume that 1 mol of any gas occupies 22.4 L)
- The ^{13}C NMR of the dicarboxylic acid has signals at 73 ppm and 175 ppm.

Determine the structure of the acid. Show your working for all calculations and justify your final answer linked to the data provided.

(ii) After the addition of 2.19 mL of $KOH(aq)$ in the titration described in part (i), the titration mixture had pH of 2.50. The equation for the reaction occurring in the flask up to this point in the titration is:



Calculate pK_{a1} of acid H_2X . K_{a1} is the equilibrium constant for the reaction:



Q14 Organic (NZIC 2018)

Compound **A** ($M^+ = 172$ m/z) reacts with dilute sulfuric acid to give compounds **B** and **C**. One of these has strong absorptions in the infrared spectrum at 1720 cm^{-1} and 3200 cm^{-1} . The other has a strong absorption at 3350 cm^{-1} . Compound **C** ($M^+ 86$ m/z) is converted to compound **D** by reacting with concentrated sulfuric acid followed by treatment with hydrogen gas in the presence of a metal catalyst. Reaction of compound **C** with acidified potassium dichromate produces compound **E**. Reaction of Compound **B** with concentrated sulfuric acid results in compounds **F** and **G**, which are constitutional isomers. Reaction of compounds **F** and **G** with hot, concentrated acidified potassium permanganate, $\text{MnO}_4^-/\text{H}^+$, results in compounds **H** and **I** respectively with both reactions generating bubbles of gas that turn lime water cloudy. Compounds **H** and **I** react with 2 and 1 mol equivalents of aqueous sodium hydroxide, $\text{NaOH}(\text{aq})$, respectively.

^{13}C NMR spectra are provided below for all of Compounds **A to I** (See Appendix 2)

INFORMATION

The reaction of an alkene with acidified potassium permanganate, KMnO_4/H^+ , results in the breaking of the double bond. The reaction products depend on the number of hydrogen atoms present on each of the double-bonded carbon atoms. If there are no hydrogen atoms on a double bonded carbon atom, a ketone is formed at this carbon. When one hydrogen atom is present on a double bonded carbon atom, a carboxylic acid is formed and when there are two hydrogen atoms present, carbon dioxide gas is produced.

Oxalic acid (ethanedioic acid) also reacts with warmed, acidified, potassium permanganate to give two mole equivalents of CO_2 gas.

Give the structural formulae of Compounds **A to I**, and justify our answer, including annotating the spectra provided to indicate any significant peaks that assist in your decisions about the identity of the compounds.

The following question provide practice at determining the structures of organic molecules from data provided but do not include spectroscopy data.

Q15 Organic (NZEST Scholarship)

An optically active compound **A**, $\text{C}_7\text{H}_{12}\text{O}_2$, when treated with H_2/Pt gave compound **B**, $\text{C}_7\text{H}_{14}\text{O}_2$, which is not optically active. Refluxing **B** with $\text{NaOH}(\text{aq})$ gave compound **C** ($\text{C}_5\text{H}_{12}\text{O}$) and **D** ($\text{C}_2\text{H}_3\text{O}_2\text{Na}$). Both **C** and **D** are optically inactive. **C** gives **E** ($\text{C}_5\text{H}_{10}\text{O}$) on treatment with acidified potassium dichromate. **E** does not react with Benedict's solution or ammoniacal silver nitrate. **C** is converted by concentrated H_2SO_4 into a mixture of two stereoisomers, **F** and **G** (C_5H_{10}).

Give structural formulae for compounds **A – G**, and the systematic names for compounds **C– G**.

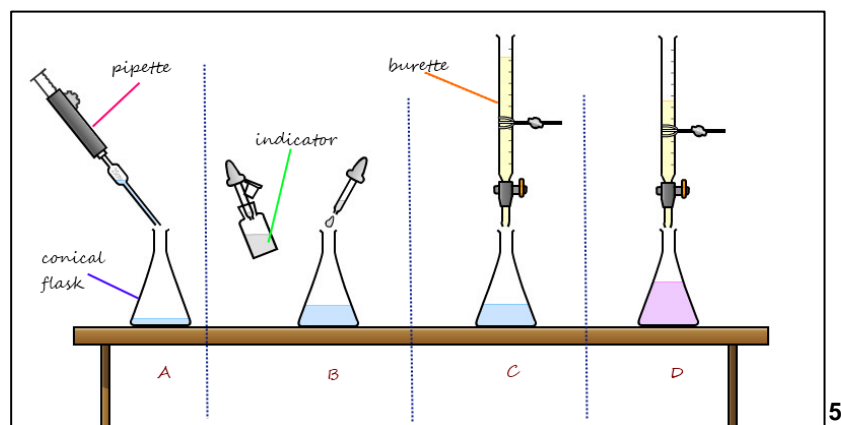
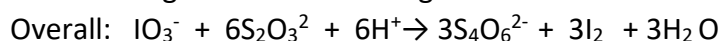
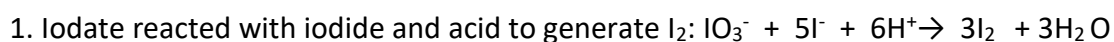
APPENDIX 1: TITRATION NOTES

- Titrations can be performed when a reaction goes to completion as long as the end-point can be observed.
- Useful reactions include: acid-base, redox, precipitation, complexometric
- More sophisticated titrations may involve: multiple reactions where the titration is carried out on the product of a previous reaction involving the unknown, or a back titration.
- Skills from AS2.2 include: making standard solutions, carrying out titrations, calculating concentrations including for diluted solutions, stoichiometric relationships, understanding how to ensure accurate results

Redox reactions often have convenient end points because of colour of reactants is different from products.

- For example, the permanganate ion is particularly convenient because the appearance or disappearance of its intense colour is an ideal criterion for the end-point of the reaction
e.g. $6\text{H}^+ + 2\text{MnO}_4^- + 5(\text{COOH})_2 \rightarrow 10\text{CO}_2 + 2\text{Mn}^{2+} + 8\text{H}_2\text{O}$
- Iodine is widely used as a reagent for the volumetric determination of strong reductants such as tin(II) chloride (SnCl_2), and thiosulfate ($\text{S}_2\text{O}_3^{2-}$). A starch indicator is used to determine the end point of the reaction. Starch is blue in the presence of iodine.
- However, neither iodine nor sodium thiosulfate are suitable as primary standards so it is necessary to generate the iodine from a suitable primary standard and then titrate the iodine produced against the unknown solution. For example, to standardise a solution of sodium thiosulfate, $\text{Na}_2\text{S}_2\text{O}_3$, iodine can be generated by reaction with a known volume of a potassium iodate solution, $\text{KIO}_3(\text{aq})$ and the resulting iodine titrated against the $\text{Na}_2\text{S}_2\text{O}_3$. KIO_3 is a 'good' primary standard

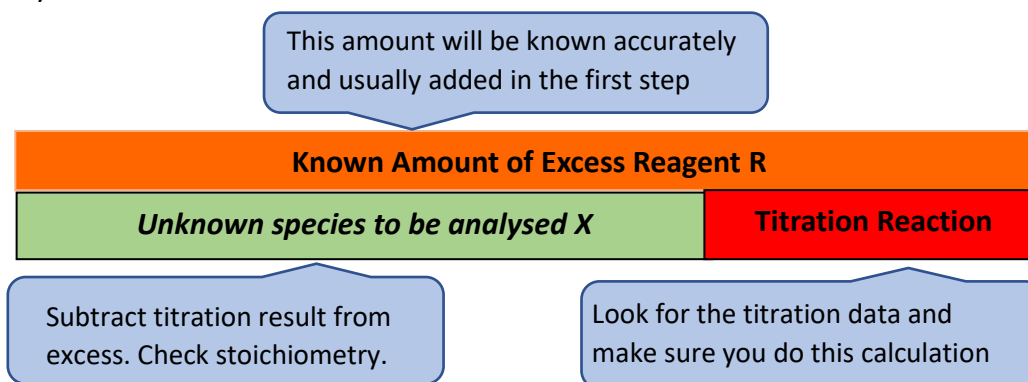
Reactions are:



⁵ <https://practical-chemistry.com/practical-work/chemistry/quantitative-chemistry/titration-acid-base-simple/>

BACK TITRATIONS

- Back titrations are used when reactions are slow OR there are competing reactions OR there is no easy way to detect the end point
- A measured amount of a reagent **R**, that will react with a sample of an unknown solution, **X**, is added in excess (more than is needed to completely react with the sample) and all at once.
- The amount of unreacted reagent **R** is determined by titrating with a standard solution.
- The amount of unknown **X** in the sample is calculated from the difference in the amount of **R** added and the amount left after the reaction, using stoichiometric principles.
- The following diagram shows the relationship between the titration and the unknown sample that is to be analysed.



Worked example Back Titration

25.00 mL of 0.100 mol L⁻¹ NaOH were added to 10.00 mL of a solution of NH₄Cl. 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 with 0.0521 mol L⁻¹ H₂SO₄. 15.50 mL of H₂SO₄ were required for complete reaction. Calculate the concentration of the NH₄Cl solution.

Answer

Initial reaction: NH₄Cl + NaOH → NH₃ + H₂O + NaCl

$$n(\text{NaOH})_{\text{added}} = c \times V = 0.100 \text{ mol L}^{-1} \times 2.50 \times 10^{-2} \text{ L} = 2.50 \times 10^{-3} \text{ mol}$$

Titration reaction: 2NaOH + H₂SO₄ → 2H₂O + Na₂SO₄

$$n(\text{H}_2\text{SO}_4) = 0.0155 \text{ L} \times 0.0521 \text{ mol L}^{-1} = 8.0755 \times 10^{-4} \text{ mol}$$

$$n(\text{NaOH})_{\text{unreacted}} = 2 \times 8.0755 \times 10^{-4} = 1.615 \times 10^{-3} \text{ mol}$$

Subtract unreacted NaOH from $n(\text{NaOH})_{\text{added}}$ to NH₄Cl solution (excess)

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

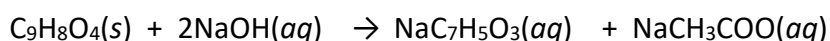
Calculation $c(\text{NH}_4\text{Cl(aq)})$: NH₄Cl + NaOH → NH₃ + H₂O + NaCl

$$n(\text{NaOH})_{\text{reacted}} = n(\text{NH}_4\text{Cl}) = 0.88 \times 10^{-3} \text{ mol}$$

$$\text{Original NH}_4\text{Cl sample is 10.00 mL} \quad c(\text{NH}_4\text{Cl}) = 0.88 \times 10^{-3} \text{ mol} / 0.0100 \text{ L} = 0.088 \text{ mol L}^{-1}$$

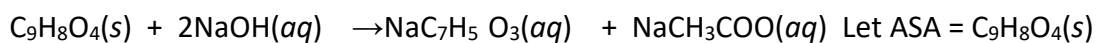
Back Titration Practice Problem (adapted from NZIC 2020)

The mass of acetylsalicylic acid, $C_9H_8O_4$, in an aspirin tablet can be determined by refluxing the tablet with a known amount of excess aqueous sodium hydroxide, $NaOH(aq)$, to hydrolyse the ester group. The unreacted sodium hydroxide is then titrated with a standard solution of hydrochloric acid, $HCl(aq)$. The equation for the reaction is:

**Method:**

One aspirin tablet was ground up and added to 20.00 mL of $0.4000 \text{ mol L}^{-1}$ sodium hydroxide solution, $NaOH(aq)$. The mixture was heated under reflux for 15 minutes. The resulting solution was transferred quantitatively to a 250.0 mL volumetric flask and diluted to the mark. A 20.00 mL sample of the diluted solution was titrated with $0.01500 \text{ mol L}^{-1}$ HCl using phenolphthalein as indicator. The average titre was 13.31 mL. Determine the mass of acetylsalicylic acid (ASA) initially present in the tablet.

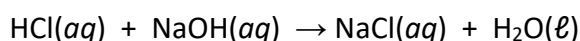
$$M(\text{acetylsalicylic acid}) = 180.16 \text{ g mol}^{-1}.$$

Answer

$$V(\text{aspirin reaction}) = 250.0 \text{ mL}$$

$$n(OH)_{\text{added}} = 0.02000 \times 0.4000 = 8.000 \times 10^{-3} \text{ mol (in 250 mL)}$$

$$\text{Titration (after hydrolysis) } V = 20.00 \text{ mL}$$



$$n(HCl) = 0.01331 \times 0.01500 = 1.997 \times 10^{-4} \text{ mol} = n(NaOH)_{\text{left}}$$

$$\text{In 250.0 mL } n(NaOH)_{\text{left}} = (0.2500 \text{ mL} / 0.02000 \text{ mL}) \times 1.997 \times 10^{-4} \text{ mol} = 2.496 \times 10^{-3} \text{ mol}$$

Amount of NaOH reacted with ASA

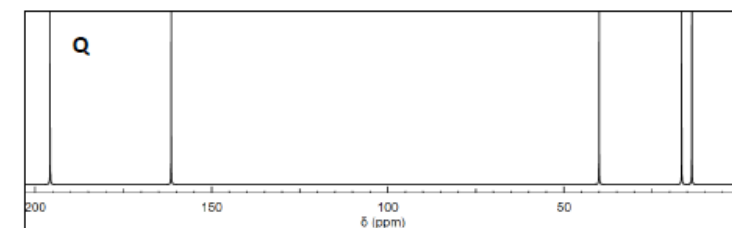
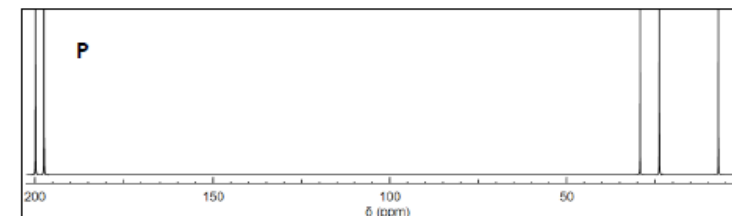
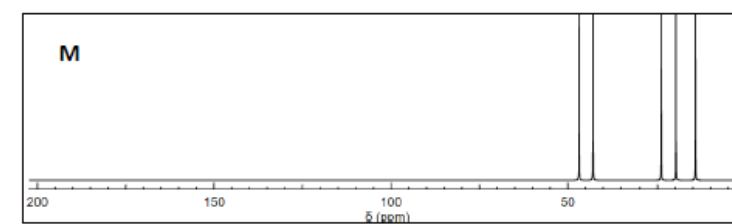
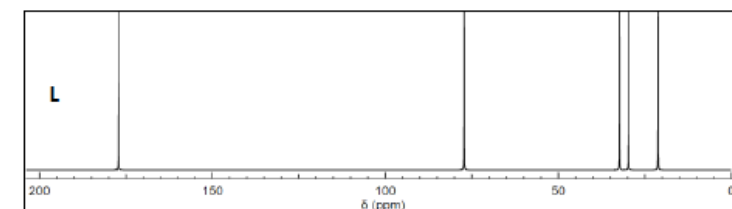
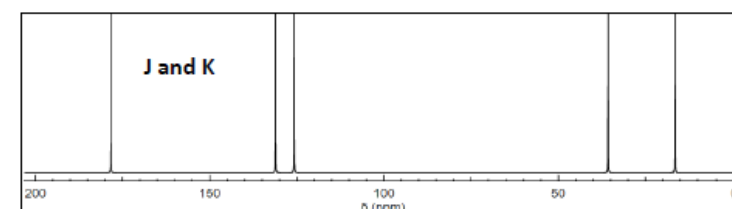
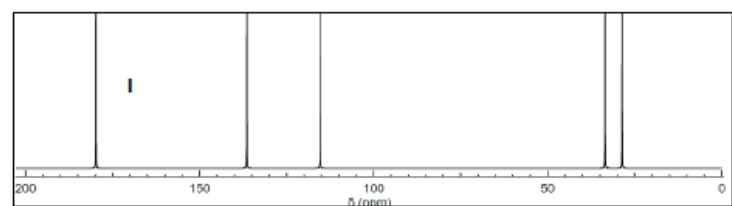
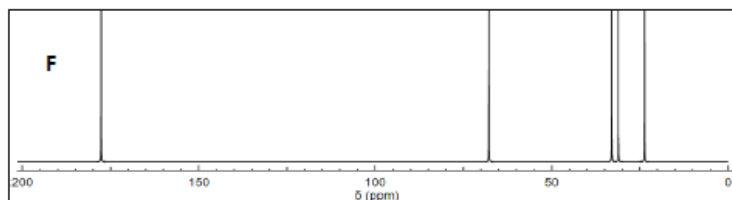
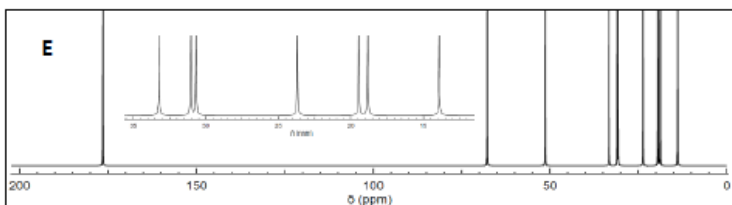
$$n(NaOH)_{\text{reacted}} = n(OH)_{\text{added}} - n(NaOH)_{\text{left}} = 8.000 \times 10^{-3} \text{ mol} - 2.496 \times 10^{-3} \text{ mol} = 5.504 \times 10^{-3} \text{ mol}$$

$$\text{From initial reaction equation: } n(\text{ASA}) = \frac{1}{2}n(NaOH) = 2.752 \times 10^{-3} \text{ mol}$$

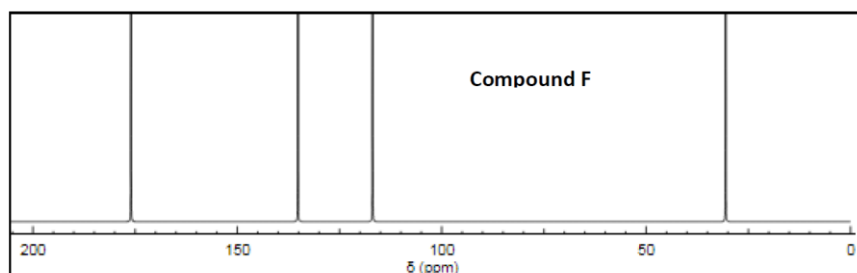
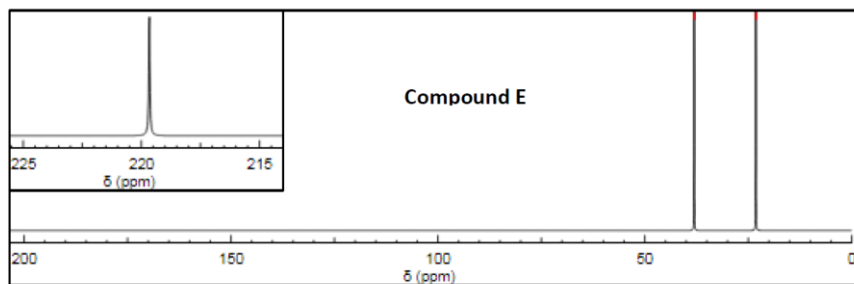
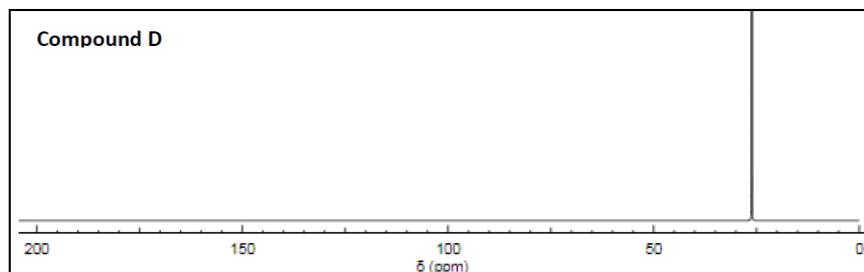
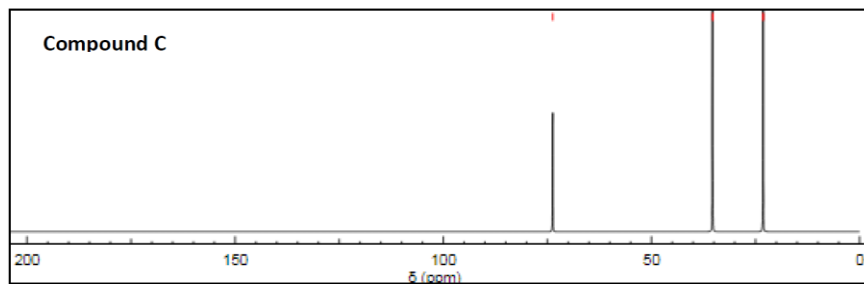
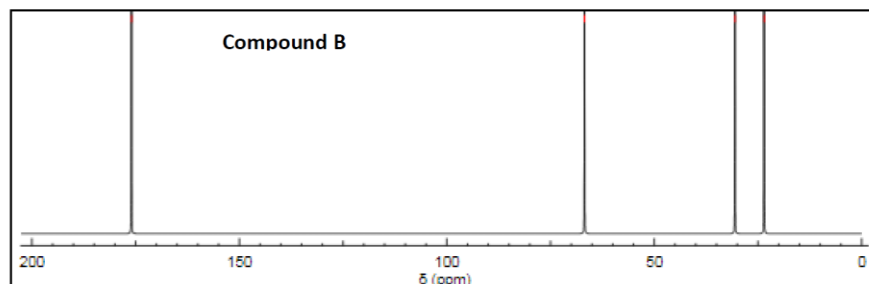
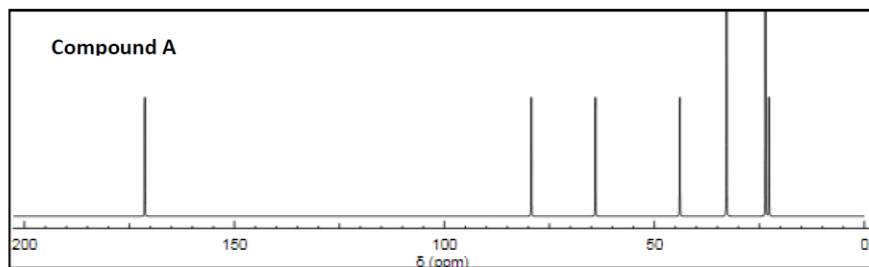
$$m(\text{ASA}) = 2.752 \times 10^{-3} \text{ mol} \times 180.16 \text{ g mol}^{-1} = 0.4958 \text{ g}$$

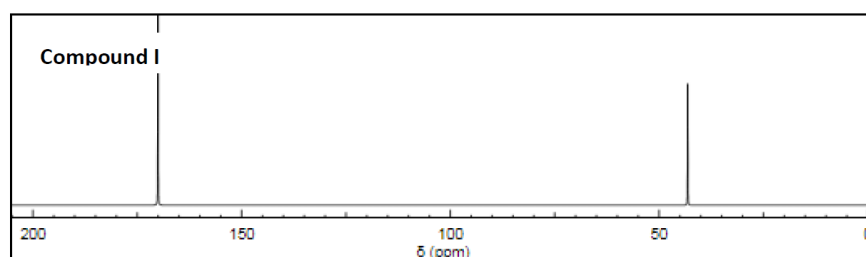
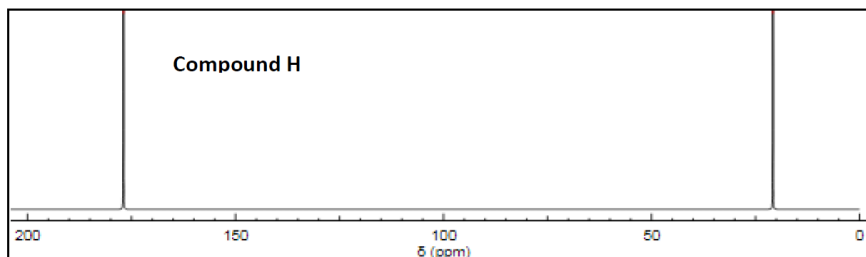
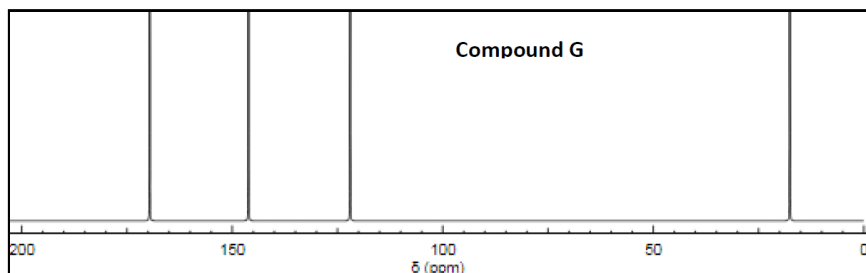
APPENDIX 2 -¹³C NMR Spectra

Problem Solving Worked Example 4

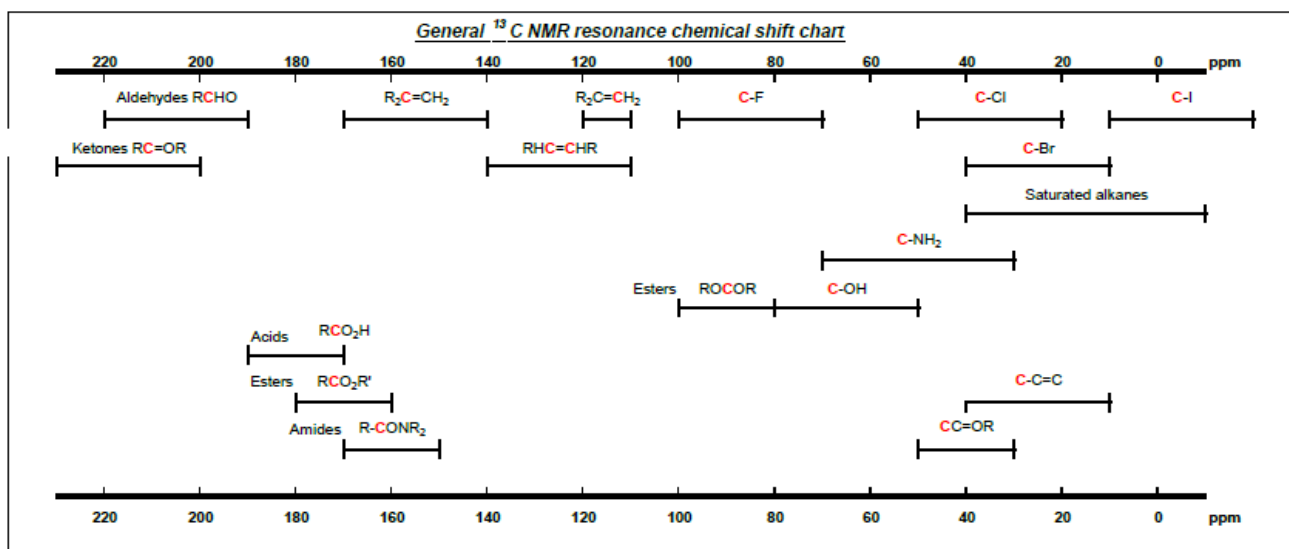


Problem Solving Practice Exercise 14





¹³C NMR RESONANCE SHIFTS



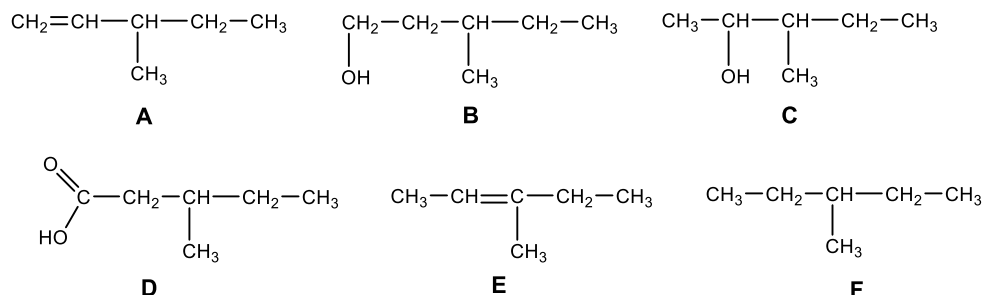
APPENDIX 3 - ANSWERS

Problem Solving Worked Example 5

A is optically active. Reacts with $\text{H}_2\text{O}/\text{H}^+$ to produce two alcohols, B and C. Hence A is an unsymmetrical alkene. A also reacts with H_2/Pt to produce a non-chiral molecule.

B is oxidised with $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$. There is an increase in the number of O atoms suggesting an acid is produced. Hence B is a primary alcohol.

C, an alcohol, is eliminated by concentrated H_2SO_4 to produce to alkene products. Hence C is an un symmetrical secondary alcohol



Problem Solving Worked Example 5 - discussion

Links between structures and information provided:

The ^{13}C NMR spectrum for **E** has 10 signals, which means 10 distinct carbon environments. The corresponding spectra for **F** and **M** show 5 signals suggesting there is no symmetry to consider due to branching.

The initial hydrolysis reaction implies **E** is either ester or amide. Since both **F** and **G** (products of the hydrolysis reaction) react with NaOH, **E** must be an amide (ester would produce acid and alcohol which will not react with NaOH). There is also evidence of an N atom in Compound **M** (see below).

The ^{13}C NMR for Compound **F** has peaks at 180 ppm for an acid and at 70 ppm for an alcohol. The M^+ peak for **F** is 118 suggesting there is a 5 carbon chain when the -OH and -COOH groups in the molecule are taken into account.

Reacting **F** with concentrated H_2SO_4 produces 4 products. From the ^{13}C NMR for Compounds **I** and **J** (and **K** since it is a geometrical isomer of **J**) there are peaks between 115 and 140 ppm for C=C, so there are 3 elimination products suggesting **F** contains a secondary alcohol. The ^{13}C NMR for **L** has no evidence for C=C suggesting that the removal of water has resulted in the formation of a cyclic ester as indicated by the C=O peak at 175 ppm and the C-O peak at 78 ppm.

The reaction of **G** with NaOH produces **M** which has an M^+ peak with an odd number implying the presence of an N atom in the molecule. Hence **G** will be the protonated amine (from the hydrolysis reaction) and **M** the amine. Compound **M** has 5 signals in the ^{13}C NMR and after the Hofmann reaction gives 2 products so (see (a)) is likely a secondary amine. The products **N** and **O** will be alkenes

The ^{13}C NMR spectrum for **P** shows two signals around 200 ppm typical of a C=O group (aldehyde or ketone) and there is no peak at around 180 ppm which would be expected for an acid. This supports **N** as pent-2-ene and **O** as pent-1-ene - oxidation produces a terminal -OH group that is further oxidised to a carboxylic acid (signal in the ^{13}C NMR at 165 ppm) so **Q** has acid and ketone.