Week 1

CHEM1102 Worksheet 1: Introduction to Carbon Chemistry

Model 1: Bonding in Organic Molecules

Here is a partial periodic table. The shaded elements are the focus of organic chemistry. The number above each column indicates the **number of covalent bonds that an element in that column will typically make**.

1	2	0	0	0	0	0	0	0	0	0	0	3	4	3	2	1	0
H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Sr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

Figure 1. Partial Periodic Table

Critical thinking questions

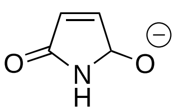
1. How many bonds does carbon typically make? Draw a molecule composed of only C and H with exactly <u>two C atoms</u> and <u>some number of H atoms</u> in which both C and H are making their typical number of bonds.

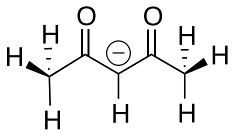
2. Nitrogen typically forms three bonds. Given that each bond involves two electrons, and nitrogen obeys the octet rule, how many valence electrons are unaccounted for?

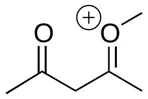
3. Free electrons, like bonding electrons, take up space. How does this lone pair of electrons affect the shape of a molecule like NH_3? (Try to draw it in 3-D.)

Sometimes atoms will form more or less than their typical number of bonds. In these cases the atoms are said to carry a formal charge (either + or -).

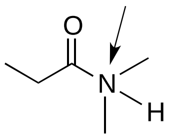
4. Here are a few examples. How does the typical number of bonds formed and the actual number of bonds formed relate to the formal charge? Can you write this as a formula[*]?

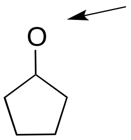


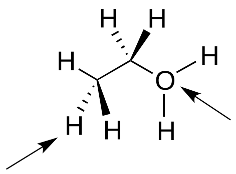




5. Determine the formal charges on the atoms indicated below.







Remember: formal charges must ALLWAYS be indicated when you are drawing molecular structures.

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[*] This formula works well for heteroatoms (atoms other than C and H) but care must be taken when determining the formal charge on C, as we will see next week.

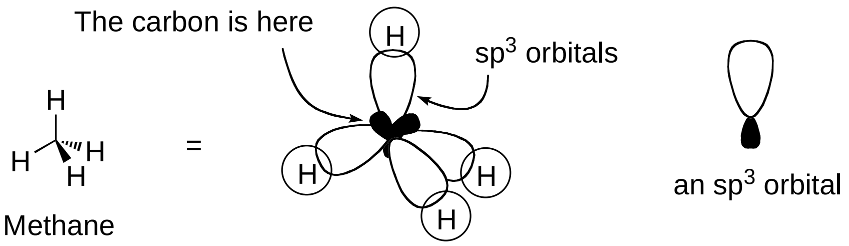
Model 2: Hybridization

There's an apparent paradox in the bonding of carbon:

a) The valence electrons of a carbon atom sit in atomic orbitals that are different in energy (what are they?)
b) The tetrahedral carbon in methane has four identical bonds to H's

So it seems like the electrons are different, but the bonds are the same..?

We resolve this by saying that the carbon orbitals (and the electrons in them) *mix* to form new orbitals. So the 2s and the three 2p orbitals can mix together to form four orbitals that are all the same. These overlap with the hydrogen 1s orbitals to form four identical bonds. This kind of orbital mixing, to produce hybrid orbitals, is known as ***hybridization***.



Critical thinking questions

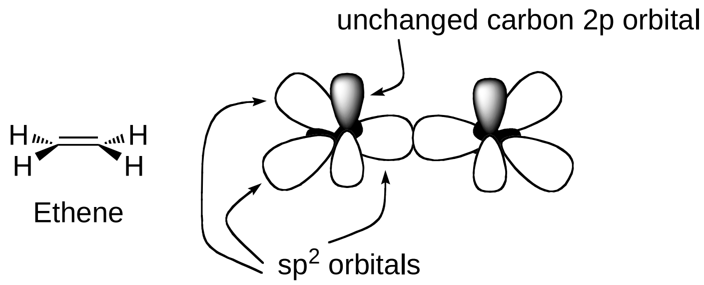
1. Is it obvious why these orbitals are called *sp*^{3} orbitals?

Carbon is also able to use its 2*s* orbital and *two* of its *p* orbitals to form new orbitals.

2. How many new, mixed orbitals would result from this? How would these orbitals arrange themselves around carbon?

3. What might you call these orbitals?

An example of this kind of mixing is found in ethene:



4. Note that a *p* orbital is left over. Are there electrons in this *p* orbital? The adjacent carbon is also in the same situation, so can these *p* orbitals combine?

5. Is this kind of bond (π-bond) stronger or weaker than the σ-bond formed by the overlap of the *sp*^{2} hybridized orbitals? Why?

6. How many bonds are there between the two carbons of ethene? Can you relate this to the stick structure above?

Model 3: Naming Organic Molecules

Critical thinking questions

1. You find a bottle in the lab labeled dimethylpentane. This name is ambiguous, so draw (using stick notation) all the possible structures consistent with this name.

2. You should have drawn 4 structures in Q3. Pick one of these and try to give it an unambiguous name.

Convention has it that compounds are numbered from the end nearest the functional group that provides the root of the name (the alkene in 1-butene, the alcohol of 1-butanol). Where there are no such functional groups, numbering of the parent chain starts from the end nearest a branch.

3. Is your answer to Question 2 consistent with this convention? If not, try to name it again.

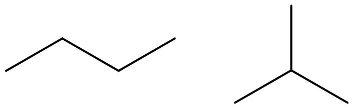
4. Name the other molecules in your answer to Question 1.

Learning to name organic molecules is a bit like learning a foreign language. There is no substitute for practice!

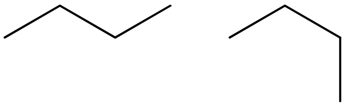
CHEM1102 Worksheet 2: Isomerism and Reactions

Model 1: Isomerism

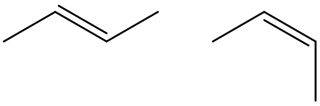
There are three broad classes of isomers.



Constitutional



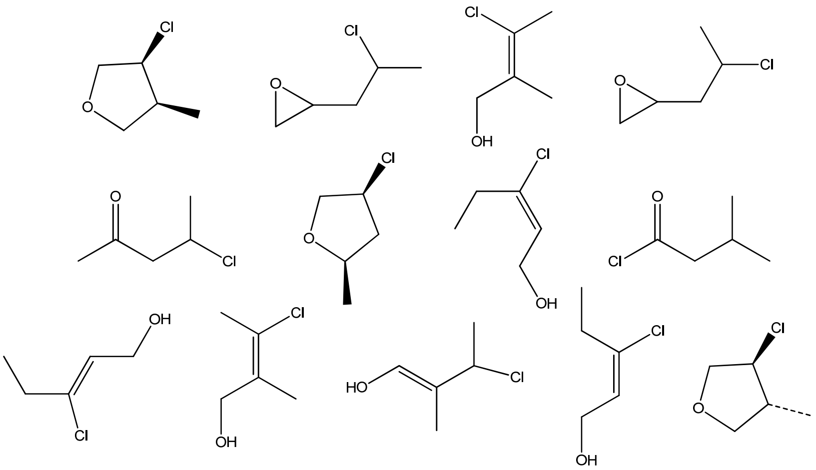
Conformational



Configurational

- **Constitutional** isomers have the same formula but different connectivity.
- **Conformational** isomers differ only by rotation about a single bond. They interconvert freely at all but extremely low temperatures (ie they are identical).
- **Configurational** isomers (**Stereoisomers**) have the same connectivity but cannot be interconverted through single bond rotation. Bond breaking and bond formation are required for interconversion.

Here are some molecules all with the formula C_5H_9ClO



Critical thinking questions

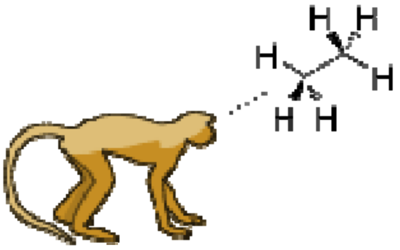
1. Circle at least 7 constitutional isomers

2. Identify and *draw* two pairs of conformational isomers

3. Identify and *draw* three pairs of configurational isomers. Assign them as *E*/*Z* or *cis*/*trans*.

4. **Extension:** How many different functional groups can you identify?

5. To understand conformers, it helps to look at the molecule from different angles. Imagine you (or in this case, a monkey) were looking at ethane along the central C-C bond:



Sketch what you would see. By doing this explain what you think might be meant by the term *staggered conformation*.

6. Can you draw a conformation of ethane that might be higher in energy? What might you call this?

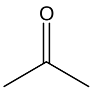
These drawings of molecules obtained by looking along the bonds like this are called *Newman projections*.

Model 2: Polar Reactions

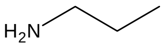
In many covalent bonds, the electrons are not distributed evenly due differences in the electronegativity of the two atoms involved. We use partial charges (δ⁺, δ⁻) to denote the resultant polarisation of the bond.

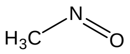
Critical thinking questions

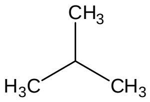
1. Determine the partial charges on the following molecules. In each case, do you expect the polarization effect to be large or small?



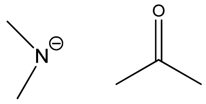
$H_3C—Cl$







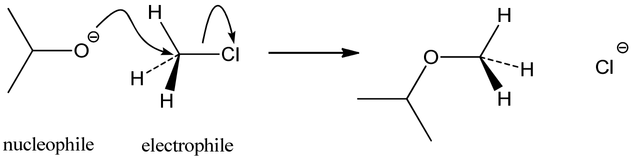
2. We know that there is an attractive force between positively and negatively charged objects. With this in mind, it would seem sensible that the negatively charged nitrogen below would react with the slightly positive carbon of the carbonyl.



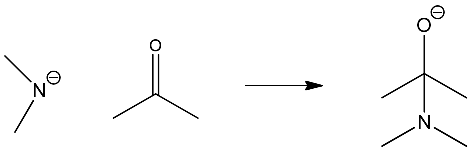
We know from Worksheet 1 that carbon typically forms four bonds. If we form a new bond between the nitrogen and the carbonyl carbon what else needs to happen?

3. Which bond most is likely to break and why?

Chemists use "curly arrows" to track the movement of electrons in a reaction. Convention has it that the arrow starts at the source of the electrons (a lone pair or a bond) and finishes where the electrons end up (in a bond or as a lone pair on an atom).



4. Try using curly arrows to describe the movement of electrons in Q2.



This is an example of a polar reaction, the most common type of reaction in organic chemistry (and the only kind you will see this year). Polar reactions always involve the interaction between an electron rich component (**nucleophile**) and an electron deficient component (**electrophile**).

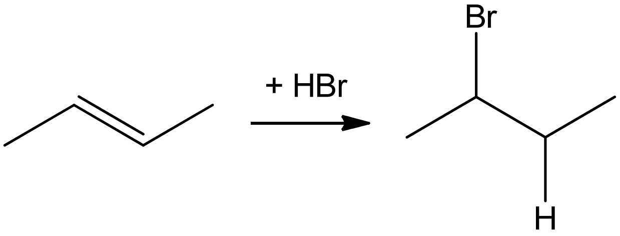
5. Identify the electrophile and the nucleophile in two schemes above.

If you can identify the potential electrophiles and nucleophiles in a reaction, you can almost always work out what the outcome of the reaction should be. No memorization required!

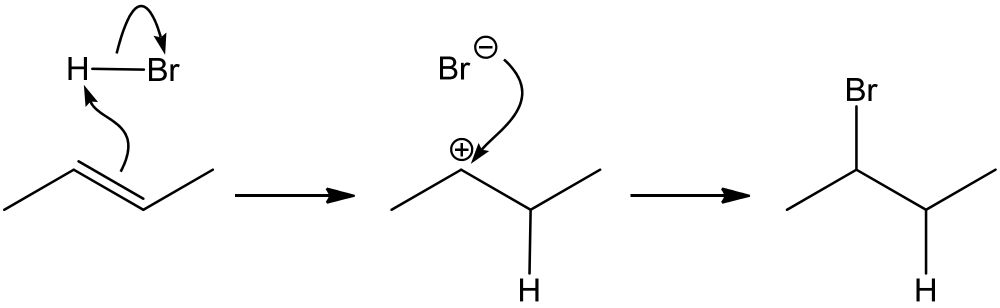
CHEM1102 Worksheet 3: Addition and Substitution Reactions

Model 1: Addition to Symmetrical Alkenes and Alkynes

In Worksheet 2, we saw that the double bond of an alkene is made up of one strong σ-bond and one weak π-bond. The process in which this π-bond is broken and two new σ-bonds are formed in its place is called an ***addition*** reaction.



The addition reaction usually takes place in two steps. In the first step, an intermediate is formed called a ***carbocation***.



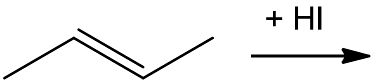
Critical thinking questions

1. In this reaction is the alkene acting as an electrophile or a nucleophile?

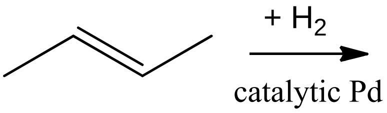
2. Highlight the bonds that are breaking in one colour, and the newly formed bonds in another.

3. Using the scheme above as a model, determine the outcome of the following reactions:

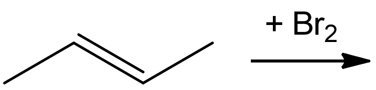
(a)



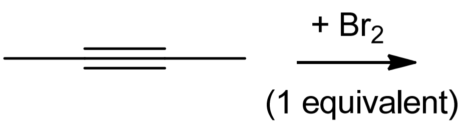
(b)



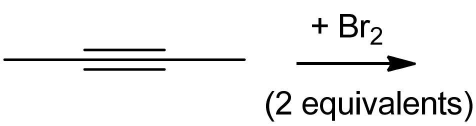
(c)



(d)



(e)

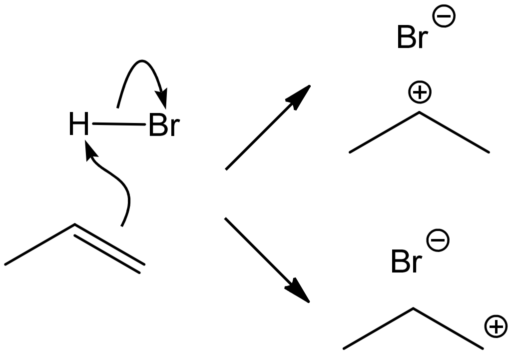


Model 2: Addition to Unsymmetrical Alkenes and Alkynes

The alkene used in Model 1 was *symmetrical*: it had the same groups at the two ends of multiple bond.

For *unsymmetrical* alkenes, with different groups at the two ends of the multiple bond, two carbocations may be formed in the first step of the reaction, as illustrated in the scheme opposite.

Because of this, there are *two* possible products. However, experimentally, one is formed in much greater amount than the other.



Critical thinking questions

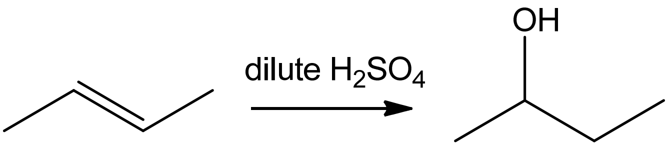
1. Draw and name the products arising from each of these carbocations.

2. Given that the alkyl groups (CH_n groups) stabilize carbocations, which carbocation do you expect to be the most stable in the scheme above?

3. Given your answers to Q2, which of the two products you drew in Q1 will be the major product?

This is Markovnikov's rule. It states that in an addition to an unsymmetrical alkene, the hydrogen will go predominately to the end that already has the most hydrogen atoms.

Another reaction you would have seen is the hydration of alkenes which is carried out using aqueous sulfuric acid. This is also an addition reaction but H_2SO_4 is *not* added across the double bond.



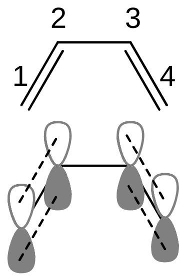
4. What is being added across the double bond? (Remember that atoms are added to *both* ends.)

5. What is the role of the H_2SO_4?

Model 3: Resonance and Electrophilic Aromatic Substitution

The π-bond in an alkene arises from the overlap of *p* orbitals on adjacent C atoms. The structure of 1,3-butadiene is normally drawn with π-bonds between C1 and C2 and between C3 and C4 due to overlap of their *p*-orbitals.

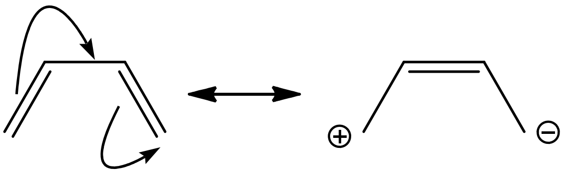
This structure suggests that there is no overlap, and so no *π* bonding, between the *p* orbitals of C2 and C3.

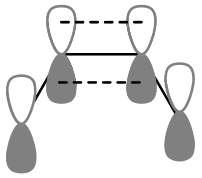


Critical thinking questions

1. Is this a realistic picture of the bonding in 1,3-butadiene?

Indeed, we could also draw the structure like below. The double headed arrow is used to show that the two Lewis structures are both possible.

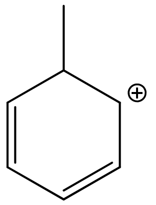


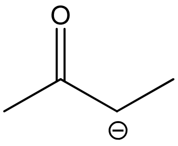


2. Do you think this resonance form is stable? Why?

The reality, of course, is somewhere in between – each C-C bond is more than a single bond, but slightly less than a double bond. It is hard to picture "one-and-a-bit" bonds, so chemists like to draw the different **resonance structures** instead. Resonance structures differ only in the location of electrons, *not* in the position of nuclei.

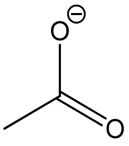
3. Draw resonance structures for the following:

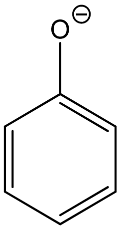


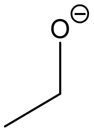


4. Do you think the molecules above are more or less stable than typical carbocations and carbanions?

5. Acetic acid is a stronger acid than phenol and phenol is a stronger acid than ethanol. Draw resonance structures for the following anions and use them to explain the relative acidities of the conjugate acids.

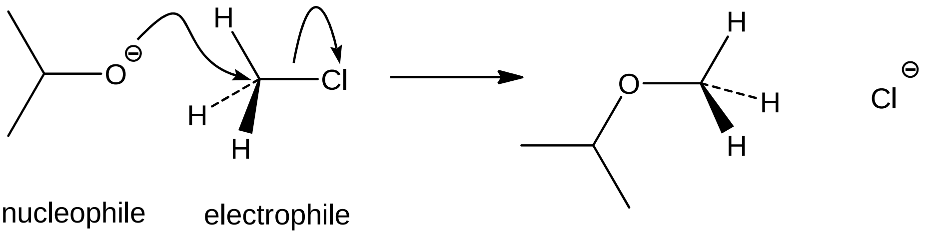






Model 4: Nucleophilic Substitution

In Worksheet 2, you practiced drawing curly arrows in the reaction below in which substitution occurs.



Critical thinking questions

1. Here it has been drawn as a one step (concerted) process. Can you draw an alternative two-step mechanism? (*Hint*: make sure you never draw *more* than 4 bonds to carbon so break a bond first.)

2. The first mechanism is called S_N2, the second S_N1. Can you suggest what each component of these names might refer to?

Examples of past exam questions

CHEM1102 2008-N-12 November 2008

Marks

- Consider the compound **J** below.

J

What is the systematic name for compound **J**.

1

Draw a constitutional isomer of **J**.

1

Draw a configurational isomer of **J**.

1

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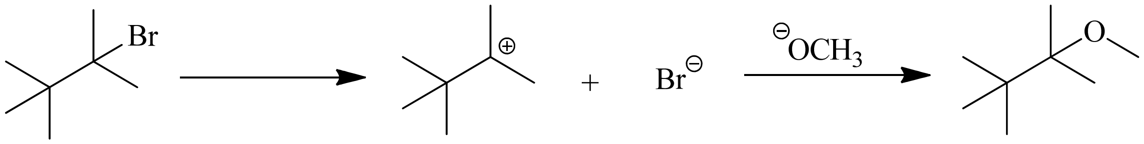
Marks

2

- Complete the following mechanism by adding curly arrows to illustrate the bonding changes that take place.



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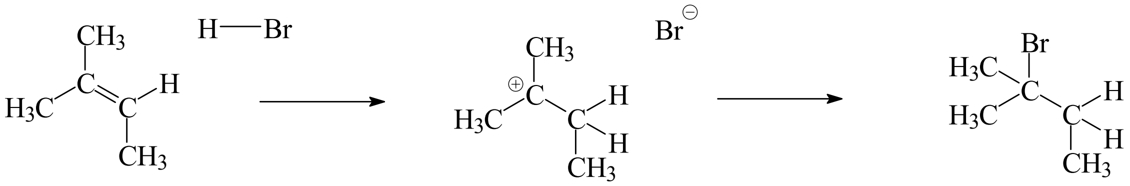
Marks
2

- The incomplete proposed mechanism for the reaction of 2-methyl-2-butene with HBr is shown below. Complete the mechanism by adding curly arrows to illustrate the bonding changes that take place.



Which one of the two reactants is the electrophile?

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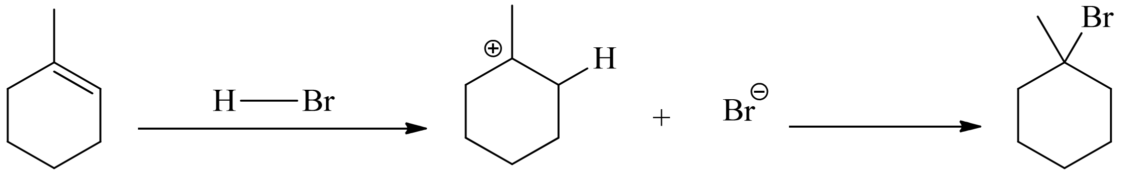
3

- Give the mechanism of the reaction that occurs when 1-methylcyclohexene is converted to 1-bromo-1-methylcyclohexane by the addition of HBr. Give the structure of the intermediate carbocation that is formed and indicate (with curly arrows) all the bonding changes that occur.



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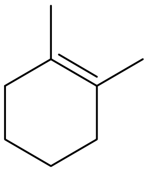
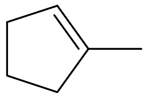
Marks
2

- Complete the following table. Make sure you indicate any relevant stereochemistry.

Starting Material	Reagents / Conditions	Major Organic Products
	H_2/Pd/C (catalyst)	
	aqueous H_2SO_4	

Week 2

CHEM1102 Worksheet 4: Spectroscopy Workshop (1)

Model 1: Infrared (IR) Spectroscopy

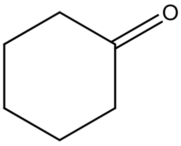
You have seen in lectures how bonds stretch and bend. A light wave of the correct frequency will be in resonance with a bond in motion and transfer its energy to this motion, like a parent pushing a swing. Light absorbed by the molecule in this manner falls in the infrared range. The frequencies at which some bonds stretch is quite similar in different molecules so **IR spectroscopy can be used to identify bonds, and hence functional groups**, in a molecule.

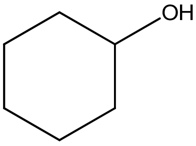
The table below lists IR absorption frequencies for some common bonds found in organic molecules:

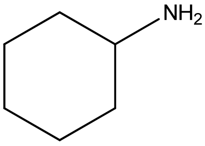
Bond	alcohol O-H	alkane C-H	carbonyl C=O	amine N-H	alkyne C≡C
Absorption Range (cm^{-1})	3200-3650 (strong, broad)	2840-3000 (strong)	1690-1760 (strong)	3100-3500	2100-2260

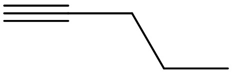
Critical thinking questions

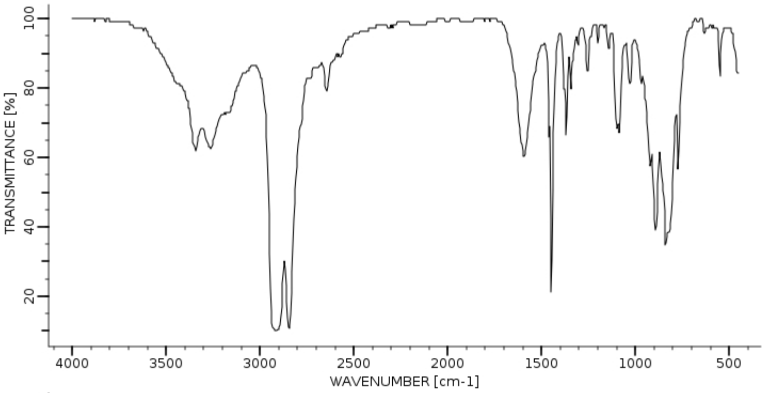
1. Use the characteristic stretching frequencies to match the four compounds below to their IR spectrum.

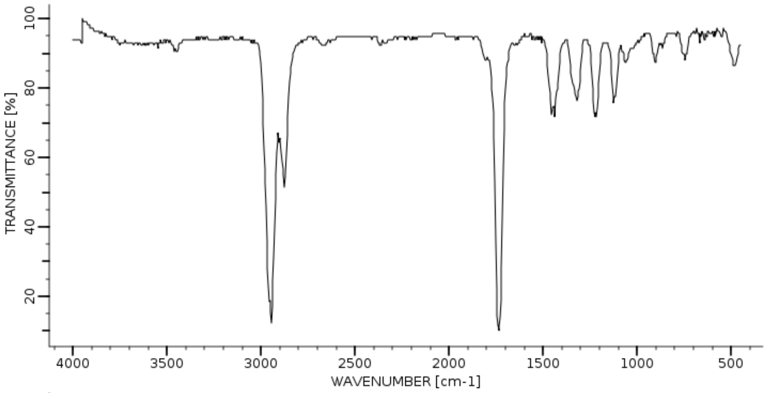


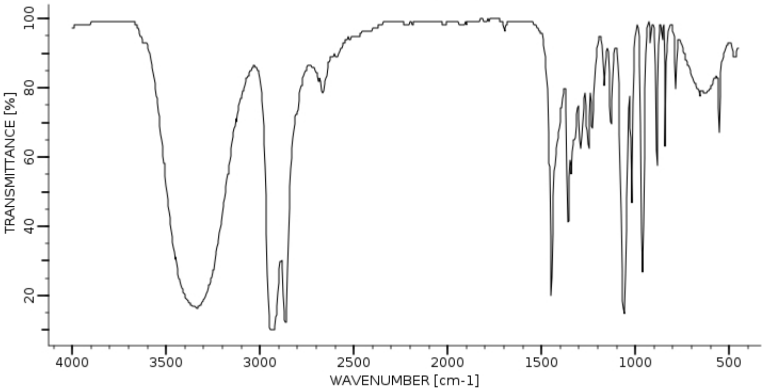


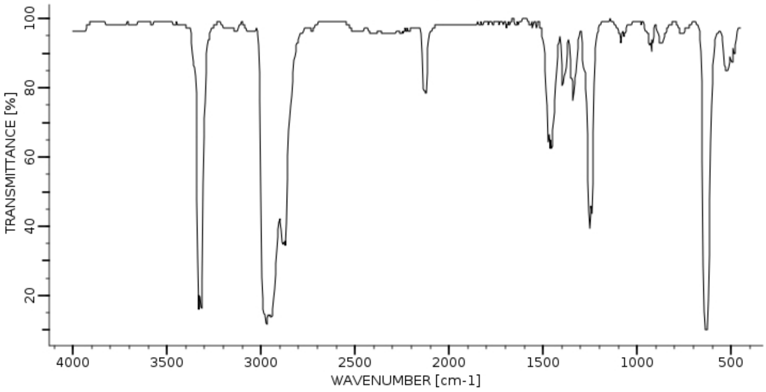








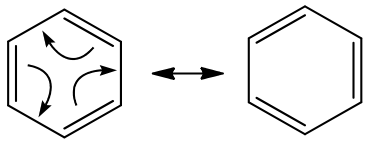




Model 2: UV-Visible Spectroscopy

In Worksheet 3, you saw how a chain of double bonds, each separated by exactly one single bond could be drawn in different resonance forms. This pattern of double-single-double bonds is called ***conjugation***.

Benzene is the classic example of a conjugated molecule.

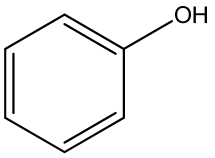


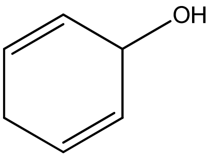
In CHEM1101, you learned about molecular orbitals. In conjugated molecules, the energy needed to excite an electron from the *highest occupied molecular orbital* (HOMO) to the *lowest unoccupied molecular orbital* (LUMO) is in the ultraviolet or even in the visible region of the spectrum.

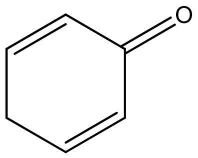
For conjugated systems, this LUMO-HOMO energy difference falls in the UV-Vis range.

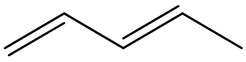
Critical thinking questions

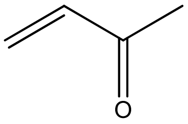
1 Which of the molecules below are conjugated?

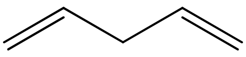












2. Circle the molecules above which would show a peak in the UV-Vis spectrum?

3. How useful do you think a UV-Vis spectrum is in identifying organic molecules?

Model 3: ^{1}H NMR Spectroscopy - Chemical Shifts

NMR spectroscopy (most often ^{13}C and ^{1}H, other nuclei as well) **is the most powerful tool for identifying organic molecules**. This is due to its sensitivity. Each unique carbon or hydrogen will give rise to a specific **signal** (peak), with a characteristic **chemical shift** (position) in the NMR spectrum[*].

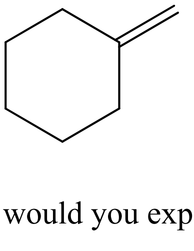
Nuclei give rise to identical signals only when they are in the same **chemical environment**. This occurs when:

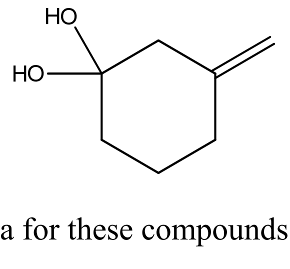
(i) they are attached to exactly the same atoms (e.g. the 4 hydrogen atoms of CH_4 are equivalent and give rise to only one peak)

(ii) are related by symmetry (e.g. the two CH_3 groups in propane are equivalent).

Critical thinking questions

1. Indicate each H environment in the molecules below. (*Hint*: you should first draw them on!)





2. How many signals would you expect in the ^{1}H spectra for these compounds?

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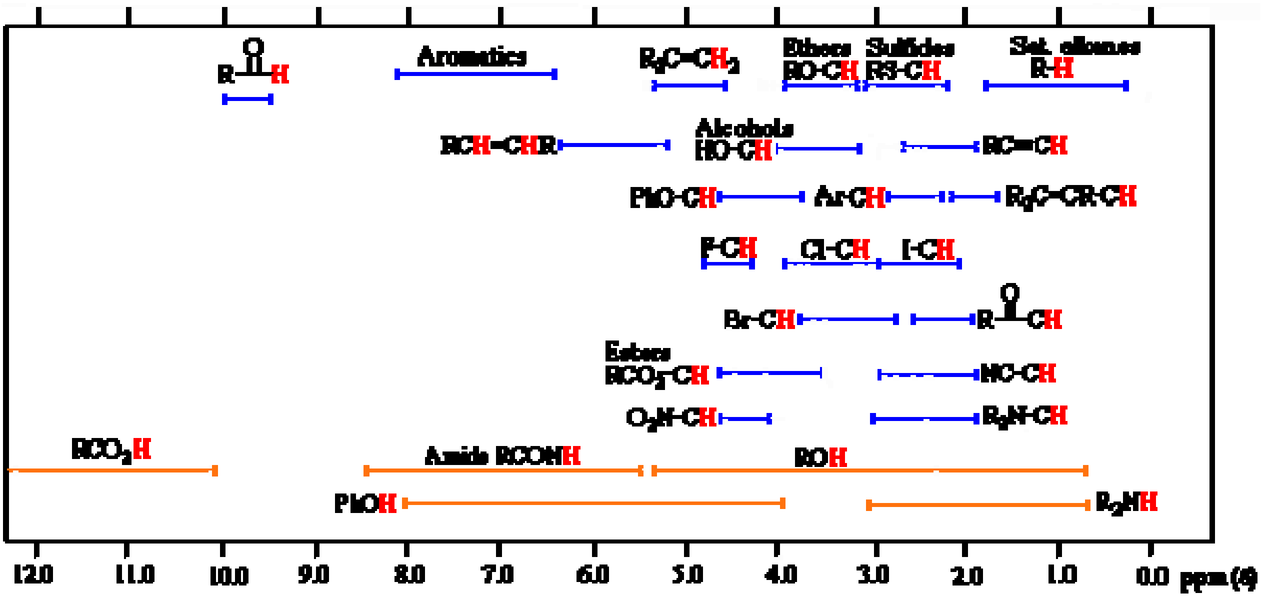
[*] For a more in depth analysis of the material in Models 3 – 4, see the online resources on eLearning.

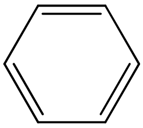
The chemical shift tells us what other atoms are nearby. If the ^1H is bonded, or near, to an electronegative atom like O, N or a halide, the electron density around the nucleus is lowered and its chemical shift is *increased*.

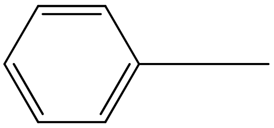
The *hybridization* of the carbon atom to which the ^1H is bonded is also important. A ^1H bonded to an *sp*^{3} C atom (e.g. in an alkane) has a smaller chemical shift than a ^1H bonded to an *sp*^{2} C atom (e.g. in an alkene or carbonyl).

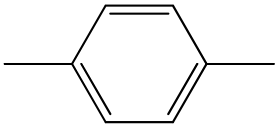
The figure below shows the characteristic chemical shifts (δ) for ^1H atoms in common groups, with R = alkyl and Ar = aromatic.

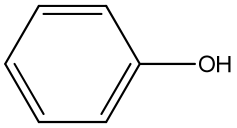


3. Predict the *number* of signals and the approximate *chemical shifts* for the molecules below.









Model 4: ^1H NMR Spectroscopy - Coupling

^1H NMR spectra have an added level of complexity. A signal may be "split" by the presence of ^1H atoms on adjacent carbon atoms.

- the signal due to a ^1H next to a CH group appears as a 2 peaks (*doublet* with relative heights 1:1)
- the signal due to a ^1H next to a CH_2 group appears as 3 peaks (*triplet* with relative heights 1:2:1)
- the signal due to a ^1H next to a CH_3 groups appears as 4 peaks (*quartet* with relative heights 1:3:3:1)

Note: equivalent protons do not split each other – i.e. a signal is not split by the protons giving rise to the signal. Hence, in the ^1H NMR spectrum for ethane, in which all of the hydrogen atoms are equivalent, consists of one signal which is a singlet.

Critical thinking questions

1. What is the relationship between the number of peaks into which a signal is split and the number of hydrogen atoms on the adjacent carbon atoms?

2. How many hydrogen atoms must there be on adjacent carbon atoms if the signal is a singlet?

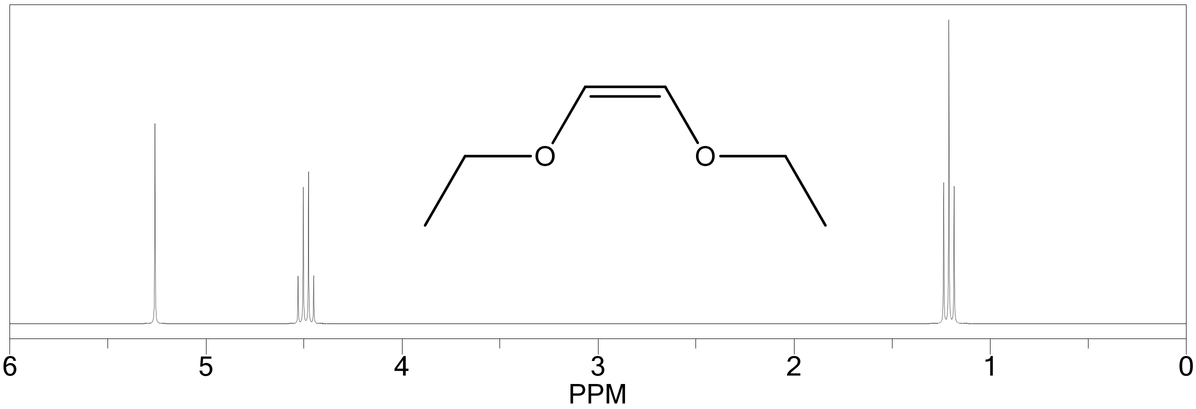
3. The ^1H atoms on the central carbon atom in propane are next to two $–CH_3$ groups. Into how many lines would you expect their NMR signal to be split?

Model 5: ^{1}H NMR Spectroscopy - Integration

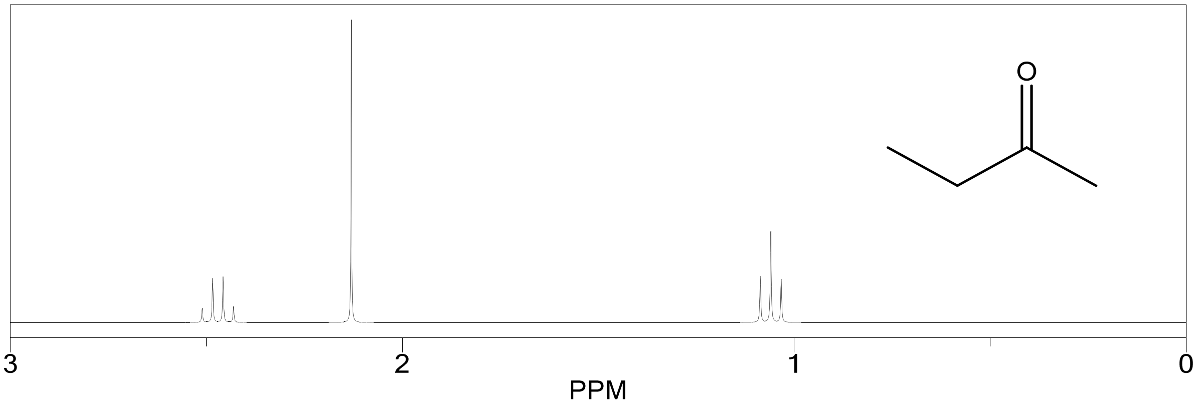
The height of a peak (specifically the *integral* of the area under the peak) is related to the number of protons it represents. If the ratio of the integrals of two peaks is 2:3, the ratio of protons represented by those peaks is also 2:3.

Critical thinking questions

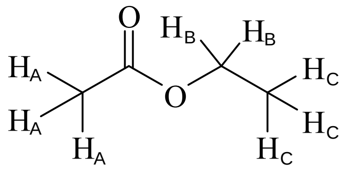
1. Assign the peaks of the ^{1}H NMR spectrum of (*Z*)-1-2,diethoxyethane, shown below, and explain the spectrum in much details as you can, including the relative position of the signals, the splitting and the relative sizes of the peaks..

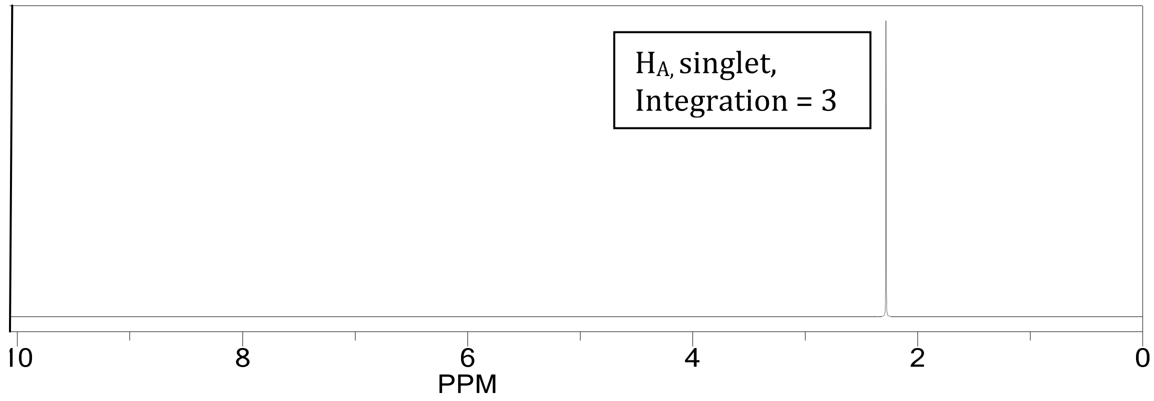


2. Repeat this exercise for butanone



3. Sketch the resonances you would expect to observe for protons H_B and H_C in the ^{1}H NMR spectrum of the compound opposite. Ensure that the approximate chemical shifts, as well as peak splittings and signal integrations are incorporated in your answer. (The resonance for H_A is provided as a guide.)




$H_{A,}$ singlet,
Integration = 3

CHEM1102 Worksheet 5: Spectroscopy Workshop (2)

Model 1: Mass Spectrometry

Mass spectrometry allows us to determine the molecular weight of a compound. However, it is a highly destructive technique, and molecules will often break up into smaller fragments. These fragments can further help in the identification of the compound.

For example, a CH_2CH_3 group has a mass of 27, so a peak at 27 might indicate the presence of a CH_2CH_3 group.

Critical thinking questions

1. A compound containing carbon, hydrogen and nitrogen displays a molecular ion peak in its mass spectrum at m/z 41 and a fragment ion at m/z 15. Give the structure of a compound which is consistent with these data.

Model 2: Combined Use of Mass Spectrometry and IR, UV-Visible and NMR Spectroscopy to Identify Unknown Compounds.

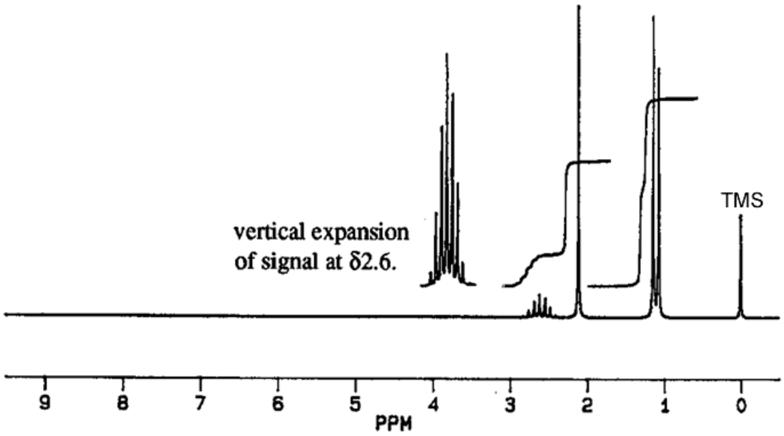
Commonly, all of these techniques are used to identify an unknown or newly synthesized compound as unambiguously as possible. The compound must be consistent with each spectrum. Each technique has its own strengths:

- mass spectrometry – helps to identify the molecular mass and, through the fragment pattern, can also be used to identify group that are present (such as $–CH_3$ or $–C_6H_5$).
- UV – Visible spectroscopy – identifies the presence / absence of conjugation such as aromatic rings
- IR spectroscopy – identifies the presence of common bonds, especially C=O and O-H
- NMR – identifies types of atoms present (chemical shifts), relative numbers of each atom type (integration) and which groups are bonded together (coupling).

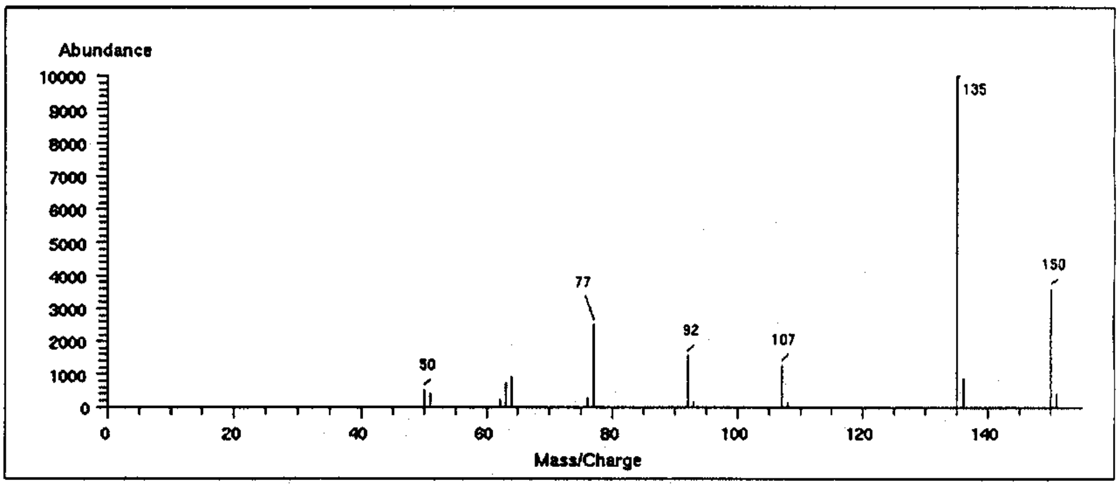
When performing this task, it is common to go through each piece of evidence to identify the parts of the molecule and to put them together. This can be a cyclical procedure with each spectrum analyzed at more than once.

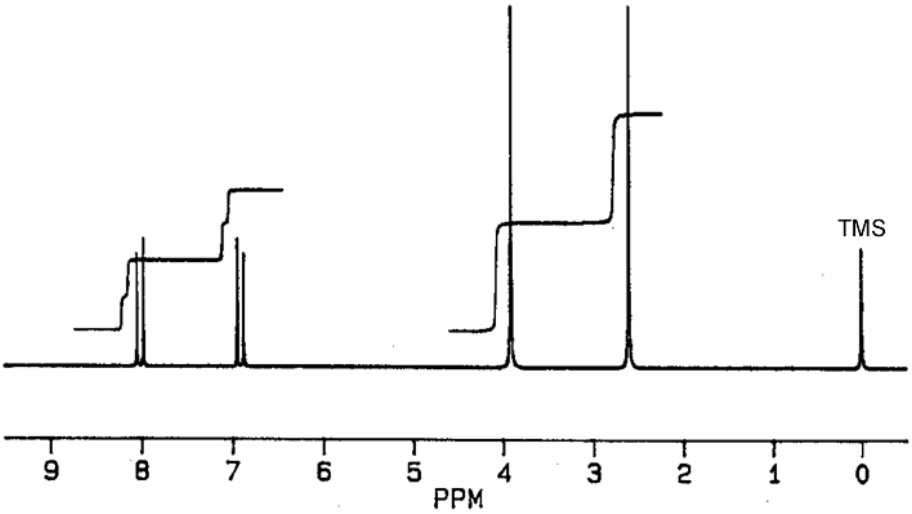
Critical thinking questions

1. A compound has a strong absorption near 1720 cm^{-1} in its infrared spectrum and a parent ion at *m/z* 86 in its mass spectrum. Its ^1H NMR spectrum is given below. Give a structure consistent with these data.



2. A compound of molecular formula $C_9H_{10}O_2$ has a strong absorption in the ultraviolet spectrum around 265 nm, and strong absorptions in the infrared spectrum at 1670 cm^{-1} and 2900 cm^{-1}. The mass spectrum and ^1H NMR spectrum are given below. Give a structure consistent with these data.


Abundance
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
50
77
92
107
135
150
0
20
40
60
80
100
120
140
Mass/Charge


TMS
9
8
7
6
5
4
3
2
1
0
PPM

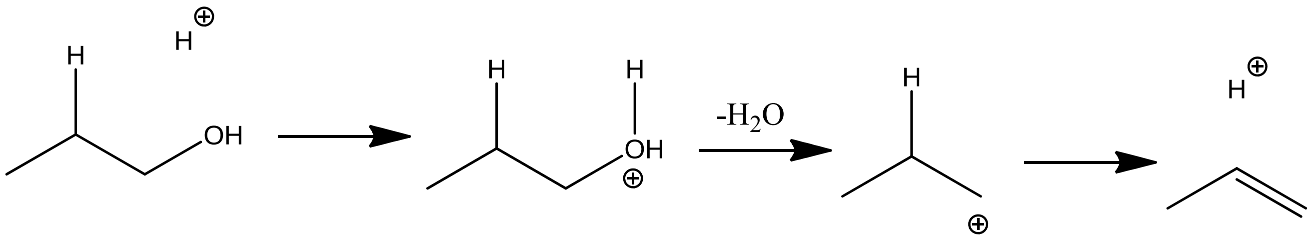
CHEM1102 Worksheet 6: Elimination Reactions and Chirality

Model 1: Elimination Reactions

In Worksheet 3, you saw how the C=C bonds undergo electrophilic addition reactions in which a group is added to each end of the double bond and the π bond is lost. Elimination reactions are the opposite: a group is lost from each end of a C-C bond to form a C=C double bond. *Hydration* is a special example of addition: H is added to one end and OH added to the other of the C=C bond. *Dehydration* is the opposite and is a special example of elimination: H is removed from one end and OH removed from the other end of the C-C bond.

Critical thinking questions

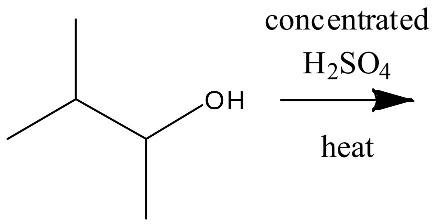
1. Complete the mechanism for the dehydration of water from 1-propanol to form propene by adding curly arrows.



2. The first step involves protonation of the alcohol. Why is this step necessary?

3. What is the overall role of H^+ in the reaction?

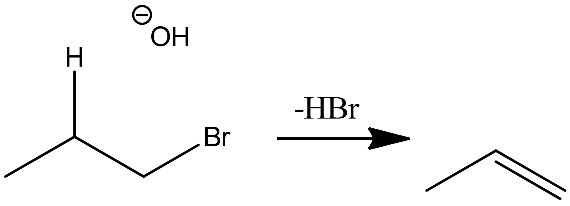
4. There are two possible alkenes formed in the elimination reaction below. Draw both.



5. *More* substituted alkenes are *more* stable. Indicate the likely *major* and *minor* products in Q4.

This is an example of Zaitsev's rule: the major product of an elimination reaction will be the more substituted alkene

The acid-catalysed dehydration reaction in Model 1 is a common way to make alkenes. A second way is through base-catalysed elimination:



This is an example of an E2 reaction whereas the acid-catalysed elimination in Model 2 is an E1 reaction.

6. Complete the mechanism by adding curly arrows.

7. Explain the E1 and E2 nomenclature, using what you know about S_N1 and S_N2 reactions from Worksheet 3.

Model 2: Enantiomers and Diastereomers

You may need a molecular model set for these activities.

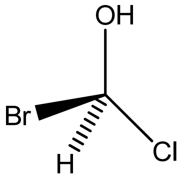
In Worksheet 2, you investigated constitutional, conformational and configuration isomers.

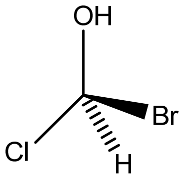
Critical thinking questions

1. Draw two examples of configurational isomers, one involving a double bond and one involving a ring.

These are ***diastereomers***: they are not identical and they are not mirror images. Configurational isomers that are not identical but *are* mirror images are called ***enantiomers***.

2. Using a model kits, construct the isomers below with a carbon at the centre (black) and 4 different coloured balls to represent the 4 groups bonded to it. Satisfy yourself and every member of your group that the two models are different (i.e. cannot be made the same just by being turned over).

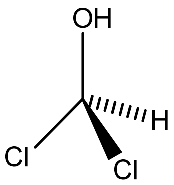


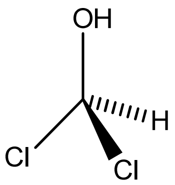


3. On *one* model, swap two of the balls. What is the relationship between the two models now?

4. On *one* model, swap a second pair of balls. What is the relationship now?

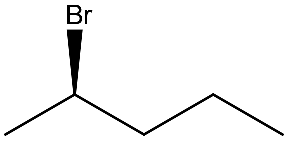
5. Make the models below and repeat these exercises. What do you notice?

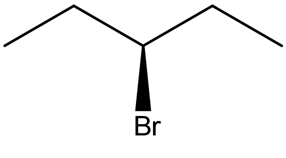


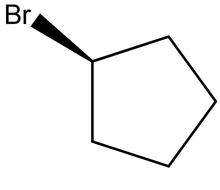


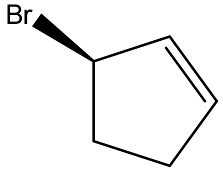
6. When a molecule can exist in 2 enantiomeric forms, it is said to be ***chiral***. From your experiments above, can you suggest a key requirement for molecules to be chiral?

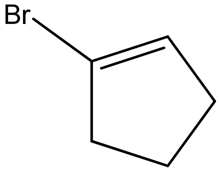
7. Identify the molecules below as chiral or achiral (= non-chiral).









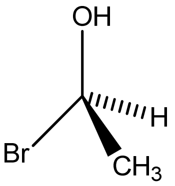


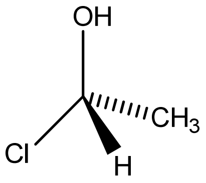
Just as (*E*) & (*Z*) and *cis* & *trans* are used to distinguish between diastereomers, (*S*) & (*R*) are used to denote the stereochemistry for the two enantiomers of a chiral molecule.

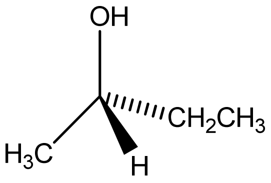
To assign the a*bsolute stereochemistry*,

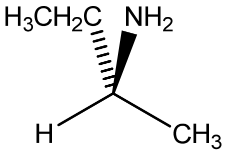
(i) Number the four substituents on the chiral centre in terms of priority (the same rules apply as for double bond isomers here)
(ii) Draw the molecule with the *lowest priority group pointing into the page*
(iii) Count around the remaining groups from highest priority to lowest:
(iv) Assign the stereochemistry as (*R*) if these numbers are ordered clockwise and (*S*) if these numbers are ordered anti-clockwise.

8. Assign the absolute stereochemistry of the following molecules (some may need to be redrawn, use the model kit if you need to). Name them, including (*R*) or (*S*) at the beginning.

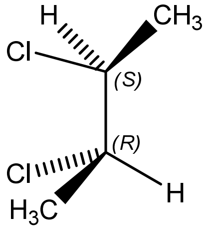








Things become more complex when the molecule contains a second (or third or fourth. …) chiral centre. One isomer of 2,3-dichlorobutane is shown below. It has two chiral centres with the absolute configurations shown.



9. Draw the other forms of 2,3-dichlorobutane in the space above.

10. Identify the relationships between *each pair*. *Hint:* they will either be enantiomers, diastereomers or the same. The pair that are the same as each other are not isomers – this is the ***meso form***.

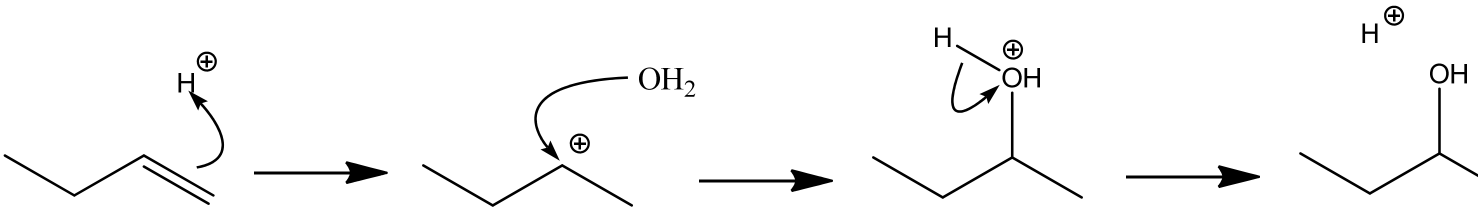
11. **Extension:** If you replace one of the chlorine groups with bromine and repeat the exercise, will you still get a pair of meso compounds? (Try to do this as a thought experiment first, then draw out the structures if you need to.)

Model 3: Stereochemistry and Reactions

Now that you are familiar with the different types of isomers, you can start looking at the stereochemical outcomes of the reactions that you have studied.

Critical thinking questions

1. Label the starting material, the carbocation intermediate and the product in the reaction below as chiral or achiral.

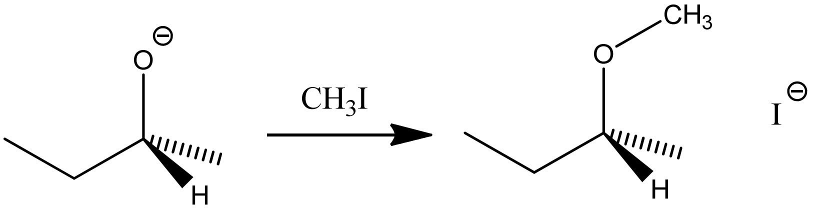


2. Imagine that water attacks the carbocation intermediate from above the plane of the page, draw the product and assign the stereochemistry. Repeat, this time imagining that water has attacked from below.

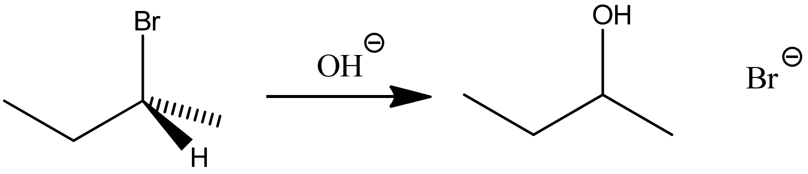
3. Which of these enantiomers do you think will actually be the product of this reaction?

Creating a chiral molecule from an achiral molecule generally leads to a 50:50 mixture of both enantiomers. **This is called a racemic mixture**.

4. The reaction below is an S_N2 reaction and leads to the formation of an ether. Do you expect the product to be (*R*), (*S*), a racemic mixture or achiral? Why?



5. **Extension:** The substitution reaction below goes *via* an S_N2 mechanism. Draw the product in 3D and assign the stereochemistry of both reactant and product.

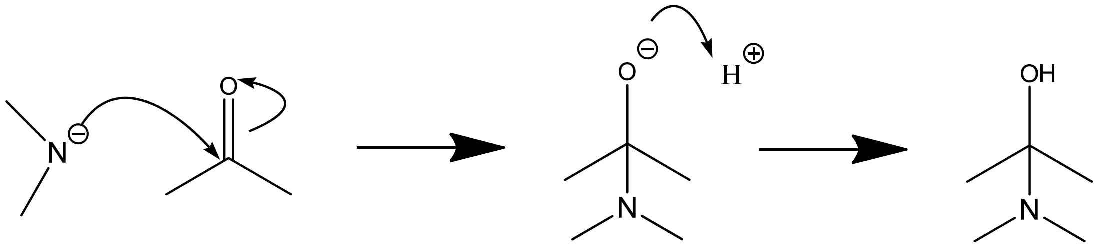


Week 3

CHEM1102 Worksheet 7: Reactions of Carbonyls and Acid Derivatives

Model 1: Addition to a Carbonyl

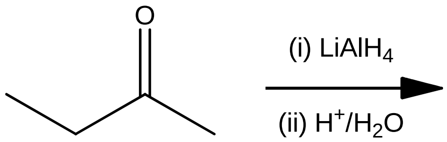
In Worksheet 2, you looked at the following reaction:

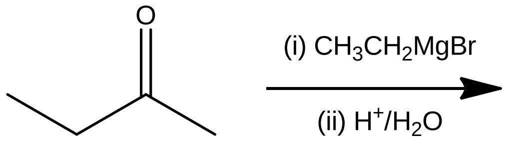


The addition of a nucleophile to a carbonyl carbon is a very general reaction. The C=O bond is very polar and the C end is very easily attacked by a nucleophile.

Critical thinking questions

1. Using the model above, predict the outcome of the following reactions. (*Hint*: $LiAlH_4$ reacts as if it contains the hydride ion, H^-, and CH_3CH_2MgBr reacts as it contains the carbanion, $CH_3CH_2^-$)

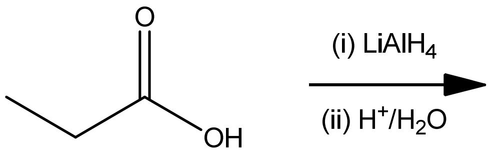




2. Describe the products of the above reaction as (*R*), (*S*), racemic or achiral.

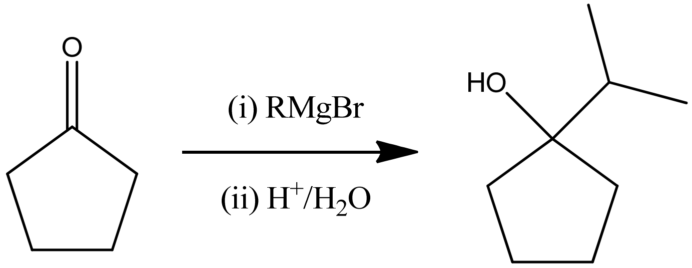
3. Do you expect aldehydes to be more or less electrophilic than the corresponding carboxylic acids? Explain.

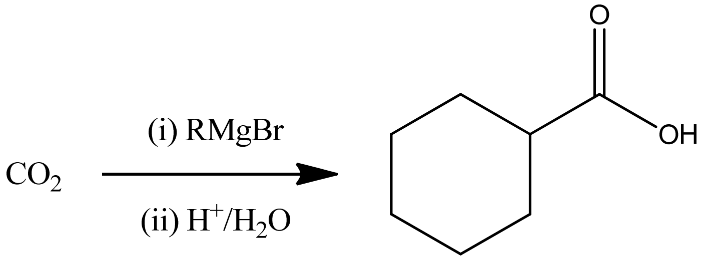
4. Based on this, predict the outcome of the reaction below.



Grignard reagents (RMgBr) are excellent nucleophiles, and are a very good way to form new carbon-carbon bonds.

5. Identify the appropriate Grignard reagent to complete the following reactions.

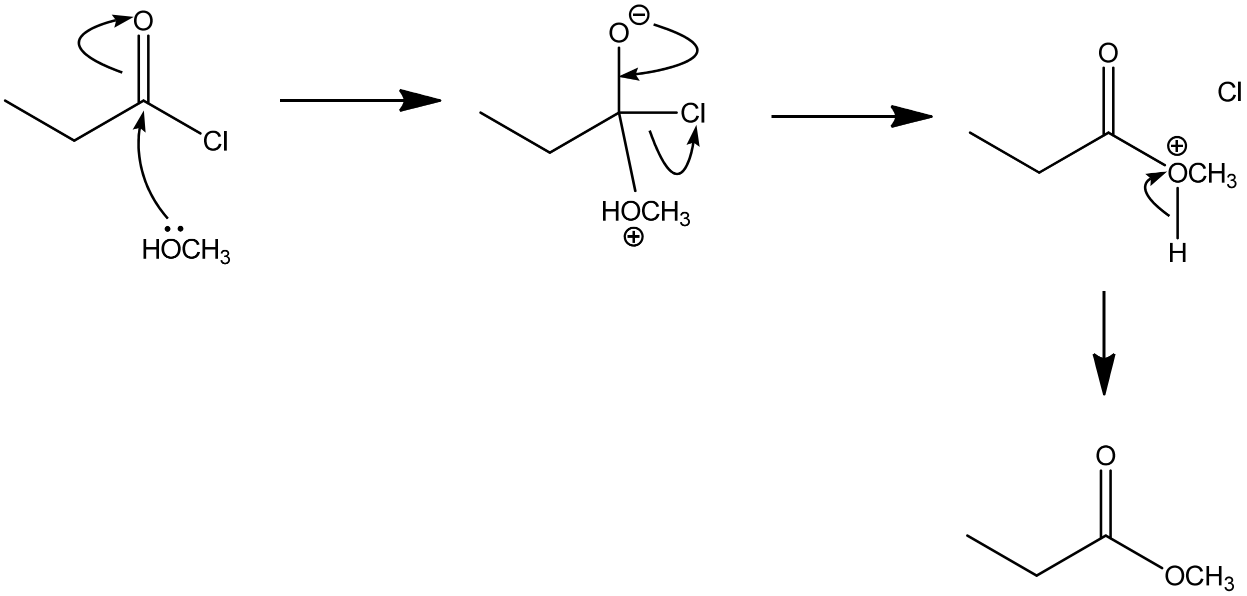




Extension: In each case, the addition of the nucleophile was followed by addition of acid. What purpose does this serve? Why are they not added at the *same* time?

Model 2: Carboxylic Acid Derivatives

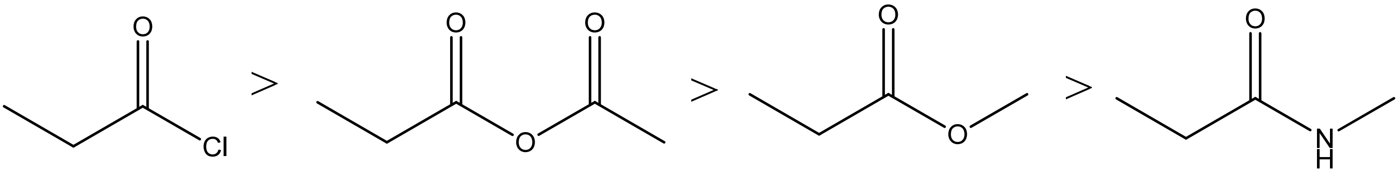
Carboxylic acid derivatives are formed from the condensation of a carboxylic acid with a second functional group, such as an alcohol or an amine. In some cases they can be formed directly. More often, the carboxylic acid must be converted to a more reactive intermediate, such as an acid chloride but the **process of condensation is essentially the same**:



Critical thinking questions

1. Using the reaction above as a model, try to devise a mechanism for the condensation of an acid chloride with an amine to form an amide.

Here are the common carboxylic acid derivatives, arranged from most reactive to least reactive.



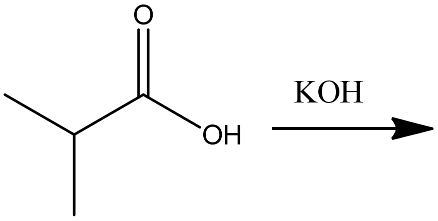
A carboxylic acid derivative can *only* be converted to form a *more* stable derivative.

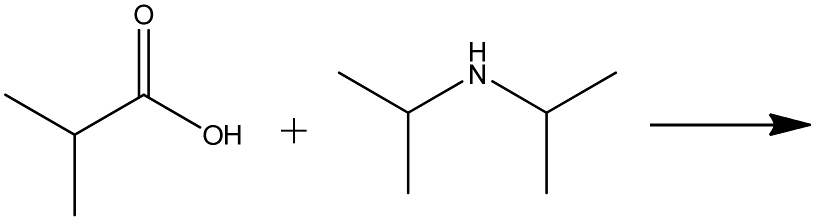
2. How might you convert an ester into an amide? (*Hint*: look at your answer to Question 1).

3. What is the by-product of this reaction?

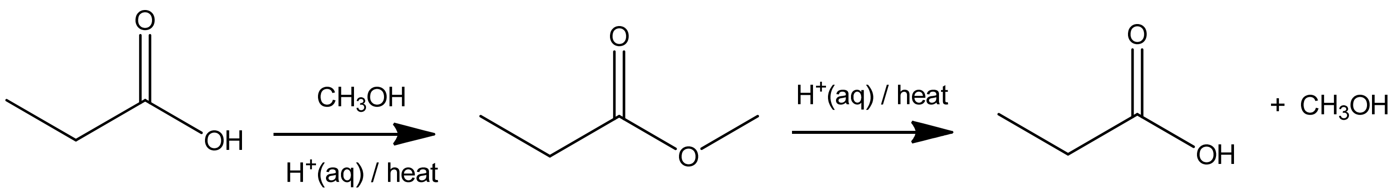
Extension: By considering how the substituents will affect the partial charge on the carbon atom of the carbonyl group, explain the trend in reactivity of the derivatives shown above.

4. Carboxylic acids are, as the name suggests, capable of undergoing acid-base reactions. We also know that amines are basic. Use this to predict the outcome of the following reactions.



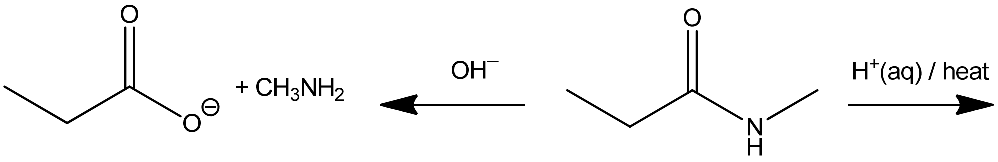


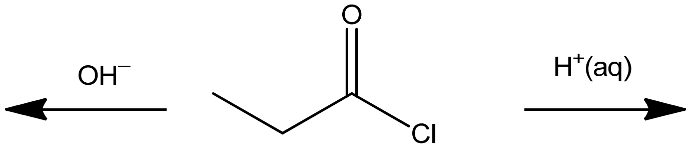
The scheme below shows the *condensation* of a carboxylic acid and an alcohol to give an ester, followed by *hydrolysis* of the ester back to the carboxylic acid and alcohol. Hydrolysis can be catalysed by acid or base.

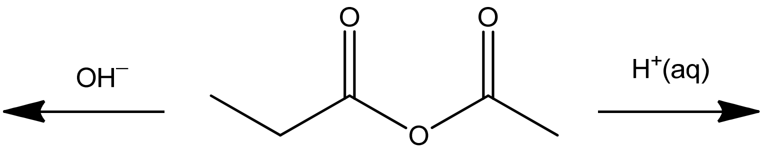


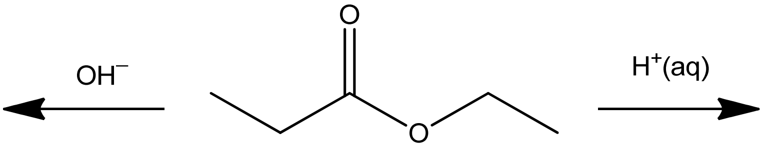
5. Overall, what is being removed or added in each step? How does this relate to the names we give these reactions (condensation and hydrolysis)?

6. Complete the schemes bellow.









7. An acid chloride can be hydrolysed using just water, whereas hydrolysis of an amide requires an acid (or base) and heat. Explain the origin of the difference.

Now make yourself a revision summary sheet and / or flashcards to help you remember the key transformations studied in this course. This might include:

- alkenes and alkynes - electrophilic addition of HX to alkenes and alkynes (X = H, Cl, Br, I, OH) (including the prediction of the major product using Markovnikov's rule),
- alcohols – acid/base reactions, oxidation reactions and acid catalysed elimination (including the prediction of the major product using Zaitsev's rule).
- amines – acid/base reactions and use in substitution reactions,
- alkyl halides – use in substitution reactions and base catalysed elimination (including the prediction of the major product using Zaitsev's rule)
- aldehydes and ketones – nucleophilic addition, reduction and oxidation
- carboxylic acid derivatives – acid/base reactions, nucleophilic substitution and reduction

Week 4

CHEM1102 Worksheet 8: Acids and Bases

Model 1: pH

Water is able to act as both an acid and a base and it is possible for water to react with itself in an acid-base reaction called the *autoprotolysis* or *autoionization* of water:

$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$$

The equilibrium constant for this reaction $K_w = [H_3O^+(aq)][OH^-(aq)]$. At 25 °C, $K_w = 1.0 \times 10^{-14}$. Several definitions have proven to be useful:

$$pH = -\log_{10}[H_3O^+(aq)], \qquad pOH = -\log_{10}[OH^-(aq)] \qquad pK_w = -\log_{10}K_w$$

Significant figures: when using logs, the number of significant figures is determined by the number of decimal points. The number to the left of the decimal point is *not* significant.

Critical thinking questions

1. During the course of a titration, a student measures the pH several times. What is $[H_3O^+(aq)]$ for each pH value below? (Actually calculate $[H_3O^+(aq)]$ – do *not* leave in the form 10^x).

pH	**0.50**	**1.50**	**2.50**	**3.50**	**4.50**	**5.50**	**5.75**
$[H_3O^+(aq)]$							

2. What is the effect of the number to the left of the decimal point in the pH on $[H_3O^+(aq)]$?

3. What is the effect of the number to the right of the decimal point in the pH on $[H_3O^+(aq)]$?

Model 2: Strong and Weak Acids

A **strong acid** is one that is essentially 100% dissociated in water: if 1.0 mole of the acid is added to enough water to make a 1.0 L solution, the solution will have $[H_3O^+(aq)] = 1.0$ M and will be pH = 1.

A **weak acid** is one that is *significantly* less than 100% dissociated in water: if 1.0 mole of the acid is added to enough water to make a 1.0 L solution, the solution will have $[H_3O^+(aq)] < 1.0$ M and will be pH > 1.

When an acid HA is placed in water, $H_3O^+(aq)$ ions are produced according to the reaction:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

Critical thinking questions

1. What are the *major* species present in a solution of a strong acid like HCl?

2. What are the *major* species present in a solution of a weak acid like CH_3COOH?

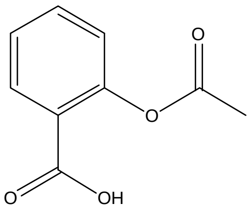
3. Under what pH conditions would $CH_3COO^-(aq)$ be the *dominant* species in a solution of CH_3COOH?

4. Write down the equilibrium expression, K_a, for CH_3COOH.

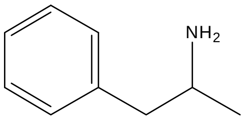
5. What are the *major* species present in a solution of a weak base like CH_3NH_2?

6. Under what pH conditions would $CH_3NH_3^+(aq)$ be the *dominant* species?

7. The extent of ionization of a drug helps determine how it is distributed in the body because ions are less likely to cross cell membranes than uncharged molecules. Are the two drugs below likely to be absorbed in (i) the acid environment of the stomach or (ii) the basic environment of the intestine?



aspirin



amphetamine

Model 3: Conjugate Pairs

Certain pairs of molecules are related through their acid and base properties. These pairs are described as a **conjugate acid-base pair**. They differ by *a single proton*. A base has *one less proton* than its conjugate acid. An acid has *one more proton* than its conjugate base.

Acid	Base
H_2CO_3	HCO_3^-
HCO_3^-	CO_3^{2-}
H_3O^+	H_2O
H_2S	HS^-

Critical thinking questions

1. (a) What is the conjugate base of H_2O?

   (b) What is the conjugate acid of H_2O?

2. Write the formula of the conjugate bases of the following acids:

   (a) CH_3COOH (b) NH_4^+ (c) $CH_3NH_3^+$

3. Write the formula of the conjugate acids of the following bases:

   (a) H_2S (b) HS^- (c) S^{2-}

Model 4: A Solution Containing a Weak Acid

As a **weak acid** is *significantly* less than 100% dissociated in water, an equilibrium must be considered:

$$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq) \qquad K_a = \frac{[H_3O^+(aq)][A^-(aq)]}{[HA(aq)]}$$

Calculating the pH requires that the equilibrium value of $[H_3O^+(aq)]$ be first calculated. To do this, the 'ICE' approach covered in CHEM1101 can be followed. Consider a 2.0 M solution of CH_3COOH:

	CH_3COOH (aq)	H_2O(l)	$\rightleftharpoons$	CH_3COO^-(aq)	H_3O^+(aq)
initial	2.00	large		0	0
change	$-x$	$-x$		$+x$	$+x$
equilibrium	$2.00 - x$	large		$+x$	$+x$

As hardly any weak acid dissociates, x is *very* small and so $2.00 - x \approx 2.00$. Using this approximation, the equilibrium constant can then be written down as:

$$K_a = \frac{[CH_3COO^-(aq)][H_3O^+(aq)]}{[CH_3COOH]} = \frac{x^2}{2.00-x} \approx \frac{x^2}{2.00} \quad \text{and so } x = [H_3O^+(aq)] = \sqrt{K_a \times 2.00}$$

After working out $[H_3O^+(aq)]$, the pH and percentage dissociation of the weak acid can be calculated:

$$pH = -\log[H_3O^+(aq)] \quad \text{and} \quad \%\ \text{dissociation} = \frac{[H_3O^+(aq)]}{[CH_3COOH]_{\text{initial}}} \times 100\%$$

Critical thinking questions

1. What are the initial and final concentrations of CH_3COOH in the ICE table above? How are they related when the small x approximation is used?

2. Using your answer to Q1, write down a formula for x for any dilute weak acid.

3. Calculate the pH and percentage dissociation of the acetic acid as it is diluted ($K_a = 10^{-4.76}$).

(a) 2.00 M pH =

% dissociation =

(c) 0.500 M pH =

% dissociation =

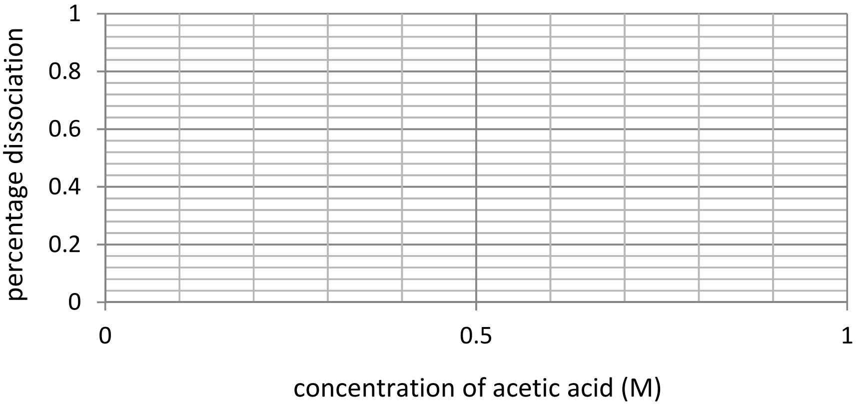
(b) 1.00 M pH =

% dissociation =

(d) 0.250 M pH =

% dissociation =

4. Complete the graph below showing how the percentage dissociation changes with the initial concentration. What are the *major* species present in a 1.00 M solution of acetic acid?



5. *Carefully* explain in words what happens to the amount of dissociation of a weak acid as it is diluted.

CHEM1102 Worksheet 9: Weak Acids and Titrations

Model 1: Addition of a Strong Acid to a Weak Base

In Worksheet 8, you used an "ICE" approach to work out the pH of a solution containing a weak acid. For example, you worked out that a 0.500 M solution of $CH_3COOH(aq)$ has a pH of 2.531.

If a strong base, such as NaOH, is added to this solution, it will react with the weak acid.

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(aq)$$

As long as the amount of $OH^-(aq)$ added is *less* than the amount of $CH_3COOH(aq)$ present, the solution will contain both $CH_3COO^-(aq)$ and left over $CH_3COOH(aq)$. A solution like this containing both a weak acid and its conjugate base is a buffer and its pH is given by the *Henderson-Hasselbalch* equation:

$$\text{pH} = \text{p}K_a + \log\frac{[\text{base}]}{[\text{acid}]} = \text{p}K_a + \log\frac{[CH_3COO^-(aq)]}{[CH_3COOH(aq)]}$$

Critical thinking questions

1. If 0.100 mol of NaOH(s) is added to a 1.00 L solution of 0.500 M CH_3COOH, it will react to form a solution which is 0.100 M in $CH_3COO^-(aq)$ and 0.400 M $CH_3COOH(aq)$. What is the pH of this solution? ($\text{p}K_a$ (CH_3COOH) = 4.76).

2. Complete the table below showing the concentrations of $CH_3COOH(aq)$ and $CH_3COO^-(aq)$ and the pH of the solution as more NaOH(s) is added to this solution.

Amount of NaOH(s) added (mol)	0.000	0.100	0.200	0.300	0.400	0.500
$[CH_3COOH(aq)]$ (M)	0.500	0.400				
$[CH_3COO^-(aq)]$ (M)	0.000	0.100				
pH	2.531					

3. To react completely with the original CH_3COOH, 0.500 mol of NaOH must be added. What is the pH of the solution when exactly *half* this amount is added?

4. How can you obtain the value for pK_a for an acid?

Model 2: Neutralizing a Weak Acid

Model 1 describes the pH changes as a strong base is added to a solution containing a weak acid. The strong base reacts with the weak acid leading to a solution containing the conjugate base of the weak acid and any left over acid. The *equivalence* point occurs when enough base has been added so that there is no acid left.

At this point, the solution contains the conjugate base and essentially none of the original acid.

The conjugate base will then set up its own equilibrium:

$$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH(aq) + OH^-(aq) \qquad K_b = \frac{[CH_3COOH(aq)][OH^-(aq)]}{[CH_3COO^-(aq)]}$$

From the chemical equation:

$$[CH_3COOH(aq)]_{equilirium} = [OH^-(aq)]_{equilirium}$$

As hardly any base reacts, $[CH_3COO^-(aq)]_{equilibrium} \approx [CH_3COO^-(aq)]_{initial}$ and so:

$$K_b = \frac{[OH^-(aq)]^2}{[CH_3COO^-(aq)]_{initial}} \qquad \text{and} \qquad [OH^-(aq)] = \sqrt{K_b \times [CH_3COO^-(aq)]_{initial}}$$

After working out $[OH^-(aq)]$, the pOH can be calculated:

$$pOH = -\log[OH^-(aq)]$$

Finally, the pH can then be calculated using pH = 14.00 – pOH.

Critical thinking questions

1. To react completely with the original CH_3COOH in Q5, 0.500 mol of NaOH must be added. What will be $[CH_3COO^-(aq)]$ when this occurs?

2. Calculate the pH of the solution the reaction produced in Q1.
(*Hint*: remember that $pK_a + pK_b = 14.00$ or $K_a \times K_b = 10^{-14.00}$)

3. Correct your entry in the final column of the table in Model 1 if required!

4. What is the pH at the equivalence point of the titration of a *strong* acid with a strong base?

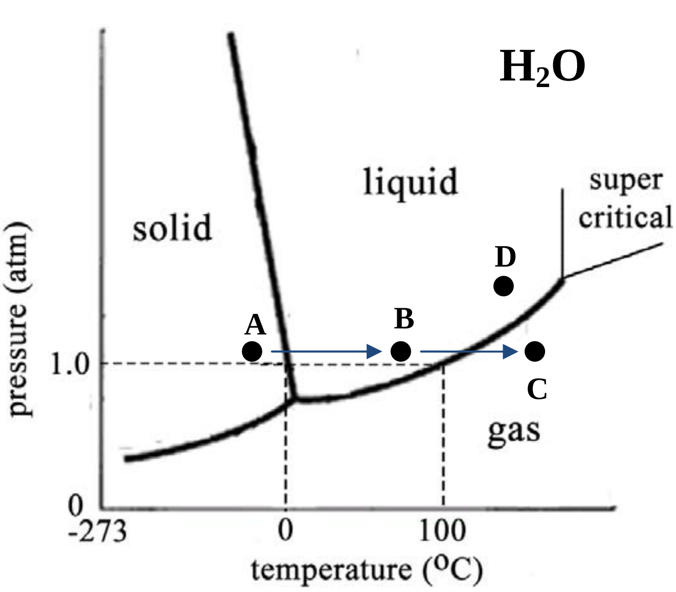
5. Is the pH at the equivalence point of the titration of a *weak* acid with a strong base less than or higher than 7?

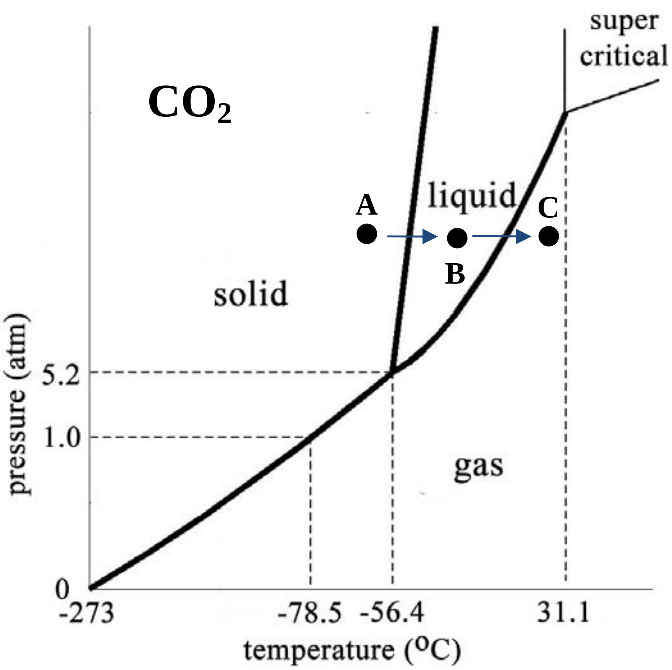
Week 5

CHEM1102 Worksheet 10: Making a Perfect Snowball

Model 1: Phase Diagrams for Water and Carbon Dioxide

The *phase diagrams* for H_2O and CO_2 are shown below. A phase diagram summarizes the behaviour of a substance and different temperatures (*x* axis) and pressures (*y* axis). The different areas of the diagram represent conditions under which the material is a gas, liquid or solid. The thick, solid lines represent the transitions between these phases.





For example, point **A** on both diagrams represents a temperature and pressure in which the substance is a solid (*ice*). If the temperature is increased and the pressure is not changed, the substance moves to point **B** (liquid) and then to point **C** (gas). Along the way it passes through the solid line separating 'solid' from 'liquid' (*melting*) and through the solid line separating 'liquid' from 'gas' (*boiling* or *vapourizing*).

Critical thinking questions

1. Water in a car radiator when the engine overheats is both very hot and under pressure. Point **D** on the water phase diagram represents this situation. What phase is water in at point **D**?

2. If the radiator cap is removed, the pressure will decrease to atmospheric pressure. What is likely to happen to the water? Draw another point (**E**) and an arrow on the phase diagram to illustrate this process.

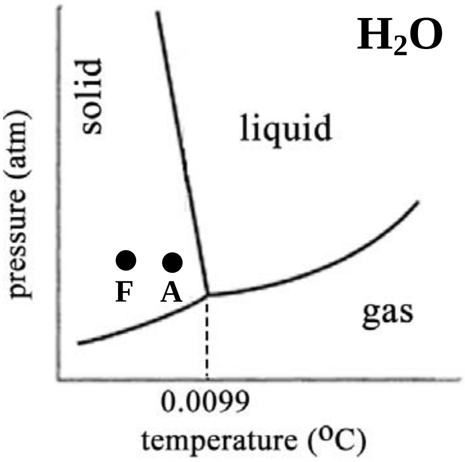
3. Sequestration involves storing CO_2, produced by burning fossil fuels, underground as a liquid. How could this be done? Draw two points and an arrow on the phase diagram of CO_2 to illustrate this process occurring at 25 °C.

Model 2: Under Pressure

Snow is very loose and there is an art to make it into a snowball capable to being thrown. To make a perfect snowball, you scoop up snow in a gloved hand and squeeze it between your cupped hands.

The explanation for this lies in the almost unique[*] phase diagram of water. The thick line representing the solid-liquid transition slopes to the left for water. As shown in Model 1 for CO_2, it normally slopes to the right.

This peculiarity is associated with the lower density of solid water compared to liquid water: water ice floats in a glass of water but dry ice sinks in liquid CO_2.



Critical thinking questions

1. On a particular winter’s day, the temperature is just below freezing. The snow you pick up is at point **A** on the phase diagram. When you squeeze the snow, what will happen to it? Draw another point (**G**) and an arrow on the phase diagram to illustrate this process.

2. Before throwing the snowball, you release the pressure. Describe what will happen and add another arrow to the phase diagram to illustrate this process.

3. The temperature even on a summer’s day at the South Pole is very cold (around -25 °C). On worlds such as Ganymede, Pluto or Mars, the temperature can be a low as -120 °C. Point **F** represents snow on a very cold day. Can ice be welded by hand compression from this point?

4. Mars is usually so cold that CO_2 exists as a solid. By first predicting what happens if you squeeze dry ice at point **A** on its phase diagram (see Model 1), suggest whether it is possible to make a snowball of dry ice.

---

[*] There are other materials that have solid-liquid transition lines that slope to the left but these tend to be under conditions where humans cannot survive. You could, for example, make a plutonium snowball by squeezing plutonium dust at 640 °C. Just don’t take too big a handful.

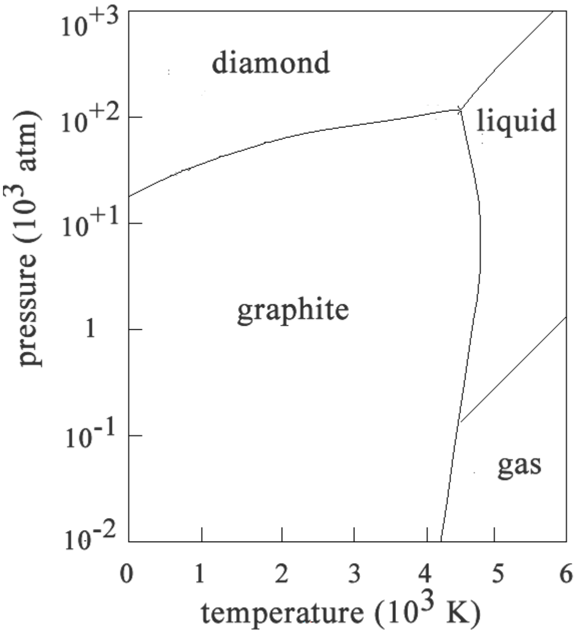
Model 3: Allotropes and Pressure

Many elements can exist as different structural forms called *allotropes*. Allotropes have different physical properties, including densities, and their stability depends on the temperature and pressure. Phase transitions between these forms can occur as well as between them and the liquid and gaseous forms of the element.

The phase diagram opposite is that of carbon showing regions due to diamond and graphite.

It shows that graphite is more stable than diamond at lower pressures and diamond is more stable than graphite at higher pressures.

There are 2 triple points on the phase diagram.



Critical thinking questions

1. Describe the phase change(s) that occur when graphite at room temperature and pressure is heated to 5000 K.

2. Label the 2 triple points and describe which phases are in equilibrium at each.

   (i)

   (ii)

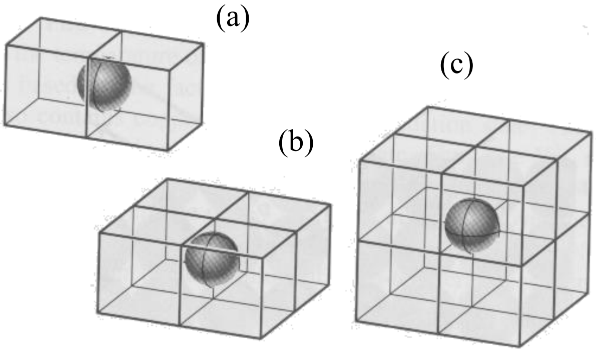
3. Is the phase diagram consistent with graphite or diamond being more dense? Explain your answer.

4. Explain how your answer to Q3 is compatible with your knowledge of the structures of these 2 allotropes.

CHEM1102 Worksheet 11: The Solubility Product and Structures & Stoichiometry

Model 1: The Unit Cell

In metals and ionic solids, the atoms are arranged in very ordered arrangements. The number of atoms in such a solid is enormous: if you were sitting on one, you would see atoms in every direction as far as you can see. The best way to describe the structure is to look for the smallest repeating unit. This is called the *unit cell*. The structure of the solid can be built from the unit cell by stacking them together in three dimensions.



The simplest unit cells are cubes. These are packed together, as shown opposite, like bricks to make up the infinite, three dimensional structure. Atoms on the corners, edges and faces of a unit cell are shared by more than one unit cell:

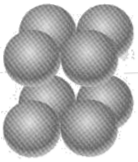
(a) an atom on a *face* is shared by *two* cells so only *half* belongs to each of the cells

(b) an atom on an *edge* is shared by four cells so only a *quarter* belongs to each of the cells

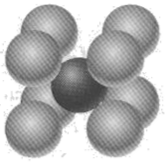
(c) an atom on a *corner* is shared by eight cells so only an *eighth* belongs to each of the cells

Critical thinking questions

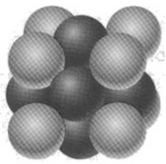
1. The picture opposite shows the *simple cubic* unit cell, which only has atoms on the *corners* of the cube. What is the *net* number of atoms belonging to the unit cell? (*Hint*: how many atoms are on the corners and how much of each one *belongs* to the cell



2. The picture opposite shows the *body centred* unit cell, which has an atom at the *centre* as well as atoms on the *corners* of the cube. What is the *net* number of atoms in the unit cell?



3. The picture opposite shows the *face centred* unit cell, which has atoms on the *faces* and on the *corners* of the cube. What is the *net* number of atoms in the unit cell?

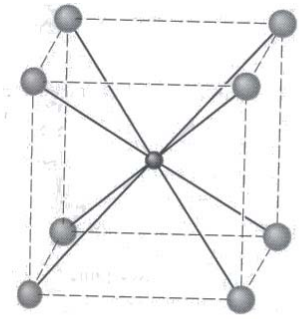


Model 2: The Unit Cell and Stoichiometry

The unit cell opposite is of caesium chloride. It contains Cl^- at the corners of the cube and Cs^+ at the centre.

The caesium ion is completely in the cell:

- number of caesium ions in cell = 1



From Model 1, only an eighth of atoms on the corners belong to the cell. Hence:

- number of chloride ions in cell = $8 \times \frac{1}{8} = 1$

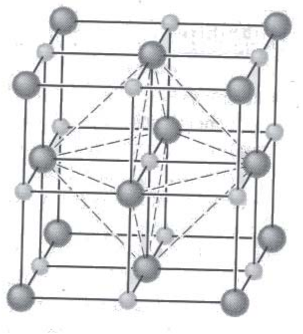
The unit cell contains 1 caesium and 1 chloride and so the formula is CsCl.

Critical thinking questions

1. The picture overleaf shows the structure of NaCl.

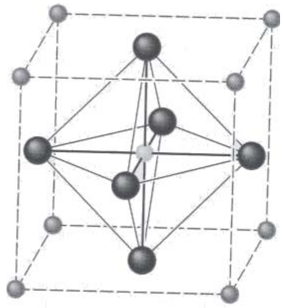
(a) The larger spheres represent Cl atoms. These are located on the *corners* and *faces* of the cube. How many Cl atoms are in the cell?

(b) The smaller spheres represent Na atoms. These are located on the *edges* and at the *centre* of the cube. How many Na atoms are in the cell?



(c) Is this cation : anion ratio consistent with the formula NaCl?

2. The picture opposite is the perovskite structure which is very important in minerals and in superconductors. It contains *three* different types of atoms.



(a) There is a Ti atom at the *centre* (light grey). How many Ti atoms in the cell?

(b) There are Ca atoms (dark grey) at each *corner*. How many Ca atoms are in the cell?

(c) There are O atoms (black) on each *face*. How many O atoms are in the cell?

(d) What is the formula of the mineral?

(e) What is the oxidation number of the titanium?

Model 3: The solubility product

If as much solid has dissolved as is possible, the solution is saturated and equilibrium has been established.

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

The equilibrium constant is known as the '**solubility product**' and given the symbol $\boldsymbol{K_{sp}}$:

$$K_{sp} = [Mg^{2+}(aq)][OH^-(aq)]^2$$

It involves only the aqueous ions with the concentration of each raised to the power by which they appear in the dissolution reaction. The concentration of the solid is constant so does not appear in K_{sp}. This is only true if solid is present: if there is no solid present, the solution is *not* saturated and the reaction is *not* at equilibrium.

Critical thinking questions

1. Write down the solubility product for the following salts:

   (a) $AgCl(s)$: $K_{sp} =$

   (b) $Ag_2SO_4(s)$: $K_{sp} =$

   (c) $PbCl_2(s)$: $K_{sp} =$

2. $PbCl_2$ is not very soluble in water with $K_{sp} = 1.6 \times 10^{-5}$. The number of moles of $PbCl_2$ that dissolve in a litre of water is called the *molar solubility*.

   (a) If x moles of $PbCl_2$ dissolve in 1.00 L of water, what will be $[Pb^{2+}(aq)]$ and $[Cl^-(aq)]$ in terms of x?

   (b) K_{sp} of $PbCl_2$ is 1.6×10^{-5}, using your answer to Q1(c) and Q2(a), work out $[Pb^{2+}(aq)]$ and $[Cl^-(aq)]$.

3. In terms of its K_{sp}, what is the molar solubility of $Fe(OH)_3$? (*Hint*: consider the procedure you followed in Q2 and think about the effect of the stoichiometry on the calculation.)

4 Order the following salts from lowest to highest solubility.

(a) $SrSO_4$ ($K_{sp} = 2.8 \times 10^{-7}$) (b) $Zn(OH)_2$ ($K_{sp} = 4.5 \times 10^{-17}$)

(c) PbI_2 ($K_{sp} = 8.7 \times 10^{-9}$) (d) MnS ($K_{sp} = 5 \times 10^{-15}$)

Model 4: To dissolve or not to dissolve?

The solubility product gives the *maximum* values of the ion concentrations that are allowed. If their concentrations are such that their product is *less* than K_{sp}, then more solid can dissolve.

If $[Mg^{2+}(aq)][OH^{-}(aq)]^2 < K_{sp}$ then more solid can dissolve

If their concentrations are such that their product is *more* than K_{sp} then the concentrations must reduce: precipitation *must* occur.

If $[Mg^{2+}(aq)][OH^{-}(aq)]^2 > K_{sp}$ then precipitation must occur

The value of the product can thus be used to predict whether dissolution or precipitation can occur. Because of its importance, it is called the '**ionic product**' and given the symbol Q_{sp}:

$$Q_{sp} = [Mg^{2+}(aq)][OH^{-}(aq)]^2$$

If $Q_{sp} < K_{sp}$ then dissolution will occur. If $Q_{sp} > K_{sp}$ then precipitation will occur.

Critical thinking questions

1. A solution is made by mixing 500.0 mL of 0.12 M NaOH solution with 500.0 mL of 0.10 M $Mg(NO_3)_2$. K_{sp} is 1.8×10^{-11}

   (a) Assuming that no reaction occurs, what will $[Mg^{2+}(aq)]$ and $[OH^{-}(aq)]$ be after mixing?

   (b) Write down the value of the ionic product, Q_{sp}.

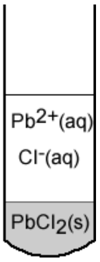
   (c) Does a precipitate form?

2. For each of the following experiments, predict whether or not a precipitate of MgF_2 will form. K_{sp} $MgF_2(s) = 6.4 \times 10^{-9}$

   (a) 500.0 mL of 0.050 M $Mg(NO_3)_2$ is mixed with 500.0 mL of 0.010 M NaF

   (b) 500.0 mL of 0.050 M $Mg(NO_3)_2$ is mixed with 500.0 mL of 0.0010 M NaF.

Model 5: Le Châtelier's Principle and Solubility



If the concentration of a reactant is increased, the equilibrium responds by producing more products.
If the concentration of a product is increased, the equilibrium responds by producing more reactant.

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$PbCl_2$ is not very soluble in water. The picture shows a test tube containing a saturated solution of lead chloride in contact with a precipitate of solid.
The effect on this solubility of adding $Pb^{2+}(aq)$ or $Cl^-(aq)$ ions from another source is called the *common ion effect*.

Critical thinking questions

1. Write down the solubility product expression, K_{sp}, for lead chloride.

2. Sodium chloride dissolves completely to give $Na^+(aq)$ and $Cl^-(aq)$ ions. If sodium chloride is added to the saturated solution, what would be the effect on the solubility of lead chloride? (*Hint:* consider how the equilibrium written above would shift, according to Le Châtelier's principle, when these ions are added).

3. If sodium chloride is added so that $[Cl^-(aq)] = 0.5$ M, rearrange your K_{sp} expression to give $[Pb^{2+}(aq)]$.

4. What is the effect of adding extra $PbCl_2(s)$ to the test tube? (Be careful!)

Model 6: Solubility and pH

Metal hydroxides dissolve to give metal ions and hydroxide ions. The position of the equilibrium (i.e. the solubility) is very sensitive to pH since this controls $[OH^-(aq)]$. For example,

$$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$$

All forms of life depend on iron and the concentration of iron in the oceans and elsewhere is one of the primary factors limiting the growth rates of the most basic life forms. One reason for the low availability of iron(III) is the insolubility of $Fe(OH)_3$ which has a K_{sp} of only 1 x 10^{-39}.

Critical thinking questions

1. Write down the expression for the solubility product, K_{sp}, for $Fe(OH)_3$.

2. The pH of the oceans is currently 8.179. Use this to work out $[OH^-(aq)]$.

3. If x moles of $Fe(OH)_3$ dissolve in 1.00 L of water, $[Fe^{3+}(aq)] = x$ mol L^{-1}. Use your answers to Q1 and Q2 to work out x in the ocean.

4. If the amount of CO_2 in the atmospheres increases, the pH of the oceans will *decrease* due to the equilibrium below. What will happen to $[Fe^{3+}(aq)]$?

$$CO_2(g) + H_2O(l) \rightleftharpoons HCO_3^- + H_3O^+(aq)$$

5. The concentration of Fe^{3+} in our blood is about 10^{-6} M. Assuming a typical blood pH of 7.4, calculate the concentration of free Fe^{3+} in our blood and account for any difference with the actual concentration.

Week 6

CHEM1102 Worksheet 12: Coordination Chemistry

Model 1: The oxidation number and electronic configuration of transition metal cations in coordination compounds

The sum of the charges of the metal cation and its ligands adds up to give the charge of the complex ion. If the complex ion is charged, this is balanced by counter ions.

The number of valence electrons on an atom is equal to its group number. In a cation, the oxidation number is equal to the number of these electrons which have been removed. Transition metal cations have a configuration d^z where z is the number of valence electrons *left over after ionization*:

> **z = number of valence electrons on atom – charge of cation**
>
> **= group number – oxidation number**

For example:

(a) Ni is in group 10 so Ni^{2+} has (10 – 2) = 8 valence electrons left: it has a d^8 configuration.
(b) Cr is in group 6 so Cr^{3+} has (6 – 3) = 3 valence electrons left: it has a d^3 configuration.

Critical thinking questions

1. Complete the 'oxidation number' column of the table below by working out the oxidation number of each of the transition metal cations.
2. Complete the '*d* configuration' column in the table by working out z for each of the transition metal ions.

Model 2: To minimize repulsion, electrons occupy orbitals singly before they pair up

There are five *d*-orbitals and, as each orbital can accommodate two electrons, there is space for a maximum of ten electrons The electrons are added to these orbitals using Model 2. This has been completed for the complexes in the first three rows of the table.

If this process leads to unpaired electrons, the complex is *paramagnetic* and is attracted towards magnetic field. If there are no unpaired electrons, the complex is *diamagnetic* and is repelled by magnets.

Critical thinking questions

1. Show the electron configuration for the transition metal cation using the box notation in the table.
2. Indicate if the complex is paramagnetic or not in the final column of the table.

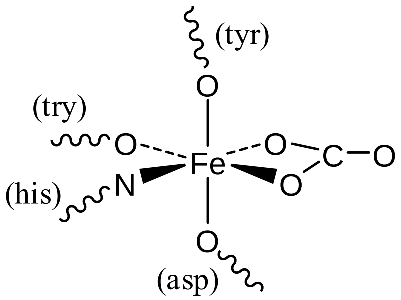
Coordination Compound or Complex	Oxidation Number	*d* Configuration	Electron Arrangement	Paramagnetic?
$K_2[NiCl_4]$	+2	d^8	[↑↓] [↑↓] [↑↓] [↑] [↑]	Yes
$[Cr(en)_3]Br_3$	+3	d^3	[↑] [↑] [↑] [ ] [ ]	Yes

$Na[MnO_4]$			☐☐☐☐☐	
$(NH_4)_2[CoCl_4]$			☐☐☐☐☐	
$[Cr(NH_3)_5(H_2O)]Cl_3$			☐☐☐☐☐	
$[Zn(en)_2Cl_2]$			☐☐☐☐☐	

*en is $NH_2CH_2CH_2NH_2$ and can bond through lone pairs on *both* N atoms.

Model 3: Iron in Biology (1): Transferrin

Iron is found in many biological molecules. Typical of its coordination chemistry in fairly recently evolved systems is *transferrin*, which is used to transport iron in the blood. The Fe(III) atom is bonded to O and N atoms through five ligands: 4 amino acids and 1 carbonate anion (CO_3^{2-}).



Critical thinking questions

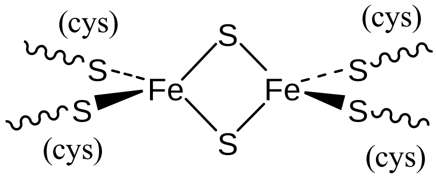
1. How many unpaired electrons will the Fe(III) atom have?

2. What is the coordination number and approximate geometry of the Fe(III) atom. Describe how this is achieved with 5 ligands.

3. The Fe(III) is released in a cell by a decrease in the pH. Use your knowledge of acid-base chemistry to suggest what the effect of low pH will be on the ligands in the complex.

Model 4: Iron in Biology (2): Ferredoxins

Iron-sulfur clusters are widespread in biology and date further back in evolutionary time. They contain Fe(II) and/or Fe(III) ions coordinated by S atoms, the simplest of which is shown opposite. They are involved in redox reactions in which the oxidation numbers of the iron atoms change.



Critical thinking questions

1. What are the coordination numbers and approximate geometries of the Fe atoms?

2. How many unpaired electrons will a Fe(II) atom and a Fe(III) atom have?

3. Given your answer to Q2, suggest why magnetic studies indicate no *net* unpaired electrons when both iron atoms are present as Fe(III) in this cluster.

4. Using your answer to Q3, predict the *net* number of unpaired electrons in the reduced form containing one Fe(II) and one Fe(III).

CHEM1102 Worksheet 13: Coordination Chemistry and Introduction to Kinetics

Model 1: Naming Coordination Compounds

The name of a coordination compound consists of two parts: the complex ion and the counter ions:

- The cation is named *before* the anion.
- The *number* of counter ions is not specified, as it can be inferred from the charge of the complex.
- There is a *space* between the names of the cation and anion so we can tell which is which.

The name of the complex ion is written as *one word*, with *no space* between its parts. To name the complex ion, follow steps 1-6:

1. Neutral ligands use the name of neutral molecule. For example, the molecule $NH_2CH_2CH_2NH_2$ is ethylenediamine and this is also used when it is a ligand. There are three common exceptions to this rule:
    - H_2O – aqua
    - NH_3 - ammine (*note the double m to distinguish it from* RNH_2 *amine ligands*)
    - CO - carbonyl
2. Negatively charged ligands use the name of the anion with the last letter changed to 'o'. Examples include:

anion name	name when coordinated	anion name	name when coordinated
fluoride	fluorido	hydroxide	hydroxido
chloride	chlorido	iodide	iodido
bromide	bromido	nitrate	nitrato
oxide	oxido	sulfide	sulfido

3. The ligands are named first, in alphabetical order according to the name of the *ligand*.
4. Numerical prefixes based on the Greek, di-, tri-, tetra-, penta-, hexa- are used to indicate the presence of more than one of any given ligand. These prefixes are *disregarded* for the purpose of determining the order of listing ligands in the name. Double vowels such as in "hexaaqua" and "pentaammine" are retained.
5. The name of the complex ion is completed with that of of the metal ion. The name of the metal ion includes its oxidation number and this is given by Roman numerals written in brackets. There is *no space* between *any* part of the name of the complex ion, including the metal atom and its oxidation number.
6. If the complex ion is *negatively* charged, the name of the metal ion is changed with 'ate' added to the name of the metal atom. When the metal name ends in 'um', the metal's name is first stripped to the second last consonant. The oxidation number is written after 'ate'.
7. For historic reasons, some elements are given their Latin names (stripped to the second last consonant) when present in complex anions:

metal	metal name in an anionic complex	metal	metal name in an anionic complex
iron	ferrate	gold	aurate
copper	cuprate	lead	plumbate
tin	stannate	antimony	stibnate

Examples

A. $[Co(NH_3)_5(OH_2]Cl_2$:

- The compound contains the complex ion $[Co(NH_3)_5(OH_2)]^{2+}$ and two Cl^- counter ions.
- The complex ion contains 5 ("penta") ammonia ligands ("ammine") and 1 water ligand ("aqua").
- Alphabetically, “ammine” is before “aqua”.
- The oxidation number is +2 so the metal ion is cobalt(II) (with no space between the element and its oxidation number)
- Hence, the complex ion is pentaammineaquacobalt(II), This is written as one word with no spaces.
- Counter ions are not bonded to the complex ion and are written as a separate word. The complex ion is a cation and thus *precedes* the anion in the name. There is a space between cation and anion so they can be distinguished.
- The compound is **pentaammineaquacobalt(II) chloride.**

B. $Cs_2[CuCl_4]$:

- The compound contains the complex ion $[CuCl_4]^{2-}$ and two Cs^+ counter ions.
- The complex ion contains 4 ("tetra") Cl^- ligands ("chlorido").
- The complex ion is an anion so the ending "ate" is used. For copper, the "cuprate" is used.
- The oxidation number is +2 so the metal is cuprate(II).
- Hence, the complex ion is **tetrachloridocuprate(II)**. This is written as one word with no spaces.
- Counter ions are not bonded to the complex ion and are written as a separate word. The complex ion is a anion and thus the counter cation *precedes* the anion in the name. There is a space between cation and anion so they can be distinguished.
- The compound is **caesium tetrachloridocuprate(II).**

Critical thinking questions

1. Name the complex ions below.

   (a) $[CoCl(NH_3)_5]^{2+}$

   (b) $[AuCl_3(OH)]^-$

   (c) $[CrCl_2(OH_2)_4]^+$

   (d) $[Ru(NH_3)_5(OH_2)]^{3+}$

2. Name the coordination compounds below:

   (a) $[CoCl(NH_3)_5]Cl_2$

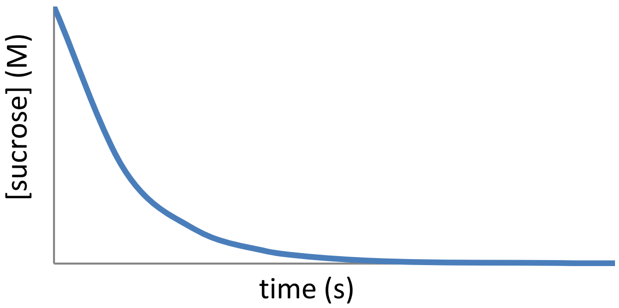
   (b) $K[AuCl_3(OH)]$

   (c) $[CrCl_2(OH_2)_4]Cl$

   (d) $[Ru(NH_3)_5(OH_2)]Br_3$

   (e) $[Ni(en)_3]I_2$ (en = ethylenediamine)

Model 2: Rate of Reaction



The figure opposite shows how the sucrose concentration changes when it reacts with acid according to the reaction below:

$\text{sucrose} + H_3O^+ \rightarrow \text{fructose} + \text{glucose}$

The rate of the reaction can be measured by measuring the *change* in the concentration of sucrose, H_3O^+, fructose or glucose over *time*:

$$\text{rate} = -\frac{\Delta[\text{sucrose}]}{\Delta t} = -\frac{\Delta[H_3O^+]}{\Delta t} = +\frac{\Delta[\text{fructose}]}{\Delta t} = +\frac{\Delta[\text{glucose}]}{\Delta t}$$

Critical thinking questions

1. What are the units of rate?

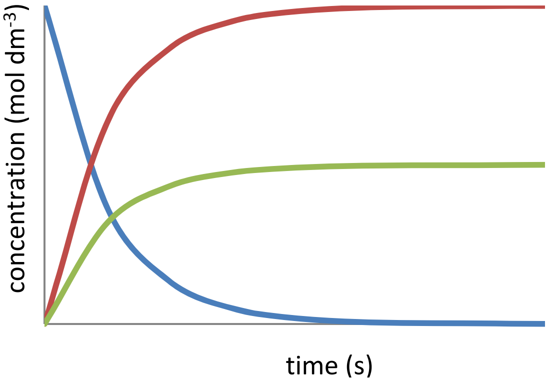
2. Sketch on the figure above how the concentration of *fructose* will be changing over the same time period.

3. Why is there a minus sign before $\Delta[\text{sucrose}]/\Delta t$ and $\Delta[H_3O^+]/\Delta t$ and a plus sign in front of $\Delta[\text{fructose}]/\Delta t$ and $\Delta[\text{glucose}]/\Delta t$ in the equation above for the rate?

4. The change in concentration with time of the reactants and products for the reaction below is shown in the figure opposite.

   $2NO_2(g) \rightarrow 2NO(g) + O_2(g)$

   Label each curve with the chemical it represents.



Model 3: The Rate Law

The rate of reactions are often found to be proportional to the concentration of each *reactant* raised to some power:

$\text{rate} \propto [\text{reactant}_i]^{x_i}$

x_i is called the *order* of the reaction with respect to reactant$_i$ and is commonly an integer such as 0, 1 or 2. The order of the reaction is the sum of all x_i: order = $\sum_{i=1}^{n} x_i$

The relationship between the rate of a reaction and the concentration of the reactants is known as the rate law. For the hydrolysis of sucrose in Model 2, for example, it is found to be

$\text{rate} \propto [\text{sucrose}][H_3O^+]$ or $\text{rate} = k\,[\text{sucrose}][H_3O^+]$

k is the rate constant and is simply the proportionality constant.

Critical thinking questions

1. What happens to the rate of a reaction if the initial concentration of the reactant is doubled for each value of *x* below?

   (a) $x = 2$ (b) $x = 1$ (c) $x = 0$

2. For the hydrolysis of sucrose, what happens to the rate of the reaction for each of the changes to the initial concentrations of the reactants below?

(a) [sucrose] is doubled but $[H_3O^+]$ is not changed.

(b) [sucrose] is not changed but $[H_3O^+]$ is doubled.

(c) Both [sucrose] and $[H_3O^+]$ are doubled.

3. Lactose can be decomposed into galactose and glucose through acid hydrolysis or using the enzyme lactase. In the basic environment of the intestine, only the enzyme catalysed decomposition is possible and lactose intolerance in humans arises from a deficiency of lactase. In the acidic environment of the stomach, however, hydrolysis should still occur and much research has been devoted to its study.

The table below shows the results from 3 experiments in which the initial rate of lactose decomposition was measured at different initial concentrations of lactose and acid.

experiment	initial rate ($M\ s^{-1}$)	$[\text{lactose}]_0$ (M)	$[H_3O^+]_0$ (M)
(1)	0.00116	0.01	0.001
(2)	0.00232	0.02	0.001
(3)	0.00464	0.01	0.004

(a) Between experiments (1) and (2), how were $[\text{lactose}]_0$ and $[H_3O^+]$ changed? What effect did this have on the rate?

(b) Between experiments (1) and (3), how were $[\text{lactose}]_0$ and $[H_3O^+]$ changed? What effect did this have on the rate?

(c) Using your answers to Q1 and to parts (a) and (b), determine the values of x and y in the rate law.

$$\text{rate} = k[\text{lactose}]^x[H_3O^+]^y$$

(d) Between experiments (2) and (3), how were $[\text{lactose}]_0$ and $[H_3O^+]$ changed and what effect did this have on the rate? Check that this is consistent with your rate law.

(e) Using your rate law and any one of the experiments, determine the value of the rate constant, *k*. Remember that a measurement is meaningless without a unit.