

PART IA Chemistry Notes

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This note is for Cambridge first year course "Part IA Chemistry" in Natural Sciences. The lecturers were Prof. Peter Wothers, Prof. Deborah Longbottom, Prof. Steven Lee, Prof. James Keeler and Dr Daniel Beauregard, each led us through some topics. While listening to lectures, completing worksheets, attending supervision sessions and enjoying practicals, I wrote this note for better memorization of knowledge, since I was, still is, and (I expect) will be, poor in chemistry. Also, it is likely that I constantly made mistakes throughout this note, I would be grateful if someone could kindly point it out and email me directly as soon as possible.

I would particularly like to express my sincere thanks to Prof. Deborah Longbottom, who tried her best to make lectures so clear that no one could understand even a word.

I want to express my sincere thanks to my family members, who spared no effort to support me, to Jesus College who pulled me out from the summer pool, to all the lecturers who delivered knowledge and kindly answered all the questions after lectures, and to my girlfriend, the great biologist Ms. Jinghao Yan, who provided precious suggestions and offered a lot of help during the academic year. In fact, most of this note was completed during the time we studied together in Quincentenary Library and Rosemary Murray Library.

Part I

**The Shapes and Structures
of Molecules - 1**

This part covers the contents of course A: the shapes and structures of molecules, and some additional topics in my practical and supervision sessions as well. As it is the first part of Part IA Chemistry, it is designed to lay a solid foundation for more specific knowledge. It is not hard, but it is going to be time-consuming. The key thing is: one should always think from a variety of perspectives when trying to solve a problem.

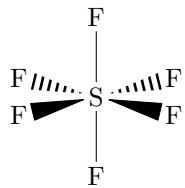
Chapter 1

Representing Molecules

1.1 Inorganic molecules

Inorganic molecules normally have relatively small sizes, and the bonds between atoms can vary from ordinary σ bonds to ionic bonds. Though the types of interactions are different, we always draw a line between two atoms to indicate that there are some connections happening. Remember that, in both organic and inorganic chemistry, our drawn structure can only relatively represent the true structure in a molecule, since the nuclei and electrons are oscillating in complex patterns, and the uncertainty principle forbids us from knowing both their position and momentum accurately.

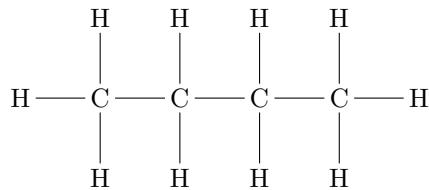
A simple way to predict the number of bonds around a molecule is to count the electrons. S has 6 electrons so it normally forms 2, 4 or 6 bonds, leaving 2 pairs, 1 pair and 0 pair of free electrons, respectively. However, this does not work on CB_4H_8 , because hydrogen simply can't have 2 bonds! In the coming sections, you will see that our representation methods are not "true" at all, but they do make life a lot easier when trying to picture structures in head.



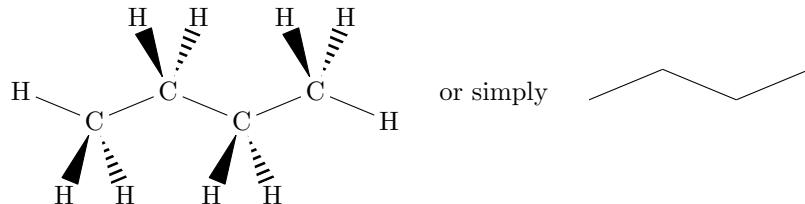
The drawn structure of SF₆

1.2 Organic molecules

Generally, organic molecules are built up by a carbon-based structure, with each carbon forming 4 bonds around it. One thing to remember is university students are required to include hybridization into their figure, which means, instead of drawing



we should draw more informatively like



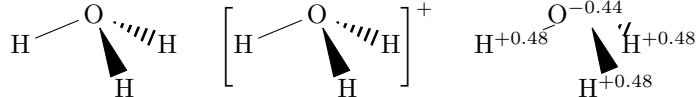
Note that the bonds coming in and out of the plane should be united on the same side of the vertical line.

1.3 Formal charges

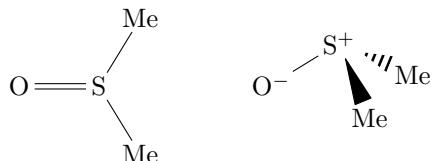
We can work out formal charges in the following way:

1. Find the number of electrons associated with a particular atom, N_e .
2. Find the number of valence electrons associated with neutral atom, N_v .
3. Calculate the formal charge, $(N_v - N_e)$.

The most common example is the hydrogen iron, H^+ , or formally, H_3O^+ .



The first figure does not show anything about formal charges, the second shows net charge of the iron, which is acceptable, the final one is a proper way to draw H_3O^+ . Disappointingly, we don't usually have the data of charge distribution for a given ion, so we accept the second representation, but highly recommend students to think it in the way of the final representation.



Another great example is dimethyl sulfoxide ($(CH_3)_2SO$), by calculating N_e and N_v we can see that there must be a lone pair around S. Therefore, instead of the misleading structure on the LHS, we should draw the **relatively** correct one on the RHS.

1.4 Naming compounds

We will only talk about organic compounds, in other words, the IUPAC naming method. Since the method is clearly explained in Wikipedia page, we will just skip those rules and just write down a useful table.

Name	Molecular formula	Number of possible isomers
methane	CH ₄	0
ethane	C ₂ H ₆	0
propane	C ₃ H ₈	0
butane	C ₄ H ₁₀	2
pentane	C ₅ H ₁₂	3
hexane	C ₆ H ₁₄	5
heptane	C ₇ H ₁₆	9
octane	C ₈ H ₁₈	18
nonane	C ₉ H ₂₀	35
decane	C ₁₀ H ₂₂	75

Chapter 2

Determination of Molecular Structure

There are many ways to determine a molecular structure, they are often combined and eventually lead us to a final answer. That is because in organic chemistry the final mixture we get often include a lot of similar compounds, our goal is to determine and separate them apart.

In practice we will encounter a total of six methods, each gives us data in different aspects, and in practical sessions we will learn some ways to separate the mixture.

The six methods are: X-ray diffraction, nuclear magnetic resonance (NMR), IR spectroscopy, UV-visible spectroscopy, microwave spectroscopy and mass spectrometry.

2.1 X-ray crystallography

We can use X-ray diffraction to determine the structure of a molecule because the spacing between atoms is generally around 1\AA , which is exactly the wavelength range of X-ray. This method will give us a map of electron density, and we can certainly determine the basic structure with it.

Apart from the position of bonds, we can guess out which atom is there as well. Since oxygen is more electronegative than carbon, we will see more circles around the oxygen. Also, there will be more lines along a double bond than a single bond, since double bonds are formed by overlapping 2 orbits.

The **advantages** of X-ray crystallography are:

1. The **ultimate method** of structural information.
2. Gives locations of all atoms.

The **disadvantages** are:

1. Need to be crystals.
2. Need to be good quality crystals (though 1mm in diameter is enough).
3. Sometimes hard to locate hydrogen atoms because they are the least electronegative ones.

You may be curious about how this is done, the answer will be given in solid state physics notes. It's stupid to talk about it at this stage. However, it's interesting to think about the equipment generating high-energy X-ray. Ordinary glass will just melt if penetrated by X-ray at that high energy density, and diffraction will happen in almost all crystal materials, which hugely affects our result (yes we can cancel it out with simple mathematics if the window is a perfect crystal, but we can't afford making one at that size). Clever chemists came up with the idea of using hydrogen since they have the lowest electron density but failed in practice. They turned to helium and lithium, unsurprisingly, they failed again and again. Eventually, we use pure beryllium to make the window and it worked quite well.

2.2 Mass spectrometry

This is probably the most effective way to determine the exact molecular formula. The idea in theory is rather simple:

$$M_{\text{molecule}} = \sum_i n_i m_i \quad (2.1)$$

If we are able to measure m_i to enough decimal places (actually $1/10^7$ can be achieved), we will be able to figure out how many atom i are there in the molecule. This may not be mathematically right (we have more unknown variables than equations), but considering the fact that one kind of isotope can only have one value in the same apparatus, our method seems reasonable.

2.2.1 Measuring method

Let's take a brief look about how to measure the molecular masses. There is a picture showing a typical mass spectrometry equipment. After introducing the sample into the instrument, the sample is vaporized automatically because it is near vacuum in the ion source. Then the molecules will be ionized by strong electromagnetic field provided by the ionizing filament. By focusing the ions onto detectors using uniform magnetic field, the apparatus can output a mass spectrum, where each peak represents an ion.

Nowadays we measure the time of an ion going through fixed distance to calculate the molar mass, mainly because we can measure time a lot more accurately than several decades before, and partly because we cannot produce a perfectly uniform magnetic field.

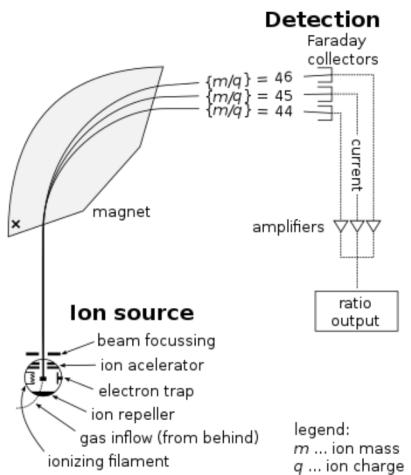


Figure 2.1: Old fashioned mass spectrometer

Furthermore, the methods of ionizing have changed. One can fire high energy electrons to the vapor and knock electrons out of the molecules, which generally leads to M^+ .

2.2.2 Electrospray

Another way to do it is **electrospray**. In this technique the sample is introduced into the equipment as charged aerosol droplets. When the solvent evaporates, the molecule will be left with an ion stuck on. Sodium ion, MeO^- and CH_3CO_2^- are commonly used examples.

When calculating molar mass, remember to remove the mass of added ion, or take the escaping electron into account.

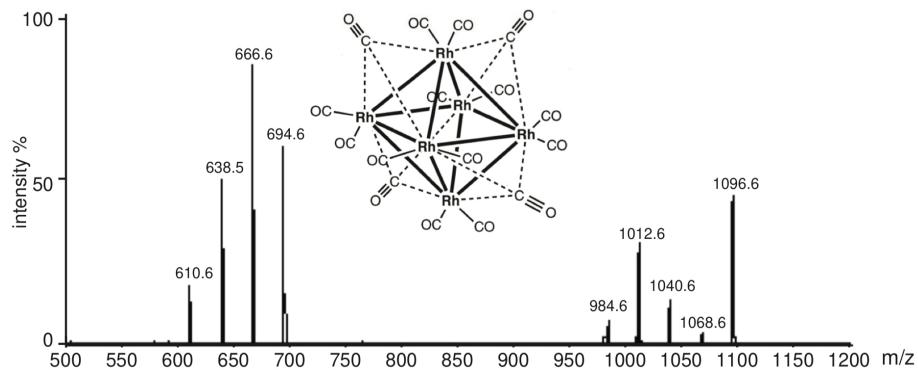
2.2.3 Mass spectrum

So far you must be expecting a neat and clean mass spectrum of a molecule, however it is not the case.

Ionized molecules carry net charge, which pull them out of energy favored states. The molecules will begin to **fall apart**. Therefore when you look at the mass spectrum of $[\text{Rh}_6(\text{CO})_{16} + \text{MeO}^-]$, you will find the peaks of $[\text{Rh}_6(\text{CO})_{16} + \text{MeO}^-]$, $[\text{Rh}_6(\text{CO})_{15} + \text{MeO}^-]$, $[\text{Rh}_6(\text{CO})_{14} + \text{MeO}^-]$, and $[\text{Rh}_4(\text{CO})_4 + \text{MeO}^-]$ $[\text{Rh}_4(\text{CO})_3 + \text{MeO}^-]$, etc.

The **advantages** of mass spectrometry are:

1. Gives precise molecular formula.
2. Excellent for analysis of mixtures.

Figure 2.2: Mass spectrum of $[\text{Rh}_6(\text{CO})_{16} + \text{MeO}^-]$

3. Tiny sample needed (I bet the police like this).

The **disadvantage** is:

1. Often difficult to interpret because of the "falling apart" process.

Remember that the spectrum is related to your apparatus, which means your data will fit only if you compare them with previous data from that particular apparatus, this rule works for all six methods.

Also, this method is called mass **spectrometry**, not mass spectroscopy for a reason. You will understand immediately after reading the next subsection.

2.3 A quick note on spectroscopy

The electromagnetic spectrum tells us the relationship between each type of "light". Electromagnetic wave with higher frequency carries larger energy per photon, and as we can see from Fig 1.3, has greater ability to influence the inner part of atoms.

2.4 Infrared (IR) spectroscopy

2.4.1 Basic theory

Infrared spectroscopy is closely related to normal modes in multi-dimensional harmonic oscillation. The basic idea will be covered in Part IB Physics A, but if you want to take a look in advance I would recommend Goldstein's Classical Mechanics.

Traditionally, what we normally get is a **transmission spectra**, but now it's increasingly to see an **absorption spectra**, in which all peaks are pointing upwards. Ideally these two spectra satisfy mirror symmetry, but we will see that there are small differences between them.

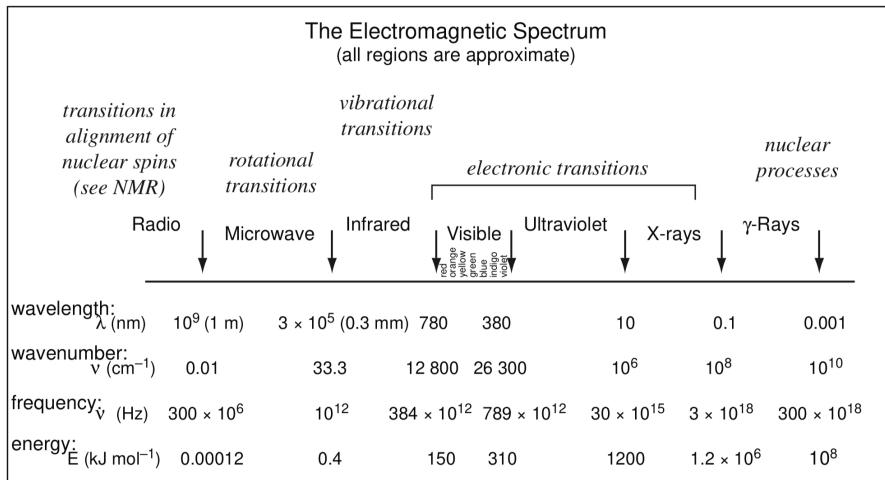


Figure 2.3: The approximate electromagnetic spectrum

The frequency in the plot is in wavenumbers and has unit cm^{-1} . with simple calculation we can show that it is proportional to frequency ν and the quantized energy $E = h\nu$ as well.

$$\tilde{\nu} = \frac{1}{\lambda} \frac{1}{100} = \frac{\nu}{100c} \propto \nu \quad (2.2)$$

Just like what we did in classical mechanics, no matter how complex the molecule is, the equations always become

$$k + \omega^2 m = 0, \quad (2.3)$$

thus we can guess our wavenumbers can be represented by

$$\tilde{\nu} = \frac{1}{2\pi c} \sqrt{\frac{k_f}{\mu}}, \text{ where } \mu = \frac{m_1 m_2}{m_1 + m_2}. \quad (2.4)$$

Note that μ is in kg and c is $3 \times 10^{10} \text{ cm s}^{-1}$.

In this equation, μ and constants are all easy to find, the only unknown is the force constant, k_f , which can only be found through experiment. However, we can predict that it is in positive correlation with bond strength, since the physical meaning of k_f is Hooke's coefficient.

2.4.2 Typical regions

Now let's make our way through the horizontal axis from high frequency to low frequency. Firstly, $4000 \sim 2500 \text{ cm}^{-1}$, the X-H **single bond** region. Then we have $2500 \sim 2000 \text{ cm}^{-1}$ for **triple bonds**, including double bond with formal charges such as $\text{C}^- = \text{O}^+$. $2000 \sim 1500 \text{ cm}^{-1}$ is the region for **double bonds**, and **fingerprint region** is below 1500 cm^{-1} .

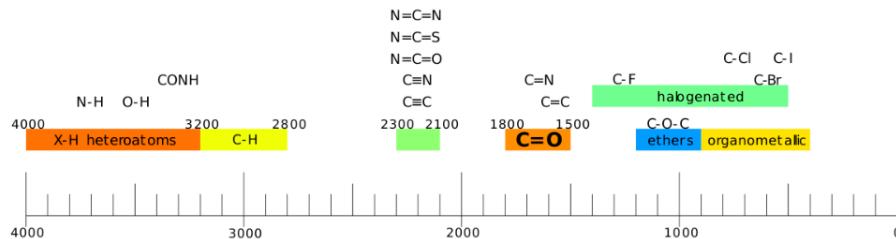


Figure 2.4: Typical region for different bonds in IR spectroscopy

For atoms in the same period, we can predict their relative relation by comparing their reduced masses, μ . You may come up with the question "why is that?", the answer is for atoms in different period, the matching between p-orbits are different, such as C = O and C = S, the $2p$ orbital of carbon and $3p$ orbital of sulfur can't match as perfectly as two $2p$ orbitals, thus the π -bond is relatively weaker. However, the reduced mass is bigger. So in general we cannot predict which one has the larger wavenumber.

Finally, the fingerprint region. Its properties are obvious from its name - each compound leaves its own "fingerprint" in this region. However, some kinds of bond, either relatively weak or hard to drive (the electric dipole is too small), can fall into this region, but they are still easy to read and identify because their peak is significantly high, and one bond can be related to different normal modes.

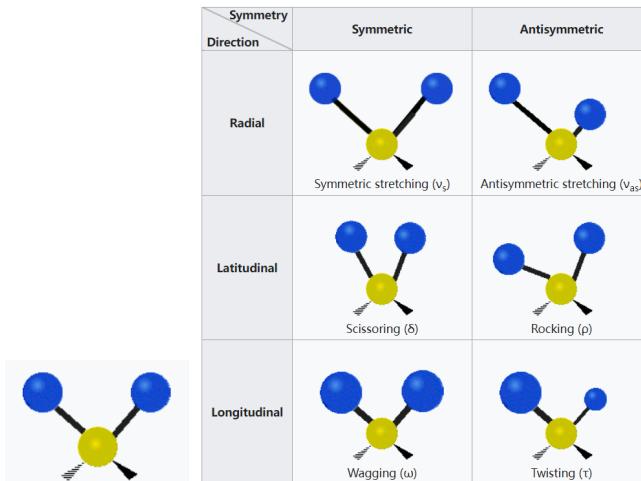


Figure 2.5: Different stretching patterns

2.4.3 Stretching patterns

Let's take a look at some stretching patterns, each corresponds to a normal mode. The pair we will usually discuss is symmetric and antisymmetric stretching. Other patterns normally disappear in noise or hide themselves in the fingerprint region.

"Whilst the frequency at which a bond absorbs depends on its strength, exactly how big¹ the peak is depends on the dipole moment of the bond" (Peter Wothers). That means **symmetric stretches in symmetric molecules** don't show themselves in absorption spectrum. But luckily, we can use **Raman spectroscopy**, which look at frequencies of light scattered by the molecule, to determine the existence of such bonds.

Personally I don't agree with this point. I discussed with my supervisor and we believe it is reasonable to say that dipole contributes to frequency. We will come back to this when talking about conjugation.

Now it is time to summarize what we've collected in the lectures. We will discuss part by part below the table.

No.	Bond	Stretch	Wavenumber	Description
1	CH	symmetric	3374	in ethyne
2	CH	antisymmetric	3287	in ethyne
3	CH	trans bend	612	in ethyne
4	CH	Sics bend	729	in ethyne
5	CH		2900~3200	typically just less than 3000
	CH		~3250	specifically sp carbon
6	NH		~3300	
7	NH ₂	symmetric	~3300	
8	NH ₂	antisymmetric	~3400	
9	OH		~3300	VERY broad
10	OH		~3600	sharp when shielded
11	C = C		1635~1690	generally weak
12	C = C		1450~1625	in benzene, weak
13	NO ₂	symmetric	~1350	in the fingerprint region
14	NO ₂	antisymmetric	~1530	easier to spot
15	C = O		~1715	ketone
16	C = O		1750~1820	CH ₃ COCl
17	C = O		1600~1690	CH ₃ CONH ₂
18	C = O		~1730	CH ₃ COOH
19	C = O		~1745	CH ₃ COCH ₃
20	C = O		~1730	CH ₃ CHO
21	CN		~2250	triple bond
22	CC		2100~2250	triple bond

1~4. This is about different stretching patterns in ethyne. Not surprisingly both trans and sics fall into fingerprint region, but it is odd that symmetric

¹Intensity.

stretch has larger wavenumber than antisymmetric. By the lecturer, this is just a happy coincidence. However, physics is always lying behind freaking chemistry. If you work out the problems in Lev Landau's Classical Mechanics you will find the answer.

5~6. Nitrogen is more electronegative than carbon, so force constant is a lot larger, it wins even if nitrogen is heavier.

7~8. This is a typical case of dipole contributing to force constant. In antisymmetric stretch we are moving two identical bonds but in symmetric stretch the total dipole of the NH₂ group is equal to a single N-H dipole, which leads to a decrease in force constant. However, this is entirely my PERSONAL idea, if something is wrong, please contact me.

9~10. OH is really broad because of the influence of hydrogen bond. The more hydrogen bonds there are, the broader it will be. One way to understand this is: hydrogen bond is withdrawing electron from the OH bond, thus strengthening it. However, the interaction has a lot of freedom so different OH groups are interacting with different numbers of ... other things, making the spectrum broad like a bell curve.

11~20. Finally we arrive at conjugation, and its competition with electronegativity. In benzene we have a ${}^6_6\Pi$ and you can picture it as: instead of 3 double bonds, we now have 6 one-and-a-half bonds in a ring. Of course $1.5 < 2$. Conjugation is right now just another name of existence of Π bond. Similarly, in NO₂ we have ${}^3_3\Pi$. Conjugations can add up, also, conjugation can happen as long as there is a pi-sigma-pi structure, no matter between triple & double, double & double or triple & double.

15~20 are all about competing among factors. Let's compare CH₃COCl and CH₃COOH, why does the former group has larger wavenumber, given that oxygen is more electronegative than chlorine? The answer is in the presence of oxygen, there is a clear conjugation (${}^3_3\Pi$), but the 3p orbit of chlorine can't match perfectly with the 2p orbit of carbon. In a nutshell, **conjugation can more effectively reduce the shifting effect caused by electronegativity in CH₃COOH**.

However, electronegativity does not always win the game, in CH₃CONH₂ it failed to give a shift in wavenumber, and conjugation wins.

We can use it to identify different isomers. An clear example is between 3-Butyn-2-one and 3-Butyn-1-ol. The former one has conjugation between triple bond and double bond, but the latter does not. Therefore you can predict one of them having a peak at ~ 1715 while the other having ~ 1680 .

In 17, NH₂ group is donating electron density. In 20, hydrogen is weakly donating electron density. Comparing 19 and 20, you will see that conjugation can be added, thus OCH₃ is more capable of withdrawing electrons than OH group. In a word, groups withdraw electron density strengthen C = O double bond, groups donating electron density weaken C = O double bond.

21~22. Same as 5~6, you can predict it yourself.

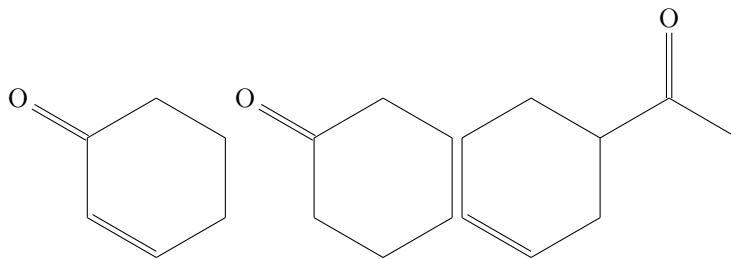


Figure 2.6: Conjugated and non-conjugated ketones

2.4.4 Special cases

The first one on the left hand side is called conjugated ketones, it has wavenumber 1690, 25 smaller than normal ketones at the right. Conjugation lowers the base frequency by 20~30.

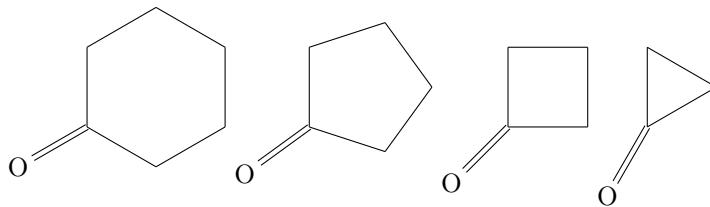


Figure 2.7: 6-ring → +30 → 5-ring → +35 → 4-ring → +35 → 3-ring.

Due to vibration, the smaller the size of the ring, the higher the stretching frequency.

2.4.5 Summary

bond strength	molar mass	electric dipole	conjugation	electronegativity	ring
+	-	0 but intensity	-	+	-

2.5 Nuclear Magnetic Resonance Theory

2.5.1 Basic knowledge

Certain nuclei posses spin and as a result it can have interaction with external magnetic field. When placed in a strong magnetic field the interaction will give rise to a set of nuclear spin energy levels. Radiowaves of the appropriate frequency cause transition between these energy levels and this gives rise to the NMR signal.

To create strong magnetic field, superconductivity coil is always used, therefore, though our sample remains as liquid solutions during the experiment, the machine works at a very low temperature (probably just a few K).

The nuclear spin is specified by the nuclear spin quantum number, I . It may take values of non-negative half-integers. A nucleus with spin I gives rise to $(2I + 1)$ different energy levels. Each of the $(2I + 1)$ levels takes values from I to $-I$ in integer steps.

e.g. When $I = 3/2$, $m_l = \frac{3}{2}, \frac{1}{2}, -\frac{1}{2}, -\frac{3}{2}$.

The **general way to predict I** is:

1. Odd mass number \rightarrow half-integral spin.
2. Even mass number + odd numbers of protons \rightarrow integral spin.
3. Even mass number + even numbers of protons \rightarrow zero spin.

Basically, NMR tests whether the "freedom" of a nuclei, nuclei in different environments show different frequencies in NMR spectrum.

We quote the resonance frequency of a line as its shift from an agreed reference compound (usually TMS, $\text{Si}(\text{CH}_3)_4$), expressed as a fraction to compensate for the magnetic field strength. The frequency is described (for easy reading) in units **part per million** (ppm).

$$\delta = 10^6 \times \frac{\text{frequency of resonance} - \text{frequency of reference}}{\text{frequency of reference}} \quad (2.5)$$

While the relative separation of different kinds can be compared in the same plot, the exact difference in energy between the different spin states depends on the strength of the external magnetic field. Intuitively, the stronger the external magnetic field, the larger the energy separation. Actually, energy separation is perfectly proportional to the external field, but different kinds of atoms have different separation in the same external field.

2.5.2 Local magnetic field

Apart from external magnetic field, the exact difference in energy depends on the local magnetic field. For example, in a benzene ring, the local field in the ring is smaller than the external field, while the local field outside the ring is larger, due to the ${}^6\text{II}$ diamagnetic effect.

Another example of electrons shielding nuclei is simple one-carbon compounds.



Figure 2.8: Compounds with decreasing frequency in ${}^{13}\text{C}$ NMR

Molecule	Chemical shifts (ppm)
CH_3CH_3	7
CH_3Cl	26
CH_2Cl_2	54
CHCl_3	77
CCl_4	96

For example, carbons that are more shielded show smaller (or more negative) shifts, while carbons that are attached to electronegative groups show larger shifts.

2.5.3 Equivalent nuclei

Equivalent nuclei only shows one peak in the NMR spectrum. That is not surprising because they are all in the same environments, so by symmetry all influences vanish.

2.6 Carbon-13 NMR

2.6.1 Typical scale

Carbon-13 NMR spectra usually run from 0 to 200 ppm, which can be divided into four regions in the table below. Or, to be clearer:

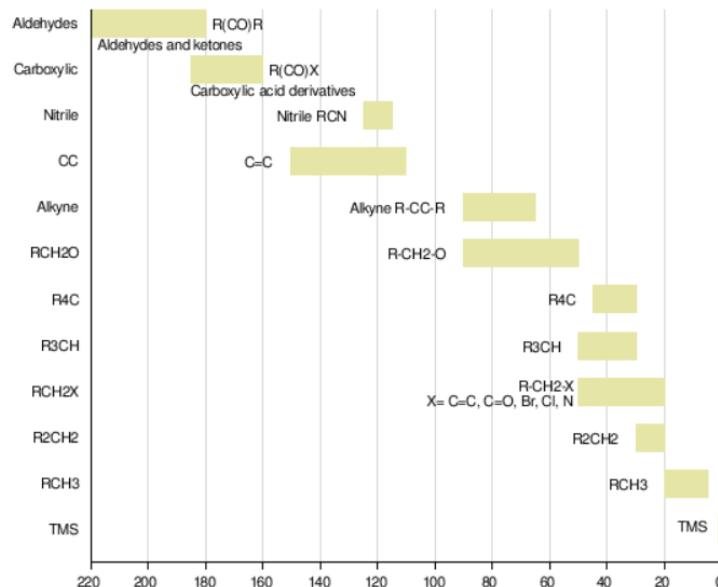


Figure 2.9: Typical chemical shifts in carbon-13 NMR

Region (ppm)	Carbon
0~50	sp ³ carbons
50~100	sp ³ carbons with very electron withdrawing groups attached
100~150	sp ² carbons
150~200	sp ² carbons with very electron withdrawing groups attached
~70	sp carbons

By "very electron withdrawing", we typically mean oxygen. In fact, sp³ carbon with nitrogen attached often gives only ~40 ppm.

2.6.2 Intensity

The intensity, or size, of a carbon-13 NMR signal is determined by several factors. Two main factors are the **number of protons attached**, and the **number of carbons in the same environment**.

2.6.3 Coupling

Coupling is a phenomenon caused by the dependence of local magnetic field. The extra field given by the spin moment of nearby atoms creates difference in chemical shifts. These shifts are usually only a few Hz, but rather important because it allows us to make many predictions.

C-H coupling is rarely seen because in normal cases carbon-13 NMR spectrum is proton-decoupled.

C-C coupling is also rarely seen, not because it does not exist, but because the natural abundance of carbon-13 is only 1 percent. Therefore C-C coupling will only give signals that are 200 times lower than the main signal, and always vanish in noise.

In contrast, **coupling between carbon and fluorine are commonly seen**. The difference is denoted by $^aJ_{A-B}$, in which a is the number of bonds connecting atoms A and B.

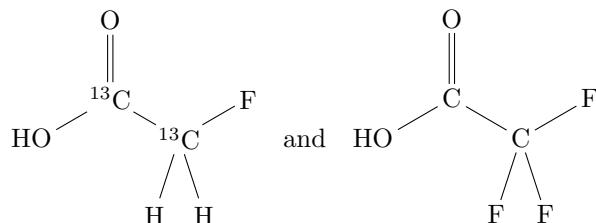


Figure 2.10: Fluoroacetic acid and trifluoroacetic acid.

Fig 2.10 shows the structure of **radiative** fluoroacetic acid. In its carbon-13 NMR spectrum, we should be able to see both $^1J_{C-F}$ and $^2J_{C-F}$. Furthermore, there is still coupling between two carbons, so a separation of $^1J_{C-C}$ must be added, resulting in a doublet of doublets.

There are more funny examples, Fig 2.10 also shows the structure of trifluoroacetic acid, where three C – F coupling exists, resulting in two quartets ($^2J_{C-F}$ and $^3J_{C-F}$).

As long as the coupling types and constants are the same, the ratio of the intensities can be predicted by the traditional Yang Hui's Triangle. However, it is not the case when coupling constants are different, even if they are all 2J . Here is a typical example. In the structure of PF₃, all the fluorine atoms are

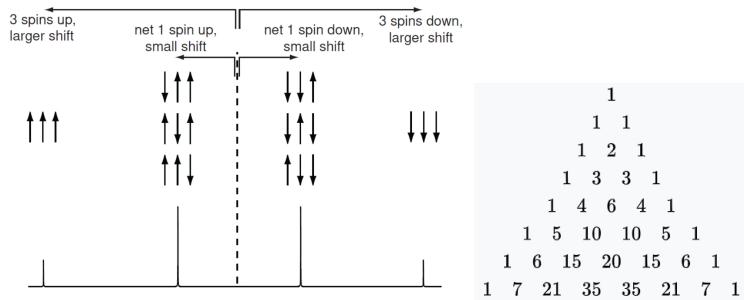


Figure 2.11: Yang Hui's triangle, also known as the Pascal's triangle, can be used to predict ratio of intensities.

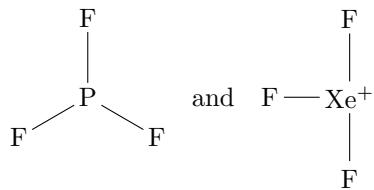


Figure 2.12: PF_3 and XeF_3^+

equivalent because it has planar triangular shape. However, XeF_3^+ has the so-called "T-shape", in which three fluorine atoms are not equivalent. Therefore, its ^{129}Xe NMR would be a triplet of doublets (td).

Note that larger coupling constants goes first (td is different from dt).

2.6.4 Decoupling

Normally all carbon-13 NMR plots are proton-decoupled, because we want to have more intensity in a single carbon peak. A proton-coupled carbon-13 NMR give us more information on how many protons are attached to that carbon.

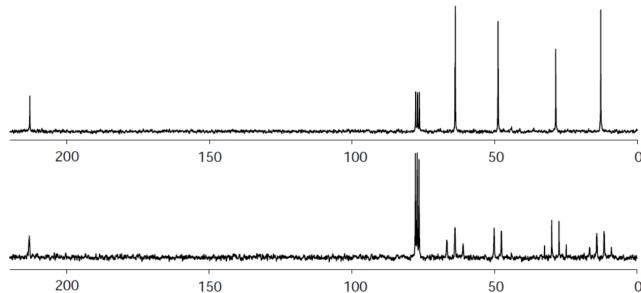


Figure 2.13: Example of a proton-decoupled carbon-13 NMR (top) and a proton-coupled one.

In the given example, fig 2.13, the five environments have 0,2,1,3,3 protons attached, respectively.

There is another disadvantage of proton-coupled NMR plot. if carbon signals are close, the separated peaks can overlap and mislead us. To solve this, we can ask our NMR spectrometer to get the best of both worlds – to do an experiment called the **Attached Proton Test, APT**.

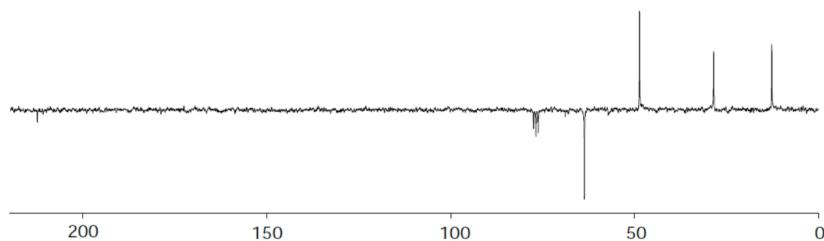


Figure 2.14: APT result of the same compound.

How this works need not concern us, but the result is that the peaks from the carbon atoms with an even number of protons attached, 0 or 2, point one way (**the same way as the deuterated solvent**, this is how we identify the sides) and the carbon atoms with an odd number of protons, 1 or 3, point the other way.

Satellites Consider the NMR spectra for chloroform, CHCl_3 . When recording a carbon-13 NMR every carbon-13 is attached to a spin 1/2 proton and so unless we applied broadband proton decoupling, coupling to the proton would mean the carbon-13 signal would appear as a doublet. In contrast, when recording a proton NMR spectrum of chloroform, most protons in the sample are attached to spin-zero carbon-12 and so no coupling is observed. However, in 1% of the sample, the proton is attached to a carbon-13 which means if we looked very closely at the baseline, we just might see the tiny fraction that appears as a doublet.

However, **the carbon-13 satellites are always lost in background** because the natural abundance of carbon-13 is really low. **However, it is not the case when it comes to other elements.** Therefore, when coupling forms do not fit to the Yang Hui's triangle, it may due to natural abundance.

2.7 Proton NMR

We study proton NMR in a different way, because coupling matters a lot here. The integrated area under peaks can give us enough information about how many protons are evolved in the measurement, and at the end we will have a glance at typical scales, which is seldomly used in practices.

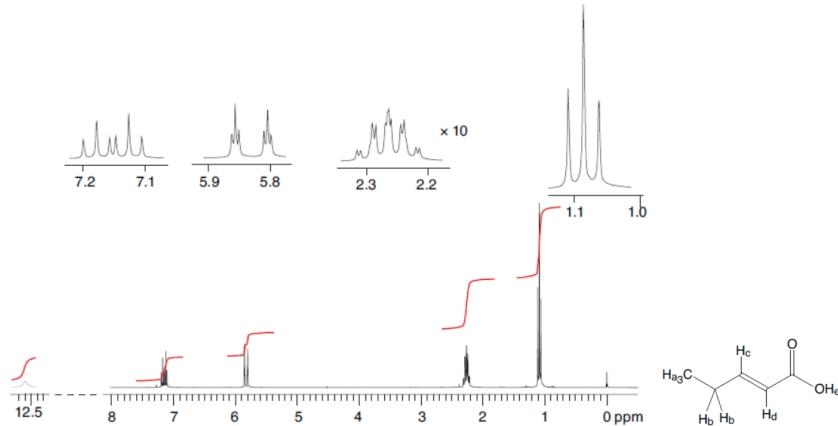
2.7.1 Coupling

Proton has spin 1/2, so there are coupling between them as long as there are in different environments. Normally, the coupling does not go farther than 3 bonds, but in some cases it can. We will go through them in a minute.

Typical coupling constants are shown in the table below:

Coupling type	Coupling constants (Hz)
$^3J_{\text{H}-\text{H}}$	7
$^3J_{\text{H}-\text{H}}$ trans	17~18
$^3J_{\text{H}-\text{H}}$ sics	12~13
$^2J_{\text{H}-\text{H}}$ on sp^2 carbon (geminal)	0~3
$^2J_{\text{H}-\text{H}}$ on sp^3 carbon (geminal)	8~13~18

How to align NMR? Here is an example:



$\delta = 12.6\text{ppm}$, $I = 1\text{H}$, wide singlet (near oxygen), H_e

$\delta = 7.15\text{ppm}$, $I = 1\text{H}$, dt, $^3J_{\text{H}-\text{H}} = 17, 7\text{Hz}$, H_c

$\delta = 5.82\text{ppm}$, $I = 1\text{H}$, dt, $^3J_{\text{H}-\text{H}} = 17\text{Hz}$, $^4J_{\text{H}-\text{H}} = 3\text{Hz}$, H_d

$\delta = 2.26\text{ppm}$, $I = 2\text{H}$, qn d, $^3J_{\text{H}-\text{H}} = 7\text{Hz}$, $^4J_{\text{H}-\text{H}} = 3\text{Hz}$, H_b

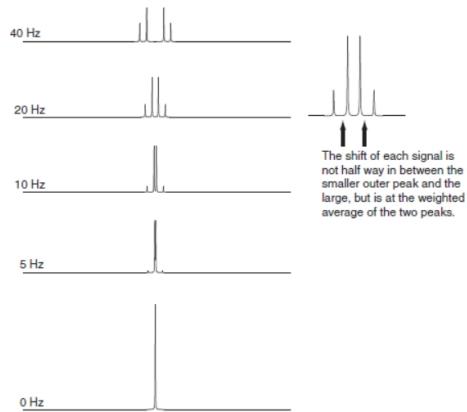
$\delta = 1.08\text{ppm}$, $I = 3\text{H}$, t, $^3J_{\text{H}-\text{H}} = 7\text{Hz}$, H_a

Note that the chemical shift in ppm (part per million). This is either the centre of a signal, or the weighted average of a roofed doublet. Only for unresolved multiplets should a range be given. But the respective coupling constants in Hz for each of the splittings.

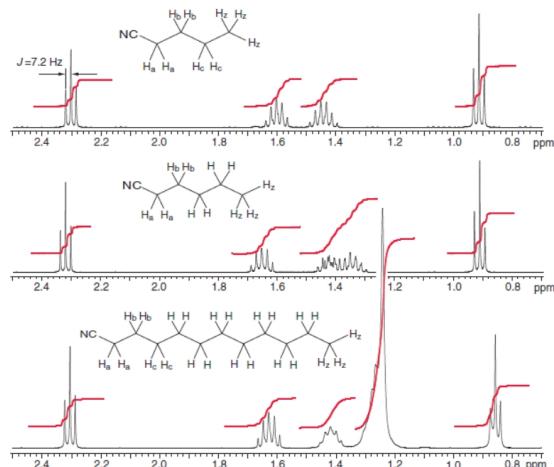
Also, **multiplets** can be seen in various conditions. For example, a triplet bond would work as a wave guide and may encourage 4J or even 5J , aromatic rings may also play similar roles.

Roofing For two signals that are coupling to each other, it is found that the intensity of the outermost lines decreases, while the innermost lines increase.

This effect is known as roofing and how strong the effect is depends on the difference between the two signals that are coupling. **The closer the two signals are, the stronger roofing is.** If the difference of two signals is 0Hz, the resultant signal would be a singlet.



Signals overlap Unfortunately, life is not always so straightforward, more often signals overlap and cannot be easily assigned.



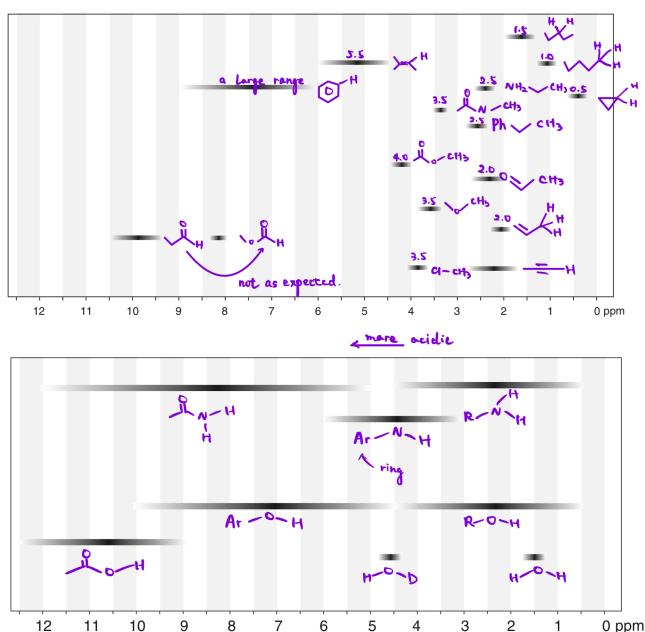
2.7.2 Integrated area under groups of peaks

Rules are simple - **The integrated area under a peak suggests the number of protons in that experiment.** To be specific, it is the ratio that matters. Here is an example:

A proton NMR plot of a compound with 8 protons is given, but we have no idea what the structure is. Imagine that there are 4 peaks, the ratio of the integrated areas is 1:1:3:3. It is therefore easy to tell that we have two methane groups and two carbon with 1 proton attached.

Satellites Satellites such as carbon-13 satellite effect exists in proton NMR, but always lost in background.

2.7.3 Typical scale



- The shift of protons in methyl groups are generally around 0.5 ppm less than those in alkyl chains.
- The shift of protons on a three-membered ring are unusually low. Such signals usually are complicated due to different couplings on the ring.
- Protons on a sp^2 carbon usually have a shift of around 2.5 ppm.
- Protons on a carbon (connected to oxygen) usually have a shift about 1 ppm greater than those on a carbon (connected to nitrogen). **If the oxygen or nitrogen is conjugated with a carbonyl, the shift of these protons increases further.²**

²For more information, refer to the Karplus Equation.

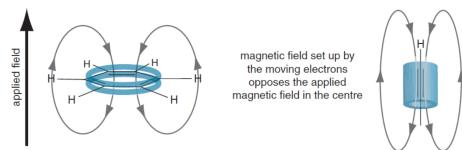


Figure 2.15: The shifts of protons directly attached to aromatic rings have greater shifts than alkene protons, while the proton of a terminal alkyne has a much lower-than-expected shift. These are due to the local magnetic fields set up by the electrons as they move in the π -systems.

Exchangeable protons There are exchangeable protons due to hydrogen bonds. They have wide shift ranges. The exact shift depends on the amount of hydrogen bonding for the proton concerned. This in turn depends on the particular compound, the solvent the spectrum is recorded in, the concentration of the sample, and the temperature.

Despite the wide range of shifts, these signals are easy to spot since they are usually much broader than other signals (see subsection 2.7.1). **D₂O shake**³ is the tech to solve the problem. After the shake, the broad singlet will disappear because deuterated protons resonate at a completely different frequency.

Also, if the possibility of hydrogen-bonding is removed by preparing a very dilute solution in an extremely dry solvent, coupling through an oxygen or nitrogen atom may be observed.

2.7.4 Coupling to spins greater than 1/2

Coupling to spins greater than 1/2 is normally not observed, because the spin states rapidly interconvert due to a process called **relaxation**. This rapid interconversion is so rapid that compared to the frequency of our apparatus, it always averages to zero. However, there are still examples where relaxation is slow.

The carbon resonance appears as a triplet because of the coupling to the deuterium. The nuclear spin for deuterium is $I = 1$, which means that there are 3 different spin states ($2I + 1$).

The number of lines into which a signal is split by coupling to n equivalent nuclei of spin I is given by the formula $(2nI + 1)$. We can no longer use a simple Pascal's triangle to work out the intensities of the lines – these are best found by constructing a tree diagram.

2.8 Summary

We have learned 4 technologies to determine information of molecules:

³Shaking the NMR sample prepared in a solvent with a little deuterated water

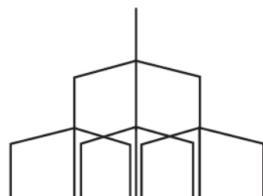


Figure 2.16: Deuterated dichloromethane appears as a quintet, ratio 1 : 2 : 3 : 2 : 1; it comes at 54ppm. Notice that no coupling is observed to the chlorine nucleus in the spectra, even though both the naturally occurring isotopes, chlorine-35 and chlorine-37, have spin $I = \frac{1}{2}$. Chlorine nuclear spin states relax too quickly for any coupling to be seen.

X-ray crystallography;
Mass spectrometry;
Infrared spectroscopy (IR);
Nuclear Magnetic Resonance (NMR).

The first two technologies are seldomly seen in tripos questions. Normally a tripos question consists of several IR and NMR plots, and asks you to fully align the spectrum and guess out the structures of molecules. This is always time-consuming, but it is relatively easy - JUST DO IT!

Part II

The Shapes and Structures of Molecules - 2

Chapter 3

Quantum Mechanical Theory on Atomic Structures

This chapter is a collection of several articles I wrote for revision.

3.1 Hydrogen-Like Atoms and Quantum Numbers

The first article is a daily review on quantum mechanics. Also, if someone taking PART IA Chemistry *Shapes and structures of molecules (part two)* needs a physical view of atoms, this article should also be helpful in some ways.

3.1.1 Preparation

These are fundamental knowledge that you should at least be able to recognize when you run into them.

Mathematical concepts

Linear algebra, commutation relations, complex numbers, factorization, trigonometric functions, ordinary differential equations, partial differential equations, spherical harmonics.

Physical concepts

Harmonic oscillator, energy, momentum, angular momentum, Hamiltonian, Lagrangian, Plank's constant, spin, mirror and rotational symmetry, degeneracy, quantum numbers.

3.1.2 Harmonic Oscillator

This section is an example of how to do factorization in quantum mechanics. You can skip this section and it won't affect further reading in any way.

The Hamiltonian of harmonic oscillator is

$$H = \frac{p^2}{2m} + \frac{m\omega^2 x^2}{2}, \quad (3.1)$$

which gives rise to the Schrödinger equation

$$i\hbar \frac{\partial}{\partial t} \psi = \left[\frac{\hbar^2}{2m} \nabla^2 + \frac{m\omega^2 x^2}{2} \right] \psi. \quad (3.2)$$

Solving this equation will lead us straightly to spherical harmonics, but in order to apply factorization in later concepts, we will use it now.

Re-write H as

$$H = \hbar\omega \left[\left(\sqrt{\frac{m\omega}{2\hbar}} x + \frac{ip}{\sqrt{2\hbar m\omega}} \right) \left(\sqrt{\frac{m\omega}{2\hbar}} x - \frac{ip}{\sqrt{2\hbar m\omega}} \right) + \frac{1}{2} \right], \quad (3.3)$$

in which $[x, p] = i\hbar$ was used. By dimensional analysis we conclude that

$$\left(\sqrt{\frac{m\omega}{2\hbar}} x + \frac{ip}{\sqrt{2\hbar m\omega}} \right) \left(\sqrt{\frac{m\omega}{2\hbar}} x - \frac{ip}{\sqrt{2\hbar m\omega}} \right) \quad (3.4)$$

is just a number (because it shares the same dimension as $1/2$). For simplicity we define two operators which form a "complex conjugate" pair (in higher dimensions it should be "Hermitian conjugate", $H^\dagger = (H^T)^*$) as

$$a = \sqrt{\frac{m\omega}{2\hbar}} x + \frac{ip}{\sqrt{2\hbar m\omega}}, \quad a^\dagger = \sqrt{\frac{m\omega}{2\hbar}} x - \frac{ip}{\sqrt{2\hbar m\omega}}, \quad (3.5)$$

which allows us to write

$$H = \hbar\omega \left(a^\dagger a + \frac{1}{2} \right) = \hbar\omega \left(n + \frac{1}{2} \right) \quad (3.6)$$

and

$$N = a^\dagger a = \frac{H}{\hbar\omega} - \frac{1}{2}, \quad N|n\rangle = n|n\rangle. \quad (3.7)$$

To find eigenvalues of a and a^\dagger , we can solve the equation

$$a|n\rangle = c|n-1\rangle \quad (3.8)$$

by

$$\langle n | a^\dagger a | n \rangle = |c|^2 = \langle n | N | n \rangle = n^2, \quad (3.9)$$

which gives us $a|n\rangle = \sqrt{n}|n-1\rangle$ and $a^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$.

After factorization, the traditional approach is to consider commutation relations, by plugging in $[x, p] = i\hbar$ we obtain

$$\begin{aligned}[N, a] &= -a \\ [N, a^\dagger] &= a^\dagger \\ [a, a^\dagger] &= 1.\end{aligned}$$

Interestingly, by applying these we can discover some interesting properties of a and a^\dagger . For example,

$$\begin{aligned}Ha|\psi\rangle &= ([H, a] + aH)|\psi\rangle \\ &= (\hbar\omega[N, a] + aH)|\psi\rangle \\ &= (-\hbar\omega a + aH)|\psi\rangle \\ &= -\hbar\omega a|\psi\rangle + Ea|\psi\rangle \\ &= (E - \hbar\omega)|\psi\rangle.\end{aligned}$$

This indicates that operator a reduces the total energy by $\hbar\omega$. Similarly, you can find that operator a^\dagger increases the total energy by $\hbar\omega$. So what we do by applying a and a^\dagger is climbing up and down a ladder with integer steps. For some deep mathematical reasons we cannot take non-integer steps (I don't understand this, I tried to take non-integer steps, but I failed). Also, because energy must be positive definite, our n cannot be less than zero.

The properties of creation and annihilation operator (a^\dagger and a , respectively) give us great weapon to solve the Schrödinger equation in a more elegant way. We can focus only on the zero state ($n = 0$).

By definition of zero state,

$$\langle x|a|0\rangle = \sqrt{\frac{m\omega}{2\hbar}} \left\langle x \left| \left(x + \frac{ip}{m\omega} \right) \right| 0 \right\rangle = 0 \quad (3.10)$$

we obtain

$$\psi_0 = \langle x|0\rangle = \frac{1}{\pi^{1/4}\sqrt{x_0}} \exp\left[-\frac{1}{2}\left(\frac{x}{x_0}\right)^2\right]. \quad (3.11)$$

By adding a^\dagger to the middle, wave function of all states can be obtained.

3.1.3 Angular Momentum

The general concepts of angular momentum are extremely similar to our harmonic oscillator. We construct two operators J_\pm as

$$\begin{aligned}J^2 &= J_x^2 + J_y^2 + J_z^2 \\ J_\pm &= J_x \pm iJ_y\end{aligned}$$

By commutation relations

$$[J^2, J_i] = 0 \quad (3.12)$$

$$[J^2, J_{\pm}] = 0 \quad (3.13)$$

$$[J_i, J_j] = i\hbar\epsilon_{ijk}J_k \quad (3.14)$$

$$[J_+, J_-] = 2\hbar J_z \quad (3.15)$$

$$[J_z, J_{\pm}] = \pm\hbar J_{\pm}, \quad (3.16)$$

we compare J_+, J_- with a^\dagger, a , and write our eigenstates as $|a, b\rangle$, where a are eigenvalues of J^2 and b are eigenvalues of J_z .

Physically, $|b|$ can never be larger than $\sqrt{|a|}$, so there must be maximum and minimum values of b . Note that

$$J_- J_+ |a, b_{\max}\rangle = (J^2 - J_z^2 - \hbar J_z) |a, b_{\max}\rangle = 0, \quad (3.17)$$

therefore,

$$a - b_{\max}^2 - \hbar b_{\max} = 0. \quad (3.18)$$

For similar reasons,

$$a - b_{\min}^2 + \hbar b_{\min} = 0. \quad (3.19)$$

Then it is easy to observe

$$b_{\max} = -b_{\min} \quad (3.20)$$

and

$$b_{\max} = b_{\min} + n\hbar. \quad (3.21)$$

We define $j = n/2$ so that $a = \hbar^2 j(j+1)$, we also write $m = b/\hbar$. Now we have two dimensionless integers to describe the angular momentum of an atom. Note that these parameters came from natural commutation relation, and was defined to make equations readable.

In atoms, angular momentum has two completely separate parts: orbital angular momentum and spin angular momentum. We will denote orbital angular momentum by L , spin angular momentum by S .

3.1.4 Hydrogen-Like Atoms

In classical mechanics, we used effective potential to reduce a 2 dimensional question to 1 dimension. We can still use the same method in quantum mechanics, because the equation of motion (Schrödinger equation) depends only on Hamiltonian. Therefore our equation is

$$i\hbar\partial_t\psi = \left[-\frac{\hbar^2}{2mr^2}\nabla^2 + \frac{l(l+1)\hbar^2}{2mr^2} + V(r) \right] \psi, \quad (3.22)$$

where $l(l+1)\hbar^2$ is the eigenvalue of the square of orbital angular momentum L^2 .

This is a typical partial differential equation. But in physics we are definitely not going to solve it using partial differential equation theory. We will bet our life on ψ being separable, which means we assume ψ can be written as

$$\psi = R(r)\Theta(\theta)\Phi(\phi). \quad (3.23)$$

Radial part

The radial part of Schrödinger equation is

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dR}{dr} \right) + \left[\frac{2m}{\hbar} \left(E + \frac{Ze^2}{2\pi\varepsilon_0 r} \right) - \frac{l(l+1)}{r^2} \right] R = 0, \quad (3.24)$$

which defines the **principal quantum number** n , which determines the energy

$$E_n = -\frac{1}{2} mc^2 \alpha^2 \frac{Z^2}{n^2}. \quad (3.25)$$

In this equation α is the coefficient of fine structure, whose value is surprisingly close to $1/137$ (pure coincidence).

As for the radial wave function, it is a kind of Laguerre polynomials.

$$R_{nl}(r) = \sqrt{\left(\frac{2Z}{na_0}\right)^3 \frac{(n-l-1)!}{2n(n+l)!}} e^{-\frac{Z}{na_0}r} \left(\frac{2Z}{na_0}r\right)^l L_{n-l-1}^{2l+1} \left(\frac{2Z}{na_0}r\right), \quad (3.26)$$

in which a_0 is the Bohr radius.

Spherical part

The spherical part is spherical harmonics, which is not surprising considering the symmetry of space. In other words,

$$\frac{1}{\sin \theta} \frac{d}{d\theta} \left(\sin \theta \frac{d\Theta}{d\theta} \right) + \left[l(l+1) - \frac{m^2}{\sin^2 \theta} \right] \Theta = 0 \quad (3.27)$$

$$\frac{d^2\Phi}{d\phi^2} + m^2\phi = 0, \quad (3.28)$$

the functions Θ and Φ can be combined and represented as

$$Y_{lm}(\theta, \phi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_l^m(\cos \theta) e^{im\phi}. \quad (3.29)$$

P_l^m is the associated Legendre polynomials.

3.1.5 Conclusion

Please, please do not ask how to solve those equations.

Principal quantum number, n

The principal quantum number is defined in the radial part, and it is one-to-one correlated with energy eigenvalues. That's why different orbits in the same "layer" have the same **energy**.

Azimuthal quantum number, l

This number is also called quantum number of orbital angular momentum, satisfying $L^2|\psi\rangle = l(l+1)|\psi\rangle$. **It specifies the magnitude of orbital angular momentum.**

Magnetic quantum number, m_l

The magnetic quantum number has nothing related to the m in spherical harmonics, but it is the m in our equation $m = b/\hbar$. **It specifies the orientation of orbital angular momentum.** We label it by l because it can only vary between l and $-l$, taking integer steps.

Spin quantum number, m_s

It specifies the orientation of spin angular momentum. We haven't come across spin quantum number yet. But it follows the rules of angular momentum. To explain the origin of spin, we have to know the standard model, which is unfortunately beyond my academic ability. Therefore we won't discuss it in detail.

3.2 Helium Atom

In the previous article we made our way through harmonic oscillator, and took a glance at hydrogen-like atoms. In this note, we will carry on and introduce a number of new theories that allow us to deal with more complex atoms.

The basic idea of the process is:

$$\begin{aligned} \text{Theory} &\rightarrow \text{More complex system} \rightarrow \text{Introduce new theory} \\ &\rightarrow \text{More complex system} \rightarrow \text{Introduce new theory} \rightarrow \dots \end{aligned}$$

This cycle literally has no ends, so our solution, no matter how accurate we get, remains as approximation. Though we can get infinite decimal places in theory, no one has ever done it yet, not even supercomputer series.

Now let's begin!

3.2.1 A Brief Review on Perturbation Theory

Curious logic: perturbation theory is a theory for perturbations

We talked about the idea of how to refine our theory based on rather simple models - a cycle that has no ends. In some sense, perturbation theory shares the same logic with that cycle. In this theory, we expand perturbation into sum of infinite series, each term at an order, we take the zero order only to obtain a zero-order solution, then plug in the original equation to get higher-order solutions. The final answer will be sum of infinite number of solutions, each one at an order.

What perturbation theory allows us to do, is treat our new problems as perturbations to the simpler system. We do perturbation theory every time until there is no other problems to be found.

One can repeat this cycle because perturbations can be added linearly - this is something related to group theory and we are not going in detail (in case I make stupid mistakes).

The general theory is rather vague in form, so let's discuss two examples.

How to deal with perturbations mathematically - 1. Hamiltonian

In time-independent non-degenerate cases, perturbation theory is nothing but solving an equation using numerical methods.

We separate our Hamiltonian into two parts, the first part H_0 is the so-called "zero order" term, and the second part V is our perturbation.

$$H = H_0 + V, \quad (3.30)$$

where

$$H_0|n^{(0)}\rangle = E_0|n^{(0)}\rangle \quad (3.31)$$

gives us the zero-order solution, which is an exact solution when perturbation term is "turned off". The entire problem can be solved if we know how to solve

$$(H_0 + V)|n\rangle = E_n|n\rangle, \quad (3.32)$$

but unfortunately we don't.

For clearer notation we add a factor $\lambda \in [0, 1]$ to represent how much perturbation is "turned to". For instance, when $\lambda = 0$ we have zero perturbation, the problem can be solved using (1); when λ equals or close to 1, we have "full strength" perturbation, which means we have to take a few more higher order solutions, or we just cannot use perturbation theory. The Hamiltonian is now written as

$$(H_0 + \lambda V)|n\rangle = E_n|n\rangle. \quad (3.33)$$

Also for clearer notation, we define energy shift of the n th state as

$$\Delta_n = E_n - E_n^{(0)}. \quad (3.34)$$

We simply need to figure out what Δ_n is because $E_n^{(0)}$ is assumed to be solvable.

Our basic Schrödinger equation is

$$(E_n^{(0)} - H_0)|n\rangle = (\lambda V - \Delta_n)|n\rangle, \quad (3.35)$$

which is basically

$$\langle n^{(0)}|\lambda V - \Delta_n|n\rangle = 0. \quad (3.36)$$

Suppose that we define a complementary projection operator

$$\phi_n = 1 - |n^{(0)}\rangle\langle n^{(0)}| = \sum_{k \neq n} |k^{(0)}\rangle\langle k^{(0)}|, \quad (3.37)$$

we can expand $(\lambda V - \Delta_n)|n\rangle$ as

$$(\lambda V - \Delta_n)|n\rangle = \phi_n(\lambda V - \Delta_n)|n\rangle. \quad (3.38)$$

Therefore (6) can be re-written as

$$|n\rangle = c_n(\lambda)|n^{(0)}\rangle + \frac{1}{E_n - E_n^{(0)}}\phi_n(\lambda V - \Delta_n)|n\rangle \quad (3.39)$$

where $c_n(\lambda) = \langle n^{(0)}|n\rangle$. In order to make normalization correct, we should have $\langle n|n\rangle = 1$, but in perturbation theory we set $\langle n^{(0)}|n\rangle = 1$ as well. We can always do this if we are not worried about the overall normalization because the only effect of setting $c_n \neq 1$ is to introduce a common multiplicative factor. That allows us to write

$$\Delta_n = \lambda\langle n^{(0)}|V|n\rangle. \quad (3.40)$$

At this stage we have combined everything we need in (10) and (11), the basic idea is to expand $|n\rangle$ and Δ_n in the powers of λ and then match the appropriate coefficients. This is justified because (10) and (11) are identities which hold for all values of $\lambda \in [0, 1]$.

We begin by expanding eigenstates $|n\rangle$ and Δ_n as

$$\begin{aligned} |n\rangle &= |n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \lambda^2|n^{(2)}\rangle + \dots \\ \Delta_n &= \Delta_n^{(0)} + \lambda\Delta_n^{(1)} + \lambda^2\Delta_n^{(2)} + \dots \end{aligned} \quad (3.41)$$

in which $\Delta_n^{(0)} = 0$. Therefore it is easy to see that

$$\Delta_n^{(N)} = \langle n|V|n^{(N-1)}\rangle. \quad (3.42)$$

Now we expand (10) using (12) and (13)

$$\begin{aligned} |n\rangle &= |n^{(0)}\rangle + \\ &\frac{\phi_n}{E_n^{(0)} - H_0} \left(\lambda V - \lambda\Delta_n^{(1)} - \lambda^2\Delta_n^{(2)} - \dots \right) \left(|n^{(0)}\rangle + \lambda|n^{(1)}\rangle + \dots \right) \end{aligned} \quad (3.43)$$

To powers of λ , we have

$$|n^{(1)}\rangle = \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle. \quad (3.44)$$

Armed with $|n^{(1)}\rangle$, we can simply write

$$\Delta_n^{(2)} = \langle n|V \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle \quad (3.45)$$

$$\begin{aligned} |n^{(2)}\rangle &= \frac{\phi_n}{E_n^{(0)} - H_0} V \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle \\ &- \frac{\phi_n}{E_n^{(0)} - H_0} \langle n^{(0)}|V|n^{(0)}\rangle \frac{\phi_n}{E_n^{(0)} - H_0} V |n^{(0)}\rangle. \end{aligned} \quad (3.46)$$

We can repeat this process to get $|n^{(N)}\rangle$ but normally the first two terms should be enough.

How to deal with perturbations mathematically - 2. Propagator

Similar to what we did to Hamiltonian and energy eigenstates, we can expand the propagator as

$$K = K^{(0)} + K^{(1)} + K^{(2)} + \dots \quad (3.47)$$

and our final propagator will be

$$\begin{aligned} K(b, a) = & K^{(0)}(b, a) - \frac{i}{\hbar} \int K^{(0)}(b, c)V(c)K^{(0)}(a, c)d\tau_c \\ & + \left(-\frac{i}{\hbar}\right)^2 \iint K^{(0)}(b, c)V(c)K^{(0)}(c, d)V(d)K^{(0)}(d, a)d\tau_c d\tau_d + \dots \end{aligned} \quad (3.48)$$

Interestingly, when we extract the first order terms out of the expansion, it becomes

$$K = K^{(0)}(b, a) - \frac{i}{\hbar} \int K^{(0)}(b, c)V(c) \left[K^{(0)}(c, a) - \frac{i}{\hbar} \int K^{(0)}(c, d)V(d)K^{(0)}(d, a)d\tau_d + \dots \right] d\tau_c + \dots \quad (3.49)$$

That means if we consider perturbation as a kind of scattering, the physical meaning of $K^{(i)}(b, a)$ is the probability amplitude of the event "our particle starts from A and goes to B , experiencing i times of scattering". The total propagator, therefore not surprisingly, should be $K = \sum_i K^{(i)}$ (R. Feynman).

3.2.2 Helium Atom

Ground state at zeroth order

The basic Hamiltonian of an electron outside helium nucleus is

$$H_i = \frac{p_i^2}{2m_e} - \frac{e^2}{4\pi\varepsilon_0 r_i} + \frac{e^2}{8\pi\varepsilon_0 r_{12}}, \quad i = 1, 2. \quad (3.50)$$

In this equation, we have already made some approximations. First of all, the nucleus is assumed to be stationary, and we ignored all forces except Coulomb forces. However, this Hamiltonian still can't give us a simple answer, we will ignore the electron-electron interaction part first to form our ground-state Hamiltonian.

$$H_i = \frac{p_i^2}{2m_e} - \frac{e^2}{4\pi\varepsilon_0 r_i}, \quad i = 1, 2. \quad (3.51)$$

The total Hamiltonian can be constructed using linear superposition

$$H|n_1, l_1, m_1\rangle|n_2, l_2, m_2\rangle = (E_1 + E_2)|n_1, l_1, m_1\rangle|n_2, l_2, m_2\rangle, \quad (3.52)$$

and the answer is

$$E_1 + E_2 = -\left(\frac{1}{n_1^2} + \frac{1}{n_2^2}\right) R_\infty Z^2 \quad (3.53)$$

simply because our Hamiltonian is in the same form as that of electrons in hydrogen-like atoms.

The ground state, $|100\rangle$, can be easily determined

$$|\psi\rangle = \frac{1}{\sqrt{2}} (|100\uparrow\rangle|100\downarrow\rangle - |100\downarrow\rangle|100\uparrow\rangle) \quad (3.54)$$

Single excited state at zeroth order

Since we have two identical electrons (different spins, but central symmetric), our single-excited state can be written as

$$|100\rangle|2lm\rangle \quad \text{or} \quad |2lm\rangle|100\rangle, \quad (3.55)$$

and it is connected to the eigenvalue

$$E_1 = -\frac{5}{4}Z^2R_\infty. \quad (3.56)$$

Double excited state and ionization

”Naturally, traditional quantum mechanics just practice” (adapted from Su-permind Taichi master Ma Baoguo). Double excited state is nothing but put another electron in $n = 2$ state.

$$|2lm\rangle|2lm\rangle \Rightarrow E_2 = -\frac{1}{2}Z^2R_\infty \quad (3.57)$$

But that gives rise to a problem - He^+ is a hydrogen-like atom with energy eigenvalue $E_0(\text{He}^+) = -4R_\infty$. Clearly, $E_2(\text{He}^{**}) > E_0(\text{He}^+)$, which means our double-excited helium can only exist for a very short period and it will automatically ionize to a helium ion and a free electron.

3.3 Multi-Electron Atoms

Moving further, the most important contributions to the Hamiltonian for an N -electron atoms are:

$$H = H_0 + H_1 + H_2, \quad (3.58)$$

in which,

$$\begin{aligned} H_0 &= \sum_{i=1}^N \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} \right] \\ H_1 &= \sum_{i < j}^N \frac{e^2}{4\pi\epsilon_0 r_{ij}} \\ H_2 &= \sum_{i=1}^N \xi_i(r_i) \mathbf{L}_i \cdot \mathbf{S}_i \end{aligned} \quad (3.59)$$

The term H_0 is the sum of N independent hydrogen-like Hamiltonians. It therefore possesses eigenstates which are products of N single-particle hydrogen-like states of the form $|n\ell m_\ell\rangle|sm_s\rangle$

The energies and degeneracies of these single-particle states depend only on the principal quantum number n :

$$E_n = -\frac{Z^2}{n^2}R_\infty, \quad g = \sum_{\ell=0}^{n-1} 2(2\ell+1) = 2n^2. \quad (3.60)$$

Note that **Pauli exclusion principle** must hold in this situation.

Example Consider the 2p subshell with $n = 2$ and $\ell = 1$, the six available single-particle states are

$$|m_\ell\rangle|n_s\rangle = |+1\rangle|\downarrow\rangle, |+1\rangle|\uparrow\rangle, |0\rangle|\downarrow\rangle, |0\rangle|\uparrow\rangle, |-1\rangle|\downarrow\rangle, |-1\rangle|\uparrow\rangle, \quad (3.61)$$

If the subshell contains six electrons, only one overall state consistent with identical particle exchange symmetry can be formed:

$$|\psi\rangle = \frac{1}{\sqrt{6!}} \begin{vmatrix} |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle & |+1\rangle|\uparrow\rangle \\ |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle & |+1\rangle|\downarrow\rangle \\ |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle & |0\rangle|\uparrow\rangle \\ |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle & |0\rangle|\downarrow\rangle \\ |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle & |-1\rangle|\uparrow\rangle \\ |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle & |-1\rangle|\downarrow\rangle \end{vmatrix}, \quad (3.62)$$

which produces a unique, antisymmetric overall wavefunction.

Every one of the $6!$ items in the wave function has

$$m_L = \sum_{i=1}^6 (m_\ell)_i = 0, \quad m_S = \sum_{i=1}^6 (m_s)_i = 0, \quad (3.63)$$

thus

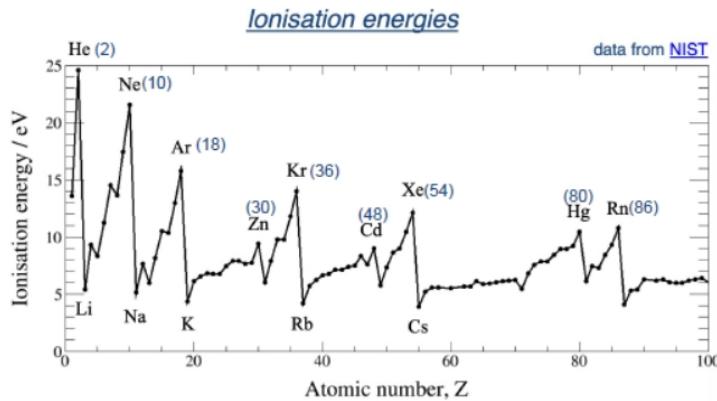
$$m_J = m_L + m_S = 0 \Rightarrow J = L = S = 0, \quad (3.64)$$

which suggests that the overall six-electron state has zero total angular momentum.

It is not possible to construct a totally antisymmetric wave function for a multi-electron state if the subshell is **full**. Generally, a full subshell has zero total angular momentum, so the total angular momentum of an atom is effectively determined by just a small number of outer (valence) electrons (in the outermost unfilled subshell).

Ionisation energies can give us an insight on stability of an atom. One may explain them qualitatively using high school knowledge.

Just like what we did in hydrogen-like atoms, we must find some kind of theory to treat the remaining terms of our Hamiltonian. Now H_1 is too large to be treated as a perturbation, so we use a method called the **central-field approximation** (CFA): assume that the electron-electron repulsion term contains a large spherically symmetric component arising from the "core" electrons. We



apply this approximation to make our Hamiltonian "repartitionable" in a way that perturbation theory is allowed to be applied.

The Hamiltonian is repartitioned as $H = H'_0 + H'_1$, where

$$\begin{aligned} H'_0 &= \sum_{i=1}^N \left[-\frac{\hbar^2}{2m_e} \nabla_i^2 - \frac{Ze^2}{4\pi\epsilon_0 r_i} + U_i(r_i) \right] \\ H'_1 &= \sum_{i < j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} - \sum_{i=1}^N U_i(r_i) \end{aligned} \quad (3.65)$$

thus H'_1 is small enough to be seen as perturbation.

By assuming the solution has the form of a single Slater determinant

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \psi_1(\mathbf{r}_1) & \psi_1(\mathbf{r}_2) & \cdots & \psi_1(\mathbf{r}_N) \\ \psi_2(\mathbf{r}_1) & \psi_2(\mathbf{r}_2) & \cdots & \psi_2(\mathbf{r}_N) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_N(\mathbf{r}_1) & \psi_N(\mathbf{r}_2) & \cdots & \psi_N(\mathbf{r}_N) \end{vmatrix} \quad (3.66)$$

we can work out a series of results, which is available [here](#).

One can easily find out configuration quantum numbers from the data.

Coupling Schemes LS coupling and jj coupling would be mentioned elsewhere as it is not related to IA chemistry.

3.4 Summary

No offense, but chemists always say things but don't explain any ***** thing. That is why this chapter exists - to provide a more quantitatively understanding of atomic structures.

Chapter 4

Chemical View of Atomic Orbitals

With knowledge on how to denote electron configurations and simple quantum mechanics, it is possible to measure how much energy is needed to remove a single electron from an atom. The technic to achieve this is called **photoelectron spectroscopy**. You may guess which kind of electromagnetic wave is used¹.

Using photoelectron spectroscopy, it is easy to verify the degeneracy of states with the same principal quantum number.

4.1 Orbitals and Quantum Numbers

As previously mentioned², there are four quantum numbers, each representing a unique property of electrons (orbitals).

Principal quantum number, n Specifies which **shell** is being referred to. n takes integer values $1, 2, 3, 4, \dots$ and is always placed at the front in notations because it is the most important quantum number. For a single-electron system³, the value of n alone determines the energy of the electron.

Angular momentum quantum number, l Also called the azimuthal quantum number, specifies which **subshell** we are referring to. l takes integer values $0, 1, 2, \dots, n - 1$, and each value of l has a different letter associated with it.

value of l	0	1	2	3	4	5
letter associated	s	p	d	f	g	h

l determines the orbital angular momentum of the electron

$$L = \hbar\sqrt{l(l+1)}. \quad (4.1)$$

¹Most commonly X-rays, according to section 2.3.

²In chapter 3.

³Hydrogen-like atom.

Magnetic quantum number, m_l Specifies which **orbital** we are referring to. m_l takes integer steps from $-l$ to $+l$ ($2l + 1$ steps in total).

For an s orbital	$l = 0$	$m_l = 0$	1 orbital
For a p orbital	$l = 1$	$m_l = -1, 0, 1$	3 orbitals
For a d orbital	$l = 2$	$m_l = -2, -1, 0, 1, 2$	5 orbitals
For an f orbital	$l = 3$	$m_l = -3, -2, -1, 0, 1, 2, 3$	7 orbitals

Spin quantum number, m_s Specifies the **orientation of spin** angular momentum. All electrons have same spin: $s = 1/2$, but orientation may differ. m_s takes integer steps from $-s$ to s , resulting in a total of 2 orientations: \uparrow and \downarrow .

Summary The first three quantum numbers define the orbital the electron is in, and the last number tells us about the spin of the electron

As previously mentioned, an electron in a hydrogen-like atom has energy

$$E_n = -\frac{m_e e^4}{8\epsilon_0^2 h^2} \frac{Z^2}{n^2} = -R_H \frac{Z^2}{n^2}, \quad (4.2)$$

that means orbitals with higher energy also have more degenerate states. We will start with the easiest one.

4.1.1 1s orbital, $(n, l, m_l) = (1, 0, 0)$

From section 3.1, it is clear that

$$\begin{aligned} R_{10}(r) &= \sqrt{\frac{1}{2}} \left(\frac{2Z}{a_0} \right)^3 e^{-\frac{Z}{a_0} r} \\ Y_{00}(\theta, \phi) &= \sqrt{\frac{1}{4\pi}} = \text{const.} \end{aligned} \quad (4.3)$$

Since $Y_{00} = \text{const}$, the distribution is spherically symmetric. The wave function

$$\psi_{1s}(r, \theta, \phi) = \psi_{1s}(r) = \sqrt{\frac{1}{\pi}} \left(\frac{Z}{a_0} \right)^3 e^{-\frac{Z}{a_0} r} \quad (4.4)$$

is just an exponential decay. Considering the **Radial Distribution Function**

$$\text{def. } P = \int \text{RDF } dr \Rightarrow \text{RDF} = 4\pi r^2 [R(r)]^2, \quad (4.5)$$

One can quickly find out the physical meaning of a_0 : the electron is most likely be found there, if $Z = 1$. a_0 is called **Bohr Radius**.

4.1.2 2s orbital, $(n, l, m_l) = (2, 0, 0)$

$$R_{20}(r) = \sqrt{\frac{1}{8} \left(\frac{Z}{a_0}\right)^3} e^{-\frac{Z}{2a_0}r} \left(2 - \frac{Z}{a_0}r\right)$$

$$Y_{00} = \sqrt{\frac{1}{4\pi}} = \text{const.}$$
(4.6)

It has identical spherical symmetry, except the RDF has changed into:

$$\text{RDF}_{2s} = \frac{1}{2}\pi r^2 \left(\frac{Z}{a_0}\right)^3 e^{-\frac{Z}{a_0}r} \left(2 - \frac{Z}{a_0}r\right)^2.$$
(4.7)

If $Z = 1$, RDF is zero at twice the Bohr radius.

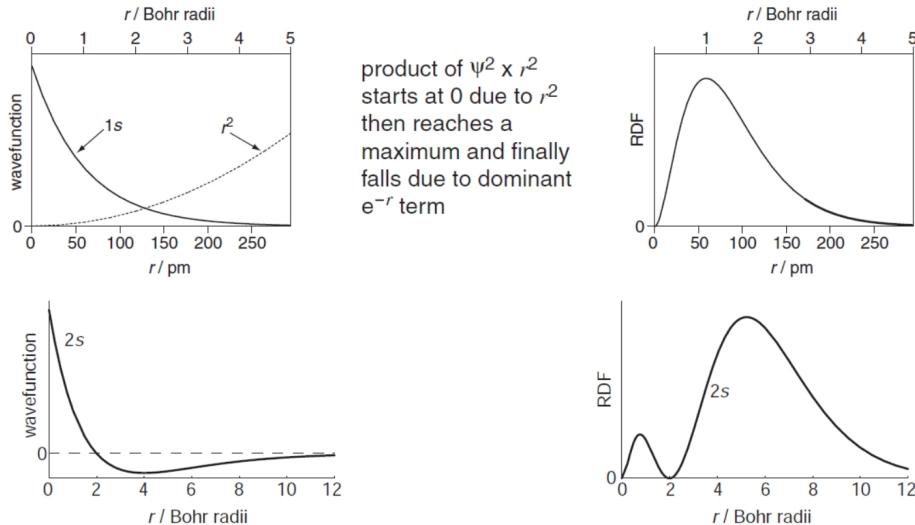


Figure 4.1: Wave function and RDF of 1s and 2s orbital.

4.1.3 2p orbitals, $(n, l, m_l) = (2, 1, (-1; 0; 1))$

There are 3 orbitals in the 2p subshell.

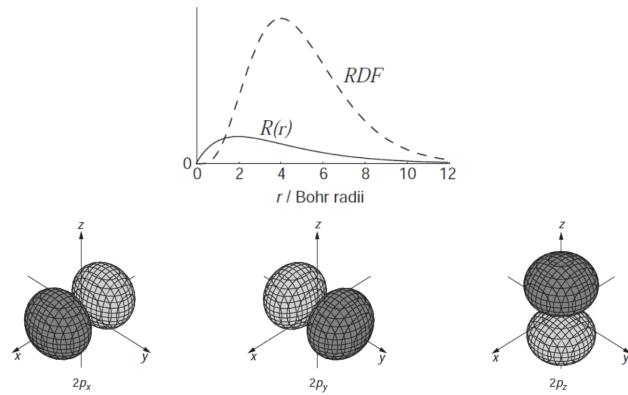
$$R_{21}(r) = \sqrt{\frac{1}{12} \left(\frac{Z}{a_0}\right)^3} e^{-\frac{Z}{2a_0}r} \left(\frac{Z}{a_0}r\right)$$

$$Y_{1,-1}(\theta, \phi) = \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi}$$

$$Y_{10}(\theta, \phi) = \sqrt{\frac{3}{4\pi}} \cos \theta$$

$$Y_{11}(\theta, \phi) = -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}.$$
(4.8)

This leads to axisymmetrical orbits



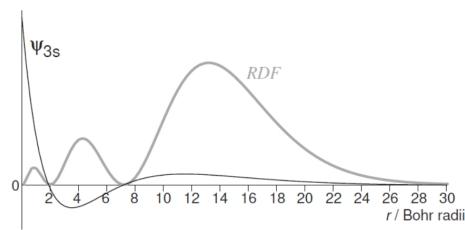
4.1.4 3s orbital, $(n, l, m_l) = (3, 0, 0)$

Due to the properties of spherical harmonics, we can already predict that the 3s orbital is spherically symmetric.

$$R_{30} = \sqrt{\frac{1}{3} \left(\frac{2Z}{3a_0} \right)^3} e^{-\frac{Z}{3a_0}r} \left(\frac{1}{2} \left(\frac{2Z}{3a_0}r \right)^2 - \frac{2Z}{a_0}r + 3 \right) \quad (4.9)$$

$$Y_{00} = \sqrt{\frac{1}{4\pi}}.$$

The solutions of $\text{RDF} = 0$ are $\frac{r}{a_0} = 0$ and solutions of $x = \frac{r}{a_0}$, $2x^2 - 18x + 27 = 0$.

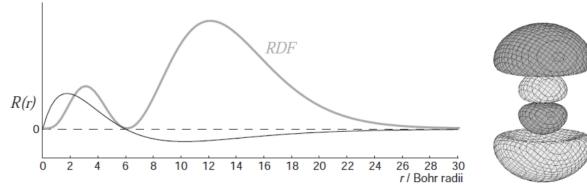


4.1.5 3p orbitals, $(n, l, m_l) = (3, 1, (-1; 0; 1))$

The angular form should be identical compared to 2p orbitals, but we have another radial node.

$$\begin{aligned}
 R_{31} &= \sqrt{\frac{1}{24} \left(\frac{2Z}{3a_0}\right)^3 \frac{2Z}{3a_0}} r e^{-\frac{Z}{3a_0}r} \left(4 - \frac{2Z}{3a_0}r\right) \\
 Y_{1,-1}(\theta, \phi) &= \sqrt{\frac{3}{8\pi}} \sin \theta e^{-i\phi} \\
 Y_{10}(\theta, \phi) &= \sqrt{\frac{3}{4\pi}} \cos \theta \\
 Y_{11}(\theta, \phi) &= -\sqrt{\frac{3}{8\pi}} \sin \theta e^{i\phi}.
 \end{aligned} \tag{4.10}$$

Resulting in similar shapes:

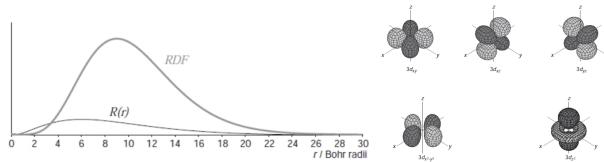


4.1.6 3d orbitals, $(n, l, m_l) = (3, 2, (-2; -1; 0; 1; 2))$

This is the first d orbital we have encountered.

$$\begin{aligned}
 R_{32} &= \sqrt{\frac{1}{30} \left(\frac{2Z}{3a_0}\right)^3} e^{-\frac{Z}{3a_0}r} \left(\frac{2Z}{3a_0}r\right)^2 \\
 Y_{2,-2}(\theta, \phi) &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{-2i\phi} \\
 Y_{2,-1}(\theta, \phi) &= \frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{-i\phi} \\
 Y_{20}(\theta, \phi) &= \frac{1}{4} \sqrt{\frac{5}{\pi}} (3 \cos^2 \theta - 1) \\
 Y_{21}(\theta, \phi) &= -\frac{1}{2} \sqrt{\frac{15}{2\pi}} \sin \theta \cos \theta e^{i\phi} \\
 Y_{22}(\theta, \phi) &= \frac{1}{4} \sqrt{\frac{15}{2\pi}} \sin^2 \theta e^{2i\phi}.
 \end{aligned} \tag{4.11}$$

The plots are straight forward:



4.1.7 Summary - Nodes

Total number of nodes in hydrogen-like atom orbitals depends only on the principal quantum number n ,

$$\text{total number of nodes} = n - 1. \quad (4.12)$$

It is a combination of angular and radial nodes. We have l angular nodes and the rest are radial nodes.

total number of nodes	=	angular	+	radial
$n - 1$	=	l	+	$(n - l - 1)$

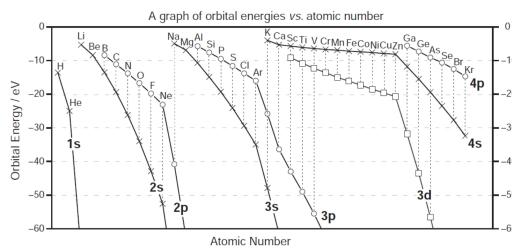
4.2 Electron Configuration

In real atoms hydrogen-like atom model will break. The most famous example is that 4s comes before 3d in K. With larger atomic number, the exact ordering rapidly becomes complicated and is impossible to predict without the aid of a computer.

There is a graph showing some orbital energies, from which we can generalize the following:

- Orbital energy decreases across a period due to increased Z_{eff} .
- Core electrons have very low⁴ energy and take little part in reactions.

The trends in the orbital energies are reflected in the ionization energies and electronegativities (which increase with increasing Z_{eff}) and also in their atomic radii (which decrease with increasing Z_{eff}). We shall now see how these trends affect the chemical bonding between atoms.



⁴In other words, very hard to knock them out from an atom.

Chapter 5

Quantum Mechanical Theory on Molecular Structures

This chapter is also a collection of articles I wrote for revision.

5.1 The Born-Oppenheimer Approximation

A molecule consists of electrons and nuclei. Electrons are light, negatively charged and moves relatively freely; while nuclei are heavy, positively charged and more constrained by different kinds of forces. Because of those differences, we can treat electrons and nuclei separately, which leads to **the Born-Oppenheimer approximation**.

- When studying eigenstates of electron system, treat nuclei as fixed mass points.
- When studying nuclear motion¹, assume that electrons respond instantly to the changes in nuclear positions².

The Hamiltonian for a molecule is of the form

$$H = \sum_{n=1,2,\dots} \frac{p_n^2}{2m_e} + \sum_{N=a,b,\dots} \frac{p_N^2}{2m_N} + V(\{r_n\}, \{R_N\}), \quad (5.1)$$

thus the Shrödinger equation is

$$\left[-\frac{\hbar^2}{2m_e} \sum_{n=1,2,\dots} \nabla_n^2 + V(\{r_n\}, \{R_N\}) \right] \Psi(\{r_n\}, \{R_N\}) = E(\{E_N\}) \Psi(\{r_n\}, \{R_N\}). \quad (5.2)$$

¹Such as molecular rotations and vibrations.

²In other words, assume that nuclei moves very slowly.

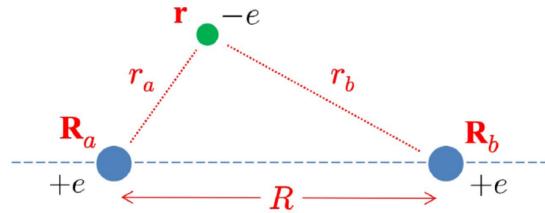
As molecular conformation is varied, by changing the nuclear positions, the ground state energy can be minimised to find the equilibrium conformation for those positions.

5.2 H_2^+ Ion

This ion only consists of two protons and an electrons, which makes it the simplest of all molecules.

$$H = -\frac{\hbar^2}{2m_e} \nabla_r^2 + \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{R} - \frac{1}{r_a} - \frac{1}{r_b} \right) \quad (5.3)$$

The Schrödinger equation can be solved exactly, but is complicated, which is



not what we want. Instead, we will use the Rayleigh-Ritz variational method. As a trial wave function, we take a linear combination of two hydrogen-like ground state atomic wave functions.

$$\begin{aligned} \psi_{\text{trial}}(r; R, Z') &= \alpha_a \psi_a(r) + \alpha_b \psi_b(r) \\ \psi_{a,b}(r) &= \left(\frac{\beta^3}{\pi} \right)^{1/2} \exp(-\beta|R_{a,b} - r|), \quad \beta = \frac{Z'}{a_0} \end{aligned} \quad (5.4)$$

Explicitly, the trial wave function is

$$\psi(x, y, z) = \sqrt{\frac{\beta^3}{\pi}} [\alpha_a e^{-\beta r_a} + \alpha_b e^{-\beta r_b}], \quad (5.5)$$

where

$$\begin{aligned} R_a &= (0, 0, -R/2) & r_a^2 &= x^2 + y^2 + (z + R/2)^2 \\ R_b &= (0, 0, +R/2) & r_b^2 &= x^2 + y^2 + (z - R/2)^2 \end{aligned}$$

For this choice of trial wave function, there are four variational parameters:

- the coefficients α_a , α_b
- the proton-proton separation R
- an effective nuclear charge Z' .

The variational method requires us to minimise the energy to find the overall minimum energy E_{\min} ³.

For any given values of R and Z' , the coefficients α_a , α_b can be obtained by solving the Rayleigh-Ritz secular equation

$$\det(H - E_{\min}S) = 0, \quad (5.6)$$

where H and S are symmetric 2×2 matrices

$$S = \begin{pmatrix} 1 & S_{ab} \\ S_{ab} & 1 \end{pmatrix}, \quad H = \begin{pmatrix} H_{aa} & H_{ab} \\ H_{ba} & H_{bb} \end{pmatrix} \quad (5.7)$$

with matrix elements

$$\begin{aligned} S_{aa} = S_{bb} &= 1, \quad S_{ab} = S_{ba} = \langle \psi_a | \psi_b \rangle \\ H_{aa} &= \langle \psi_a | H | \psi_a \rangle = H_{bb} = \langle \psi_b | H | \psi_b \rangle \\ H_{ab} &= H_{ba} = \langle \psi_b | H | \psi_a \rangle. \end{aligned} \quad (5.8)$$

The secular equation for the energy E is therefore

$$\begin{vmatrix} H_{aa} - E & H_{ab} - ES_{ab} \\ H_{ab} - ES_{ab} & H_{aa} - E \end{vmatrix} = 0 \quad (5.9)$$

The resulting eigenstates have $\alpha_a = \pm \alpha_b$. Gerade eigenstates are even under interchange $a \leftrightarrow b$, but ungerade eigenstates are odd under interchange $a \leftrightarrow b$ ⁴.

$$\begin{aligned} \psi_g &= \frac{\psi_a + \psi_b}{\sqrt{2(1 + S_{ab})}}, \quad E_g = \frac{H_{aa} + H_{ab}}{1 + S_{ab}} \\ \psi_u &= \frac{\psi_a - \psi_b}{\sqrt{2(1 - S_{ab})}}, \quad E_u = \frac{H_{aa} - H_{ab}}{1 - S_{ab}} \end{aligned} \quad (5.10)$$

We want to find the minima of energies, in this case⁵, the lowest state turns out to be $|\psi_g\rangle$. It is a **single, stable minimum**, which is quite exciting.

The proton-proton separation and bound state energy can also be predicted.

Name	Predicted Value	Measured Value
R_0	106.0pm	106.0pm
E_0	-15.96eV	-16.4eV

Not surprisingly, the approximation on R_0 works much better than that on E_0 .

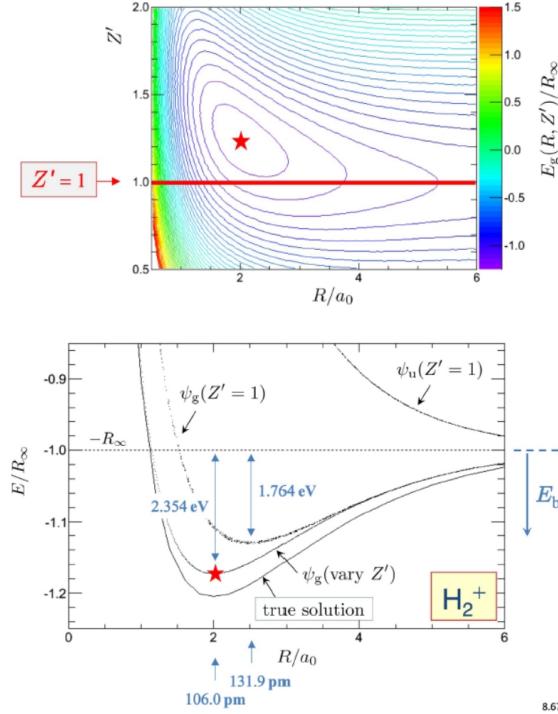
A simple check to our approximation is to take the limit

$$\lim_{R \rightarrow \infty} E_0(R) = -13.6\text{eV}. \quad (5.11)$$

³In chemistry, with $Z' = 1$, the trial wave function is an example of a molecular orbital, and the approximation method is known as **Linear Combination of Atomic Orbitals (LCAO)**.

⁴This is why we use g and u in chemistry when labeling molecular orbitals. The standard labeling of $|\psi_g\rangle$, $|\psi_u\rangle$ are σg , σ_u^* .

⁵After several pages of calculation



5.3 H_2

Different from H_2^- , the H_2 molecule cannot be solved exactly, and is much more complex.

$$H = -\frac{\hbar^2}{2m_e} (\nabla_1^2 + \nabla_2^2) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{R} + \frac{1}{r_{12}} - \frac{1}{r_{a1}} - \frac{1}{r_{a2}} - \frac{1}{r_{b1}} - \frac{1}{r_{b2}} \right) \quad (5.12)$$

We shall treat H_2 as a sum of two independent H_2^+ Hamiltonians plus a term

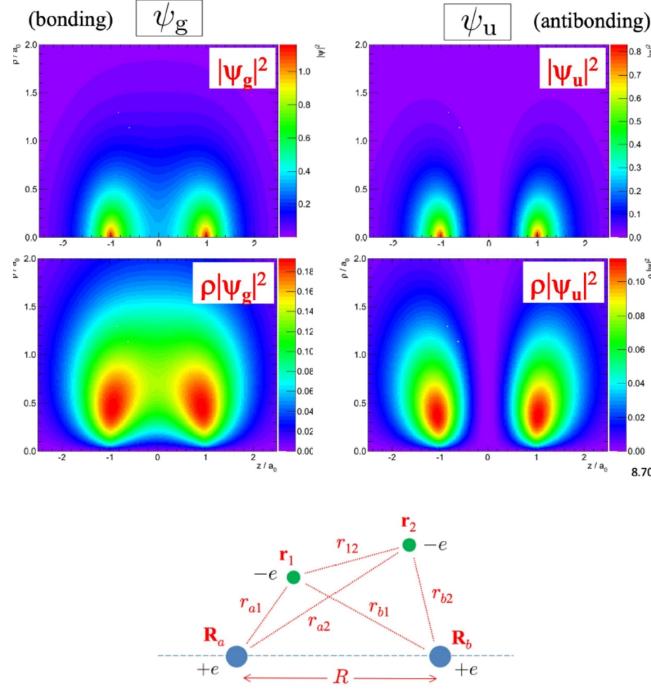
$$\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_{12}} - \frac{1}{R} \right).$$

In the absence of this term, the H_2 eigenstates are products of two H_2^+ molecular orbitals

$$\psi_g(r_1)\psi_g(r_2), \psi_g(r_1)\psi_u(r_2), \psi_u(r_1)\psi_g(r_2), \psi_u(r_1)\psi_u(r_2), \quad (5.13)$$

so $\psi_g(r_1)\psi_g(r_2)$ would be the ground state. However, the two-electron state $|\psi_g(r_1)\rangle|\psi_g(r_2)\rangle$ is symmetric under interchange $1 \leftrightarrow 2$ so must be combined with antisymmetric $S = 0$ spin singlet state.

$$|\psi\rangle = \psi_g(r_1)\psi_g(r_2) \times \frac{1}{\sqrt{2}} (|\uparrow\rangle_1|\downarrow\rangle_2 - |\downarrow\rangle_1|\uparrow\rangle_2) \quad (5.14)$$



As usual, we use the variational method to estimate the ground state energy.

$$\begin{aligned}\psi(r_1, r_2) &= \frac{\beta^3}{2\pi(1+S)} (e^{-\beta r_{a1}} + e^{-\beta r_{b1}}) (e^{-\beta r_{a2}} + e^{-\beta r_{b2}}) \\ S &= \left(1 + \beta R + \frac{1}{3}(\beta R)^2\right) e^{-\beta R}, \quad \beta = \frac{Z'}{a_0}.\end{aligned}\quad (5.15)$$

The minimum is clearly

$$\langle E \rangle = \langle g; g | H | g; g \rangle \propto \langle a + b; a + b | H | a + b; a + b \rangle. \quad (5.16)$$

For H₂, the molecular binding energy E_b is defined in relation to two infinitely separated ground state H atoms,

$$E_b = -2R_\infty - E_0. \quad (5.17)$$

Choosing a correct effective nuclear charge, $Z' = 1.192$, we obtain a minimum approximately at

Name	Predicted Value	Measured Value
R_0	73.0pm	74.1pm
E_b	3.49eV	4.75eV

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The error of E_b is too large to accept. The problem is $\psi_g\psi_g$ is not a good representation of the true ground state. Expanding the product gives⁶

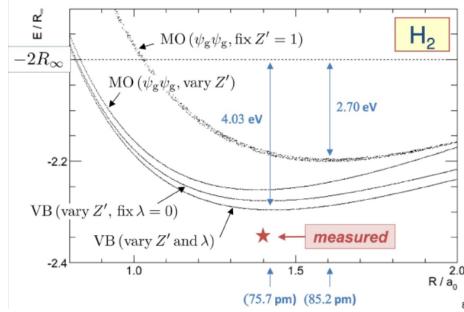
$$\psi_g\psi_g \propto (\psi_a\psi_b + \psi_b\psi_a) + (\psi_a\psi_a + \psi_b\psi_b). \quad (5.18)$$

The first term means electrons are shared between two protons (covalent bonding), but the second term shows that each proton holds two electrons and doesn't share any (ionic bonding). The 1 : 1 ratio between the two states gives that we are equally likely to get an H^+ and an H^- when we split the molecule, as we are to get two H atoms⁷.

Do variational method again and we obtain

Name	Predicted Value	Measured Value
R_0	75.7pm	74.1pm
R_0	4.03eV	4.75eV

which is a better, but still not-so-good approximation.



The results so far are listed in the table below:

trial wavefunction	fix	vary	Z'	λ	R/pm	BE/eV
MO	Z', λ	R	1.0	1.0	85.2	2.70
MO, variable charge	λ	Z', R	1.192	1.0	73.0	3.49
VB, variable charge	λ	Z', R	1.167	0.0	74.6	3.78
variable λ and charge		λ, Z', R	1.195	0.26	75.7	4.03
James & Coolidge					74.1	4.73 ± 0.02
Experiment					74.1	4.75

⁶ r_1 always comes first

⁷IRL this is unlikely due to electron-electron repulsion

Chapter 6

Chemical View of Molecular Orbitals

The energy of a diatomic system varies with the internuclear distance. The relations is called Lenard-Jones potential:

$$U(r) = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] \quad (6.1)$$

But special properties appears when chemical bond forms. Therefore we must consider quantum-mechanically the properties of electrons, which was discussed in the last chapter.

In **homonuclear diatomics**, such as H_2 , H_2^+ , LCAO¹ together with factorization skills was used to calculate the minimum ground state energy. However, chemists found an easier way to understand the whole thing.

6.1 Diatomic Molecules

6.1.1 Combining wave functions

Two wave functions can add **in-phase** or add **out-of-phase**.

Adding in-phase always increase electron density between atoms, therefore it is more energetically favorable². Also, electron(s) between atoms help to hold atoms together. For a number of reasons, the "in-phase" state is called **bonding orbital**, while the other is the **anti-bonding orbital**. The result may be summarized using the following plot.

Although the quantum-mechanical calculation is a bit hard, there are simple rules to predict things in chemistry.

¹Linear combination of atomic orbitals, in case one forgets.

²"Energetically favorable" is so loved by some biologists that they use this phrase to explain everything in life.

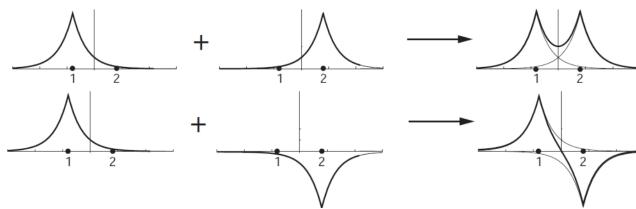


Figure 6.1: Simple version of wave function combination, adding in-phase (upper one) and adding out-of-phase.

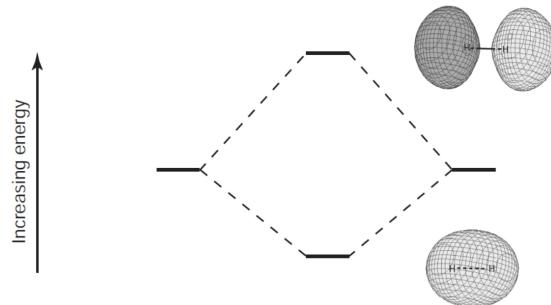


Figure 6.2: Bonding and anti-bonding molecular orbitals in a diatomic H_2 .

- Combining n AOs results in n MOs³.
- One molecular orbital (the bonding MO) is lower in energy than the atomic orbitals, the other (the anti-bonding MO) is higher.

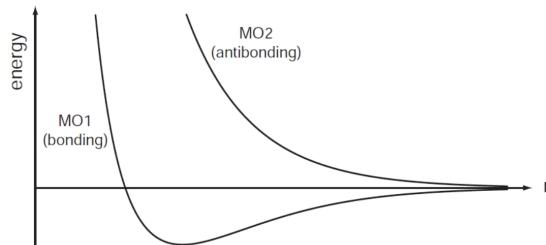


Figure 6.3: $E_{\text{anti-bonding}} - E_{\text{zero}} > E_{\text{zero}} - E_{\text{bonding}}$ at the same radius.

When exciting H_2 , one electron will move from bonding MO to the anti-bonding one. The important point is, that with one electron in the bonding and one in the antibonding MOs, the total energy is always positive. At any point, the energy can decrease by increasing the bond length. Eventually, the bond breaks entirely to form two hydrogen atoms.

³AO for atomic orbital, MO for molecular orbital.

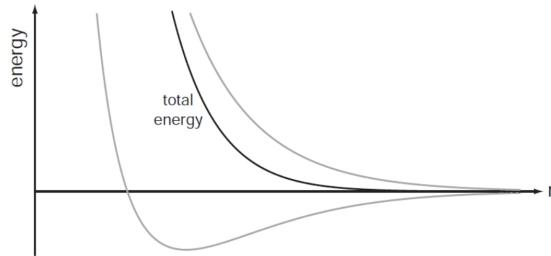


Figure 6.4: With one electron in the bonding and one in the antibonding MOs, the total energy is always positive.

Using similar words, we can explain why He_2 does not exist. It has two electrons in bonding MO and 2 in anti-bonding MO, The total energy of the MOs is greater than zero, therefore He_2 is unstable with respect to helium atoms.

6.1.2 Bond order

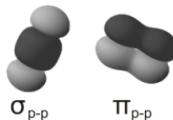
A useful concept to consider when trying to work out if a bond forms is the bond order, The electrons in anti-bonding MOs cancel out the bonding gained by having electrons in bonding MOs, hence the difference between the number of electrons in bonding MOs and the number in anti-bonding MOs will tell us if the species is stable or not. The $1/2$ is there because electrons always comes in pairs inside a chemical bond.

$$\text{Bond order} = \frac{1}{2} (\text{electrons in bonding MOs} - \text{electrons in antibonding MOs}) \quad (6.2)$$

In simple molecules, bond order is the number of bonds between two atoms.

6.1.3 Labeling bonds

σ and π bonds When two s orbitals combine, it can only form a single kind of MOs, because s orbitals are spherically symmetrical. However, when it comes to p orbitals, we must consider how they combine. Consider two sets of p orbitals meet in the y direction. p_y s will form a σ bond, but p_x s or p_z s will form a π bond.

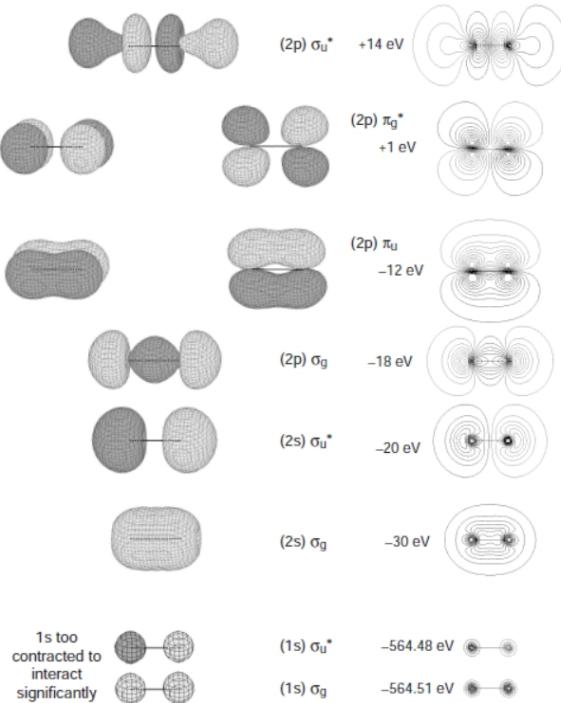


Central symmetry The second label depends on how the sign of the wave function changes through the **center of inversion**. If the wave function does not switch sign at opposite coordinates, it is said to be ungerade (even), if the wave function does switch sign at opposite coordinates, it is said to be gerade (odd). We use *u* for ungerade and *g* for gerade.

This symmetry label only applies to molecules that possess a centre of inversion in the first place and so could be used for N₂ but not for CO, for example.

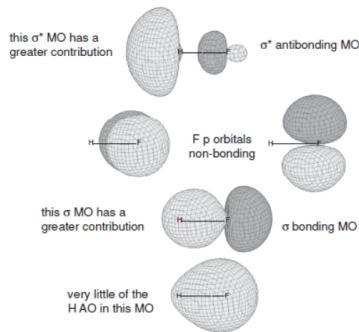
Bonding or not If the MO is anti-bonding, we will write a * on the top-right of σ or π .

6.1.4 Examples



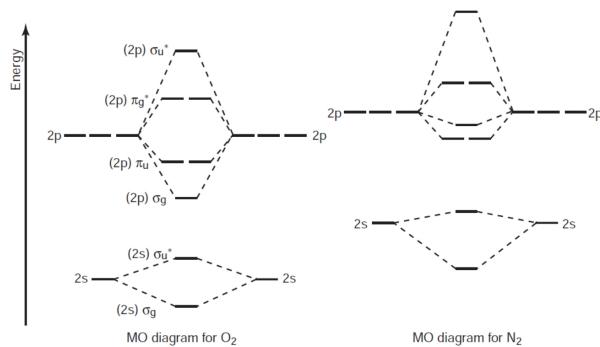
The MOs for oxygen is symmetrical because energy levels in two oxygen atoms are the same. However, things are more complicated in non-symmetric molecules, such as HF.

The energy level diagram and the MO pictures both show that most of the electrons in HF are concentrated around the fluorine atoms rather than the hydrogen atom. In other words, the HF bond is **polarized towards the fluorine**.



6.1.5 sp mixing

sp mixing is a phenomenon that happens in homodiatomic atoms at and below N_2 . Basically the 1σ MOs and 2σ MOs repel each other, resulting in a form of



Actually, the repulsion exists in all atoms, but only at and below N_2 can $(2p)\sigma_g$ override $(2p)\pi_u$.

For heteronuclear diatomics, it is not generally possible to predict how significant the effects of sp mixing will be without considerable computation.

6.2 Large Molecules

6.2.1 H_3^+ , an example

As usual, combining 3 AOs will give rise to 3 MOs, they are called bonding, non-bonding and anti-bonding respectively. If one want to estimate the energy levels and distances between nuclei, LCAO must be used again.

6.2.2 Hybridization

Hybridization allows us to mix a number of atomic orbitals on the same atom to create hybrid atomic orbitals (HAOs) which point directly towards the atoms

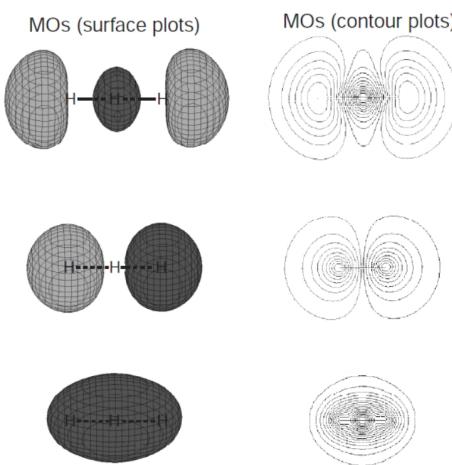
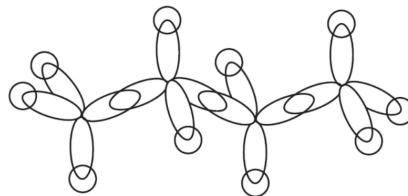


Figure 6.5: Note that anti-bonding has 2 nodes, and non-bonding has 1 node.

we wish to construct bonds with.

For example, in methane, we no longer consider the carbon as having an s orbital and three p orbitals but four equivalent sp^3 HAOs, each pointing to the corner of a regular tetrahedron. Each HAO can overlap with one of the hydrogen 1s AOs in-phase to give a bonding MO and out-of-phase to give an anti-bonding MO.

In this way we suggest a possible (actually quite useful) structure of C_4H_{10} .



It is **EXTREMELY** important to know that shape always comes first. **If the shape is known, so is the hybridization.** Now you must understand why we study how to determine shapes and structures of molecules in the first place!

Advantages of Hybridization

- Simplifies the bonding scheme.
- Gives more directional HAOs that point towards the bonding atoms or where we think of the lone pairs as pointing.

- Gives molecular orbitals in which electrons are not delocalized over many atoms but instead the bonding electrons are localized in between two atoms and the lone pair electrons centered on the atom.
- More useful when trying to draw mechanisms.

Disadvantages of Hybridization

- Simple hybridization does not give the best picture of the different energy levels within the molecule.
- Encourages a localized view of electrons whereas **in reality the electrons are spread over many atoms**.

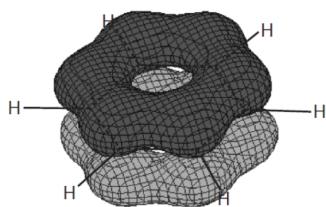
The last point is extremely important - though resonance and conjugation are used to overcome this disadvantage, one may still fail to consider electrons as globally as possible.

Hybridization	Geometry	Bond Angle	Example
sp	linear	180	BeF ₂
sp ²	trigonal planar	120	BF ₃
sp ³	tetrahedral	109.5	CF ₄
sp ² d or p ² d ²	square planar	90	Pt(Cl) ₂ (NH ₃) ₂
sp ³ d or spd ³	trigonal bipyramidal	90 and 120	PF ₅
sp ³ d ²	octahedral	90	SF ₆

6.2.3 Delocalized systems - Conjugation

Following concepts in the disadvantages of hybridization, we look at systems in which electrons can not be seen as fully localized.⁴

The most famous example of such a system is the Π_6^6 in benzene. But it is such trivial that it will be a waste of time if we just talk about it here.



So let's look at something easier. Consider butadiene, C₄H₆. If someone asks you to identify the HOMO and LUMO⁵ of that molecule, here are the right things to do:

First, count electrons while describe and draw the molecular structure.

⁴In this subsection some tips on Tripos exams are given, one may ignore it if he or she doesn't need.

⁵HOMO for Highest Occupied Molecular Orbital, LUMO for Lowest Unoccupied Molecular Orbital.

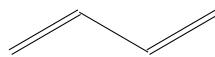


Figure 6.6: The first plot you should draw in your exams.

In this molecule, each carbon is sp^2 hybridized. What concerns us is its Π_4^4 system.

Second, identify orbitals.

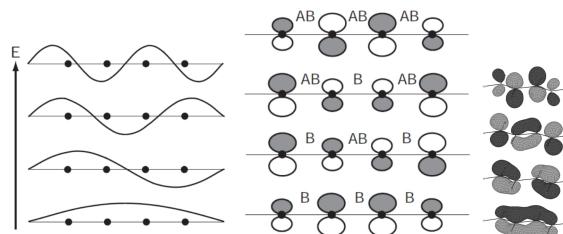


Figure 6.7: The second plot you should draw in your exams.

Note that there are 4 electrons in those orbitals, namely orbital 2π is the HOMO, while 3π is the LUMO. Problem Solved!

6.2.4 Predicting structures by minimizing energies

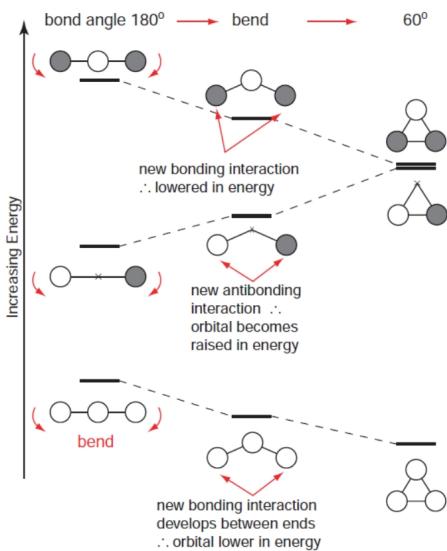
In all of the examples we have looked at we have assumed the shape of the molecule and then looked at the molecular orbitals it would have. However it is possible (but complicated!) to theoretically predict from scratch the shape a molecule will adopt. In essence we simply assume a starting geometry for a molecule, work out its energy and then alter the geometry slightly and recalculate the energy again. We keep repeating this process until the energy of the molecule is at a minimum. This usually requires considerable computer power and is not something that can be simply worked out on paper. However, we can illustrate how the process works by returning to the very simple H_3^+ ion.

It is clear that there is a three-centered two-electron bond, namely Π_3^2 , in that structure.

A Trick for Tripos The HOMO and LUMO can be identified in simple molecules following simple tricks.

Energy levels : Bonding < Non – bonding & lone pairs < Anti – bonding

That's why a O – C – C – N structure's HOMO is always at N's side. Also, gaps between π^* and π are smaller than σ^* and σ .



6.3 Reactions as HOMO-LUMO Interactions

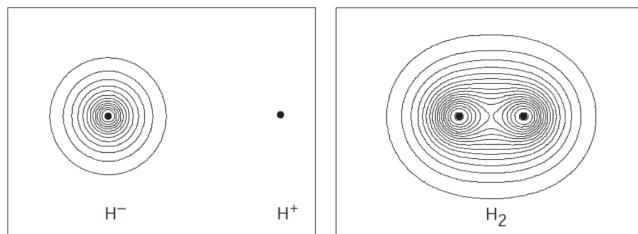
Considering from molecular orbitals, the highest energy electrons in one species may be lowered in energy by interacting with a second species. That may be regarded as the true meaning of reactions.

For a possible chemical reaction, basic rules, such as electron conservation and atom conservation, must be satisfied. But in order to find the correct mechanism, we must consider in addition the shapes of the molecular orbitals.

6.3.1 Example: $\text{H}^+ + \text{H}^- \rightarrow \text{H}_2$

This time shapes of orbitals do not matter very much because 1s orbitals are spherically symmetric.

The initial attraction between the two oppositely charged ions is electrostatic, but the interaction does not lead to an ionic bond but a covalent one where the two electrons are shared equally between the two nuclei. This is shown by the electron density contour maps:



6.3.2 Curly arrows

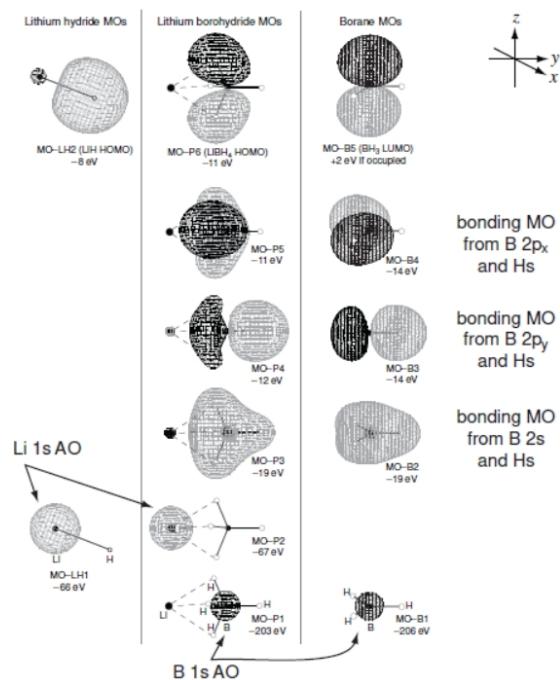
Curly arrow is a kind of way to illustrate the redistribution of electrons. A half, or **fish-hook curly arrow** represents the "movement" of an electron. The word movement was quoted because in reality the electron does not move from an atom to another⁶.

An example is the reaction $\text{LiH} + \text{BH}_3 \rightarrow \text{LiBH}_4$.

Let us first consider the MOs for LiH . The lowest energy orbital, MO-LH1 , at -66eV , is essentially just the $1s$ AO on lithium (it is just off the graph on page 19). This AO is too contracted and too low in energy to interact with the hydrogen atom in LiH or indeed any atoms in the product and so remains essentially unchanged during the reaction.

The Highest Occupied MO in LiH , MO-LH2 , is a result of the interaction between the lithium $2s$ AO and the hydrogen $1s$ AO. Consulting the graph on page 19, we see that the hydrogen $1s$ AO is considerably lower in energy than lithium $2s$ AO hence the bonding MO formed (MO-LH2) has a greater contribution from the hydrogen atom than from the lithium atom. This is clearly seen in the orbitals's appearance.

The very lowest energy orbital in both BH_3 and LiBH_4 is the $1s$ atomic orbital on the boron at *ca.* -203eV . It is considerably lower in energy than the lithium $1s$ since boron has a greater Z_{eff} . It too remains essentially unchanged during the reaction.



The MOs labelled MO-B2 , B3 and B4 in BH_3 are all bonding between the boron and the hydrogen atoms. These are all delocalised MOs: MO-B2 is a combination of

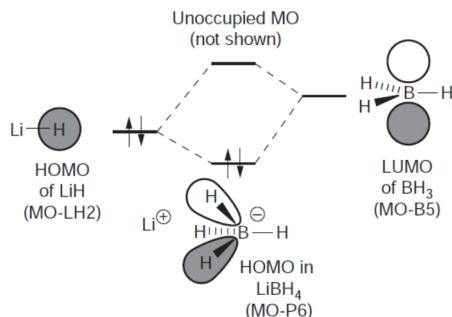
⁶It is shared by all atoms in the molecule, remember?

the boron 2s and the hydrogen 1s orbitals; MOs B3 and B4 are combinations of the boron $2p_y$ and $2p_x$ AOs with the hydrogen 1s orbitals. Because the three hydrogen atoms in planar BH_3 lie in the nodal plane of the boron's $2p_z$ orbital, there can be no net interaction between these orbitals. Thus MO-B5 is simply the (vacant) $2p_z$ AO of the boron.

Note that instead of using the boron 2s, $2p_x$ and $2p_y$ AOs separately to form delocalized bonding MOs with the hydrogens, we could have come up with a similar picture by considering the boron atom in BH_3 to be sp^2 hybridized. In either scheme, the Lowest Unoccupied MO in BH_3 , the boron $2p_z$, remains exactly the same.

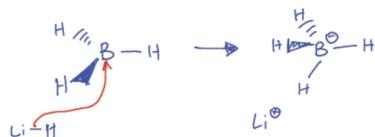
In the product, LiBH_4 , MOs P3, P4 and P5 are essentially just modified versions of the orbitals B2, B3 and B4 in BH_3 ; they have the same approximate forms and energies even though they are now involved in bonding four hydrogen atoms in the product rather than just the three in the reactant, BH_3 .

The highest energy electrons in the reactants, at -8eV , were in MO-LH2 MO of the lithium hydride. The highest energy electrons in the product, at -11eV , are in MO-P6. However, the form the HOMO in the LiBH_4 does not resemble the HOMO in LiH but is much closer in form to the LUMO in BH_3 . MO-P6 is a bonding MO, consisting of a bonding interaction between the boron $2p_z$ with the hydrogens. We can show its formation from the interaction between the BH_3 LUMO and the LiH HOMO:



In BH_3 there are three pairs of electrons contributing to the three B–H bonds. In the product, LiBH_4 , there are four pairs contributing to the four B–H bonds. The orbital interactions show that it is the electrons in the HOMO of the LiH (which are more associated with the hydrogen rather than the lithium) that end up contributing to the B–H bonding in the product (in MO-P6).

The curly arrow diagram should look as



These arrows suggest that the electrons that were in the bond between the lithium and the hydrogen (but more associated with the hydrogen) end up con-

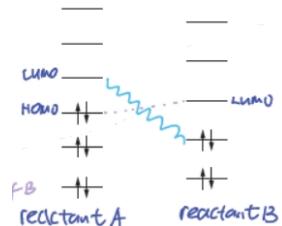
tributing to a new bond between the boron and the hydrogen. This is consistent with what the MO interactions are telling us.

One of the most important interactions is that between the HOMO of one reactant and the LUMO of the other. This interaction will lead to a net lowering in energy of the most energetic electrons.

6.3.3 HOMO-LUMO interactions

There are no net interactions between other molecular orbitals, because only interactions between HOMO and LUMO can cause a net lowering in energy of the most energetic electrons. Again, the lowering in energy of the electrons is a key driving force behind why the reaction takes place.

It is easy to picture that there are two pairs of HOMO-LUMOs, we should choose the pair with smaller energy gaps, as the dashed line in the following figure shows. That is why we choose HOMO and LUMO following the trick in [6.2.4](#).



6.3.4 Nucleophilic addition to the carbonyl group

This is a kind of reaction that a general nucleophile, Nu^- attacks the carbonyl carbon, forming a new bond and simultaneously breaking the C-O π bond.

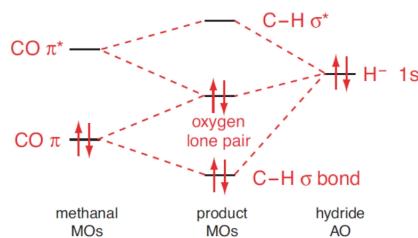
All of the reactions may be represented by the general equation:



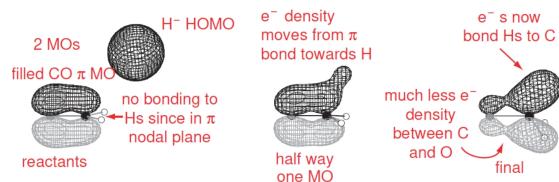
The carbonyl carbon bears a partial positive charge due to the influence of the electronegative oxygen atom attached to it. Hence there is an initial electrostatic attraction between the negatively charged nucleophile and the carbon. For example, in the reaction between carbonyl and hydride, this can be written in the form of:

The important result is that overall, the energy of the electrons is lowered during the reaction which explains why it takes place.

Considering the reaction with structure, the **attacking angle** is the angle between C=O double bond at carbon's side, and the anti-bonding orbital, which is about 107° . The reason is not only the direct attack (overlap) to the C=O



π^* , but also a bit of repulsion from the π bond. The two reasons combine and give an angle at about 107° .



For this reason, the following reaction cannot happen (the possible attacking angle is too small).



More will be seen in the third part of our note.

Part III

Reactions and Mechanisms in Organic Chemistry

Chapter 7

Fundamental Knowledge

The lecture believed that organic chemistry is "an excellent training for those who wish to become medicinal chemists but so much more besides: organic molecules are everywhere, from crop sprays to vitamins, dyes to smells and washing powder to recreational drugs and bombs". Surly organic chemistry is mostly for chemists and biologists, but a particular nerdy biologist¹ refused to study chemistry. So the burden fell on my shoulders, I had to carry it alone, even though I hate it so much.

I don't expect this part of my note will be particularly interesting because the content is just some rubbish with no logic at all. But I will try my best to go through all of the things we studied at lectures and during supervisions.

7.1 Representing Molecules - Chirality

Representations are a kind of language, the ultimate goal is to let others understand what we are talking about without using any kind of social languages. The representation system must be worldwide accepted and unified. In fact chemists had succeeded in building the empire.

The basic rules have been introduced at the beginning of this note, but here are more things to consider:

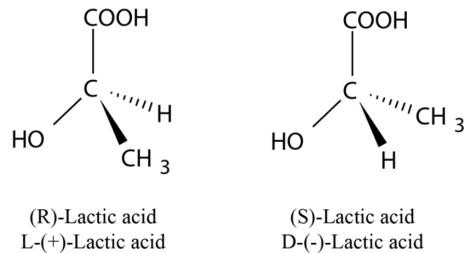
Chirality is important because it impacts all kinds of properties². **Enantiomers** are mirror images of one another but they do not necessarily have the same properties.

The most famous example is **lactic acid**, or more formally 2-Hydroxypropanoic acid. Lactic acid is a chiral compound with a carbon chain composed of a central (chiral) atom and two terminal carbon atoms. A hydroxyl group is attached to the chiral carbon atom while one of the terminal carbon atoms is part of the carboxylic group and the other atom is part of the methyl group.

¹The one I mentioned at the beginning of this note.

²A better way to say "physical, chemical and biological properties".

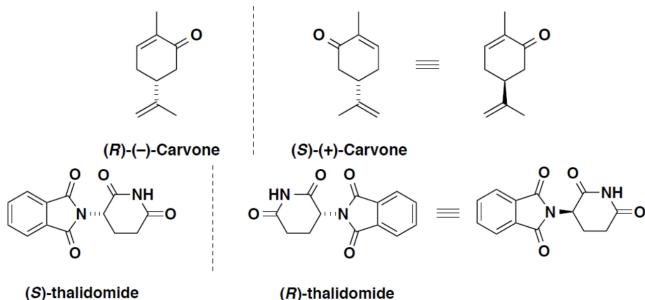
Two optically active isomeric forms of lactic acid exist: L(+) form, also named (S)-lactic acid, and D(-) form, or (R)-lactic acid. **L(+) -lactic acid is the biological isomer**, which plays a key role in human bodies³.



We must state its chiral property in our plot, for this reason the figure above used "dashed" sticks and "sharp" sticks to show the relative positions.

Apart from biological properties, there are simple ways to identify purified lactic acid solutions. When shone by polarized light, one kind of lactic acid bends light to a direction and the other bends light to the opposite direction. They also have different melting points.

Here are other examples:



These plots are following **Stereochemical notation**, it is simply what we said earlier, just another name.

7.2 Functional Groups

7.2.1 Reasons of using functional groups

There are several reasons why it is reasonable to use functional groups instead of other models.

- C-H bonds and C-C σ bonds are too strong to break in an organic chemistry condition, also they are not so polarized.

³During anaerobic exercise, lactate produced in skeletal muscles is transferred to the liver for gluconeogenesis, the newly formed glucose is transferred back to the muscles for respiration.

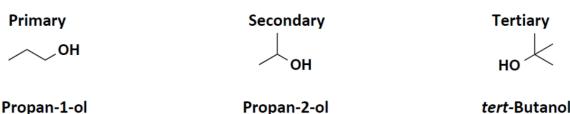
- C-X σ bonds (where X is a heteroatom⁴) are polarised and reactive towards nucleophilic attack, which make them much easier to break in a chemical reaction.

A functional **group** is how we describe those reactive C-X **bonds**.

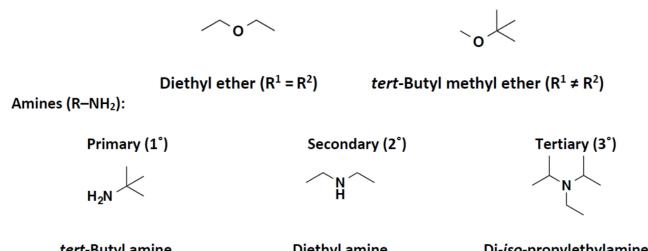
7.2.2 Categories

In part IA chemistry, we are concerned about 4 types of C-X bonds: alcohols, ethers, amines and halides. We will use R to represent alkyl groups⁵, and Ar for an aromatic ring.

Alcohols (R-OH):



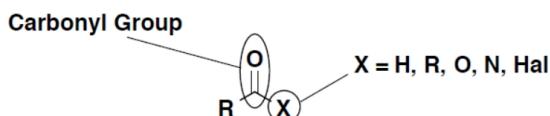
Ethers (R^1-O-R^2); R^1 and R^2 can be different or the same:



Halides (R-Hal):



We are also interested in groups with π bonds present, such as carbonyl groups, alkenes and alkynes. **Carbonyl** is a general structure, specifically aldehydes, ketones, carboxylic acids, esters, amides and acid halides.



⁴Atoms other than C and H.

⁵Groups that consists only with carbon and hydrogen

Names	aldehydes	ketones	carboxylic acids	esters	amides	acid halides
-X	-H	-R	-OH	-OR	-N	-Hal

Anhydrides are dehydrated carboxylic acids, generally R₁ and R₂ are different but quite often they are the same because of the dehydration process.

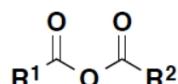


Figure 7.1: General structure of anhydrides.

Alkenes and alkynes are just the double and triple bond between carbons, because they are also reactive, they can be called as functional groups.

Nitriles are -CN, a structure that is commonly seen in different attaching reactions.

Having gone through many different functional groups, it is now possible to identify, go through and label all the functional groups on a more complex molecule. So it is time to meet them in chemical reactions.

7.2.3 Synthesis and Retrosynthesis

I have no idea for what ***** reason synthesis is called synthesis⁶. But this is how the world works, we must ***** take it.

- Aldehydes and ketones can be reduced to alcohols (NaBH₄).
- Carboxylic acids react with alcohols to give esters (R'OH, HCl).
- Alcohols react with anhydrides to give esters (C₄H₆O₃, H⁺).
- Carboxylic acids can be converted to acid chlorides (SOCl₂).
- Acid chlorides can be converted into amides (R'NH₂).

The plots are not given in order to familiarize those names.

In order to get a target compound, we use these rules to find our reactant, this is called **retrosynthesis**. Basically retrosynthesis is the inverse reaction of synthesis.

In the previous part we have discussed two kinds of organic chemical reactions: substitution and nucleophilic addition. In those examples we considered only the HOMO-LUMO interactions (maybe a little electrostatic interaction), but in reality there are more things to think about:

⁶Things would be a lot better if we study chemistry in Chinese.

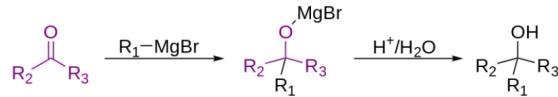
- HOMO-LUMO interactions, as usual.
- Electrostatic interactions.
- Hardness and softness, and hence whether a reaction is FMO⁷ or electrostatic driven.
- Orbital coefficients.
- Symmetry.

Clearly, the best bonding interaction is between the HOMO of nucleophile and LUMO of electrophile. In other words, **nucleophile gives out electrons, electrophile love electrons** and receive them. Also, it is obvious that bonds are stronger in those with higher potential differences between HOMO and LUMO, because it would result in a much larger drop in the total energy.

7.3 Grignard Reaction

7.3.1 Definition and mechanism

Grignard reaction is the easiest way to **extend carbon chain**⁸. The basic mechanism is shown below:



Compounds with structure RMgX is called **Grignard reagents**. In a Grignard reaction, the R group would eventually attach to the targeting carbonyl carbon and X would just dissolve in our solution, which is a good thing. In normal cases, X is chosen to be Br.

Though it seems simple to use the reaction, the mechanism is still a myth. Here we provide a possible mechanism that is accepted by most people.

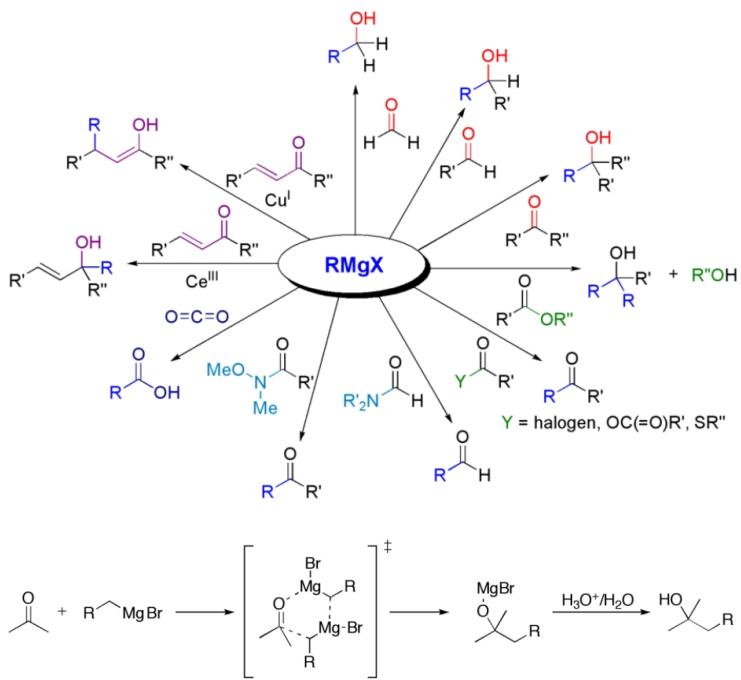
Because carbon is more electronegative than magnesium, the carbon attached to magnesium acts as a nucleophile and attacks the electrophilic carbon atom in the polar bond of a carbonyl group. The addition of the Grignard reagent to the carbonyl group typically proceeds through a six-membered ring transition state, as shown below:

The Grignard reaction must be completed under **anhydrous conditions**⁹. Otherwise, the reaction will fail because the Grignard reagent will dissolve and act as a **base** rather than a **nucleophile** and pick up a labile proton rather than attacking the electrophilic site. This will result in no formation of the desired

⁷Frontier Molecular Orbital, basically HOMO and LUMO.

⁸This reaction won 1921 Nobel Prize in chemistry

⁹No water and even no -OH group (alcohol).



product as the R-group of the Grignard reagent will become protonated while the MgX portion will stabilize the deprotonated species.

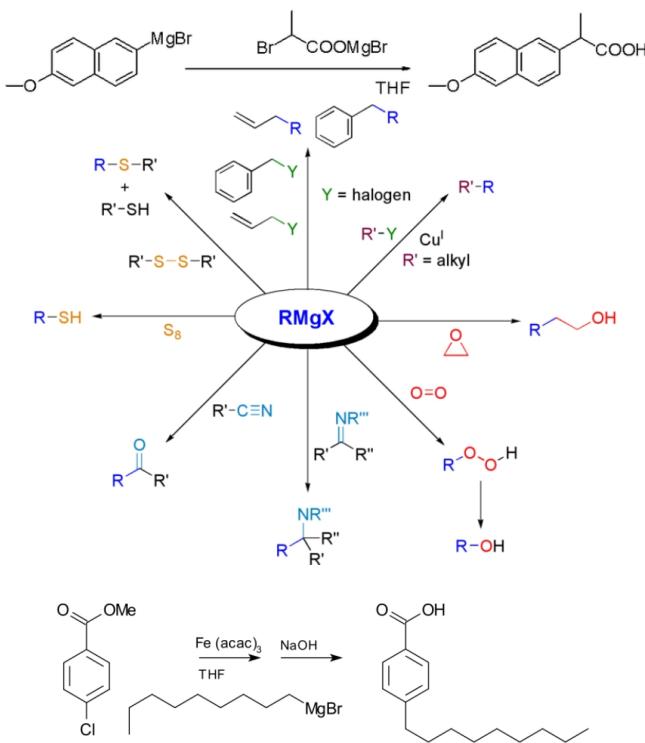
To prevent this, Grignard reactions are completed in an inert atmosphere to remove all water from the reaction flask and ensure that the desired product is formed. Additionally, if there are acidic protons in the starting material, one can overcome this by protecting the acidic site of the reactant by turning it into an ether or a silyl ether to eliminate the labile proton from the solution prior to the Grignard reaction.

7.3.2 More on Grignard reagents

Apart from what we said before, Grignard reagents are nucleophiles in nucleophilic aliphatic substitutions for instance with alkyl halides in a key step in industrial **Naproxen** production:

When water exists, Grignard reagents serve as a base. Grignard reagents are basic and react with alcohols, phenols, etc. to give alkoxides (ROMgBr). The phenoxide derivative is susceptible to formylation by paraformaldehyde to give salicylaldehyde.

Grignard reagents do not typically react with organic halides, in contrast with their high reactivity with other main group halides. In the presence of metal catalysts, however, Grignard reagents participate in C-C coupling reactions. For example, nonylmagnesium bromide reacts with methyl p-chlorobenzoate to give p-nonylbenzoic acid, in the presence of Tris(acetylacetonato)iron(III)



($\text{Fe}(\text{acac})_3$), after workup with NaOH to hydrolyze the ester, shown as follows. Without the $\text{Fe}(\text{acac})_3$, the Grignard reagent would attack the ester group over the aryl halide.

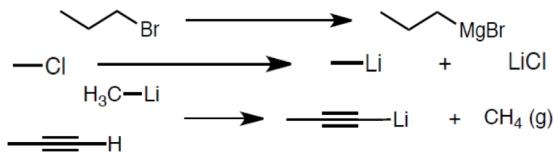
7.3.3 Synthesis of Grignard reagents

Grignard reagents (only magnesium based organometallics are called Grignards) are made by reacting **alkyl**, **aryl** or **vinyl** (attached to double bond) **halides** (chlorides, bromides or iodides may be used) with magnesium ‘turnings’.

Alkynyl derivatives can also be made (CC triple bond attached) but in a slightly different way. For reasons which will be unravelled later on, it is possible to deprotonate alkynes with simple alkyl, aryl or vinyl organometallics. Most commonly, the reagent used will be a simple alkyl organolithium or Grignard reagent.

Organolithium compounds are made by a similar process, with an equal variety of species that can be generated: alkyl, vinyl or aryl halides (chlorides, bromides or iodides) are reacted with lithium. Each reaction requires two equivalents of lithium and generates one equivalent of the desired organolithium plus one equivalent of the lithium halide salt.¹⁰

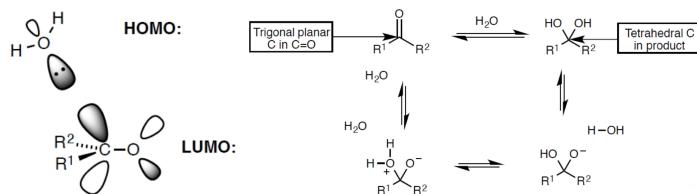
¹⁰Mechanisms of these reactions are beyond IA level.



7.4 Reactions with Water and Alcohols

7.4.1 Aldehydes or ketones with water

When ketone meets water, C=O double bond will turn into two -OH groups, which is an obvious possibility. Interestingly, you can think of it as HOMO-LUMO interactions, but you can also regard it as electron translation caused by electrostatic interactions. Both are right because there are no right answers in chemistry, only approximations.

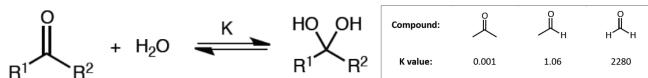


Not all aldehydes and ketones form significant amounts of hydrate: indeed, significant concentrations of hydrate are usually only formed from aldehyde.

The reason for this is that as we increase the size of the 'R' groups attached to the C of the C=O, it is harder to form the hydrate because we move from a bond angle of 120° in the starting material to one of $109^\circ 28'$ in the hydrate: it is harder to form the hydrate product with larger 'R' groups as **steric clash** (Van de Waals strain) in the product is greater than in the starting carbonyl compound.

However, it is not only sterics that play a part in this: **ring strain** factors must also be considered. Specifically, if there is a strained ring, e.g. cyclopropyl, hydrate formation will be favourable due to a release of ring strain with decreased bond angle.

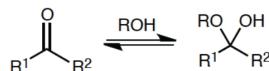
To illustrate some of these statements, the relative K values for a group of aldehydes and ketones can be compared for general hydrate equilibrium:



7.4.2 Aldehydes or ketones with alcohols

Aldehydes and ketones also react with alcohols, initially in exactly the same way as water did but this time, the initial product of that reaction is a hemiacetal.

Overall, R-OH has been added across the carbonyl group, the mechanism is exactly the same as that with water.



7.4.3 Catalysis

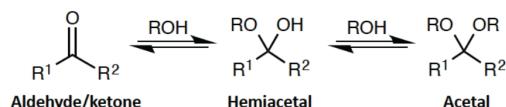
A catalyst increases the rate of a chemical reaction but emerges from the reaction unchanged, but it doesn't mean the reaction can still happen with catalysis generally. Sometimes catalysis is also a necessary reactant, only taht it formed again in the system later on.

Acid catalysts work by making the carbonyl group more electrophilic, while **base catalysts** work by making the nucleophile more nucleophilic¹¹.

7.4.4 Acetal formation

Here is an example of choosing catalysis. Note that every step of acetal formation is reversible, so we must choose a good catalysis to make one direction favorable.

To push the acetal formation through to completion, we must use an excess of alcohol and/or remove water from the reaction mixture as it forms, by distillation, for example. Although hemiacetal formation can be catalysed by acid or base, acetal formation can only be catalysed by acid because an OH group must be made into a good leaving group for it to work. This cannot happen under basic conditions.



Therefore in the first step we use alcohol and **acid or base catalysis**, but in the second step we must use **alcohol and acid catalysis**. To make both reactions happen in a satisfactory rate, we should choose acid catalysis.

Also, note that the first step does not need re-arranging but the second step does. Do not mess up, this is a usual mistake in the exams. For the anti-reaction, the first step needs re-arranging and then H₂O attacks C=O π*, because sp² carbon (made by re-arranging) is flat and less crowded, thus it is easier for water to attack it.

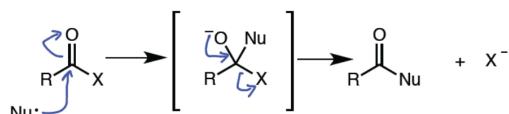
Why is base not successful for this transformation? Under basic conditions, you cannot make a good leaving group. You can straightforwardly access the hemiacetal but at that point, there is only base to departure the hemiacetal, nothing to make the OH⁺ and have it left.

¹¹This is another way to define acid and base.

7.5 Acidity, Basicity and Leaving Group Ability

We consider acidity, basicity and leaving group ability because we want to find out which compound reacts first in a complex system. In reality, there is no "first" or "second" because molecules don't line up to react with each other. The so-called sequential order is just an effective way to evaluate the final equilibrium¹².

7.5.1 Leaving groups



The situation here is different from before (when we had aldehydes and ketones) because now, the group 'X' is present. In the scheme shown, 'X' is a group that can be easily **expelled** from a molecule, taking with it a negative charge (usually). We refer to groups of this type as **leaving groups**. Examples of this type of group are Cl^- , RO^- and RCO_2^- : the best types are those that **can easily stabilise negative charge**.

Taking a closer look at the structures, it can be concluded that substitutions at trigonal planar carbonyl groups go through a tetrahedral intermediate and then onto a trigonal planar product. In the above reaction scheme, the tetrahedral intermediate is unstable, in contrast to earlier reactions seen: for example, addition of a Grignard reagent to an aldehyde or ketone. Why is that? To figure it out, we consider two typical examples: Formation of an ester from an acid chloride, and addition of a Grignard reagent to a ketone.

Comparing different leaving groups, we can find that **the most acidic conjugate acid will most likely have the most stable anion and this is then likely to be the best leaving group from our tetrahedral intermediate**. In the latter example, the conjugated acid of three functional groups on the central carbon are all not acidic, so there are no sensible leaving group, therefore the tetrahedral product is relatively stable.

7.5.2 pH scale

There are several ways to define acids and bases, among them the simplest reads: An **acid** is a species with a tendency to lose a proton; a **base** is a species with a tendency to gain a proton.

pH scale is a way to quantitatively study acidity and basicity based on that definition. The pH value of a water solution is defined by the equation

$$\text{pH} = -\log c(\text{H}_3\text{O}^+). \quad (7.1)$$

¹²Actually all reactions happen together, but those strongly acidic or basic products react again to give the original reactant.

The region we normally use is $0 \sim 14$, in which $\text{pH} = 7$ is defined to be neutral because it is the pH of solvent - water itself. However, one should not say that pH is limited to this region. Strong acidic or basic conditions can easily be achieved.

Indeed, this definition brought many shortcomings, it tells us nothing about how strong one acid might be in relation to another because it depends on the concentration of the acid, the structure of the acid and the solvent. Some bases are extremely strong that they can't exist in water because water is acid to them, but can in some organic solvents where they act as strong bases, vice versa.

In order to measure acidity and basicity, we use a modified equilibrium constant, $\text{p}K_{\text{a}}$, defined by

$$\text{p}K_{\text{a}} = -\log \left(\frac{c(\text{H}_3\text{O}^+)c(\text{A}^-)}{c(\text{HA})} \right). \quad (7.2)$$

The advantage of using $\text{p}K_{\text{a}}$ is that it is a consistent value when temperature and solvent don't change. The smaller $\text{p}K_{\text{a}}$ is, the stronger the acidity, the better the leaving group.¹³ Note that highly electronegative atoms can increase acidity of nearby protons. There are more to be seen at the end of this chapter.

Esters		25
Ammonia/Amines		33-36
Hydrogen ²⁶		35
Allylic Proton ²⁷		43
Alkene ²⁷		44
Benzene ²⁷		ca. 43
Alkanes ²⁷		48-60

7.5.3 Conjugated acid-base pair

A deprotonated acid is a base. That is because deprotonation is a reversible reaction so the product tends to gain protons. Similar thing happens to bases. Therefore in the equation



the HA and A^- are called a conjugated acid-base pair. It is obvious, from $\text{p}K_{\text{a}}$, that the more acidic an acid, the less basic its conjugated base.

¹³Recall the tricks in Gaokao, they are EXTREMELY useful.

7.5.4 Anion Stability

It is important to understand why one anion is more stable than another. Indeed, stabilisation of anions can occur through several pathways and this is the final piece of information we need to have in hand before we return to the reactions of the carbonyl group and cover them with confidence. Again, it is **a balance of many factors**.

Electronegativity Generally, as we increase the electronegativity of the atom upon which a negative charge sits, we increase the stability of the anion.

Second Row Hydride (XH _n):	CH ₄	NH ₃	H ₂ O	HF
Electronegativity of X	2.55	3.04	3.44	3.98
pK _a	48	33	16	3
Conjugate Base	CH ₃ ⁻	NH ₂ ⁻	OH ⁻	F ⁻

Increase Electronegativity of X →

Therefore, increase electronegativity will decrease pK_a and thus increase anion stability.

Delocalization The more resonance forms we can draw¹⁴, the greater the stability of the anion.

Chlorine Based Acid	HOCl	HClO ₂	HClO ₃	HClO ₄
pK _a	7.5	2	-1	-10
Conjugate Base	ClO ⁻	ClO ₂ ⁻	ClO ₃ ⁻	ClO ₄ ⁻

Therefore, increase delocalization will decrease pK_a, increase acidity and increase anion stability. Note that, this is related to their ability to exist in **planar forms**. If a pair of atoms are both flat¹⁵, their acidity can be compared using our trick, otherwise, we cannot compare them unless they have much similarity in structures. That is simply because planar forms lead to better overlap of π orbitals, thus creating more chances of resonance.

A-H bond the weaker the A–H bond, the stronger the acid.

Group VII Acids (HX)	HF	HCl	HBr	HI
HX Bond Dissociation Energy (kJ/mol)	565	429	363	295
pK _a	3.2	-7	-9	-10

Therefore, decrease bond length will decrease pK_a and thus increase anion stability.

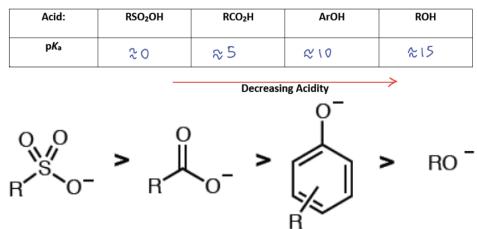
¹⁴The more delocalized is the negative charge.

¹⁵Which means the bonds bind atoms together and no part can rotate.

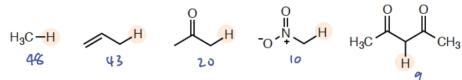
7.5.5 Explaining relative pK_a values

This subsection consists of several examples.

For a series of oxygen acids, in order to explain the change in pK_a , we must look at the anions generated following deprotonation and discuss **both** how they are stabilised and which has the most effective form of stabilisation (this should follow the pK_a value ordering).

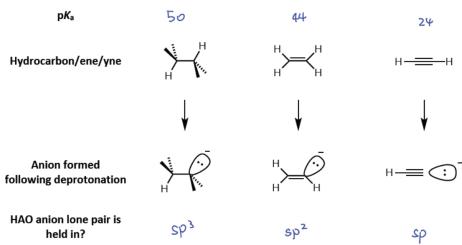


Carbon acids can also be compared in similar ways. Generally, these are weaker than oxygen acids because carbon is less electronegative than oxygen but they can also vary in terms of pK_a : if the negative charge can be delocalised from carbon onto a more electronegative element(s) such as oxygen or nitrogen, the conjugate base will be stabilised and the acid will be stronger.



7.5.6 Hybridization

As s-orbitals are held closer to the nucleus than p-orbitals, the electrons in s-orbitals are lower in energy and more stable. Therefore, the more s-character an orbital has, the more tightly held are the electrons in it, which results in the following pattern.



Compound Name	Conjugate Acid → Conjugate Base	pK _a
Hydriodic Acid	HI → I ⁻	-10
Hydrobromic Acid	HBr → Br ⁻	-9
Protonated Ketone		-7.3
Hydrochloric Acid	HCl → Cl ⁻	-7
Protonated Ether		-3.6
Sulfuric Acid	H ₂ SO ₄ → HSO ₄ ⁻	-3
Carbocations		-3
Protonated Alcohol		-2.4
Hydronium Ion		-1.7
Nitric Acid	HNO ₃ → NO ₃ ⁻	-1.3
Tosic Acid		-1.3
Hydrofluoric Acid	HF → F ⁻	3.2
Hydrogen Nitride (Hydrazoic Acid)	HN ₃ → N ₃ ⁻	4.7
Carboxylic Acid		4.8
1,3-dialdehyde		5
Protonated Pyridine		5.2

Carbonic Acid	$\text{H}_2\text{CO}_3 \longrightarrow \text{HCO}_3^-$ (bicarbonate)	6.4
Hydrogen Sulfide	$\text{H}_2\text{S} \longrightarrow \text{HS}^-$	7
1,3-Diketone		9
Hydrogen Cyanide	$\text{HCN} \longrightarrow \text{CN}^-$	9.1
Ammonium Ions		9.2
Phenol		10
Nitromethane		10
Bicarbonate	$\text{HCO}_3^- \longrightarrow \text{CO}_3^{2-}$	10.3
Thiols		10.5
Protonated Amines		10.6
Hydrogen Peroxide	$\text{HOOH} \longrightarrow \text{HOO}^-$	11.6
1,3-Diester		12
Cyclopentadiene		15
Amides		15
Water	$\text{H}_2\text{O} \longrightarrow \text{HO}^-$	15.7
Primary Alcohols		15.9
Tertiary Alcohols		18
Ketones		20
Alkynes		24

Chapter 8

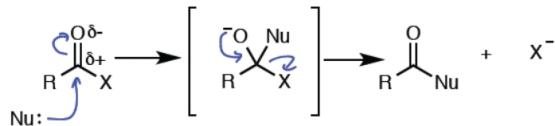
Theory of Nucleophilic Substitutions at Carbonyl Group

We've discussed too many trivial details that I have forgot everything. No matter, let's have a short review:

After learning how to correctly represent molecules, we were introduced to a number of functional groups, and saw some example of transformations between them. Then we learned how to use Grignard reaction to extend carbon chain. In order to do experiments, we must know what compounds can react with typical solvents such as water and alcohols. In those solutions, theories on acidity, basicity and leaving groups allow us to predict possible products. In short, nucleophilic substitution is just a process of adding a nucleophile and kicking off a good leaving group on the same carbon.

To lay a more solid foundation, it is time to use an example and explain it with all that we have learnt. We choose one of the simplest type of reaction in organic chemistry: nucleophilic substitution at the carbonyl group.

The reactivity of this type of system is usually based upon the natural polarity of the carbonyl group ($\delta+$ on carbon, $\delta-$ on oxygen). The general reaction mechanism of this type is given below.



It is obvious that there are three major factors that determine whether this mechanism will operate and they must all be considered when thinking about

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the reactivity of any carbonyl compound:

- Strength of the incoming nucleophile.
- Reactivity of the carbonyl group.
- Leaving group ability.

We will discuss one by one.

8.1 Strength of the Incoming Nucleophile

Generally, **the higher the pK_a of HNu , the better the nucleophile Nu** . Basically, a species which will readily form new bonds to hydrogen (i.e. not very acidic, a strong base with a high pK_a value) will also readily form bonds to carbon. This also means that **good nucleophiles are poor leaving groups**.

Nucleophile (Nu^-)	Conjugate Acid (HNu)	Conjugate Acid pK_a (Nucleophile pK_{sh})	Type of Nucleophile
R^-	RH	50	Good
NH_2^-	NH_3	33	Good
RO^-	ROH	16	Good
R_2N^-	R_2NH^+	10	OK
RCOO^-	RCOOH	5	Poor
ROH	ROH_2^+	-3	Poor
Cl^-	HCl	-7	Poor

↑
Increasing Nucleophile Strength

8.2 Reactivity of the Carbonyl Group

The overall strength of the positive charge and hence the reactivity of the carbonyl group is governed by **two** major factors, which must be considered together¹.

8.2.1 The inductive effect

The inductive effect relates to the relative **electronegativity** of the group (X) adjacent to the carbonyl carbon and withdrawal of electron density through the σ -framework. If we only considered this effect, we could assume that the more electronegative the group adjacent to the carbonyl carbon: **the greater the +ve charge on the carbonyl carbon, the more reactive it should be towards nucleophilic attack**.

¹One should be familiar with them because we have discussed them a lot in sections related to IR spectroscopy. This section is, indeed, relative to IR.

8.2.2 The conjugative effect

The conjugative effect involves delocalisation of the lone pair from the attached group (X) into the π^* of the carbonyl system. Overall, conjugation reduces the +ve charge on the carbonyl carbon and makes the C=O less reactive towards nucleophilic attack.

8.2.3 Summary

An example (which was given before) is oxygen, nitrogen and chloride. Oxygen has the best electronegativity because of two reasons: first, it has more Z_{eff} than nitrogen; second, it better matches the carbon p orbitals than chloride².

To summarize:

	C=O IR Stretch
Acid chloride	1790-1815
Anhydride	1800-1850, 1740-1790
Ester	1735-1750
Amide	1630-1680
Carboxylate Anion	1550-1630
<i>[Conjugated - 30]</i>	

8.3 Leaving group ability

In the last chapter we learnt how to compare leaving group ability, it is straightforward that

Carbonyl Derivative	$\text{R}-\text{C}(=\text{O})-\text{Cl}$	$\text{R}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{R}$	$\text{R}-\text{C}(=\text{O})-\text{OR}'$	$\text{R}-\text{C}(=\text{O})-\text{NR}'\text{R}''$
Leaving Group	Cl^-	RCO_2^-	$\text{R}'\text{O}^-$	$\text{R}'\text{R}''\text{N}^-$
Conjugate Acid	HCl	RCO_2H	$\text{R}'\text{OH}$	$\text{R}'\text{R}''\text{NH}$
pK_a	-7	5	16	23
\rightarrow Decreasing leaving group ability				

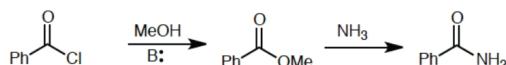
What we now need to do is combine these three variables.

²Chloride is a bad lone pair donor because of this reason.

8.4 Illustrating the Principles

Just like acids and bases, we can get less reactive compounds from more reactive ones. Following this thought, we can determine the reactivity of the carbonyl compound.

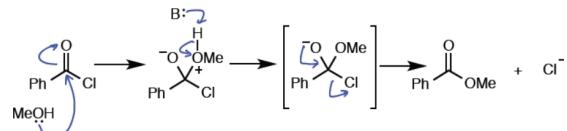
Given that, we know that the following reactions can happen: From which



we know that acid chloride is more reactive than ester, and ester is more reactive than amide. But this does not explain why it would happen, we will try to fill in the details.

8.4.1 Converting an acid chloride to an ester

First, just paste the mechanism using curly arrows.



Next, we need to consider our three variables to explain why this is likely to happen:

1. Reactivity of the carbonyl group: Cl is very electron withdrawing and not good at conjugative donation into the C=O so this acid chloride carbonyl carbon is very d+ and very reactive.
2. Strength of the incoming nucleophile: relatively poor.
3. Leaving group ability: excellent (pK_a of HCl is -7).

Apart from the leaving group ability, it is good habit to check we are using the most reactive leaving group³. In the tetrahedral intermediate, there are three leaving groups. In this case it is fairly clear that chloride is going to be "pushed out".

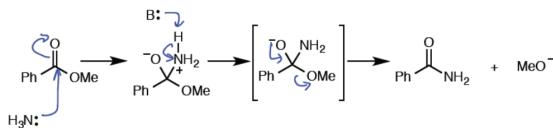
A quick summary: we have very reactive carbonyl, relatively poor nucleophile (MeOH) and a good leaving group. The reaction is very likely to work.

8.4.2 Converting an ester to an amide

Follow similar steps.

The three variables:

³If not, there will be a reaction but the product would be different.



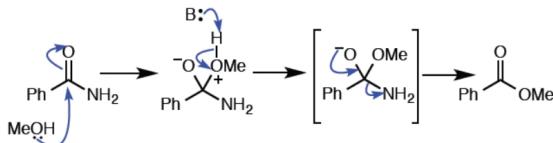
1. Reactivity of the carbonyl group: OMe is inductively withdrawing and not a very strong π -donor so this ester carbonyl carbon is quite $\delta+$ and quite reactive.
2. Strength of the incoming nucleophile: OK.
3. Leaving group ability: OK.

Again, there are three possible leaving groups, and we are surely using the most reactive one.

Summary: we have quite reactive carbonyl, OK nucleophile, OK leaving group. The reaction is likely to work but **will require more forcing conditions** than ester formation from acid chloride.

8.4.3 Predicting impossible reactions

Would this reaction work?



In this case:

1. Reactivity of the carbonyl group: not very reactive (amides are the least reactive derivative, due to the dominant conjugative effect).
2. Strength of the incoming nucleophile: relatively poor.
3. Leaving group ability: the order is exactly the same as it was when we were forming an amide from an ester (we are looking at the reverse reaction now). Leaving group ability is unchanged from before and therefore, it is very unlikely that NH_2^- will leave to give the ester.

Conclusions: if we only considered the reactivity of the carbonyl and the strength of the nucleophile, we might find reason to say that under forcing conditions, this reaction might be persuaded to work. However, when we look at leaving group ability, the difference is so vast between the potential leaving groups, we can only conclude one thing about our conversion from amide to ester. Therefore, this reaction will **not** work.

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In order to answer any question of this type, the same method of analysis can be used: as long as you know the three things you need to consider and have a good handle on leaving group ability, you can be confident of the right outcome.

This is the end of PART IA Chemistry in Michaelmas term!

Enjoy the vacation!

Merry Christmas & Happy New Year!

Part IV

Reactions and Mechanisms in Organic Chemistry Again

Chapter 9

Nucleophilic Substitution at the Carbonyl Group

Last term we took a glance at the theory of nucleophilic substitution at carbonyl groups. This term we will go further to realistic reactions.

9.1 Review

The reaction ability of a nucleophilic substitution is determined by three major factors:

1. Strength of the incoming nucleophile.
2. Reactivity of the carbonyl group.
3. Leaving group ability.

The strength of incoming nucleophile could be determined by estimating pK_a^1 , so does the leaving group ability.

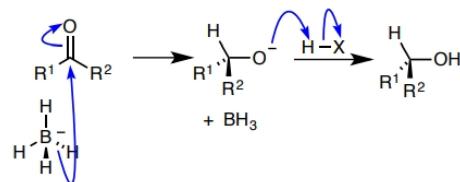
However, the reactivity of the carbonyl group is a balance between inductive and conjugative effect. Inductive effect states that, the greater the +ve charge on the carbonyl group, the more reactive it should be towards nucleophilic attack. However, conjugation reduces +ve charge on the carbonyl carbon, thus it fights against inductive effect. Generally, Ester is a balance of two effects, with C = O IR stretch $1735 \sim 1750 \text{ cm}^{-1}$. While more reactive carbonyl groups have larger IR stretches.

In the last section of chapter 8 we used several examples to illustrate our theory. But did not generalize the conditions for possible reactions. In this chapter we will look at reactions with four kinds of nucleophile and give a summary at the end.

¹Larger pK_a means it is a stronger nucleophile and a weaker leaving group.

9.2 Reactions with Hydride Reducing Reagents

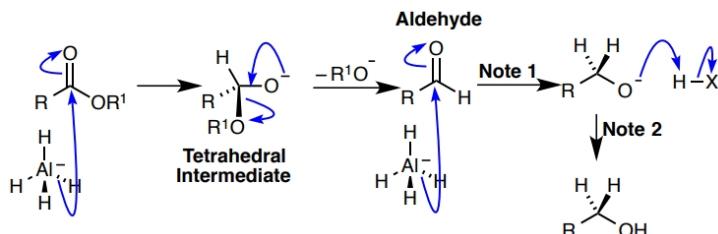
What actually happens now is we want to attack the carbonyl group with H^- , but H^- cannot exist alone, it must be "carried" by something else. The mildest agent that can be used here is **sodium borohydride**, NaBH_4 .



Clearly the reaction consists of an attack and a protonation², and the final product is always alcohol. However, this reagent does not always work. For less reactive carbonyl groups we may need to change for a wilder reagent than NaBH_4 , such as **borane** or **lithium aluminium hydride**³. The application of different agents are summarized in the following table.

	$\text{R}-\text{C}(=\text{O})-\text{Cl}$	$\text{R}-\text{C}(=\text{O})-\text{O}-\text{R}$	$\text{R}-\text{C}(=\text{O})-\text{R}'$	$\text{R}-\text{C}(=\text{O})-\text{OR}'$	$\text{R}-\text{C}(=\text{O})-\text{NR}'\text{R}''$	$\text{R}-\text{C}(=\text{O})-\text{OH}$
NaBH_4	Y	Y	Y	Slow	N	N
LiBH_4^*	Y	Y	Y	Y	N	N
LiAlH_4	Y	Y	Y	Y	Y**	Slow (use BH_3)

As a general principle, always use the **mildest** reagent possible for safety reasons.



Reductions using these agents often do not stop at the first step. Because the tetrahedral intermediate may contain good leaving groups and an aldehyde⁴,

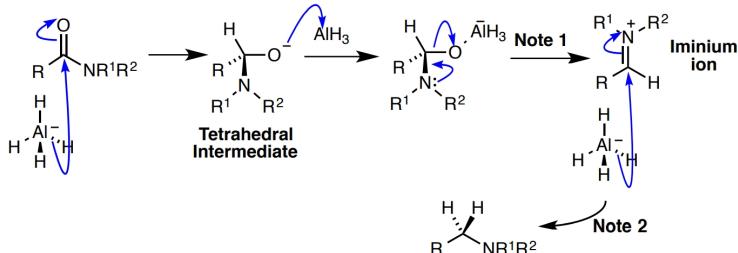
²Note that HX can be any proton donor, things such as H_3O^+ are accepted.

³Lithium aluminium hydride is very reactive and has caused many a laboratory fire. It is incompatible with water and should ONLY be used as a reducing agent when one of this strength is necessary. In contrast, lithium borohydride can be used in alcoholic solutions and has chemoselectivity for esters over amides.

⁴Intro-molecular reactions always happen first.

which is more reactive to nucleophilic attack, will form. Therefore the reaction continues and the aldehyde will be turned into an alcohol.

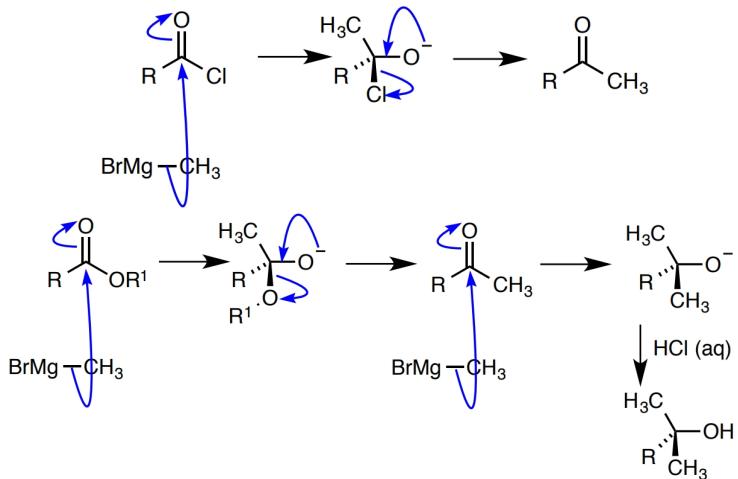
The reduction of amides to amines is a bit more complicated.



The mechanistic difference arises because the tetrahedral key intermediate does not have such a good leaving group. The iminium ion which is then formed is analogous to the aldehyde in the reduction of esters by LiAlH₄ and is reduced very quickly to the amine product, rather than an alcohol.

9.3 Reactions with Organometallic Reagents

In previous sections we discussed on organometallic (Grignard) reagents and their reactions with aldehydes and ketones to produce alcohols. The lithium and magnesium-based reagents discussed are a good source of carbanions, and the mechanism is similar: nucleophilic attack⁵ and protonation.

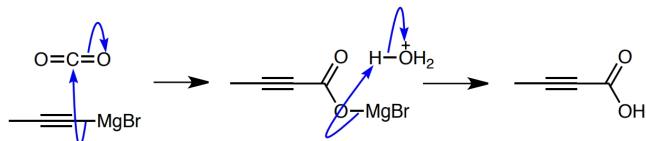


For the reason stated in the footnote, if you intend to make a ketone product,

⁵Similarly, there could be double attacks, and this is related to product estimates. If a much more reactive carbonyl is produced by the first attack, the product will contain little carbonyl intermediate.

you need to use the acid chloride or anhydride to begin with, instead of ester, in order to control the single addition of nucleophile to the starting material. In contrast, if you intend to make an alcohol by double addition, you will need to use the ester and 2eq of nucleophile.

Organometallic reagents can also react with carbon dioxide to form carboxylic acids.



Here is a summary for the products and how much reagents were used.

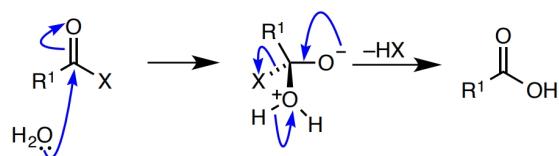
Starting material	$\text{R}-\text{C}(=\text{O})-\text{Cl}$	$\text{R}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{R}$	$\text{R}-\text{C}(=\text{O})-\text{R}^2$	$\text{R}-\text{C}(=\text{O})-\text{OR}^2$	$\text{R}-\text{C}(=\text{O})-\text{OH}$	$\text{O}=\text{C}=\text{O}$
Product following reaction with $\text{R}'\text{MgBr}$ or $\text{R}'\text{Li}$	$\text{R}-\text{C}(=\text{O})-\text{R}'$ (1 eq) $\text{R}-\text{C}(=\text{O})-\text{R}'$ (2 eq)	$\text{R}-\text{C}(=\text{O})-\text{R}'$ (1 eq) $\text{R}-\text{C}(=\text{O})-\text{R}'$ (2 eq)	** $\text{R}-\text{C}(=\text{O})-\text{R}'$ OH $\text{R}-\text{C}(=\text{O})-\text{R}'$ (2 eq)	**, $\text{R}-\text{C}(=\text{O})-\text{R}'$ OH $\text{R}-\text{C}(=\text{O})-\text{R}'$ (2 eq)	*** $\text{R}-\text{C}(=\text{O})-\text{OMgBr}$ or $\text{R}-\text{C}(=\text{O})-\text{OLi}$	** $\text{R}-\text{C}(=\text{O})-\text{OH}$

9.4 Reactions with Water

There are two kinds of reactions with water: reactions with water alone and with water and some acid or base mediated help.

9.4.1 Reactions with water alone

For different kinds of carbonyl groups, the mechanism is the same.



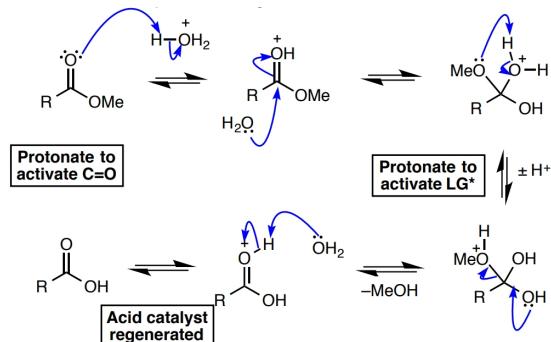
Reaction	Conditions
$\text{R}-\text{C}(=\text{O})-\text{Cl} \xrightarrow{\text{H}_2\text{O}} \text{R}-\text{C}(=\text{O})-\text{OH}$	Fast at 20 °C
$\text{R}-\text{C}(=\text{O})-\text{O}-\text{C}(=\text{O})-\text{R} \xrightarrow{\text{H}_2\text{O}} \text{R}-\text{C}(=\text{O})-\text{OH}$	Slow at 20 °C
$\text{R}-\text{C}(=\text{O})-\text{OR}' \xrightarrow{\text{H}_2\text{O}} \text{R}-\text{C}(=\text{O})-\text{OH}$	Only on heating with an acid catalyst or base.
$\text{R}-\text{C}(=\text{O})-\text{NR}'\text{R}'' \xrightarrow{\text{H}_2\text{O}} \text{R}-\text{C}(=\text{O})-\text{OH}$	Only on prolonged heating with strong acid or base.

However, the conditions for different carbonyl groups may vary, which are summarized below.

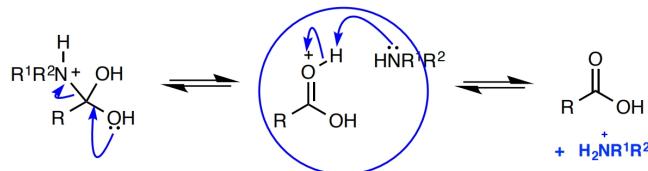
Note that, both the reactivity of the carbonyl group and the leaving group ability decreases as we go down the group. For the acid halides / anhydrides, the reactions can perfectly happen. But for esters and amides further aid are required.

9.4.2 Acid-mediated hydrolysis

For an ester, the acid works as a **catalyst**. The reaction was done by first protonating the carbonyl oxygen⁶ and then protonating the leaving group⁷.



In the amide case things are different. 1eq of acids is used up.



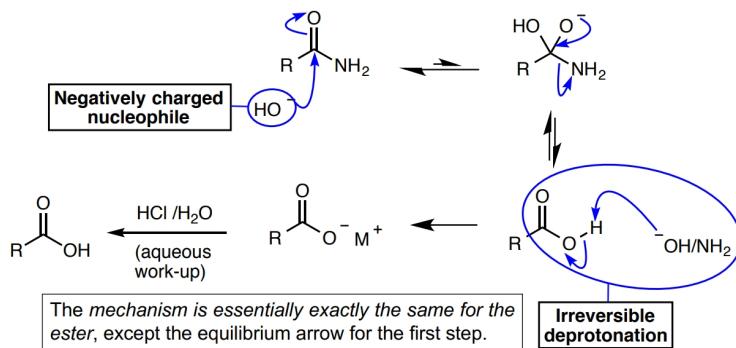
⁶Making it more susceptible to attack by nucleophile.

⁷Lower its pK_a.

9.4.3 Base-mediated hydrolysis

Sometimes there are reasons we cannot use acid in our system. Then base is needed to complete the reaction. The mechanism of these reactions are also the same overall: Creating a negatively charged nucleophile⁸ and deprotonating the carboxylic acid product, pulling the equilibrium over irreversibly towards the hydrolysis products.

For amides, the reaction mechanism is



"The arrow for the first step" refers to the fact: In amide case, more of the initial tetrahedral intermediate goes back to starting material; in the ester case, the equilibrium is approximately even.

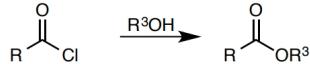
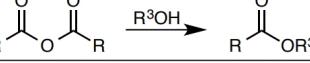
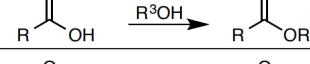
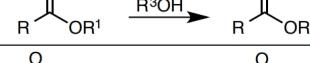
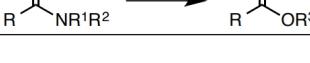
Here is a summary for the acid and base-mediated reactions with water.

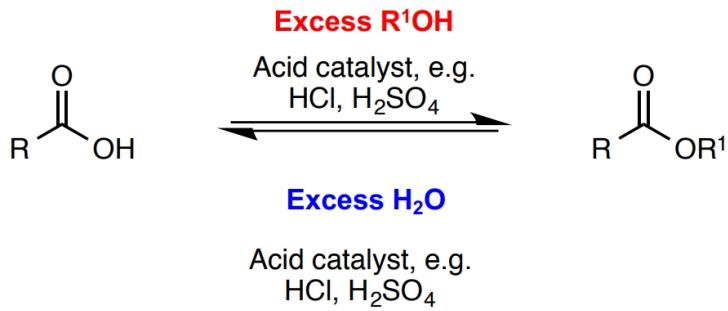
Reaction and Example Conditions	Comments
$\text{R}-\text{C}(=\text{O})-\text{OR}' \xrightarrow[\text{100 } ^\circ\text{C, 30 mins}]{\text{HCl, H}_2\text{O}}$	Acid-mediated: usually requires heat for a short period. H^+ regenerated during course of reaction: truly catalytic.
$\text{R}-\text{C}(=\text{O})-\text{NR}'\text{R}'' \xrightarrow[\text{100 } ^\circ\text{C, 3 hrs}]{\text{H}_2\text{SO}_4, \text{H}_2\text{O}}$	Acid-mediated: usually requires heat for extended period. At least one equivalent acid required to protonate amine generated at the end of reaction: not catalytic in acid.
$\text{R}-\text{C}(=\text{O})-\text{OR}' \xrightarrow[\text{100 } ^\circ\text{C, 30 mins}]{\text{NaOH, H}_2\text{O}}$	Base-mediated: both require heat, esters usually for a shorter period than amides. At least one equivalent of base is required to deprotonate carboxylic acid product at end of reaction: not catalytic in base.
$\text{R}-\text{C}(=\text{O})-\text{NR}'\text{R}'' \xrightarrow[\text{100 } ^\circ\text{C, 3 hrs}]{\text{NaOH, H}_2\text{O}}$	

⁸Making it more reactive.

9.5 Reactions with Alcohols

Due to the hydroxyl group in alcohols, the reactions should obviously be similar to that of water. The conditions for comparable reactions are also similar.

Reaction	Conditions
	Fast at 20 °C
	Slow at 20 °C
	Only on heating with an acid catalyst.
	Transesterification: on heating with an acid or base catalyst.
	Not usually a good way to make an ester. Difficult even with added acid or base.



- **ester** by having an *excess of alcohol* present
- **carboxylic acid** by having an *excess of water* present

9.6 Special Notes

For reactions with carboxylic acids, the organometallic species (or amides, etc.) always attack first with the O-H bond instead of the carbonyl carbon. This is driven by the strong dipole of the O-H bond. In basic alcoholic conditions, deprotonate first.

Before everything, determine the condition of the reaction. Is it basic or acidic. In acidic conditions no O⁻ are allowed.

9.7 Hard and Soft Nucleophiles and Electrophiles

Soft nucleophiles are large, they react very quickly with saturated carbon⁹ but poorly at carbonyl groups. They have a high-energy HOMO and are often uncharged or spread diffusely over large orbitals.

The small HOMO-LUMO gap means reactions are dominated by FMO interactions. Low charge density means electrostatics are not important.

Hard nucleophiles are small, they¹⁰ attack carbonyl groups rapidly, have their electrons concentrated close to the nucleus (a low HOMO), and are usually charged with high charge density.

The large HOMO-LUMO gap means reactions cannot be dominated by FMO interactions. High charge density means electrostatics are much more important, but orbitals are still used for reactions to occur.

⁹Connecting the bridge between this chapter and the next.

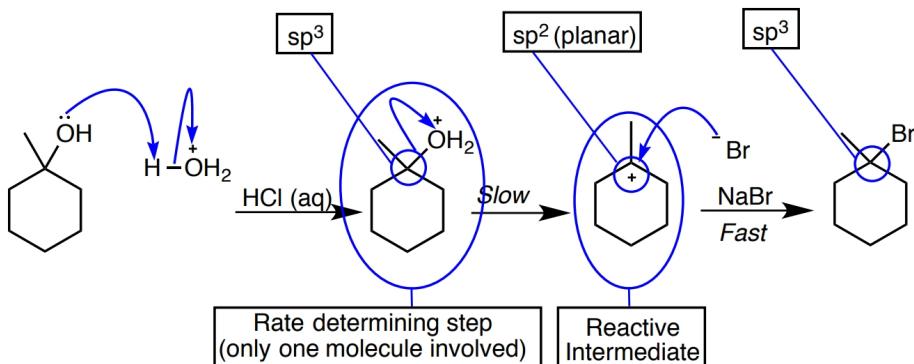
¹⁰By steric chemistry.

Chapter 10

SN1 and SN2 reactions

SN1 and SN2 reactions, or nucleophilic substitution at saturated carbon, often use soft nucleophiles. The two kinds are divided by mechanism and kinetics.

SN1 Nucleophilic substitution unimolecular / first order.



Formation of the carbocation is the rate-determining step and therefore, the rate of reaction will depend only on the concentration of the substrate,

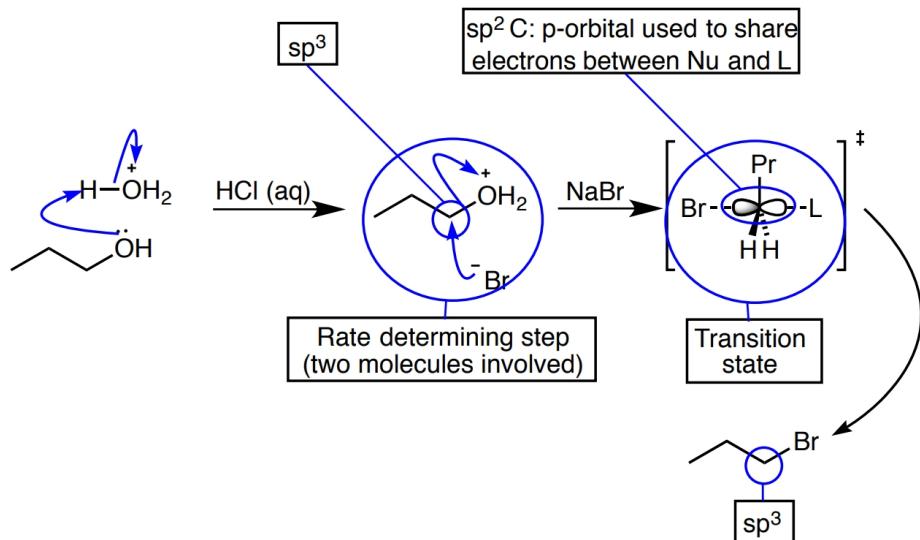
$$\text{rate} = k_1[\text{RL}]. \quad (10.1)$$

For steric chemistry, it is worthwhile to notice that SN1 reactions goes from tetrahedral starting material to planar carbocation, then back to tetrahedral.

SN2 Nucleophilic substitution bimolecular / second order.

Now the rate determining step has two molecules involved. The rate of reaction will depend on both the substrate and the nucleophile,

$$\text{rate} = k_2[\text{RL}][\text{Nu}]. \quad (10.2)$$



For SN2 it is different, we have a transition state¹ where both incoming nucleophile and leaving group are attached. This means that the other three groups must flip sides, the chirality of the central carbon has been changed. Clearly, that sets limit to SN2 reactions, if the chirality of carbon is locked, SN2 cannot happen no matter how reactive the incoming nucleophile is.²

Now we are going to discuss the influencing factors of SN1 and SN2 reactions. There are four major factors:

1. Substrate Structure;
2. Nucleophile;
3. Leaving group;
4. Solvent.

We will go step by step for either of the reactions.

10.1 Substrate Structure

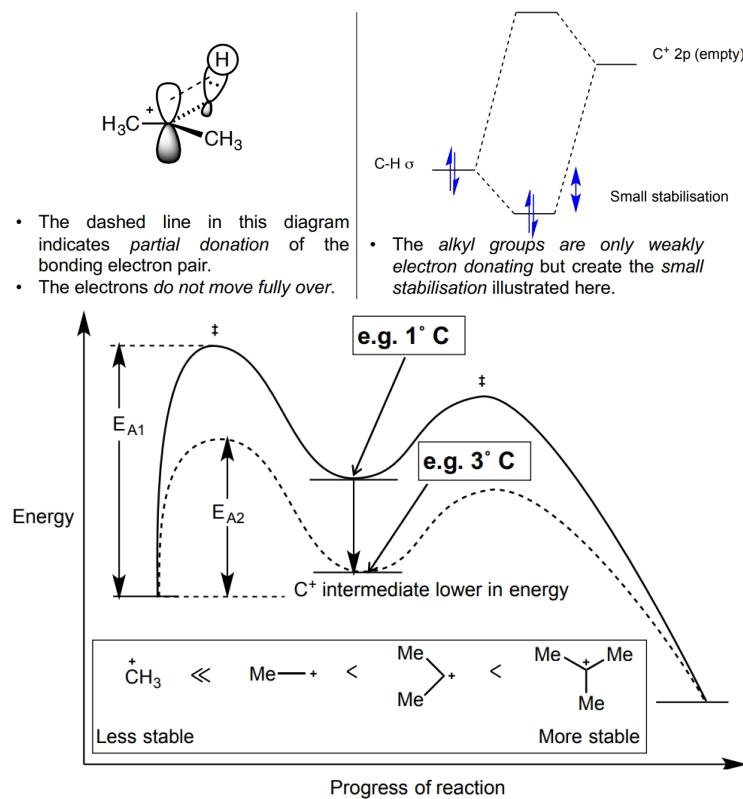
Steric hindrance SN1 reactions become more likely the more substituents there are on the carbon center being attacked by the nucleophile, but this is because of stabilisation of the carbocation rather than anything to do with steric hindrance and is covered below.

¹Not an intermediate! An intermediate is still a local minimum in the energy plot, while a transition state is at the peak of energy.

²The reaction still have chance to happen though other mechanisms.

However, SN₂ become less likely the more substituents there are on the carbon center being attacked by the nucleophile. Increased steric hindrance makes approach of the nucleophile more difficult.

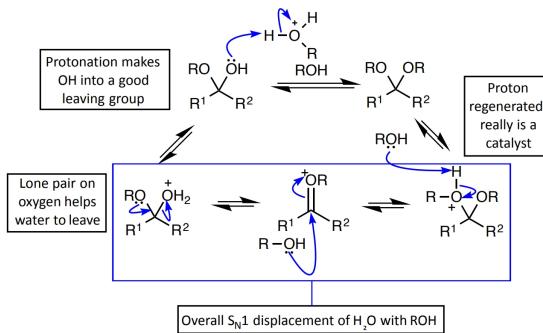
Hyperconjugation for SN₁ The crowd around carbon have bonds attached to them, and these bonds could contribute to the stabilisation of intermediate, which will lead to the increase in reaction speed.



Note that, in the exam everyone is expected to draw precisely the partial donation, especially where it is from. Hyperconjugation can also be remembered as σ bond donation. The bonds does not really overlap with the p orbital so it is a partial donation.

π bond and lone pair donation for SN₁ These factors dominates the stability of intermediate, playing a greater role than hyperconjugation. For π bonds, the more double bonds into which the positive charge can conjugate, the more stabilised the carbocation.

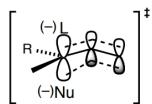
Lone pair donation is the strongest of all. But it is usually not a donating process, it is more likely that the lone pair assists in the departure of the leaving group.



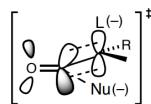
Adjacent double bonds for SN2 We all know that stabilising delocalisation is possible from either filled or vacant orbitals, therefore both electron-donating and electron-withdrawing substituents are able to stabilise SN2 transition state³

Two major types of group which stabilise the transition state in SN2 reactions are:

Adjacent double bonds, C=C
e.g. vinyl or phenyl group



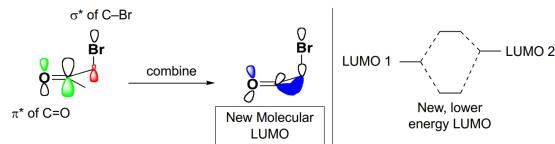
Adjacent carbonyl group



- Stabilised by adjacent $\pi_{C=C}$ and $\pi^*_{C=C}$
- Same for benzyl group but more stabilisation.
- Possible to invoke both electron withdrawal and donation as stabilising factor (donation from $\pi_{C=C}$ pictured).

- Stabilised by adjacent $\pi^*_{C=O}$
- Only possible to invoke electron withdrawal as stabilising factor (C=O cannot donate electrons due to very strong pull by O)

Carbonyl groups for SN2 For the carbonyl group, another factor is also at work. Considering the starting material molecular orbitals, a new lower energy LUMO is formed, which is lower in energy than either the original σ^* or π^* and thus σ more reactive starting material is created. Both the carbonyl and the carbon-bromine bond are more reactive.



Naturally the different relative reactivity can influence the position where nucleophile attack. Just as what we did in year 8 for different acids, the most reactive one thermodynamically reacts first. Therefore be careful when choosing the position of SN2 happening.

³Therefore lower the excitation energy.

A brief summary is given here:

R-Cl:					
Relative Rate:	0.02	79	200	200	100,000
Comments:	Steric hindrance	π -conjugation in TS but more hindered than Me	Least hindered	More π -conjugation in TS than allyl combats hindrance	C=O conjugation in TS

→ Increasing rate

For substrates with alkyl groups attached:

Substrate:	Me-X				
Substrate Type:	Me	1°	2°	3°	'neopentyl'
S_N1 Mechanism:	Bad	Bad	Poor	Excellent	Bad
S_N2 Mechanism:	Excellent	Good	Poor	Bad	Bad

For substrates with groups other than simple alkyl groups attached:

Electrophile:					
Substrate Type:	Allylic ²⁴	Benzylic			
S_N1 Mechanism:	Good	Good	Good	Bad	Bad
S_N2 Mechanism:	Good	Good	OK but S _N 1 better ²⁵	Excellent	Possible but slow.

Stereochemical outcome In SN1 the nucleophile can attack the planar intermediate on both sides, therefore the product is always a mixture of two chiralities. However, in SN2 there can only be a single enantiomer for reasons discussed at the beginning of the section.

10.2 Nucleophile

For SN1 reactions, the nucleophile is not so important because the rate does not rely on it anyway⁴. But in SN2 the nucleophile is very important.

However, different from what we discussed in carbonyl chemistry, the strength here is not reflected by its pK_a value anymore. Instead, we must consider both:

⁴See the rate determining step and the rate equation above.

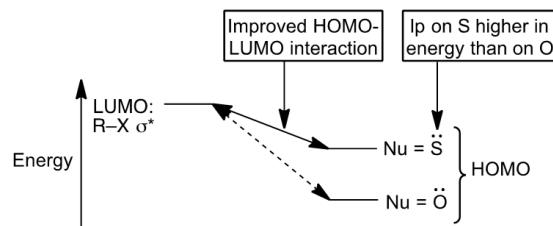
1. Electrostatic attraction, and
2. Bonding orbital interactions.

In carbonyl chemistry, the carbon-oxygen double bond is driven by electrostatics. HOMO-LUMO interactions must also occur but polarity and electrostatics are the major driving force.

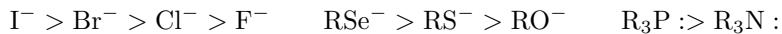
However, the small difference in electronegativity show that the electrostatic component is much less important in the SN2 process. Rather, reactions must be dominated by HOMO-LUMO interactions⁵.

If the electrophile is the same in both cases, generally the lower down the periodic table the nucleophilic atom is found, the larger the atom, the closer in energy are the HOMO of nucleophile and LUMO of electrophile, the better the HOMO-LUMO interaction between nucleophile and substrate and the more favourable the SN2 reaction process.

For example, the sulfur vs oxygen case:



Some of the most commonly found patterns are illustrated below:



Special case When the atom forming the bond is the same over the range of nucleophiles, the nucleophilicity does parallel basicity. Therefore we can use pK_a values in this case.

Oxyanion Nucleophile:	OH^-	PhO^-	AcO^-	TsO^-
Conjugate Acid:	H_2O	PhOH	AcOH	TsOH
Approximate pK_a:	16	10	5	-1.3

$\xrightarrow{\hspace{10em}}$
Decreasing nucleophilicity

10.3 Leaving group

The leaving group is important in both SN1 and SN2 reaction processes because departure of the leaving group is involved in the rate determining step of both mechanisms. Two major types of leaving groups are discussed.

⁵This indicates that soft nucleophile will often react best in the SN2 reaction process.

10.3.1 Halides

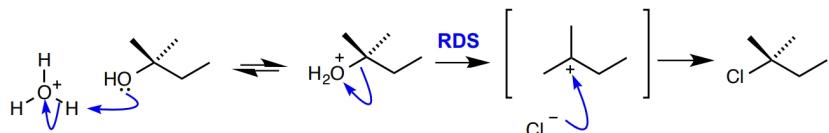
The main factors are clearly the C-X bond strength and halide ion stability⁶.

Halide:	Fluorine	Chlorine	Bromine	Iodine	Decreasing BS →
C-X Bond Strength (kJ mol ⁻¹): ²⁹	118	81	67	54	
pK _a of HX:	+3	-7	-9	-10	Increasing acidity → Increasing LG ability

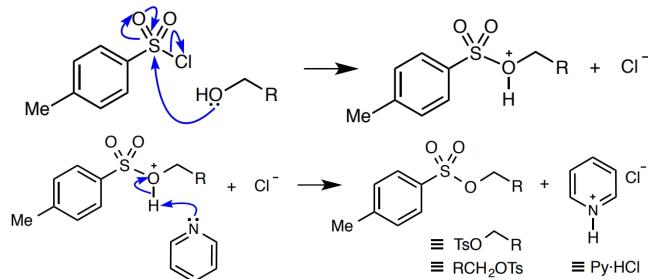
10.3.2 OH derivatives

The point to consider OH derivatives is OH⁻ not usually react as a whole⁷. To make OH a good leaving group, we can choose protonation or sulfonate ester formation.

Protonation The key point is that the rate determining step in the mechanism is the loss of water.



Sulfonate ester formation One of the most widely used methods of making an OH group into a good leaving group is to transform it into a sulfonate ester. We use, and ALWAYS use para-Toluenesulfonates (tosylates, OTs).

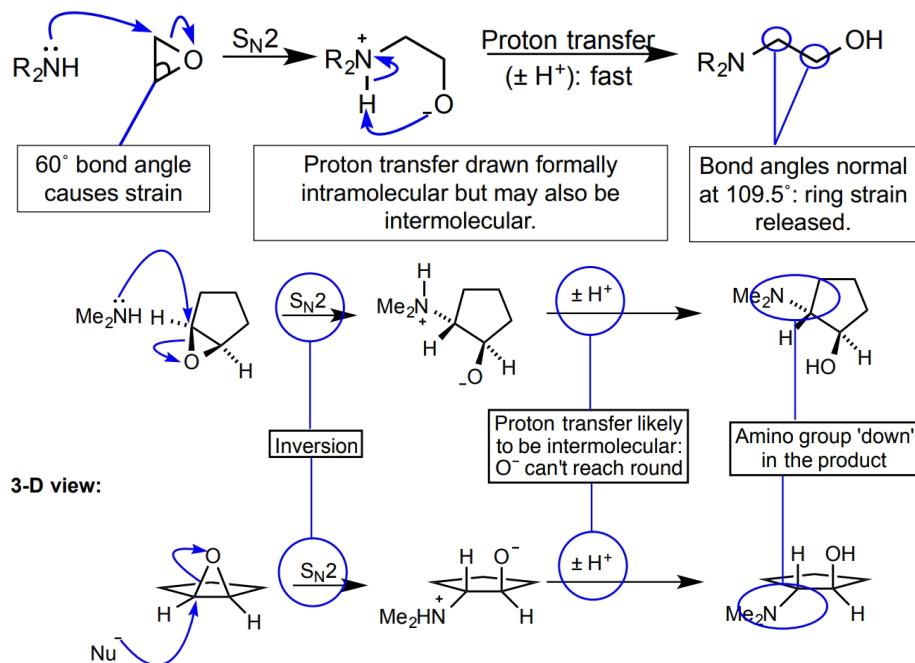


⁶Use pK_a.

⁷Because of the dipole of course.

10.3.3 Epoxides

The mechanism is given below:



10.4 Solvent

SN1 reaction process favours polar protic solvents, while SN2 favours polar aprotic solvents. If one can choose solvent to be the nucleophile, one should always do that to increase the reaction speed and yield.

10.5 From Dr Kim Liu, my supervisor

SN1 vs SN2: some rules, which everybody knows. But the key is thresholds - nobody seems to tell you these. Big general rule - **SN1 only happens if SN2 cannot happen.**

My rules:

1. sp² cannot ever react by SN1 nor SN2 - orbits just don't work.
2. 1° carbocation NEVER forms.
3. 3° never SN2.
4. SN1 likely in RO – CH₂ – X type molecules (acetal-like mechanism).

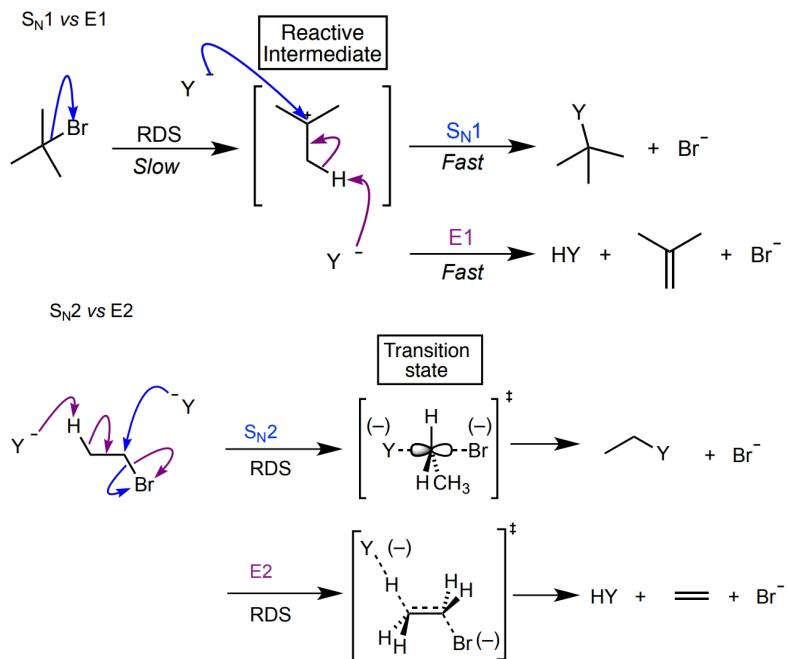
Then:

1. Improving leaving group does not really make SN1 more likely than SN2.
2. Poor nucleophiles do not automatically exclude SN2.
3. Alphahalo ketones are almost always SN2.
4. Grignards almost always SN2.
5. Very strong soft nucleophiles such as Iodide and Thiolates almost always do SN2.
6. 2° nucleophilic are poor.

Chapter 11

C=C Double Bond Formation: Elimination Mechanisms

Why we need to study C=C double bond formation and why we need to put it here? The fact is, **in both SN1 and SN2 reactions, an alternative pathway may occur**. These pathways are known as E1 and E2 elimination pathways.



The difference is, in E1 and E2 our original nucleophile acts as base. It is clear that elimination occurs when Y^- attacks at a hydrogen instead of a carbon but the key to this section is to understand how to predict which is more likely in each case.

In each section we will discuss a factor that can help us determine the reaction mechanism.

11.1 Rate of Reaction

The rate laws of E1 and E2 reactions are exactly the same as SN1 and SN2 processes. For E1,

$$\text{rate} = k_1[\text{RL}]. \quad (11.1)$$

For E2,

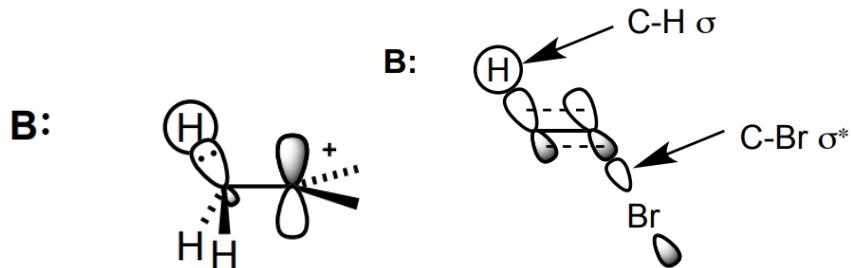
$$\text{rate} = k_1[\text{RL}][\text{Nu}]. \quad (11.2)$$

11.2 Orbitals

In an E1 elimination process, the C-H bond attached to the proton being removed must be parallel to the empty p orbital for best overlap. The two HOMO-LUMO interactions:

- Lone pair of B with C-H σ^* ;
- C-H σ bond with empty p orbital

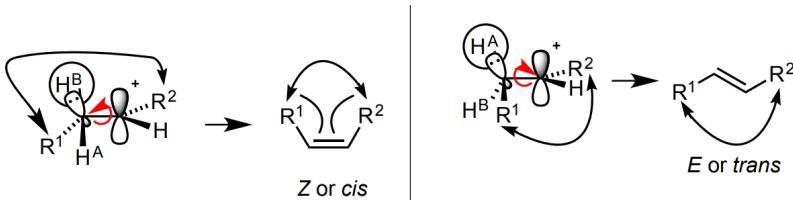
are therefore connected well.



In an E2 elimination, the C-H σ bond and C-Br σ^* must be antiperiplanar to one another. As the top-right picture shows.

11.3 Stereochemical Outcome

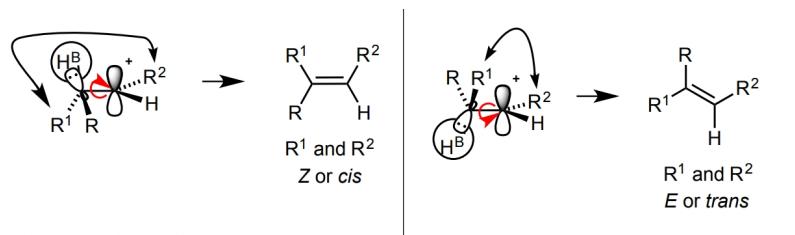
Due to the restricted rotation of the double bond, two kinds of products could be formed from a single elimination process, trans (E) or cis (Z).



- higher energy arrangement of R groups in cation intermediate
- greater steric clash in Z/cis product
- lower energy arrangement of R groups in cation intermediate
- less steric clash in E/trans product

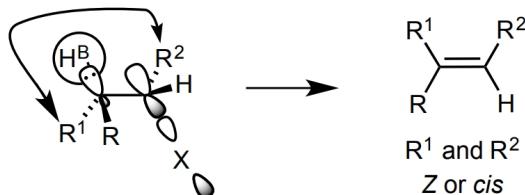
In an E1 process, the trans (E) isomer is always the major product due to thermodynamical reasons. But the overlapping is equally possible.

If there are more R groups, the case is more complicated, but the major product will always be the one in which there is the least steric clash.



- This product will dominate when the group 'R¹' is smaller than 'R', i.e. minimise steric clash between R and R².
- This product will dominate when the group 'R¹' is larger than 'R', i.e. minimised steric clash between R¹ and R².

The E2 process will be limited by the antiperiplanar condition. So there is only one product that can be formed.



11.4 Leaving Groups

Everything in the SN1 & SN2 leaving group discussion applies to the E1 & E2 leaving group dependence. A table here summarises this.

Most of this is straightforward but there is one group that requires a little more detail: the quaternary ammonium salt. Their synthesis is very straightforward and simply involves quaternisation of an amine to the salt by an SN2

Leaving Group:	Halide (Usually Br ⁻ /I ⁻)	OH ⁻	⁺ OH ₂	TsO ⁻	⁺ NR ₃
E1 Mechanism:	Good	Never	Good (OH under acidic conditions)	Good	Good
E2 Mechanism:	Good	Never	Never (E2 always carried out under basic conditions) ⁴⁴	Good (convert OH to OTs for successful E2)	Good

reaction with an alkyl halide. Elimination then occurs by an E1 or E2 mechanism, analogous to other leaving groups.

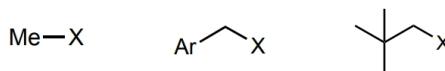
11.5 Factors that Determines Whether Elimination or Substitution Occur

Note that E1 and E2 are NOT directly related to SN1 and SN2, respectively. A reaction, for example, can occur through SN1 can have both E1 and E2 side products.

11.5.1 Substrate structure

Electrophile:						
Substrate Type:	1°	2°	3°	α-alkoxy	Allylic	Benzyllic
E1 Mechanism:	No ⁴⁵	OK	Good	Good	Good	Good
E2 Mechanism:	Good	OK	Also possible ⁴⁶	Also possible ⁴⁶	Also possible ⁴⁶	Also possible ⁴⁶

Substrates which *cannot* eliminate by either E1 or E2 mechanism are shown below:

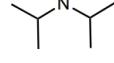
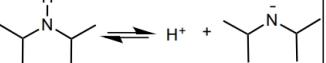


The bottom three cannot react through E1 or E2 because if you try to draw the elimination mechanism (neither E1 nor E2 are possible) with these substrates, you will find that there are no hydrogens in the right place for the usual mechanistic pathway to take place.

11.5.2 Basicity of the Nucleophile

The general guideline is that strong bases give mainly elimination where weak ones give nucleophilic substitution. Therefore, if Y⁻ is a strong base, elimination usually occur; if Y⁻ is a weak base, substitution usually occur. The basicity can

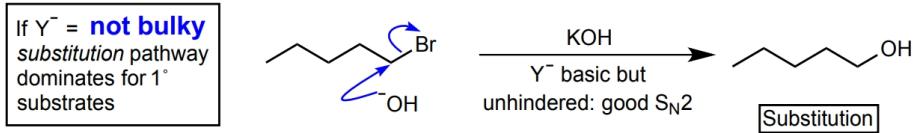
be derived by referring to the pK_a value, larger pK_a means stronger basicity. The summary is given below:

Base	Relevant Equation	pK_a of Conjugate Acid	Base Strength
EtOH	$\text{HX} \rightleftharpoons \text{H}^+ + \text{X}^-$ $\text{EtOH}_2^+ \rightleftharpoons \text{H}^+ + \text{EtOH}$	-2.4	Weak
H_2O	$\text{H}_3\text{O}^+ \rightleftharpoons \text{H}^+ + \text{H}_2\text{O}$	-1.7	Weak
OH^- (e.g. in NaOH)	$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$	15.7	Quite strong
EtO^- (e.g. in NaOEt)	$\text{EtOH} \rightleftharpoons \text{H}^+ + \text{OEt}^-$	15.9	Quite strong
 (e.g. in LiNPr_2 = LDA)		36	Strong
Bu^- (e.g. in BuLi)	$\text{Bu}-\text{H} \rightleftharpoons \text{H}^+ + \text{Bu}^-$ (Butane)	50	Very strong

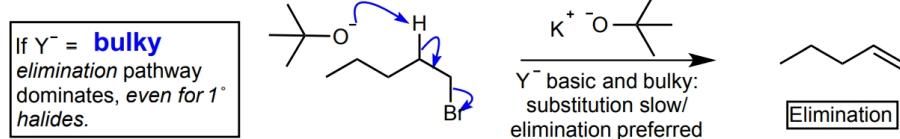
11.5.3 Sizes of the nucleophile

Accessing the more exposed α -hydrogen atom in an elimination reaction is much easier than the $\text{S}_{\text{N}}2$ attack. Therefore, as soon as we start using basic nucleophiles which are also bulky, elimination becomes preferred over substitution, even for primary halides.

Treat with KOH (OH^- = unhindered base/nucleophile):



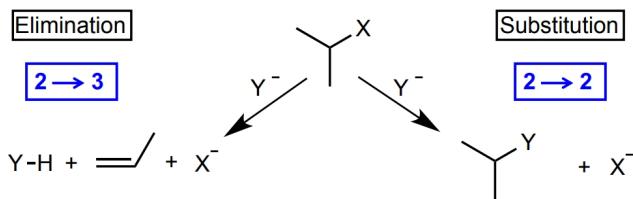
Treat with ${}^t\text{BuOK}$ (${}^t\text{BuO}^-$ = hindered base/nucleophile):⁴⁸



11.5.4 Temperature

Higher temperatures tend to favour elimination over nucleophilic substitution, the fundamental reason for which lies in entropy: because two molecules become three in an elimination and two molecules form two in a substitution, ΔS is greater for elimination than for substitution.

$\Delta G = \Delta H - T\Delta S$. Then a reaction where ΔS is more positive becomes more favourable, i.e. ΔG becomes more negative. Eliminations should be favoured at



high temperature in that case and indeed, they are usually conducted at room temperature or above.

11.5.5 Summary

Here is a summary for elimination vs substitution.

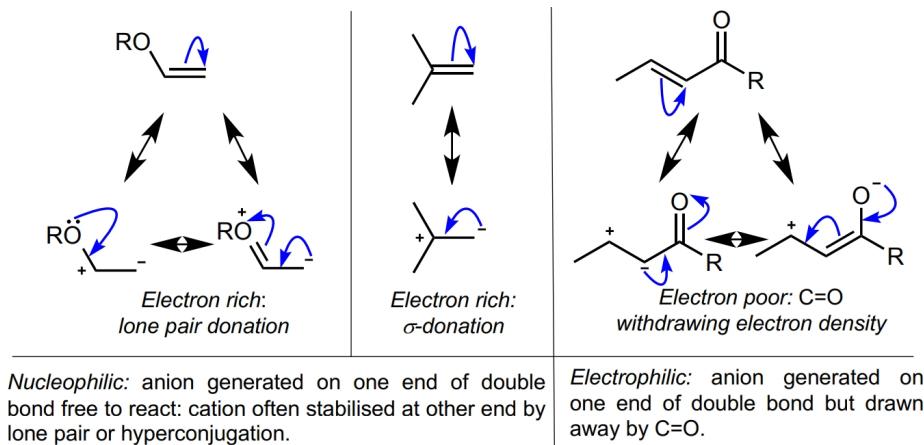
Nucleophile/Base Type →		Poor e.g. H ₂ O, ROH	Weakly basic e.g. I ⁻ , RS ⁻	Strongly basic unhindered e.g. EtO ⁻	Strongly basic hindered e.g. 'BuO ⁻
Substrate Structure ↓					
Methyl	Me—X	No reaction	S _N 2	S _N 2	S _N 2
Primary (unhindered)		No reaction	S _N 2	S _N 2	E2
Primary (hindered)		No reaction	S _N 2	E2	E2
Secondary		S _N 1, E1 (slow)	S _N 2	E2	E2
Tertiary		S _N 1 or E1	S _N 1 or E1	E2	E2

- R-X derivatives where R = Me cannot eliminate, as there are no appropriately placed protons. Therefore reactions always proceed via an SN2 process regardless of nucleophile choice.
 - Increasing branching favours elimination over substitution: increased carbocation stability for E1 and increased numbers of protons available for elimination by either mechanism.
 - Strongly basic hindered nucleophiles always eliminate unless elimination is not possible.
 - Good (weakly basic) nucleophiles give SN2 substitution unless the substrate is tertiary, in which case the intermediate cation can eliminate by E1, as well as substitute by SN1.
 - In cases where there may be a competition between E1 and SN1, choose high temperature to favour E1: this will raise the importance of entropy in the free energy of the reaction.

Chapter 12

Reactions of π Bonds: Electrophilic Attack and Hydrogenation

In terms of their overall reactivity, double bonds can be nucleophilic or electrophilic, depending upon which substituents are attached to them.

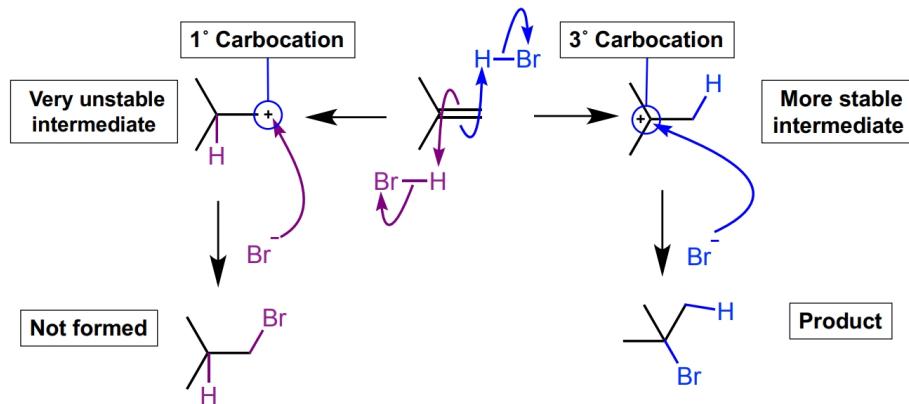


We will study a number of types of electrophilic addition to electron rich double bonds.

12.1 Electrophilic Addition of H–X

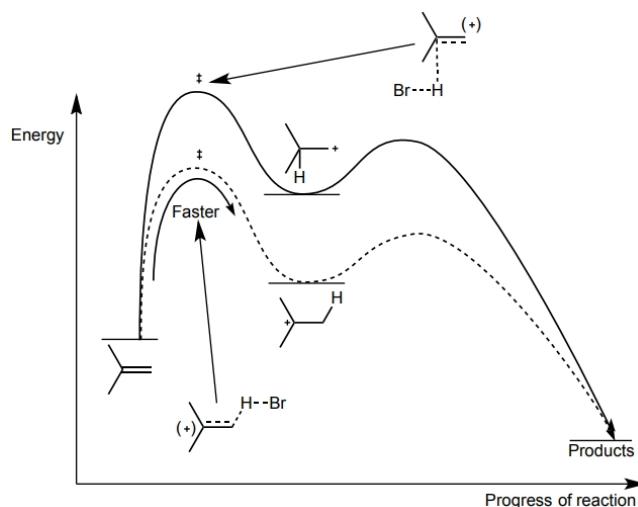
The reaction mechanism is quite straightforward, the double bond donates an electron to the hydrogen, and the H–X bond breaks. However, it is important

to think about which side the hydrogen will be added to, especially when there are two possible outcomes.



It is clear that the addition product will be the one that originates from the most stable carbocation intermediate. The question now is how to define 'stable'. The answer is fairly simple: the factors covered previously regarding carbocation stability all apply here.

As always, we can look at this question in the thermal dynamical rather than kinetic way. The higher energy reactive carbocation intermediate has a higher energy transition state on the path to its formation. On the other side, Formation of more stabilised carbocation intermediate during the RDS is faster due to the lower energy pathway via the lower energy transition state.



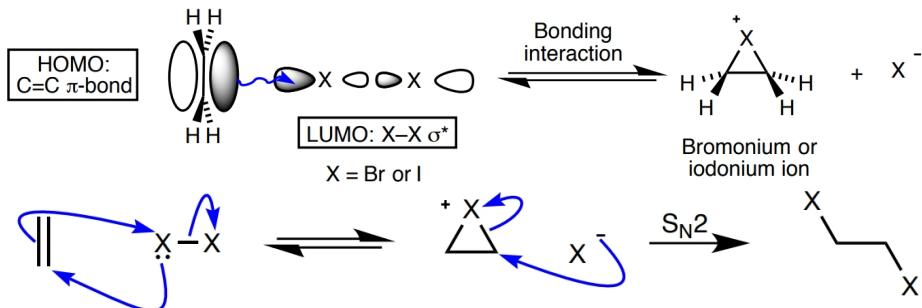
Generally, the presence of more alkyl groups enhances the rate of reaction,

which is due to the possibility to form a more stable carbocation intermediate¹.

Alkene:	=	<i>n</i> Bu				
Relative Rate of Reaction:	1	100	1750	5700	13000	1900000

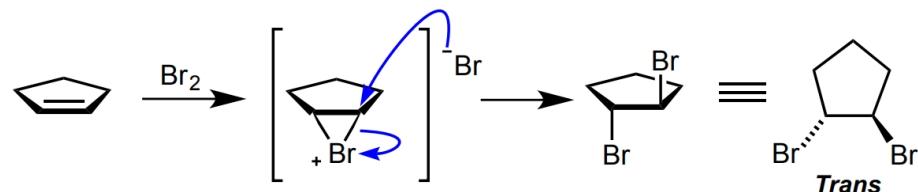
12.2 Bromination and Iodination

The initial HOMO-LUMO interaction for this step is between the p-bond (HOMO) and the empty X–X σ^* . Overall, the reaction follows the mechanism:



The bromonium/iodonium ion is itself an electrophile however, and is usually attacked very quickly by the bromide/iodide ion, forming the 1,2-dihalogenated product via an S_N2 mechanism between a pair of electrons on the nucleophilic halide anion (HOMO) and the C–X σ^* (LUMO).

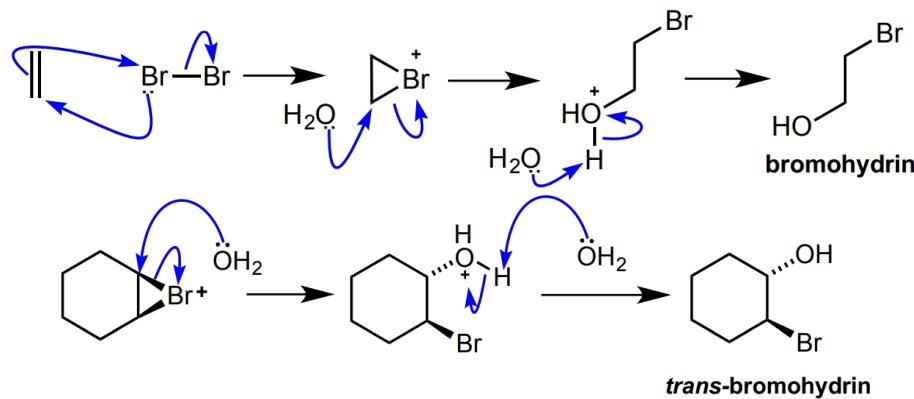
In the case of a ring system, as S_N2 is restricted by steric chemistry, the resultant isomer is only trans.



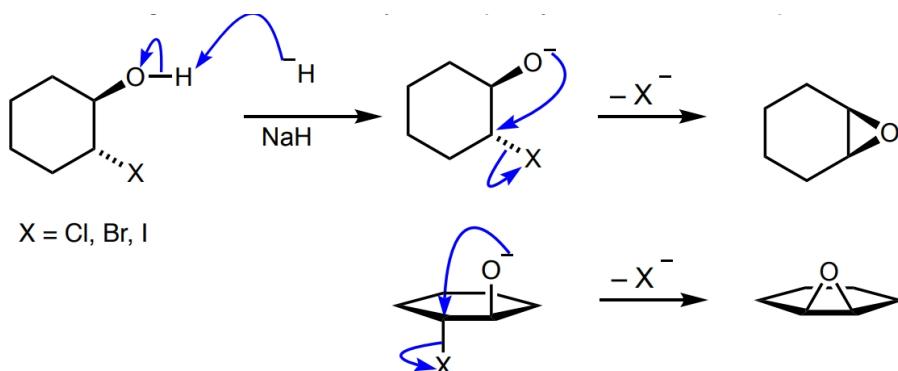
¹The presence of more alkyl groups also makes the double bond more electron rich and therefore more nucleophilic and more reactive.

12.3 Halohydrin Formation and Reaction

Due to the low dipole moment of Br-Br bond, the reaction is initially driven by the lone pair on Br. Also, because of the large amount of water present, rather than the intermediate bromonium ion being attacked by bromide, it is water that attacks and then gives the bromohydrin product. The steric chemistry is the same - always trans.

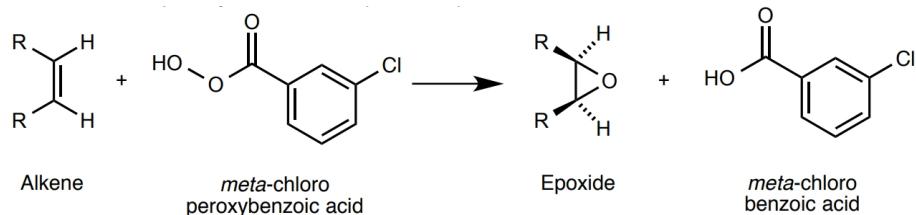


Another useful process may be the formation of epoxides from a transhalohydrin starting material: if a halohydrin ($X = \text{Cl}, \text{Br}, \text{I}$) is treated with base, the alcohol is deprotonated and a rapid $\text{SN}2$ reaction follows: the halide is expelled as the leaving group and an epoxide is formed. This can be done on linear or cyclic substrates but in the case of the trans-halohydrin product formed on the 6-membered ring, the stereochemistry is set up very well to react in this process:



12.4 Epoxidation

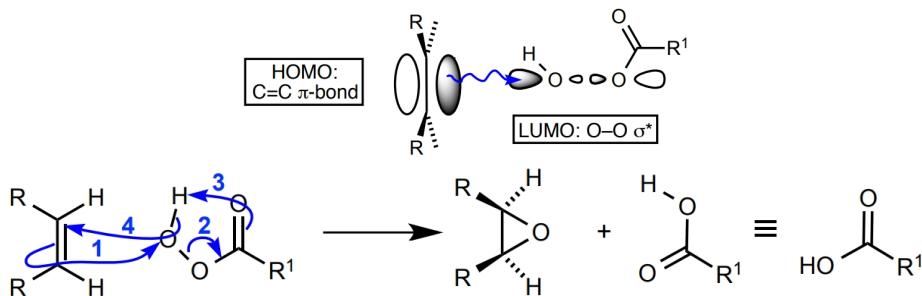
m-CPBA (meta-chloroperoxybenzoic acid) is the most commonly used material for forming epoxides from double bonds.



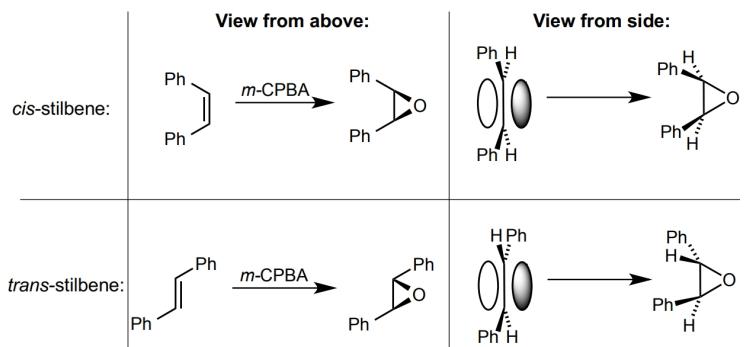
Overall, one oxygen atom is transferred from the peroxy-acid (weak O–O bond) to the alkene with the concurrent formation of two new C–O bonds and a carboxylic acid.

The mechanism consists of several parts:

- The electron rich double bond is the HOMO and the O–O σ^* is the LUMO.
- The special arrangement by m-CPBA.

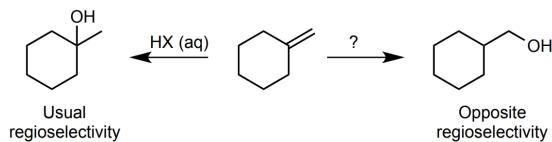


Since the mechanism differs from SN₂, both trans and cis outcomes are possible.

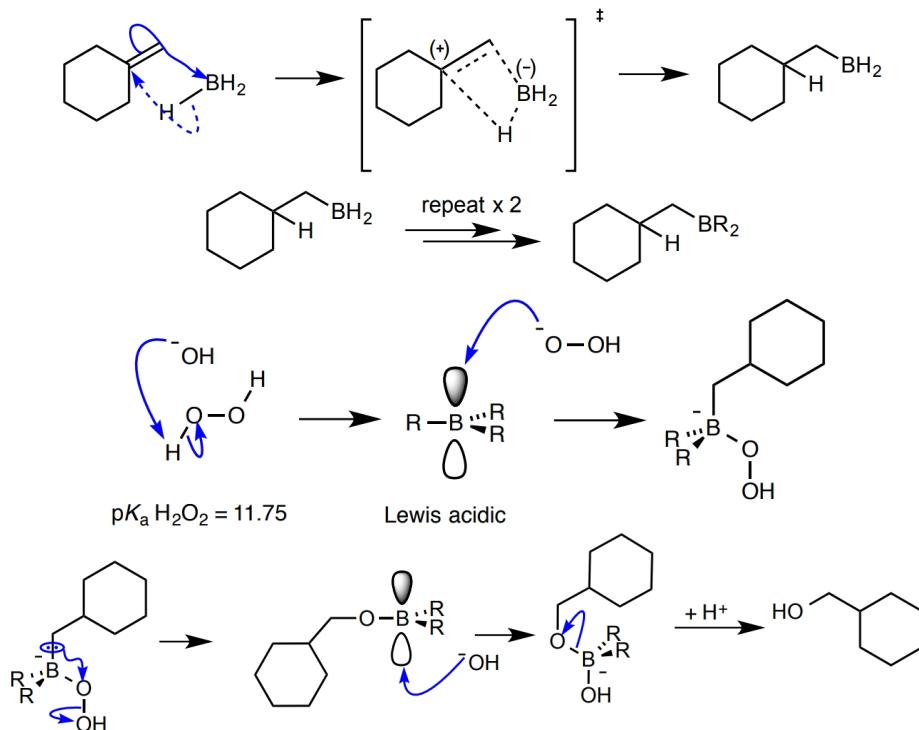


12.5 Hydroboration: Addition of Water with Opposite Regioselectivity

Being able to reverse the natural selectivity of an alkene substrate in the addition of water is arguably of great utility. The chemist can then choose reaction conditions that obtain the desired product. Whilst formation of an alcohol through reaction with aqueous acid will provide a product with typical 'Markovnikov selectivity', the question arises of how to achieve the opposite regioselectivity.



The alcohol products can be made into leaving groups, which could then lead to other products so knowing how to choose the regioselectivity from this one reaction type is in itself very useful.



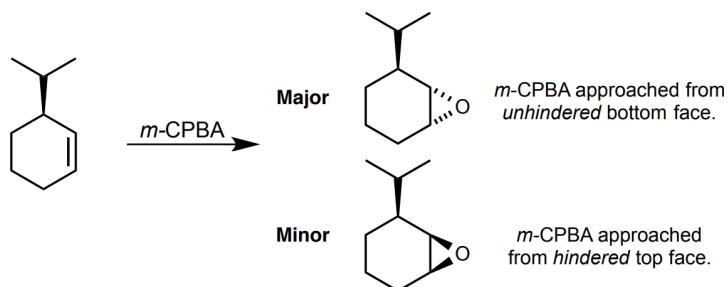
For a typical reaction with the use of borane, the steps are:

- Borane align with double bond and attacks it.
- The procedure repeats twice.

- The aqueous mixture of base and hydrogen peroxide generates hydroperoxide anion, which adds to the empty p-orbital of boron.
- A strange re-arrangement and boron leaves to form the product.

Because the boron and hydrogen add to the double bond in an essentially concerted process, the stereochemical outcome from the reaction process overall is the syn addition of H and OH to the double bond.

Note that, there is the possibility for that group to hinder the approach of the incoming electrophile, whether that is bromine, m-CPBA or borane and it can also effect which face of a double bond which becomes hydrogenated. Essentially, whatever the reaction taking place, the less hindered face becomes favoured over the more hindered face.



And this is the end of the Organic Chemistry part.

The End

1. Organic Chemistry: Background and Relevance ✓
2. Functional Groups in Synthesis ✓
3. Synthesis and Retrosynthetic Analysis (The Disconnection Approach) ✓
4. Mechanism in Organic Chemistry ✓
5. Nucleophilic Addition to the Carbonyl Group ✓
6. Acidity, Basicity and pK_a ; Leaving Group Ability ✓
7. Nucleophilic Substitution at the Carbonyl Group: Principles ✓
8. Nucleophilic Substitution at the Carbonyl Group: Reactions ✓
9. Hard and Soft Nucleophiles and Electrophiles ✓
10. Nucleophilic Substitution at Saturated Carbon: S_N1 and S_N2 Reactions ✓
11. C=C Double Bond Formation: Elimination Mechanisms ✓
12. Reactions of π -bonds: Electrophilic Attack (and Hydrogenation) ✓

Part V

Physical Chemistry:
Kinetics and
Thermodynamics

Chapter 13

Kinetics of Chemical Reactions

13.1 Rate of Reaction

As we all know, the rate of reaction is defined as change in concentration per unit time. Usually, the rate of reaction refers to the instantaneous rate, defined as

$$\text{rate} = \frac{dc}{dt}. \quad (13.1)$$

The unit is of course $\text{mol m}^{-3} \text{ s}^{-1}$, but usually we use $\text{mol dm}^{-3} \text{ s}^{-1}$ instead. Please note that it can be dangerous treating with units so be careful in exams.

The problem now is, for different reactants and products, the rate may differ. This leads to an improved version of definition

$$\text{rate} = \frac{1}{\nu_A} \frac{d[A]}{dt}, \quad (13.2)$$

where ν_A is the stoichiometric coefficient of species A in the balanced chemical equation. Note that, for reactants the rate is always positive and for products always negative.

13.1.1 Rate law and rate constants

The rate of a reaction is often of form

$$r = k[A]^a[B]^b \dots, \quad (13.3)$$

note that this was concluded from experimental results so does not mean anything. It is only useful when combining with the definition of rate. For more complicated reactions, the rate law may vary greatly.

The rate constant, k , depends on a lot of things and will be discussed based on classical theories in further sections¹. What we know from experiments now is

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (13.4)$$

where E_a is the activation energy per unit mole and A is the pre-exponential factor.

For a positive activation energy, the rate constant increases with temperature,

$$\ln k = \ln A - \frac{E_a}{RT}. \quad (13.5)$$

And a plot of $\ln k$ against $1/T$ is appropriate for discussion because both A and E_a could be calculated from it.

From the plot it is clear that A is the rate constant at infinite temperature (or when $RT \gg E_a$), it sets a limit (usually maximum) for rate constants.

13.1.2 Equilibrium constants

When a reversible reaction reaches equilibrium, the rates for back and forward reactions should be the same,

$$k_f[A][B] \cdots |_{\text{eq}} = k_r[C][D] \cdots |_{\text{eq}}. \quad (13.6)$$

The equilibrium constant is defined by

$$K_{\text{eq}} = \frac{k_f}{k_r} = \left(\frac{[C][D]}{[A][B]} \right)_{\text{eq}} \quad (13.7)$$

13.2 Collision Theory

In classical thermodynamics, ideal gas obeys Maxwell and Boltzmann distributions, the mean speed is given by

$$\bar{c} = \sqrt{\frac{8k_B T}{\pi m}}. \quad (13.8)$$

Considering the relative motion of two molecules, the mean relative speed is therefore

$$\bar{c}_{\text{rel}} = \sqrt{\frac{8k_B T}{\pi \mu}}, \quad \mu = \frac{m_A m_B}{m_A + m_B}. \quad (13.9)$$

The collision rate, measuring the number of total collisions per unit volume and unit time, is

$$Z_{AB} = c_A c_B N_A^2 \sigma \bar{c}_{\text{rel}}, \quad (13.10)$$

¹The problem is definitely quantum-mechanical, but classical value should be a good approximation for gases.

where σ is the collision cross-section, often taking the value $\pi(r_A + r_B)^2$.

Let's assume that each collision leads to a product², the number of moles of product formed per unit time per unit volume, is $Z_{AB} \exp(-E_a/RT)/N_A$. Further assume that the rate law is second ordered, $r = k_2 c_A c_B$,

$$k_2 = N_A \sigma \bar{c}_{\text{rel}} \exp\left(-\frac{E_a}{RT}\right). \quad (13.11)$$

From the equation, it is clear that $A = N_A \sigma \bar{c}_{\text{rel}}$. This result can be counter-intuitive because it depends on temperature, but setting a limit to a temperature-dependent value k . Luckily, the exponential factor has a much stronger temperature dependence and this tends to swamp the weak temperature dependence of A .

The fraction of sufficiently energetic collisions which lead to reaction is called the steric factor p .

$$p = \frac{A_{\text{experiment}}}{A_{\text{collision theory}}} \quad (13.12)$$

By intuition it is much less than 1. However, if the molecules interact over greater distances than the radii found from gas kinetic theory would indicate, the steric factor can exceed 1.

13.3 On Simple Rate Laws

13.3.1 First-order rate laws

Reactions with rate law $r = k_1[A]$ are called first-order reactions. From the definition of rate we have the differential equation

$$\frac{d[A]}{dt} = -k_1[A]. \quad (13.13)$$

This of course leads to

$$\ln[A] = -k_1 t + \ln[A]_0. \quad (13.14)$$

The half-life is therefore $t_{1/2} = \ln 2/k_1$.

For the product B , $[B]_t = [A]_0 - [A]_t$ naturally holds.

13.3.2 Second-order rate laws

For an arbitrary second-order reaction, $r = k_2[A][B]$, the differential equation can be complicated to solve, especially when $[A]_0 \neq [B]_0$. However, when the rate law is of form $r = k_2[A]^2$, the steps are easy.

$$\begin{aligned} \frac{d[A]}{dt} &= -k_2[A]^2 \\ \frac{1}{[A]} &= \frac{1}{[A]_0} + k_2 t \end{aligned} \quad (13.15)$$

²which is clearly not precise, as chemistry always does.

Naturally a plot of $1/[A]$ against t should be drawn to find a straight line. The half-life is therefore $t_{1/2} = 1/k_2[A]_0$ ³.

For reactions with rate law $r = k_2[A][B]$ and initial condition $[A]_0 = [B]_0$, the equation is the same because

$$\frac{d[A]}{dt} = \frac{d[B]}{dt}. \quad (13.16)$$

13.3.3 Isolation method

Isolation method is a way to simplify complicated rate laws. The central idea is to make measurements with one reagent in great excess⁴, and regard the concentration as constant. Usually this can simplify rate laws to pseudo first or second order.

The only thing to mind is that the original rate constant has to be determined with the help of the 'constant' concentration.

13.3.4 Differential method

If the rate law is of the form

$$r = k[A]^n, \quad (13.17)$$

then an appealing method of finding the value of the order, n , is to plot the log of the rate against the log of $[A]$,

$$\ln r = \ln k + n \ln[A]. \quad (13.18)$$

Such a graph will have slope n .

The drawback is that rather than plotting a function of concentration we have to plot rates, and rates are much harder to measure than concentrations. Therefore obtaining an accurate slope is not at all easy.

In one of our practical sessions, we used differential method in a well-designed electrical chemistry reaction. The result was $n = 0.94$ for a first order reaction (quite accurate). This is because the reaction went on extremely slowly under mild conditions, which is not possible to achieve for many reactions.

13.4 Ways of Obtaining Kinetic Data

As we want to get concentration as a function of time, the measurement of concentrations must be instantaneous, and we have to do this in a mixture without interfering with it. There are several ways to deal with ordinary reactions, and extra care must be taken when dealing with fast reactions.

³We often use the dependence of half life on initial conditions to distinguish first and second order reactions.

⁴Typically more than 50 times the concentration of the other.

13.4.1 Light absorbance

When shined with UV light, the extent to which light is absorbed is related directly to the concentration of the absorbing species by the Beer-Lambert Law:

$$I = I_0 e^{-\varepsilon cl}, \quad (13.19)$$

where I_0 is the intensity of the light entering the medium, I is the intensity of light exiting the medium, and l is the path length through which the light passes, c is the concentration and ε is the extinction coefficient.

Typically, a glass or quartz 'cuvette' of known dimensions (commonly 1 cm thick) is used for solutions. The absorbance, A , is defined by

$$A = \log \frac{I_0}{I} = \varepsilon cl. \quad (13.20)$$

It can be read out directly from spectrophotometers, and turned into absolute concentrations by this equation. Usually this is done by measuring the absorbance of a series of solutions of known concentrations and then simply plotting A against c , the slope is εl . If we are studying first order processes then only a relative measure of concentration is needed, so it is sufficient just to know the absorbance.

Absorbance measurements are very convenient, they are non-invasive, rapid and can easily be automated. As different species absorb at different wavelengths it is possible to study different molecules in a reaction mixture. However, UV/vis absorptions tend to be rather broad, especially in solution. So it is possible that more than one species will absorb at a given wavelength. The same principle applies to IR measurements.

Proton NMR can also be used to monitor concentrations, as under the right conditions the peak height is proportional to concentration. It has the advantage that individual chemical species can easily be followed, but NMR is not very sensitive so as an analysis method it is not very fast.

13.4.2 Conductivity measurements

Ions in solution conduct electricity and the resistance of such a solution depends on the concentration of the ions and their identity. In fact, the conductance is directly proportional to the concentration of the ions.

13.4.3 Gas pressure

In reaction we will generally have a mixture of gases, and so we can talk about the partial pressure of gases, p_i . By Dalton's law, the total pressure is the sum of the partial pressures,

$$p = \sum_i p_i. \quad (13.21)$$

In a reaction involving gases, the only measurable pressure is the total pressure exerted by the system. We need to find other relations to relate partial

pressures to total pressure. That includes initial condition and rate relations. You will find the "formation of three lines"⁵ in Gaokao useful for discussion.

13.4.4 Electrochemistry

As we have seen, the EMF generated by an electrochemical cell depends on the concentration of the species in the cell. By constructing a cell with an appropriate electrode it is possible to measure the concentration of a wide variety of ions in the solution. Such electrodes can give both absolute and relative measurements of concentration. They are non-invasive, sensitive to particular ions (selective) and have a rapid response.

An example is that, the voltage produced by a bromine cell is

$$E = E^0 - \frac{RT}{2F} \ln \frac{[\text{Br}^-]^2}{[\text{Br}_2]}. \quad (13.22)$$

13.4.5 Chemical methods

Concentration, of course, can be measured by classical methods such as titration. Such methods are rather slow, and so it is usually necessary to extract some of the reactions mixture and then stop (quench) the reaction so that no further reaction takes place during the analysis. Example of such quenching procedures might be sudden cooling or chemical removal of one of the reagents.

A more sophisticated chemical analysis uses a gas chromatogram (GC), possibly in conjugation with a mass spectrometer. A gas chromatogram separates the components of a mixture by using an inert carrier gas to sweep them down a column which is packed with some sort of porous solid material. Different components travel at different speeds down the tube and so are detected at different times after injecting the sample, their concentrations can thus be measured separately.

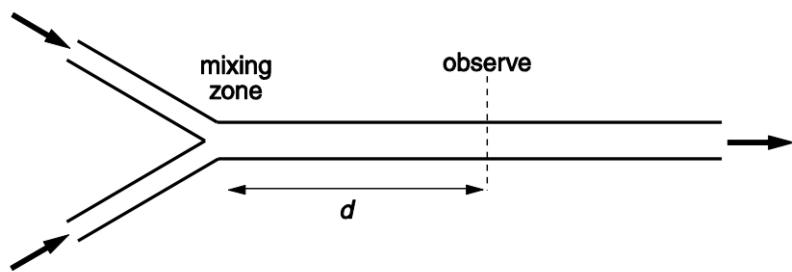
13.4.6 Studying fast reactions

Whatever method we choose for monitoring the concentration of the reacting species we also have to consider how the reagents are going to be mixed and the reaction initiated. This is a serious problem for fast reactions. It is no good if it takes 1 second to mix the reagents if the reaction is over in 100 ms! Further, our method of measuring concentration has to be fast enough to make measurements over the time scale of the reaction. A great deal of effort has been put into developing methods for measuring such fast reactions; we will consider some of these here.

Continuous flow The idea here is to flow the reagents together (they can be gases or solutions), and after mixing let them continue to flow down the reaction tube. Different distances down the tube correspond to different times after

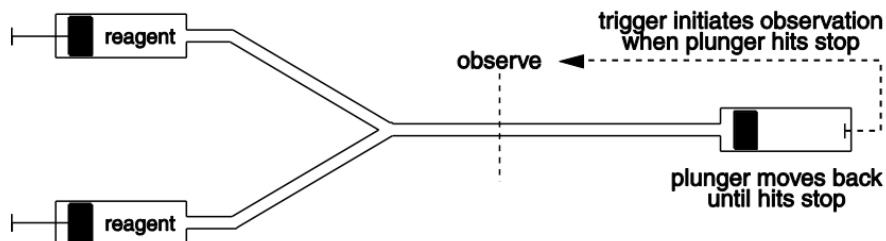
⁵San Duan Shi

mixing and initiating the reaction. As the reagents are constantly replenished, we can take our time in making observations at any distance (and hence time). Essentially the method is a way of achieving rapid mixing and then being able to monitor the reaction at leisure, rather than in “real time”. Mixing can be complete in under 1 ms, so reactions with half-lives on the ms timescale can be studied. A typical flow velocity is 10ms^{-1} , so a distance of 1 cm corresponds to 1 ms of reaction. Usually the reaction is monitored by spectrophotometry, which is a very rapid technique. The main disadvantage of this method is that you need lots of reagents, particularly if you are trying to observe a fast reaction where the flow rate needs to be high.



The method is perhaps used more in the gas phase; in this case the flow is created by pumping on the “waste” end of the tube and supplying gases at the other.

Stopped flow This apparatus is similar in conception to the continuous flow method, in that the reagents are flowed together to ensure rapid mixing. However, the difference is that the reacting mixture pushes a plunger back until it hits a stop; then the flow is halted and measurement, at a fixed point, is initiated (again, usually using spectrophotometry). Observations are made at a point at which mixing is complete. The stopped flow method is only used for solutions.



In contrast to continuous flow, stopped-flow requires measurements in real time. However, it has the advantage of not requiring large amounts of reagents (as little as 1 cm^3 may be sufficient). Generally the time resolution is a little faster than for continuous flow.

13.4.7 Flash photolysis

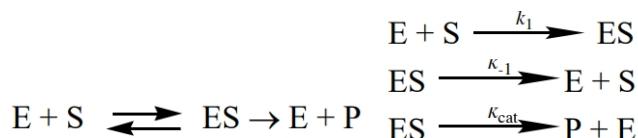
The idea of this method is to use a short, intense flash of light (now often from a laser) to generate some reactive species, typically free radicals. Then, the reaction of these species with other reagents present in the system is monitored, usually spectrophotometrically. This is a useful method for studying the fast reactions of radicals; there is no mixing problem as the reagents are generated *in situ*. However, measurements do have to be made in “real time”, so rapid detection is needed.

13.5 Analysing the Kinetics of Complex Reactions

A set of reaction steps is called the mechanism. Each of the reactions which comprise the mechanism is called an elementary step, it is elementary in the sense that we believe that it takes place in a single reactive encounter between the species involved. The elementary steps are thus the basic building blocks of a complex reaction and cannot be broken down further. A mechanism can be defined as a proposed set of elementary steps which account for the overall features of the reaction.

Rate Law for complex reactions can be divided into elementary rate laws. For sequential reactions, we have to determine the rate determining step (RDS) and then use isolation method to work out the final rate law.

Enzyme kinetics and the Michaelis-Menten equation The molecules which bind to the enzyme, that is the reagents are called substrates. The reactions are



We assume that ES is in the steady state and use

$$\frac{d[ES]}{dt} = 0 \quad (13.23)$$

to generate the final differential equations.

We know the initial concentration of enzyme, but once the reaction is under way the free enzyme concentration will be less than this as some has become ES. At any time the total amount of free and bound enzyme is equal to the initial concentration of enzyme. Then we get the Michaelis-Menton equation,

$$r = \frac{k_{\text{cat}}[E]_0[S]}{[S] + K_M}, \quad K_M = \frac{k_{-1} + k_{\text{cat}}}{k_1}. \quad (13.24)$$

The Michaelis constant, K_M , is equal to the substrate concentration which gives a velocity of half its maximum value. And a plot of $1/V$ against $1/[S]$ is appropriate since

$$\frac{1}{V} = \frac{1}{V_{\max}} + \frac{K_M}{V_{\max}} \frac{1}{[S]}. \quad (13.25)$$

The Michaelis-Merton scheme is just the simplest one which explains saturation kinetics. Many enzymes show a more complex behaviour, for example if the catalysis involves several steps. In addition, as the reaction is assumed to proceed in the steady state, the experiment does not give individual values for k_1 and k_{-1} , to find these we would need to perform experiments outside the steady state region.

13.6 Arrhenius parameters for complex reactions

Since the rate constant can be written in exponential forms, as given by Arrhenius equation. Therefore, the combination of rate constants can also be written in exponential forms. In this form, we could determine the activation energy for the whole reaction, the pre-exponential parameter, and the temperature dependence.

13.7 Chain Reactions

In a chain reaction, chain carriers are molecules that carry forward the reaction. And reactions are called chain propagation steps as they are the steps which carry on the chain and lead to the formation of product. The reaction which generates the chain carrier is called the initiation step. Processes which destroy chain carriers are called termination steps.

Some reactions have chain branching steps, these are steps in which one chain carrier reacts in such a way as to give rise to two or more carriers.

The chain length is defined by the average number of times that the closed cycle of steps which produce products is repeated per chain carrier. It can be written in terms of rates:

$$l = \frac{\text{rate of overall reaction}}{\text{rate of initiation}}, \quad (13.26)$$

which is equivalent to the definition above.

Chapter 14

Energetics and Equilibria

Special and sincere thanks to Professor James Keeler. His handout was clear enough to be used as notes, with just a little re-arrangement.

14.1 Entropy and the Second Law

The second law of thermodynamics governs whether or not a process is spontaneous. There are several possible statements of this law, but the one we will use is

In a spontaneous process the entropy of the Universe increases.

It is not possible to prove this law, all we can say is that the experience is that it is true.

The problem now is to define entropy.

From a molecular interpretation, the particles satisfy Boltzmann distribution,

$$n_i = n_0 e^{-\varepsilon_i/kT}, \quad (14.1)$$

where it is assumed that the lowest energy level, with $i = 0$, has energy 0. n_0 is the population of this level.

Boltzmann distribution says that as the energy of a level increases its population decreases. Levels whose energies are much greater than kT have vanishingly significant populations. The ground level is always the most highly populated. As the temperature is raised, molecules move to higher energy levels.

Entropy was defined by Boltzmann as

$$S = k_B \ln \Omega, \quad (14.2)$$

where Ω is the total possible number of microscopic combination states, and k_B is the Boltzmann constant. It is now clear that

- supplying energy as heat to the molecules increases W and hence increases the entropy;

- increasing the number of energy levels available, for example by increasing the volume of a gas, increases W and hence increases the entropy;
- the entropy increase resulting from supplying a certain amount of energy is greater the lower the temperature of the system.

These relations are clearer considering the classical definition of the change of entropy,

$$dS = \frac{\delta q_{\text{rev}}}{T}. \quad (14.3)$$

Note that, the small amount of energy absorbance must be under reversible conditions.

We divide the Universe into two parts:

- the system, which is the thing we are interested in;
- the surroundings, which are the rest of the Universe.

The entropy change of the Universe ΔS_{univ} is written as the sum of the entropy change of the system and that of the surroundings,

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}. \quad (14.4)$$

Once ΔS_{univ} has been calculated in this way we can use the second law to decide whether or not the process is spontaneous.

ΔS_{sys} can be calculated from ΔH and ΔG , we will discuss it afterwards.

If the system is closed (matter cannot be exchanged between the system and the surroundings), any heat transfers are reversible from the point of view of the surroundings, therefore $dS_{\text{surr}} = \delta q_{\text{surr}}/T_{\text{surr}}$, and $q_{\text{surr}} = -q_{\text{sys}}$. Also, we will assume that the system and the surroundings are in thermal equilibrium, meaning that they have the same temperature, therefore

$$\Delta S_{\text{univ}} = \Delta S_{\text{sys}} - \frac{\delta q_{\text{sys}}}{T_{\text{sys}}}. \quad (14.5)$$

A process for which $\Delta S_{\text{univ}} = 0$ is at equilibrium, meaning that there is no tendency for further change. In the case of liquid water freezing to ice we can compute the temperature at which $\Delta S_{\text{univ}} = 0$.

14.2 The First Law of Thermodynamics

We all know that $U = Q + W$, where W is the work done by the surroundings, and Q is the heat absorbed by the system. In other words, **energy cannot be created or destroyed but is just transformed from one form into another**. Note that, heat and work are path function, but internal energy is a state function.

Because the value of a state function depends only on the state of the system, and not on how that state was arrived at, it is meaningful to measure

and tabulate the numerical values of such functions. In this course we will come across several state functions and will see how they can be measured for chemical substances. We will also go on to see how such tabulated data can be manipulated to give information about reactions. One way of viewing thermodynamics is that its aims to identify state functions which have particularly useful properties.

14.3 Ideal Gas

The ideal gas law is $pV = nRT$, where R is the gas constant, $R = 8.3145 \text{ JK}^{-1}\text{mol}^{-1}$. If the gas is expanding, the work done on the gas is simply

$$\delta w = -p_{\text{ext}} dV. \quad (14.6)$$

However, different path of expansion can lead to different results.

Expansion against constant external pressure Since $p = \text{const}$, the work done is $w = -p_{\text{ext}}(V_2 - V_1)$.

Reversible isothermal expansion of an ideal gas Isothermal means temperature is constant, which leads to $pV = \text{const}$, and

$$w = -nRT \ln \frac{V_2}{V_1}. \quad (14.7)$$

What is happening in this isothermal expansion is that the work done in the expansion is exactly compensated for by the heat flowing in. If no heat flowed in, some of the internal energy would have to be converted to work, and as a result the temperature of the gas would drop. However, we specified that the process had to be isothermal, so heat must be supplied in order to maintain the temperature (internal energy) of the gas.

Indicator diagram is just a p - V plot.

The heat involved can be calculated from the first law of thermodynamics. In a reversible process the magnitude of the heat is a maximum. And the q_{rev} in the definition of entropy is the maximized heat in the corresponding reversible process.

14.4 Internal Energy, Enthalpy, Heat Capacity and Absolute Entropy

The internal energy change, ΔU , is equal to the energy as heat under constant volume conditions; while the enthalpy change, ΔH , is equal to the energy as heat under constant pressure conditions. Clearly,

$$\Delta U = \delta q - pdV, \quad \Delta H = \delta q + Vdp, \quad \delta q = TdS \quad (14.8)$$

The molar heat capacity is defined using the relation

$$\delta q = nC_m \Delta T, \quad (14.9)$$

while in different conditions it can also be written as

$$\Delta U = nC_{V,m} \Delta T, \quad \Delta H = nC_{p,m} \Delta T. \quad (14.10)$$

Equivalently,

$$C_{V,m} = \left(\frac{dU}{dT} \right)_V, \quad C_{p,m} = \left(\frac{dH}{dT} \right)_p. \quad (14.11)$$

Although we often treat heat capacities as constants, it is found that the heat capacity does vary with temperature, although generally not too strongly. To get around this, heat capacities are often expressed in the parametrized form

$$C(T) = a + bT + \frac{c}{T^2}. \quad (14.12)$$

Note that, to find the entropy under constant pressure condition, just replace δq with dH since H is a state function. Often entropy is the subtraction of absolute entropy

$$S(T) = n \int_0^T \frac{C_{p,m}(T')}{T'} dT'. \quad (14.13)$$

Clearly,

$$S(T_2) - S(T_1) = nC_{p,m} \ln \frac{T_2}{T_1}. \quad (14.14)$$

14.5 Gibbs Free Energy

The Gibbs free energy is defined by $G = H - TS$, which leads to the Master Equation

$$dG = -SdT + Vdp. \quad (14.15)$$

But this equation is of little use in chemistry, especially when dealing with chemical reactions. That is because ΔH and ΔG are often directly measurable and the aim is usually to calculate ΔS .

At a constant temperature, $V = \frac{dG}{dp}$,

$$(\Delta G)_T = nRT \ln \frac{p_2}{p_1}. \quad (14.16)$$

At a constant pressure, $-S = \frac{dG}{dT}$,

$$\frac{d}{dT} \left(\frac{G}{T} \right) = -\frac{H}{T^2}. \quad (14.17)$$

For a mixture of gas, the total Gibbs energy is the direct sum of parts

$$G_{m,i} = G_{m,i}^\circ + RT \ln \frac{p_i}{p^\circ}, \quad G = \sum_i n_i G_{m,i}(p_i), \quad (14.18)$$

where p_i is the partial pressure for the i -th part.

Chemical potential is just the molar Gibbs free energy, therefore

$$\mu_i(c_i) = \mu_i^\circ + RT \ln \frac{c_i}{c^\circ}, \quad (14.19)$$

where c° is the standard concentration 1 mol L⁻¹.

14.6 Chemical Reactions

14.6.1 The Δ_r symbol

The reason that we have to think about having a large amount of the reaction mixture is so that when the reaction takes place in the way specified above the amounts of each species do not change significantly. In thermodynamics the term composition is used to describe a particular ratio of the species involved in a reaction. Therefore $\Delta_r H$ can be described as the enthalpy change when the reaction proceeds according to the stoichiometric equation under conditions of constant composition. The specification of constant composition is important because some thermodynamic quantities depend on the composition. The quantities $\Delta_r G$ and $\Delta_r S$ are defined in a similar way.

The quantity known as the standard enthalpy change ($\Delta_r H^\circ$) is more commonly encountered (and similarly for the entropy and Gibbs energy). It is defined by the enthalpy change when all species being in their standard states. It is important to realise that as the standard state implies the pure substance, this standard enthalpy change is for pure (unmixed) reactants going to pure (unmixed) products.

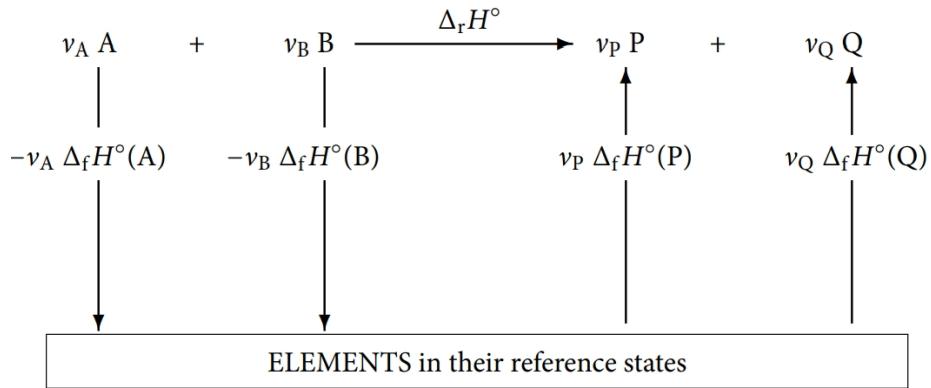
14.6.2 Standard states and standard enthalpy change

The standard state of a substance is the pure form at a pressure of one bar and at the specified temperature. The standard enthalpy of formation of a compound, $\Delta_f H^\circ$, is the standard enthalpy change for a reaction in which one mole of the compound is formed from its constituent elements, each in their reference states. The reference state is the most stable state of that element at a pressure of 1 bar. As noted above, the temperature must be stated.

For example, at 298 K the reference state of nitrogen is N₂ gas (as opposed to nitrogen atoms) and the reference state of carbon is graphite. With this definition the standard enthalpy of formation of elements in their reference states is zero.

The standard enthalpy change for any reaction can be computed from standard enthalpies of formation in a way which is best visualized as a cycle:

The arrows on the left show the conversion of the reactants to their elements in their reference states. The enthalpies are therefore minus the standard enthalpies of formation; note that these have to be multiplied by the stoichiometric



coefficients ν_i . The arrows on the right show the formation of the products from the elements in their reference states. It follows from the cycle that

$$\Delta_rH^\circ = \sum_i \nu_i \Delta_fH^\circ(i) - \sum_j \nu_j \Delta_fH^\circ(j). \quad (14.20)$$

14.6.3 Standard entropy and Gibbs energy change

Similar to standard enthalpy change,

$$\Delta_rS^\circ = \sum_i \nu_i \Delta_fS^\circ(i). \quad (14.21)$$

Once we have Δ_rH° and Δ_rS° for a reaction, it is simple to calculate standard Gibbs energy of formation, Δ_fG° , using the equation

$$\Delta_rG^\circ = \Delta_rH^\circ - T\Delta_rS^\circ. \quad (14.22)$$

14.6.4 Variation of Δ_rH° with temperature

Typically, tabulated values of Δ_rH° are at 298 K, but with the aid of heat capacity data it is possible to convert these values to another temperature.

Using the equations for heat capacity at constant pressure,

$$\frac{d\Delta_rH^\circ}{dT} = \Delta_rC_p^\circ, \quad (14.23)$$

where, for the general reaction,

$$\Delta_rC_p^\circ = \sum_i \nu_i C_{p,m}^\circ(i) - \sum_j \nu_j C_{p,m}^\circ(j). \quad (14.24)$$

We saw before that if we assume that the heat capacity does not vary with temperature in the range T_1 to T_2 . Overall, the Δ_rH° at a different temperature is

$$\Delta_rH^\circ(T_2) = \Delta_rH^\circ(T_1) + \Delta_rC_p^\circ[T_2 - T_1]. \quad (14.25)$$

14.6.5 Variation of $\Delta_r S^\circ$ with temperature

The argument is just the same and we again assume that the heat capacity does not vary with temperature in the temperature range.

$$\Delta_r S^\circ(T_2) = \Delta_r S^\circ(T_1) + \Delta_r C_p^\circ \ln \frac{T_2}{T_1}. \quad (14.26)$$

14.7 Chemical Equilibrium

14.7.1 Equilibrium constants

As usual, equilibrium constant is written as

$$K = \frac{\prod_p [P]^{\nu_p}}{\prod_q [Q]^{\nu_q}}. \quad (14.27)$$

For particular reaction and at a given temperature the equilibrium constant has a certain value. A reaction mixture at equilibrium will always have concentrations such that the right hand side of the equation above is equal to this value of K_c , regardless of the initial concentration of the reagents.

In formal thermodynamics the equilibrium constant is defined in such a way that it is dimensionless. This is achieved by dividing each concentration term by an (agreed) standard concentration.

For a reaction involving gases the concentrations of the species are expressed as their partial pressures, and each partial pressure is divided by the standard pressure p° so that the expression for K is

$$K = \frac{\prod_p \left(\frac{p_p}{p^\circ}\right)^{\nu_p}}{\prod_q \left(\frac{p_q}{p^\circ}\right)^{\nu_q}}. \quad (14.28)$$

For reactions in solution the equilibrium constant is expressed in terms of concentrations, with each being divided by c° .

The standard pressure and concentration are used to make equilibrium constants dimensionless and therefore can be used for comparing the limit productivity of reactions.

14.7.2 Conditions for chemical equilibrium

To be simple, at chemical equilibrium,

$$\Delta_r G = \sum_p \nu_p \mu_p - \sum_q \nu_q \mu_q = 0. \quad (14.29)$$

We will not talk further into this because it should already be covered in the physics courses.

14.7.3 $\Delta_r G^\circ$ and equilibrium constants

By writing μ as $\mu^\circ + RT \ln(p_i/p^\circ)$ and plug into the equation above. We get

$$\Delta_r G = \Delta_r G^\circ + RT \ln \frac{\prod_p \left(\frac{p_p}{p^\circ} \right)^{\nu_p}}{\prod_q \left(\frac{p_q}{p^\circ} \right)^{\nu_q}}, \quad (14.30)$$

and the equilibrium condition is

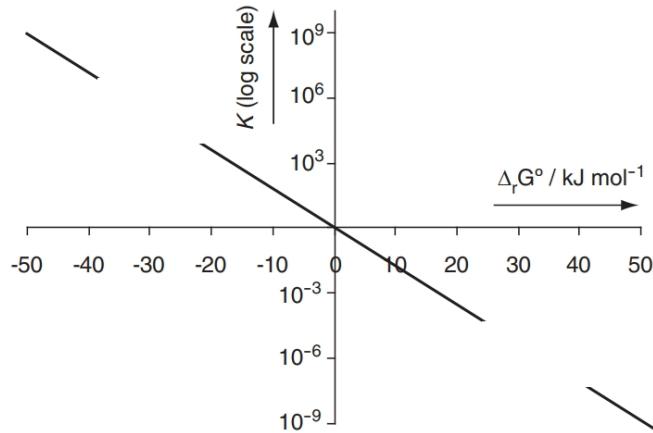
$$\Delta_r G^\circ + RT \frac{\prod_p \left(\frac{p_p}{p^\circ} \right)^{\nu_p}}{\prod_q \left(\frac{p_q}{p^\circ} \right)^{\nu_q}} = 0, \quad \Delta_r G^\circ = -RT \ln K. \quad (14.31)$$

Combining the condition with $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$,

$$K = \exp \left(\frac{-\Delta_r G^\circ}{RT} \right) = \exp \left(\frac{-\Delta_r H^\circ + T\Delta_r S^\circ}{RT} \right). \quad (14.32)$$

It is very important to realize that a reaction with positive $\Delta_r G^\circ$ will still go to products to some extent; it is just that at equilibrium the reactants will be favoured. Sometimes this can cause confusion as $\Delta_r G$ must be negative for a spontaneous process.

Due to the exponential relationship between $\Delta_r G^\circ$ and the equilibrium constant, quite small changes in $\Delta_r G^\circ$ cause large changes in the equilibrium constant. This is illustrated on the graph below where K is plotted on a logarithmic scale. For this plot the temperature is taken as 298 K; the magnitude of the slope of the graph decreases as T increases.



At 298 K, once $\Delta_r G^\circ$ is more negative than about -40 kJ mol^{-1} , the equilibrium constant has become so large that the reaction goes essentially completely to products. Similarly, once $\Delta_r G^\circ$ is more positive than about $+40 \text{ kJ mol}^{-1}$, the equilibrium constant is so small that essentially no products are formed.

14.7.4 Influencing equilibrium

The famous Le Chatelier's principle always speaks the truth of nature.

**When a system in equilibrium is subjected to a change,
the composition of the equilibrium mixture
will alter in such a way as to counteract that change.**

(14.33)

Various kinds of changes can be envisaged, such as concentration, pressure and temperature. With the tools we have developed so far we are now able both to explain how Le Chatelier's principle arises and put it on a quantitative basis.

Temperature is certainly an important influencing factor, beginning from equations

$$\Delta_r G^\circ = -RT \ln K, \quad \Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ, \quad (14.34)$$

we can see that $\Delta_r G^\circ$ is strongly temperature dependent on the count of the second term, and so the equilibrium constant is definitely temperature dependent. It is important to realise that this temperature dependence is not given by $\Delta_r G^\circ = -RT \ln K$ alone as $\Delta_r G^\circ$ is temperature dependent.

By simply replacing $\Delta_r G^\circ$ with $\Delta_r H^\circ - T\Delta_r S^\circ$, we can see that

$$\ln K = -\frac{\Delta_r H^\circ}{R} \frac{1}{T} + \frac{\Delta_r S^\circ}{R}, \quad (14.35)$$

which says is that the way in which K varies with temperature is determined by the sign of $\Delta_r H^\circ$. Of course, an $\ln K$ vs $1/T$ plot here is helpful to determine the sign of $\Delta_r H^\circ$, and therefore the possibility of reaction happening. It should be a straight line assuming $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are independent of temperature. As it is simple to measure the equilibrium constant at different temperatures, we can indirectly determine the standard enthalpy.

Note that, for Graphical method for determining $\Delta_r H^\circ$ from the variation of K with temperature. A long extrapolation is needed to find $\Delta_r S^\circ$ from the intercept, so it may be preferable to compute $\Delta_r G^\circ$ from the measured values of K and then use $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ to find $\Delta_r S^\circ$.

ΔH is equal to the heat absorbed, at constant pressure. This implies another way to determine $\Delta_r H^\circ$ directly for reaction that goes completely to results. However, for reactions of $K \approx 1$, the measurement could be very hard as the reaction simply does not go to completion.

If we want to go along the indirect way, it will be easy if we can predict the variation of equilibrium constant against temperature. Starting from the equation

$$\frac{d}{dT} \left(\frac{\Delta_r G^\circ}{T} \right) = -\frac{\Delta_r H^\circ}{T^2}, \quad (14.36)$$

and replacing $\Delta_r G^\circ$ with $-RT \ln K$, we arrive at the van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta_r H^\circ}{RT^2}. \quad (14.37)$$

This equation says that if $\Delta_r H^\circ$ is positive, i.e. an endothermic reaction, $d \ln K / dT$ is positive and so the equilibrium constant increases with temperature, and vice versa. These are exactly the conclusions we reached earlier in this section. In other words, if a reaction absorbs heat, it favours high temperature.

If we integrate the equation above,

$$\ln K_2 - \ln K_1 = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \quad (14.38)$$

in which we assumed that $\Delta_r H^\circ$ does not vary with temperature, we can also see proofs for our conclusions. This equation gives us a way to convert equilibrium constants from a temperature to another.

Pressure is another influencing factor which plays the major role when gases appears in either side of the reaction.

Since $\Delta_r G^\circ$ is defined under standard conditions (a pressure of one bar), it follows that K does not vary with the actual pressure. However, this does not mean that the composition of the equilibrium mixture does not change when the pressure is altered.

One way of viewing what happens is to say that when the pressure is changed, the composition changes in order to keep K constant. This leads to the 'San Duan Shi' again, this technique is always helpful when treating reactions with changing compositions. Often a degree of dissociation, α , is assumed. 'San Duan Shi' is set out and there will be two independent ways to construct K , a $K = K$ equation can therefore be used to find α out.

14.8 Electrochemistry

Chemical reactions involving reduction and oxidation can be thought of as involving the transfer of electrons, and with suitable intermediates a cell could be made, and electrons will travel through an external circuit to provide voltage, current, etc.

This cell turns the energy available from the chemical reaction (in fact the Gibbs energy) into an electrical current; this is of great practical importance as this principle is the basis of electrical batteries. However, we will be more interested not in the current that we can extract from the cell but the electric potential (sometimes called the electromotive force, EMF, or loosely the 'voltage') that the cell develops between its electrodes under conditions of zero current flow.

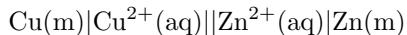
14.8.1 Cell conventions

Half-cell reactions and couples We all know that a half-cell reaction evolves electrons and reagents at a pole only. This helps us determine which thing is oxidized and which reduced.

Cell conventions When discussing a cell, we follow several conventions:

- The cell is written on paper, thus identifying clearly the left- and right-hand half cells.
- Each half cell reaction is written as a reduction i.e. with the electrons on the lefthand side of the reaction.
- Having written the left- and right-hand half cell reactions as reductions involving the same number of electrons, the conventional cell reaction is found by taking (RHS half-cell reaction) - (LHS half-cell reaction).
- The cell potential is that of the RHS measured relative to the LHS.

The cell notation, for example



indicates the crucial things in a cell: reagents, their phases, and the liquid junction.

14.8.2 Thermodynamic parameters from cell potentials

It can be shown¹ that, at constant temperature and pressure, the cell potential E is related to $\Delta_r G_{\text{cell}}$ for the conventional cell reaction according to:

$$\Delta_r G_{\text{cell}} = -nFE, \quad \text{at constant } p \text{ and } T. \quad (14.39)$$

In this relationship, F is the Faraday constant, which is the charge on one mole of fundamental charges; $F = 96485 \text{ C mol}^{-1}$; n is the number of electrons involved in the balanced chemical equation which represents the cell reaction.

This is an exceptionally important relationship as it relates the cell potential (which can easily be measured) with a voltmeter, to the useful thermodynamic parameter, $\Delta_r G_{\text{cell}}$.

Once we have found $\Delta_r G_{\text{cell}}$ it is easy to find $\Delta_r S_{\text{cell}}$, since

$$\Delta_r S_{\text{cell}} = - \left(\frac{\partial \Delta_r G_{\text{cell}}}{\partial T} \right)_p = nF \left(\frac{\partial E}{\partial T} \right)_p. \quad (14.40)$$

Therefore the entropy change of the cell reaction can be found simply from the temperature coefficient of the cell potential. In practice, all we would need to do is to measure the cell potential over a range of temperatures, plot the graph of E vs T , and then take the slope.

Once we determined G and S , H can easily be found. Therefore we achieved our goal of obtaining thermodynamical values using electrical potential.

¹In the additional material of the course.

14.8.3 The Nernst Equation

Since $\Delta_r G_{\text{cell}}$ depends on concentration, we want to know how they relate to each other. The Nernst equation predicts this dependence of the cell potential on concentration. Before deriving the Nernst equation we need to consider how chemical potentials depend on concentration.

By defining an dimensionless quantity called activity, a_i , in the equation for chemical potential of a reagent in ideal solutions,

$$\mu_i(a_i) = \mu_i^\circ + RT \ln a_i. \quad (14.41)$$

We can see that when $c_i \rightarrow 0$, the ideal solution behaves more and more like a mixture of gases, therefore $a_i \rightarrow c_i/c^\circ$. At first, this seems like an odd definition, but it turns out that chemical potentials are experimentally measurable, for example from electrochemical cells.

For ions in solution, Debye–Hückel theory gives reasonable estimates of the activities in terms of concentrations, but this theory lies well beyond the scope of this course. So for now we will simply assume that in any calculations activities can be replaced by concentrations. We will, however, continue to write activities in our expressions.

$$\begin{aligned} \Delta_r G_{\text{cell}} &= \Delta_r G_{\text{cell}}^\circ + RT \ln K \\ &= \Delta_r G_{\text{cell}}^\circ + RT \ln \frac{\prod_i a_i^{\nu_i}}{\prod_j a_j^{\nu_j}} \\ \Rightarrow E &= E^\circ - \frac{RT}{nF} \ln \frac{\prod_i a_i^{\nu_i}}{\prod_j a_j^{\nu_j}}, \end{aligned} \quad (14.42)$$

where the final line is the Nernst Equation. The fraction on the RHS of the Nernst equation has the same form as an equilibrium constant i.e. ‘products over reactants’. However, it is not an equilibrium constant as the activities are not necessarily those at equilibrium.

Nernst equation can be listed for half cells, but note that the electrons are not considered in them. Once we have the Nernst equation for both half cells, the total EMF can be calculated from

$$E = E_{1/2}(\text{RHS}) - E_{1/2}(\text{LHS}). \quad (14.43)$$

In the same way,

$$E^\circ = E_{1/2}^\circ(\text{RHS}) - E_{1/2}^\circ(\text{LHS}). \quad (14.44)$$

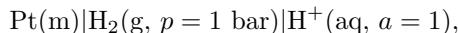
Given that standard half-cell potentials are tabulated, this is the way in which we can determine the standard potential of any cell.

14.8.4 Standard half-cell potentials

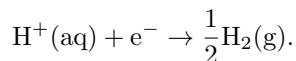
It is not possible to measure a half-cell potential on its own as the potential of any cell will always be the difference of two half-cell potentials. A table of

standard half-cell potentials can be drawn up by defining one of the half-cells to have zero potential and then referencing all other half-cell potentials to this. Since all calculations involve a difference in half-cell potentials, this arbitrary choice of a zero point will not cause any problems.

The electrode whose standard potential is taken as zero is the standard hydrogen electrode (SHE), at all temperatures.



and the half-cell reaction was



The standard half-cell potential of an electrode is defined as the potential developed by a cell in which the left-hand electrode is the standard hydrogen electrode and the right hand electrode is the one under test; all species are present at unit activity.

Extensive tabulations of standard half-cell potentials are available in Atkins' *Physical Chemistry*. As the cell potential is essentially a value for Δ_rG , we expect it to depend strongly on temperature. Therefore the tabulated data are at a specified temperature, most commonly 298 K.

14.8.5 Spontaneous cell reaction

In previous pages we talked about the conventional cell reaction. That is seriously not a good idea² since it doesn't always represent the reaction truly happening. The actual reaction that would take place if current were allowed to flow - called the spontaneous cell reaction - is found by inspecting the sign of the cell potential.

- If the cell potential is negative, the spontaneous reaction is the reverse of the conventional reaction;
- if the cell potential is positive, the spontaneous reaction is the same as the conventional reaction.

Note that cell potentials are affected by the concentrations of the species involved, so under some circumstances the direction of the spontaneous cell reaction can be reversed simply by altering the concentrations of the ions.

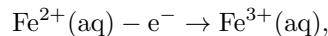
14.8.6 Types of half cells

Metal and ion Nothing special, but be careful about which phase the ions are in.

²In my opinion, conventional cell reaction shouldn't even exist, but for exams I still noted them down.

Gas and ion These consist of the gas in contact with a solution containing related ions; an inert Pt electrode provides the electrical contact. The ions can be anions or cations³.

Redox The oxidized and reduced species are both present in solution; an inert Pt electrode provides the electrical contact. The most common example is the half reaction⁴



and



Metal, insoluble salt and anion These consist of a metal coated with a layer of the insoluble salt formed by the metal and the anion which is in the solution. The commonest example is the combination silver, silver chloride, chloride anion.

Another commonly encountered electrode is that between liquid mercury, solid mercurous chloride (mercury(I) chloride) and chloride anions. The mercurous chloride is made up in a paste with liquid mercury and then floated on top of mercury. This electrode is called the calomel electrode.

Liquid junctions If it is the case that the solutions in the two half-cells are different, then a problem arises in that for the cell to produce a potential the two solutions must be in contact. However, they must not mix as then the reaction would take place without the electrons moving round the external circuit. The ‘join’ between the two solutions is called a liquid junction.

Typically such a junction is handled in practice by having a porous barrier between the two solutions; this allows contact but prevents rapid mixing. The problem with this arrangement is that a potential, called a liquid junction potential, may be set up across the barrier. It turns out that this potential detracts from the cell potential and so the measured potential will not be correct.

Liquid junction potentials can be minimised by using a salt bridge. This is a tube containing, typically, a concentrated solution of KCl or KNO₃; the ends of the tube dip in the solutions which form the cell and the KCl solution is kept in the tube by glass sinters at each end. Such a salt bridge provides electrical contact between the solutions and minimizes the liquid junction potential.

14.8.7 Assessing redox stability using electrode potentials

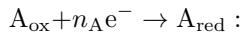
One of the very useful things we can do with a table of standard electrode potentials is to use them to assess the relative stability of different species with

³When dealing with water, we assume that it is initially pure and does not contribute to H⁺ and OH⁻ ions, unless specially denoted.

⁴Note that the equation is not acceptable by convention but in my opinion it is totally fine.

respect to oxidation and reduction. This is just a way to verify the electrochemical series we learned in high school. The more positive the standard potential, the more strongly oxidizing a couple is said to be.

For a A_{ox} and A_{red} couple,



- the greater the half-cell potential, the more strongly oxidizing A_{ox} becomes;
- the more negative the half-cell potential, the more strongly reducing A_{red} becomes.

The electrochemical series is simply the redox couples listed in order of standard half cell potentials, with the most positive at the top and the most negative at the bottom; a selection of couples arranged in this way is shown in the table opposite (data at 298 K).

The electrochemical series

A_{ox}	A_{red}	E° / V
A_{ox} is a strong oxidizing agent		
F_2	F^-	+2.866
MnO_4^-	Mn^{2+}	+1.507
$\text{Cr}_2\text{O}_7^{2-}$	Cr^{3+}	+1.232
O_2	OH^-	+0.401
Sn^{4+}	Sn^{2+}	+0.151
Fe^{3+}	Fe	-0.037
Zn^{2+}	Zn	-0.7618
Mg^{2+}	Mg	-2.372
Li^+	Li	-3.040
A_{red} is a strong reducing agent		

Since E is related to the standard Gibbs energy of the cell, $\Delta_r G_{\text{cell}}$, the cell potential gives us the Gibbs energy change per electron. So, by comparing cell potentials, we are really comparing Gibbs energy changes which have been corrected for the number of electrons involved. This is why we do not need to worry about the actual number of electrons involved in the redox couple.

14.8.8 More applications

Concentration cells A concentration cell has the same electrode on the RHS and LHS, but with different concentrations or pressures of the species involved.

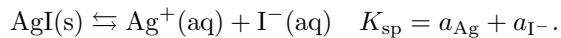
The cell produces a potential which depends on the ratio of the concentrations in the two half cells.

Thermodynamical parameters of ions Addition to what we mentioned: the $\Delta_r H^\circ$ and $\Delta_r G^\circ$ for elements in there reference states are zero. For ions in solution, we introduce the additional conventions that

$$\Delta_f H^\circ(\text{H}^+) = \Delta_f G^\circ(\text{H}^+) = 0. \quad (14.45)$$

In any experiment we will only be able to determine the difference of enthalpies or Gibbs energies of ions, so in order to establish values for individual ions we need to fix a zero point of the scale. Assigning the value 0 to H^+ is arbitrary, but as only differences are measurable we are free to choose the origin to be where we like.

Solubility product of AgI AgI is a sparingly soluble salt whose solubility is determined by the solubility product, K_{sp} , which is defined as the equilibrium constant for the dissolution reaction



But K_{sp} can also be related to $\Delta_r G_{\text{cell}}$ by $\Delta_r G_{\text{cell}} = -RT \ln K_{\text{sp}}$. Therefore, from E we can obtain K_{sp} eventually.

This is the end of PART IA Chemistry in Lent term!

Enjoy the exams!

Bibliography

- [1] Peter Wothers: *The Shapes and Structures of Molecules, Handout 1,2.* 2023.
- [2] Deborah A. Longbottom: *Reactions and Mechanisms in Organic Chemistry, Handout 1,2.* 2023.
- [3] J. J. Sakurai, Jim Napolitano: *Modern Quantum Mechanics, Second Edition.* Cambridge University Press. 2017.
- [4] P. Alvarez Cartelle: *Advanced Quantum Mechanics, Handout 1,2, Slides 6,7,8.* 2023.
- [5] Lei Sun: *Chemistry Handouts for High School Students.* 2022.
- [6] Ruize Li: *Physics Olympiad Outline.* 2022.
- [7] Shuqing Huang: *Thermodynamics.* Higher Education Press.
- [8] Peter Atkins and Julio De Paula and James Keeler: *Physical Chemistry, 11th Edition.* Oxford University Press.
- [9] James Keeler: *Energetics and Equilibria, Handout.* 2024.