

FINAL

EXAM

NOTES

N U C L E A R

C H E M I S T R Y

TOPIC ONE: NUCLEAR CHEMISTRY (LECTURES 1-5)

LECTURE 3: RADIOACTIVITY & NUCLEAR DECAY AND HALF-LIFE & CARBON DATING

LECTURE 4: NUCLEAR STABILITY, PREDICTING RADIOACTIVE MODES OF DECAY

Activity and half-life: for a given number atomic nuclei: a low activity correspond to a small decay constant and long half-life and then high activity corresponds to large decay constant and a short half-life.

LO: USE EQUATIONS TO CALCULATE QUANTITIES SUCH AS ACTIVITY, MOLEAR ACTIVITY, SPECIFIC ACTIVITY AND HALF-LIFE

Activity: the activity (A) of a radioactive sample is a specific measure of the rate of decay, defined as the number of nuclei that disintegrate per second. The unit of activity is the Becquerel (1 Becquerel = 1 second). Activity is proportional to the number of nuclei in the sample. $A = kN$ where k is the decay constant. Then the final and initial activity are also related by exponential decay $A = A_0 e^{-kt}$

Specific activity and molar activity

Specific activity is the activity per gram of radioactive nuclide and Molar activity is the activity per mole of radioactive nuclide

Half life equation

$$N = N_0 e^{-kt}$$

where N = number of nuclei, N_0 = initial number of nuclei, k = decay constant, t = time

We can solve this equation for a specific time-point - the half-life. At this time-point, $t = t_{1/2}$ and $N = N_0/2$

Substituting into our original equation gives:

$$\frac{N}{2} = N_0 e^{-kt_{1/2}} \rightarrow 2 = e^{kt_{1/2}} \rightarrow \ln 2 = kt_{1/2}$$

$\therefore t_{1/2} = \frac{\ln 2}{k}$ This explains why a large half-life corresponds to a small decay constant (and activity)

LO: USE AND MANIPULATE EQUATIONS DESCRIBING EXPONENTIAL DECAY

The equation for carbon dating

We have seen that: $A = A_0 e^{-kt} \quad t_{1/2} = \frac{\ln 2}{k}$

We can therefore replace k with $\ln 2/t_{1/2}$ to give:

$$A_t = A_0 e^{-\frac{t}{t_{1/2}}} \rightarrow \frac{A_t}{A_0} = e^{-\frac{t}{t_{1/2}}}$$

but $t_{1/2}$ of ^{14}C is known (5730 yr), but the method had to be experimentally calibrated (using a tree ring). This yielded a value of 8033 $\ln(t/t_{1/2})$ (rather than the theoretical value of 8267).

LECTURE 4: NUCLEAR STABILITY, PREDICTING RADIOACTIVE MODES OF DECAY

LO: EXPLAIN THE FACTORS THAT GOVERN NUCLEAR STABILITY

TWO main parameters govern nuclear stability: 1. The size of the nucleus and 2. The composition of the nucleus (neutrons:protons), also termed the N:Z ratio. **The N:Z ratio:** Zone of stability - all known stable nuclides fall inside the zone of stability. The zone has a N:Z ratio near to 1, but 'bends' towards more neutrons per proton as the nucleus gets larger. RULE: unstable isotopes must decay towards the zone of stability, finally falling below 209Bi.

Radioactive decay mechanisms 1

Radioactive nuclei undergo spontaneous decay by various mechanisms. In all nuclear reactions, both mass number and charge are balanced.

1. α decay $\text{^{208}Bi} \rightarrow \text{^{204}Po} + \text{^{4}He}$
2. β^- decay $\text{^{208}Bi} \rightarrow \text{^{208}Tl} + \text{e}^- + \bar{\nu}_e$
3. Proton (β^+) decay $\text{^{208}Bi} \rightarrow \text{^{207}Po} + \text{e}^+ + \nu_e$ (beta plus decay)

LO: PREDICT MODE RADIOACTIVE DECAY FOR GIVEN UNSTABLE NUCLEUS

Radioactivity \rightarrow Atomic nuclei is divided into two types 1) stable and 2) radioactive.

Why are some unstable and others stable? Because the stability of a nucleus involves the competition between two forces. One force: Electrostatic repulsion - between protons acts to push these nucleon apart over a long range.

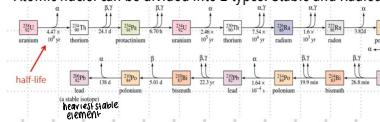
Second force: The strong nuclear force - which is a short range attraction between all nucleons.

How do the electrostatic and strong nuclear forces influence decay? 1. In nuclides with too few neutrons, the electrostatic repulsion overwhelms the strong nuclear attraction. 2. As the nucleus gets larger, the long-range electrostatic repulsion between the protons accumulates and eventually overwhelms the strong nuclear attraction. 3. Where there are too many neutrons, the nucleus is also unstable.

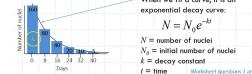
LECTURE 3: RADIOACTIVITY & NUCLEAR DECAY AND HALF-LIFE & CARBON DATING

LO: RECALL THAT ALL RADIOACTIVE NUCLIDES HAVE DIFFERENT RATES OF DECAY

Atomic nuclei can be divided into 2 types: Stable and Radioactive.



e.g. ^{131}I has a half-life of 8 days, so if we start with 160 nuclei, the decay will look like this:

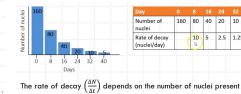


When we fit a curve, it is an exponential decay curve:

$$N = N_0 e^{-kt}$$

 N = number of nuclei
 N₀ = initial number of nuclei
 k = decay constant
 t = time

Worksheet questions 1 and 2



The rate of decay ($\frac{dN}{dt}$) depends on the number of nuclei present

Radioactive nuclei undergo spontaneous decay to eventually become stable nucleus

Half-life: the decay of an unstable nuclide is characterised by its half-life, which is the time required for half of the nuclei in a sample to undergo a decay event.

The decay constant (k) is characteristic of the amount of the particular radioactivity nuclide, and does not depend on the amount of the sample.

e.g. 117 g of U-234 has an activity of $1.05 \times 10^6 \text{ Bq}$. This corresponds to a specific activity of:

$$\frac{1.05 \times 10^6 \text{ Bq}}{117 \text{ g}} = 12400 \text{ Bq g}^{-1}$$

And a molar activity of: $\frac{1.05 \times 10^6 \text{ Bq}}{117 \text{ g} / 234 \text{ g mol}^{-1}} = 2.90 \times 10^4 \text{ Bq mol}^{-1}$

Activity and half life: for a given number atomic nuclei: a low activity correspond to a small decay constant and long half-life and then high activity corresponds to large decay constant and a short half-life.

Such as ACTIVITY, MOLEAR ACTIVITY, SPECIFIC ACTIVITY AND HALF-LIFE

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Substituting into our original equation gives:

$$\frac{N}{2} = N_0 e^{-kt_{1/2}}$$

$\therefore t_{1/2} = \frac{\ln 2}{k}$ This explains why a large half-life corresponds to a small decay constant (and activity)

The process of carbon dating

1. Measure the C-14 activity of the archaeological sample (this is A₁)
2. Measure the C-14 activity of an equivalent modern-day sample (this is A₂)
3. Substitute these values into the equation for C-14 age:

$$t = 8033 \times \ln \left(\frac{A_1}{A_2} \right)$$

C-14 dating is only appropriate for objects less than 60000 years old.

Radioactive decay sequences

Decay from ^{238}U

A radioactive decay sequence (e.g. ^{238}U) can be represented more concisely as a graph of atomic number versus neutron number.

α decay is shown as a decrease of two protons (Z) and two neutrons (N).

β^- decay is shown as a decrease of one neutron and an increase of one proton.

Isotopes (same Z, different N) lie along vertical lines in this graph.

Radioactive decay mechanisms 2

Beta capture is followed by emission of a γ -ray to restore full two-body energy to the system lost by the beta capture by the captured electron. A proton is emitted, forming a neutron.

Simple emission of a neutron, which changes M but leaves Z unchanged.

This is a high frequency radiation that often accompanies the other forms of decay. No change in M or Z is associated with γ -emission on its own.

Radioactive decay mechanisms 3

What actually happens in the nucleus?

1. α decay loss of two protons and two neutrons $\text{Ni}, \text{Z} \downarrow$
2. β^- decay $[\text{p}] \rightarrow [\text{p} + \bar{\nu}_e] \text{ Ni}, \text{Z} + 1, \text{N} \uparrow$
3. Positron (β^+) emission $[\text{p}] \rightarrow [\text{p} + \nu_e] \text{ Ni}, \text{Z} + 1, \text{N} \uparrow$
4. Electron capture $[\text{n}] \rightarrow [\text{n} - e] \text{ Ni}, \text{Z} + 1, \text{N} \uparrow$

N:Z ratio

$\frac{N}{Z} >$ zone of stability

$\frac{N}{Z}$ 1 and/or Z 1

e.g. α decay, neutron emission

$\frac{N}{Z} <$ zone of stability

$\frac{N}{Z}$ 1 and/or Z 1

e.g. β^+ decay, electron capture

$\frac{N}{Z} <$ zone of stability

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TOPIC ONE: NUCLEAR CHEMISTRY (LECTURES 1-5)



LECTURE 5: CONSEQUENCES AND USES OF RADIOACTIVITY

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LO: EXPLAIN WHY IONISING RADIATION CAUSES BIOLOGICAL DAMAGE

Radiation produced by radioactive decay: is very high energy. Causes the ionisation of matter by ejecting an electron from an atom; highly penetrating radiation passes through matter.

Why is radiation damaging? 50-70% of the body is made of water, meaning that a large proportion of the reaction will be with water. Water is ionised to a cation and an electron. Free radicals are very reactive, and damage: for example DNA strands -> genetic damage, Cancer or Cell membranes -> cells break apart

LO: EXPLAIN THE MAIN FACTORS THAT CONTRIBUTE TO THE SEVERITY OF RADIATION DAMAGE

The effects of radiation damage depend on three factors:

Types of radiation

Length & source of exposure:

2. Length of exposure:

short term (acute) - this is called radiation poisoning, high doses in short times cause acute cell damage and often death

Long term (chronic): Radiation-induced cancer. Anything that interrupts DNA can lead to cancer.

3. Source of exposure:

Internal exposure: ingestion or inhalation, Alpha and Beta are the most dangerous, most gamma radiation escapes the body.

External exposure: Alpha and Beta radiation can't penetrate through air and skin, gamma radiation can penetrate skin and is more dangerous.

LO: EXPLAIN WHY RADIOACTIVE ISOTOPES ARE USEFUL IN CANCER THERAPY AND IMAGING, AND IDENTIFYING THE MOST USEFUL TYPES OF RADIATION

Cancer therapy: ionising radiation can be used to kill cancerous cells. Two methods are used to ensure that only cancer cells are killed. 1. Focussing ionising radiation onto the tumour

2. Internal administration of radiopharmaceutical - the radio pharmaceutical must be targeted to the tumour and uses alpha and Beta emitters, which have short-range effects. Attaching radionuclides to antibodies can treat target radio pharmaceutical to other cells or organs

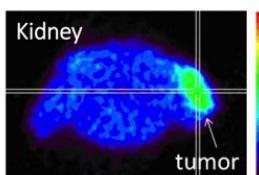
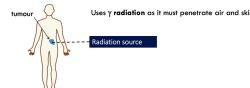
Imaging = radio imaging uses radiation emitted from within the body to map the body. The radiation must be highly penetrating so

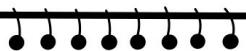
that it can be detected and is not harmful to the patient - requires gamma radiation. Distribution of the radioisotope is imaged by

Scintillation counting. For example Technetium-99m imaging - technetium is the lightest element with no stable isotopes. Technetium-99 is ideal for imaging because: it can be easily incorporated into many drugs, it can easily be prepared from Mo-99, it does not change its chemistry when it decays and it emits only highly-penetrating gamma rays, not harmful alpha and Beta particles. Another example is PET imaging- Positron emission tomography (PET) uses radionuclide that emits positrons. Inside the body, the positron reacts with an electron, producing two high energy gamma rays, which are detected outside the body. The most common PET imaging agent is Fludeoxyglucose (FDG), in which an oxygen atom of glucose is replaced by Fluorine-18. FDG is used to observe parts of the body that uses high levels of glucose (e.g. tumours, brain).

Ionisation of a single molecule requires 10 eV, so each unit of radiation can ionise a large number of molecules

Type of radiation	Aprox. energy	No. ionised molecules
Alpha (α)	5 MeV	5×10^5
Beta (β)	0.05 to 1 MeV	5×10^6 to 1×10^7
Gamma (γ)	1 MeV	1×10^8





LECTURE 6: QUANTUM THEORY ELECTRONS ARE WAVES



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LO: CALCULATE THE ENERGY OF A PHOTON FROM ITS WAVELENGTH AND ITS WAVELENGTH FROM ITS ENERGY

The photoelectric effect:

Light can eject from a metal, but only if its frequency is above a threshold frequency (characteristic for each metal).

Classically, for light as a wave, its energy is proportional to the square of its amplitude. For particles, energy is proportional to frequency.

Light is electromagnetic radiation that has both wave and particle (photons) nature. The amount of energy (quantum) in each photon is determined by its frequency, ν (nu) or wavelength, λ (lambda). hence, c is the speed of light, $3.0 \times 10^8 \text{ m s}^{-1}$.

$$E = h\nu = h \frac{c}{\lambda}$$

Planck's constant
 $6.626 \times 10^{-34} \text{ Js}$

LO: CALCULATE THE MOMENTUM OF PARTICLE FROM ITS WAVELENGTH AND WAVELENGTH OF THE PARTICLE FROM ITS MOMENTUM

Matter waves: if light can behave as a wave and a particle (photoelectric effect), why shouldn't matter (electrons) also have wave properties. De Broglie reasoned that the momentum ($m \times$ velocity of a particle, mv) of a particle should be related to its wavelength in the same way as a photon. From Einstein's special theory of relativity, for a photon (zero rest mass) its momentum, p , is related to its energy by $p=E/c$.

From quantum theory, the energy of a photon is given by $E=hc/\lambda$.

Applying the same two equations to a particle gives the wavelength of a matter wave.

$$\frac{\lambda}{p} = \frac{\hbar}{mv} \quad M = \text{mass} \quad V = \text{velocity} \quad \hbar = \text{Planck's constant } 6.626 \times 10^{-34} \text{ Js}$$

LO: CALCULATE ENERGY LEVELS FOR ONE-ELECTRON (HYDROGEN-LIKE) ATOMS

The hydrogen atom has a set of allowed energy given by the equation: $E_n = -\frac{E_k}{n^2}$

The Rydberg constant = $2.18 \times 10^{-18} \text{ J}$

$$E_n = -\frac{E_k}{n^2} = -E_k \frac{1}{n^2} \quad n = 1, 2, 3$$

\hookrightarrow allowed energies in quantum mechanics are often written in terms of a set of quantum numbers such as 'n'

Only certain specific values of E are allowed. Values between $-E_k$ ($N=1$) and $-E_k/4$ ($n=2$) cannot be observed

Allowed energies for H

The lowest allowed energy of the hydrogen atom ($n=1$) is $E_1 = -2.18 \times 10^{-18} \text{ J}$.

$$\text{For } n=2, E_2 = -5.45 \times 10^{-18} \text{ J}$$

$$\text{For } n=3, E_3 = -2.42 \times 10^{-18} \text{ J}$$

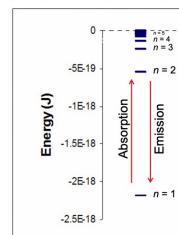
As n increases, E_n approaches the energy of unbound electron, or 0.

LO: RELATE ABSORPTION AND EMISSION OF PHOTONS TO CHANGE IN ENERGY LEVELS

Spectroscopic lines:

Visible atomic emission spectral discrete spectral wavelengths called lines. Bohr (1913) applied quantum theory to the structure of the atom and proposed an atomic model in which the electrons are in discrete orbitals. Thus, an atom cannot lose energy continuously, but must do so in quantum jumps between different orbits.

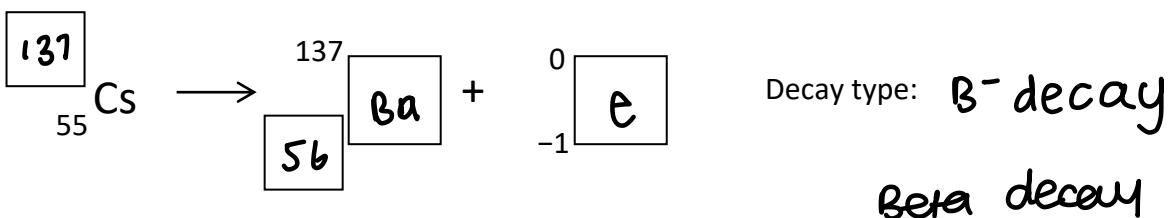
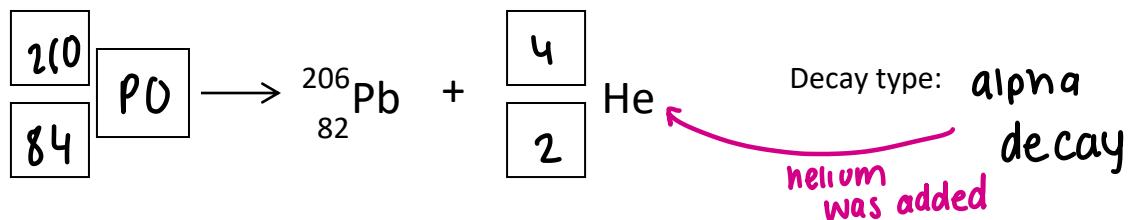
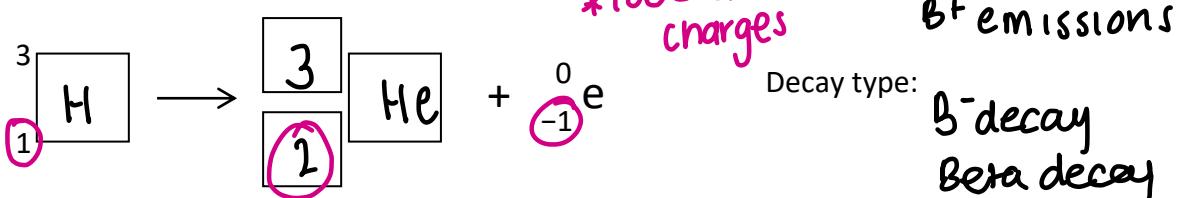
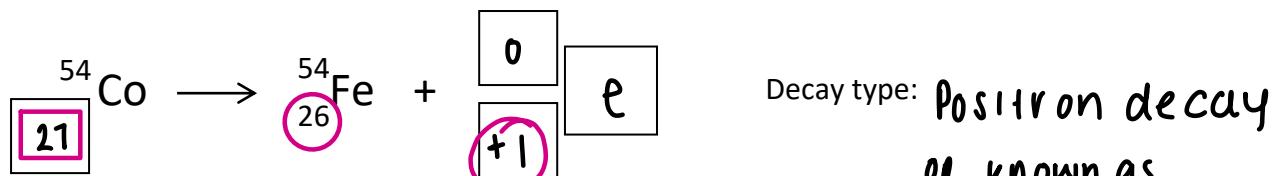
When shining a photon of light onto an atoms it will cause a discrete jump an electron will jump from one orbital level to another. When that energy source is removed and the system relaxes back down to equilibrium it will emit light by jumping from $n=2$ to $n=1$.



CHEM1111 worksheet – Lecture 4

Modes of nuclear decay

1. Complete the following equations, and identify the type of radioactive decay in each.

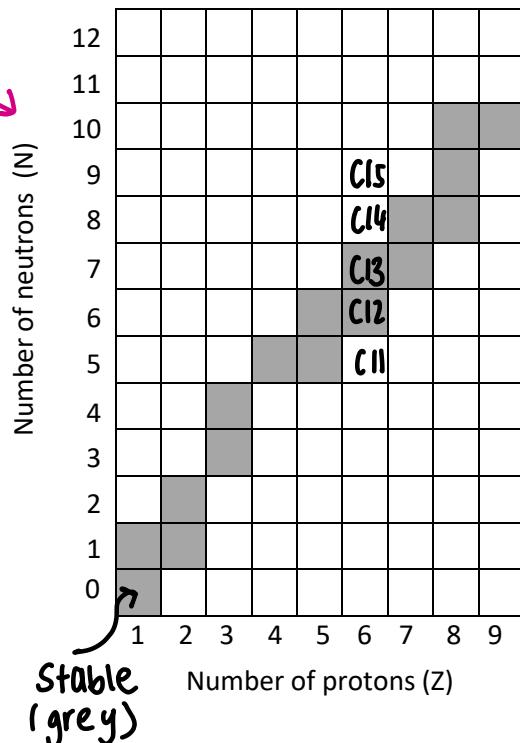


2. Carbon has five known isotopes, with mass numbers of 11, 12, 13, 14 and 15.

(a) Fill in the first two lines of the following table for each isotope

Isotope	Carbon-11	Carbon-12	Carbon-13	Carbon-14	Carbon-15
Number of protons	6	6	6	6	6
Number of neutrons	$11-6=5$	$12-6=6$	$13-6=7$	$14-6=8$	$15-6=9$
Stable?	No	Yes	Yes	No	No

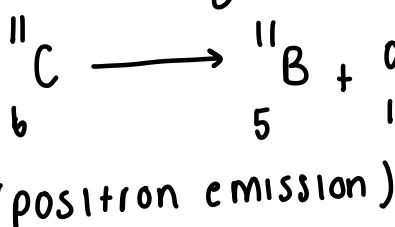
(b) Mark each isotope on the following graph. The zone of stability is shown in grey.



(c) Fill in line 3 of the table, predicting the stability of each of the nuclei

(d) For each of the **unstable** nuclei, decide whether the nucleus has too many protons or too many neutrons. Which mode of decay will the nucleus undergo? Write an equation, and mark the transformation on the graph above.

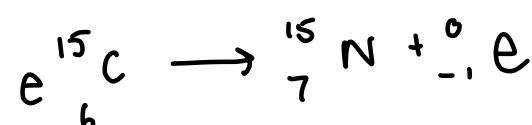
C-11 = Not enough



C-14 = loose one



C-15 = loose one



CHEM1111 worksheet – Lecture 5

Consequences and uses of radioactivity

Fill in the table with the desired properties for radioisotopes used for different purposes:

	Internally-administered cancer therapy	Gamma-ray imaging	Positron emission tomography
Type of radiation used	$\alpha \rightarrow$ Alpha $\beta^- \rightarrow$ Beta	γ gamma	${}^0_1 e^+$
Reason	Short penetration Acts locally	Camera is external to the body long penetration	produce gamma γ ${}^0_1 e^+ + {}^0_{-1} e^- = 2\gamma$
Ideal half-life (s, h, d, or y)?	hours or days	hours	hours
Reason	Needs to persist long enough to do damage	Needs to persist long enough to get the area of concern but not so long as to cause damage.	Needs to persist long enough to get the area of concern but not so long as to cause damage restrict life time
Example radioisotope	Thyroid cancer ${}^{131}_5 I$	Technetium-99m ${}^{99m}_{43} Tc$	Fluorine ${}^{18}_9 F$

CHEM1111 worksheet – Lecture 6

Quantum atoms

1. Relationships between energy, frequency and wavelength.

Data: Planck's constant, $h = 6.626 \times 10^{-34} \text{ J s}$

Speed of light, $c = 3.0 \times 10^8 \text{ m s}^{-1}$

- a. Microwave ovens typically operate at a frequency of $2.45 \times 10^9 \text{ s}^{-1}$ (2.45 GHz). Calculate the wavelength of this microwave radiation.

$$V = \frac{C}{\lambda} \quad 2.45 \times 10^9 = \frac{3.0 \times 10^8}{\lambda} \quad \lambda = \frac{3.0 \times 10^8}{2.45 \times 10^9}$$

$V = \text{velocity/frequency}$
 $C = \text{speed of light}$
 $\lambda = \text{wavelength}$

$$= 0.122 \text{ m} \\ \times 100 \\ = 12 \text{ cm}$$

- b. Calculate the energy of a green laser, which has a wavelength of 532 nm.

$$E = \frac{h \times c}{\lambda} \quad E = \frac{6.626 \times 10^{-34} \text{ Js} \times 3.0 \times 10^8 \text{ ms}^{-1}}{532 \times 10^{-9} \text{ m}}$$

$E = \text{Energy}$

$h = \text{Planck's constant (J s)}$

$c = \text{speed of light (meters/seconds)}$

$\lambda = \text{wavelength (nm)}$ must change
to meters

$$\boxed{\text{Energy} = 3.7 \times 10^{-19} \text{ J}}$$

$$532 \text{ nm} \div 1000000000 = 532 \times 10^{-9} \text{ m}$$

- c. Calculate the wavelength and frequency of an X-ray photon with an energy of $8.0 \times 10^{-16} \text{ J}$.

Find wavelength (nm):

rearranged

$$E = \frac{h \times c}{\lambda} \quad \lambda = \frac{h \times c}{E}$$

$$\lambda = \frac{6.626 \times 10^{-34} \text{ J s} \times 3.0 \times 10^8 \text{ ms}^{-1}}{8.0 \times 10^{-16} \text{ J}}$$

$$\text{wavelength } (\lambda) = 2.5 \times 10^{-10} \text{ m} \\ \times 1000000000 \\ 25 \text{ nm}$$

$$\boxed{\text{Wavelength} = 25 \text{ nm}}$$

Find Frequency:

$$V = \frac{c}{\lambda}$$

$$V = \frac{3.0 \times 10^8 \text{ ms}^{-1}}{2.5 \times 10^{-10} \text{ m}}$$

$$\boxed{\text{frequency} = 1.2 \times 10^{18} \text{ s}^{-1}}$$

2. Quantum chemistry: relating mass and energy. Consider an electron ($m = 9.11 \times 10^{-31}$ kg) and a proton ($m = 1.671 \times 10^{-27}$ kg) both travelling in a vacuum at $v = 5.0 \times 10^6$ m s $^{-1}$.

- a. Using the de Broglie relation, predict which of these particles will have the longest wavelength. Why?

Broglie relation: Wavelength (λ) is proportional to its momentum (mv)

$$\lambda = \frac{h}{mv}$$

electron mass = 9.11×10^{-31} kg (weighs less)

proton mass = 1.671×10^{-27} kg (weighs more)

—

∴ The electron has less mass and therefore will have a longer wave length

- b. Calculate the wavelength of the electron in m and nm.

$$\lambda = \frac{h}{mv} \quad \lambda = \frac{6.626 \times 10^{-34} \text{ Js}}{9.11 \times 10^{-31} \times 5.0 \times 10^6 \text{ m s}^{-1}}$$

$$\lambda = 1.45 \times 10^{-10} \text{ m} \times 100000000000$$

$$= 14.5 \text{ nm}$$

- c. Calculate the kinetic energy of this electron ($E = \frac{1}{2}mv^2$).

$$E = \frac{1}{2} \times mv^2$$

$$E = \frac{1}{2} \times 9.11 \times 10^{-31} (5.0 \times 10^6)^2$$

$$\therefore \text{Kinetic energy} = 1.14 \times 10^{-17}$$



School of Chemistry

Chemistry 1A (CHEM1111)

Tutorial 2 (Week 2): Nuclear Chemistry

Model 1: Radioactive Decay

A nuclide is a particular nuclear species with a specified number of protons and neutrons. The six most important ways in which radioactive nuclides decay are:

- (a) α decay: the nucleus loses an α particle (${}^4_2\text{He}^{2+}$)
- (b) β^- decay: a neutron in the nucleus is converted into a proton and an electron. The electron is ejected from the nucleus.
- (c) Positron or β^+ emission: a proton in the nucleus is converted into a neutron and a positron. The positron is ejected from the nucleus.
- (d) Electron capture: the nucleus captures an electron. This reacts with a proton in the nucleus to produce a neutron.
- (e) Neutron emission: loss of a neutron.
- (f) Gamma or γ decay: emission of high energy photons. This often accompanies the other decay mechanisms.

Critical thinking questions

1. For each of the decay routes, complete the table below showing the effect on the nucleus.

	type of decay	change in number of neutrons (N)	change in number of protons (Z)
(a)	α decay	reduced by 2	reduced by 2
(b)	β^- decay	-1	+1
(c)	β^+ emission	+1	-1
(d)	electron capture	+1	-1
(e)	neutron emission	-1	No change
(f)	γ decay	No change	No change

2. What nucleus is produced when the following nuclear decays occur?

- (a) $^{238}_{92}\text{U}$ undergoes α decay: $^{234}_{90}\text{U}$
- (b) $^{14}_6\text{C}$ undergoes β^- decay: $^{14}_7\text{N}$
- (c) $^{11}_6\text{C}$ undergoes β^+ emission: $^{11}_7\text{N}$
- (d) $^{55}_{26}\text{Fe}$ undergoes electron capture: $^{55}_{25}\text{Fe}$
- (e) $^{12}_4\text{Be}$ emits a neutron: $^{12}_4\text{Be}$
- (f) $^{99m}_{43}\text{Tc}$ undergoes γ decay: $^{99m}_{43}\text{Tc} + \gamma$ (gamma)

3. By first working out the number of neutrons (N) and the number of protons (Z) before and after the nuclear decays in question 2, what is the effect of the decay on the mass number and on the ratio N / Z ?

	type of decay	change in mass number	change in N / Z
(a)	α decay	Reduced 4 (-4)	↑
(b)	β^- decay	0	↓
(c)	β^+ emission	0	↑
(d)	electron capture	0	↑
(e)	neutron emission	Reduced 1 (-1)	↓
(f)	γ decay	0	0

Model 2: Predicting the Mode of Decay

Figure 1 on the next page shows a plot of the number of neutrons (N) vs the number of protons (Z) for *stable* nuclides. Clearly, a key factor in determining stability is the N / Z ratio.

The nuclides form a narrow **band of stability**:

- very few stable nuclides exist with $N / Z < 1$
- for light nuclide ($Z \leq 10$), $N / Z \approx 1$
- The N / Z ratio of stable nuclides gradually increases as Z increases with $N / Z = 1.15$ for $^{56}_{26}\text{Fe}$, $N / Z = 1.28$ for $^{107}_{47}\text{Ag}$ and $N / Z = 1.49$ for $^{184}_{74}\text{W}$.
- All nuclides with $Z > 82$ are unstable.

An unstable nuclide generally decays in a mode that shifts its N / Z ratio towards the band of stability.

Critical thinking questions

4. Why is $^{31}_{15}\text{P}$ much more stable than $^{30}_{15}\text{P}$?

$^{31}_{15}\text{P}$ has $N = (31 - 15) = 16$ and $Z = 15$, so $N/Z = 1.1$

$^{30}_{15}\text{P}$ has $N = (30 - 15) = 15$ and $Z = 15$, so $N/Z = 1.0$

$\therefore ^{31}_{15}\text{P}$ as
 $N/Z = 1.1$
 which is > 1.0

5. Nuclides *above* the band of stability in Figure 1 have an N / Z ratio which is too high. Using your answer to question 3, which of the six modes of decay might such a nuclide undergo to approach the band of stability? Fill in your answer in the box on the figure overleaf.
6. Nuclides *below* the band of stability in Figure 1 have an N / Z ratio which is too low. Using your answer to question 3, which of the six modes of decay might such a nuclide undergo to approach the band of stability? Fill in your answer in the box on the figure overleaf.
7. Nuclides with $Z > 82$ are beyond the band of stability and are unstable. Using your answer to question 3, which of the six modes of decay might such a nuclide undergo? Fill in your answer in the box on the figure overleaf.

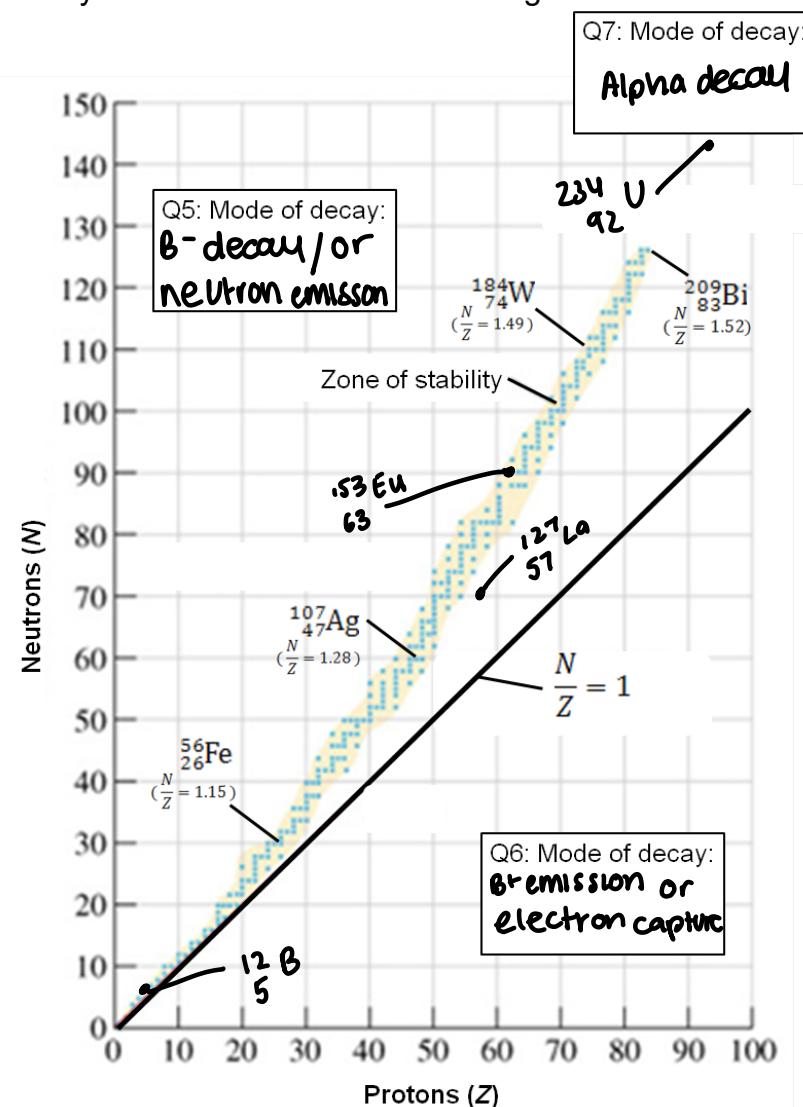


Figure 1. Plot of the number of neutrons (N) vs the number of protons (Z) for the stable nuclides.

8. Sketch each of the following nuclides on Figure 1, calculate their N/Z ratios and hence predict their stability. For the unstable (radioactive) nuclides, predict the mode(s) of nuclear decay they are likely to undergo.

use to graph on x axis

(a) $\text{^{12}_{\underline{5}}B}$ $12-5=7$, $\frac{N}{Z} = \frac{7}{5} = 1.4$ too high so B^- decay

(b) $\text{^{153}_{\underline{63}}Eu}$ $153-63=90$, $\frac{N}{Z} = \frac{90}{63} = 1.43$ Stable in this region No decay needed

(c) $\text{^{234}_{\underline{92}}U}$ $234-92=142$, $\frac{N}{Z} = \frac{142}{92} = 1.5$. Because $Z > 83$ it is too heavy Alpha decay to decrease total mass

(d) $\text{^{127}_{\underline{57}}La}$ $127-57=70$, $\frac{N}{Z} = \frac{70}{57} = 1.2$ too low will undergo B^+ emission or electron capture

Model 3: Calculating radioactive decay and half-life, $t_{1/2}$ and activity

Radioactive isotopes undergo exponential decay as described by the following equation:

$$N(t) = N_0 e^{-kt} \quad (1)$$

The half life of a given radioisotope is the time required for half of the original number of nuclei (N_0) to decay (i.e. the time after which half of the original sample remains). Half-life can be described by the following equation:

$$t_{1/2} = \frac{\ln 2}{k} \quad (2)$$

The activity of a radioactive sample is the number of disintegrations it undergoes per second. It depends on the number of particles present.

$$A = k N \quad (3)$$

Critical thinking questions

9. What does each symbol in equation 1 mean? What are the SI units of each symbol?

$N(t)$ = nuclei after a period of time (t), SI unit = seconds (s)

N_0 = initial number of nuclei, SI unit (t) = (s)

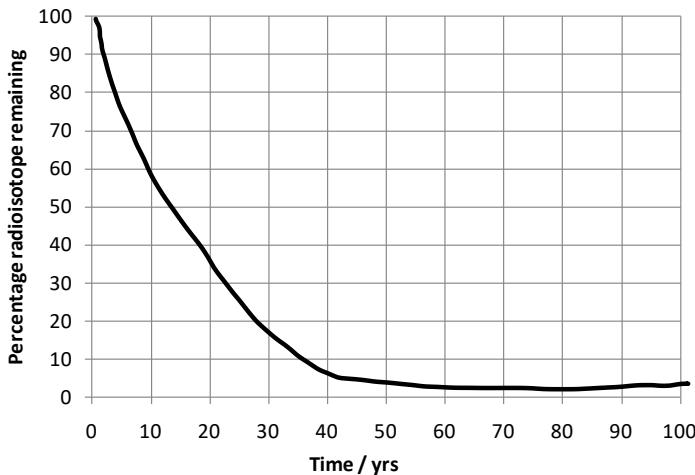
k = decay constant (s^{-1}) = s⁻¹ unit

t = time (s) - s⁻¹ unit.

10. What does each symbol in equation 2 mean? What are the SI units of each symbol?

$t_{1/2}$ = half life, SI unit (s)

k = decay constant, SI unit (s^{-1})



12. The decay constant (k) for ^{131}I is $1.0 \times 10^{-6} \text{ s}^{-1}$. Calculate the half-life of ^{131}I in seconds, and in days.

$$t_{1/2} = \frac{\ln 2}{k} = t_{1/2} = \frac{\ln 2}{1.0 \times 10^{-6}}$$

natural log
 look up a converter
 $t_{1/2} = 6.9 \times 10^5 \text{ s}$ days
 $t_{1/2} = 8.0 \text{ days}$

13. What does each symbol in equation 3 mean? What are the SI units of each symbol?

k = decay constant (s^{-1})

N = number of nuclei

A = activity per second, SI unit (s^{-1} or Bq)

14. What is the value of N when calculating molar activity, A_M ?

Avogadro's number = 6.02×10^{23}

15. A 10.0 mg sample of ^{201}TI has an activity of $7.9 \times 10^{13} \text{ Bq}$. What is the decay constant for ^{201}TI ? What is the half-life of ^{201}TI , in seconds?

$$k = \frac{A}{N}$$

$\uparrow N = 201 \text{ g/mol}$

sample = 10.0 mg/mol

$\therefore 201 \times 1000 = 201000$

$10 \div 201000 = 4.975 \times 10^{-5} \text{ mol}$

x AvO number

$4.975 \times 10^{-5} \times 6.022 \times 10^{23}$

$N = 3.00 \times 10^{19}$

$$k = \frac{A}{N} = k = \frac{7.9 \times 10^{13}}{3 \times 10^{19}}$$

$$= 2.6 \times 10^{-6} \text{ s}^{-1}$$

$$t_{1/2} = \frac{\ln 2}{2.6 \times 10^{-6}}$$

$$t_{1/2} = 2.6 \times 10^5 \text{ s}$$



THE UNIVERSITY OF
SYDNEY

Wave
theory

School of Chemistry

Chemistry 1A
(CHEM1111)

Tutorial 3 (Week 3): The Energy Levels of Electrons

Model 1: Electron Energy

For an atom or ion with a nuclear charge of Z and **one** electron, the energy of the electron is given by the equation below:

$$E_n = -(2.18 \times 10^{-18} \text{ J}) \times \frac{Z^2}{n^2}$$

where $n = 1, 2, 3, 4\dots$. The different values of n correspond to the *allowed* energies that the electron can have. These energies are called “energy levels”. The lowest energy level has $n = 1$ and is called the “ground state”. All other energy levels are called “excited states”. The average distance of an electron from a nucleus is also controlled by the value of n :

$$r_{\text{average}} = (0.529 \times 10^{-10} \text{ m}) \times \frac{n^2}{Z}$$

Critical thinking questions

1. The hydrogen atom has atomic number $Z = 1$. Using the equations above for the energy and average distance of an electron from a nucleus (r_{average}), complete the table below for hydrogen.

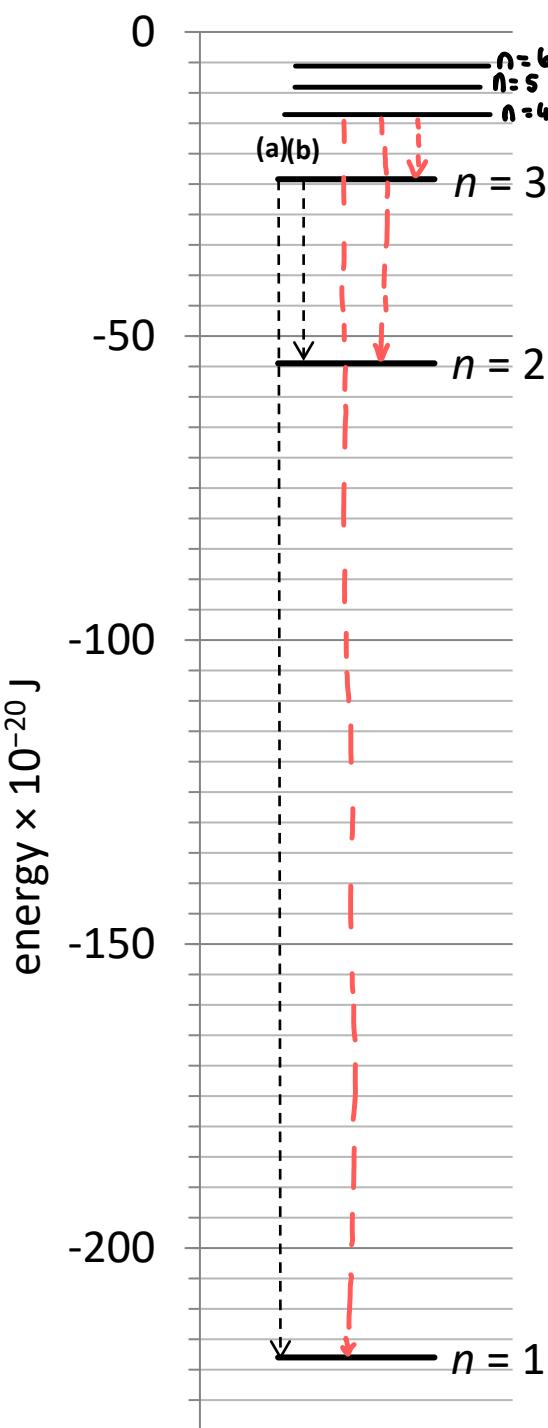
n	$E_n (\text{J})$	$r_{\text{average}} (\text{m})$
1	-218×10^{-20}	0.529×10^{-10}
2	-54.5×10^{-20}	2.12×10^{-10}
3	-24.2×10^{-20}	4.76×10^{-10}
4	-6.06×10^{-20}	8.46×10^{-10}
5	-1.52×10^{-20}	13.2×10^{-10}
6	-3.81×10^{-20}	19.0×10^{-10}

$$-(2.18 \times 10^{-18}) \times \frac{1^2}{n^2} \leftarrow$$

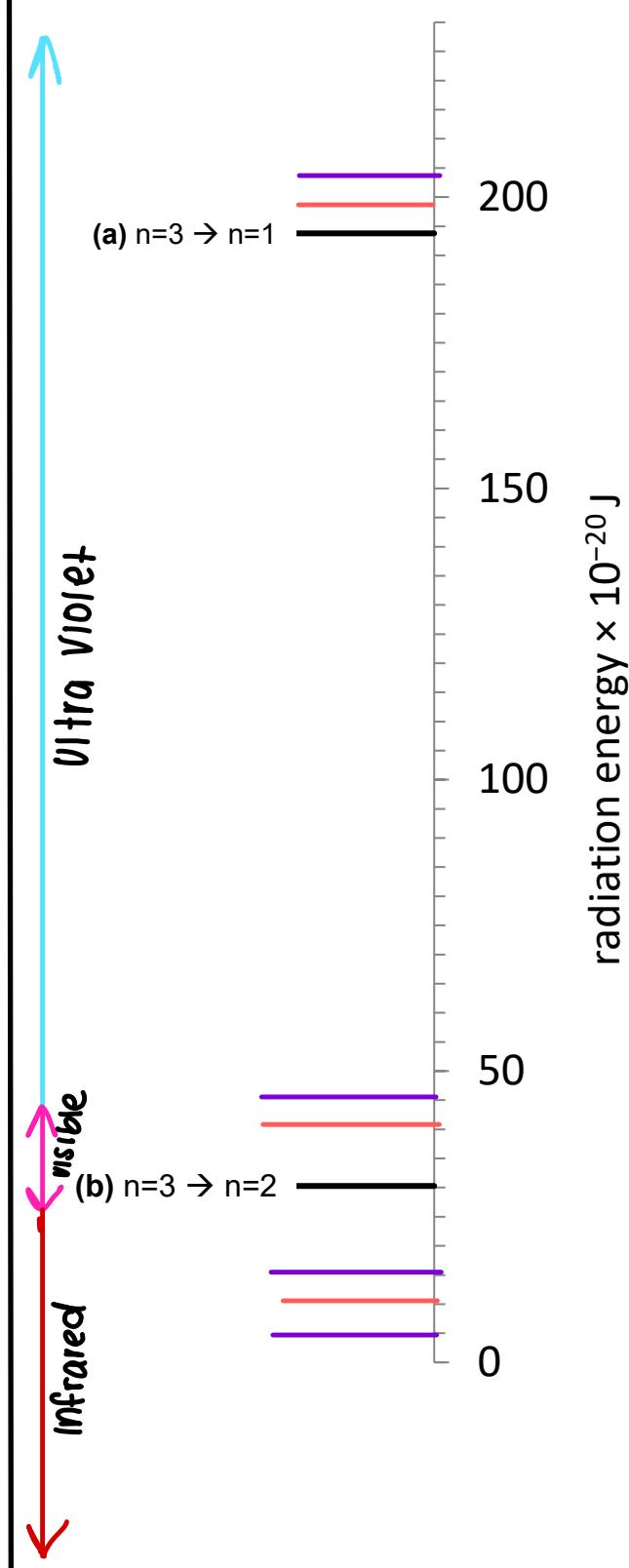
$$\leftarrow (0.529 \times 10^{-10}) \times \frac{Z^2}{1}$$

2. The horizontal lines on the graph on the next page shows the energy levels for $n = 1, 2$ and 3 . Using the values you calculated for E_n , add the energy levels for $n = 4$ to 6 .

Energy levels of the H atom



Atomic Spectrum of the H atom



3. Describe *in words* to your neighbour what happens to the energy levels and the average distance of the electron from the nucleus as n increases. When you have agreed on this, write down your description in a grammatically correct sentence below.

**When gets bigger the energy approaches 0
this means that when energy increases n will increase.**

4. As n gets larger and larger (approaches infinity) what happens to the energy and average distance from the nucleus?

As n gets larger and goes towards infinity, the energy goes towards zero and the average distance between the electron and the nucleus increases.

5. How would these energy levels change for other hydrogen-like ions, e.g. Li^{2+} ?

$\text{Li}^{+3} \rightarrow Z = 3 \text{ protons, } r = (0.529 \times 10^{-10}) \frac{1^2}{3}$ | Each energy would become more negative as $Z = \text{charge on the nucleus}$. This would mean that the energy levels would be lower on the graph.

Model 2: Atomic Spectroscopy

The electron in a hydrogen atom will be in the $n = 1$ level (the “ground state”). However, if energy is provided, an excited H atom is formed in which the electron is in a level with $n > 1$. The electron in this “excited” atom quickly moves (“relaxes”) to a *lower* level and the excess energy is lost (“emitted”) as electromagnetic radiation.

For example, if the excited atom is formed with its electron in the $n = 3$ level, the electron can fall into the $n = 2$ or into the $n = 1$ level. This is shown by the dotted vertical lines on the graph. The energy lost is the *difference* between the two energy levels involved: it is equal to the *length* of the dotted line.

If the electron moves from (a) $n = 3$ to $n = 1$, the energy emitted is equal to $194 \times 10^{-20} \text{ J}$ and (b) $n = 3$ to $n = 2$, the energy emitted is equal to $30 \times 10^{-20} \text{ J}$. These energies can be measured on the graph or calculated using the values in the table on the previous page.

The energy of the emitted light for jumps (a) and (b) is shown by the horizontal lines on the graph of the right hand side overleaf.

Critical thinking questions

6. If the excited atom is formed with the electron in the $n = 4$ level, add dotted lines to the graph on page 2, showing how the electron can relax.
7. For each of these jumps, work out the energy of the emitted light (using the space below) and mark it using a horizontal line on the right hand graph on page 2. **THIS COLOUR
change = final - initial**

$$\begin{aligned} n=4 \longrightarrow n=3 & - 24.2 \times 10^{-20} - (-13.6 \times 10^{-20}) = 10.6 \times 10^{-20} \text{ J} \\ \longrightarrow n=2 & - 54.5 \times 10^{-20} - (-13.6 \times 10^{-20}) = 40.9 \times 10^{-20} \text{ J} \\ \longrightarrow n=1 & - 218 \times 10^{-20} - (-13.6 \times 10^{-20}) = 204 \times 10^{-20} \text{ J} \end{aligned}$$

numbers from table on page 11

8. Repeat questions 6 and 7 for an excited atom formed with the electron in the $n = 5$ level. Space is provided below for working out. **THIS COLOUR**

$$n=5 \longrightarrow n=4 \quad -13.6 \times 10^{-20} - (-8.72 \times 10^{-20}) = 4.88 \times 10^{-20} \text{ J}$$

$$n=3 \quad -24.2 \times 10^{-20} - (-8.72 \times 10^{-20}) = 15.5 \times 10^{-20} \text{ J}$$

$$n=2 \quad -54.5 \times 10^{-20} - (-8.72 \times 10^{-20}) = 45.8 \times 10^{-20} \text{ J}$$

$$n=1 \quad -218 \times 10^{-20} - (-8.72 \times 10^{-20}) = 209 \times 10^{-20} \text{ J}$$

9. The right hand graph represents the energy of the emitted radiation for the hydrogen atom. You have drawn its "atomic spectrum".

Light with energy *less* than $28 \times 10^{-20} \text{ J}$ is the infrared region. Light with energy *greater* than $50 \times 10^{-20} \text{ J}$ is ultraviolet. Visible light lies between these values. Mark these regions on your spectrum.

10. What is the relationship between the energy (E) and wavelength (λ)?

- (a) What wavelengths correspond to the upper and lower limits of visible light given above?

$$7.1 \times 10^{-7} \text{ m (710 nm)} \text{ to } 4.0 \times 10^{-7} \text{ m (400 nm)}$$

- (b) What colours correspond to these limits (see table below)?

Red to violet

11. What do the lines in the visible part of the spectrum have in common?

$$n=2$$

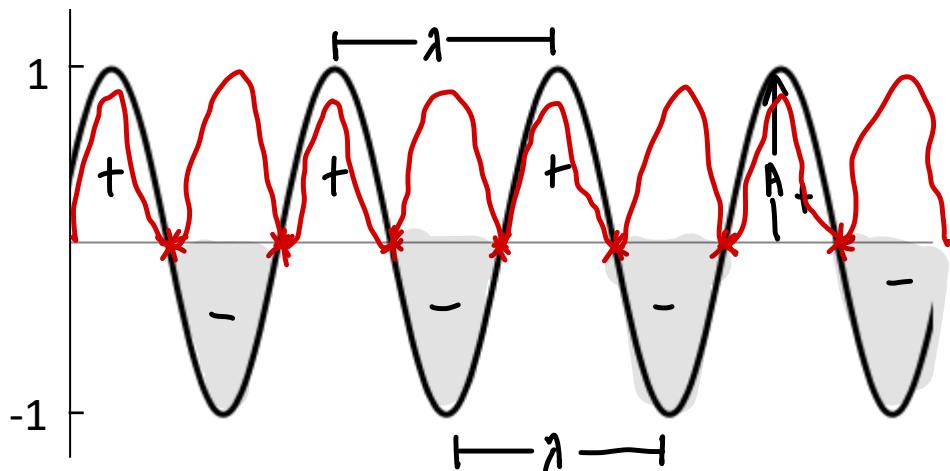
12. What do the lines in the ultraviolet part of the spectrum have in common?

$$n=1$$

colour	red	orange	yellow	green	blue	violet
wavelength (nm)	630–750	690–630	560–590	480–560	430–480	400–430

Model 3: Light and Waves

The picture below shows a light wave. The wavelength is the distance between peaks (or the distance between troughs). The amplitude is the height of the wave counted from 0 (= height of a peak or depth of a trough). We cannot see these waves. Instead, our eyes detect the *intensity* of the light which is given by the *square* of the wave.



Squaring means multiplying the wave at each point by itself, remembering that positive \times positive and negative \times negative are both positive.

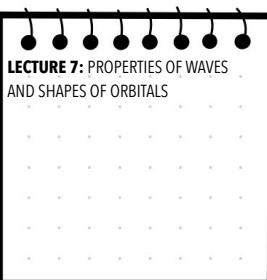
Critical thinking questions

13. On the diagram, indicate the wavelength (λ) and the amplitude (A) of the wave.
14. Put an asterisk ("*") to mark the positions where the amplitude of the wave changes its sign. These are 'nodes'.
15. Peaks are where the wave is positive. Troughs are where the wave is negative. Label these with "+" and "-" signs respectively. *Lightly shade* the "-" areas.
16. On top of the picture, draw a sketch of the *intensity* of the light.

↑
Square the
Waves
↓
Note: this IS
ASSUMING
the amplitude
IS 1

A T O M I C

S T R U C T U R E



LECTURE 7: PROPERTIES OF WAVES AND SHAPES OF ORBITALS

LECTURE 7: PROPERTIES OF WAVES AND SHAPES OF ORBITALS

Electrons are waves and particles

Niels Bohr postulates a set of circular orbits for electrons with specific, discrete radii and energies where electrons could move. But electrons do not move in circular orbits, instead, the discrete energy levels are a direct consequence of wave behaviour.

Why is there a minimum energy?

In the Bohr model the lowest energy electron in an atom is assumed to follow an orbit closest to the nucleus. However in classical theory an orbiting charged particle radiates energy. Thus the electron should lose energy and spiral into the nucleus.

The fundamental energy

On any musical instrument it is impossible to play a note lower than the fundamental (lowest possible pitch). The energy of the fundamental of any standing wave depends on the degree of confinement. What confines an electron wave in an atom? Electrostatic attraction to the nucleus

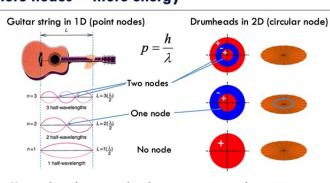
LO: RECALL THE BORN INTERPRETATION OF THE ELECTRON WAVE

An electron wave function in itself is not the informative. The quantity we are interested in is the probability of finding the electron at a particular point in space (electron density), which is given by the square of wave function.

Wave function squared is always positive, so the probability of finding an electron is positive, regardless of the sign of the wave. **Analogy:** light (which also moves in a wave). We cannot measure the amplitude, but we can measure the intensity (brightness), which is the square of the amplitude (photo density)

LO: UNDERSTAND THE REPRESENTATION OF WAVES AS CROSS-SECTIONAL GRAPHS, CONTOUR PLOTS AND LOBE REPRESENTATIONS

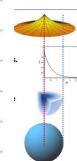
More nodes = more energy



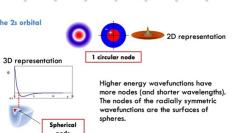
as the wave length gets shorter the momentum gets bigger
the nodes that the wave length has the more energy - that corresponds to shorter wave length and high Kinetic energy

LO: DRAW LOBE REPRESENTATION OF S ORBITALS

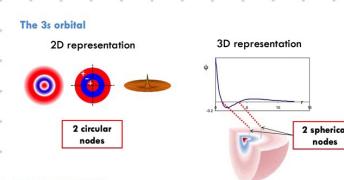
Lowest (1s)



2s



3s



orksheet questions 2 and 3

LO: RECALL THAT S ORBITALS HAVE N-1 NODES

1s orbital

This orbital can be represented as a radial function - this plot shows the amplitude of 1s wave function, plotted as a function of distance, r , away from nucleus. The max amplitude is at the nucleus. Or as gradient or contour. The intensity of the shading indicates the the amplitude of the wave function, which max at the nucleus and decreases with increasing r . Or simply as a lobe. The spherical lobe indicates how far a certain level of electron density extends from the nucleus.

The 2s orbital

Higher energy wave function have more nodes (shorter wavelengths). The nodes of the radially symmetric wave functions are the surface of spheres. **Has one node**

The 3s orbital

Has 2 nodes.

LO: EXPLAIN WHY ORBITALS SIZE INCREASES WITH ENERGY

Becomes higher in energy as the size increases because the distances from the nucleus increases

LO: IDENTIFY THE PRINCIPAL QUANTUM NUMBER

Principle quantum number, n

1s	$n = 1$, zero nodes, $E = -E_0(Z^2/1^2)$	$n = 1$ nodes
2s	$n = 2$, one spherical node, $E = -E_0(Z^2/2^2)$	
3s	$n = 3$, two spherical nodes, $E = -E_0(Z^2/3^2)$	
4s	$n = 4$, three spherical nodes, $E = -E_0(Z^2/4^2)$	

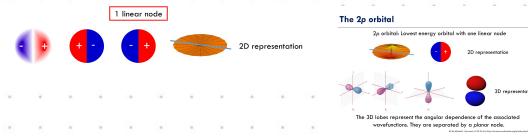


LECTURE 8: SHAPES OF P AND D ORBITALS

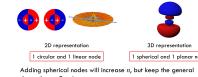
LECTURE 8: SHAPES OF P AND D ORBITALS

Linear Nodes

Drum heads can also generate asymmetrical standing waves of various kinds. In the simplest kind of harmonic the membrane is halved, making linear nodes and in 3D we will observe a planar node. The lowest energy p-orbital ($2p$) already has a node so has more energy than $1s$ orbital. It also has a higher energy because it is larger and its electron are hence on average further away from the nucleus.



3p orbitale



LO: UNDERSTAND THE MEANING OF THE ORBITAL QUANTUM NUMBERS N,L,M CI AND DESIGNATION OF ORBITALS SUCH AS 1S, 3D, 4F

Anhalt momentum quantum number

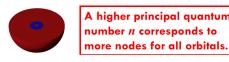
The principle quantum number can't differentiate between 2p and 2s. As we have seen from the de Broglie relation, free electrons have nothing momentum and wavelength. Electron bound in orbitals also have angular momentum, which is described by additional quantum numbers. Like energy, angular momentum is quantised into discrete values. Spherically symmetric (s) orbitals have 0 angular momentum. Other shapes of orbitals do have angular momenta, that are integer multiples of $h/2\pi$. This integer is the orbital angular momentum quantum number, l . I may take on any values between 0 and $n-1$. For $n=1$, $l=0$ only an s orbital is possible, for $n=2$, $l=0$ (s orbitals) or 1 (p orbitals)

Magnetic quantum number, m ,

The number of orbitals with a given angular momentum quantum number l is determined by their shape. For example, for the p orbitals we have 3 different orientations p_x, p_y and p_z . This is characterised by the magnetic quantum number m or m_l , m can take any integer value between $-l$ and l , and describe the orientation of the orbital. For $l=0, m=0$ (s orbital), for $l=1, m=-1, 0, +1$ (three p orbitals). for a given l , there are always $2l+1$ orbitals. Quantum states or wave function of equal energy are referred to as degenerate. The $2p_x, 2p_y$ and $2p_z$ orbitals are degenerate.

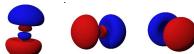
3d orbitals

When $n=3$, l can be 0 (one 3s). 3s orbitals have two spherical nodes.

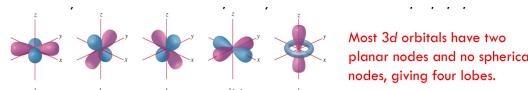


A higher principal quantum number n corresponds to more nodes for all orbitals.

Or $l=1$ (there 3p orbitals) 3p orbitals ($3p_x$, $3p_y$, $3p_z$) have one planar nodes and one spherical nodes

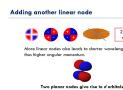


Or $l=2$ (d orbitals) $3d$ orbitals have more lobes than $2p$ orbitals, and their shape is obviously different, for d -orbitals, m may take on five values: $-2, -1, 0, 1, 2$. Most $3d$ orbitals have two planar nodes and no spherical nodes, giving four lobes.



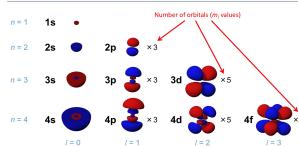
Most 3d orbitals have two planar nodes and no spherical nodes, giving four lobes.

LO: RECOGNISE THE REPRESENTATION OF WAVES AS A CROSS-SECTIONAL GRAPH, CONTOUR PLOT AND LOBES



10. RECOGNISE THE SHAPES OF ATOMIC ORBITALS

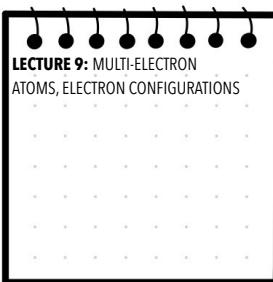
s, p, d and f orbitals and quantum numbers



10: DEDUCE THE NUMBER OF NODAL PLANES AND SPHERES FOR A S P OR D ORBITAL

Q. DRAW THE LORE REPRESENTATION FOR A B ORBITAL.

LECTURE 9: MULTI-ELECTRON ATOMS, ELECTRON CONFIGURATIONS



Spin quantum number, m_s

- describe the spin of the electron
- each electron behaves like a magnet, so with an odd number of electrons may be deflected in an homogeneous magnetic field

Multi-electron atoms:

For one-electron (also referred to as hydrogen-like atoms), the energy of orbitals is determined by its principal quantum number, n .

For multi-electron systems, n is no longer sufficient to predict energy levels. We have to consider:

- Electron-electron repulsion: when we have more than one electron, the electrons within an orbital repel each other.
- Orbital shielding: when an orbital is occupied, it shields the interaction of the outer orbital with the nucleus. This alters the energy levels of the orbitals. Orbital shielding depends on the shape of the orbital: $s < p < d < f$.

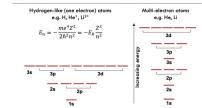
LO: EXPLAIN ORBITAL SHIELDING AND ITS EFFECTS

After He, the $n=1$ orbital is full, we now need to which orbital ($2s$ or $2p$) has lower energy, for a 1-electron atom, $2s$ and $2p$ have the same energy. For an atom with more than one electron, electrons in orbitals closer to the nucleus shield electron that are further away, shielding has the effect of decreasing the positive attraction from the nucleus, raising its energy. The $2s$ orbital has a lobe closer to the nucleus than the $2p$ orbital, so it is less shielded and therefore has lower energy.

LO: WRITE THE ELECTRON CONFIGURATION OF ATOMS AND IONS FROM THE S AND P BLOCKS

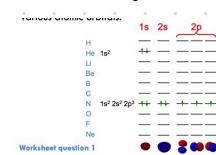
Electron configuration are often represented in an orbital diagram, which explicitly shows the number of electrons and indicates their spins in various atomic orbitals

Hydrogen like vs. multi-electron



Filling higher orbitals

The same rules apply for the orbitals filling as we deduced for $n=2$. First the $3s$ orbitals are filled then $3p$. As the angular momentum quantum number, l , increases, the orbitals extended further from the nucleus. This means that the energy of an orbital increases with l for a given n . This effect is big enough that the energy of the $4s$ orbital is lower than the $3d$. The order of the filling:



Valence electrons

The classic model of the atom includes the concept of electron 'shells'. The outmost shell of electrons, outside the rare-gas core (Noble gas configuration) are called the valence electrons. Electronic configuration can also be written in short hand form using noble gases as shown below. Valence electrons are important in the formation of chemical bonds. They will lie in the same group in the periodic table, and form compounds with the same group in the periodic table and form compounds with the same stoichiometry. Noble gases are unreactive because they contain filled electron shells.

LO: IDENTIFY ANY ELEMENT FROM THE ELECTRIC CONFIGURATION OF ITS ATOM OR ION

Electron configuration: Using the atomic orbitals obtained for the hydrogen atom, we fill orbitals beginning with the lowest energy, for helium (2 electrons):

Electron 1 - $1s$ orbital ($n=1, l=0, m_l=0$) with $m_s = +\frac{1}{2}$ (or $-\frac{1}{2}$)

Electron 2 - $1s$ orbital ($n=1, l=0, m_l=0$) with $m_s = -\frac{1}{2}$ (or $+\frac{1}{2}$)

The ground state electron configuration of He is written as $1s$. (For H it is written as $1s$).

LO: PARAPHRASE THE PAULI EXCLUSION PRINCIPLE, AUFBAU PRINCIPLE AND HUND'S RULE

Pauline exclusion and Aufbau principles:

The quantum state of an electron is specified by the orbital quantum numbers n, l , and m_l , plus an electron spin quantum number m_s .

Rule 1: The PAULI EXCLUSION PRINCIPLE says that no two electrons in an atom may be in the same quantum state

In other words, no two electrons can have the four quantum numbers n, l, m_l and m_s .

Rule 2: The AUFBAU PRINCIPLE states that electrons in atoms (and molecules) generally exist in their lowest possible energy state. This is called the ground state

Hund's Rule:

After Be, the $1s$ and $2s$ orbitals are full. The $2p$ orbital are next. If we remember the shape of the p orbitals, then having one electron in each p orbital will keep the electron as far from each other as possible. This is a way of accounting for the repulsive potential energy between electrons. HUND'S RULE: the lowest energy electron configuration in orbitals of equal energy is the one with maximum number of unpaired electrons with parallel spins.

Summary of rules

Pauli Exclusion Principle. No two electrons in an atom may be in the same quantum state $\{n, l, m_l, m_s\}$

Aufbau Principle. Electrons generally adopt the lowest possible energy configuration.

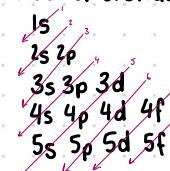
Orbital Shielding. For orbitals of equal n , those nearest the nucleus have the lowest energy: $s < p < d < f$...

Hund's Rule. Maximise the number of parallel unpaired electron spins in degenerate orbitals.

LO: RECOGNISE THE CONSEQUENCES OF HUND'S RULE ON THE DETAILED ELECTRONIC CONFIGURATION OF AN ATOM



Order of orbitals



E _g	[He] 2s ² 2p ²	O ₂ ⁻	Cl ₂
C	[He] 2s ² 2p ²	CO ₂	Cl ₂
N	[He] 2s ² 2p ³	NO ₂	Cl ₂
O	[He] 2s ² 2p ⁴	NO ₂	Cl ₂
F	[He] 2s ² 2p ⁵	NO ₂	Cl ₂
Ne	[He] 2s ² 2p ⁶	NO ₂	Cl ₂

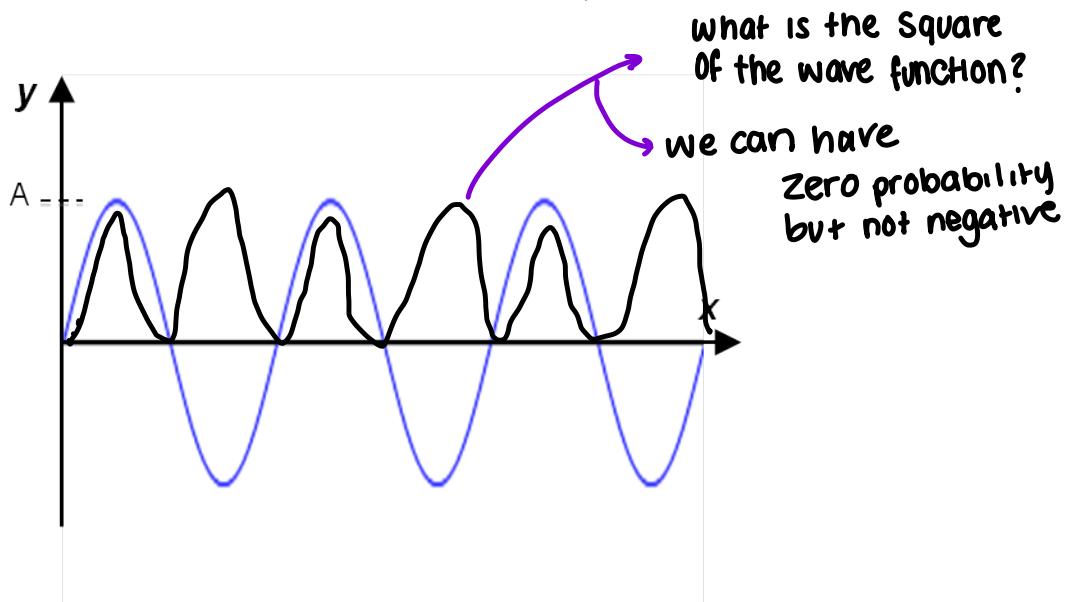
CHEM1111 worksheet – Lecture 7

Electron waves

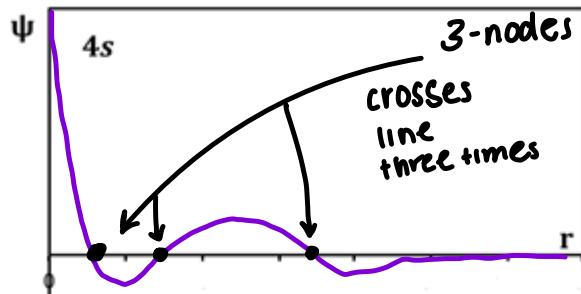
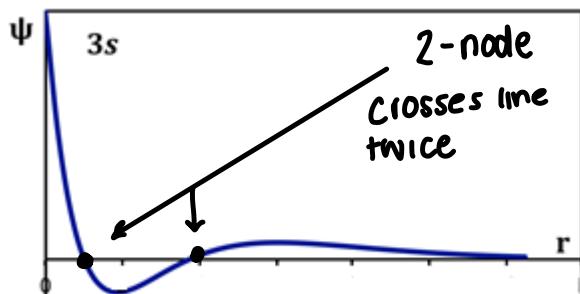
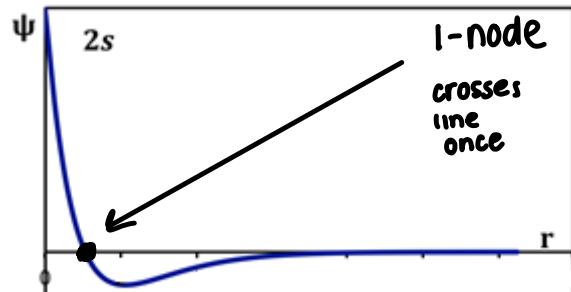
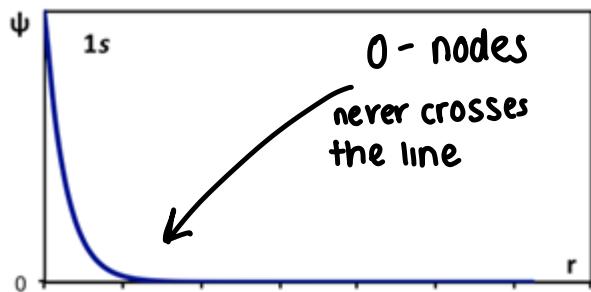
1. The graph below shows a 1-dimensional light wave, y vs. x using the following equation.

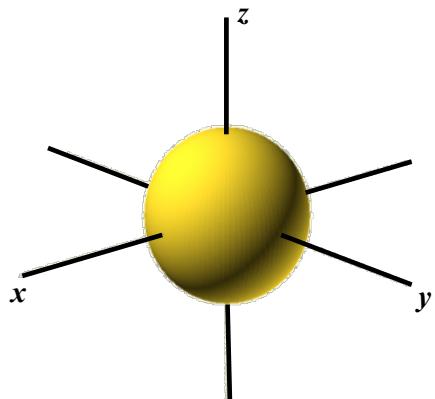
$$y = A \sin\left(\frac{2\pi}{\lambda} x\right)$$

On the same graph, sketch the plot of the squared form of the wave i.e. y^2 vs. x .



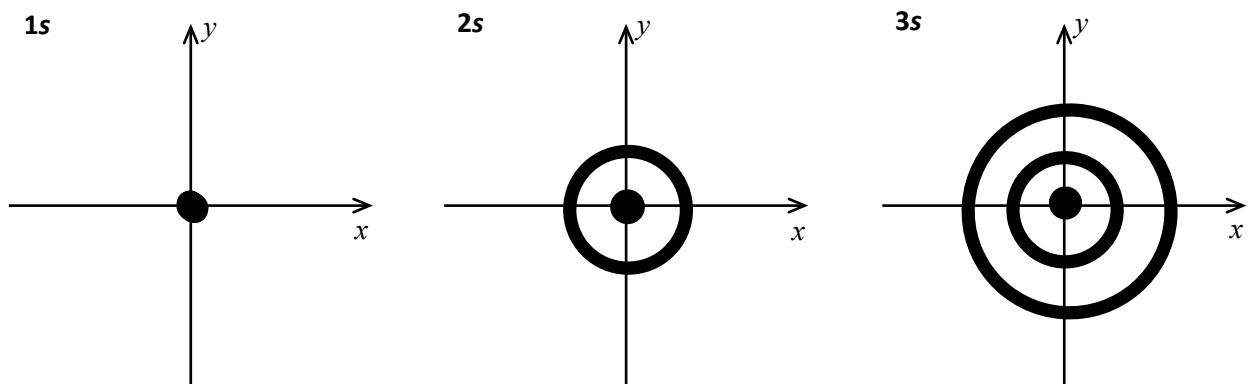
2. The radial functions of the 1s, 2s and 3s orbitals are shown below. Predict the radial function for the 4s orbital.





The 90% boundary surface diagram of an s orbital is shown to the left, which represents the solid surface, which encloses 90% of the electron density. Within this region, the electron density will vary depending on the principal quantum number, n .

3. Imagine that you take a cross-section of the orbital on the x-y plane (for $z = 0$). Draw the resulting electron density for a 1s orbital, 2s orbital and 3s orbital.



How would this change if you were to travel along the y-axis

→ It would look the same as they are spherical

The more nodes it has the more energy
e.g 3s has higher energy than 2s

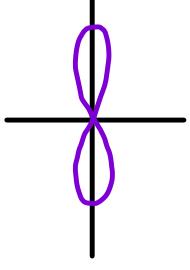
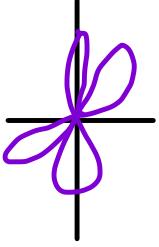
CHEM1111 worksheet – Lecture 8

Atomic orbitals

- Fill in the following table.

	1s	2s	3s	2p	3p	3d
Principal quantum number (n)	1	2	3	2	3	3
Total number of nodes $n-1 = \text{total number of nodes}$	$1-1=0$	$2-1=1$	$3-1=2$	$2-1=1$	$3-1=2$	$3-1=2$
Number of planar nodes	0	0	0	1	1	2
Number of spherical nodes	0	1	2	0	1	0
Orbital angular momentum quantum number ($l = \text{total } n. \text{ nodes}$)	0	0	0	1	1	2
Magnetic quantum numbers (m_l) $l-l=$	0	0	0	1, 0, -1	1, 0-1	$2, 1, 0$ $-1, -2$
Number of orbitals of this type	1	1	1	3	3	5

2. Look at the following orbitals on the Hydrogenic Atom Viewer (), and fill in the table.

	$2p_x$	$4p_z$	$3d_{yz}$
Number of planar nodes	1	1	2
Number of spherical nodes	0	2	0
Total number of nodes	1	$4-1=3$	2
n	2	4	3
l	1	1	2
Sketch of orbital			

CHEM1111 worksheet – Lecture 9

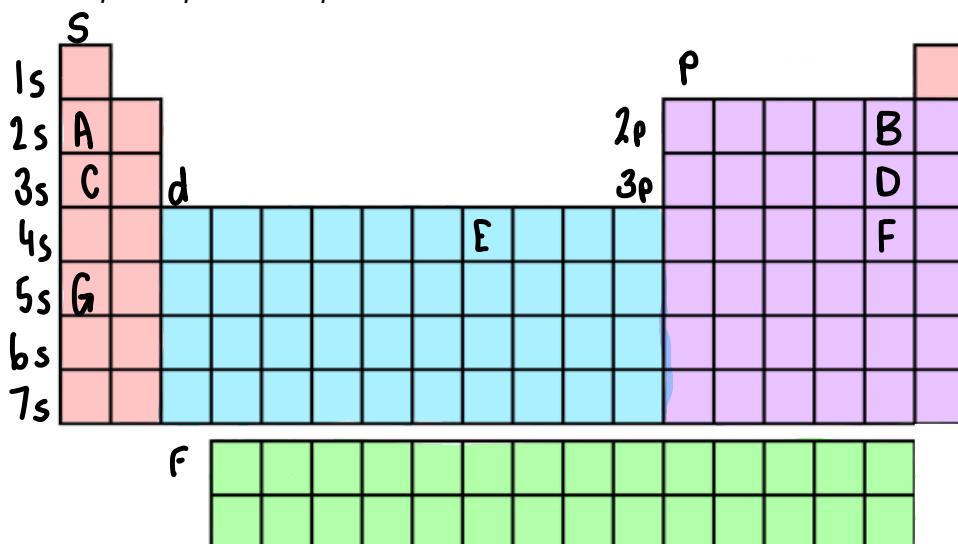
Multi-electron atomic configurations

1. Complete the electronic configurations for the first ten elements and fill in the orbital diagrams, showing distribution of electrons between the orbitals. Nitrogen is completed for you as an example.

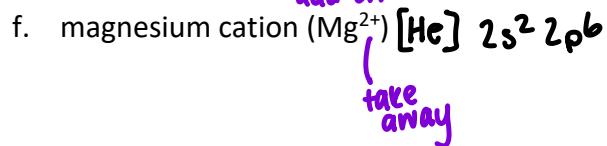
	$1s$	$2s$	$2p$
H	1	—	— — —
He	11	—	— — —
Li	11	1	— — —
Be	11	11	— — —
B	11	11	1 — —
C	11	11	1 1 —
N	$1s^2 2s^2 2p^3$	11	1 1 1
O	11	11	1 1 1
F	11	11	1 1 1
Ne	11	11	1 1 1

2. On the following periodic table, label the *s*, *p*, *d*, *f* blocks and then mark where you would find atoms with electronic configuration:

- a. $1s^2 2s^1$
 - b. $1s^2 2s^2 2p^5$
 - c. $1s^2 2s^2 2p^6 3s^1$
 - d. $1s^2 2s^2 2p^6 3s^2 3p^5$
 - e. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$
 - f. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$
 - g. $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$



3. Write out the electronic configuration of the following atoms and ions:



take away

4. For the atoms and ions in question 3, write out their configurations in shorthand form (in terms of the noble gas configuration).

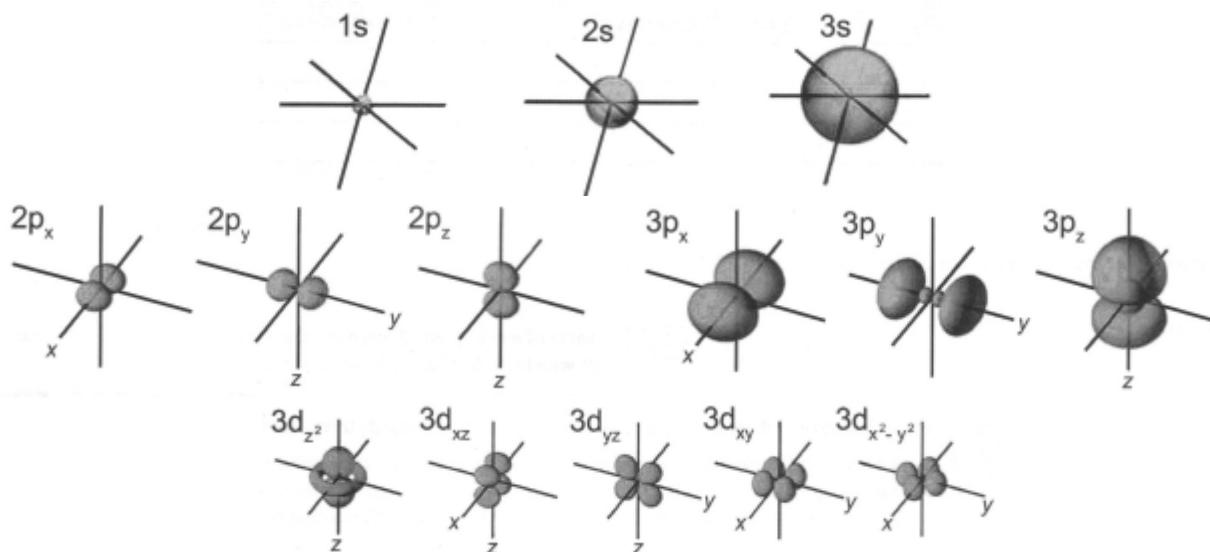
Tutorial 4 (Week 4): Quantum Chemistry

Model 1: Atomic Orbitals and Quantum Numbers

The wave functions for electrons in atoms are given the special name ‘atomic orbitals’.

As we explored last week, the energy levels of hydrogen-like (one-electron) atoms are determined by a single quantum number, n . For other atoms, more quantities are involved in determining the shape and orientation of the atomic orbitals; the *angular momentum quantum number*, l , and *magnetic quantum number*, m_l .

Name	Characterises	symbol	Allowed values
Principal	Size and energy. Total $n-1$ nodes.	n	$n = 1, 2, 3, \dots$
Angular Momentum	Shape. Energy in multi-electron atoms. l planar nodes.	l	$l = 0, 1, 2, \dots, n-1$
Magnetic	Orientation	m_l	$m_l = -l, 1-l, \dots, 0, \dots, l-1, l$
Spin	Electron spin	m_s	$m_s = \pm \frac{1}{2}$



Critical thinking questions

- Which quantum number identifies the shape of an orbital?
- For each value of $n = 2, 3$ and 4 , what are the possible values for l , and what labels correspond to these orbitals?

n	Possible l values	Orbital labels
1	0	s
2	0, 1	s, p
3	0, 1, 2	s, p, d
4	0, 1, 2, 3	s, p, d, f

- For each value of $l = 0, 1, 2$, what are the possible values for m_l , and what are the labels for the orbitals with this set of m_l values?

l	Possible m_l values	Orbital labels
0	0	s
1	-1, 0, 1	2p _x , 2p _y , 2p _z
2	-2, -1, 0, 1, 2	3d _{z²} , 3d _{xz} , 3d _{yz} , 3d _{xy} , 3d _{x²-y²}
3	-3, -2, -1, 0, 1, 2, 3	7f

- How many *planar nodes* (a plane where electron density is zero) do s, p and d orbitals have?

$$S = 0$$

$$P = 1$$

$$D = 2$$

- What is the relationship between the value of the angular momentum quantum number and the number of such *planar nodes*?

The number of planer nodes is equal to the value of the angular momentum quantum number, l .

- How many *spherical nodes* do each of these orbitals have: 2s, 3p_z, 3d_{x²-y²}?

$$\begin{array}{lll} n-l-1 & 2s: & 3p_z \quad 3d_{x^2-y^2} \\ & 2-1=1 & 2-1=1 \quad 1-1=0 \end{array}$$

Model 2: Atomic orbitals in multiple-electron atoms

Critical thinking questions

7. Discuss with your group and write down definitions of

a. *The Aufbau Principle*

orbitals are filled with electrons in order of energy with the lowest energy orbital getting filled first.

b. *Pauli Exclusion Principle*

no two electrons may have the same set of quantum numbers.

Each orbital can accommodate no more than 2 electrons. These two electrons will have Opposite spin (m_s)

c. *Hund's Rule*

In a set of orbitals with the same energy, electrons may not be spin-paired until each orbital contains one electron

8. Fill in the ground state electronic configuration for a carbon atom on the diagram to the right.

a. Why isn't the electron configuration of carbon $1s^2 2s^3 2p^1$?

Pauli principle

b. Why isn't it $1s^2 2s^2 2p_x^2$?

Hund's rule: Can't spin pair until all $2p$ have electrons

9. In atomic orbital diagrams, a horizontal line indicates a single atomic orbital. Based on the Pauli Exclusion Principle, what is the maximum number of electrons that can be drawn on a single line?

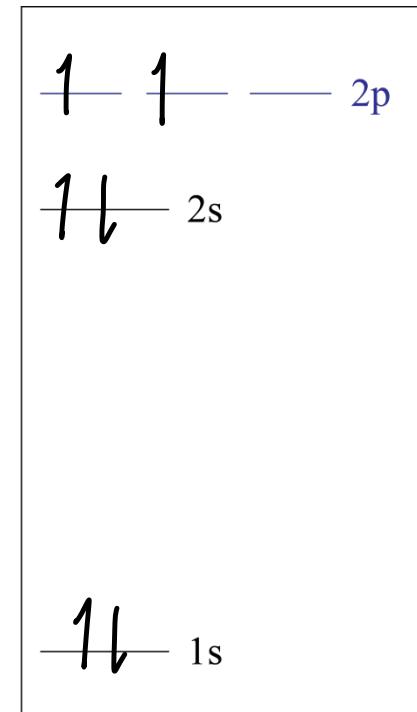
2 electrons

10. How many electrons can there be in the $1s$ orbital? How will this change for a $2s$ or $3s$ orbital?

maximum of 2 electrons

11. How many electrons can there be altogether in the $2p$ orbitals? How will this change for $3p$ and $4p$?

p orbitals always have 6



12. The following ground state electron configurations disobey one of the rules that you defined in question 7. State what is wrong with each configuration, and write the correct configuration.

a) $1s^2 2s^2 2p^6 3s^2 3p^4 4s^1$ ISSUE: $3p^4$ not full — underfull

correct: $1s^2 2s^2 2p^6 3s^2 3p^5$

b) $1s^2 2s^2 2p^6 3s^2 3p^7$ ISSUE: $3p^7 \rightarrow$ overfilled electrons

correct: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$ ISSUE: $3d^2 \rightarrow$ fill 4s before 3d

correct: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$

d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 3f^2$ ISSUE: $3f^2 \rightarrow$ 3f does not exist, f orbitals don't start until 4th

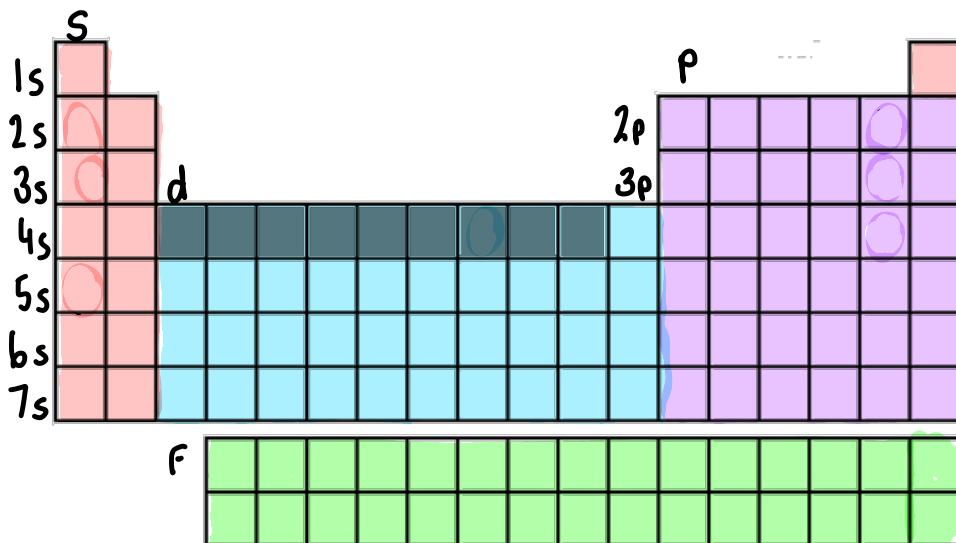
correct: $1s^2 2s^2 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^2$

Model 3: Electronic Configurations in Atoms and Ions

Atoms are arranged in the periodic table in blocks according to the orbital that is being filled.

Critical thinking questions

13. On the periodic table below, mark the s block, the p block, the d block and the f block.



14. The row shaded in grey corresponds to a partially-filled 3d orbital. Which orbital is filled before this? What is the reason for this order?

Atom or ion	Number of protons	Number of electrons	Electron configuration	Noble gas configuration (shorthand electron configuration)
Cl	17	17	$1s^2 2s^2 2p^6 3s^2 3p^5$	[Ne]3s ² 3p ⁵
Ar	18	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	[Ar]
K	19	19	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	[Ar]4s ¹
Ca	20	20	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	[Ar]4s ²
Cl ⁻	17	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	[Ar]
K ⁺	19	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	[Ar]
Ca ²⁺	20	18	$1s^2 2s^2 2p^6 3s^2 3p^6$	[Ar]
Zn	30	30	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	[Ar]4s ² 3d ¹⁰
Sr	38	38	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2$	[Kr]5s ²
Sr ²⁺	38	36	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$	[Kr]

15. Complete the table above. Chlorine has been completed for you as an example.

16. *Isoelectronic* refers to species that have the same electron configuration. From the table above, identify the isoelectronic species.

Ar, Cl⁻, K⁺, Ca²⁺

17. Suggest an atom or ion that would be isoelectronic with Sr²⁺.

Kr, Rb⁺, Br⁻, Se²⁻

18. The periodic table allows us to predict which atoms will have similar chemical properties. From the table above, which atom or ion will have similar chemical properties to Ca?

Sr

19. Elements whose atoms have one electron in the valence s orbital are called alkali metals. Which element(s) from the table above are alkali metals?

K

20. Elements whose atoms have five electrons in their valence p orbitals are called halogens. Which element(s) from the table above are halogens?

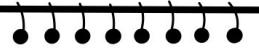
Cl

21. Elements in the d block are called transition metals. Which element(s) from the table above are transition metals?

Zn

MOLECULAR ORBITAL THEORY

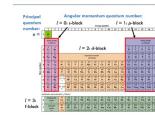
M O L E C U L A R
O R B I T A L
T H E O R Y

**LEARNING OUTCOMES**

1. RECOGNISE TRENDS IN THE PERIODIC TABLE, SUCH AS ATOMIC RADII, IONIC RADII AND IONISATION ENERGIES
2. UNDERSTAND AND EXPLAIN REASONS FOR THESE TRENDS
3. USE TRENDS TO PREDICT REACTIVITY

1. RECOGNISE TRENDS IN THE PERIODIC TABLE, SUCH AS ATOMIC RADII, IONIC RADII AND IONISATION ENERGIES

Periodic table

**Anionic Radii**

When forming an anion, electrons are usually added to the same orbitals. More electrons \rightarrow more electronic repulsion
General rule: anions (negative ions) of atom always have bigger atoms than the original atom

Cationic Radii

When forming a cation, electrons are removed from the outer orbital. Now the valence orbital is closer to the nucleus \rightarrow cations are smaller than the original atom
Ionisation Energy

Ionisation energy (E_i) is the amount of energy required to remove an electron completely from an atom. Ionisation requires input of energy, so energy will always be positive. Larger Z_{eff} = electrons held more tightly to nucleus, electrons are harder to remove and higher ionisation. Across the period \rightarrow electrons are attracted more strongly by nucleus and higher ionisation.

Down the periodic group \rightarrow electrons are added to orbitals that are further from nucleus, weaker nucleus attraction and lower ionisation.

Electron affinity

Energy required to add an electron to a neutral atom to construct an anion. When electron affinity is large that mean the atom likes to take on the extra electron. The halide ions like to do this as it completes their electron shells

2. UNDERSTAND AND EXPLAIN REASONS FOR THESE TRENDSEFFECTIVE NUCLEAR CHARGE

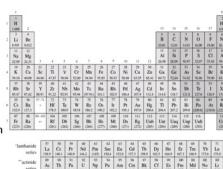
Nuclear charge (Z) = number of protons in nucleus

Effective nuclear charge (Z_{eff}) = positive charge felt by an electron in a multi-electron atom.

Electrons in the outer orbitals are partially shielded from the nuclear charge resulting in a weaker attraction and a lower Z_{eff} .

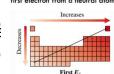
3. USE TRENDS TO PREDICT REACTIVITY**Metals vs non-metals****METALS**

Elements have a very low ionisation energy (readily lose electrons)



NON-METALS
Elements have an affinity for electrons (readily gain electrons)

The first ionisation energy is the energy required to remove the first electron from a neutral atom.



Decreases

Increases

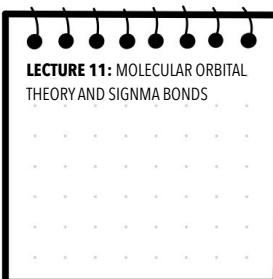
Largest

Smallest

Decreases

Increases</p

LECTURE 11: MOLECULAR ORBITAL THEORY AND SIGMA BONDS



LECTURE 11: MOLECULAR ORBITALS THEORY

LO: EXPLAIN HOW ELECTRON SHARING LEADS TO LOWERING OF ELECTRONIC ENERGY IN TERMS OF INCREASING THE DE BROGLIE WAVELENGTH

Covalent bonding

As atoms come together, electrons begin to be shared between two nuclei. Wavelength is increased, so energy is decreased (de Broglie).

When nuclei are too close together, nuclei repel each other.



bond length

The equilibrium (minimum energy) bond length is approx 1 Å. The Angstrom (Å) is a unit to discuss atomic distances. 1 Å = 10^{-10} m (= 0.1 nm). The Bohr Radius is the most probable distance between a proton and an electron in a H atom. The Bohr radius is 0.53 Å.

Number of orbitals

Electron an atom are described by atomic orbitals 2 electron can occupy each atomic orbitals. Electrons in a molecule are described by molecular orbital 2 electrons can occupy each molecular orbitals (one spin up and one spin down)

Total number of atomic orbitals in a component atom = number of molecular orbitals

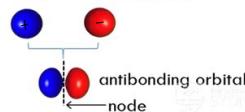
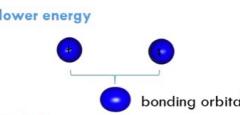
Mixing of orbitals

In σ orbitals \rightarrow 2 x molecular orbitals

The two molecular orbitals arise from mixing of orbitals in different phases.

When two 1s orbitals in the same phases mix, the result is an orbital with

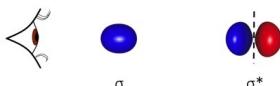
When two 1s orbitals in the opposite phase mix, the result is an orbital with a node with a node, i.e. higher energy



LO: RECOGNISE A σ ORBITAL AND A σ^* ORBITAL

Sigma (σ) orbitals and bonds

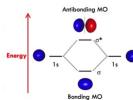
Looking along the bind axis, these orbitals look round, like s orbitals. Orbitals of this type are called sigma (σ) orbitals (the Greek leere for s). Bonding orbital area; antibonding orbitals are (Sigma-star). Bonds that result from sigma orbitals are called sigma bonds



LO: RECOGNISE A BONDING OR ANTBONDING ORBITAL FROM THE LOBE REPRESENTATION

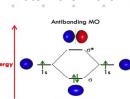
Bonding and antibonding orbitals

In general, atomic orbitals form pairs of bonding and antibonding molecular orbitals, one without a node between the nuclei (bonding) and one with a node between the nuclei (antibonding)



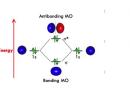
The H₂ molecule

The electron from each H atom are in the bonding orbitals. The electrons in H₂ have lower energy than the electrons in 2 H atoms.

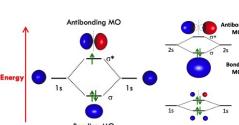


The He dimer

In He₂, the 4 electrons fill both the bonding and antibonding orbitals. The electrons in He₂ do not have lower energy than the electrons in 2 He atoms \rightarrow this molecule does not form.

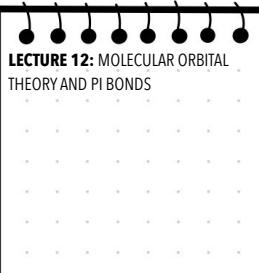


In He₂, the bonding orbital has 2 electrons and the antibonding orbitals has 1. The electrons in He₂ have lower energy than the electrons in 1 He atom and 1 He+ ion atoms \rightarrow this molecule can be observed.



Li₂

The 2s orbitals form molecular orbitals in the same way as 1s orbitals – a bonding MO and an antibonding MO. In Li₂, the 1s orbitals do not contribute to bonding, because both the bonding and anti-bonding orbitals are completely filled and hence cancel. Only valence electrons determine bonding.



LECTURE 12: MOLECULAR ORBITAL THEORY AND PI BONDS

LECTURE 12: MOLECULAR ORBITAL THEORY AND PI BONDS

Molecular orbitals of Be₂

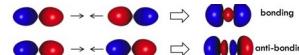
The electrons fill both the bonding and antibonding orbitals. The electrons in Be₂ do not have lower energy than the electrons in 2 Be atoms → this molecule is not stable



Mixing p-orbitals

There are 3 types of p orbital.

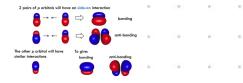
1 pair of p orbitals will have an end-on interaction



LO: RECOGNISE A σ ORBITAL, A π ORBITAL A NON-BONDING ORBITAL

Molecular orbitals are classified according to their symmetry. Looking end-on, a molecular orbital may resemble an s-orbital, or a σ -orbital. Those without a node in the plane containing both nuclei resemble an s-orbital and are denoted σ -orbitals. Those with a node in the plane containing both nuclei resemble a p-orbital and are denoted π -orbitals.

2 pairs of p orbitals will have side-on interaction



Sigma and pi orbitals

p atomic orbitals give rise to both σ and π molecular orbitals



The orbitals that arise from side-on interactions of p orbitals have the same energy - they called degenerate orbitals

The exact order of σ and π bond energies can change depending on the element

LO: IDENTIFY THE VALENCE ELECTRONS AND ORBITAL IN DIATOMIC MOLECULES

LO: PREDICT ELECTRONIC CONFIGURATION FOR DIATOMIC MOLECULES, GIVEN A MOLECULE ORBITAL (MO) ENERGY DIAGRAM

LO: EXPLAIN THE DIFFERENCE BETWEEN PARAMAGNETISM AND DIAMAGNETISM

Magnetism in molecules

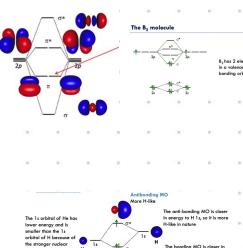
Paramagnetic molecules have unpaired electrons and a net magnetic moment. Such substances will be drawn into magnetic fields, e.g. O₂.

Diamagnetic molecules do not have unpaired electrons, and have no magnetic moment. They are weakly repelled by magnetic fields, e.g. N₂.

LO: PREDICT WHETHER A MOLECULE WILL BE DIAMAGNETIC OR PARAMAGNETIC FROM ITS ORBITAL ENERGY DIAGRAM

Heteronuclear molecules

The mixing of different atomic orbitals gives rise to asymmetric molecular orbitals. Why is the 1s orbital of He lower in energy than the 1s orbital H? This is because He has a 2+ so the electrostatic energy reaction between the electron and the nucleus ups the charge on the nucleus making it more stable increasing the cool-on reaction and thus lowering the energy

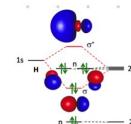


LO: DISTINGUISH BETWEEN POLAR AND APOLAR BONDS IN DIATOMIC MOLECULES AND RELATE IT TO ELECTRON ATTRACTION OF A NUCLEUS (ELECTRONEGATIVITY)

LO: PREDICT RELATIVE BINDING ENERGIES AND BOND LENGTHS FROM BOND ORDER

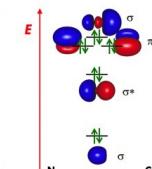
Molecular orbitals in HF

In HF, the closest orbital in energy to H 1s is one of the F 2p orbitals, so this gives rise to the σ and σ^* orbitals. The other 2p orbitals are nonbonding, and they remain atomic in appearance. The F 2s orbital is only slightly distorted, and can be regarded as non-bonding



Molecular orbitals in CN-

CN- is isoelectronic with N₂ (same number of electrons). Note that the lower-lying orbitals are polarised towards the nitrogen. This is because nitrogen has a greater nuclear charge than carbon, so draws the electrons more strongly in the MO. A net polarisation of charge gives rise to a molecular dipole.

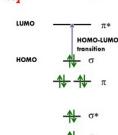


LO: RECALL THE MEANING OF HOMO AND LUMO AND DETERMINE THE LOWEST ENERGY ELECTRONIC TRANSITION

HOMO = Highest Occupied Molecular Orbital. LUMO = Lowest Unoccupied Molecular Orbital.

The lowest energy electronic transition of a molecule is the HOMO-LUMO transition.

N₂



LECTURE 13: MOLECULAR ORBITALS IN SOLIDS

LECTURE 13: MOLECULAR ORBITALS IN SOLIDS

Orbitals in a molecule

Core Electrons: Electrons in these orbitals are unaffected by the presence of neighbouring atomic nuclei. Their energy is practically the same as in an isolated atom.

σ or single covalent bond: Electrons in these orbitals are delocalised between neighbouring nuclei. The electron density is highest along the internuclear axis.

Non-bonding (nb) orbitals: are localised on only one atom and do not affect bonding.

π bonds: Electrons in these orbitals lower the energy of the molecule. They are delocalised between multiple nuclei in lobes on opposite sides of the inter-nuclear axis. They are responsible for double and triple bonds.

LO: RECALL THAT THE NUMBER OF MOLECULAR ORBITALS INCREASE WITH THE NUMBER OF ATOMS IN THE MOLECULE

Number of orbitals

Electrons in an atom are described by atomic orbitals. A maximum of 2 electrons can occupy an atomic orbital. Electrons in a molecule are described by molecular orbitals. A maximum of 2 electrons can occupy a molecular orbital.

Total number of atomic orbitals = number of molecular orbitals

As we increase the number of atoms, the number of molecular orbitals increases. We define bond order as:

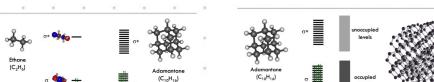
Bond order = $\frac{1}{2}$ (No. of bonding electrons – No. of antibonding electrons)

Bonding orbitals \rightarrow electron goes down in energy relative to where they had been in the atom. Anti-bonding \rightarrow forced up into a higher energy state. Both bonding and anti-bonding: cancel each other out energetically.

LO: RECOGNISE THAT INTERACTIONS OF σ -ORBITALS GIVE RISE TO A VALENCE BAND AND σ^* ORBITALS GIVE RISE TO A CONDUCTION BAND IN COVALENT NETWORKS

From Ethane to adamantine

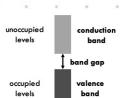
Has bonding and antibonding structures \rightarrow increases number of possible states when going from little to big.



LO: USE, DEFINE AND EXPLAIN THE CONCEPTS OF CONDUCTION BAND, VALENCE BAND, BAND GAP, HOLE, ACCEPTOR LEVEL, DONOR LEVEL, N-DOPING AND P-DOPING

Electronic band structure

Network solids have electronic bands rather than molecular orbitals. The band of occupied orbitals is called the valence band. The band of unoccupied orbitals is called the conduction band. The energy gap between these bands is the band gap. The band gap is the minimum energy a network solid must absorb to promote an electron from the valence band to the conduction band.

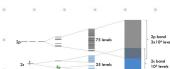
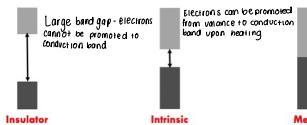


Conductivity: In order for an electron to conduct electricity, it must have access to an unoccupied energy level. The valence band of diamond is full, so electrons in the valence band cannot move as there are no nearby empty orbitals. In order for diamond to conduct electricity, it must absorb enough energy to promote electrons from the valence band into the conduction band.

Conductivity in metals:

Metals do not have a band gap. Valence and conduction bands overlap, so metals can conduct electricity

Conductivity in insulators:



Graphite and diamond

Diamond and graphite are allotropes of carbon. They have very different electronic structures.

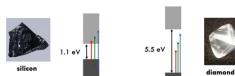
Graphite	Diamond
High conductivity	High resistivity
High thermal conductivity	Low thermal conductivity
Black	White
Graphene	Diamond

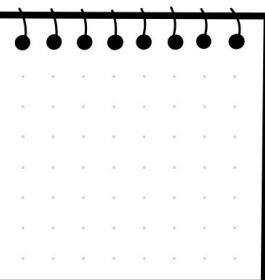
Graphite has a hexagonal lattice structure, while diamond has a cubic lattice structure. Diamond has a large band gap, making it a good insulator, whereas graphite has a small band gap and is a conductor.

LO: EXPLAIN THE RELATIONSHIP BETWEEN BAND GAP AND ELECTRICAL AND OPTICAL PROPERTIES

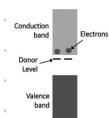
Band gaps and colour

The gap of a network solid determines its colour for example silicone: has a small band gap and can absorb all visible light and appears black. Diamonds have a large band gap so it absorbs no light and appears transparent

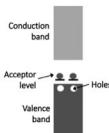


LO: EXPLAIN HOW N- OR P-DOPING GIVES RISE TO CONDUCTIVITY OF ELECTRONS AND HOLESN-type doping

In n-type doping, there are extra negative charge carriers, (i.e. electrons). This is achieved by substituting with an element to the right on the periodic table, which has more electrons. e.g. substituting Si with P. The extra electrons reside in donor levels, just below the conduction band. As the material is heated, these electrons are promoted to the conduction band, and vastly outnumber any holes in the valence band.

P-type doping

In p-type doping, there are fewer electrons, and more positive charge carriers, (i.e. holes). This is achieved by substituting with an element to the left on the periodic table, which has fewer electrons. e.g. substituting Si with Al. The electron poor atoms generate acceptor levels, just above the valence band. Valence band electrons are promoted to the acceptor levels, leaving holes in the valence band. In a p-type semiconductor, the major conduction is due to holes.

LO: EXPLAIN WHY THE CONDUCTIVITY OF SEMICONDUCTORS INCREASES WITH TEMPERATURETypes of semiconductors

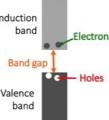
Intrinsic semiconductor: When the band gap is small, electrons can be promoted to the conduction band, leaving electrons in the conduction band and holes in the valence band. e.g. silicon, germanium.

Extrinsic semiconductor: Many applications require stable conductivity at all temperatures. This can be achieved by doping – substituting some atoms.

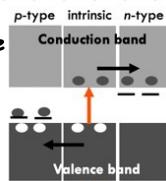
There are two types of doping – n-type and p-type.

Solar cells

Solar cells can be generated by combining an intrinsic semiconductor with both p-type and n-type extrinsic semiconductors.



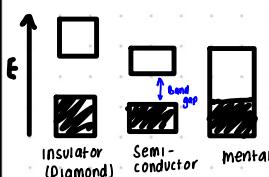
As electrons move the holes left by electrons in the valence band also change position.



Electrons travel to the conductive band of n-type semiconductors

TOPIC SEVEN: MOLECULAR ORBITAL IN SOLIDS (LECTURE 13)

The absorption of light promotes electrons from the valence to the conduction band of the intrinsic semiconductor



Note: To increase conductivity you must decrease the band gap.

↳ This is done by doping.

↳ There are two types of doping

Intrinsic semi-conductor → pure

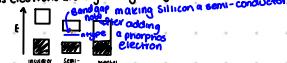
Extrinsic semi-conductor → contains dopants

n-type semi-conductor: adds an electron (makes sense as electrons are negatively charged)

↳ For example: Silicon

$Si + P$ adds an electron to get an

$s^2 p^2 s^2 p^3$ n-type semiconductor



p-type semi-conductor: removes an electron (this adds a positive charge)

↳ For example: Silicon

$Si + Al$ removes an electron creating

$s^2 p^2 s^2 p^1$ a positive charge.

Note: To know if a combination will be p-type or n-type semiconductors?

If the doping agent is to the right of the element it will be n-type

If the doping agent is to the left of the element it will be p-type.

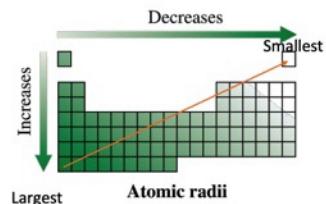
CHEM1111 worksheet – Lecture 10

Periodic table and periodic trends

1. For each of the following pairs, predict which atom is larger (has a bigger radius).

a. Si or Cl

b. S or Se



2. Predict whether the following atoms will be smaller or larger than As.

a. P **Smaller**

b. Ge **larger**

c. Se **smaller**

d. Sb **larger**

3. For each of the following pairs, predict which is larger.

a. Li or Li^+

b. F or F^-

c. Na^+ or F^-

d. Ca^{2+} or S^{2-}

Because you 'add' an extra electron it is more spread out making anions always larger than the normal state

4. For each of the following pairs, predict which will have the largest ionisation energy.

a. H or He

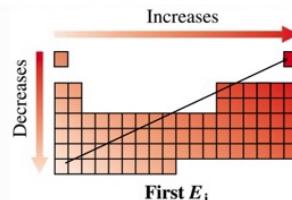
b. He or Ne

c. K or Ca

d. Br or Kr

e. N or P

The **first ionisation energy** is the energy required to remove the first electron from a neutral atom



5. The first ionisation energies of Mg, Al and Si are shown below.

Element	Atomic number	E_i (kJ mol ⁻¹)	Atom configuration	Cation (+ charge) configuration
Mg	12	738	$1s^2 2s^2 2p^6 3s^2$	$1s^2 2s^2 2p^6 3s^1$
Al	13	577	$1s^2 2s^2 2p^6 3s^2 2p^1$	$1s^2 2s^2 2p^6 3s^2$
Si	14	786	$1s^2 2s^2 2p^6 3s^2 2p^2$	$1s^2 2s^2 2p^6 3s^2 2p^1$

take one away

- a. Fill in the electronic configurations for the atoms and the 1+ cations.
- b. Which ionisation energy does not fit in with the trends we have learnt?

Aliminium,

- c. Provide an explanation for this anomaly.

as it goes down in ionisation as it has a complete subshell.

6. Identify the elements based on the following clues.

- a. Has a smaller atomic radius than hydrogen.

Helium as it has two protons and pulls them closer

- b. Not a noble gas. Has a first ionisation energy larger than both nitrogen and oxygen.

Flurien - has more protons in nucleus

- c. Has the smallest atomic radius of the metalloids (i.e. B, Si, Ge, As, Sb, Te, Po).

B - it is in the second period.

- d. Has a partially filled $3p$ subshell and prefers to exist as the 2- anion.

S^{-2}

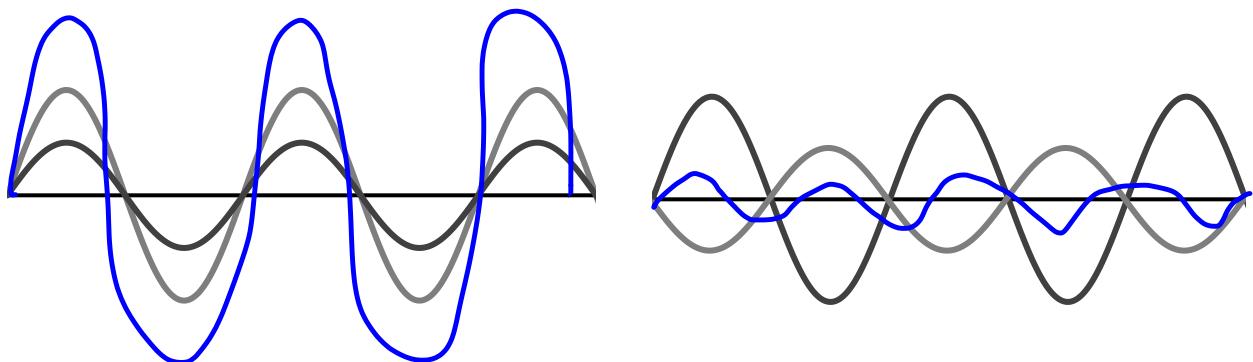
- e. Has one electron in its valence s orbital. Has a lower first ionisation energy than rubidium.

Caesium - its shell is further out so the attraction is weaker

CHEM1111 worksheet – Lecture 11

Molecular Orbital Theory

1. For the following pairs of waves, sketch the sum of the two waves

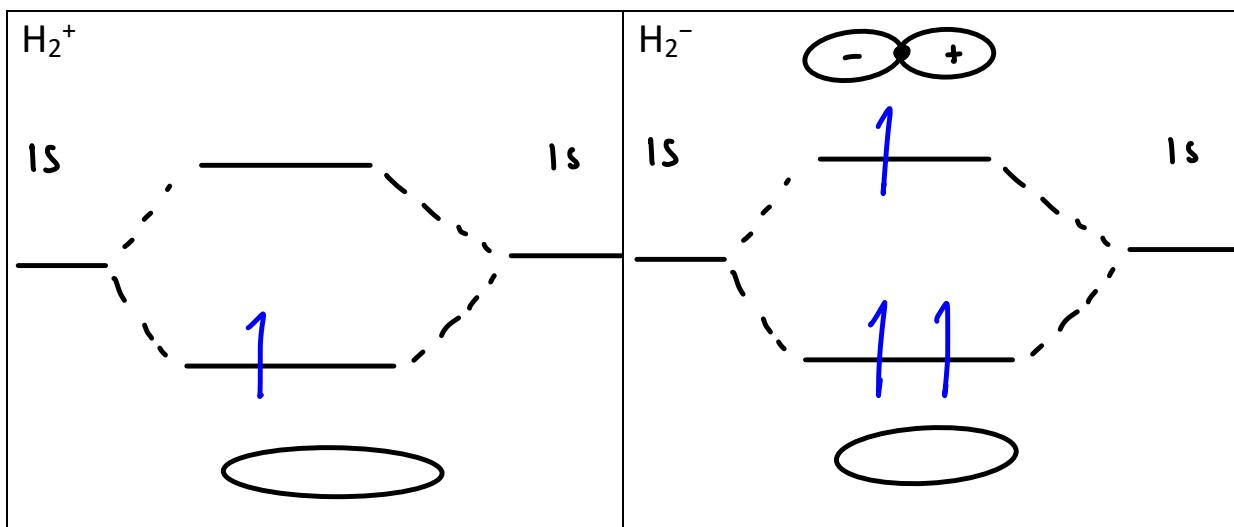


2. Predict whether the following molecules form stable bonds:

- a) H_2^+ (the second most abundant molecule in the universe! – after H_2),
 b) H_2^-

Approach:

- i. Sketch out a MO diagram

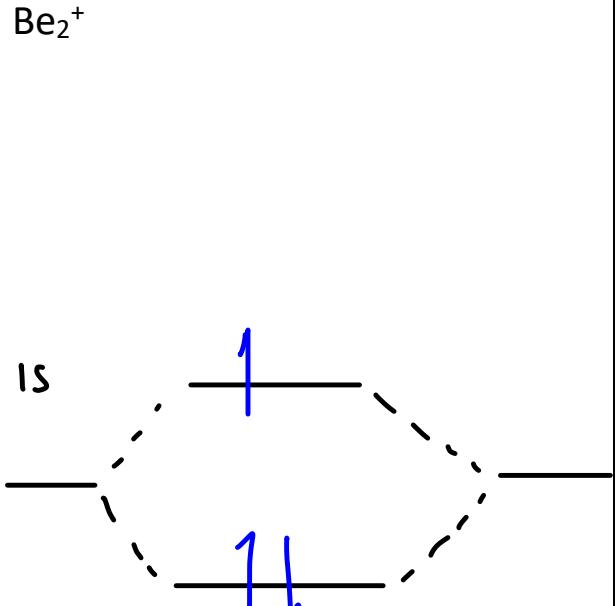
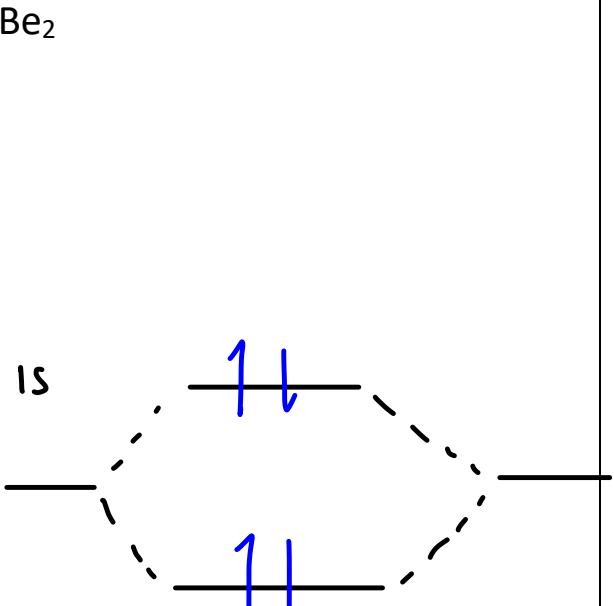


- ii. Work out how many electrons are in each
 iii. Fill the energy levels in the diagram with electrons

Draw the lobe representation of the molecular orbitals in H_2^- .



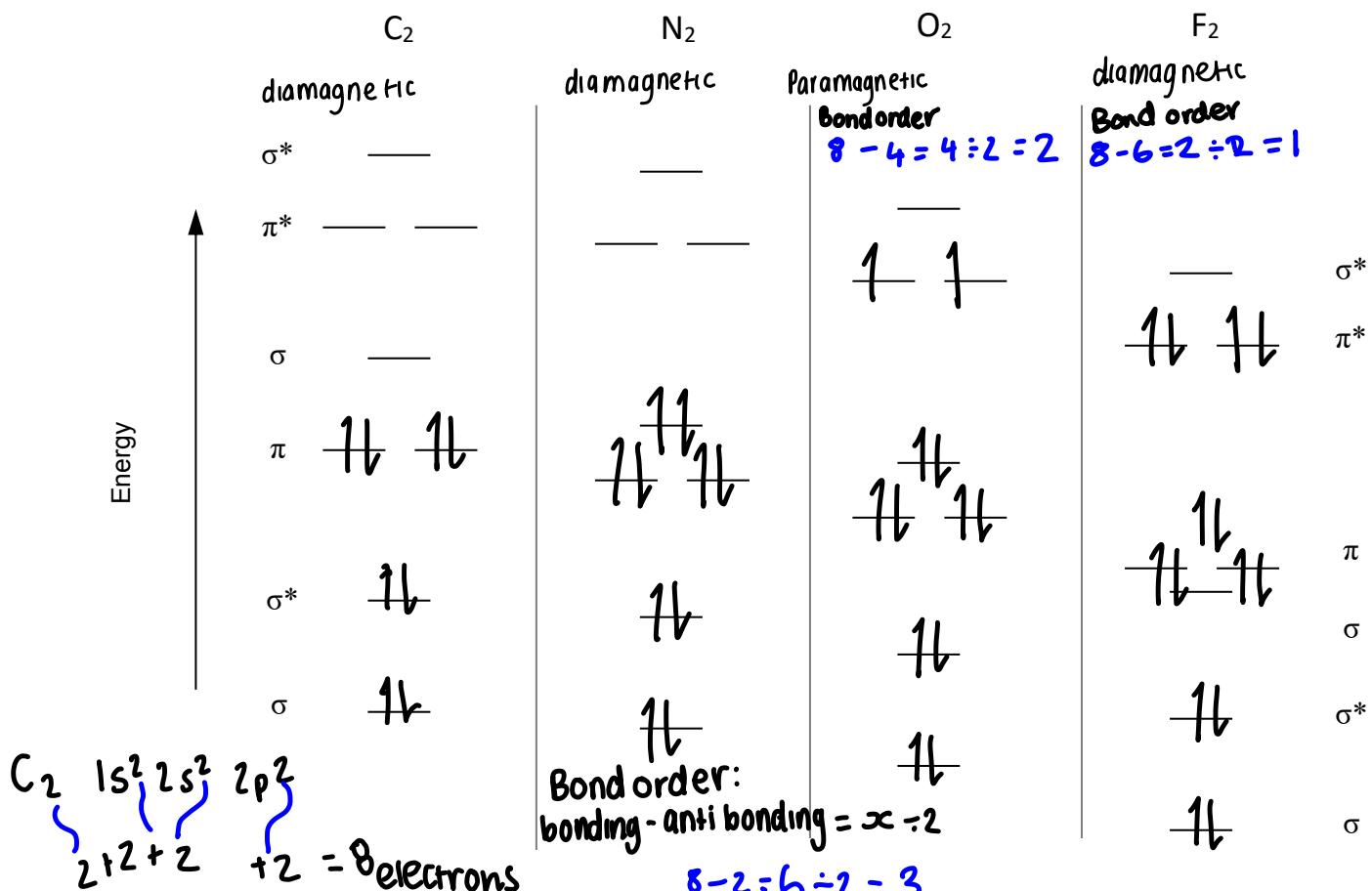
2. Follow the same steps as in question 1 to predict the stability of Be_2^+ and Be_2 .

Be_2^+	Be_2
 <p>There are more bonding electrons than there are antibonding so $1 + 1$ is stable but only low</p>	 <p>not stable as there are equal antibonding and bonding electrons and they cancel each other out</p>

CHEM1111 worksheet – Lecture 12

Molecular orbitals

1. The following diagram shows the molecular orbital energy levels for the **valence** electrons in the homonuclear diatomic molecules C₂, N₂, O₂ and F₂.



a) Complete the diagram by filling in the remaining **valence** electrons for each molecule.

b) Decide whether each molecule will be paramagnetic or diamagnetic.

c) Explain why the energy of the orbitals decrease going from left to right across the periodic table.

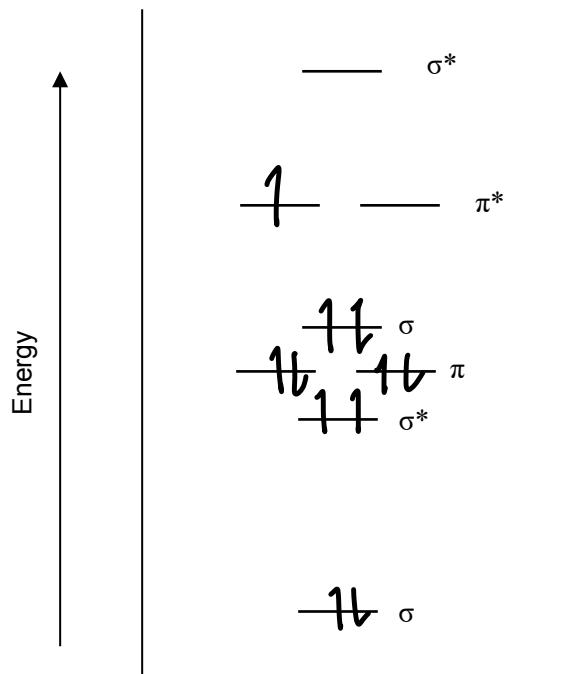
Increase of nuclear charge

2. The NO molecule plays an important signalling role in the human body.

- a) How many valence electrons are there in NO?

$$\begin{array}{l} N = 5 \\ O = 6 \end{array} \quad 5 + 6 = 11 \text{ valence}$$

- b) The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the NO molecule. Indicate on this diagram the ground state electronic configuration of NO using the arrow notation for electron spins.



- c) Is the NO molecule diamagnetic or paramagnetic?

Paramagnetic

- d) Would removing an electron from NO to form NO^+ strengthen or weaken the bond between the two atoms? Explain your answer.

More stable and stronger

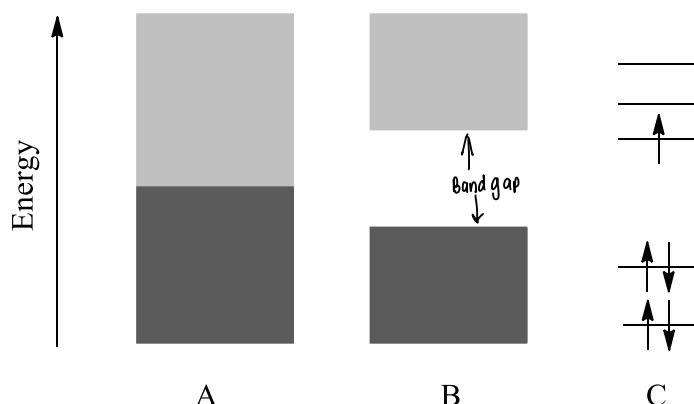
CHEM1111 worksheet – Lecture 13

MO in solids

1. Explain what is meant by the term "band gap".

The difference in Energy between the top of the valence band and the bottom of the conduction Band.

2. The diagram below shows the band structure of two solid elements, A and B. Dark grey denotes filled electron energy levels, light grey denotes unfilled levels. Also shown are the atomic energy levels (valence electron orbitals only) of another element, C.



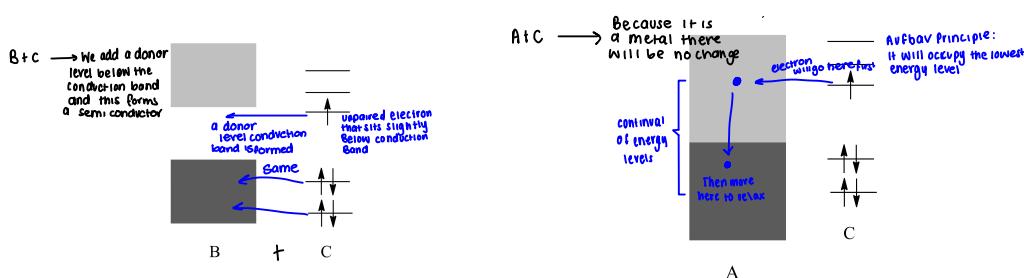
- a. Describe the electrical properties of elements A and B, explaining your reasoning.

A = conductor / metal as there is no bandgap

B = Semiconductor there is a band gap

C = molecule : paramagnetic insulator

- b. If a small amount of element C is deliberately added to each of A and B, describe what effect this will have on the electrical properties of each. Give reasons.



3. Will the following combinations form p-type or n-type semiconductors?

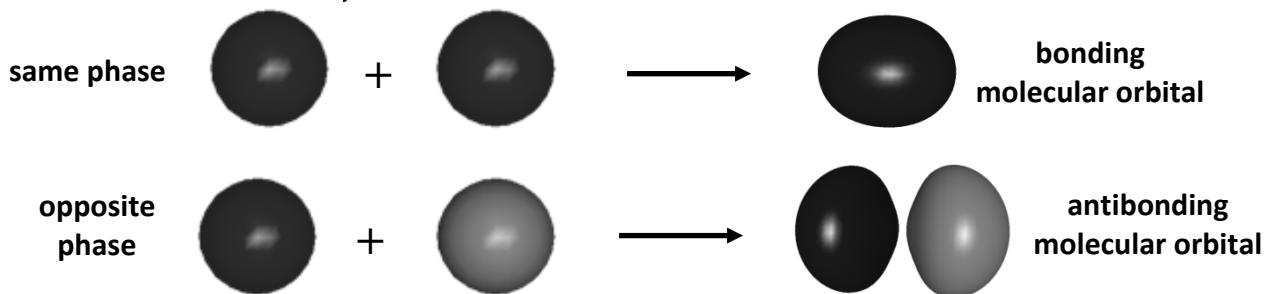
- silicon doped with arsenic → n-type conductor (arsenic is to the right of silicon)
- germanium doped with aluminium → p-type conductor (aluminium is a group to the left of germanium)
- diamond doped with boron → p-type (Boron sits in a group to the left of diamonds)
↳ Carbon

Tutorial 5 (Week 5): Molecular Orbitals, Bonding and Atomic Spectroscopy

Model 1: Molecular Orbitals

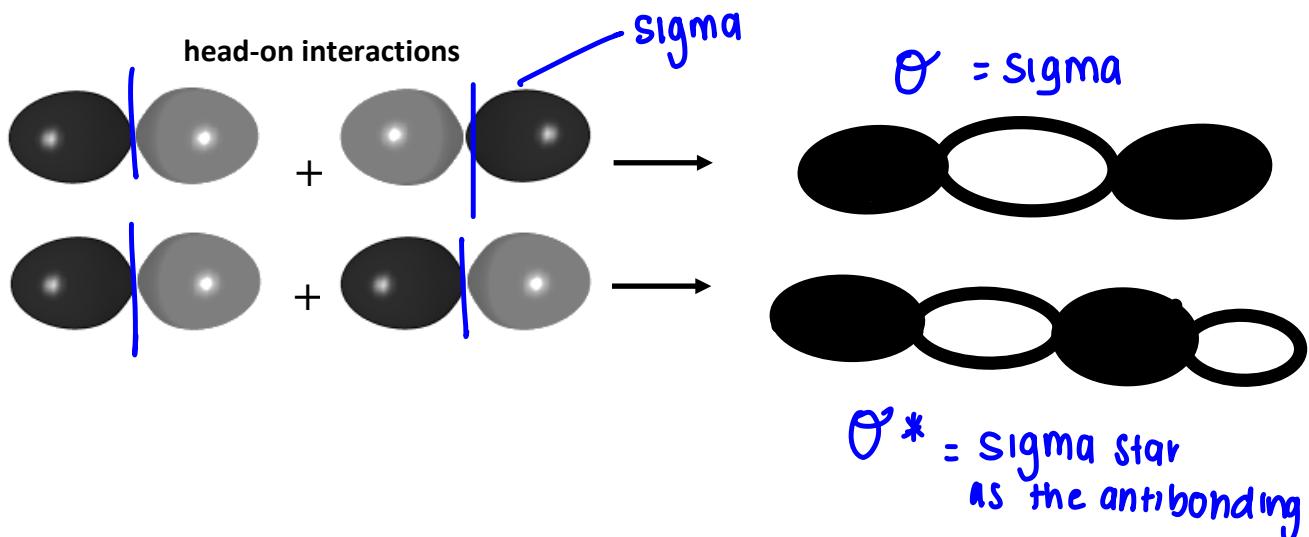
Molecular orbitals are formed from combinations of atomic orbitals. When orbitals are combined, they can either add in phase (same sign) or out of phase (opposite signs). This gives rise to two molecular orbitals. The bonding molecular orbital results from addition of lobes with the same phase, while the antibonding molecular orbital results from addition of lobes with opposite phase. The latter will have a node between the nuclei.

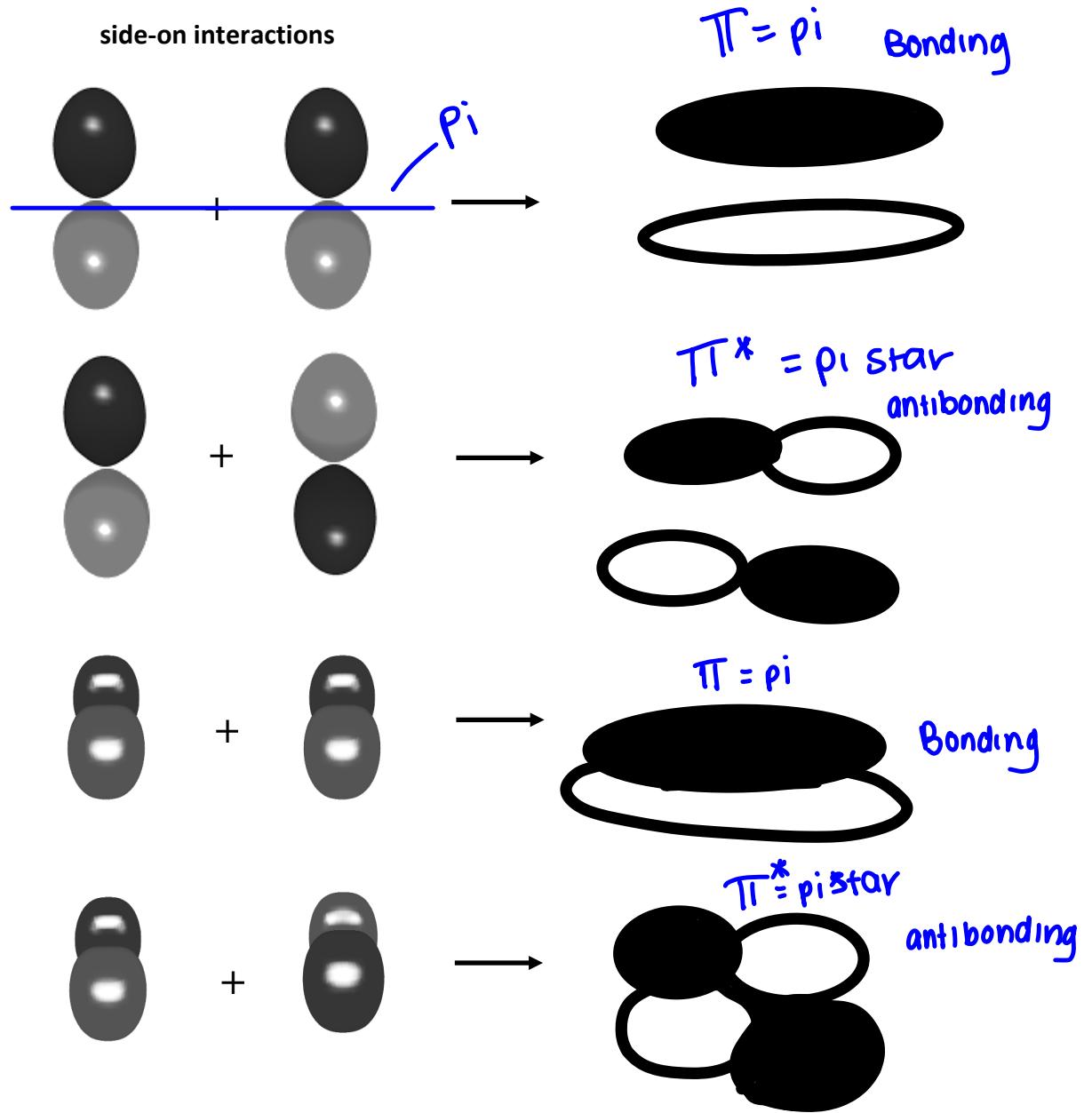
For example, two 1s orbitals can combine to give rise to a bonding and an antibonding orbital in the following way:



In the same way, p atomic orbitals can combine to give molecular orbitals. The shape of the orbitals will depend on the orientation of the interaction. p orbitals can either combine in a head-on fashion, or a side-on fashion.

1. Draw the molecular orbital that results from interaction of the following p orbitals.

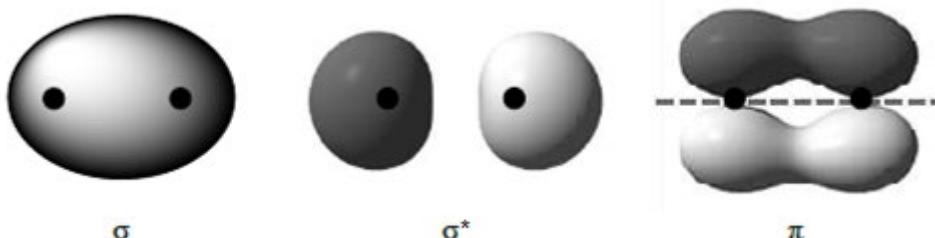




- Indicate whether the molecular orbitals that you have drawn in question 1 are bonding or antibonding orbitals.

Model 2: σ , σ^* , π , and π^* Orbitals

Molecular orbitals describe the properties of electrons in molecules and a knowledge of them gives insight into the reactivity and stability of compounds. Commonly, molecular orbitals are described as being σ (pronounced 'sigma') or π (pronounced 'pi'). The pictures below show two examples of σ orbitals and one example of a π orbital in a diatomic molecule. The black dots (\bullet) show the position of the nuclei.

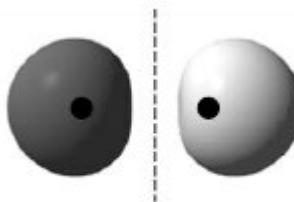


σ orbitals are symmetric around a line joining the two nuclei. π orbitals have a node along this line: they are zero along the *horizontal* dotted line shown above.

When electrons occupy a **bonding orbital**, they strengthen the bond. When electrons occupy an **antibonding orbital**, they weaken the bond.

Anti-bonding orbitals, such as the one drawn opposite, have a nodal plane between the nuclei: they are zero along the *vertical* dotted line shown.

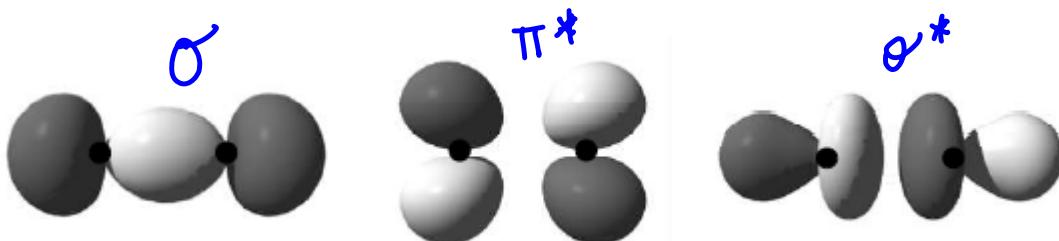
An asterisk ("*") is added to the σ or π label to show



this.

Critical thinking questions

3. Label the orbitals below as σ , σ^* , π , or π^* .



4. For the orbitals that you drew in question 1, assign labels of σ , σ^* , π , or π^* .

Model 3: Molecular Orbital Diagrams

The figure opposite is a *molecular orbital diagram*, or MO diagram, for a diatomic molecule made of second row elements. Each orbital is represented by a line, showing its energy, and may hold a maximum of 2 electrons.

Note that there are 2 π orbitals and 2 σ^* orbitals and this is represented by 2 lines in each case.

The valence electrons of the two elements are placed in these orbitals, starting from the lowest energy orbitals at the bottom.

For example, as a B atom has 3 valence electrons, the diatomic molecule B_2 has 6 valence electrons. These are placed as shown on the diagram. 2 electrons occupy σ , 2 electrons occupy σ^* and 2 electrons occupy the π orbitals.

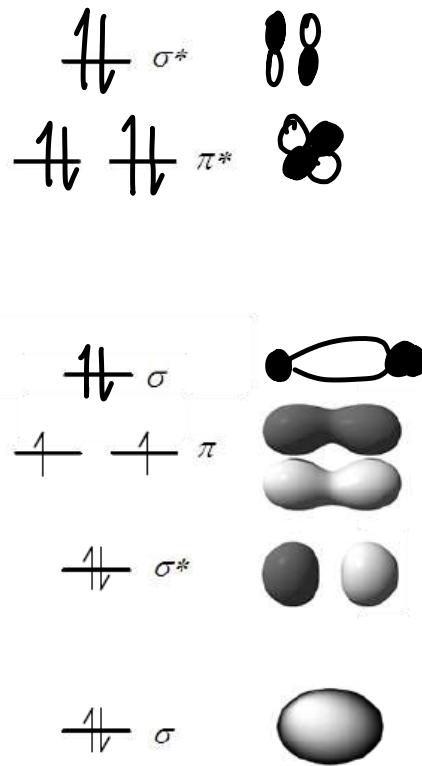
The last 2 electrons occupy one π orbital each as this keeps the electrons further away from each other. The completed MO diagram correctly predicts that the B_2 molecule has 2 unpaired electrons and is, as a result, *paramagnetic*.

Once the electrons have been added to the diagram, the *bond order* can be worked out by first counting up the number of bonding and anti-bonding electrons and then calculating:

$$\text{bond order} = \frac{1}{2} (\text{number of bonding electrons} - \text{number of anti-bonding electrons})$$

For B_2 , there are 4 bonding electrons (2 in σ and 2 in π) and 2 anti-bonding electrons (in σ^*) and so:

$$\text{bond order} = \frac{1}{2} (4 - 2) = 1$$



Critical thinking questions

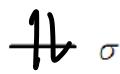
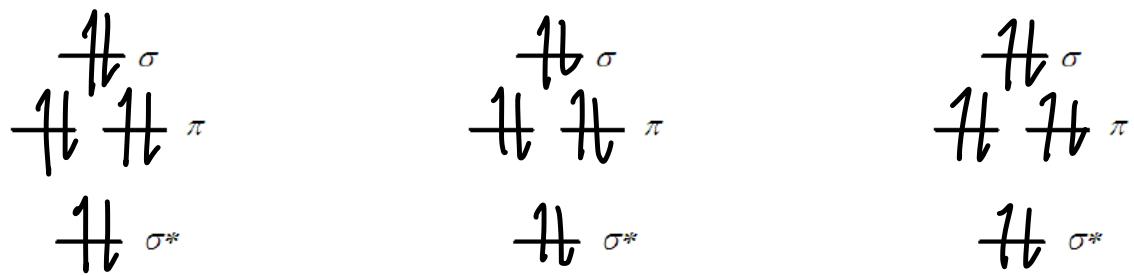
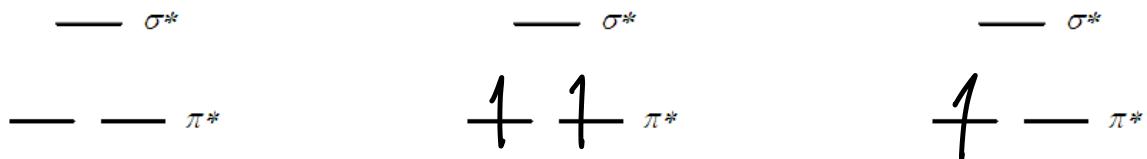
5. Using the labels as a guide, sketch the remaining orbitals from Model 1 on the diagram above.
6. Add electrons to the diagram on the next page so that it shows the occupation for N_2 . Calculate its bond order.
7. Add electrons to the diagram on the next page so that it shows the occupation for O_2 . Calculate its bond order.

8. What combinations of bonds (σ and/or π) normally make up double and triple bonds?

double = 1 σ 1 π

Triple = 2 π 1 σ

9. What is the bond order of nitric oxide (NO)?



N₂

N = 5 valence
 $\times 2 = 10$ electrons

Bond order:

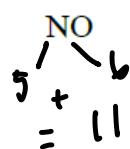
$$8 - 2 = 6 \div 2 = 3$$

O₂

6 valence
 $\times 2 = 12$

Bond order

$$8 - 4 = 4 \div 2 = 2 \quad 8 - 3 = 5 \div 2 \\ 2.5$$

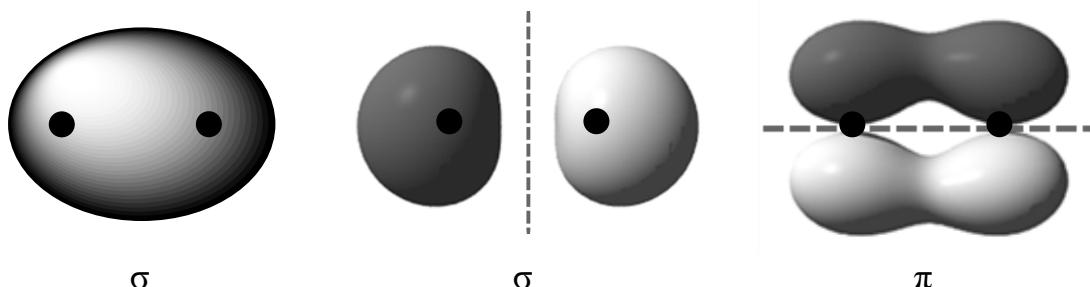


Bond order

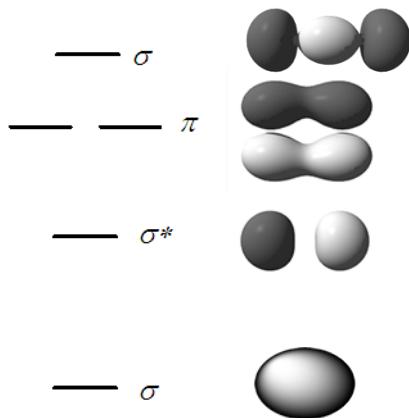
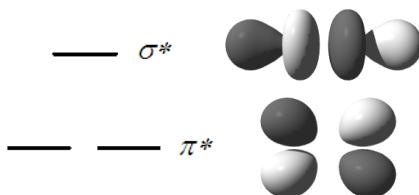
Molecular Orbital Diagrams

σ and π orbitals

- When electrons occupy a **bonding orbital**, they strengthen the bond. When electrons occupy an **anti-bonding orbital**, they weaken the bond. Anti-bonding orbitals have a nodal plane between the nuclei: they are zero along the *vertical* dotted line shown.
- σ orbitals are symmetric around a line joining the two nuclei. π orbitals have a node along this line: they are zero along the *horizontal* dotted line shown below.



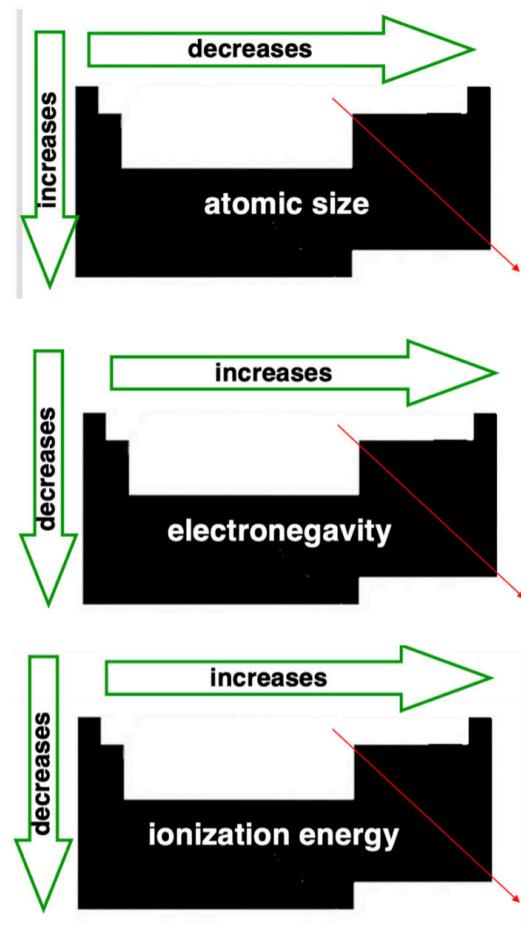
- Molecular orbital diagrams show the energies of molecular orbitals. They are filled with the valence electrons by following the principles:
 - Fill from the lowest to the highest levels.
 - Two electrons can occupy each level.
 - Electrons keep apart by occupying separate levels before pairing up.



- The **bond order** can be worked out by first counting up the number of bonding and anti-bonding electrons and then calculating:

$$\text{bond order} = \frac{1}{2} (\text{number of bonding electrons} - \text{number of anti-bonding electrons})$$

Periodic Properties



Cations:

- Smaller than the atom from which they are made
- Get smaller as +ve charge increases

Anions:

- Larger than the atom from which they are made
- Get larger as -ve charge increases

BONDING

VSEPR

INTERMOLECULAR

FORCES

LECTURE 14: ATOMIC SPECTROSCOPY AND MOLECULAR SPECTROSCOPY

LECTURE 14: SPECTROSCOPY

Spectroscopy

Spectroscopy is the study of the interaction of matter with electromagnetic radiation. There are many different forms of spectroscopy. The type of electromagnetic radiation used, instrumentation, and sample preparation determines the information that will be obtained.

LO: Understand the relationship between absorption and observed colour.

Colour

White light is a combination of all colours. Black materials absorb all the visible light which is shone on them. White materials absorb no visible light. The colours of other objects are due to the particular wavelengths of light that they absorb. A solid that absorbs red light and reflects all the other colours will appear green. A solid that absorbs green light is perceived by us as a red colour. A Newton's colour wheel lets us predict the colour that will be observed.

Methyl orange is a pH indicator that is a different colour in acidic and basic form.

Terms to describe colour

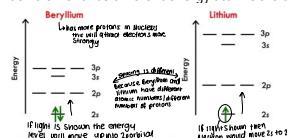
Transparent materials allow all light to pass through (e.g. air, water, clear glass). Translucent materials allow some light to pass through, but the light is scattered (e.g. frosted glass, some plastics). Opaque materials do not let any light pass through. Light is reflected on

absorbed (e.g. wood, stone, metals). The designation of a material as coloured or colourless is separate from these terms. An opaque and colourless material will be white, while a transparent and colourless material will be clear.

LO: Relate absorption and emission of photons to changes in electron energy levels.

Atomic spectroscopy

Each element has different energy atomic orbitals, so the energy gaps between these orbitals will depend on the element.



at can also be used to get an element to emit a colour/ wavelength. However this only done when the electron has already moved up to other orbital and then moved back down. It is the transition form moving back down that light is emitted. This is called emission spectroscopy

LO: Calculate emission and absorption wavelengths from energy levels.

Atomic spectrum of hydrogen

The emission spectrum of hydrogen is composed of discrete wavelengths, or "spectral lines". This shows that the gaps between energy levels are fixed, and was early evidence that the energy of the electron in the atom is quantised.



In 1885, Balmer showed that the wavelengths of the visible spectral lines follow the equation:

$$\frac{1}{\lambda} = E_R \left(\frac{1}{n^2} - \frac{1}{2^2} \right) \quad \text{where } E_R = \text{Rydberg's constant, } 2.18 \times 10^{-18} \text{ J}$$

} Energies for different transitions and what wavelength of light would come out.

Energies of one-electron atom

Hydrogen is a special case as it has one electron, so energy levels are defined only by the principal quantum number, n, and can therefore be calculated using the Rydberg formula shown below

$$E_n = -E_R \frac{1}{n^2}$$

LO: Use the Beer-Lambert law.

Quantities from absorbance

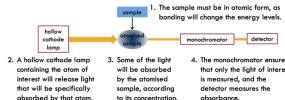
Spectroscopy is useful in identifying elements or molecules. It is also useful for determining concentrations or quantities.

The Beer-Lambert law relates absorbance to concentration:

$$A = \epsilon cl$$

LO: Identify constraints on analysis by atomic absorption spectroscopy (AAS).

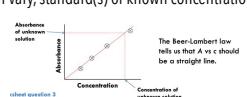
Atomic absorption spectroscopy (AAS) uses the characteristic absorption wavelengths of each element to determine concentrations of elements.



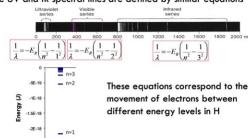
LO: Describe how the hollow cathode lamp operates, and why it is central to sensitive AAS measurements.

AAS and the Beer-Lambert law

Because the light emitted by the cathode lamp can vary, standard(s) of known concentration must be run at the same time as the unknown. Often, a calibration curve is constructed, using number of solutions of different concentration.



The UV and IR spectral lines are defined by similar equations



$n=1$: ultraviolet series

$n=2$: visible series

$n=3$: infrared series

This also applies to other "hydrogen-like"

cations (with only one electron), such as He+, $E_n = -E_R \frac{Z^2}{n^2}$, N6+, for which the equation is shown below.

$A = \text{absorbance}$. This is related to how much light can pass through a solution. Higher absorbance \rightarrow less light gets through (a darker solution).

$c = \text{concentration}$. A more concentrated coloured solution will absorb more light.

$\epsilon = \text{molar extinction coefficient}$. For a given molecule, this is a constant.

$l = \text{path length}$. How far the light has to travel. If light has to travel through more solution, then more will be absorbed.



LO: Relate electronic absorbance and emission spectra to electronic structure.

LO: Describe the process of molecular spectroscopy.

Molecular spectroscopy

HOMO = Highest Occupied Molecular Orbital

LUMO = Lowest Unoccupied Molecular Orbital.

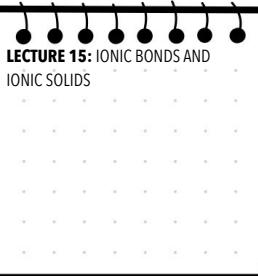
The lowest energy electronic transition of a molecule is the HOMO-LUMO transition. The absorption of light of this energy will result in promotion of an electron.

LO: Compare and contrast atomic and molecular spectroscopy

Molecular spectroscopy using the same principles: Molecules absorb specific wavelengths of light according to orbital energies. Beer-Lambert law applies.

Unlike atomic absorption spectroscopy: Molecular spectroscopy does not require atoms to be atomised, as it measures the energy of electrons in molecules, not atoms.





LECTURE 15: IONIC BONDS AND IONIC SOLIDS

LECTURE 15: IONIC BONDS AND IONIC SOLIDS

LO: Describe and explain the periodic trends in electronegativity.

Trends in the periodic table

Electronegativity was introduced by Linus Pauling as an arbitrary scale - the ability of a particular atom to attract bonding electrons. Each element has electronegativity on scale between 0 and 4. An electronegativity of 4 is assigned to fluorine as the most electronegative element. If two compounds have an electronegativity difference of >1.5, they will form an ionic compound. More than one electron may be gained/lost but >3 electrons not common. Atoms gain or lose electrons to become isoelectronic to the nearest noble gas (tend to have fully filled valence shells).

LO: Explain the origin of ionic bonding.

Ionic bonding is the long-range electrostatic attraction between cation (+) and anion (-), together with the short-range repulsion between electrons in adjacent ions. The equilibrium distance between cation and anion nearest neighbours occurs when the potential energy is a minimum. That is, when the attractive and repulsive forces are exactly equal and opposite. Electrostatic interactions are isotropic - meaning they are the same in all directions - and they are long-ranged (decay as r^{-1}). Firstly a shell of oppositely charged ions (counterions) is attracted to surround a central ion. This in turn attracts another shell of their counterions etc.... This structure continues to grow leading to ionic crystals rather than small molecules.

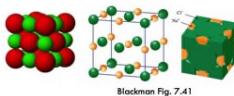
LO: Explain why ionic interactions lead to crystals rather than small molecules.

Packing ions into crystals

An ionic crystal is an organised lattice of cations and anions. Many different arrangements of ions can form depending on ionic radii. All ionic crystals share one characteristic - oppositely-charged ions are nearest neighbours. It is the attraction between oppositely charged ions that makes the crystal stable.

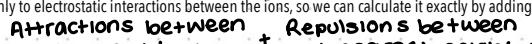
Packing arrangements

Tendency to close pack the anions and relative sizes of the ions determine the arrangements of ions in an ionic solid.



NaCl adopts a face-centred cubic (fcc) array

- Cl⁻ at corners and faces of cube; Na⁺ in spaces in between), due to a large difference in ionic radii.
- Smaller Na⁺ (1.02 Å) can fit into the spaces (interstices) between closely packed larger Cl⁻ (1.81 Å).



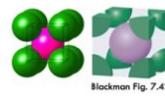
The negative value denotes that energy of the crystal lattice is lower than that of the ions. This same idea as the negative potential energy that binds a H_2 molecule to two protons.

Two protons nucleus

LO: Explain the meaning of the term "lattice energy".

Lattice energy

The lattice energy is the energy change when gas phase ions combine to form a crystal lattice. e.g. For



Blockman Fig. 7.42

CsCl adopts a primitive cubic array

- Cs⁺ at centre; 8 Cl⁻ anions at corners, due to similar ionic radii.
- Cs⁺ (1.61 Å) is big enough to fit more than 6 Cl⁻ anions around it.
- This packing is less stable than fcc array.

This denotes the energy change accompanying the formation of 1 mole of Lattice

The energy of a crystal lattice is due only to electrostatic interactions between the ions, so we can calculate it exactly by adding up all of the pairs of interactions between ions as long as we know their distances:

Attractions between nearest neighbours + Repulsions between next nearest neighbour.

LO: Explain how ionic radii influence crystal structure, and why they differ from atomic radii.

Factors affecting lattice energy

The larger the energy the stronger the lattice is. The next-nearest, next-next-nearest, etc. neighbour distances all depend only on the geometry of the lattice (i.e. square, triangular, hexagonal..., which includes the number of neighbours), and the nearest neighbour distance.

Lattice energy depends on a number of factors:

1. The sum of the anion and cation radii e.g. The lattice energy of KF ($r\text{F}^- + r\text{K}^+ = 2.69 \text{ \AA}$) is greater than that of NaI ($r\text{I}^- + r\text{Na}^+ = 3.22 \text{ \AA}$).
2. The charge on the ions e.g. MgO has a much higher lattice energy (3795 kJmol⁻¹) than LiF (1030 kJmol⁻¹).
3. The arrangement of ions e.g. NaCl (face-centred cubic; 788 kJmol⁻¹); CsCl (primitive cubic; 657 kJmol⁻¹)

LO: Calculate energy levels for one-electron atoms (worksheet)

LO: Understand how the lattice energy is influenced by size and charge of the ions

Lattice energies of ionic compounds

Lattice energies vary between ionic compounds

cation	F ⁻	O ²⁻	Cl ⁻	I ⁻	S ²⁻
Li ⁺	1030	854	798	730	2791
Na ⁺	910	769	732	682	2481
K ⁺	808	705	671	632	2238
Rb ⁺	774	680	651	617	2163
Mg ²⁺	2913	2326	2097	1944	3795
Ca ²⁺	2609	2223	2132	1965	3414
Sr ²⁺	2476	2127	2008	1937	3217
Ba ²⁺	2341	2033	1950	1851	3029

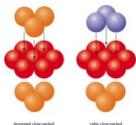


High affinity for electron (readily gain electrons)
Apart from noble gases



$\text{Mg}^+ \rightarrow \text{Mg}^{2+}$
 $\text{Al} \rightarrow \text{Al}^{3+}$

Note: charge is always shown on the top right.
The sign comes after the element name.



Face-Centred Cubic
Simple Cubic
Body-Centred Cubic

LECTURE 16: COVALENT BONDS AND LEWIS STRUCTURES

LO: DRAW OUT PLAUSIBLE LEWIS STRUCTURES FOR SIMPLE POLYATOMIC MOLECULES

Polyatomic molecules

Earlier we described bonding in diatomic molecules in terms of the molecular orbitals. For polyatomic molecules, the MOs become much more complicated and often involve many atoms.

Lewis bonding:

Simple models to allow us to determine the connectivity in and structure of molecules. Phrased as a set of rules/algorithm for structure-writing. A chemical bond is thought of as a pair of electrons shared between two atoms; atoms share bonds to achieve a full valence shell ($8 e^-$). Developed in 1916. Before the nuclear structure of the atom was understood. Before the wave nature of the electron was discovered. Before molecular orbital theory was developed. Still widely used by chemists to represent molecules and bonds. Extremely useful but incomplete model → need to use it judiciously and understand its limitations as well as its strength

A simple strategy for drawing molecular structures:

- Step 1: Count the total number of valence electrons in the molecule.
- Step 2: Draw single bonds between the atoms. (Assume $2 e^-$ each)
- Step 3: Count how many electrons are left and assign them as lone pairs to fill the valence shells (usually $8 e^-$). **Octet rule:** Start with outer atoms.
- Step 4: If there are incomplete valence shells, form multiple bonds to complete them.

Lewis Structure of simple molecules

Lewis Structure of hypochlorous acid (HClO)

$\text{H} - \ddot{\text{O}} - \text{Cl}$:
O has 2 lone pairs
Cl has 1 lone pair.
In polyatomic molecules, the centre atom is the one that needs to share the greatest number of electrons.

Lewis Structure of oxygen molecule (O_2)

$\ddot{\text{O}} = \ddot{\text{O}}$:
O has double bond
Bond order: 2
Each O atom has 2 lone pairs
Filled valence shells

LO: ASSIGN BOND ORDERS BASED ON SHARING OF ELECTRONS, RESONANCE STRUCTURES AND FORMAL CHARGES

Resonance structure and delocalisation of electrons

Sometimes the Lewis model allows several valid structures e.g. O_3



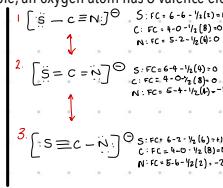
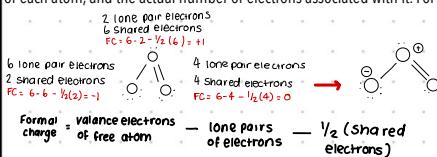
This structure satisfies the Lewis rules, but it is disregarded because three members of the O₃ molecule are equivalent.

(but they are equivalent)

These resonance structures are equivalent representations of bonds that are "in-between" single and double bonds. We use a double headed arrow, not equilibrium arrows () for resonance. In ozone, this means that both O-O bonds are equivalent, and we have an average bond order of 3/2 or 1½. Remember that electrons are really delocalised between more than two nuclei in molecular orbitals. Resonance is simply a way to describe this in terms of Lewis structures.

Formal charge:

Formal charge is the charge assigned to an atom in a molecule, assuming that electrons are shared equally between atoms. → It is the difference between the number of valence electrons of each atom, and the actual number of electrons associated with it. For example, an oxygen atom has 6 valence electrons. In the ozone molecule:



Formal charge can be used to decide the most likely Lewis structure from a number of possibilities. Step 6: Minimise the formal charges on all atoms. Structure 3 has larger formal charges → unlikely.

Structures 1 and 2 have the same formal charges (just in different places) → compare electronegativities. N is more electronegative than S, so structure 2 is more likely than structure 1. But, both 1 and 2 are seen in nature

Lewis structures of simple molecules

- Step 1: Count the total number of valence electrons in the molecule.
- Step 2: Draw single bonds between the atoms. (Assume $2 e^-$ each)
- Step 3: Count how many electrons are left and assign them as lone pairs to fill the valence shells (usually $8 e^-$). **Octet rule:** Start with outer atoms.
- Step 4: If there are incomplete valence shells, form multiple bonds to complete them.
- Step 5: If there is more than one plausible structure, then we consider both (all) to be resonance structures.
- Step 6: Minimise the formal charges on all atoms.

Worksheet question 2

LO: EXPLAIN THE RELATIONSHIP BETWEEN RESONANCE AND ELECTRON DELOCALISATION IN MOLECULAR ORBITALS

Lewis structures allow us to draw out plausible or reasonable structures for connectivity in molecules and ions and to get some insight into bond orders and electron distributions. Octet rule: atoms share electrons in order to have filled valence shells, i.e. adopt the electron configuration of the following noble gas.

- A filled valence shell for H contains 2 electrons.
- A filled valence shell for all other main group elements contains 8 electrons.
- Elements in the 3rd, 4th etc. rows may have extra linkages, but they still obey the octet rule.
- Elements at the beginning of a row may not achieve a full valence shell

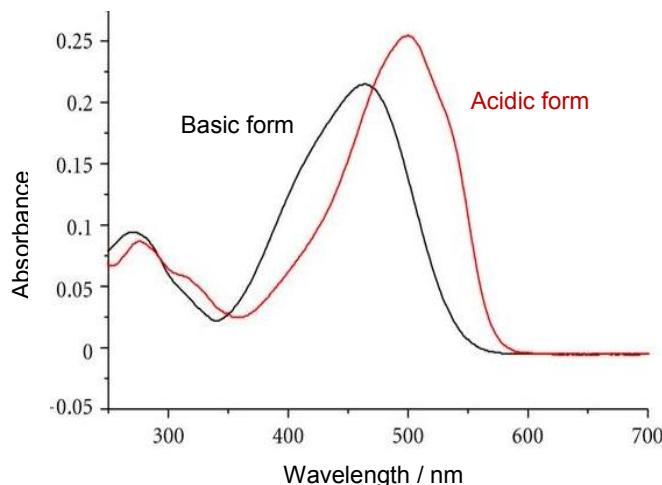
Summary of rules

- Step 1: Count the total number of valence electrons in the molecule.
- Step 2: Draw single bonds between atoms. (Assume $2 e^-$ each)
- Step 3: Count how many electrons are left and assign as lone pairs to fill valence shells (usually $8 e^-$). **Octet rule:** Start with outer atoms.
- Step 4: If there are any incomplete valence shells, form multiple bonds to complete them.
- Step 5: If there is more than one plausible structure, then we consider both (all) to be resonance structures.
- Step 6: Minimise the formal charges on all atoms.

CHEM1111 worksheet – Lecture 14

Spectroscopy

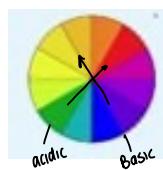
1. The absorbance spectra of methyl orange in its acidic and basic forms are shown below.



a) Predict the colour of methyl orange in its acidic and basic forms.

Acidic form $\lambda_{\max} \approx 500 \text{ nm}$ \therefore Green absorption = appears red

Basic form $\lambda_{\max} \approx 450 \text{ nm}$ \therefore Blue/violet = appears orange/yellow



b) What do you observe when a green laser pointer is pointed at the two solutions?

Acidic form (Red) absorbed the light

The basic form (orange) transmitted light

2. The most intense line(s) in the emission spectra for Li, Na and K are given below.

From the values of energy, calculate the wavelength emitted and predict the colour of light.

$$E = hc/\lambda$$

$$h = 6.626 \times 10^{-34} \text{ Js}$$

$$c = 2.998 \times 10^8 \text{ ms}^{-1}$$

a. Lithium $- 2p^1 \rightarrow 2s^1 \Delta E = 2.96 \times 10^{-19} \text{ J}$

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ ms}^{-1}}{2.96 \times 10^{-19} \text{ J}} = 6.71 \times 10^{-7} \text{ m}$$

$$= 671 \times 10^{-9} \text{ m}$$

$$= 671 \text{ nm}$$

(emission Red light)

b. Sodium $3p^1 \rightarrow 3s^1$ $\Delta E = 3.37 \times 10^{-19} \text{ J}$

$$\lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ ms}^{-1}}{3.37 \times 10^{-19} \text{ J}} = 5895 \times 10^{-9} \text{ m} \\ = 589 \text{ nm}$$

emits yellow/orange

c. Potassium $4p^1 \rightarrow 4s^1$ $\Delta E = 2.59 \times 10^{-19} \text{ J}$ ①
 $5p^1 \rightarrow 4s^1$ $\Delta E = 4.91 \times 10^{-19} \text{ J}$ ②

$$\textcircled{1} \quad \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ ms}^{-1}}{2.59 \times 10^{-19} \text{ J}} = 767 \times 10^{-9} \text{ m} \\ = 767 \text{ nm}$$

emits white
(invisible)

$$\textcircled{2} \quad \lambda = \frac{hc}{E} = \frac{6.626 \times 10^{-34} \text{ Js} \times 2.998 \times 10^8 \text{ ms}^{-1}}{4.91 \times 10^{-19} \text{ J}} \\ = 405 \times 10^{-9} \\ = 405 \text{ nm}$$

emits violet

3. Atomic Absorbance Spectroscopy

The US Environmental Protection Agency limits lead in drinking water to a maximum of 15 parts per billion (ppb). 1 part per million (ppm) = 1 mg/kg 1 ppb = 1 mg/1000kg.

An atomic absorbance spectrometer with a path length of 1 cm is used to measure lead levels in a tap water sample. The sample gives an absorbance reading of 0.0068. A reference C = 0.100 ppm standard solution gives A = 0.165.

a. Calculate the extinction coefficient (ϵ) for the standard solution.

$$A = \epsilon c \ell \longrightarrow \epsilon = \frac{A}{c \ell} \longrightarrow \frac{0.165}{0.100 \times 1} = 1.65$$

$$\epsilon = 1.65 \text{ ppm}^{-1} \text{ cm}^{-1}$$

b. Using this ϵ value, what is the lead concentration of the unknown tap water sample?

$$A = \epsilon c \ell \rightarrow c = \frac{A}{\epsilon \ell} \longrightarrow \frac{0.0068}{1.65 \text{ ppm}^{-1} \text{ cm}^{-1} \times 1 \text{ cm}} = 4.12 \times 10^{-3} \text{ ppm} \\ = 4.12 \text{ ppb}$$

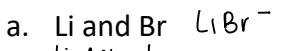
c. Is the concentration of lead in this sample within safe (US) limits?

4.12 ppb ✓ yes safe

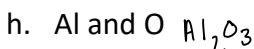
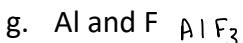
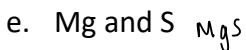
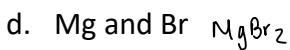
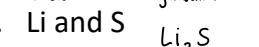
CHEM1111 worksheet – Lecture 15

Ionic bonding

1. Predict the formula of the ionic compound that will be formed between the following pairs of ions:



Li is in group 1 it
loses an electron



2. In the demonstration, we are going to observe the characteristic emission of four different metal salts – strontium nitrate, barium chloride, sodium chloride and copper (II) chloride. The reaction involves potassium chlorate, which is a strong oxidising agent, and sugar, which is easily oxidised and is a good source of energy. The reaction is started by using concentrated sulfuric acid as a catalyst.

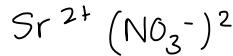
- a. If the formula for potassium chlorate is KClO_3 , what is the charge on the polyatomic ion chlorate? $\text{K}^+ \text{ClO}_3^-$

Good electron donors
are on the left of the
periodic table; s^1 , s^2 and
 d (transition) elements.

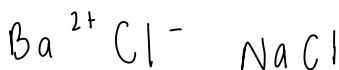
1+ 2+	Commonly found ions	2- 1-
	1+, 2+ or 3+	

Good electron
acceptors are on the
right of the periodic
table; p^2 , (p^4) .

- b. The formula of strontium nitrate is $\text{Sr}(\text{NO}_3)_2$. What is the charge on the nitrate anion?



- c. Write the formulae for barium chloride and sodium chloride.



3. From the table of lattice energies below:

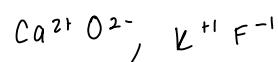
TABLE 5.1 Lattice energies for a number of ionic compounds. All values are in kJ mol^{-1} .

Cation	Anion				
	F^-	Cl^-	Br^-	I^-	O^{2-}
Li^+	1030	834	788	730	2799
Na^+	910	769	732	682	2481
K^+	808	701	671	632	2238
Rb^+	774	680	651	617	2163
Mg^{2+}	2913	2326	2097	1944	3795
Ca^{2+}	2609	2223	2132	1905	3414
Sr^{2+}	2476	2127	2008	1937	3217
Ba^{2+}	2341	2033	1950	1831	3029

- a. What is the trend in lattice energies of fluoride salts of alkali metals? Explain this trend.

As you go down a group the lattice energy gets smaller, this because the radius increases. and this gives a smaller charge density

- b. Give one reason why CaO has a larger lattice energy than KF .



CaO has larger charges so higher lattice energy

- c. In an ionic lattice of KCl , which ion will be larger?

Number of electrons is the same

K has more proton originally

So therefore smaller so

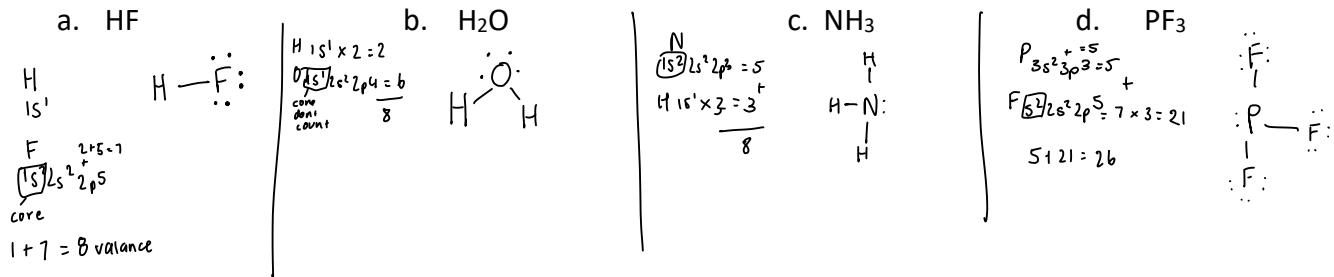
Cl is larger.

1. Know valence electrons
2. Join atoms with bond
3. distribute the remaining to the most electro negative atoms

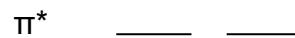
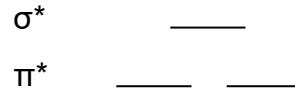
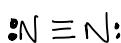
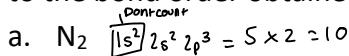
CHEM1111 worksheet – Lecture 16

Lewis structures

1. Draw Lewis structures for:



2. Draw Lewis structures of the following molecules and assign the bond orders. Then fill in the molecular orbital diagram for N₂ and calculate the bond order. How does it compare to the bond order obtained from the Lewis structure?

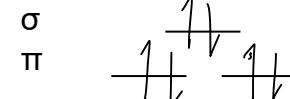
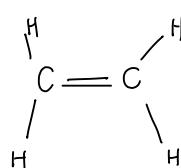


- b. Ethene (C₂H₄)

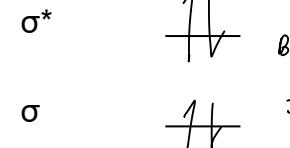
$$C = [1s^2]2s^22p^2 = 4 \times 2 = 8$$

$$H = 1s^2 \times 4 = 4$$

$$4 + 8 = 12$$

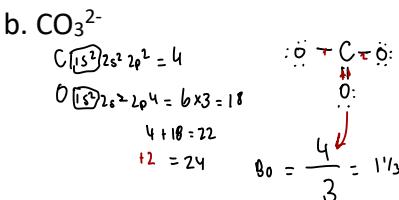
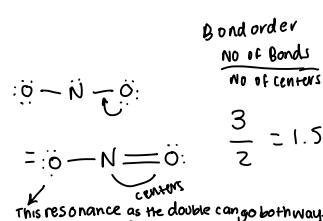
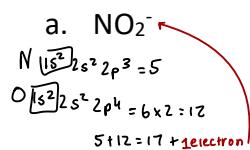


$$BO = \frac{6-2}{2} = 2$$



$$BO = \frac{6-2}{2} = 2$$

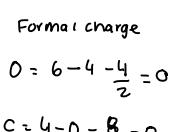
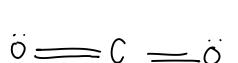
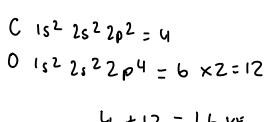
3. Draw Lewis structures for the following molecules and assign the bond order.



4. Assign formal charges to the Lewis structures in question 4.

5. Draw three possible Lewis structures each of these molecules, assign formal charges and determine which is/are the preferred structure(s):

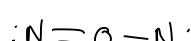
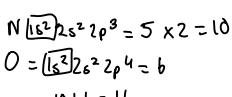
- a. CO₂



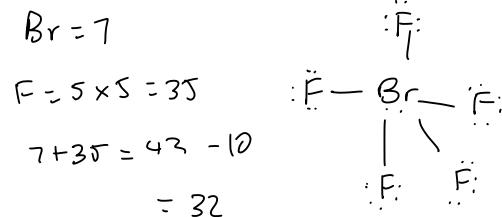
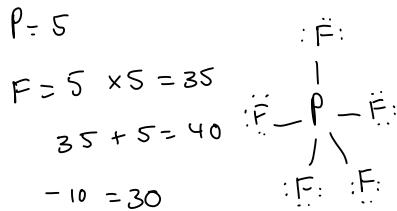
Ressonance structure
 $C = 4 - 0 - \frac{8}{2} = 0$

MUST obey octet rule
and have formal charge of 0

- b. N₂O

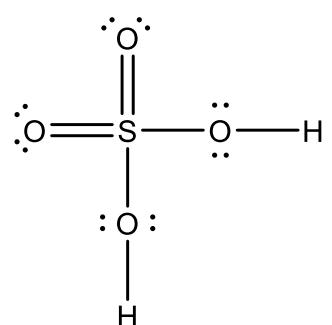


6. Draw Lewis structures for:



7. The Lewis structure of sulfuric acid, H_2SO_4 , is commonly drawn with an expanded octet for sulfur, as shown.

a. Annotate the structure with bond orders and formal charges for each atom.



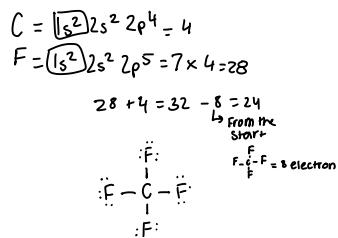
b. Draw an alternative Lewis structure for H_2SO_4 that obeys the octet rule and assign bond orders and formal charges.

CHEM1111 worksheet – Lecture 17

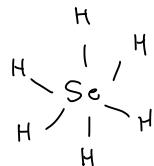
VSEPR theory

1. Draw Lewis structures for the following molecules:

a. CF_4

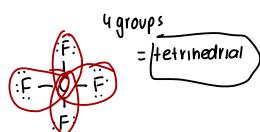


b. SeH_6

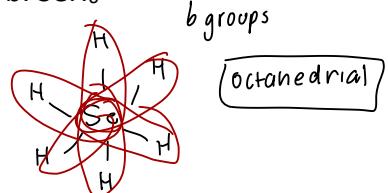


2. Predict the molecular shape for the molecules in Q1

a. CF_4

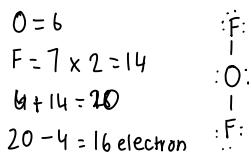


b. SeH_6

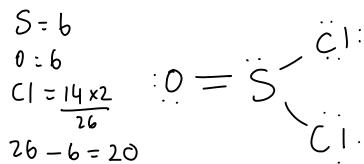


3. Draw Lewis structures for the following molecules.

a. OF_2

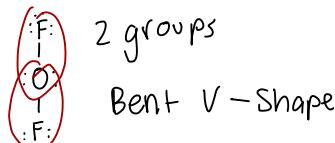


b. SOCl_2

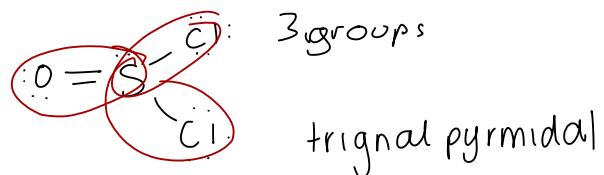


4. Predict the molecular shape for the molecules in Q3

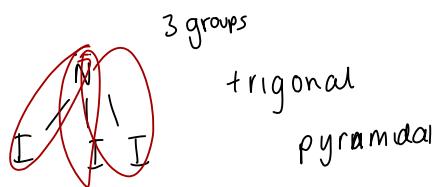
a. OF_2



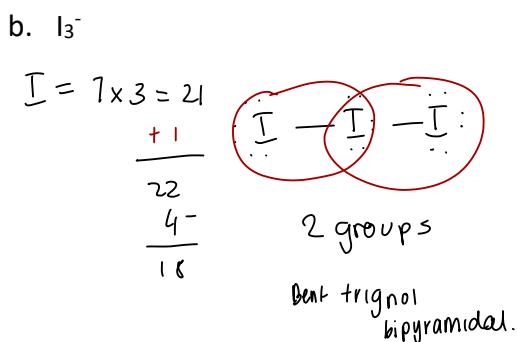
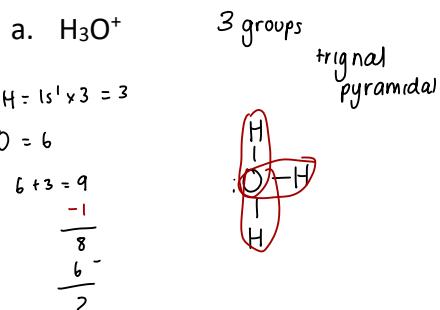
b. SOCl_2



5. Nitrogen triiodide (NI_3) is extremely unstable and can violently explode with the slightest touch. Draw the Lewis structure of NI_3 and predict its molecular shape



6. For the following ions draw the Lewis structure(s) and predict the molecular shape





School of Chemistry

Chemistry 1A (CHEM1111)

Tutorial 6 (Week 6): Lewis Structures

Model 1: Simple Compounds of C, N, O and F

The octet rule tells us that C, N, O and F will form covalent bonds so that they are surrounded by eight electrons. For C, N, and O, this can give rise to compounds with single or multiple bonds.

Critical thinking questions

1. The following table shows some common simple molecules containing C, N, O or F. For the atom in **bold**, fill in the number of single, double and triple bonds surrounding it, and the number of lone electron pairs.

Compound	Number of single bonds	Number of double bonds	Number of triple bonds	Number of lone electron pairs
$\begin{array}{c} \text{H} & \text{H} \\ & \backslash \\ \text{C} & / \\ & \backslash \\ \text{H} & \text{H} \end{array}$	4	0	0	0
$\begin{array}{c} \text{H} \\ & \text{C}=\ddot{\text{S}}: \\ & \text{H} \end{array}$	2	1	0	2
$\text{H}-\text{C}\equiv\text{P}:$	1	0	1	1
$\begin{array}{c} \text{H} & \text{H} \\ & \backslash \\ \text{H}-\ddot{\text{N}} & / \\ & \backslash \\ \text{H} & \text{H} \end{array}$	3	0	0	1
$\begin{array}{c} \ddot{\text{N}} \\ \text{H}-\text{C}-\text{H} \\ \text{H} \end{array}$	3	1	0	1
$:\text{N}\equiv\text{N}:$	0	0	1	2
$\begin{array}{c} \text{H} \\ :\ddot{\text{O}} \\ \text{C}-\text{H} \\ \text{H} \end{array}$	5	0	0	2
$:\ddot{\text{O}}-\ddot{\text{N}}-\text{H}$	1	1	0	3
$:\ddot{\text{F}}-\text{H}$	1	0	0	3

2. Based on your answers in the Q1, fill in the following table to show how many lone electron pairs and how many bonds C, N, O and F need to have to satisfy the octet rule. For total number of bonds, count a triple bond as 3 and a double bond as 2 (e.g. 1 triple bond + 1 single bond = 4).

Atom	Number of lone electron pairs	Total number of bonds
C	0	4
N	1	3
O	2	2
F	3	1

Model 2: Formal Charge

For some molecules, not every atom can have its preferred number of bonds and lone electron pairs. Formal charge can be a useful concept in determining the most likely Lewis structure for a compound. In general, preferred structures will have minimised formal charges on each atom.

In order to calculate the formal charge of an atom in a molecule, three things must be determined:

- the number of valence electrons of the element
- the number of electrons that the atom has in lone pairs
- the number of electrons that the atom shares in bonds

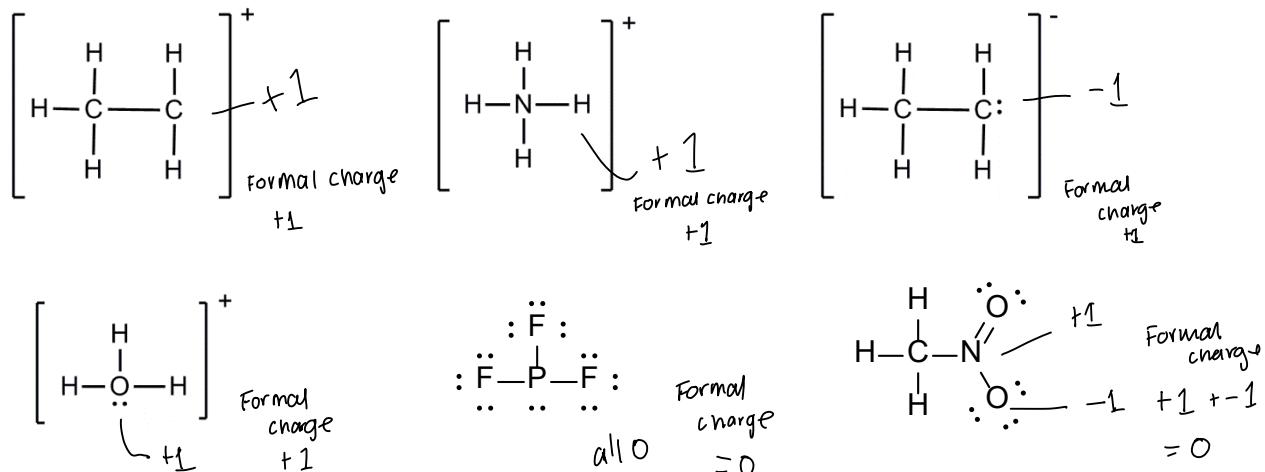
Formal charge can be calculated by the following formula:

$$\text{Formal charge} = (\text{valence electrons}) - (\text{lone pair electrons}) - \frac{1}{2} (\text{shared electrons})$$

A negative formal charge means that an atom has more electrons than it does in atomic form, while a positive formal charge means that it has fewer electrons.

Critical thinking questions

3. For the following Lewis structures, determine the formal charge of each atom.



4. For the species in question 3, determine the sum of the formal charges. How does this relate to the overall charge of the compound?

Model 3: Lewis Structures

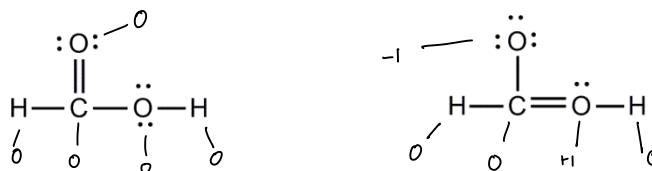
Lewis structures can give us information about the connectivity between atoms in molecules.

The steps for drawing Lewis structures are:

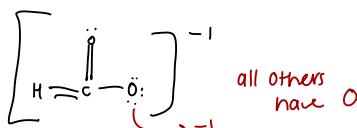
- Step 1.** Count the total number of valence electrons on the molecule
Step 2. Draw single bonds between the atoms
Step 3. Count how many electrons are left and assign them as lone pairs to fill the valence shells
Step 4: If there are unfilled valence orbitals, share the lone pairs to fill the valence orbitals
Step 5: If there is more than one possible plausible structure, then we consider both (all) to be resonance structures

Critical thinking questions

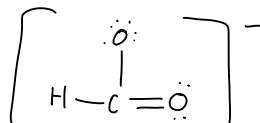
5. Formic acid has a formula of CH_2O_2 . Two possible Lewis structures are shown below. Calculate the formal charges on all atoms in the two structures, and predict which Lewis structure better reflects the structure of formic acid.



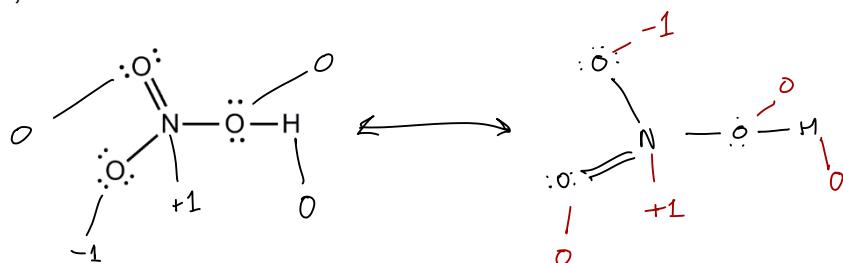
6. Formic acid can lose the H bound to the oxygen atom as H^+ , to give the conjugate base, formate (CHO_2^-). Draw the resulting ion, and calculate the formal charges of each atom.



7. There is a second resonance form of formate, in which the other oxygen atom has the negative charge. Draw the other resonance form, based on your answer to question 6.



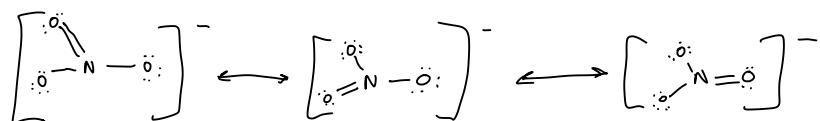
8. One resonance structure of nitric acid is shown below. Calculate the formal charges on each atom, and draw the other resonance structure.



9. What are the bond orders of the three N-O bonds in nitric acid, taking into account the resonance forms?

The two N-O bonds have bond orders of 1.5, the N-OH bond order is 1

10. The proton of nitric acid can be removed to give the nitrate anion, NO_3^- . Draw the Lewis structures of all the resonance forms of nitrate.



Model 4: Lewis Structures for Organic Molecules

Organic molecules contain carbon and hydrogen and may also contain other atoms such as O and N. The ability of C, N and O to make single and multiple bonds means that there is a huge number of possible organic molecules.

Critical thinking questions

11. Draw the Lewis structures of the molecules below. Make sure that you use all of the electrons that are available.

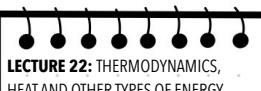
	Lewis Structure
(a) C_3H_8	$ \begin{array}{ccccc} & \text{H} & \text{H} & \text{H} \\ & & & \\ \text{H} & - \text{C} & - \text{C} & - \text{C} & - \text{H} \\ & & & \\ & \text{H} & \text{H} & \text{H} \end{array} $
(b) H_2CO	$ \begin{array}{c} \text{H} \\ \backslash \\ \text{C} = \ddot{\text{O}} \\ / \\ \text{H} \end{array} $
(c) CH_3OCH_3	$ \begin{array}{ccccc} & \text{H} & & \text{H} \\ & & & \\ \text{H} & - \text{C} & - \text{O} & - \text{C} & - \text{H} \\ & & & \\ & \text{H} & & \text{H} \end{array} $

12. Complete the Lewis structures of the molecules below by filling in multiple bonds and lone electron pairs. The molecules are not charged.

glycine (an amino acid)	guanine (nitrogen base in DNA)	aspirin

THERMO-

DYNAMICS

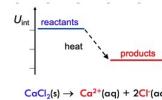
**LO: DEFINE SYSTEMS, SURROUNDING AND UNIVERSE FOR SIMPLE THERMODYNAMIC PROCESSES**

- System – the part of the universe we are focussed on
For us, the chemical reaction: e.g. $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$
- Surroundings – everything else
- System + surroundings = The Universe
- Internal energy (U) – the total energy (potential and kinetic) of the system

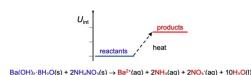
LO: RELATE THE DIFFERENCE IN INTERNAL ENERGY OF REACTANTS AND PRODUCTS TO THE SIGN OF THE CHANGE IN INTERNAL ENERGY FOR EXOTHERMIC AND ENDOHERMIC REACTIONS**Chemical reactions and energy – exothermic reactions**

Many reactions release heat – exothermic

- Products have lower internal energy (U) than reactants:
- $U_{\text{int}}(\text{products}) < U_{\text{int}}(\text{reactants})$ so
 $\text{Change} = \Delta U_{\text{int}} = U_{\text{int}}(\text{products}) - U_{\text{int}}(\text{reactants}) < 0$

**Chemical reactions and energy – endothermic reactions**

- Some reactions require heat to be supplied - endothermic
- Products have greater internal energy than reactants:
- $U_{\text{int}}(\text{products}) > U_{\text{int}}(\text{reactants})$ so
 $\text{Change} = \Delta U_{\text{int}} = U_{\text{int}}(\text{products}) - U_{\text{int}}(\text{reactants}) > 0$

**LO: USE THE FIRST LAW OF THERMODYNAMICS TO CALCULATE CHANGE IN INTERNAL ENERGY ACCOMPANYING HEATING AND EXPANDING AN IDEAL GAS****Heat and work**

The energy changes in a chemical reaction are not confined to heat (q):

- Expansion and compression of gas
- Light
- Electrical

First Law of Thermodynamics:

- The change in internal energy of a chemical system is the sum of heat absorbed (q) by and the work (w) done on the system: $\Delta U_{\text{int}} = q + w$

Work Arising from Expansion or Compression

- The work done on or by a system can take many forms.
- One common form of work in systems in contact with the atmosphere arises when the system changes its volume V , either



- The work w done on the system due to a volume change ΔV in contact with a pressure P is then given by:

$$w = -P \times \Delta V$$

- Why the negative sign? Think about compression:

- Work is done to the system and its energy increases:
 $w > 0$ when $\Delta V < 0$ (i.e. compression)
- We have to include a minus sign to ensure that this relation holds

The meaning of the 1st law

The realization that heat is a form of energy, the idea embodied in the 1st Law of Thermodynamics, was one of the great achievements of 19th century science.

In the same way that the discovery of the gas laws in the 17th and 18th centuries allowed for the inclusion of gases as a form of matter and so lead to the idea of the chemical transformation of matter - the 1st Law's inclusion of heat as a form of energy allows us to describe the chemical transformation of energy.

**LECTURE 24:**

USING ENTHALPIES OF FORMATION AND FUEL EFFICIENCY

LO: DEFINE STANDARD STATES

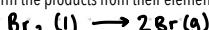
Standard conditions and enthalpy of formation

Standard conditions are universally understood to be: Pressure = 1 atm, temperature = 298 K, concentration = 1 mol L⁻¹. When these conditions apply, a 'o' is added to the thermochemical symbol: e.g. ΔH° , $\Delta_f H^\circ$, and $\Delta_{comb} H^\circ$.The enthalpy of formation of a compound is the enthalpy change when it is made from the stable form of its elements at these conditions: C(s) + 2H₂(g) → CH₄(g) $\Delta_f H^\circ$ = -74.8 kJ mol⁻¹Methane is made from carbon and hydrogen. At 1 atm and 298 K, the stable forms are graphite (C(s)) and diatomic gaseous H₂(g) respectively.**LO: COMBINE ENTHALPIES OF FORMATION TO WORK OUT THE ENTHALPY CHANGE FOR CHEMICAL REACTIONS****LO: COMBINE ENTHALPIES OF REACTION TO WORK OUT THE ENTHALPIES OF FORMATION**

Enthalpy of formation and Hess's law

Formation equations can be combined to calculate enthalpies we haven't (or can't) measure. For example: CFCIBr₂(g) + light → CFCI(g) + 2Br(g). Decompose the reactants into elements in their standard states:CFCIBr₂(g) → C(s) + Br₂(l) + ½F₂(g) + ½Cl₂(g). As the reaction is the reverse of the formation of CFCIBr₂(g), the enthalpy change is -DfH_o (CFCIBr₂(g)): DH_o = -DfH_o (CFCIBr₂(g)) = +184 kJ mol⁻¹

Form the products from their elements in their standard states:

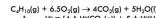


- As the reaction leads to 2Br(g), the enthalpy change is 2DH_o (Br(g)): $\Delta H_2^\circ = 2\Delta_f H(Br(l)) = +223.74 \text{ kJ mol}^{-1}$
- C(s) + ½F₂(g) + ½Cl₂(g) → CFCI(g) = +31 kJ mol⁻¹

In general:

$$\Delta_{actual} H^\circ = \sum \Delta_f H^\circ(\text{products}) - \sum \Delta_f H^\circ(\text{reactants})$$

Examples:



$$\Delta_{actual} H^\circ = [(1\Delta_f H(C_2H_6(g)) + 3/2\Delta_f H(O_2(g))) - (2\Delta_f H(CO_2(g)) + 3\Delta_f H(H_2O(l)))]$$

Note: $\Delta_f H(O_2(g)) = 0$ as formation of an element from itself requires no energy!

$$\begin{aligned} & \text{Combine: (1) + (2) + (3)} \\ & CFCIBr_2(g) + \text{Br}_2(l) + \frac{1}{2}F_2(g) + \frac{1}{2}Cl_2(g) \\ & \rightarrow C(s) + 2Br(g) + \frac{1}{2}F_2(g) + \frac{1}{2}Cl_2(g) + 2Br(g) + CFCI(g) \end{aligned}$$

$$\begin{aligned} & \Delta H^\circ = \Delta H^\circ + \Delta H_2^\circ + \Delta H^\circ \\ & = [(1\Delta_f H(CFCIBr_2(g)) + (2\Delta_f H(Br(l)) + (3\Delta_f H(F_2(g)) + (1/2\Delta_f H(Cl_2(g)))] \\ & = (-\Delta_f H(CFCIBr_2(g)) + (2\Delta_f H(Br(l)) + \Delta_f H(CFCI(g)) \end{aligned}$$

LO: EXPLAIN THE ADVANTAGES AND DISADVANTAGES OF DIFFERENT FUELS**LO: WORK OUT THE EFFICIENCY OF FUELS**

LECTURE 25: ENTROPY AND SPONTANEITY

LO: UNDERSTANDING THAT THE DIRECTION OF SPONTANEOUS CHANGE IS NOT ACCOUNTED FOR BY THE 1ST LAW

Spontaneity

The 1st Law cannot tell us anything about spontaneity. e.g. heat flowing from hot to cold or heat flowing from cold to hot - both satisfy the 1st Law but only heat flowing from hot to cold actually occurs spontaneously. Why?

First Law of Thermodynamics: The change in internal energy of a chemical system is the sum of heat absorbed (q) by and the work (w) done on the system: $\Delta U_{\text{int}} = q + w$

Explain spontaneous processes like the flow of heat from high T to low T.

Clausius connected heat flow q with entropy change: ΔS by $\Delta S = q/T$

Heat flow q into a system increases its entropy. The lower the temperature, the bigger the increase Rudolf Clausius in entropy.

A chemical reaction proceeding towards equilibrium is an example of spontaneous change.

Entropy (S) is a thermodynamic quantity that describes the number of arrangements that are available to the system in a given state.

Mathematically: $S = k \ln W$ (W = number of ways molecule can be in a range in a particular configuration and k =Boltzmann constant: $1.38 \times 10^{-23} \text{ J/K}$)



LO: UNDERSTAND THAT CLAUSIUS' DEFINITION OF ENTROPY CHANGES IN TERMS OF A Q AND T ASSOCIATES HEAT FLOW FROM HIGH TO LOW T WITH THE REQUIREMENTS THAT THE TOTAL ENTROPY MUST INCREASE IN A SPONTANEOUS PROCESS.

LO: UNDERSTAND THE STATEMENT OF LAW 2

In a spontaneous process, the entropy of the universe must increase: $\Delta S_{\text{universe}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$

The universe becomes more disordered and like the first law of thermodynamics, the second Law can never be violated. For any process to occur spontaneously, the total entropy must increase. For now, take the 2nd Law simply as a condition which, if applied, always predicts the outcome we actually observe. In a spontaneous process, decreases in the entropy of the system can only occur if increases in the entropy of the surroundings outweigh them, remembering that a the second law must always be obeyed: $\Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0$. The essential role of the surroundings is to either add heat to the system or remove heat.

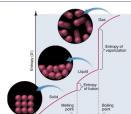
LO: KNOW THE 'TRENDS IN ENTROPY' (SLIDE 8)

Entropy is zero at absolute zero

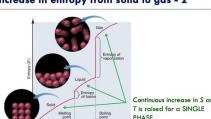
A material at $T = 0 \text{ K}$ is defined as having an entropy of zero. This statement is called the 3rd Law of Thermodynamics. It provides a reference point from which all other entropies can be measured. Entropy increases in a material when the temperature increases. Entropy increases when molecules go from a dense state (liquids and solids) to the gas state. Entropy decreases when an ideal gas is compressed at constant temperature

LO: CALCULATE ENTROPY CHANGE USING STANDARD ENTROPY TABLES

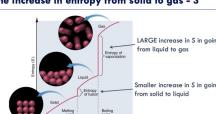
The increase in entropy from solid to gas - 1



The increase in entropy from solid to gas - 2



The increase in entropy from solid to gas - 3



LO: UNDERSTAND THE IMPORTANCE OF ACCOUNTING FOR ENTROPY CHANGE IN THE SURROUNDINGS AS WELL AS THE SYSTEM.

The importance of the surroundings - 1

- In an isolated system (e.g. a thermos flask)
$$\Delta S_{\text{total}} = \Delta S_{\text{system}}$$

- But for an open system (e.g. any reaction in contact with a heat bath)
$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

The surroundings here might be the atmosphere, a heat bath, etc.

The importance of the surroundings - 2

2nd Law of Thermodynamics:

$$\boxed{\text{For any spontaneous process: } \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0}$$

We can calculate ΔS_{system} and $\Delta S_{\text{surroundings}}$ separately, and hence determine spontaneity using the 2nd Law

CHEM1111: Worksheet – Lecture 22

Model 1: Heat in or heat out: q

- If a reaction *requires* heat (q), it absorbs it from the surroundings. If you hold a beaker containing such a reaction, the heat is taken from your hands and they feel cold. Such reactions are called **endothermic**.
- If a reaction *releases* heat, it transfers it to the surroundings. If you hold a beaker containing such a reaction, the heat is transferred to your hands and they feel hot. Such reactions are called **exothermic**.
- If there is only a change in **heat energy** during a reaction, then the change in the internal energy, $\Delta U_{\text{int}} = q$.

Critical thinking questions

When $\text{CaCl}_2(\text{s})$ is dissolved in water, the reaction is **exothermic**.

1. How would the temperature of the water change as $\text{CaCl}_2(\text{s})$ dissolves?
The temperature would increase = $\Delta T_{\text{temperature}} > 0$
2. The chemical ‘system’ in this case is the Ca^{2+} and Cl^- ions and the waters that they interact directly with. The ‘surroundings’ is the rest of the water molecules. Has the chemical system gained or lost energy?
lost energy
3. Is the change in the internal energy of the system, ΔU_{int} , positive or negative?
negative $\Delta U_{\text{internal}} < 0$
4. Complete the table opposite by putting ‘+’ or ‘-’ to show the sign of ΔU_{int} and q for exothermic and endothermic reactions.

reaction type	ΔU_{int}	q
exothermic	-	-
endothermic	+	+

Model 2: Work: w

- If work, *is done to a system*, energy is transferred to it and its **internal energy increases**: $w > 0$.
- If work is *done by a system*, it loses energy and its internal energy *decreases*: $w < 0$

Critical thinking questions

1. If a gas is compressed by applying pressure, P , has it gained or lost energy?
Gained energy
2. Is the change in the internal energy of the system, ΔU_{int} , positive or negative?
 $\Delta U_{\text{internal}} > 0$ (positive)
3. Change in volume = $\Delta V = V_{\text{final}} - V_{\text{initial}}$. If a gas is compressed is ΔV positive or negative?
If V_{final} is small and V_{initial} is large then it will be a negative number
 $\Delta V < 0$

4. Complete the table opposite by putting '+' or '-' to show the sign of ΔU_{int} , w and ΔV for the compression and expansion of a gas.

process	ΔU_{int}	w	ΔV
compression	+	+	-
expansion	-	-	+

NOTE: Work (w) for compression is being done to the system. So it gains energy.

Work (w) for Expansion is being by the system. It loses energy.

Model 3: Work and heat together:

- First law of thermodynamics: $\Delta U_{\text{int}} = q + w$ q = heat absorbed, w = work
- Work done to or by a system due to a volume change against a constant pressure: $w = -P\Delta V$
- For a system operating against constant pressure: $\Delta U_{\text{int}} = q - P\Delta V$
- The S.I. unit for volume is the cubic metre (m^3). The S.I. unit for pressure is the Pascal (Pa), where standard pressure of 1 atm = 101.3 kPa. Constant pressure: $\Delta U_{\text{internal}} = q - P \times \Delta V$

Critical thinking questions

1. An ideal gas receives 245 J of heat and expands by $1.30 \times 10^{-3} \text{ m}^3$ against an external pressure of 60.0 kPa. What is the change in internal energy of the system?

$$q = +245 \text{ (endothermic)} \\ p = 60.0 \text{ kPa} \times 1000 = 60.0 \times 10^3 \text{ Pa} \\ \Delta V_{\text{internal}} = (+245 \text{ J}) - (60.0 \times 10^3 \text{ Pa} \times 1.3 \times 10^{-3} \text{ m}^3) \\ \Delta V = 1.3 \times 10^{-3} \text{ m}^3 \\ = 167 \text{ J}$$

2. It is more common in chemistry (and life generally) to express volumes in litres (L). How many litres are there in one cubic metre? (Hint: 1 L = 1000 cm³.)

$$1 \text{ m}^3 = 100 \text{ cm} \times 100 \text{ cm} \times 100 \text{ cm} = 1 \times 10^6 \text{ cm}^3 \\ 1 \text{ cm}^3 = 1 \text{ mL} \\ 1 \text{ L} = 10^{-3} \text{ m}^3$$

3. An ideal gas receives 245 J of heat and contracts by 1.30 L against an external pressure of 60.0 kPa. What is the change in internal energy of the system?

$$q = +245 \text{ J} \\ p = 60.0 \text{ kPa} \times 1000 = 60.0 \times 10^3 \text{ Pa} \\ \Delta V = -1.30 \text{ L} \\ 1 \text{ L} = 10^{-3} \text{ m}^3 = -1.30 \times 10^{-3} \text{ m}^3 \\ \Delta U_{\text{internal}} = (+245 \text{ J}) - (60.0 \times 10^3 \text{ Pa} \times -1.30 \times 10^{-3} \text{ m}^3) \\ = 323 \text{ J}$$

CHEM1111: Worksheet – Lecture 23

Model 1: Heat, enthalpy and internal energy

From the 1st Law we can write an expression for the change in internal energy, ΔU_{int} , for a reaction involving heat change, q , and a change in the volume of gas, V , against an external pressure P :

$$\Delta U_{int} = q - P\Delta V \quad \text{or} \quad q = \Delta U_{int} + P\Delta V \quad (1)$$

Many chemical reactions occur at constant pressure – commonly atmospheric pressure. It is useful to use **enthalpy**. The ‘heat of reaction’ or enthalpy change is the **heat change at constant pressure**:

$$\Delta H = q_P = \Delta U_{int} + P\Delta V \quad (2)$$

Critical thinking questions

- Sometimes reactions are carried out in sealed containers, so the volume is constant. Using expression (1), write an equation relating ΔU_{int} and the heat change at constant volume, q_v .

$$\textcircled{1} \quad q = \Delta_{\text{internal}} \text{ energy} + P \times \Delta V$$

↓ change in volume
 = 0

$$q_v = \Delta_{\text{internal}} \text{ energy}$$

↓ heat of constant volume

- For each of the reactions below, predict whether (i) $\Delta H > \Delta U_{int}$, (ii) $\Delta H < \Delta U_{int}$ or (iii) $\Delta H \approx \Delta U_{int}$ (*Hint: How big is ΔV and what is its sign?*)

- (a) Enthalpy of vaporisation of water.
 $\text{H}_2\text{O(l)}(100^\circ\text{C}) \rightarrow \text{H}_2\text{O(g)}(100^\circ\text{C})$
 liquid to gas means lots of expansion
 change in volume is greater than 0, The change Enthalpy will be greater than internal energy
 $\Delta V > 0 \quad \Delta H > \Delta_{\text{internal}}$
- (b) Enthalpy of condensation of water.
 $\text{H}_2\text{O(g)}(100^\circ\text{C}) \rightarrow \text{H}_2\text{O(l)}(100^\circ\text{C})$
 Gas to a liquid, change in volume is less than 0, internal energy is larger than enthalpy
 $\Delta V < 0 \quad \Delta_{\text{internal}} > \Delta H$
- (c) Enthalpy of combustion of graphite.
 $\text{C(s)} + \text{O}_2\text{(g)} \rightarrow \text{CO}_2\text{(g)}$
 Gas to Gas, change in volume is equal to 0, internal energy is same as enthalpy
 $\Delta V \approx 0 \quad \Delta_{\text{internal}} \approx \Delta H$

Model 2: Enthalpy of atomisation

When a mole of a compound is broken apart into its constituent gas phase atoms, energy is *consumed* and the energy change is called the enthalpy of atomisation ($\Delta_{\text{atom}}H$). Because energy is required, $\Delta_{\text{atom}}H > 0$ and atomisation is always **endothermic**. For example, atomisation of water corresponds to $\text{H}_2\text{O(g)} \rightarrow 2\text{H(g)} + \text{O(g)}$.

Energy is needed to break 2 O-H bonds. $\Delta_{\text{atom}}H$ values can be estimated using tabulated bond enthalpies, which are the average bond strengths from a series of related compounds. An O-H bond has an average bond enthalpy of 464 kJ mol⁻¹. As the reaction involves breaking 2 O-H bonds, $\Delta_{\text{atom}}H(\text{H}_2\text{O}) \approx 2 \times 464 \text{ kJ mol}^{-1} = 928 \text{ kJ mol}^{-1}$.

Critical thinking questions

- Use average bond enthalpies* to estimate the enthalpy of atomisation of the molecules below.



N-H bond = 391 kJ mol⁻¹
 $\Delta_{\text{H atomisation}} = 3 \times 391 = 1170 \text{ kJ mol}^{-1}$



C-H Bond = 416
 $\Delta_{\text{H atomisation}} = 416 \times 4 = 1664 \text{ kJ mol}^{-1}$



H-O Bonds = 464 × 2 = 928
 O-O Bonds = 164
 $\Delta_{\text{H atomisation}} = 928 + 164 = 1092 \text{ kJ mol}^{-1}$

NOTE: Enthalpy of atomisation is always positive

* Bond enthalpies (kJ mol⁻¹): N-H 391; C-H 416; O-O 164; O-H 464.

Forming a molecule from its gaseous atoms is the *opposite* of atomisation. As bonds are formed, energy is released: this process is always **exothermic**. For example, for water this corresponds to: $2\text{H(g)} + \text{O(g)} \rightarrow \text{H}_2\text{O(g)}$.

As 2 O-H bonds are made, 928 kJ mol^{-1} is released and $\Delta H = -928 \text{ kJ mol}^{-1}$: i.e. as the reaction is the reverse of the atomisation reaction, ΔH has the same magnitude but is opposite in sign. We can use this to work out reaction enthalpies by imagining reactions occurring in two steps:

- Break all of the bonds in the reactants. This corresponds to atomizing all of the reactants and the enthalpy change corresponds to sum of $\Delta_{\text{atom}}H$ for each reactant.
- Make all of the new bonds in the products from the atoms made in (1). The enthalpy change is $-1 \times \Delta_{\text{atom}}H$ for each product.
- The overall reaction enthalpy is then the sum of the enthalpy changes for (1) and (2).

2. Water is formed by burning hydrogen in oxygen: $\text{O}_2(\text{g}) + 2\text{H}_2(\text{g}) \rightarrow 2\text{H}_2\text{O(g)}$.

- Calculate the enthalpy change for the atomisation of the reactants[†].

$$\begin{aligned}\text{O-O Bond} &= 498 \\ \text{H-H Bond} &= 436 \times 2 = 872 \\ \Delta_{\text{Atomisation}} &= 498 + 872 = 1370 \text{ kJ mol}^{-1}\end{aligned}$$

- Calculate the enthalpy change for the formation of the products from the atoms[†].

$$\Delta_{\text{Form}} = 2(2 \times 464) = -1856 \text{ kJ mol}^{-1}$$

- Calculate the enthalpy change for the overall reaction.

$$\Delta_{\text{Reaction}} = 1370 + -1856 = -486 \text{ kJ mol}^{-1}$$

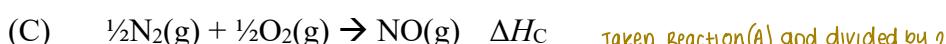
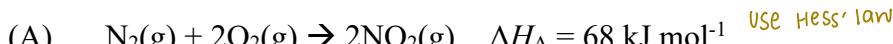
Model 3: Hess's Law

Hess's Law allows reactions with known enthalpy changes to be combined to work out enthalpy changes for unknown or difficult to measure reactions. When combining reactions, the following principles are used:

- When a reaction is reversed, the sign of ΔH is reversed.
- When a reaction is multiplied by a constant, ΔH is also multiplied by the same constant.
- When reactions are combined or added, their ΔH values are added.

Critical thinking questions

Consider the three reactions below which occur in car exhausts. The third reaction is difficult to study.



- What is the enthalpy change for reaction (D): $\frac{1}{2}\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow \text{NO}_2(\text{g})$ $\Delta H_D = \frac{68}{2} = 34 \text{ kJ mol}^{-1}$ TAKEN REACTION (B) AND REVERSED IT.
- What is the enthalpy change for reaction (E): $\text{NO}_2(\text{g}) \rightarrow \text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ $\Delta H_E = -56 = +56 \text{ kJ mol}^{-1}$ CHANGE TO (+) BECAUSE THE REACTION IS IN REVERSE
- Add reactions (D) and (E) together and work out the **net** reaction by crossing out any species that are on both sides of the equation. What is the enthalpy change ΔH_C for this reaction?

(D)	$\frac{1}{2}\text{N}_2(\text{g}) + \cancel{\frac{1}{2}\text{O}_2(\text{g})} \rightarrow \text{NO}_2(\text{g})$	34 kJ mol^{-1}
(E)	$\cancel{\text{NO}_2(\text{g})} \rightarrow \text{NO}(\text{g}) + \cancel{\frac{1}{2}\text{O}_2(\text{g})}$	56 kJ mol^{-1}
(D) + (E)	$\cancel{\frac{1}{2}\text{N}_2(\text{g})} + \cancel{\frac{1}{2}\text{O}_2(\text{g})} \rightarrow \text{NO}(\text{g})$	$\Delta_{(D+E)} = 34 + 56 = 90 \text{ kJ mol}^{-1}$

[†] Bond enthalpies (kJ mol^{-1}): O=O 498; O-H 464; N≡N 945; H-H 436; N-H 391.

CHEM1111: Worksheet – Lecture 24

Model 1: Forms of the elements under standard conditions

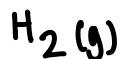
Standard conditions correspond to a temperature of 298 K and a pressure of 1 atm. These conditions are used so that scientists can compare properties of elements and compounds and know that they are referring to the same phases. For example, bromine exists as diatomic molecules in the liquid phase under these conditions. A scientist using it below 7 °C though would encounter solid bromine and a scientist using it above 60 °C would be working with gaseous bromine. The ‘standard state’ of bromine is the most stable form at 298 K and 1 atm: Br₂(l).

For processes carried out under standard conditions, a ‘o’ is added to the thermochemical quantity such as ΔH°.

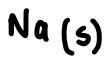
Critical thinking questions

- What are the standard states of the following elements?

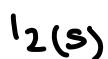
(a) H



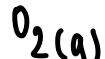
(b) Na



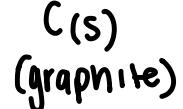
(c) I



(d) O

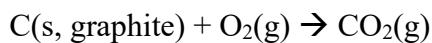


(e) C



Model 2: Standard enthalpy of formation

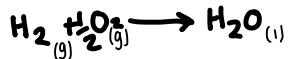
The standard enthalpy of formation of compound refers to the reaction in which it is made from its constituent elements in their standard states. For CO₂(g), for example, it is the enthalpy change for the reaction of C(s) in its standard state (graphite) with O₂(g):



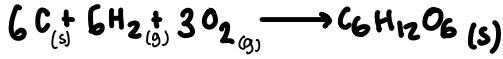
Critical thinking questions

- Write the balanced chemical equations corresponding to the enthalpy of formation of the following:

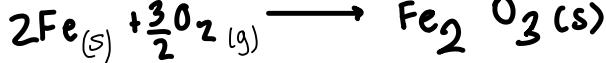
(a) H₂O(l):



(b) Glucose, C₆H₁₂O₆(s):



(c) Fe₂O₃(s):



Model 3: Using standard enthalpies of formation to calculate enthalpies of other reactions

If values are known, standard enthalpies of formation can be combined to calculate the enthalpy of any reaction using Hess’s Law from Model 3 in Lecture 23. Any reaction can be imagined to proceed via:

- Decomposition of each reactant into its elements in their standard states. This is the *reverse* of the reaction corresponds to the enthalpy of formation of the reactant and so the enthalpy change is $-1 \times$ the sum of the enthalpy of formation of each reactant: $\Delta H_1^\circ = -\sum_n \Delta_f H^\circ(\text{reactants})$.
- Formation of each product from its elements in their standard states. The enthalpy change is the sum of the enthalpies change of each product: $\Delta H_2^\circ = +\sum_n \Delta_f H^\circ(\text{products})$.

Overall:

$$\Delta_{\text{reaction}} H^\circ = \Delta H_1^\circ + \Delta H_2^\circ = \sum_n \Delta_f H^\circ(\text{products}) - \sum_n \Delta_f H^\circ(\text{reactants}).$$

Critical thinking questions

1. Using the standard enthalpy of formation data below, calculate the reaction enthalpy for the thermite reaction: $\text{Fe}_2\text{O}_3(\text{s}) + 2\text{Al}(\text{s}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + 2\text{Fe}(\text{s})$

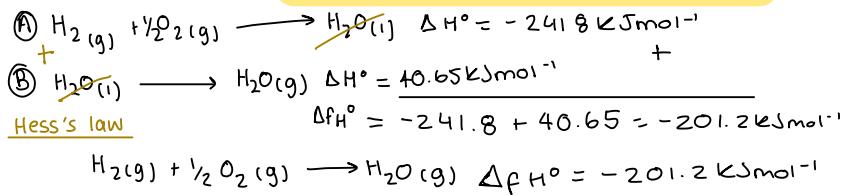
$$\begin{aligned}\Delta_f H^\circ &= \sum n \times \Delta_f H^\circ (\text{Products}) - \sum n \Delta_f H^\circ (\text{Reactants}) \\ &= \Delta_f H^\circ (\text{Al}_2\text{O}_3(\text{s}) + 2 \times \text{Fe}(\text{s})) - (\text{Fe}_2\text{O}_3(\text{s}) + 2 \times \text{Al}(\text{s})) \\ &= \Delta_f H^\circ (-1669.8 + 0) - (-822.2 + 0) = -8476 \text{ kJ mol}^{-1}\end{aligned}$$

2. Using the standard enthalpy of formation data below, calculate the reaction enthalpy for the combustion of glucose: $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \rightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{l})$?

$$\begin{aligned}\Delta_f H^\circ &= \sum n \times \Delta_f H^\circ (\text{Products}) - \sum n \Delta_f H^\circ (\text{Reactants}) \\ &= \Delta_f H^\circ (6 \times \text{CO}_2(\text{g}) + 6 \times \text{H}_2\text{O}(\text{l})) - (\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6 \times \text{O}_2(\text{g})) \\ &= \Delta_f H^\circ (6 \times -393.5 + 6 \times -241.8) - (-1275 + 6 \times 0) \\ &= \Delta_f H^\circ = -2536.8 \text{ kJ mol}^{-1}\end{aligned}$$

$\Delta_f H^\circ$ (kJ mol⁻¹): Fe₂O₃(s) -822.2; Al₂O₃ -1669.8; C₆H₁₂O₆(s) -1275.0; CO₂(g) -393.5; H₂O(l) -241.8

3. The enthalpy of vaporization of H₂O(l) is 40.65 kJ mol⁻¹. What is the enthalpy of formation of H₂O(g)?



Model 4: Rating fuels for transport

Choosing the best fuel to power cars and other forms of transport is a complex issue. Factors to consider include:

- How much energy is produced per litre?
- How difficult is it to store or transport?
- How polluting is it?
- How is it obtained?

Critical thinking questions

1. Consider the four fuels below.

Fuel	Rank from 1 to 4 in order of largest energy produced per litre	Rank from 1 to 4 in order of largest emitter of CO ₂ per kJ produced	Is this fuel a gas or liquid? (Liquids are easier to store)	What is the source of this fuel?
H ₂	4	4	gas	Electrolysis of water
CH ₄	3	3	gas	Mining
C ₂ H ₅ OH	2	1	liquid	Fermenting sugar sources
C ₈ H ₁₈	1	2	liquid	Mining

CHEM1111: Worksheet – Lecture 25

Model 1: Entropy

The change in entropy of a system is $\Delta S = q/T$, where q is the heat flow into the system and T is the absolute temperature of the system.

1. Has the entropy of the system increased, decreased or stayed unchanged in each of the following processes?
 - (i) A litre of water is cooled from 25°C to 10°C. ΔS_{system} **decreased**
Becoming more ordered
 - (ii) A litre of water at 100°C is converted in water vapour. ΔS_{system} **increased**
Becoming less ordered
 - (iii) A block of ice is heated from -15°C to -5°C. ΔS_{system} **increased**
Becoming less ordered
2. Consider two blocks of copper, each 1 kg in mass. Block 1 is at 350 K and Block 2 is at 300 K. The two blocks are placed in contact so that heat can flow between them.
 - (i) What are the signs of the heat flow into Block 1 and into Block 2?
Block 1: $q > 0$, Block 2: $q < 0$
 - (ii) Consider a heat flow of 10 J between the blocks. (This is small enough that we can ignore any change in the temperature of either block).
 - By how much has the entropy decreased in Block 1?
Clausius equation
$$\Delta S = \frac{q}{T} = \frac{-10J}{350K} = -0.029 \text{ J K}^{-1}$$
 - By how much has the entropy increased in Block 2?
Clausius equation
$$\Delta S = \frac{q}{T} = \frac{10J}{300K} = 0.033 \text{ J K}^{-1}$$
 - What is the overall change in entropy?
2nd law of thermodynamics
$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$
$$\Delta S_{\text{total}} = \Delta S_{\text{Block 1}} + \Delta S_{\text{Block 2}}$$
$$= -0.029 + 0.033$$
$$\Delta S_{\text{total}} = +0.004 \text{ J K}^{-1}$$

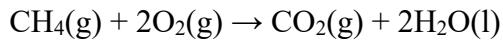
Model 2: ΔS_{total} and the 2nd Law

The 2nd Law of Thermodynamics states that for a process to occur, the total change in the entropy must be positive. Note that we must consider any entropy change of the surroundings as well as the system of interest, i.e. $\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$.

1. Under what condition will $\Delta S_{\text{total}} = \Delta S_{\text{system}}$?

$$\Delta S_{\text{surroundings}} = 0 \text{ (isolated system)}$$

2. In an exothermic process heat flows out of the system, hence the entropy of the system must decrease. How, then, can exothermic processes ever occur spontaneously? **Because the enthalpy of the surroundings will increase**
3. Consider the combustion reaction,



- (i) Calculate the entropy change ΔS_{system} at standard conditions given the following standard entropies (in $\text{J K}^{-1} \text{mol}^{-1}$):

$\text{CH}_4(\text{g})$ 186.2, $\text{O}_2(\text{g})$ 205.0, $\text{CO}_2(\text{g})$ 213.6, and $\text{H}_2\text{O}(\text{l})$ 69.9.

$$\begin{aligned}\Delta S_{\text{system}} &= \Delta S_{\text{(products)}} - \Delta S_{\text{(reactants)}} \\ &= [\Delta S(\text{CO}_2 + 2 \times \Delta S(\text{H}_2\text{O}))] - [\Delta S(\text{CH}_4) + 2 \times \Delta S(\text{O}_2)] \\ &= [213.6 + 2 \times 69.9] - [186.2 + 2 \times 205.0] \\ \Delta S_{\text{system}} &= -242.8 \text{ J K}^{-1} \text{mol}^{-1}\end{aligned}$$

- (ii) The molar heat of combustion for methane is -890.3 kJ. What is $\Delta S_{\text{surroundings}}$ for the combustion of 1 mole of $\text{CH}_4(\text{g})$ at 298 K?

$$\begin{aligned}\Delta H &= -890.3 \text{ kJ} \\ q_{\text{surrounding}} &= -q_{\text{system}} = -\Delta H \\ &= +890.3 \text{ kJ}\end{aligned}$$

Clausius equation

$$\Delta S_{\text{surrounding}} = \frac{q}{T} = \frac{890.3 \text{ kJ} \times 1000}{298 \text{ K}} = \frac{890.3 \times 10^3 \text{ J}}{298 \text{ K}} = +2988 \text{ J K}^{-1} \text{mol}^{-1}$$

- (iii) What is ΔS_{total} for the combustion of 1 mole of $\text{CH}_4(\text{g})$ at 298K?

$$\begin{aligned}\Delta S_{\text{total}} &= \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} \\ &= (-242.8) + (2988)\end{aligned}$$

$\Delta S_{\text{total}} = +2745.2 \text{ J K}^{-1} \text{mol}^{-1}$ is > 0 has not violated 2nd law.

- (iv) Would you expect ΔS_{total} for the combustion of methane to increase or decrease if we were to lower the temperature?

Increase

Model 3: ΔS_{total} and the Influence of Temperature

When working with a system in thermal contact with a surrounding held at a fixed temperature T , we can write the total entropy change as

$$\Delta S_{\text{total}} = \Delta S - \Delta H / T$$

where ΔH and ΔS are both changes for the system only. The 2nd Law states that $\Delta S_{\text{total}} > 0$ for a spontaneous process.

1. We can characterise a process by the signs of ΔH and ΔS . Fill in the Table below indicating the likelihood of spontaneity, i.e. (a) always, (b) never, (c) only at high T or (d) only at low T .

Spontaneity?	$\Delta H < 0$	$\Delta H > 0$
$\Delta S > 0$	always	only at high T
$\Delta S < 0$	only at low T	Never



THE UNIVERSITY OF
SYDNEY

School of Chemistry

Chemistry 1A
(CHEM1111)

Tutorial 9 (Week 9): Enthalpy of Reaction ($\Delta_{rxn}H$)

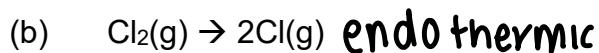
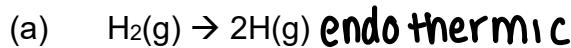
Model 1: Endothermic and Exothermic Processes

Breaking bonds requires energy to pull the atoms apart: bond breaking is endothermic ($\Delta H > 0$). When bonds are formed, energy is released – precisely the same amount of energy which would be required to break those bonds: bond making is exothermic ($\Delta H < 0$).

In most chemical reactions, bonds are broken and made. Whether a reaction is endothermic or exothermic depends on the energy required to perform the *changes* in the bonding.

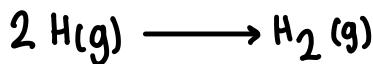
Critical thinking questions

1. Are the following reactions exothermic or endothermic?

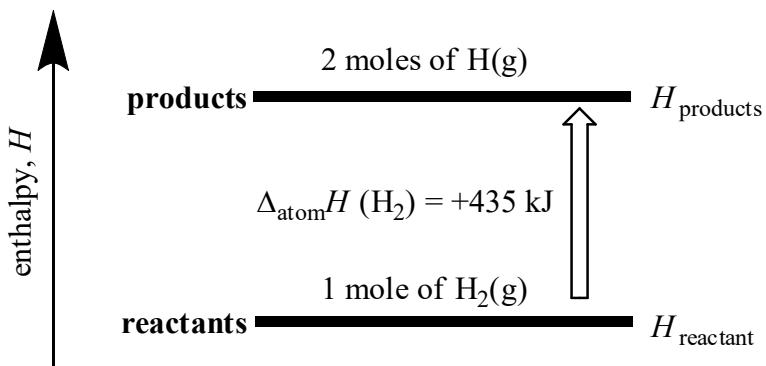


Model 2: Enthalpy of Atomization ($\Delta_{atom}H$) and Enthalpy of Atom Combination ($\Delta_{ac}H$)

When a mole of a compound is broken apart into its constituent gas phase atoms, energy is consumed and the energy change is called the enthalpy of atomization ($\Delta_{atom}H$):

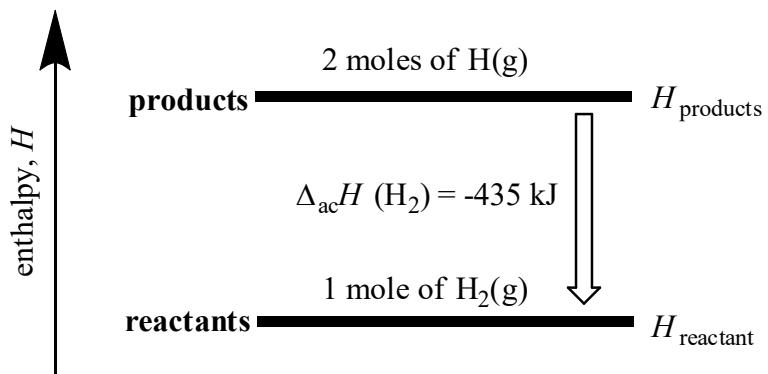


$$\begin{aligned}\Delta_{atom}H &= H(\text{products}) - H(\text{reactants}) \\ &= H(\text{atoms}) - H(\text{compound})\end{aligned}\quad (1)$$



When a mole of a compound is made from its constituent gas phase atoms, energy is released and the energy change is called the enthalpy of atom combination ($\Delta_{ac}H$):

$$\begin{aligned}\Delta_{ac}H &= H(\text{products}) - H(\text{reactants}) \\ &= H(\text{compound}) - H(\text{atoms}) \quad (2)\end{aligned}$$



Critical thinking questions

- What is the relationship between $\Delta_{\text{atom}}H$ and $\Delta_{ac}H$ for a compound like H₂?

$$\Delta_{\text{atom}}H = -\Delta_{ac}H$$

- What is the value of ΔH for the overall process of separating one mole of H₂(g) into its constituent atoms and then reforming one mole of H₂(g)?



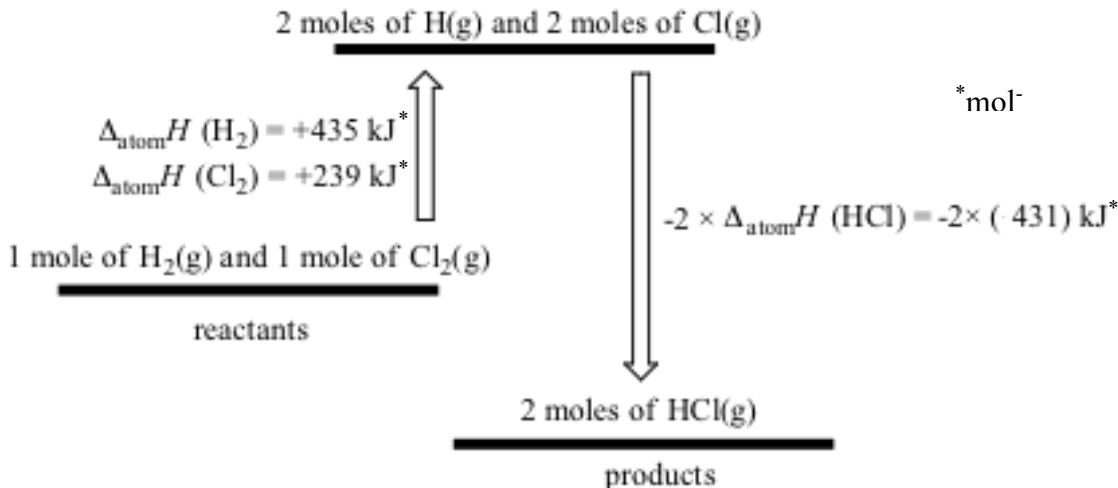
Model 3: Enthalpy of Reaction using $\Delta_{\text{atom}}H$ and $\Delta_{ac}H$

To determine the overall value of ΔH for a reaction, we can imagine the reaction taking place by:

- breaking apart all of the reactant molecules into their constituent atoms: $\Delta_{\text{atom}}H$ (reactants)
- reassembling or combining these atoms into the product molecules: $\Delta_{ac}H$ (products)

The overall enthalpy of the reaction is then the sum of these parts:

$$\Delta_{\text{rxn}}H = \Delta_{\text{atom}}H (\text{reactants}) + \Delta_{ac}H (\text{products}) \quad (3)$$



Critical thinking questions

1. Why is the ΔH associated with the upward arrow in Model 3 a *positive* number?

Involves bonds breaking only, which Requires energy

2. Why is the ΔH associated with the downward arrow in Model 3 a *negative* number?

Involves bonds making only, which Releases energy

3. What is the value of ΔH for the overall reaction in Model 3?

$$\Delta H = (239 + 435) \text{ kJ mol}^{-1} + (2 \times -431) \text{ kJ mol}^{-1} = -188 \text{ kJ mol}^{-1}$$

4. Using your answers to Model 2, rewrite the equation below so that it involves only $\Delta_{ac}H$ (reactants) and $\Delta_{ac}H$ (products).

$$\Delta_{rxn}H = \Delta_{atom}H(\text{reactants}) + \Delta_{ac}H(\text{products}) = \Delta_{rxn}H = \Delta_{ac}H(\text{products}) - \Delta_{ac}H(\text{reactants})$$

5. Using your answers to Model 2, rewrite the equation below so that it involves only $\Delta_{atom}H$ (reactants) and $\Delta_{atom}H$ (products).

$$\Delta_{rxn}H = \Delta_{atom}H(\text{reactants}) + \Delta_{ac}H(\text{products}) = \Delta_{rxn}H = \Delta_{atom}H(\text{reactants}) - \Delta_{atom}H(\text{products})$$

6. If $\Delta_{ac}H$ for the reactants is more negative than $\Delta_{ac}H$ for the products in a chemical reaction, will $\Delta_{rxn}H$ be positive or negative? Explain your reasoning.

$\Delta_{rxn}H$ will be positive if the bonds that need to be broken in the reactants are stronger than those formed in the products, the reaction is endothermic.

Model 4: Enthalpy of Reaction using Δ_fH

In Model 3, you developed a way of working out the value of enthalpy change for a reaction from the values of enthalpy of *atom* combination for the reactants and products. From Q4

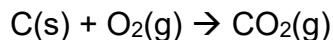
$$\Delta_{rxn}H = \Delta_{ac}H(\text{products}) - \Delta_{ac}H(\text{reactants}) \quad (4)$$

An alternative is to use the enthalpy change of formation of a compound (Δ_fH) from its *elements* in their naturally occurring forms. At room temperature and pressure, these forms are called the **standard states** of the elements and include, for example, graphite for carbon and O₂(g) for oxygen.

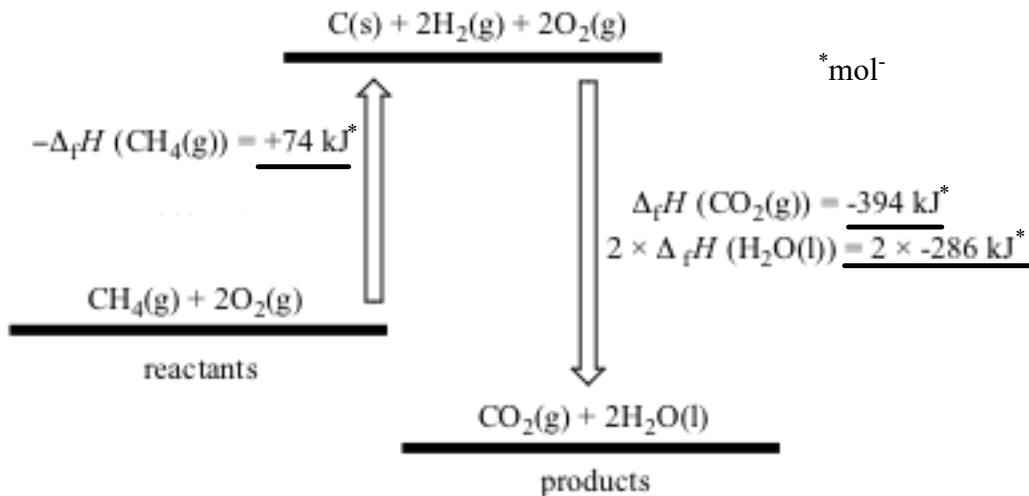
Using this method, the equation for the enthalpy of reaction becomes:

$$\Delta_{rxn}H^\circ = \Delta_fH^\circ(\text{products}) - \Delta_fH^\circ(\text{reactants}) \quad (5)$$

The enthalpy of formation of $\text{CO}_2(\text{g})$ is then the energy change for its formation from graphite and $\text{O}_2(\text{g})$:



The enthalpy change for the combustion of methane is represented on the energy level diagram below. On the left, $\text{CH}_4(\text{g})$ and $\text{O}_2(\text{g})$ are broken up into their elements in the standard states, graphite (C(s)), $\text{H}_2(\text{g})$ and $\text{O}_2(\text{g})$. This is the reverse of their formation so the energy required is $-\Delta_f H^\circ$ (reactants). On the right, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{l})$ are formed from the same elements in the same states so the energy change is $+\Delta_f H^\circ$ (products).



Critical thinking questions

1. Why are $\Delta_f H^\circ (\text{O}_2(\text{g}))$ and $\Delta_f H^\circ (\text{H}_2(\text{g}))$ both equal to 0 kJ? (Hint: what is the reaction in each case?)

$\Delta_f H^\circ \text{ O}_2(\text{g})$ is 0 as it is in its standard state ($\text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{g})$)

$\Delta_f H^\circ \text{ H}_2(\text{g})$ is 0 because the element is in its standard state ($\text{H}_2(\text{g}) \rightarrow \text{H}_2(\text{g})$)

2. What is $\Delta_{rxn} H^\circ$ for the reaction $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l})$?

Products - Reactants

Reactant Products

(standard state = 0)

$$[\Delta H^\circ_{(\text{CO}_2)} + \Delta H^\circ_{(\text{H}_2\text{O})}] - [\Delta H^\circ_{(\text{CH}_4)} + 2\Delta H^\circ_{(\text{O}_2)}]$$

$$[-393.5 + 2 \times (-286.2)] - [-74.8 + 2 \times 0] = -890.7 \text{ kJ}$$

3. Use equation (5) and the data below to calculate $\Delta_{rxn} H^\circ$ for the reaction $\text{MgO}(\text{s}) + \text{CO}_2(\text{g}) \rightarrow \text{MgCO}_3(\text{s})$.

$\Delta_f H^\circ$: $\text{MgO}(\text{s}) = -602 \text{ kJ mol}^{-1}$, $\text{CO}_2(\text{g}) = -394 \text{ kJ mol}^{-1}$ and $\text{MgCO}_3(\text{s}) = -1096 \text{ kJ mol}^{-1}$

Products - Reactants

$$\Delta_{rxn} H^\circ = ((-1090) - (-602 + -394)) \text{ kJ mol}^{-1} = 100 \text{ kJ mol}^{-1}$$

Example exam questions

- Diborane (B_2H_6) is a highly reactive compound, which was once considered as a possible rocket fuel for the US space program. Calculate the heat of formation of diborane at 298 K from the following reactions.

Reaction	ΔH_f (kJ mol ⁻¹)
1 $2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s)$	-1273
2 $B_2H_6(g) + 3O_2(g) \rightarrow B_2O_3(s) + 3H_2O(g)$	-2035
3 $H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)$	-286
4 $H_2O(l) \rightarrow H_2O(g)$	+44

Heat formation = formation of elements in standard states

Reactions (1) and (3) correspond to formation of $B_2O_3(s)$ and $H_2O(l)$

$$\textcircled{1} \Delta_f H^\circ(B_2O_3(s)) = -1273 \text{ kJ mol}^{-1}$$

$$\textcircled{3} \Delta_f H^\circ(H_2O(l)) = -286$$

To get $H_2O(l)$ to $H_2O(g)$ Reaction (4)

$$\textcircled{4} H_2O(l) \rightarrow H_2O(g) = \Delta_f H^\circ = +44$$

Thus heat formation of $H_2O(g)$ is

$$\Delta_f H^\circ(H_2O(g)) = -286 + 44 = -242 \text{ kJ mol}^{-1}$$

Reaction (2) corresponds to the combustion of $B_2H_6(s)$

Heat combustion is $\Delta_{rxn} H^\circ = [\text{Products}] - [\text{Reactants}]$

$$\Delta_{rxn} H^\circ = [(\Delta_f H^\circ B_2O_3(s)) + 3 \times (\Delta_f H^\circ H_2O(g))] - [(\Delta_f H^\circ B_2H_6(s)) + 3 \times (\Delta_f H^\circ O_2(g))] = -2035 \text{ kJ mol}^{-1}$$

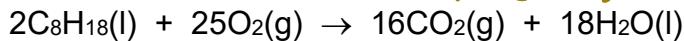
$$\text{So, } \Delta_{rxn} H^\circ = [-1273 + 3 \times (-242)] - [\Delta_f H^\circ B_2H_6(s) + 0] = -2035 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(B_2H_6(s)) = [-1273 + 3 \times (-242)] + 2035 = 36 \text{ kJ mol}^{-1}$$

Answer: **36 kJ mol⁻¹**

- The current “petrochemical economy” is based on the combustion of fossil fuels, of which octane is a typical example.

Reactants Products



Calculate the heat of combustion of octane using the supplied heat of formation data.

Data: $C_8H_{18}(l)$: -249.9 kJ mol⁻¹; $CO_2(g)$: -393.5 kJ mol⁻¹; $H_2O(l)$: -285.8 kJ mol⁻¹

Heat combustion is $\Delta_{rxn} H^\circ = [\text{Products}] - [\text{Reactants}]$

$$\begin{aligned} \Delta_{rxn} H^\circ &= [(16 \times (CO_2(g))) + (18 \times (H_2O(l)))] - [(2 \times (C_8H_{18}(l))) + (25 \times (O_2(g)))] \\ &\approx [(16 \times -393.5) + (18 \times -285.8)] - [(2 \times -249.9) + (25 \times 0)] = -10940.6 \text{ kJ mol}^{-1} \end{aligned}$$

Because the reaction is based of 2 moles of C_8H_{18} (fuel) we need get 1 mole

$$\text{Hence, } \Delta_{\text{combustion}} H^\circ = \frac{1}{2} \times -10940 = -5470 \text{ kJ mol}^{-1}$$

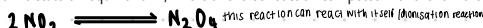
Answer: **-5470 kJ mol⁻¹**

EQUILIBRIUM

LECTURE 26: EQUILIBRIUM & EQUILIBRIUM CONSTANTS

LO: EXPLAIN THE DYNAMIC NATURE OF EQUILIBRIUM PROCESSES

Many chemical species exist in a state of "equilibrium", where a reverse reaction competes with the forward reaction.



Depending on the starting concentrations, the reaction might proceed forwards or backwards to reach equilibrium

Kinetics and equilibrium

At equilibrium, the concentrations of reactants and products do not change in time. But this does NOT mean that no further transformations are occurring.

It just means that the rates of backward and forward reactions are now equal.

LO: WRITE THE EQUILIBRIUM CONSTANT FOR ANY REACTION OR PROCESS

"At a given temperature, a chemical system reaches a state in which a particular ratio of reactant and product concentrations has a constant value." It is the ratio K_{eq} not the individual concentrations that defines equilibrium.



LO: EXPLAIN THE DIFFERENCE BETWEEN THE EQUILIBRIUM CONSTANT, K, AND THE REACTION QUOTIENT, Q.

What does Keq tell us?

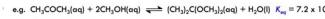
Which compounds are favoured at equilibrium?

- Small K_{eq} : equilibrium favours reactants
 - Large K_{eq} : equilibrium favours products

The reaction quotient (Q)

The reaction quotient, Q , is calculated in exactly the same way as K_{eq} , except using current concentrations rather than equilibrium concentrations.

LO: WRITE DOWN THE REACTION QUOTIENT AND USE IT TO PREDICT THE DIRECTION OF CHANGE



We put the following concentrations into a flask:

Compound	Concentration (M) Expt 1	Concentration (M) Expt 2
CH_3COCH_3	0.500	0.500
CH_3OH	10.0	0.100
$(\text{CH}_3)_2\text{C}(\text{OCH}_3)_2$	4.4×10^{-5}	0.350

Compound	Concentration (M) Expt 1	Concentration (M) Expt 2
CH_3COCH_3	0.500	0.500
CH_3OH	10.0	0.100
$(\text{CH}_3)_2\text{C}(\text{OCH}_3)_2$	4.4×10^{-5}	0.350

- As $Q \neq K_{eq}$, the reaction is not at equilibrium
 - $Q < K_{eq}$ - need to increase [product] and decrease [reactant] so the reactants proceed to the right

LECTURE 27: EQUILIBRIUM CALCULATIONS

LO: WRITE THE EQUILIBRIUM CONSTANT FOR ANY REACTION OR PROCESSES

Which reaction equation

If we start with N₂O₄ we might naturally write:

But, if we wrote the equation to make 1 mol of NO₂(g):

Or, if we wrote the equation with N₂O₄(g) as the product:

Stoichiometry matters

The equilibrium constant **must** be associated with a specific chemical process and a specific stoichiometry.

- if you multiply each component in an equation by n, you change $K_{eq} \rightarrow K_{eq}^n$

- if you reverse the chemical equation, you change $K_{eq} \rightarrow \frac{1}{K_{eq}}$

LO: USE INITIAL, CHANGE, EQUILIBRIUM (ICE) TABLES TO WORK OUT EQUILIBRIUM CONCENTRATIONS

Equilibrium for coupled reactions

Consider the following pair: $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, $K_1 = 4.5 \times 10^{-45}$

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$, $K_2 = 6.4 \times 10^4$

we can add these chemical reactions to provide an overall reaction:

$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$, $K_{total} = \frac{K_1 \cdot K_2}{K_2} = \frac{[NO_2]^2}{[N_2][O_2]^2}$

When you **add** chemical equations, you **multiply** the K's

K_{eq} - What did happen to the units?

In the last lecture we noted that K_{eq} is a unit-less quantity. How did that happen?

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ Why isn't $\frac{[NO_2]^2}{[N_2O_4]} = 0.211 \text{ mol/L}$

The answer is that the complete expression for K_{eq} is in terms of the ratio of concentrations of **pure standard-state components**, i.e.

$$K_{eq} = \frac{(NO_2)^2}{(N_2O_4)} \cdot \frac{(NO_2)^2}{(NO_2)^2} = 1$$

We choose $a^2 = 1 \text{ mol/L}$ so that for concentrations in mol/L we can simply ignore any units.

LO: CALCULATE THE VAULES OF THE EQUILIBRIUM CONSTANT FOR A REVERSE REACTION FROM ITS VALUE FOR A FORWARD REACTION, AND IF THE STOICHIOMETRY IS CHANGED

Different kinds of K_{eq}

We then use a different subscript on the K but really there is no difference to the way we treat the problem.

K_a = acid dissociation equilibrium constant;

K_b = base dissociation equilibrium constant;

K_w = water dissociation equilibrium constant;

K_{stab} = equilibrium constant for stability of a metal complex;

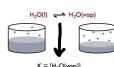
K_{sp} = solubility product.

Equilibria involving liquids and solids

$C(s) + H_2O(l) \rightleftharpoons CO(g) + H_2(g)$ the equilibrium expression can be written as $K = \frac{[CO(g)][H_2(g)]}{[H_2O(g)][C(s)]}$ But the "concentration", i.e. mol/L, of C(s) is **constant**: The "concentration" of a **solid** is its **density**, which is independent of how much substance is present. Therefore this **constant** can be incorporated into the equilibrium constant:

$$K' = \frac{[CO(g)][H_2(g)]}{[H_2O(g)]}$$

Example 2:



$$K = [H_2O]_{\text{vapour}}$$

Example 3: the decomposition of mercuric oxide



$$K = [O_2]_{\text{g}}$$

since the concentrations of **solid** HgO(s) and **liquid** Hg(l) are fixed

In summary: the concentration of fixed volume- liquid or solid - are omitted from the equilibrium expression.

LO: CALCULATE THE EQUILIBRIUM CONSTANT FOR A REACTION OBTAINED BY COMBINING TWO OTHER REACTIONS

Nuts and bolts: doing equilibrium calculations

Q: A 0.0240 mol sample of N₂O₄(g) is allowed to come into equilibrium with NO₂(g) in a 0.372 L flask at 25 °C. Calculate the amount, in moles, of NO₂ and N₂O₄ present at equilibrium (At 25 °C, $K_{eq} = 4.61 \times 10^{-3}$).



Approach:

1. Work out concentration of N₂O₄ initially

2. Let x = changes in concentration

3. Write down equilibrium in terms of x

4. Solve for x

5. Substitute x to work out final concentration or amounts

$$1. \text{ Initial concentration of } N_2O_4 = \frac{0.024 \text{ mol}}{0.372 \text{ L}} = 0.0645 \text{ mol/L}$$

$$4. K = 4.61 \times 10^{-3} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{(0.0645-x)}$$

2. Let ∞ = amount of N₂O₄ that reacts to reach equilibrium.



Initially: 0.0645

O mol/L

Change: $-x$

+2x mol/L

Equilibrium $0.0645 - x$

2x mol/L

$$3. K = 4.61 \times 10^{-3} = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(2x)^2}{(0.0645-x)} = \frac{4x^2}{(0.0645-x)}$$

$$4. x^2 + 4.61 \times 10^{-3}x - 2.973 \times 10^{-6} = 0$$

$$ax^2 + bx + c = 0$$

$$\text{Quadratic equation: } x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$5. x = 8.065 \times 10^{-3} \text{ or } -9.211 \times 10^{-3}$$

Because we know that $[NO_2] > 0$.

$$6. [N_2O_4] = (0.0645 - x) = 0.0564 \text{ mol/L}$$

$$[NO_2] = 2x = 0.0161 \text{ mol/L}$$

$$7. \text{ FINALLY } n(N_2O_4) = 0.0564 \text{ mol/L} \times 0.372 \text{ L} = 0.0210 \text{ mol}$$

$$n(NO_2) = 0.0161 \text{ mol/L} \times 0.372 \text{ L} = 0.0060 \text{ mol}$$



LECTURE 28: GIBBS FREE ENERGY AND DISTURBING EQUILIBRIUM

If the reaction is at equilibrium, then

$$Q_c = K_c \cdot \frac{[PCl_3]}{[PCl_5][Cl_2]} = 24.0$$

What would happen if we inject in more Cl₂(g)? Adding more Cl₂(g) will make Q get smaller. If Q < K then reaction shifts to the right. This decreases Cl₂(g).

If the concentration **increases**, the system acts to **consume** some of it.

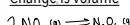
- If the concentration **decreases**, the system acts to **produce** some of it
- Changing the concentration alters **Q** and the reaction shifts so that **Q → K**
- The value of **K** does **not change**!

Change in pressure

There are 3 ways in which the pressure of a system can be changed:

1. By adding (or removing) a gaseous reactant or product: This is the same effect as changing the concentration.
2. By adding a gas that is not involved in the reaction: This does not effect the concentrations of the reactants or products. Q is not changed and the reaction does not shift.
3. By changing the volume of the container

Change is volume



If the reaction is at equilibrium, then

$$Q_c = K_c \cdot \frac{[N_2O_4]}{[NO_2]^2}$$

- If the volume available is **halved**, then [N₂O₄] and [NO₂] will both **double**
- Because we have [NO₂]², Q will **decrease**
- With **Q < K**, the reaction will shift to the right: the side with **fewer** moles of gas
- If the volume available is **doubled**, then [N₂O₄] and [NO₂] will both **halve**
- Because we have [NO₂]², Q will **increase**
- With **Q > K**, the reaction will shift to the left: the side with **more** moles of gas

LO: UNDERSTAND THAT ΔG < 0 REPRESENTS AN ALTERNATIVE STATEMENT TO THE 2ND LAW OF PARTICULAR CONVENIENCE IN CHEMISTRY.

ΔG: the Change in the Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S_{\text{system}} = -T\Delta S_{\text{total}}$$

To determine whether a process is spontaneous we can either use: ΔS_{total} > 0 or ΔG < 0.

- These two versions are equivalent statements of the 2nd Law.
- The ΔG < 0 version is the one commonly used in chemistry (and biology). Note: when ΔG = 0, it corresponds to the equilibrium state

- If the volume decreases, the system acts to decrease the number of moles present
- If the volume increases, the system acts to increase the number of moles to fill it.
- Changing the volume alters Q and the reaction shifts so that Q → K
- The value of K does not change!

LO: USE THE ΔG < 0 CONDITION TO RELATE THE EFFECT OF A CHANGE IN T TO THE SIGN OF ΔH

Keq and temperature

We have two approaches to determining the direction of spontaneous change: Q → Keq and ΔG < 0.

What is the connection? Consider the reaction: N₂(g) + 3H₂(g) ⇌ 2NH₃(g) ΔH = -92 kJ mol⁻¹

Our ΔG < 0 condition tells us that for an exothermic reaction, increasing T favours the reactants. As T increases, Keq is getting smaller

Temp (K)	K _{eq}
500	90
600	3
700	.3
800	.04

Let's consider the effect of change in T on K_{eq}

$$\ln K_{eq} = (\Delta H^\circ - T\Delta S^\circ) / RT$$

- If ΔH° < 0 then increasing T will make Keq **smaller**. The equilibrium will shift to favour the **reactants** and so to reduce the **heat released**

- If ΔH° > 0 then increasing T will make Keq **larger**. The equilibrium will shift to favour the **products** and absorbing **more heat**

LO: RECOGNISE THE RELATIONSHIP ΔG° = -RT ln K_{eq}

"If a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change."

- Increase reactant concentrations → more products produced
- Increase pressure / decrease volume → less gas produced
- Increase temperature → endothermic reaction favoured



Gibbs free energy equation

$$\Delta G = \Delta H - T \times \Delta S$$

IF

$$\Delta G = 0$$
 (equilibrium)

No exception

 $\Delta G > 0$ (Reaction is non-spontaneous) $\Delta G < 0$ (Reaction is spontaneous)

↑ what you want!

How is K related to ΔG ?

$$\Delta G = -R \times T \times \ln(K)$$

Gas constant ↑ temp ↑ natural log

Enthalpy

 ΔH enthalpy ΔH can be -ive (exothermic) +ive (endothermic)

Entropy

 ΔS entropy

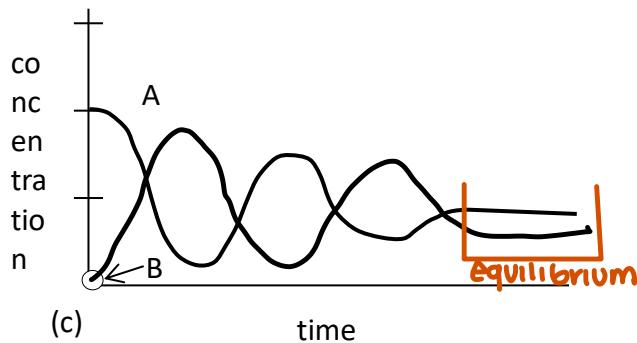
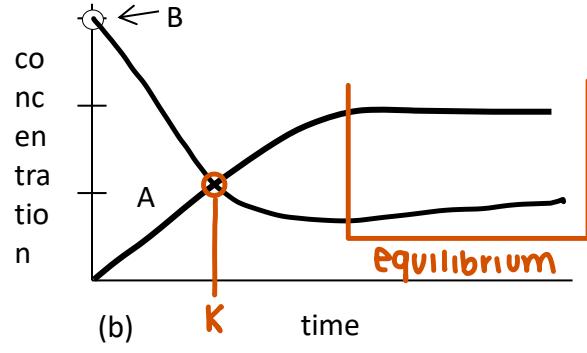
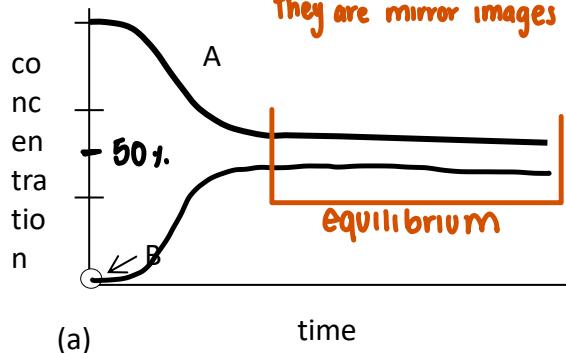
CHEM1111: Worksheet – Lecture 26

Model 1: Time Dependence of Concentrations During a Reaction

We can monitor the progress of a reaction by measuring the concentration of one or more species at regular time intervals. When the concentrations cease varying in time, the system is at equilibrium.

- Consider 3 different reactions of the form $A \rightleftharpoons B$. The 3 graphs below show the initial concentrations of A and B and the subsequent change in concentration of A with time for each reaction. Sketch the corresponding concentration of B in time in each case.

Note: Because $A = B$ ($A \approx B$)
They are mirror images



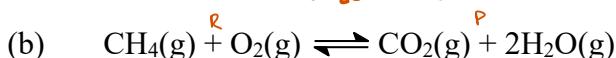
Model 2: The Equilibrium Constant K_{eq}

Write the expression for K for each of the following reactions:

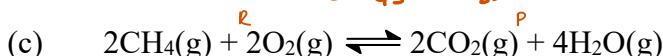
$$K_{eq} = \frac{\text{Product}}{\text{Reactants}}$$



$$K_{eq} = \frac{[H_2O]}{[H_2] \times [O_2]^{\frac{1}{2}}}$$



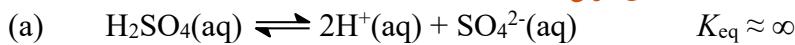
$$K_{eq} = \frac{[CO_2] \times [H_2O]^2}{[CH_4] \times [O_2]}$$



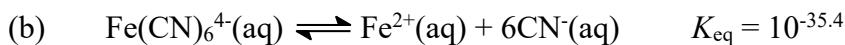
$$K_{eq} = \frac{[CO_2]^2 \times [H_2O]^4}{[CH_4]^2 \times [O_2]^2}$$

Model 3: Reactants versus Products

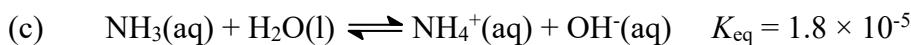
Below are some reactions with their equilibrium constants. Based on the value of the equilibrium constant for each reaction, indicate whether the reaction (i) strongly favours products, (ii) weakly favours products, (iii) strongly favours reactants, or (iv) weakly favours reactants. **NOTE: The larger the equilibrium constant (K_{eq}) the Products are favoured.**



Strongly favoured Products



Reactants are favoured strongly



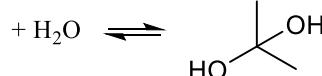
favoured Reactants



Products are weakly favoured

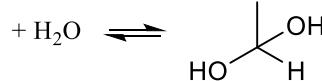
Aldehydes and ketones react with water to form hydrates. Based on the value of the equilibrium constant for each reaction, indicate whether the reaction (i) strongly favours products, (ii) weakly favours products, (iii) strongly favours reactants, or (iv) weakly favours reactants.

ketones

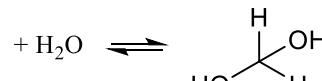
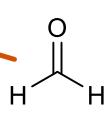


$K_{eq} = 2 \times 10^{-3}$ **Strongly favours Reactants**

aldehydes



$K_{eq} = 1.4$ **weakly favours the products**



$K_{eq} = 2.3 \times 10^3$ **strongly favours products**

What can be said about the relative stabilities of reactants and products? Would you expect 3-pentanone to have a larger or smaller equilibrium constant than acetone (2-propanone)?

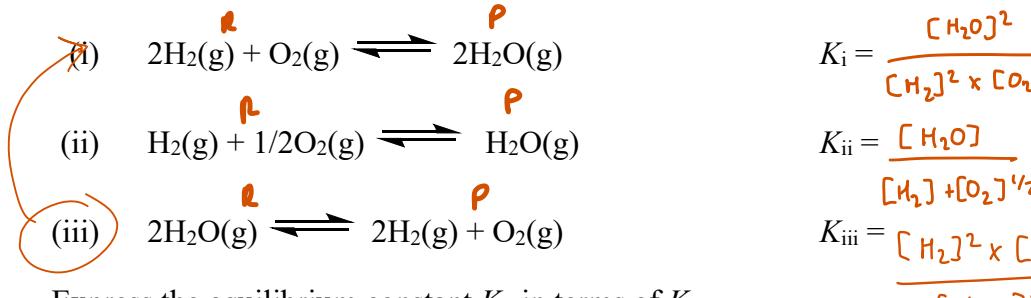
As you increase alyl chain favoure the Reactants more. So expect 3-pentanone to have a smaller equilibrium constant

CHEM1111: Worksheet – Lecture 27

Model 1: K_{eq} and Stoichiometry

The equilibrium constant for a reaction depends on the specific form of the chemical equation. Changing the chemical equation means that K_{eq} will change as well.

1. Write down the expression for K_{eq} for each of the following reactions:



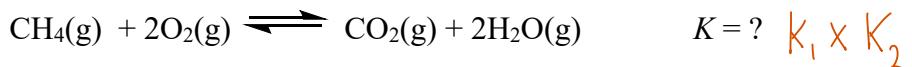
2. Express the equilibrium constant K_{ii} in terms of K_i .

$$K_{ii} = \sqrt{K_i} \quad \text{or} \quad K_{ii} = K_i^{1/2}$$

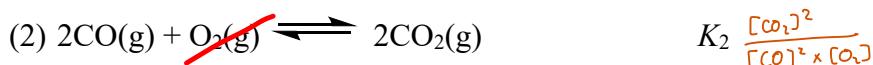
3. Express the equilibrium constant K_{iii} in terms of K_i .

$$K_{iii} = \frac{1}{K_i} \quad \text{or} \quad K_{iii} = K_i^{-1}$$

4. We would like to know the equilibrium constant K for the following reaction:



and what we are given is:



Write an expression for K in terms of K_1 and K_2 .

$$\frac{[\text{CO}] \times [\text{H}_2\text{O}]^2}{[\text{CH}_4] \times [\text{O}_2]^{3/2}} \times \frac{[\text{CO}_2]^2}{[\text{CO}]^2 \times [\text{O}_2]} = K = \frac{[\text{CO}_2] \times [\text{H}_2\text{O}]^2}{[\text{CH}_4] \times [\text{O}_2]^2}$$

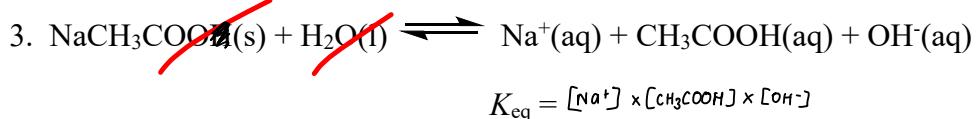
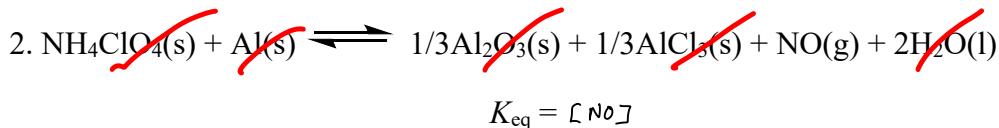
Model 2: Equilibria Involving Pure Liquids or Solids.

In the expression for the equilibrium constant, we omit the concentrations of reactants or products that are pure solids or liquids since their concentration is not altered by the reaction. For example: $\text{NaCl}(\text{s}) \rightleftharpoons \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \quad K_{\text{eq}} = [\text{Na}^+][\text{Cl}^-]$

In this case, the equilibrium constant is given a special name: it is the *solubility product*, K_{sp} .

NOTE: Liquids and Solids do not affect equilibrium constant

Write down expressions for the equilibrium constant for each of the following reactions.



Model 3: Calculations with K_{eq}

The tabulated values of K_{eq} for reactions allow us to make quantitative predictions concerning the concentrations of reactants and products at equilibrium.

1. Consider the following reaction



If, at equilibrium, $[\text{NH}_3] = 0.02 \text{ M}$, $[\text{NH}_4^+] = 0.05 \text{ M}$ and $[\text{OH}^-] = 0.6 \text{ M}$, what is the value of the equilibrium constant?

$$K_{\text{eq}} = \frac{[\text{NH}_4^+]}{[\text{NH}_3][\text{OH}^-]} = \frac{[0.05]}{[0.02][0.06]} = K_{\text{eq}} = 6.67$$

2. The two isomers, cis-stilbene and trans-stilbene, can interconvert as follows:



(a) Which isomer is favoured at equilibrium? **trans - stilbene**

(b) If we start the reaction with only 0.85 M of *cis*-stilbene present, what will be the concentration of *trans*-stilbene at equilibrium?

		<i>cis</i>	<i>trans</i>
		<i>cis</i>	<i>trans</i>
<i>cis</i>	1	0.85	0
<i>cis</i>	C	-x	+x
E		$0.85 - x$	x

$$K_{\text{eq}} = \frac{\text{trans-stilbene}}{\text{cis-stilbene}} = \frac{x}{0.85-x} = 24.0$$

$$x = 24.0(0.85-x) = 20.4 - 24.0x$$

$$\frac{25x}{25} = \frac{20.4}{25} \quad x = 0.816 \text{ M}$$

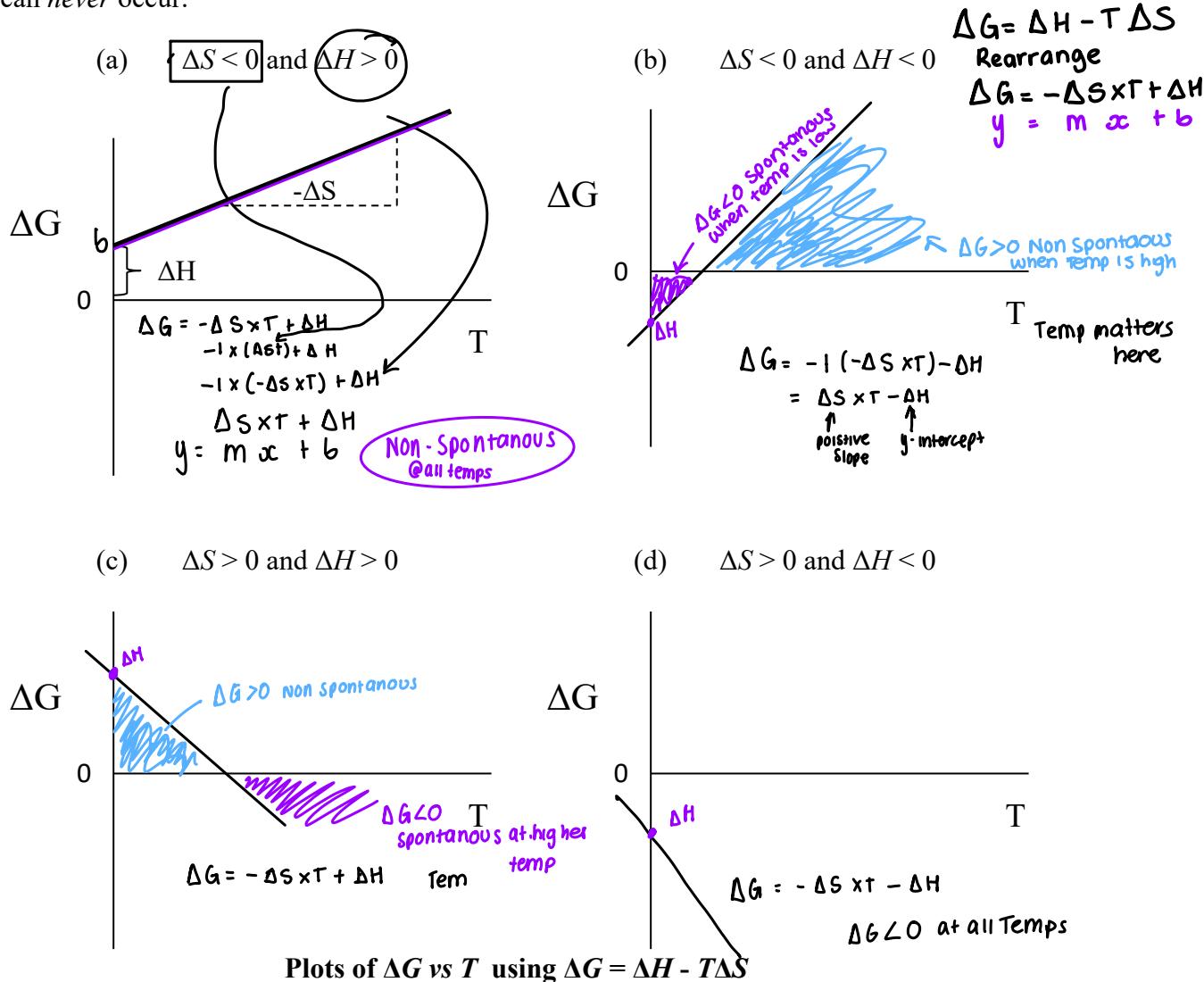
CHEM1111: Worksheet – Lecture 28

Model 1: ΔG and the Influence of Temperature

The 2nd Law condition that $\Delta S_{\text{total}} > 0$ can be re-written as $-T\Delta S_{\text{total}} < 0$. If we relabel $-T\Delta S_{\text{total}} = \Delta G$ then we have a condition for spontaneity, i.e. $\Delta G < 0$, widely used in chemistry. Since $\Delta G = \Delta H - T\Delta S$, the temperature dependence of the condition for spontaneity can be related directly to the signs of the change in enthalpy and entropy.

The temperature dependence of ΔG can be visualized by a simple qualitative graph. For example, the case where $\Delta S < 0$ and $\Delta H > 0$ would correspond to the graph (a) shown below.

Since spontaneity *requires* $\Delta G < 0$, this plot makes clear that a process with $\Delta S < 0$ and $\Delta H > 0$ can *never* occur.

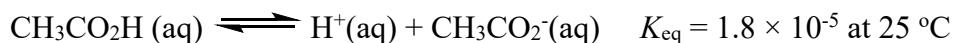


Using similar plots, sketch ΔG vs T for the cases (b) – (d) and identify the temperature range over which each process will proceed spontaneously.

Model 2: Perturbing Equilibrium by Concentration or Volume Changes

The equilibrium condition $Q = K_{\text{eq}}$ allows us to make quantitative predictions of the change in concentrations of species after we perturb an equilibrium system by changing concentrations.

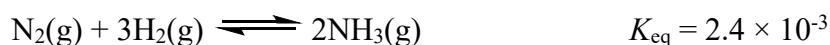
1. Consider the dissociation of acetic acid (vinegar):



- If we then add 0.1 mole of HCl to the solution, describe what will happen qualitatively to (a) $[\text{CH}_3\text{CO}_2\text{H}]$ and (b) $[\text{H}^+]$?
A It will increase as its a base to counteract the acid added
B decrease as the equilibrium needs to counteract it.
- At 50.0°C , K_{eq} is 1.6×10^{-5} . Is the reaction exothermic or endothermic?
exothermic because the K_{eq} has dropped
↳ getting rid of heat.
- Predict what will happen to $[\text{H}^+ \text{ (aq)}]$ and to the pH of vinegar as the temperature is increased. Hint: $\text{pH} = -\log_{10}[\text{H}^+ \text{ (aq)}]$.

$[\text{H}^+]$ will drop the pH will increase

2. Consider the reaction



- A system is set up so that at equilibrium we have the following concentrations:

$$[\text{NH}_3] = 0.016 \text{ M}, [\text{N}_2] = 0.25 \text{ M} \text{ and } [\text{H}_2] = 0.76 \text{ M}$$

What is the value of the reaction quotient Q if we expand the volume to twice its original value (and before any reaction is allowed to take place)?

$$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

must
use equation

$$Q = \frac{(0.008)^2}{(0.125)(0.38)^3} = 9.3 \times 10^{-3}$$

- Following this volume change, what direction will the reaction proceed?

Compare K and Q

Q is greater than K thus the

reaction
shifts to
the left.

NOTE:
If:

$Q > K$ = shifts to left

$Q < K$ = shifts to right



School of Chemistry

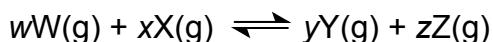
Chemistry 1A (CHEM1111)

Tutorial 10 (Week 10): Equilibrium

Model 1: The Equilibrium Constant

Many chemical reactions lead to a mixture of reactants and products. You will end up with a mixture of both $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ whether you start with pure $\text{NO}_2(\text{g})$ or pure $\text{N}_2\text{O}_4(\text{g})$. Such reactions are said to reach an equilibrium in which the amount of each substance does not change.

Consider a reaction such as that below which has been left long enough to reach equilibrium.



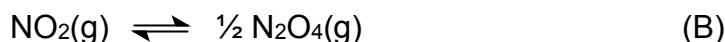
The *equilibrium constant* in terms of concentrations, K_c , is a constant at a given temperature that defines how much of each substance there will be at equilibrium:

$$K_c = \frac{[\text{Y}(\text{g})]^y [\text{Z}(\text{g})]^z}{[\text{W}(\text{g})]^w [\text{X}(\text{g})]^x}$$

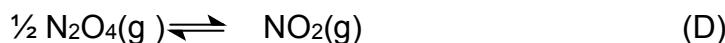
If $K_c > 1$, the mixture will contain more of the substances on the right hand side (Y and Z) of the equation.

If $K_c < 1$, the mixture will contain more of the substances on the left hand side (W and X) of the equation.

Previously, you studied the thermodynamics of the equilibrium between NO_2 and its dimer N_2O_4 . Starting from NO_2 , the formation of the dimer can be studied using one of the two equations below:



Starting from the dimer, the formation of NO_2 can be studied using one of the two equations below:



Critical thinking questions

1. Write down the expression for K_c for reactions A, B, C and D in Model 1.

$$K_c (\text{A}) = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2} \qquad K_c (\text{B}) = \frac{[\text{N}_2\text{O}_4]^{1/2}}{[\text{NO}_2]} \qquad K_c (\text{C}) = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} \qquad K_c (\text{D}) = \frac{[\text{NO}_2]}{[\text{N}_2\text{O}_4]^{1/2}}$$

2. Looking at the equations in Q1, what is the *mathematical* relationship between the different forms of K_c ?

(a) $K_c(A)$ and $K_c(B)$

$$K_c(B) = \sqrt{K_c(A)}$$

(b) $K_c(A)$ and $K_c(C)$

$$K_c(A) = \frac{1}{K_c(C)}$$

3. At equilibrium at room temperature, $[NO_2(g)] = 1.60\text{ M}$ and $[N_2O_4] = 0.20\text{ M}$. Calculate the values of $K_c(A)$ and $K_c(B)$ and $K_c(C)$ and hence confirm your analysis in Q2.

A $\frac{[0.20]}{[1.60]^2} = 0.08$ **B** $\frac{[0.20]^{1/2}}{[1.60]} = 0.28$ **C** $\frac{[1.60]^2}{[0.20]} = 12.8$

Model 2: The Reaction Quotient

The reaction quotient, Q_c , for a reaction $wW(g) + xX(g) \rightleftharpoons yY(g) + zZ(g)$, is defined as follows:

$$Q_c = \frac{[Y(g)]^y [Z(g)]^z}{[W(g)]^w [X(g)]^x}$$

It looks similar to the equilibrium constant expression. The difference is that Q_c can be calculated at any time during a reaction or if a reaction is disturbed. It is used to predict the direction in which a reaction will move.

Critical thinking questions

Consider the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$ to be at equilibrium with $[NO_2(g)] = 1.60\text{ M}$, $[N_2O_4] = 0.20\text{ M}$ and $K_c = 0.078$.

1. Predict *qualitatively* what will happen to this reaction if more NO_2 is added so that $[NO_2(g)] = 2.00\text{ M}$?

Reaction will shift to Right

2. Predict *qualitatively* what will happen to this reaction if instead NO_2 is removed so that $[NO_2(g)] = 1.00\text{ M}$?

Reaction will shift to left.

3. Calculate the values for Q_c for these two experiments.

(a) $[NO_2(g)] = 2.00\text{ M}$ and $[N_2O_4] = 0.20\text{ M}$: $Q_c = \frac{[0.20]}{[2]^2} = 0.05$

(b) $[NO_2(g)] = 1.00\text{ M}$ and $[N_2O_4] = 0.20\text{ M}$: $Q_c = \frac{[0.20]}{[1]^2} = 0.2$

4. Using your answers to Q1 - 3, what in general happens to a reaction if

(a) $Q_c < K_c$ **Reaction favours product, moves to right**

(b) $Q_c > K_c$ **Reaction favours reactants, moves to left**

Model 3: Equilibrium calculations

Model 2 gives you the tools to predict the direction in which a reaction will move if it is not at equilibrium. The concentrations that will be obtained when equilibrium is finally reached can be calculated using an ICE table: initial-change-equilibrium.

Consider the starting mixture in Q1 of Model 2: $[NO_2(g)] = 2.00 \text{ M}$ and $[N_2O_4(g)] = 0.20 \text{ M}$. These are the initial concentrations and are written in the first row of the *reaction table* below. You know from Model 2 that this reaction will shift so that some $NO_2(g)$ reacts to make $N_2O_4(g)$. We do not know *how much* will react but we *can* calculate it:

	$2NO_2(g)$	\rightleftharpoons	$N_2O_4(g)$
initial	2.00		0.20
change	$-2x$		$+x$
equilibrium	$2 - 2x$		$0.20 + x$

Critical thinking questions

- From the chemical equation: every time *one* N_2O_4 molecule is formed, *two* NO_2 molecules are lost. If $[N_2O_4(g)]$ increases by x to reach equilibrium, what will the change in $[NO_2(g)]$ be? Add this change to the second row of the table. (*Hint*: is the change positive or negative?).
- Complete the third row of the table.
- Substitute the equilibrium concentrations from the third row into your expression for $K_c(A)$ from Q1 in Model 1.

$$K_c(A) = \frac{[N_2O_4]}{[NO_2]^2} = \frac{0.20+x}{(2.00-2x)^2}$$

- You now have a *mathematical* expression to solve for x . Using $K_c = 0.078$, solve for x and hence work out the equilibrium values of $[NO_2(g)]$ and $[N_2O_4(g)]$.

$$0.078 = \frac{0.20+x}{(2.00-2x)^2}$$

\swarrow \searrow

$4.00 - 4x$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$0.078(4x^2 - 8x + 4) = 0.20 + x$$

$\downarrow 4$ $\downarrow 8x$ $\downarrow 4x^2$

$$x = \frac{-(-1.627) \pm \sqrt{(-1.627)^2 - 4 \times 0.312 \times 0.112}}{2 \times 0.312} = 0.070$$

$$0.312x^2 - 0.624x + 0.312 = 0.20 + x$$

-0.20 -0.20

$$x = \frac{-(-1.627) - \sqrt{(-1.627)^2 - 4 \times 0.312 \times 0.112}}{2 \times 0.312} = 0.070$$

$$0.312x^2 - 0.624x + 0.312 = x$$

$-1x$ $-1x$

Hence,

$$[N_2O_4] = 0.20 + 0.070 = 0.27 \text{ M}$$

$$0.312x^2 - 1.627x + 0.112 = 0$$

$$[NO_2]^2 = 2.00 - 2 \times 0.070 = 1.86 \text{ M}$$

A

B

C

$ax^2 + bx + c$

Example exam question:

- Consider the following reaction.



Marks
4

An equilibrium mixture in a 1.00 L container is found to contain $[\text{N}_2\text{O}_4] = 1.00 \text{ M}$ and $[\text{NO}_2] = 0.46 \text{ M}$. The vessel is then compressed to half its original volume while the temperature is kept constant. Calculate the concentration $[\text{N}_2\text{O}_4]$ when the compressed system has come to equilibrium. Show all working.

$$K_C = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{[0.46]^2}{1.00} = 0.21$$

	N_2O_4	\rightleftharpoons	2NO_2
I	1.00		$0.46 \times 2 = 0.92$
C	$+x$		$-2x$
E	$1.00 + x$		$0.92 - 2x$

$$0.21 = \frac{(0.92 - 2x)^2}{(2.00 + x)}$$

$$(0.92 - 2x)^2 = 0.21(2.00 + x)$$



$$0.92 \times 0.92 + 0.92x - 2x^2 - 2x \times 0.92 + -2x \times -2x \\ 0.92x^2 - 4 = -3.68x$$

$$0.92^2 = 0.8464 \\ 2x^2 = 4x^2$$

hence,

$$0.8464 - 3.68x + 4x^2 = 0.42 \\ -0.8464$$

$$-3.68x + 4x^2 = -0.43$$

$$4x^2 - 3.68x + 0.43 = 0$$

A B C

$$x = \frac{-B \pm \sqrt{b^2 - 4ac}}{2a}$$

Double concentration as volume doubles

$$x = \frac{-3.68 + \sqrt{(-3.68)^2 - 4 \times 4 \times 0.43}}{2 \times 4} = -0.85$$

$$x = \frac{-3.68 - \sqrt{(-3.68)^2 - 4 \times 4 \times 0.43}}{2 \times 4} = 0.13$$

Because you can't have - neg as a concentration for NO_2
So use $x = 0.13$

$$[\text{N}_2\text{O}_4] = (2.00 + x) \text{ M} = (2.00 + 0.13) = 2.13 \text{ M}$$

$$[\text{NO}_2] = (0.92 - 2x) \text{ M} = 0.92 - 2 \times 0.13 \\ = 0.66 \text{ M}$$

Model 4: Enthalpy ($\Delta_{rxn}H^\circ$) and Entropy ($\Delta_{rxn}S^\circ$) of Reaction

In Model 3 in week 9, you developed a way of working out the value of enthalpy change for any reaction from the values of the enthalpies of formation of the reactants and products:

$$\Delta_{rxn}H^\circ = \Delta_f H^\circ (\text{products}) - \Delta_f H^\circ (\text{reactants}) \quad (1)$$

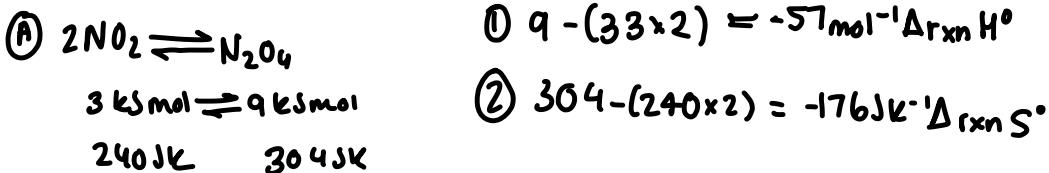
The change in entropy in a reaction can similarly be calculated as the difference in the entropies of the reactants and products:

$$\Delta_{rxn}S^\circ = S^\circ (\text{products}) - S^\circ (\text{reactants}) \quad (2)$$

Critical thinking questions

1. Using the data below, calculate $\Delta_{rxn}H^\circ$ and $\Delta_{rxn}S^\circ$ for reaction A in Model 1.

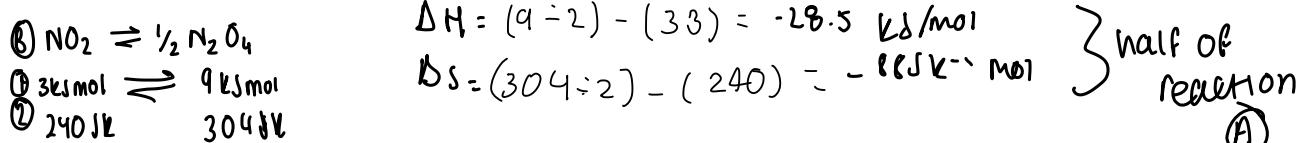
$\Delta_f H^\circ$: NO₂(g), 33 kJ mol⁻¹, N₂O₄(g) 9 kJ mol⁻¹. S° : NO₂(g), 240 J K⁻¹ mol⁻¹, N₂O₄(g) 304 J K⁻¹ mol⁻¹



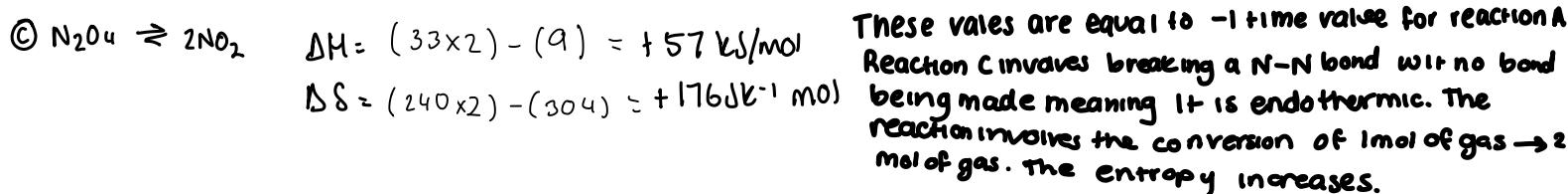
2. Explain in words the origin of the sign of $\Delta_{rxn}H^\circ$ and $\Delta_{rxn}S^\circ$ in terms of the chemical changes in the reaction.

- The reaction involves making a N-N bonds with no bonds being broken. It is exothermic
 - The reaction involves the conversion of 2 mol s of gas \rightarrow 1 mol gas. The Entropy decreases.
- H° = Chemical change in Enthalpy S° = Chemical Change in Entropy
Forming a new bond .. energy out

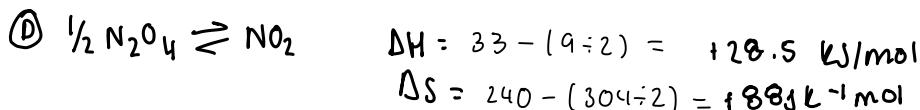
3. Calculate $\Delta_{rxn}H^\circ$ and $\Delta_{rxn}S^\circ$ for reaction B in Model 1. How are these values related to your answer to Q1?



4. Calculate $\Delta_{rxn}H^\circ$ and $\Delta_{rxn}S^\circ$ for reaction C in Model 1 and explain in words the origin of the sign of $\Delta_{rxn}H^\circ$ and $\Delta_{rxn}S^\circ$ in terms of the chemical changes in the reaction.



5. What are the values of $\Delta_{rxn}H^\circ$ and $\Delta_{rxn}S^\circ$ for reaction D in Model 1?



ORGANIC

CHEMISTRY

INTRO

LECTURE TWELVE: SHAPES, STRUCTURES AND REPRESENTATION OF ORGANIC MOLECULES

LECTURE 18: WHAT IS ORGANIC CHEMISTRY AND DRAWING ORGANIC STRUCTURES**LO: APPRECIATE THE ENORMOUS DIVERSITY AND POTENTIAL OF ORGANIC MOLECULES**

What is organic chemistry

Based around the chemistry of carbon and a few other elements such as H, N and O plus some S, P, Cl and Br. Concerns: transformations (reactivity) and creation (synthesis) of organic structure. Chemistry of life (proteins, sugars, nucleic acids); protection, improvement and even creation.

Carbon makes awesome scaffolds

Carbon has unique properties

Atomic Number 6 - 1s₂ 2s₂ 2p₂

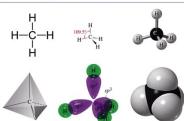
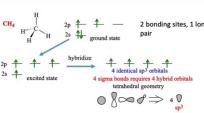
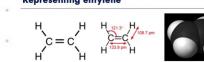
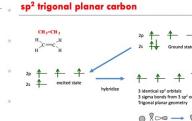
Valence of 4 and Mid-range electronegativity

C-C and C-H bonds are strong and unreactive \Rightarrow provides solid scaffolds

C can bond to itself, to metals and to heteroatoms

Geometrically flexible

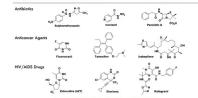
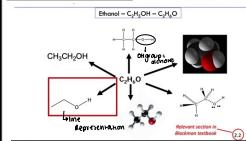
- capable of catenation - forming rings and chains and forms multiple bonds.

LO: UNDERSTAND THE BASIS OF DRAWING ORGANIC STRUCTURES**Representing Methane****sp³ Tetrahedral Carbon****Representing ethylene****sp² trigonal planar carbon****Representing molecules**

There are many ways to represent molecules

Some representations are more informative than others.

For small molecules the choice is often not critical but as the molecule gets bigger some representations are very time consuming to draw

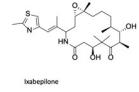
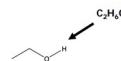
Representing molecules**So what does the picture tell us?****LO: CONVERT BETWEEN A CONDENSED MOLECULAR FORMULA AND A SKELETAL OR LINE STRUCTURE****Condensed structure****Line representation**

Advantages: Relatively simple to draw but still full of structural information

Quick to draw

Bond angles and 'heteroatoms' are represented

Disadvantages: Determining molecular formula takes time for beginners

**How line drawings work**

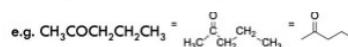
1. Lines represent bonds: 1, 2 or 3 lines for single, double, triple bonds

2. C is basis of structure (chains and rings of carbon atoms): carbon atoms not shown, assumed to be at intersections and ends of lines; C - H bonds omitted (hydrogen count assumed from valence) and All heteroatoms are shown (+ H's bound to heteroatoms)

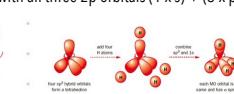
3. Valence - 4 for C and 3 for N and 2 for O and 1 for H, Cl, Br, I

4. Geometry - Use VSEPR: Indicate bond angles ($\sim 120^\circ$ or 180°)

5. In condensed formulae, atoms bonded to a C atom are listed after it

**LO: DETERMINE THE FORMULA OF A MOLECULE FROM ITS SKELETAL REPRESENTATION**

LECTURE THIRTEEN: ALKANES AND ALKENES

LECTURE 19: ALKANES & ALKENES AND HYBRIDISATION**LO: DRAW AND NAME ALANES AND ALKENES****sp³ hybridisation: alkanes -1**If the 2s orbital mixes with all three 2p orbitals ($1 \times s$) + ($3 \times p$) \rightarrow $4 \times sp^3$ i.e. $4 \times$ identical orbitals \rightarrow forms $4 \times$ single (covalent) bonds

If the 2s orbital mixes with only two 2p orbitals ...

- ($1 \times s$) + ($2 \times p$) \rightarrow $3 \times sp^2$ (+ $1 \times p$ -orbital remains unhybridised)
- i.e. 3x identical hybridised orbitals + one different one
- \rightarrow forms 3x single bonds + 1x double bond

**LO: IDENTIFY COMMON FUNCTIONAL GROUPS**

Carbon-heteroatom multiple bonds ...

Carbonyl Group

Nitrile ('Cyano') Group

Carbon Dioxide

Type of Hybridisation \Rightarrow **Carbonyl Group** oxygen and carbon are Sp^2 \Rightarrow **Nitrile ('Cyano' Group** carbon and nitrogen are Sp $\text{O}=\text{C}=\text{O}$ **Carbon Dioxide** carbon is Sp and oxygen are Sp^2

Functional groups are the "interesting bits" of a molecule ...

- C-C's and C-H's form the skeleton
- multiple bonds and heteroatoms are the 'action centres'

LO: UNDERSTAND THE HYBRIDISATION OF CARBON'S VALENCE ORBITALS AND ITS IMPORTANCE TO BONDING IN ORGANIC CHEMISTRY

Properties of alkanes

- Chemically inert (i.e. don't do a whole lot!)
- Do react with oxygen (combustion) \rightarrow used as fuels
- short-chain alkanes burn efficiently \rightarrow $\text{CO}_2 + \text{H}_2\text{O}$
- bigger alkanes don't burn as well (\rightarrow sooty flame)
- Large amounts of energy liberated in combustion
- so commonly used in fuel, e.g. natural gas, petrol, etc
- which has consequences for the planet
- Forces increase as the size of the molecule increase
- melting and boiling point increase with molecular size,
- branding lowers the melting/boiling point as it forces chains away from each other a bit more

LECTURE 20: ISOMERS AND NAMING ISOMERS

LO: UNDERSTAND THE DIFFERENCE BETWEEN CONSTITUTIONAL ISOMER AND STEREOISOMERS

Isomers have the same molecular formula to isotopes but they have DIFFERENT structures.

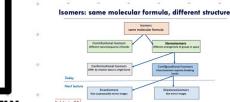
The simplest isomers are constitutional: different sequence of bonds. Then stereoisomers: they differ in 3 dimensional arrangement. Broken down further to conformation : different rotation about a single bond and is, 13kj/mol, happens at room temp and we can not separate conformational isomers.



Then configuration: inter conversion required bond breaking (double bond) and sp², 120kj/mol, requires additional energy to occur and we can separate conformational isomers.



LO: RECOGNISED CONSTITUTIONAL, CONFORMATIONAL AND DIASTEREOMERIC (CIS/TRANS OR Z/E) ISOMERS



naming a double through diastereoisomers

Either Z or E

Z: high priority atoms are the same side of double bond

E: high priority atoms on different sides of double bonds

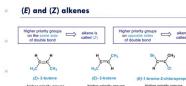
what is a high priority atom? Justified by what has the highest molecular weight

Rules:

§ Assign priority to each group on each carbon of C=C

§ The higher the atomic number of the atom attached, the higher the priority

§ If identical atoms attached, work along the chain until the first point of difference, then go by atomic number*



LO: NAME ISOMERIC STRUCTURES CORRECTLY

Isomers have different properties

- Physical and chemical properties of constitutional isomers can be very different, particularly when different functional groups are present
- For example a molecule with formula C₄H₈O may be a:

§ ketone



§ aldehyde



§ alkene/ether



§ alkene/alcohol



- Each of these functional groups has different properties and reactivity

LO: DESCRIBE ALKANE AND CONFORMATIONAL ISOMERS

Newman Projections

As we rotated through the atom through staggered and eclipsed, eclipsed needs more energy so that creates a barrier so the ability to rotate harder and harder

Conformational Isomers

Staggered alkanes

- Rotation around each C-C bond readily occurs
- Conformational isomers result
- Sometimes drawn as sawhorse projections



Newman Projections

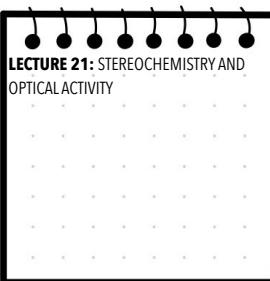
Sometimes drawn as Newman projections

- Sometimes drawn as Newman projections
- Imagine looking down the C-C bond from here
- The C-C bond is just in front of the viewer
- The C-C bond is just behind the viewer
- Which conformation is higher in energy?

Barriers to rotation

- Wedge-dash shows rotation about C-C bonds is rapid at room temperature
- Differences in energy arise from steric interactions





LECTURE 21: STEREOCHEMISTRY AND OPTICAL ACTIVITY

LO: RECOGNISE THE STRUCTURAL FEATURES IN A MOLECULE THAT RESULTS IN ENANTIOMERS

Configuration allows Isomer: Same atoms and Bonds

Configurational isomers can arise due to absence of rotation about a double bond (last lecture)

Configurational isomers can also arise when an sp³ atom has 4 different bonding partners
Chirality

An object is chiral if it is not superimposable upon its mirror image. For example, hands as if there is mirror of your left hand you can overlap that image with the right hand.

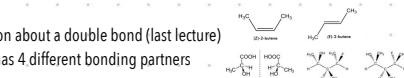


Chiral molecules

All molecules have mirror images. Some of these are special.

The molecule on the left is chiral:

- This molecule contains a stereogenic centre
- This molecule is not superimposable on its mirror image
- There is no plane of symmetry in this molecule



Definitions

Enantiomers = pair of molecules which:

- are mirror images of each other
- are not superimposable (i.e. not the same).

Enantiomers commonly contain one or more stereocentres. Stereocentre = stereogenic centre = chiral centre. Stereocentre = carbon atom with four different groups attached. Racemic mixture (racemate) = 50:50 mixture of both enantiomers

LO: IDENTIFY STEREOGENIC CENTRE(S)

Enantiomers: labels

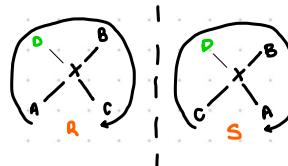
Each individual chiral centre has two possible arrangements, i.e.

There are two different labelling conventions for these two possibilities:

- i) Modern convention - enantiomers labelled as R or S
 - ii) Older convention (used for amino acids and sugars) - enantiomers labelled as L or D
- e.g. L-glyceraldehyde or R-lactic acid specify a particular enantiomer

When does chirality Matter?

Chiral molecules occur frequently with increasing molecular size. Almost all the physical properties of a pair of enantiomers are identical (melting point, boiling point, solubility, NMR, IR etc.). Enantiomers behave in an identical way when interacting with achiral objects or reagents. Enantiomers will interact & react differently with other chiral molecules



LO: APPRECIATE THE ROLE OF OPTICAL ROTATION IN CHARACTERISING ENANTIOMERS

Detecting Chirality: Optical activity

Enantiomers also differ in another interesting way ...

- Their interaction with plane polarised light
- In plane polarised light, waves oscillate in only one plane
- Generated by passing light through a polarising filter

Measuring optical activity

When plane polarised light is passed through a solution of one pure enantiomer of a compound, the plane of polarisation is rotated. The enantiomer is said to be optically active and the amount of rotation (α) is characteristic of the enantiomer

LO: DETERMINE THE MAXIMUM NUMBER OF ISOMERS POSSIBLE GIVEN N STEREOGENIC CENTRES

Enantiomers and optical activity

One enantiomer causes clockwise rotation, the other enantiomer rotates the light an equal amount in the opposite direction

- rotation in a clockwise direction is labelled (+)
- rotation anti-clockwise is labelled (-)
- racemic mixtures give an overall rotation of zero
- It isn't possible to predict which enantiomer is (+) and which (-) without performing the experiment

Remember the directional of optical rotation does not correlate with the absolute configuration of the Stereocentre

LO: UNDERSTAND HOW DIASTEREOMERS ARISE WHEN THERE ARE MULTIPLE STEREOGENIC CENTRES

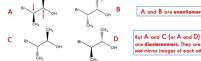
Diastereoisomers

Configurational isomers that are not enantiomers are called diastereoisomers. All achiral (i.e. non-chiral) configurational isomers are diastereoisomers.

Diastereomers with two chiral centres

Molecules that contain two or more stereogenic (chiral) centres can be either enantiomers or diastereomers. Consider the diastereomeric

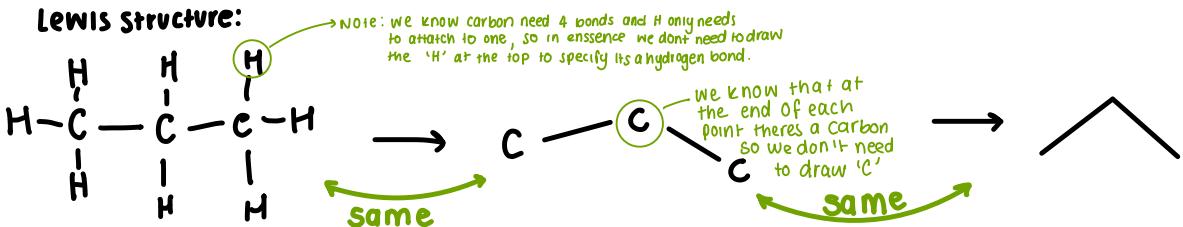
2-chiral centers



If you identify R & R then in enantiomers will be S & S, if you have R & S then the enantiomers will be S & R

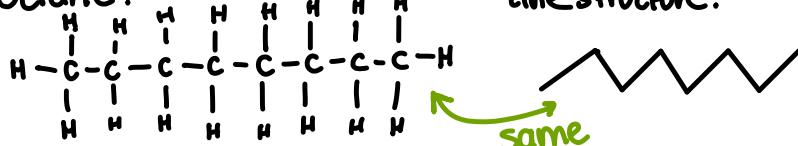
CHEM1111 Worksheet – Lecture 18

1. Propane is $\text{CH}_3\text{CH}_2\text{CH}_3$ (a chain of 3 carbons, with the number of hydrogens indicated attached to each carbon). Draw a picture to show the structure of this molecule.



Could you draw your picture quickly and efficiently? How well would this drawing method work for a bigger molecule (e.g. octane (C_8H_{18}), octadecane ($\text{C}_{18}\text{H}_{38}$) or taxol ($\text{C}_{47}\text{H}_{51}\text{NO}_{14}$))?

Octane:



How well does the picture above represent the actual structure of propane?

Badly, each carbon contains an sp^3 hybridisation

so it doesn't represent the shape of the tetrahedral right.

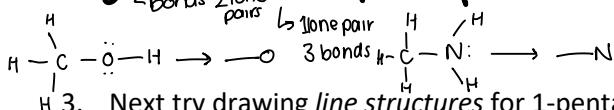
For example, the carbon is larger than hydrogen atom but you can't see that

2. Now draw a *line structure* for octane, C_8H_{18} (remember lines represent bonds, C atoms aren't shown (they're assumed to be at the intersections and ends of lines) H atoms aren't shown, and angles are drawn close to the actual bond angles.

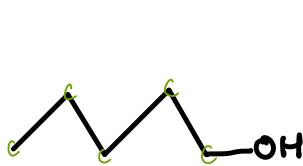
How quickly/efficiently could you draw that picture? How well does it represent the actual structure of the molecule?

Functional groups: Double bonds =

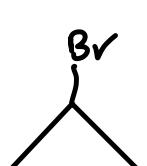
$\text{O}^{2-\text{bonds}}_{\text{2 lone pairs}} \text{N}^{-\text{3 bonds}}_{\text{1 lone pair}} \text{Triple bonds} =$



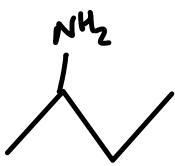
3. Next try drawing *line structures* for 1-pentanol, 2-bromopropane and 2-aminobutane.



1-pentanol
($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$)
Penta = 5
ol = alcohol

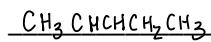
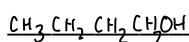
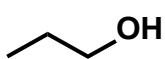
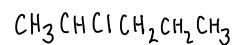
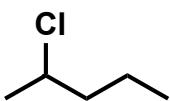


2-bromopropane
($\text{CH}_3\text{CHBrCH}_3$)
propane = 3
bromo = Br



2-aminobutane
($\text{CH}_3\text{CH}(\text{NH}_2)\text{CH}_2\text{CH}_3$)
Butane = 4
amine = NH₂

4. And now work backwards and draw *condensed formulae* (e.g. CH₃CH₂CH₃) for these structures.



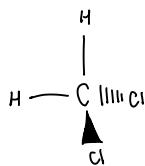
Can you name any of these three compounds?

2-chloropentane

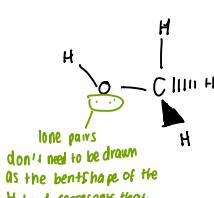
1-propanol

2-pentene

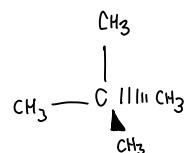
5. Try drawing 3D structures for these compounds, using wedges and dashes to show bonds coming out of/ going into the page. Determine the geometry around the underlined atoms.



dichloromethane
(CH₂Cl₂)



methanol
(CH₃OH)



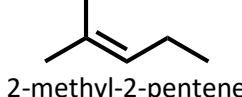
dimethylpropane
(CH₃C(CH₃)₃)

For more practice, try these extra questions ...

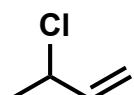
6. Work out molecular formulae (e.g. C₂H₆) for these structures. Determine the geometry around each of the carbon atoms.



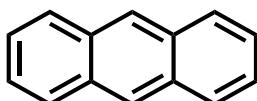
benzene



2-methyl-2-pentene



3-chloro-1-butene



anthracene

CHEM1111 Worksheet – Lecture 19

1. Methane (CH_4) has a *tetrahedral* shape. A tetrahedron is symmetrical: What does this tell you about the four C–H bonds in methane? Are they all equivalent?

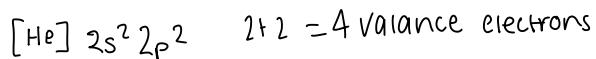
yes



What does *this* tell you about the four orbitals at carbon that are involved in forming these four bonds? Are *they* all equivalent?

yes

2. Let's look at this another way. What is the **electronic configuration** of carbon?



So which of carbon's atomic orbitals are involved in making these bonds to the hydrogens?



Would all the C–H bonds in methane be equivalent if these orbitals behaved as separate, independent orbitals (i.e. one 2s orbital + three 2p orbitals)? No

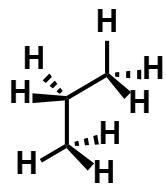
3. Let's mix some atomic orbitals. You have one s-orbital and three p-orbitals, and you hybridise them. How many different hybridised orbitals can you make (that include some s and some p)?

What is the s:p ratio in each of them? How many p orbitals are left out in each case? *Challenge*

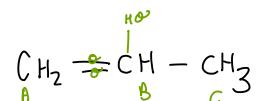
Q: There is another orbital combination that isn't mentioned in the lecture. Predict what it is.

Orbitals used	s : p Ratio	'Left Over' p-orbitals	Hybridisation
S + p	1: 3	0	sp^3
S + p	1: 2	1	sp^2
S + p	1: 1	2	sp

4. So what is the hybridization at each carbon in propane and propene shown below? Once you've answered that, match the correct name to each compound.



propane



$$\text{CA } 30^\circ + 1\pi = \text{sp}^2 = 120^\circ$$

$$\text{CB } 30^\circ + 1\pi = \text{sp}^2 = 120^\circ$$

$$\text{CC } 40^\circ \dots \text{sp}^3 = 109.6^\circ$$

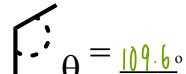


propene

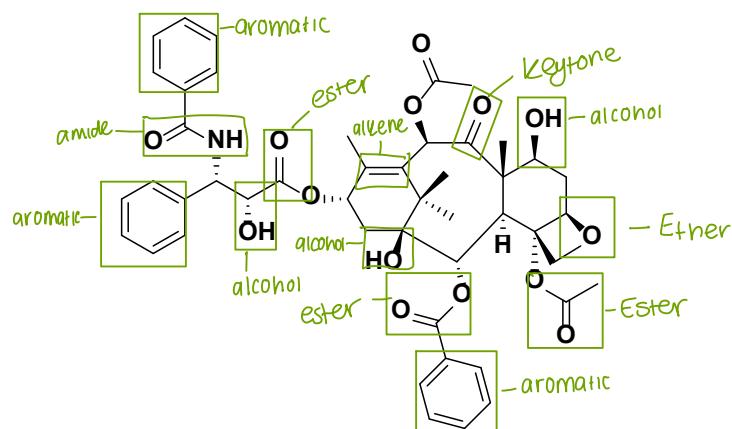
Each C has 4 single & bonds: sp^3

Bond angle: 109.6°

What is the bond angle around the central carbon in each of these compounds?



5. Circle or highlight all the functional groups in the structure of the potent anti-cancer drug known as 'Taxol' below. How many are there?



Taxol (paclitaxel)

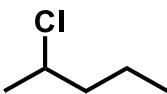
CHEM1111 Worksheet – Lecture 20

1. What are the (a) formulae and (b) names of the three compounds below.



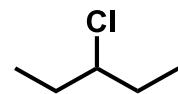
(a) $C_5H_{11}Cl$

(b) 1-chloropentane



(a) $C_5H_{11}Cl$

(b) 2-chloropentane



(a) $C_5H_{11}Cl$

(b) 3-chloropentane

2. Match the types of isomer with the right definition below.

constitutional

configurational

stereoisomer

conformational

different connectivity
(different type or sequence
of bonds)

different arrangement of
groups in space

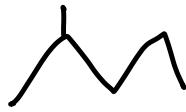
type of stereoisomer
interconversion requires
bond breaking

type of stereoisomer
interconversion via bond
rotation

3. How many constitutional isomers are there of molecular formula C_6H_{14} ? Draw them.



Hexane



2-Methylpentane



3-methylpentane



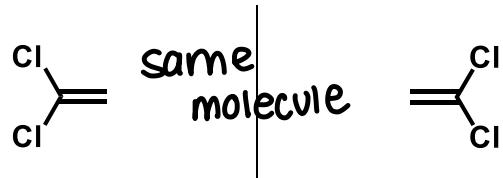
2,2 dimethylbutane



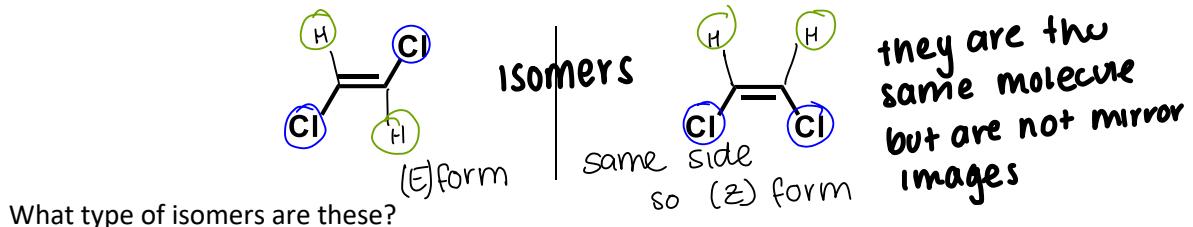
2,3 dimethylbutane

If you've got time, work out the names of the compounds you've drawn above.

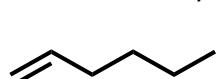
4. Are these the same compound? Why so/ why not?



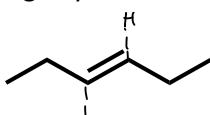
Remembering that you can't rotate around the C-C axis of a C=C bond (without breaking the π bond, which doesn't happen easily), are *these* the same compound? Why so/ why not?



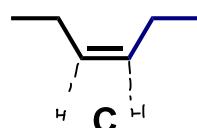
5. Now name these molecules fully (i.e. including any stereochemical descriptors, i.e. E or Z) ...



A



B



C

hex-1-ene

(E) hex-3-ene

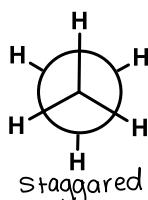
(Z) hex-3-ene

What type of isomers are

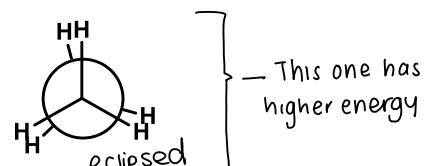
... A and B? constitutional

... B and C? configurational

6. Two conformational isomers of ethane are shown below. One of these is called the *staggered conformation*, the other is an *eclipsed conformation*. Which do you think is which? Which is higher in energy?



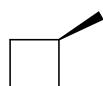
staggered



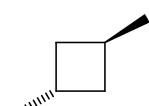
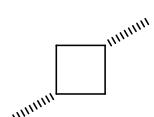
eclipsed

} This one has higher energy

7. For a bit more practice ... what type of isomerism is shown in each of these pairs of cyclobutanes?



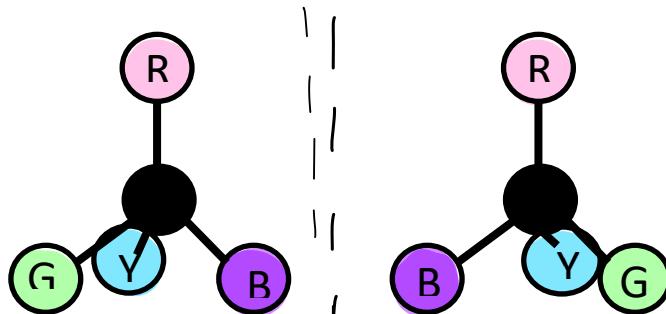




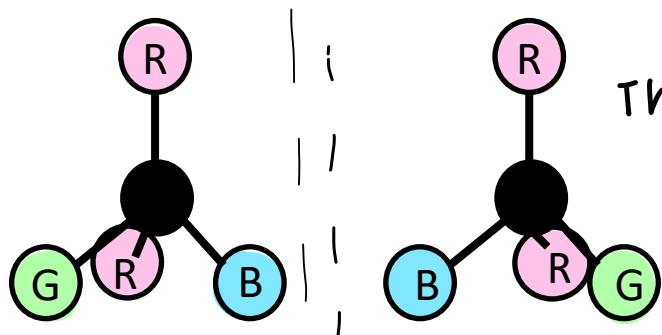
CHEM1111 Worksheet – Lecture 21

1. Consider two molecular models as depicted below. (The labels R, B, G and Y represent different colours.) In each case, determine whether the pair of molecules are enantiomers or just the same molecule rotated.

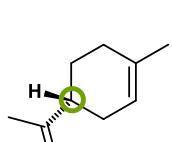
Set I



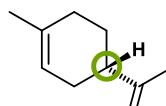
Set II



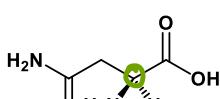
2. Highlight the stereocentres in each of these chiral molecules



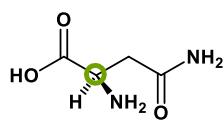
(+)-limonene
odour in oranges



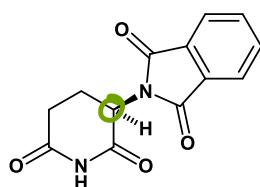
(-)-limonene
odour in lemons



L-asparagine
bitter



D-asparagine
sweet



(R)-thalidomide
mild sedative

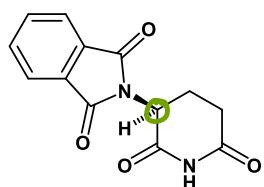
mirror plane

Our smell and taste receptors are chiral and so may differentiate between these enantiomers.

This is also true of other proteins in our bodies (see thalidomide below).

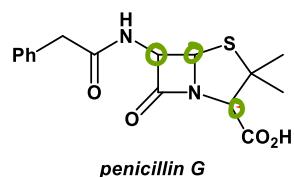
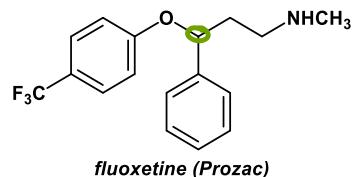
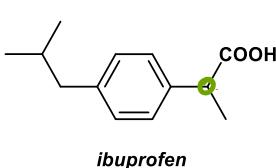
The stereochemical labels (*L*) and (*D*) are often used in biology for sugars and amino acids. In this course we will use the more general (and therefore more useful) labels (*R*) and (*S*).

See this week's videos for more about (*R*) and (*S*).

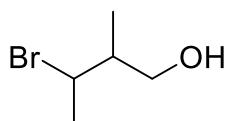


(S)-thalidomide
extreme teratogen

3. Where are the stereocentres in these well-known drug molecules?



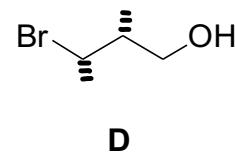
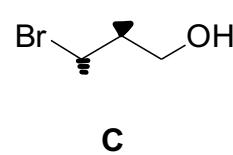
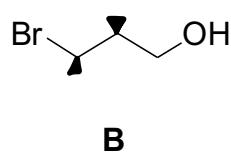
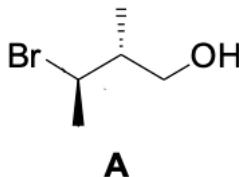
4. Consider a molecule like this one, which has two stereogenic centres. Identify the stereocentres.



# of stereogenic centres	# of different stereoisomers
2	$2 \times 2 = 4$
3	$2 \times 2 \times 2 = 8$
4	$2 \times 2 \times 2 \times 2 = 16$
n	2^n

How many different stereoisomers are possible? Complete the table for two, three, four and n stereocentres.

5. Using wedges and dashes, draw three more stereoisomers of 3-bromo-2-methylbutan-1-ol alongside the one shown below.



Which pairs are enantiomers (i.e mirror images)?

A and C

B and D



School of Chemistry

Chemistry 1A
(CHEM1111)

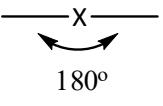
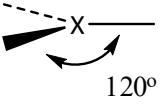
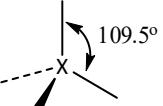
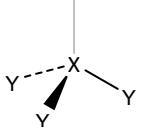
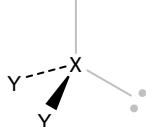
Tutorial 7 (Week 7): VSEPR and Intro Organic Chemistry

Model 1: Lewis Structures and Molecular Shape

The ‘Valence Shell Electron Pair Repulsion’ (VSEPR) model assumes that because of the repulsion between electrons, the bonds and lone pairs surrounding an atom try to get as far from each other as possible. **The shape is dictated by the arrangement of sets of electrons** (total number of bonding groups (n) and lone pairs (m) around the central atom).

The 3D-arrangements of bonds and lone pair which maximize the distance between these bonds and lone pairs are shown in the table below. The term **hybridization** is a label which indicates the number of electron areas (either lone pairs or sigma bond pairs).

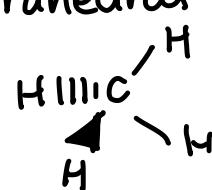
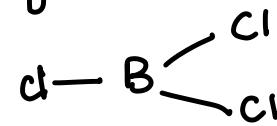
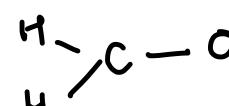
The **molecular shape** or **geometry** is the arrangement of the bonds. If lone pairs are present, they help to dictate what this arrangement is but are not included when the geometry of the molecule is described.

Electron areas n	Hybridization	Lone pairs = 0 m	Lone pairs = 1 m	Lone pairs = 2 m
2	sp	 Linear		
3	sp^2		 bent	
4	sp^3	 Tetrahedral	 trigonal pyramidal	 bent or V shaped

Critical thinking questions

1. The shapes for $n = 3, m = 1$ and $n = 4, m = 2$ are both named "bent". What are the bond angles for these two bent shapes; are they identical?

2. Complete the table below. The central atom is underlined.

System	Lewis structure	n number of Bonding groups	m lone pairs	Molecular shape (sketch and describe)
<u>CH</u> 4	$\begin{array}{c} \text{H} \\ \\ \text{H}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$ C = $[\text{1s}^2] \text{2s}^2 \text{2p}^2 = 4$ H: $s^1 \times 4 = 4$ $4+4=8$ 8 valence	4	0	tetrahedral 
<u>BCl</u> 3	$\begin{array}{c} \text{:Cl} \\ \\ \text{:Cl}-\text{B}-\text{Cl} \\ \\ \text{:Cl} \end{array}$ B = $[\text{1s}^2] \text{2s}^2 \text{2p}^1 = 3$ Cl = $[\text{1s}^2] \text{2s}^2 \text{2p}^5$ $3s^2 \text{ 3p}^5$ $5 \times 2 = 10 \times 3 = 30 + \frac{3}{3} = 33$ $\frac{33}{15}$	3	0	trigonal planar 
<u>H</u> 2CO	$\begin{array}{c} \text{H} \diagup \text{C}=\ddot{\text{O}} \diagdown \text{H} \end{array}$	3	0	trigonal planar 
<u>NF</u> 3	$\begin{array}{c} \text{F} \diagup \ddot{\text{N}} \diagdown \text{F} \end{array}$	4	1	trigonal pyramidal 
<u>SO</u> 3 ²⁻	$\begin{array}{c} \text{:O:} \diagup \text{S} \diagdown \text{:O:} \end{array}$	4	1	Trigonal pyramidal 

Model 2: Bonding in Organic Molecules

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

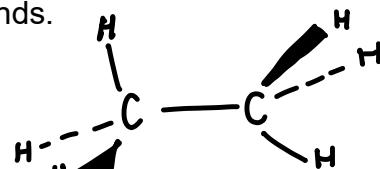
1	2	0	0	0	0	0	0	0	0	0	3	4	3	2	1	0	
H															He		
Li	Be										B	C	N	O	F	Ne	
Na	Mg										Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Sr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe

Figure 1. Partial Periodic Table

Critical thinking questions

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

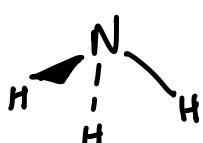
4 bonds :



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

Two

5. Non-bonding electrons – like bonding electrons – take up space. How does this lone pair of electrons affect the shape of a molecule like NH₃? (Try to draw it in 3-D.)

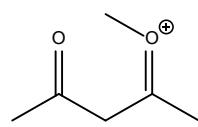
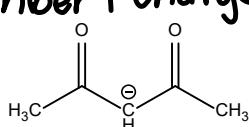
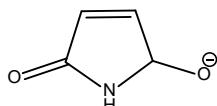


It occupies the position of a bond, causing the shape to be pyramidal rather than planar

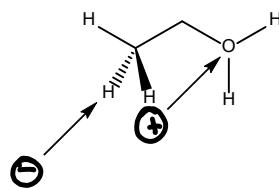
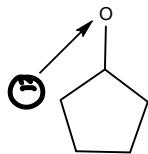
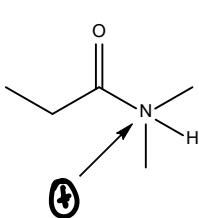
Sometimes atoms will form more or less than their typical number of bonds. In these cases, the atoms are said to carry a formal charge (either + or -).

6. Here are a few examples. How does the typical number of bonds formed, and the actual number of bonds formed relate to the formal charge?

Number of bond = typical number + charge



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

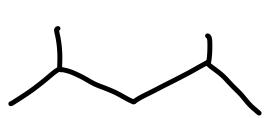


Remember: formal charges must ALWAYS be indicated when you are drawing molecular structures.

Model 3: Naming Organic Molecules

Critical thinking questions

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



2,4-dimethylpentane



2,3-dimethylpentane



2,2-dimethylpentane



3,3-dimethylpentane

9. You should have drawn 4 structures in Q8. Pick one of these and try to give it an unambiguous name.

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

10. Is your answer to Question 9 consistent with this convention? If not, try to name it again.

yes

11. Name the other molecules in your answer to Question 8.

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



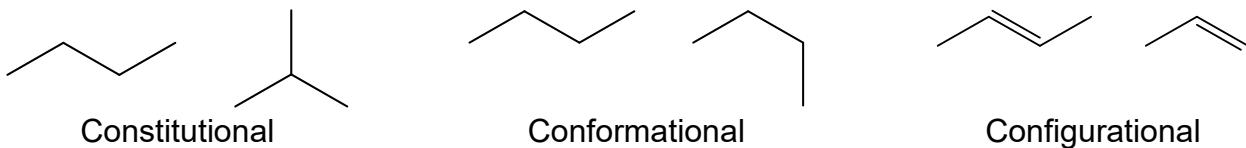
School of Chemistry

Chemistry 1A
(CHEM1111)

Tutorial 8 (Week 8): Isomerism and Chirality

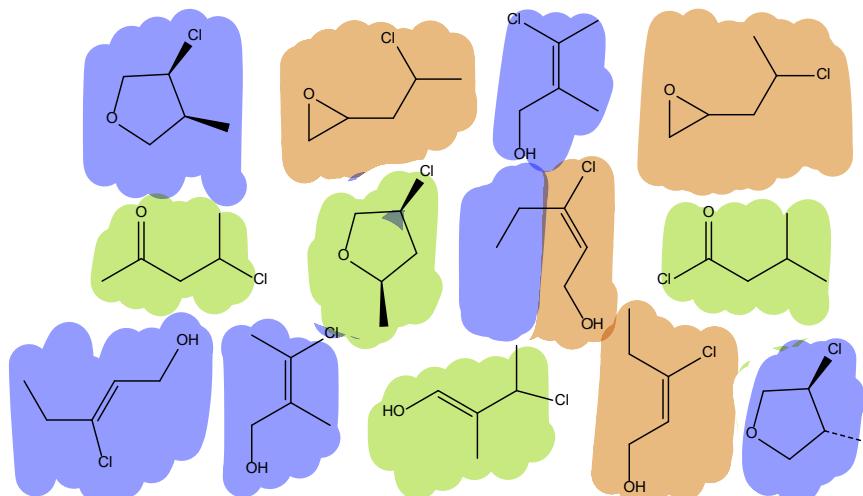
Model 1: Isomerism

There are three broad classes of isomers.



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

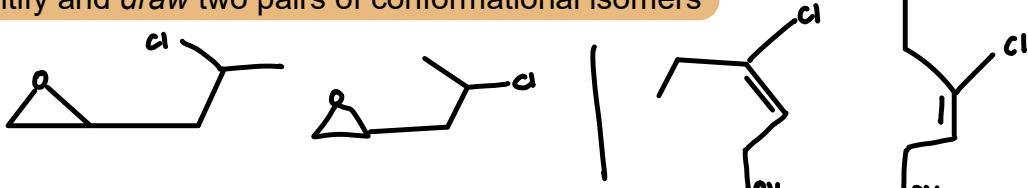
Here are some molecules all with the formula C₅H₉ClO



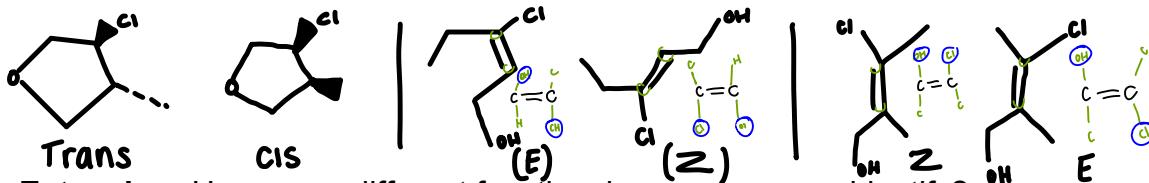
Critical thinking questions

1. Circle at least 7 constitutional isomers.

2. Identify and draw two pairs of conformational isomers



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



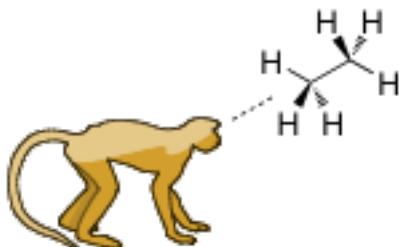
4. Extension: How many different functional groups can you identify?

Top row: (i) cycle ether and alkyl chloride, (ii) cycle ether (epoxide) and alkyl chloride, (iii) alkene, alkynyl chloride and alcohol, (iv) cycle ether (epoxide) and chloride

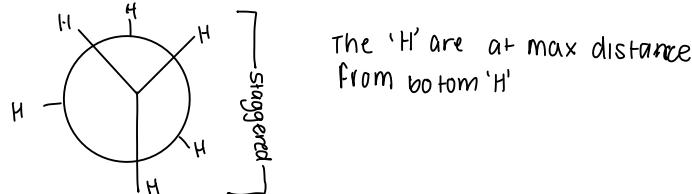
Second row: (i) ketone and alkyl chloride, (ii) cycle ether, alkene chloride, (iii) alkene, alkynyl chloride and alcohol and (iv) acyl chloride

Third row: (i) alkene, alkynyl chloride and alcohol, (ii) alkene, alkynyl chloride and alcohol, (iii) enol and alkyl chloride, (iv) alkene, alkynyl chloride and alcohol, (v) cyclic ether and alkyl chloride.

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



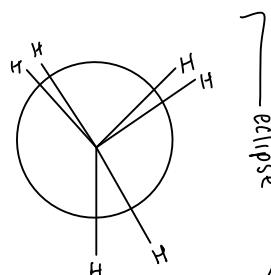
Sketch what you would see. By doing this explain what you think might be meant by the term *staggered conformation*.



The 'H' are at max distance from bottom 'H'

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

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

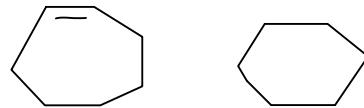
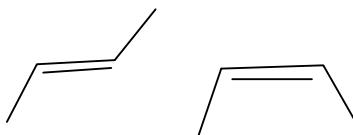


Model 2: Enantiomers and Diastereomers

You may need a molecular model set for these activities.

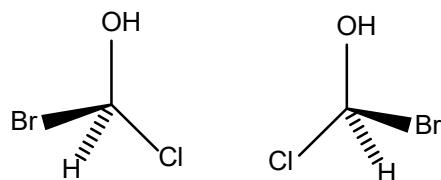
Critical thinking questions

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



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

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



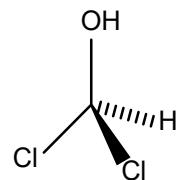
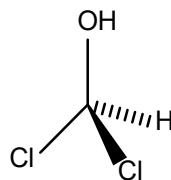
3. On one model, swap two of the balls. What is the relationship between the two models now?

Identical

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

Enantiomer

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



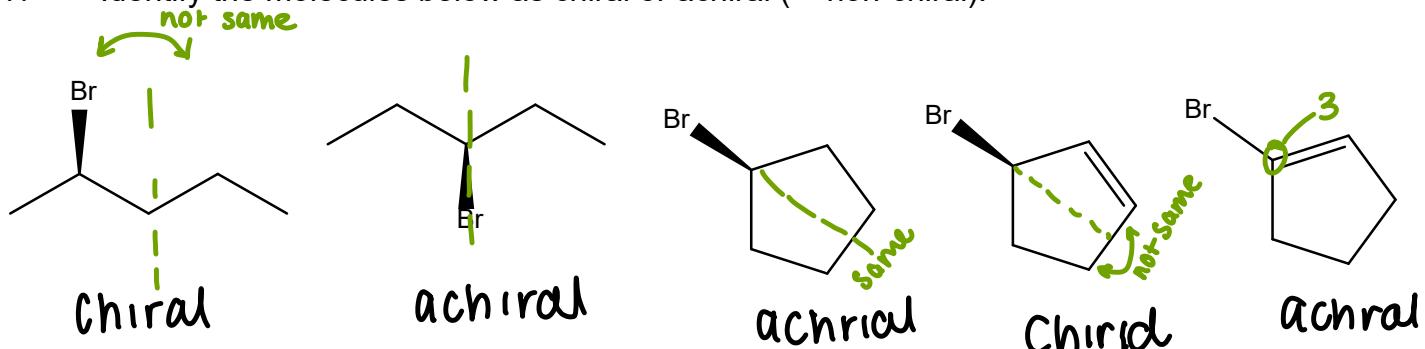
1. Identical

2. Identical

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

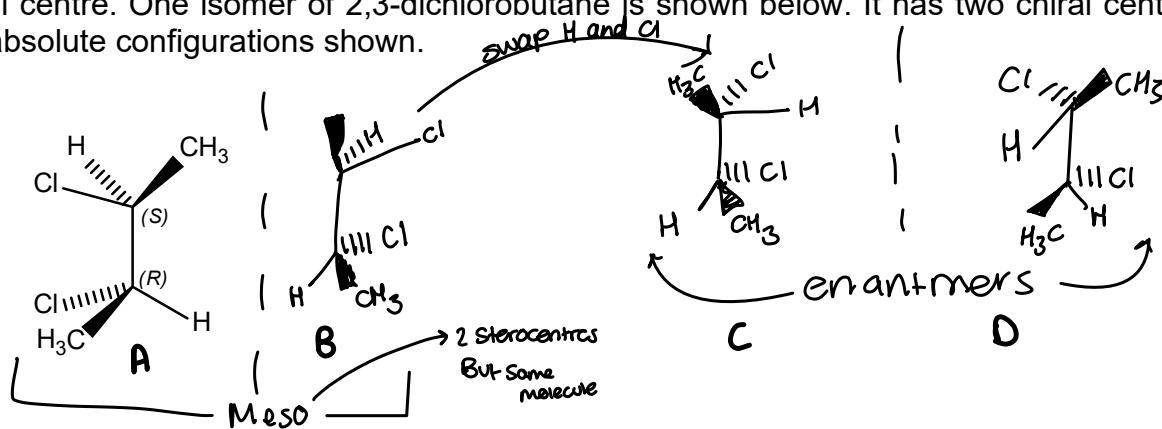
4 different groups around a tetrahedral carbon atom
in general, lack of an internal reflection plane or centre
of symmetry

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



Just as (*E*) & (*Z*) and *cis* & *trans* are used to distinguish between diastereomers, (*S*) & (*R*) are used to denote the stereochemistry for the two enantiomers of a chiral molecule. You will see these names in chemical compounds, but will learn how to assign these names in CHEM1xx2.

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



8. Draw the other forms of 2,3-dichlorobutane in the space above.
9. Identify the relationships between each pair. Hint: they will either be enantiomers, diastereomers or the same. The pair that are the same as each other are not isomers – this is the **meso form**. **A and B are identical this is called meso form**
C and D are enantiomer.
10. **Extension:** If you replace one of the chlorine groups with bromine and repeat the exercise, will you still get a pair of meso compounds? (Try to do this as a thought experiment first, then draw out the structures if you need to.)

A C I D S

3

B A S E S

LECTURE 29: REACTION OF ACIDS AND BASES AND PH

LO: LIST COMMON ACIDS AND BASES

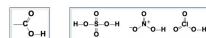
Use of common acids and bases

Substance	Formula	Use
Acetic acid	CH_3COOH	Preserving; preservative
Formic acid	HCOOH	not removable
Hydrochloric acid	HCl	irritating; irritant; bleaching agent; cleaner
Sodium hydroxide	NaOH	oven cleaner
Ammonia	NH_3	household cleaner
Sodium carbonate	Na_2CO_3	removing grease; removing the oil/grease; baking powder
Sodium hydrogen carbonate	NaHCO_3	

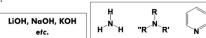
Reproduced from The Elements of Chemistry, 4e

Common types of acids and bases

- Many common acids have a proton attached to an O atom:

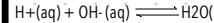


- Many bases have a free OH ion or nitrogen atom with a lone pair:



LO: DEFINE ACIDS AND BASES ACCORDING TO THE ARRHENIUS AND BRONSTED-LOWRY MODELS

Arrhenius:



ACID: H⁺-producer in aqueous solution e.g. HCl

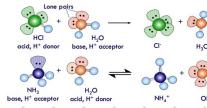
BASE: OH⁻-producer e.g. NaOH

Only applies to aqueous/water solutions

Bronsted-Lowry: $\text{H}^+ + \text{A}^- \rightleftharpoons \text{HA}$

ACID: proton donor (H⁺) e.g. HCl

BASE: proton acceptor e.g. NH₃

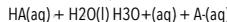


LO: APPLY EQUILIBRIA TO ACIDS AND BASES

What is H⁺(aq)?

In water: an acid (e.g., HCl) ionises to produce H⁺(aq) - actually H₃O⁺(aq), but we usually just write H⁺(aq)

Acids, bases & equilibrium



- A **STRONG** acid has equilibrium far to the right (HA is effectively completely ionised)
- A **WEAK** acid has equilibrium to the left (HA partly/mostly intact)

K_a is the **acid dissociation constant**

Conjugate acid-base pairs

Conjugate acid-base pair is of molecules that only differ by one proton

• NH₄⁺ is the conjugate acid of NH₃

it is the acid because it has one more proton

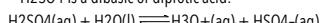
• NH₃ is the conjugate base of NH₄⁺

it is the base as it has one less proton

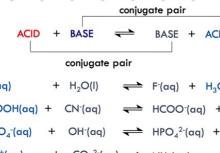
• A conjugate base has one less proton than its conjugate acid

• HS₀₄⁻: conjugate base is SO₄²⁻
conjugate acid is H₂SO₄

• H₂SO₄ is a dibasic or diprotic acid:



$$\text{Equilibrium Equation: } K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]}$$



Autotitration of Water



• Equilibrium constant given symbol and symbol

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14}$$

• Normal solution: $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ M}$

• Acids: $[\text{H}^+] > 1 \times 10^{-7} \text{ M}$

• Bases: $[\text{H}^+] < 1 \times 10^{-7} \text{ M}$

CO₂, Carbonates and Ocean Acidification



USE THE DEFINITIONS OF PH AND KW TO QUANTIFY THE ACIDITY AND BASICITY OF AQUEOUS SOLUTIONS

The pH Scale

Because the concentrations of acids and bases can vary over many orders of magnitude, it is convenient to define a logarithmic scale to compare them:

For example: If $[\text{H}^+] = 1.0 \times 10^{-6} \text{ M}$ the $\text{pH} = -\log(10^{-6}) = -(-6) = 6.00$ Hence, $\text{pOH} = 14.00 - 6.00$

$$\text{pH} = -\log_{10}[\text{H}^+]$$

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$

$$\text{PH} + \text{pOH} = 14$$

$$= 8.00 \text{ and } [\text{OH}^-] = 10^{-8.00} \text{ M}$$

The 'p' convention

$$\text{pH} = -\log_{10}[\text{H}^+]$$

$$\text{pOH} = -\log_{10}[\text{OH}^-]$$

$$\text{pK}_w = -\log_{10}K_w = 14.00 \text{ at } 25^\circ\text{C}$$

Acid: $\text{pH} < 7$

Since $K_w = [\text{H}^+][\text{OH}^-]$:

$$\log_{10}K_w = \log_{10}[\text{H}^+] + \log_{10}[\text{OH}^-]$$

$$-\log_{10}[\text{H}^+] - \log_{10}[\text{OH}^-] = -\log_{10}K_w$$

Neutral: $\text{pH} = 7$

$$\log_{10}K_w = \log_{10}[\text{H}^+] + \log_{10}[\text{OH}^-]$$

Basic: $\text{pH} > 7$

$$-\log_{10}[\text{H}^+] - \log_{10}[\text{OH}^-] = -\log_{10}K_w$$

$$\text{pH} + \text{pOH} = 14$$

$$\text{pOH} = 14 - \text{pH}$$

Temperature dependence of pH



$$\Delta S_f^\circ = 102 \text{ J K}^{-1} \text{ mol}^{-1}$$

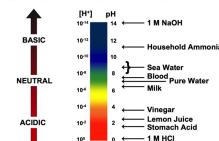
$$\Delta G_f^\circ = -55.8 - (298)(102) = -10.0 \text{ kJ mol}^{-1}$$

$$K_w = 1.0 \times 10^{-14} \text{ only at } 25^\circ\text{C}$$

• Reaction is endothermic: it is more favourable at higher temperature

$$\bullet \text{For } T > 25^\circ\text{C}, K_w > 10^{-14} \Rightarrow \text{pH} + \text{pOH} < 14 \text{ if } T = 25^\circ\text{C}$$

$$\bullet \text{For } T < 25^\circ\text{C}, K_w < 10^{-14} \Rightarrow \text{neutral pH } > 7 \text{ if } T = 25^\circ\text{C}$$



Household Ammonia
Sea Water
Blood
Pure Water
Milk
Vinegar
Lemon Juice
Stomach Acid

LECTURE: STRONG AND WEAK ACIDS AND BASES

LECTURE 30

pKa and pKb

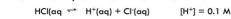


LO: EXPLAIN THE DIFFERENCE BETWEEN A STRONG AND WEAK ACID AND THE DIFFERENCE BETWEEN A STRONG AND WEAK BASE IN TERMS OF THE PERCENTAGE DISSOCIATION IN SOLUTION

Strong acids and bases

Completely ionise in water. Equilibrium lies completely to the right, $K_a \approx \infty$.

What is the pH of a 0.1 M HCl solution?

Thus $[\text{H}^+] = 0.1 \text{ M}$ and $\text{pH} = -\log_{10}[\text{H}^+] = 1.0$

Weak acids

Most acids or bases are weak and they do not completely ionise in water.

Weak bases

Equilibrium constant is called base ionisation constant, K

Tactic: calculate pOH and then pH, given K_b

• What is the pH of a 0.002 M NaOH solution?

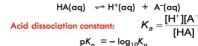
➢ Completely ionised, so $[\text{OH}^-] = 0.002 \text{ M}$ ➢ $\text{pOH} = -\log_{10}[\text{OH}^-] = -\log_{10}(0.002) = 2.7$ ➢ $\text{pH} = 14 - 2.7 = 11.3$

Strong acids

 H_2SO_4 , HCl , HBr , H_3NO_3 , HClO_4

Strong bases

All hydroxides of Groups 1 & 2 (except Be):

e.g. $\text{NaOH} \rightarrow \text{Na}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq})$ $\text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+}(\text{aq}) + 2\text{OH}^{-}(\text{aq})$ 

LO: EXPLAIN THE INCREASE IN pKa VALUES FOR DISSOCIATIONS OF THE PROTONS IN POLYPROTIC ACID

Relationship between Ka and pKa

The larger the value of K_a , the stronger the acid and the lower the value of pKa . Remember that if it has a pKa value it must be weak as it has an equilibriumwhat is the weakest acid? Phenol (10.00) as it has the lowest K_a value (highest).

what is the strongest acid? Bisulfate ion (1.991)

$$\text{Ka} = 1.02 \times 10^{-2} \text{ then } \text{pKa} = -\log_{10}(1.02 \times 10^{-2}) = 1.991$$

$$\text{pKa} = 1.991 \text{ then } \text{Ka} = 10^{-1.991} = 1.02 \times 10^{-2}$$

LO: USE pKw, pKa and pKb TO CALCULATE THE pH OF A SOLUTION CONTAINING A WEAK ACID OR BASE

Find the pH of 0.1 M acetic acid ($\text{CH}_3\text{COOH} = \text{HAc}$)

Acid Name (concn)	P	pK_a	C	pK_w
Sulfuric acid (H ₂ SO ₄)	1.02 × 10 ⁻²	2.00		
Nitrous acid (HNO ₂)	7.1 × 10 ⁻⁴	3.15		
Acetic Acid (CH_3COOH)	1.8 × 10 ⁻⁵	4.74		
Bisulfate ion (HSO_4^-)	2.3 × 10 ⁻⁷	6.4		
Phenol ($\text{C}_6\text{H}_5\text{OH}$)	1.0 × 10 ⁻¹⁰	10.00		

Since the equilibrium constant is very small we assume

$$x \ll 0.1, i.e. (0.1 - x) \approx 0.1 \\ 10^4 \approx x^2 / 0.1 \\ x^2 = 10^4 \times 0.1 = 10^{4.2} \\ x \approx \sqrt{10^{4.2}} = 10^{2.1}$$

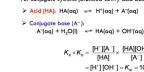
$$\begin{aligned} \text{As } \text{pH} &= -\log_{10}[\text{H}^+] \\ \text{pH} &= -\log_{10}(0.1 - x) = -\log_{10}10^{2.1} \\ &= 2.1 \end{aligned}$$

$$\begin{aligned} \text{Check: } x &= 10^{2.1} = 1.0 \times 10^{-2} \ll 0.1 \text{ or} \\ \text{or } 0.1 - x &= 0.0986 \text{ M} \sim 0.1 \text{ M} \end{aligned}$$

5% rule

Relationship between pK_a and pK_b

• For conjugate systems (Bronsted-Lowry acid-base pairs)

• We only need values of pK_a , since $\text{pK}_a = 14 - \text{pK}_b$ • Find the pK_a of 1.0×10^{-2} M HCO_3^- (weak form of carbonic acid H_2CO_3) $\text{pK}_a = 14 - \text{pK}_b = 14 - 4.3 = 9.9$ $\text{HCO}_3^- \text{ (aq)} \rightleftharpoons \text{OH}^-(\text{aq}) + \text{HCO}_3^-(\text{aq})$ Initial (I): $[\text{HCO}_3^-] = 1.0 \times 10^{-2}$ Change (C): x Equilibrium (E): $[\text{HCO}_3^-] = 1.0 \times 10^{-2} - x$ $K_a = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{HCO}_3^-]} = 10^{-2} \times \frac{x^2}{1.0 \times 10^{-2} - x} = 10^{-2} \times \frac{x^2}{1.0 \times 10^{-2}}$ $x = \sqrt{10^{-2} \times 10^{-2}} = \sqrt{10^{-4}} = 10^{-2}$ $\text{pH} = 14 - \log_{10}(10^{-2}) = 12$ $\text{pH} = 14 - 2 = 12$

Example 2 continued

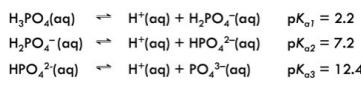
$$\begin{aligned} K_a &= [\text{H}^+][\text{HCO}_3^-] = 10^{-2} \times x^2 = 10^{-2} \times 10^{-2} = 10^{-4} \\ x &= \sqrt{10^{-2} \times 10^{-2}} = \sqrt{10^{-4}} = 10^{-2} \\ x &= 10^{-2} \text{ M} \end{aligned}$$

$$\begin{aligned} \text{As } \text{pH} &= -\log_{10}[\text{H}^+] = -\log_{10}(10^{-2}) = 2 \\ \text{pH} &= 2 \end{aligned}$$

= 8.1 (two significant figures)

LO: USE THE INCREASE IN pKa VALUE FOR DISSOCIATION OF THE PROTONS IN POLYPROTIC ACID TO PERFORM CALCULATION

Polyprotic acids



removing more protons is harder:

increasing pK_a = decreasing Ka : $\text{Ka}_1 > \text{Ka}_2 > \text{Ka}_3$

reason: harder to remove +ve charge against increasing -ve charge

- large difference in pK_a values

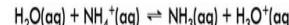
- only need to consider one equilibrium at a time
(simplifies maths!)

LECTURE 31

BUFFERS

LO: IDENTIFY CONJUGATE ACID/BASE PAIRS

Salts of weak acids:

For a conjugate acid-base pair, $pK_a + pK_b = 14.00$ at 25°CIs a solution of NaCN acidic or basic? NaCN is the salt of NaOH (strong base) and HCN (weak acid). The base "wins"; $pH > 7$. Overall reaction isDoes a solution of NH4Cl have $pH > 7$ or < 7 ?Salt of NH4OH (weak base) and HCl (strong acid)
acid "wins": $pH < 7$ and reaction is**The common ion effect**

If you add the salt on an acid to a solution of the same acid then the equilibrium will shift to towards neutral



The addition of CH3COO-: INCREASE pH

By Le Chatelier's principle the equilibrium will shift the left to remove CH3COO- and thus decreasing H3O+

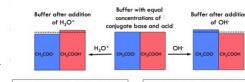
Addition of CH3COOH: DECREASE pH

By Le Chatelier's principle the equilibrium will shift the right to remove CH3COOH and thus increase H3O+.

LO: BE ABLE TO EXPLAIN WHAT BUFFERS ARE AND HOW THEY WORK

Buffer system

A solution containing both a weak acid and its salt withstands pH changes when acid or base (limited amounts) are added.

**LO: BE ABLE TO CALCULATE THE pH OF A BUFFER SYSTEM AND BE ABLE TO DESIGN A BUFFER WITH A REQUIRED pH**

Buffer systems and pH change

Consider change in pH of pure water ($pH = 7$) if we add an equal amount of 10-3 M HCl: $[\text{H}^+] = 1 \times 10^{-3} \text{ M}$ and the pH goes from 7 to 3! \rightarrow water is not a good buffer solution

Consider a buffer solution with 0.1 M each of sodium acetate (NaAc) & acetic acid (HAc):

What is the pH when 10-3 M HCl is added?

$\text{HAc}(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{Ac}^-(\text{aq})$	$K_a = 10^{-5}$
Initial: $0.1 \quad 10^{-5} \quad 0.1$	
Neutralization (I): $0.1 + 10^{-3} \quad 0 \quad 0.1 - 10^{-3}$	
Change (C): $-x \quad +x \quad +x$	
Equilibrium (E): $0.1 + 10^{-3} \quad x \quad 0.1 - 10^{-3} + x$	

$K_a = 10^{-5} = \frac{x(0.1 - 10^{-3} + x)}{0.1 - 10^{-3}} = \frac{x(0.1 - 10^{-3})}{0.1 - 10^{-3}}$
 $x = 1.02 \times K_a = 0.000102 << 0.001$
 $\text{pH} = -\log x = 4.69$

the pH hardly changes from 4.7!
Solution is buffered against pH change

Henderson - Hasselbalch equation

For a buffer solution, which contains similar concentrations of a conjugate acid/base pair of a weak acid. The dissociation of HA or protonation of A- does not lead to a significant change in the concentrations of these species. Taking logs and rearranging gives:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{initial base}]}{[\text{initial acid}]}$$

→ stay close to it using buffer zones

Buffer Preparation

If the pH of a required buffer is pK_a of available acid then use equimolar amounts of acid and conjugate baseIf the required pH differs from the pK_a then use the Henderson-Hasselbalch equation.

Buffer Capacity

Buffer capacity is related to the amount of strong acid or base that can be added without causing significant pH change.

Depends on amount of acid & conjugate base in solution:

highest when $[\text{HA}]$ and $[\text{A}-]$ are large.highest when $[\text{HA}] \approx [\text{A}-]$ Most effective buffers have acid/base ratio less than 10 and more than 0.1 \Rightarrow pH range is ± 1

Example 2
 In the $\text{H}_2\text{PO}_4^-/\text{Na}_2\text{HPO}_4/\text{Na}_3\text{PO}_4$ system, how could you make up a buffer with a pH of 7.40?

DATA: $K_{a_1} = 7.2 \times 10^{-3}$, $K_{a_2} = 6.3 \times 10^{-8}$, $K_{a_3} = 4.2 \times 10^{-13}$ To make up a buffer, we need pH near pK_a . $pK_{a_2} = 2.14$, $pK_{a_3} = 7.20$, $pK_a = 12.38$ ⇒ must use mixture of H_2PO_4^- and HPO_4^{2-} Cold gas through whole procedure
or simply use Henderson-Hasselbalch equation ...**Example 2 - continued**

$$\begin{aligned}
 \text{pH} = \text{p}K_a + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} &\rightarrow \text{require amounts} \\
 7.40 = 7.20 + \log \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} & \\
 \frac{[\text{HPO}_4^{2-}]}{[\text{H}_2\text{PO}_4^-]} = 10^{7.40 - 7.20} = 10^{0.20} &= 1.58 \\
 \therefore \text{the required ratio of } \text{Na}_2\text{HPO}_4 \text{ to } \text{Na}_3\text{PO}_4 = 1.58:1
 \end{aligned}$$

**LECTURE 32**

TITRATION CURVES AND INDICATORS

LO: UNDERSTAND STRONG ACID/STRONG BASE, STRONG BASES/STRONG ACID, WEAK ACID/STRONG BASE, WEAK BASE/STRONG ACID TITRATIONS

Strong Acid/Strong Base Titration

Strong acids completely dissociate in solution: $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^{-}(\text{aq}) + \text{H}_3\text{O}^{+}(\text{aq})$. $\text{pH} = -\log_{10}([\text{strong acid}]_{\text{initial}})$

If strong base is added, it reacts with the H_3O^{+} so $[\text{H}_3\text{O}^{+}(\text{aq})]$ is reduced: $\text{H}_3\text{O}^{+}(\text{aq}) + \text{OH}^{-}(\text{aq}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$ $\text{pH} = -\log_{10}([\text{strong acid}]_{\text{remaining}})$

Equivalence point: when the amount of added base = initial amount of acid: $[\text{H}^{+}(\text{aq})] = 10^{-7.0} \text{ M}$, $\text{pH} = 7.0$

After the equivalence point, any added base increases $[\text{OH}^{-}(\text{aq})]$: $\text{pH} = 14.00 - \text{pOH} = 14.00 - (-\log_{10}([\text{excess base}]))$

Strong Base/Strong Acid Titration

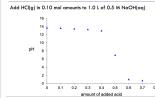
Initial pH is $\text{pH} = 14 - \text{pOH} = 14 - (-\log_{10}([\text{strong base}]_{\text{initial}}))$

At the equivalence point, $[\text{H}^{+}(\text{aq})] = 10^{-7.0} \text{ M}$, $\text{pH} = 7.00$ (at 25 °C)

After the equivalence point, $\text{pH} = -\log_{10}([\text{excess acid}])$

LO: USE TITRATION CURVES TO CHARACTERISE ACIDS AND BASES, USING pH AT THE EQUIVALENCE AND HALF-EQUIVALENCE POINTS

Strong Base/Strong Acid Titration



Weak Acid/Strong Base Titration



Weak Acid/Strong Base Titration



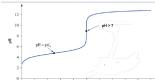
Weak Acid/Strong Base Titration



Weak Acid/Strong Base Titration



Weak Acid/Strong Base Titrations

**LO: DESIGNS AND PERFORM TITRATION EXPERIMENT TO OBTAIN pKa VALUES WITH APPROPRIATE CHOICE OF INDICATOR****Equivalence point vs end point**

Equivalence Point:

- When number of moles of added base = original number of moles of acid
- Strong acid/strong base $\text{pH} = 7$
- Weak acid/strong base $\text{pH} > 7$
- Strong acid/weak base $\text{pH} < 7$

End Point:

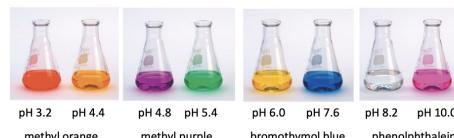
- When a colour change in the indicator is observed
- Choose an indicator that changes colour close to the equivalence point

Indicators

weak acid \rightleftharpoons base

each form has a different colour

The pH at which acid \rightarrow base depends on the pK_a of the indicator



CHEM1111: Worksheet – Lecture 29

Model 1: A Definition of Acids and Bases

Brønsted-Lowry definition:

An acid is a substance that donates a proton, H^+ , to another species.

A base is a substance that accepts a proton, H^+ , from another species.

	Reaction
(i)	$HCl(g) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$
(ii)	$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$
(iii)	$HCN(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + CN^-(aq)$

Critical thinking questions



1. (a) What chemical species are the Brønsted-Lowry acids in the *forward* reactions in the table above?
Proton donor: (i) $HCl(g)$ (ii) $H_2O(l)$ (iii) HCN
- (b) What chemical species are the Brønsted-Lowry bases in the *forward* reactions in the table above?
Proton acceptor: (i) $H_2O(l)$ (ii) $NH_3(aq)$ (iii) $H_2O(l)$
2. Is it possible for a substance to act as both an acid and a base? Explain your reasoning.
yes, H_2O can
↳ Both acid and base (amphoteric)
3. (a) What species results from the loss of a proton from the Brønsted-Lowry acid in the forward reaction (i)
 Cl^-
- (b) Does this species act as an acid or a base when the reverse of reaction (i) occurs?
Base because it picks up a proton (H)
- (c) What species results from the gain of a proton from the Brønsted-Lowry base in the forward reaction (i)
 H_3O^+ **Hydronium ion**
- (d) Does this species act as an acid or a base when the reverse of reaction (i) occurs?
Acid as it loose (H)
- (e) Repeat questions (a) – (d) for reactions (ii) and (iii). Describe any general relationship you deduce using a grammatically correct sentence.

Model 2: Conjugate Pairs

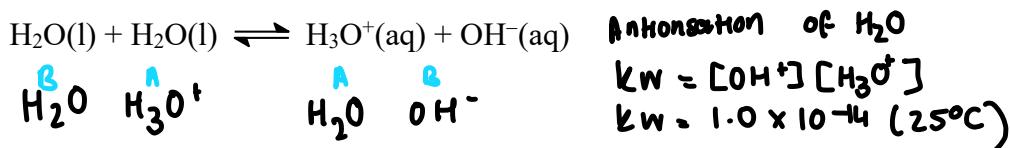
As you discovered in Model 1, certain pairs of molecules are related through their acid and base properties. These pairs are described as a **conjugate acid–base pair**. They differ by *a single proton*. A base has *one less proton* than its conjugate acid. An acid has *one more proton* than its conjugate base.

Acid	Base
H ₂ CO ₃	HCO ₃ ⁻
HCO ₃ ⁻	CO ₃ ²⁻
H ₃ O ⁺	H ₂ O
H ₂ S	HS ⁻

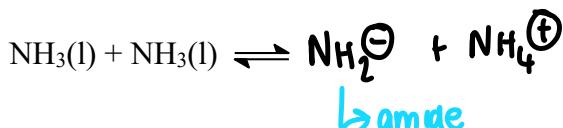
Critical thinking questions

4. (a) What is the conjugate base of H₂O? OH[⊖]
 (b) What is the conjugate acid of NH₃? NH₄[⊕]

5. There are two conjugate pairs in the following reaction. Identify *both* pairs.



6. Ammonia can also react with itself as an acid or a base. Complete the following acid–base reaction in which NH₃(l) acts as both an acid and a base:



Exercises

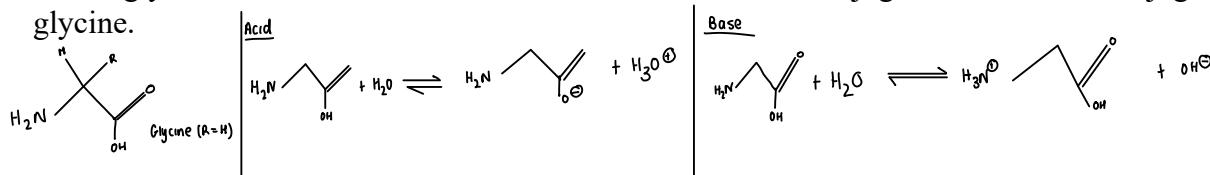
1. Write the formula of the conjugate bases of the following acids:

- (a) H₂SO₄ HSO₄[⊖] (b) HClO₄ ClO₄[⊖] (c) CH₃COOH CH₃COO[⊖]
 (d) H₃PO₄ H₂PO₄[⊖] (e) H₂PO₄⁻ HPO₄²⁻ (f) HPO₄²⁻ PO₄³⁻

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

- (a) CN⁻ HCN[⊕] (b) H₂S H₃S[⊕] (c) HS⁻ H₂S
 (d) S²⁻ HS⁻ (e) CH₃COO⁻ CH₃COOH[⊕] (f) SO₄²⁻ HSO₄⁻

3. Amino acids have both an acidic (–COOH) and a basic (–NH₂) functional group. The simplest amino acid is glycine; H₂N–CH₂–COOH. Give the structure of the conjugate acid and the conjugate base of glycine.



Zwitterion
 IS a the name of a
 Molecule with both $\text{H}_3\text{N}^{\oplus}$ and
 OH^{\ominus} ion that balance each
 Other out. So it is Neutral.

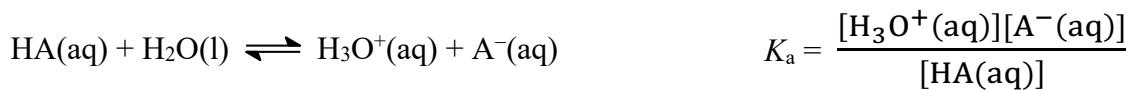
CHEM1111: Worksheet – Lecture 30

Model 1: Strong and Weak Acids

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

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

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



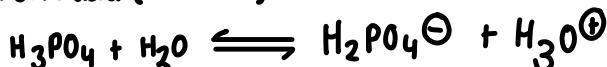
Acid Name	Molecular Formula	K_a
acetic acid	CH_3COOH	1.75×10^{-5}
carbonic acid	H_2CO_3	4.5×10^{-7}
hydrofluoric acid	HF	7.2×10^{-4}
nitrous acid	HNO_2	5.1×10^{-4}
phosphoric acid	H_3PO_4	7.1×10^{-3}

Most solutions are sufficiently dilute that the concentration of water is the same before and after the reaction with the acid.

Critical thinking questions

1. Which one of the acids in the table will produce the highest $[H_3O^+(aq)]$ for a given molarity of the acid? Write the balanced chemical equation for its reaction with water and write down the expression for K_a .

The strongest acid will have the largest K_a value
Hence;
phosphoric acid (7.1×10^{-3})



$$K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4] \times [\text{H}_2\text{O}]}$$

Ignore as H_2O is a liquid

2. Rank the acids in the table in order from strongest to weakest.

phosphoric acid (H_3PO_4) 7.1×10^{-3}
hydrofluoric acid (HF) 7.2×10^{-4}
Nitrous Acid (HNO_2) 5.1×10^{-4}
acetic acid (CH_3COOH) 1.75×10^{-5}
carbonic Acid (H_2CO_3) 4.5×10^{-7}

↑
strongest
acid

3. According to the definitions above, are HF and HNO_2 strong or weak acids?

weak because they have equilibrium constant.

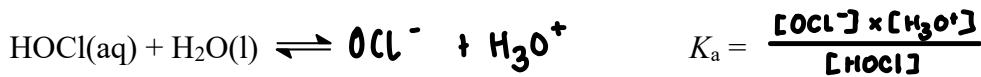
Model 2: Weak Acid Dissociation

When a weak acid is added to solution, $[H_3O^+(aq)]$ increases but the amount of dissociation is small:

Moles of HOCl Added	$[H_3O^+(aq)]$	$[OH^-(aq)]$
0.00	1.0×10^{-7}	1.0×10^{-7}
0.30	9.3×10^{-5}	1.1×10^{-10}
0.75	1.5×10^{-4}	6.8×10^{-11}
1.00	1.7×10^{-4}	5.9×10^{-11}

Critical thinking questions

1. Complete the following reaction and write down the expression for K_a .



2. 0.30 moles of HOCl added to water to make a 1.0 M solution at 25 °C. Complete the following table. (Hint: you can use the table above to work out the value of x .)

	HOCl(aq)	$[H_3O^+(aq)]$	$[OCl^-(aq)]$
initial moles	0.30	0	0
change in moles	$-x$	$+x$	$+x$
equilibrium moles	$0.30 - x$	x	x
equilibrium concentration	$(0.30 - x) / 1.0 =$ $(0.30 - 9.3 \times 10^{-5}) / 1$	$9.3 \times 10^{-5} M$	$9.3 \times 10^{-5} M$

3. Why does $[H_3O^+(aq)] = [OCl^-(aq)]$?

1:1 reaction (moles)

4. What do you notice about the value of $[HOCl(aq)]_{\text{equilibrium}}$ compared to $[HOCl(aq)]_{\text{initial}}$?

$$[HOCl]_{\text{initial}} \approx [HOCl]_{\text{equilibrium}}$$

5. Substitute $[H_3O^+(aq)] = [OCl^-(aq)]$ and your answer to question 4 into your expression for K_a to obtain an expression that only involves $[H_3O^+(aq)]$ and $[HOCl(aq)]_{\text{initial}}$.

$$K_a = \frac{[H_3O^+] \times [OCl^-]}{[HOCl]} = \frac{[H_3O^+]^2}{[HOCl]} = \frac{[H_3O^+]^2}{[HOCl]} = K_a$$

They are the same

6. Rearrange your answer to question 5 to give an equation for $[H_3O^+(aq)]$ for a weak acid. It should only involve K_a and $[HOCl(aq)]_{\text{initial}}$.

$$[H_3O^+] = \sqrt{[HOCl]_{\text{initial}} \times K_a}$$

7. Using $pH = -\log_{10}[H_3O^+(aq)]$, work out the pH of (a) a 0.30 M solution, (b) a 1.0 M solution and (c) a 3.0 M solution of HOCl(aq). $K_a = 2.9 \times 10^{-8}$ for HOCl.

(a) 0.30 M HOCl

$$[H_3O^+] = \sqrt{[HOCl]_{\text{initial}} \times K_a} \\ = \sqrt{0.30 \times (2.9 \times 10^{-8})} \\ = 9.3 \times 10^{-5} M$$

$$pH = -\log(H_3O^+) = -\log(9.3 \times 10^{-5}) = 4.0$$

(b) 1.0 M HOCl

$$[H_3O^+] = \sqrt{[HOCl]_{\text{initial}} \times K_a} \\ = \sqrt{1.0 \times (2.9 \times 10^{-8})} \\ = 1.7 \times 10^{-4}$$

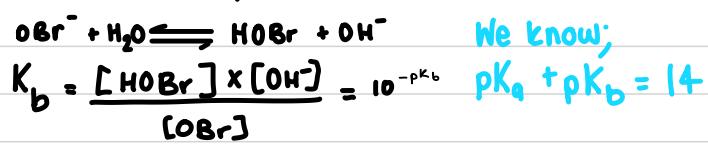
$$pH = -\log(1.7 \times 10^{-4}) = 3.77$$

(c) 3.0 M HOCl

$$[H_3O^+] = \sqrt{[HOCl]_{\text{initial}} \times K_a} \\ = \sqrt{3.0 \times (2.9 \times 10^{-8})} \\ = 2.9 \times 10^{-4}$$

$$pH = -\log(2.9 \times 10^{-4}) = 3.54$$

1. What is the pH of 0.045 M solution of KOBr? The pKa of HOB_r is 8.63



$$pK_a = 8.63 ; \quad 14 - pK_a = pK_b = 14 - 8.63 = 5.37$$
$$pK_b = 10^{-5.37}$$

$$[\text{OH}^-] = \sqrt{(K_b) \times [\text{OBr}^-]}$$
$$= \sqrt{0.045 \text{M} \times 10^{-5.37}}$$

$$[\text{OH}^-] = 4.38 \times 10^{-4} \text{M}$$

$$pOH = -\log(4.38 \times 10^{-4})$$
$$= 3.36$$

$$pH = 14 - pOH$$

$$pH = 14 - 3.36$$
$$= 10.64$$

CHEM1111: Worksheet – Lecture 31

NOTE:
The larger the K_a the
smaller the K_b
vice versa

Model 1: Acid / Base Strength of Conjugate Pairs

Acid	K_a	Conjugate Base	K_b	$K_a \times K_b = K_w$
HF hydrofluoric acid	$\frac{[H_3O^+(aq)][F^-(aq)]}{[HF(aq)]}$	F^-	$\frac{[OH^-(aq)][HF(aq)]}{[F^-(aq)]}$	$[H_3O] \times [OH^-]$
HNO ₂ nitrous acid	$\frac{[H_3O^+(aq)][NO_2^-(aq)]}{[HNO_2(aq)]}$	NO_2^-	$\frac{[OH^-(aq)][HNO_2(aq)]}{[NO_2^-(aq)]}$	$[H_3O] \times [OH^-]$
NH_4^+ ammonium	$\frac{[H_3O^+(aq)][NH_3(aq)]}{[NH_4^+(aq)]}$	ammonia	$\frac{[OH^-(aq)][NH_4^+(aq)]}{[NH_3(aq)]}$	$[H_3O] \times [OH^-]$

Critical thinking questions

- Fill out the missing entries in the table in Model 1.
- Provide an expression relating K_w to K_a and K_b of a conjugate acid – base pair. $K_w = 1.0 \times 10^{-14}$ at 298 K.

$$K_w = K_a \times K_b \quad \text{or} \quad pK_a + pK_b = pK_w$$

- How can the value of K_b for a base be determined from the value of K_a of its conjugate acid?

$$K_a \times K_b = K_w \quad \therefore K_b = \frac{K_w}{K_a}$$

- Consider two acids, HA and HX, with HA being a stronger acid than HX.
 - Which acid has a larger value of K_a ? **HA is the stronger acid**
 - Which conjugate base A⁻ or X⁻ has a larger value of K_b ? **X⁻**
 - Provide, *in words*, the relationship between the relative strength of an acid and the relative strength of its conjugate base.

The stronger the acid, the weaker the conjugate base

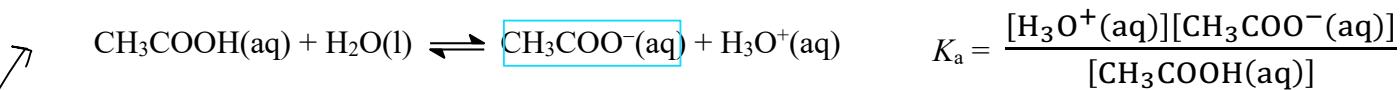
and vice - versa

NOTE: The smaller the conjugate acid
The weaker conjugate base.

The weaker
the conjugate base
the stronger
conjugate acid.

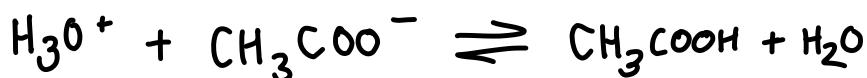
Model 2: A Mixture of a Weak Acid and its Conjugate Base

Consider a solution containing both a *weak acid* and its conjugate base. For example, if a mixture of acetic acid and sodium acetate is made up, the following equilibrium is set up:



Critical thinking questions

- $pK_a = 4.7$ for CH_3COOH . What will be the pH of a solution which is made up with *equal* amounts of CH_3COOH and CH_3COONa ?
 $K_a = \frac{[\text{H}_3\text{O}^+] \times [\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$ so, $K_a = [\text{H}_3\text{O}^+]$... $pK_a = \text{pH}$
- Write down the chemical equation for the reaction of $\text{OH}^-(\text{aq})$ with $\text{CH}_3\text{COOH}(\text{l})$.
- Explain why addition of strong base to the solution in Model 2 does not change the pH greatly.
 The CH_3COOH reacts with OH^- .
 Thus the pH change will be minimal.
- Draw a box around the *one* species that could react with a strong acid that is added to the mixture in Model 2. CH_3COO^-
- Explain why addition of strong acid to the solution in Model 2 does not change the pH greatly.



Henderson - Hasselbach equation

Exercises

A mixture of a weak acid and its conjugate base has: $\text{pH} = pK_a + \log_{10} \frac{[\text{base}]}{[\text{acid}]}$

- What be the *change* in pH if 0.1 mol of $\text{HCl}(\text{g})$ is added to 1.0 L of water?
- A buffer is made up by mixing 500. mL of 0.20 M CH_3COOH with 500. mL of 0.40 M NaCH_3CO_2 . What is the pH of the buffer? For acetic acid, $pK_a = 4.76$
- What is the *change* in pH if 0.1 mol of $\text{HCl}(\text{g})$ is added to this buffer?

$$1. [\text{pH}]_{\text{initial}} = 7$$

(pH) after addition of 0.1 mol HCl
 $[\text{H}_3\text{O}^+] = 0.1 \text{ M}$
 $\therefore \text{pH} = -\log(0.1) = 1$
 Large pH change from 7 to 1
 $\hookrightarrow 10^6$ difference in acidity

$$2.$$

$\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]}$
 needs to be in L
 $\text{pH} = 4.76 + \log \frac{0.40}{0.20}$
 Base:
 $\text{NaCH}_3\text{CO}_2 = 0.40 \text{ in } 500 \text{ mL}$
 $\div 2 = 0.20 \text{ in } 1 \text{ L}$
 Acid:
 $\text{CH}_3\text{COOH} = 0.20 \text{ in } 500 \text{ mL}$
 $\div 2 = 0.10 \text{ in } 1 \text{ L}$
 $\text{pH} = 4.76 + \log \frac{0.20}{0.10}$
 $\text{pH} = 5.06$

$$3.$$

$\text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{Cl}^-$
 thus
 $[\text{CH}_3\text{COO}^-] = 0.2 \text{ M} - 0.1 \text{ M}$
 $= 0.1 \text{ M}$
 $[\text{CH}_3\text{COOH}] = 0.1 \text{ M} + 0.1 \text{ M}$
 $= 0.20 \text{ M}$

$\text{pH} = pK_a + \log \frac{[\text{base}]}{[\text{acid}]} =$
 $\text{pH} = 4.76 + \log \frac{0.1 \text{ M}}{0.2 \text{ M}} = 4.46$

CHEM1111: Worksheet – Lecture 32

Model 1: Strong Acid / Strong Base Titration

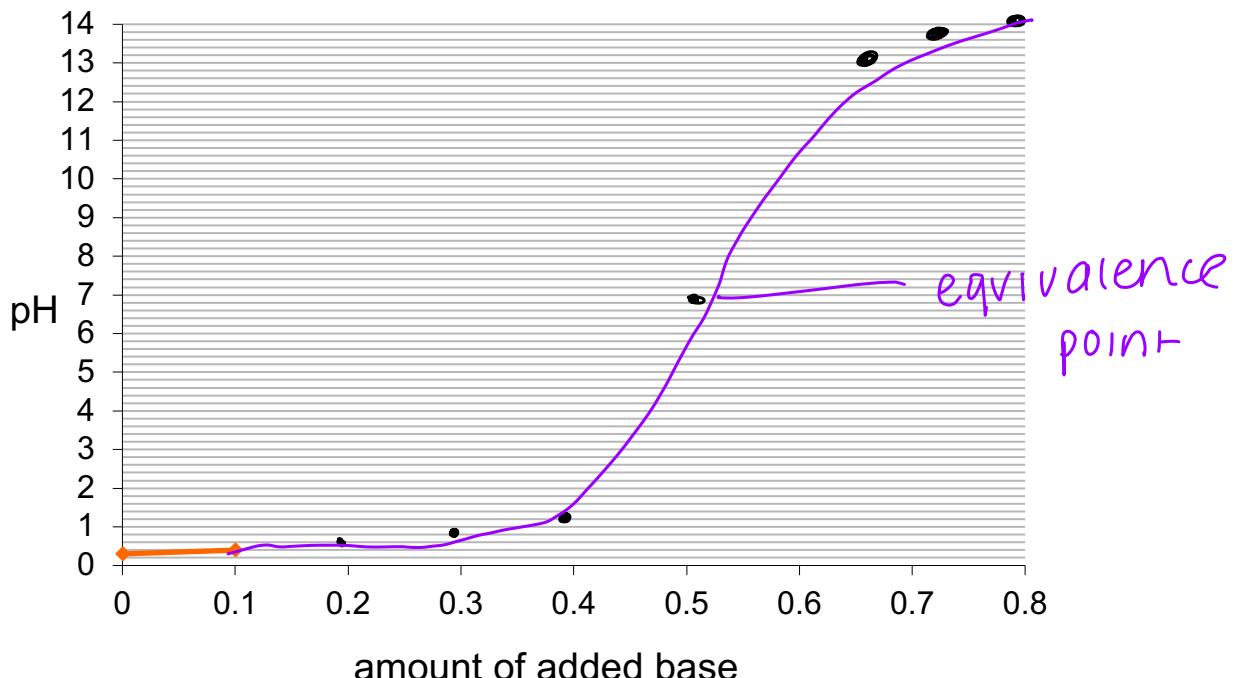
NaOH(s) - volume doesn't change is added in 0.10 mol amounts to 1.0 L of 0.50 M HCl(aq) and the pH is measured.

Critical thinking questions

1. Complete the table below showing how the pH changes during the titration in Model 1.

Moles of NaOH(s) added	Moles of H_3O^+ left	$[\text{H}_3\text{O}^+(\text{aq})]$	pH	$[\text{OH}^-]$	pOH
0.0	0.50	0.50	$-\log(0.5)$ 0.30	$2.0 \times 10^{-14} \text{ M}$	$14 - 0.30$ = 13.7
0.1	0.40	0.40	$-\log(0.4)$ 0.40	$2.5 \times 10^{-14} \text{ M}$	$14 - 0.4$ = 13.6
0.2	0.3	0.3	$-\log(0.3)$ $= 0.50$	$3.1 \times 10^{-14} \text{ M}$	$14 - 0.5$ = 13.5
0.3	0.2	0.2	$-\log(0.2)$ $= 0.70$	$5.0 \times 10^{-14} \text{ M}$	$14 - 0.7$ = 13.3
0.4	0.1	0.1	$-\log(0.1)$ $= 1$	$1 \times 10^{-13} \text{ M}$	$14 - 1$ = 13
0.5	10^{-1}	10^{-1}	7	10^{-7} M	7
0.6	—	10^{-13} M	13	0.1 M	1
0.7	—				
0.8	—				

2. Using your answer to question 1, complete the figure below. This is the titration curve for a strong acid/strong base titration.



3. What is the pH when the amount of added strong base equals the amount of initial acid? This is the 'equivalence point'.

$$\text{pH} = 7$$

0.5



At Neutralisation (equivalence point)



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 10^{-14} \text{ at } 25^\circ\text{C}$$

$$\text{So, } [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

$$\therefore [\text{H}_3\text{O}^+] = [\text{OH}^-] = 10^{-7}\text{M}$$

$$\text{pH} = -\log(10^{-7})$$

$$\text{pH} = 7$$

Buffer H-H equation

$$\text{pH} = \text{p}K_a + \log \frac{\text{base}}{\text{Acid}}$$



$$\text{pH} = 4.76 + \log \frac{0.1\text{M}}{0.4\text{M}}$$

$$\text{pH} = 4.16$$

$$\therefore [\text{H}_3\text{O}^+] = 10^{-4.16} = 6.95 \times 10^{-5}\text{M}$$

weak base **0.5** → page

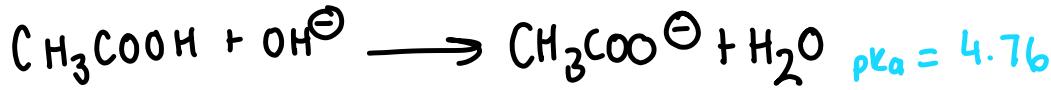
$$[\text{OH}^-] = \sqrt{K_b \times \text{base initial}}$$

$$\text{p}K_a + \text{p}K_b = 14$$

$$4.76 + \text{p}K_b = 14$$

$$\begin{aligned} \text{p}K_b &= 14 - 4.76 \\ &= 9.24 \end{aligned}$$

$$[\text{OH}^-] = \sqrt{9.24 \times 0.5\text{M}}$$



Lecture 25

Model 2: Weak Acid / Strong Base Titration

$$K_a = 10^{-4.76}$$

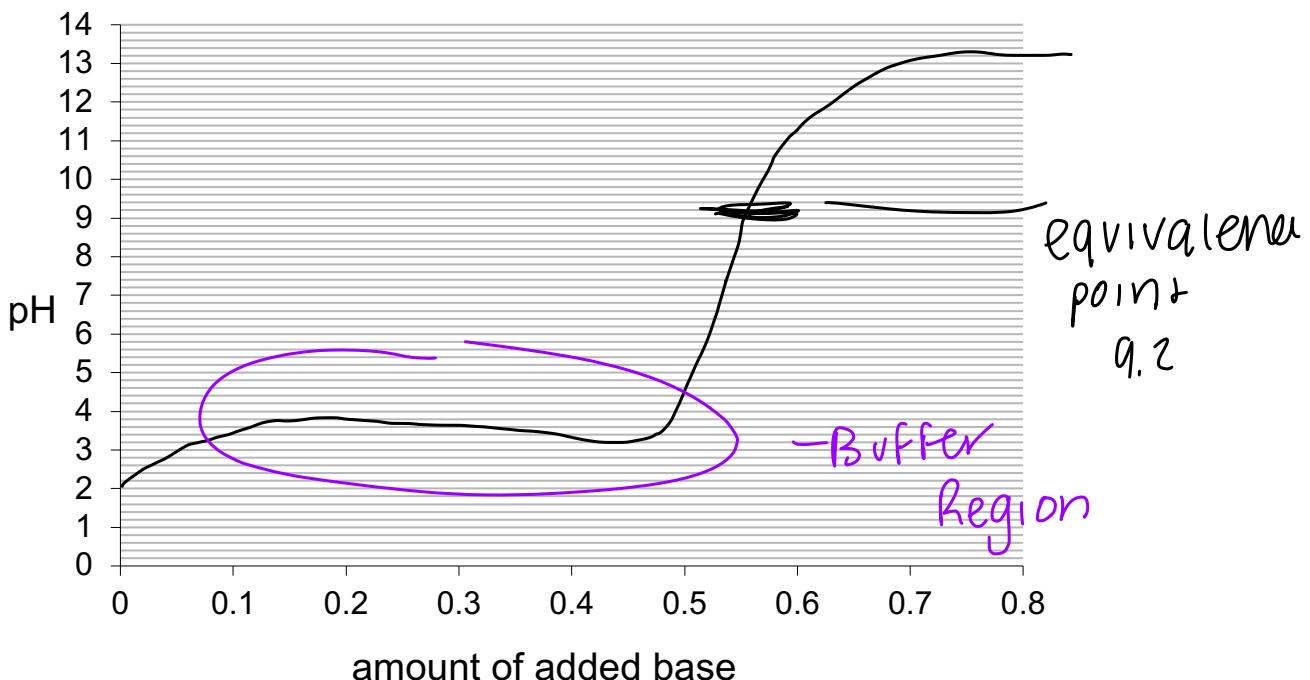
NaOH(s) is added in 0.10 mol amounts to 1.0 L of 0.50 M CH₃COOH (acetic acid) and the pH is measured.

Critical thinking questions

1. Complete the table below showing how the pH changes during the titration in Model 1.

Moles of NaOH(s) added	Moles of HA left	Moles of A ⁻ made	[H ₃ O ⁺ (aq)]	pH	[OH ⁻]	pOH
weak acid 0.0	0.50	0.00	2.95×10^{-3}	2.53	3.4×10^{-12}	11.47
Buffer 0.1	0.4	0.10	6.95×10^{-5}	4.16	1.4×10^{-10}	9.84
Buffer 0.2	0.3	0.20	3.2×10^{-5}	4.49	3.1×10^{-10}	9.51
Buffer 0.3	0.2	0.30	1.4×10^{-5}	4.85	7.1×10^{-10}	9.15
Buffer 0.4	0.1	0.40	5.3×10^{-6}	5.27	7.1×10^{-9}	8.15
weak base 0.5	0	0.5	5.8×10^{-10}	9.24	1.7×10^{-5}	4.76
Strong base 0.6						
Strong base 0.7						
Strong base 0.8						

2. Using your answer to question 1, complete the figure below. This is the titration curve for a weak acid/strong base titration.



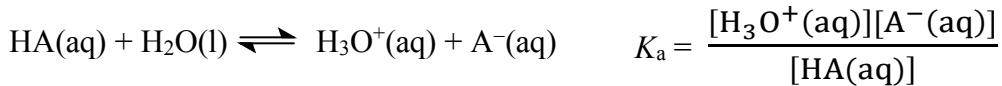
3. What is the pH when the amount of added strong base equals the amount of initial acid? This is the 'equivalence point'.

9.2

CHEM1111 Worksheet 11: Weak Acids and Equilibrium

Model 1: A Solution Containing a Weak Acid

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



Calculating the pH requires that the equilibrium value of $[\text{H}_3\text{O}^+(\text{aq})]$ be first calculated. To do this, the 'ICE' approach covered in Worksheet 10 can be followed. Consider a 2.0 M solution of CH_3COOH :

	CH_3COOH (aq)	$\text{H}_2\text{O(l)}$	\rightleftharpoons	$\text{CH}_3\text{COO}^-(\text{aq})$	$\text{H}_3\text{O}^+(\text{aq})$
initial	2.00	large		0	0
change	$-x$	$-x$		$+x$	$+x$
equilibrium	$2.00 - x$	large		$+x$	$+x$

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

$$K_a = \frac{[\text{CH}_3\text{COO}^-(\text{aq})][\text{H}_3\text{O}^+(\text{aq})]}{[\text{CH}_3\text{COOH}]} = \frac{x^2}{2.00 - x} \approx \frac{x^2}{2.00} \quad \text{and so } x = [\text{H}_3\text{O}^+(\text{aq})] = \sqrt{K_a \times 2.00}$$

After working out $[\text{H}_3\text{O}^+(\text{aq})]$, the pH and percentage dissociation of the weak acid can be calculated:

$$\text{pH} = -\log[\text{H}_3\text{O}^+(\text{aq})] \quad \text{and} \quad \% \text{ dissociation} = \frac{[\text{H}_3\text{O}^+(\text{aq})]}{[\text{CH}_3\text{COOH}]_{\text{initial}}} \times 100\%$$

Critical thinking questions

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

$$\text{Initial: } 2.00 \text{ M} \quad \text{Final}_{\text{equilibrium}} = 2.0 - x$$

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

$$x = \sqrt{K_a \times [\text{HA}]_{\text{initial}}} \quad \text{or} \quad \text{pH} = -\log_{10}(\sqrt{K_a \times [\text{HA}]_{\text{initial}}})$$

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

$$(a) 2.00 \text{ M} \quad \text{pH} = 2.23 \\ \text{pH} = -\log_{10}(\sqrt{2.00 \times 10^{-4.76}})$$

$$(c) 0.500 \text{ M} \quad \text{pH} = 2.53 \\ \text{pH} = -\log_{10}(\sqrt{0.500 \times 10^{-4.76}})$$

$$\frac{\text{amount dissociated}}{\text{initial concentration}} \times 100 = \% \text{ dissociation} = \frac{[\text{H}_3\text{O}^+]}{[\text{HA}]_{\text{initial}}} \times 100 = \frac{\sqrt{10^{-4.76} \times 2.00}}{2.00} \times 100 = 0.295$$

$$\% \text{ dissociation} = \frac{\sqrt{10^{-4.76} \times 0.500}}{0.500} \times 100 = 0.590$$

$$(b) 1.00 \text{ M} \quad \text{pH} = 2.38 \\ \text{pH} = -\log_{10}(\sqrt{1.00 \times 10^{-4.76}})$$

$$(d) 0.250 \text{ M} \quad \text{pH} = 2.68 \\ \text{pH} = -\log_{10}(\sqrt{0.250 \times 10^{-4.76}})$$

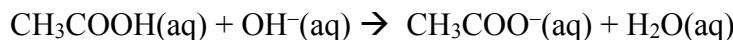
$$\% \text{ dissociation} = \frac{\sqrt{10^{-4.76} \times 1.00}}{1.00} \times 100 = 0.417$$

$$\% \text{ dissociation} = \frac{\sqrt{10^{-4.76} \times 0.250}}{0.250} \times 100 = 0.834$$

Model 2: Addition of a Strong Base to a Weak Acid

In Model 1, you used an “ICE” approach to work out the pH of a solution containing a weak acid. For example, you worked out that a 0.500 M solution of CH₃COOH(aq) has a pH of 2.531.

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



As long as the amount of OH⁻(aq) added is *less* than the amount of CH₃COOH(aq) present, the solution will contain both CH₃COO⁻(aq) and left over CH₃COOH(aq). A solution like this containing both a weak acid and its conjugate base is a buffer and its pH is given by the *Henderson-Hasselbalch* equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = \text{p}K_a + \log \frac{[\text{CH}_3\text{COO}^-(\text{aq})]}{[\text{CH}_3\text{COOH}(\text{aq})]}$$

Critical thinking questions

1. If 0.100 mol of NaOH(s) is added to a 1.00 L solution of 0.500 M CH₃COOH, it will react to form a solution which is 0.100 M in CH₃COO⁻(aq) and 0.400 M CH₃COOH(aq). What is the pH of this solution? (pK_a (CH₃COOH) = 4.76).

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]} = 4.76 + \log \frac{[0.100\text{M}]}{[0.400\text{M}]} = 4.158 \\ \text{pH} = 4.16$$

2. Complete the table below showing the concentrations of CH₃COOH(aq) and CH₃COO⁻(aq) and the pH of the solution as more NaOH(s) is added to this solution.

Amount of NaOH(s) added (mol)	0.000	0.100	0.200	0.300	0.400	0.500
[CH ₃ COOH(aq)] (M) A	0.500	0.400	0.300	0.200	0.100	0.000
[CH ₃ COO ⁻ (aq)] (M) B	0.000	0.100	0.200	0.300	0.400	0.500
pH	2.531	4.16	4.58	4.94	5.36	9.24

4.76 + log(0.100 / 0.400)

3. To react completely with the original CH₃COOH, 0.500 mol of NaOH must be added. What is the pH of the solution when exactly *half* this amount is added?

The p_a = 4.76

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

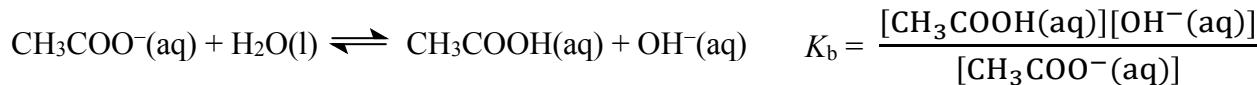
By measuring the pH when half the quantity of base needed for equivalence has been added.

Model 3: Neutralizing a Weak Acid

Model 2 describes the pH changes as a strong base is added to a solution containing a weak acid. The strong base reacts with the weak acid leading to a solution containing the conjugate base of the weak acid and any left over acid. The *equivalence point* occurs when enough base has been added so that there is no acid left.

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

The conjugate base will then set up its own equilibrium:



From the chemical equation:

$$[\text{CH}_3\text{COOH}(\text{aq})]_{\text{equilibrium}} = [\text{OH}^-(\text{aq})]_{\text{equilibrium}}$$

As hardly any base reacts, $[\text{CH}_3\text{COO}^-(\text{aq})]_{\text{equilibrium}} \approx [\text{CH}_3\text{COO}^-(\text{aq})]_{\text{initial}}$ and so:

$$K_b = \frac{[\text{OH}^-(\text{aq})]^2}{[\text{CH}_3\text{COO}^-(\text{aq})]_{\text{initial}}} \quad \text{and} \quad [\text{OH}^-(\text{aq})] = \sqrt{K_b \times [\text{CH}_3\text{COO}^-(\text{aq})]_{\text{initial}}}$$

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

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

Finally, the pH can then be calculated using $\text{pH} = 14.00 - \text{pOH}$.

Critical thinking questions

- To react completely with the original CH_3COOH in Q5, 0.500 mol of NaOH must be added. What will be $[\text{CH}_3\text{COO}^-(\text{aq})]$ when this occurs?

0.500 M of CH_3COO^-

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

$$14 - 4.76 = 9.24 \quad \text{pH} = 9.24$$

- Correct your entry in the final column of the table in Model 1 if required!
- What is the pH at the equivalence point of the titration of a *strong* acid with a strong base?

The solution will be neutral and $\text{pH} = 7$

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

At equivalence, the solution contains a weak base and is basic with $\text{pH} > 7$

CHEM1102

2006-N-5

November 2006

- Solution A consists of a 0.25 M aqueous solution of hydrazoic acid, HN_3 , at 25 °C. Calculate the pH of Solution A. The pK_a of HN_3 is 4.63.

Marks
8

I	0.25	0	0
C	$-\infty$	$+\infty$	$+\infty$
E	$0.25 - \infty$	∞	∞

As $\text{pka} = -\log(K_a)$ so,
 $K_a = 10^{-4.63}$
 $K_a = 10^{-4.63}$
 $K_a = 2.34 \times 10^{-5}$

NOTE: K_a is very small, very little HN_3 dissociates and existing so $(0.25 - \infty) \sim 0.25$

Hence, $\frac{\infty^2}{0.25} = 2.34 \times 10^{-5}$
 $\sqrt{\infty^2} = \sqrt{2.34 \times 10^{-5}}$
 $\infty = 2.42 \times 10^{-3}$

$$\text{pH} = -\log(2.42 \times 10^{-3})$$

$$\text{pH} = 2.62$$

Answer: 2.62

At 25 °C, 1.00 L of Solution B consists of 13.0 g of sodium azide (NaN_3) dissolved in water. Calculate the pH of Solution B.

N_3^- is the conjugate base of HN_3

$$\text{Thus } pK_a + pK_b = 14.00$$

$$\text{pka} = 4.63, \text{ so } 14 - 4.63 = 9.37 \text{ then } K_b = 10^{-9.37} = 4.27 \times 10^{-10}$$

Molar Mass of NaN_3 = 65.02

The number of Moles(g) = 13.00

$$\text{Number of moles} = \frac{\text{Mass}}{\text{molar mass}} = \frac{13.00}{65.02} = 0.200 \text{ mol}$$

$$0.200 \text{ mol dissolves in 1 L} = \frac{\text{number of moles}}{\text{volume}} = \frac{0.200}{1.00} = 0.200 \text{ M}$$



I	0.200	0	0
C	$-\infty$	$+\infty$	$+\infty$
E	$0.200 - \infty$	∞	∞

equilibrium constant (K_b) = $\frac{[\text{NH}_3][\text{OH}^-]}{[\text{N}_3^-]} = \frac{\infty \times \infty}{0.200 - \infty} = \frac{\infty^2}{0.200 - \infty}$

$\frac{\infty^2}{0.200} = 4.27 \times 10^{-10}$

$\sqrt{\infty^2} = \sqrt{4.27 \times 10^{-10}}$

$\infty = 2.04 \times 10^{-5}$

$\text{pOH} = -\log(2.04 \times 10^{-5}) = 5.03$

Hence,

$$\text{pH} + \text{pOH} = 14$$

$$14 - 5.03 = 8.97$$

Answer: 8.97

Solution B (1.00 L) is poured into Solution A (1.00 L) and allowed to equilibrate at 25 °C to give Solution C. Calculate the pH of Solution C.

Solution C is a buffer solution that contains both conjugate pairs: Solution A (HN_3) acid and Solution B (N_3^-) base. USE Henderson-Hasselback equation

$$\text{pH} = \text{pka} + \log \frac{[\text{base}]}{[\text{acid}]}$$

$$\text{pka} = 4.63$$

$$\text{HN}_3 = 0.25 \text{ M} \quad 4.63 + \log \frac{0.200}{0.25} = 4.53$$

$$\text{N}_3^- = 0.200 \text{ M}$$

Answer: 4.53

If you wanted to adjust the pH of Solution C to be exactly equal to 4.00, which component in the mixture would you need to increase in concentration?

To lower pH the acid concentration (HN_3) would need to increase.

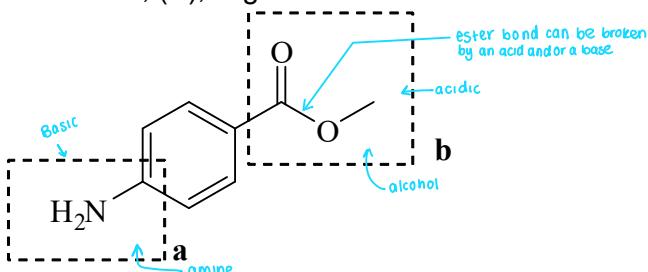


Tutorial 12 (Week 12): Acids and bases (1)

Example exam questions

- The structure of methyl 4-aminobenzoate, (**E**), is given below.

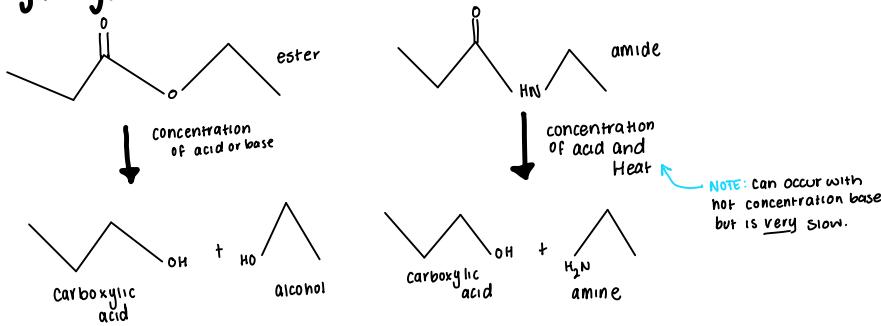
(E)



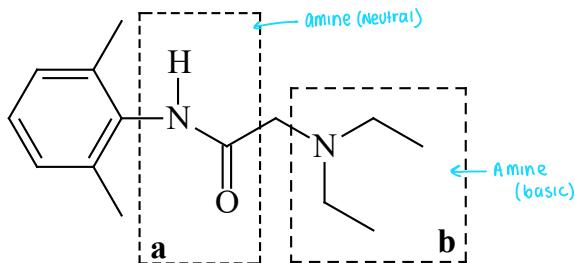
Give the structure(s) of all organic products formed when compound (**E**) is treated with the following reagents. If no reaction occurs, write "NO REACTION".

<p>cold HCl (1 M)</p> <p>reaction rate will be slower</p> <p>acidic</p> <p>not high concentration</p>		
<p>hot NaOH (4 M)</p> <p>will break ester bond fast</p> <p>basic</p> <p>high concentration</p>	<p>Hydrolysis: Carboxylic acid + alcohol</p>	<p>Treatment with base will lead to hydrolysis of an ester. In the basic solution, the carboxylic acid will deprotonate and the amine will not be protonated.</p>
<p>hot HCl (4 M)</p> <p>will break ester bond fast</p> <p>acid</p> <p>high concentration</p>	<p>Hydrolysis</p>	

Hydrolysis:

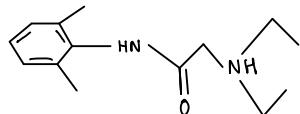


- The structure of lignocaine, a local anaesthetic, is given below.

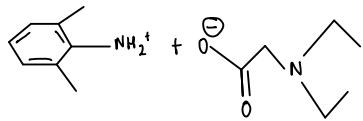


Give the structure(s) of all organic products formed when lignocaine is treated with the following reagents. If no reaction occurs, write "NO REACTION".

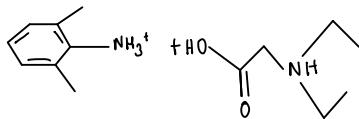
cold HCl (1 M)



hot NaOH (4 M)



hot HCl (4 M)



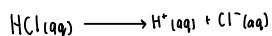
- Often pH is used to characterise acidic solutions. Give a brief definition of pH.

Marks
5

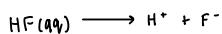
A measure of H^+ Concentration

Describe the difference between a strong acid and a weak acid.

A strong acid dissociates completely in water



A weak acid dissociates only slightly in water



In general, can pH be used to define the strength of an acid? Explain your answer.

No, all pH tells us is the concentration of H^+ . Acid Strength is through degree of ionisation (pK_a)

CARBOXYLIC

ACIDS,

POLYMERS

B I

BI-POLYMERS

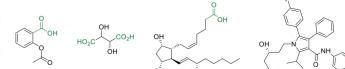
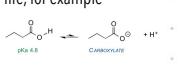
LECTURE 23: CARBOXYLIC ACIDS, ESTERS AND AMINO ACIDS

LO: UNDERSTAND THE ACID-BASE REACTIONS OF CARBOXYLIC ACIDS

Carboxylic acids

Carboxylic acids play many important roles in life, for example

Carboxylic acids are acidic

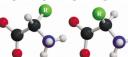
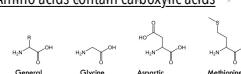


Carboxylic acids react with strong bases

They participate in acid-base reactions, which can go to completion. (the water solubility of the salts is important, and we'll come back to it)

LO: RECOGNISE THAT AMINO ACIDS INCLUDE AMINES AND CARBOXYLIC ACIDS IN THEIR STRUCTURE

Amino acids contain carboxylic acids



Source: Wikipedia contributors https://en.wikipedia.org/w/index.php?title=Amino_acid&oldid=58700000

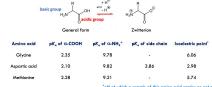
See Week 7 for the difference between these 'L' and 'D' stereoisomers

LO: UNDERSTAND THE RELATIONSHIP BETWEEN AN AMINO ACID AND ITS ZWITTERION FORM

Amino acids form zwitterions

zwitterions

When the functional group is stable and has both a positive and negative ion to stabilise it.



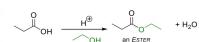
LO: UNDERSTAND THE PHYSICAL PROPERTIES OF FATS AND OILS

Fatty acids

Fatty acids are long chain carboxylic acids (C8 – C20). Saturated fatty acids have alkane chain (e.g. coconut oil, animal fats, butter). Monounsaturated fatty acids contain one double bond (e.g. olive, canola, sesame oils). Polyunsaturated fatty acids contain two or more double bonds (e.g. sunflower, soyabean oils). Fats (solid) and oils (liquid) are esters of fatty acids and an alcohol.

Making esters from carboxylic acids

It is possible to make an ester by reacting a carboxylic acid and an alcohol directly. But needs a catalyst (H⁺) and sometimes heat



Making amides by reacting carboxylic acids directly with amines generally doesn't work.

LO: RECOGNISE THE ROLE OF LONG CHAIN FATTY ACID SALTS IN SOAP

Esters in nature - fats & oils

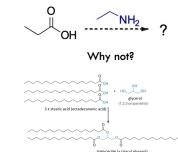
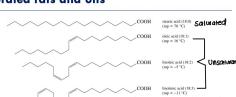
Fats are esters of long chain fatty acids and glycerol

Glycerol has 3 alcohol groups → forms a triester, so fats are also called triglycerides

Fatty acid components

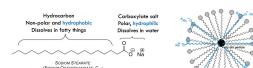


Unsaturated fats and oils



Saturated fats pack together well and tend to be solids at room temperature. (Also true of unsaturated fats with an E double bond - 'trans fats' - a side product of food processing.)

§ Unsaturated fats with a Z double bond pack less well and are liquid at room temperature. (The way that Nature makes the C=Cs means they are all Z (cis) in biosynthetically derived unsaturated fats.)



Soap

The key ingredients in soap are sodium salts of long chain fatty acids. The combination of a hydrophobic hydrocarbon chain and polar hydrophilic carboxylate group pulls grease into water. Soaps are made by heating fats with concentrated sodium hydroxide (NaOH).

Synthetic detergents

Synthetic analogues of fatty acid salts are also widely used. These are cheaper to make and have stronger grease penetrating power



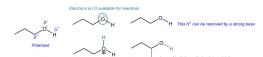
LECTURE 34: ACID/BASE PROPERTIES OF ALCOHOLS, AMINES & PHENOLS AROMATIC COMPOUNDS

LO: IDENTIFY THE MAIN FEATURES OF ALCOHOL STRUCTURES AND BONDING

Alcohols, general structure R-OH

The chemistry of alcohols is dominated by the electronegativity of O

- Attached C and H are electron-deficient as a result of being bonded to O
- OH group is polar and engages in hydrogen bonding.
- Alcohols have high boiling points (relative to alkanes, alkenes), more soluble in water.



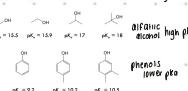
Acidity/basicity of alcohols

Alcohols are not very acidic or basic

An alcohol does not readily accept H^+ : equilibrium lies to the left. It takes a very strong base to remove the H and H^+ catalyses this reaction (ester formation)



Acidity of phenols



LO: IDENTIFY CONJUGATED AND AROMATIC PARTS OF ORGANIC MOLECULES

Conjugation

3 or more p-orbitals in an uninterrupted sequence can share electrons like an electric circuit. They are said to be conjugated or in conjugation. But conjugation alone is not enough to explain the different reactivity of benzene: and Benzene looks like it should react as $3 \times \text{C}=\text{C}$. But it doesn't.

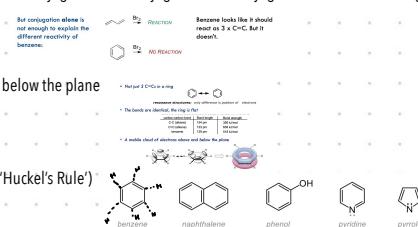
LO: RATIONALISE THE SPECIAL PROPERTIES OF AROMATIC RINGS

Aromaticity

Not just 3 C=Cs in a ring. The bonds are identical, the ring is flat and A mobile cloud of electrons above and below the plane

Aromaticity requires three things.

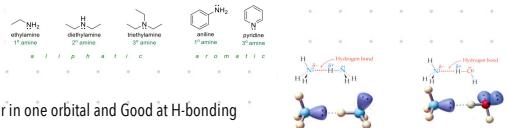
1. Aromatic systems are conjugated, but also
2. the conjugated system is cyclic, and
3. the conjugated system contains $4n+2$ p electrons (where $n = 0, 1, 2, \dots$, so 2, 6, 10, ... etc p electrons) > ('Hückel's Rule')



LO: IDENTIFY THE MAIN FEATURES OF AMINE STRUCTURE AND FUNCTION

Amines

- Amines contain ≥ 1 organic group(s) bonded to nitrogen
- general formulae RNH_2 , R_2NH , R_3N (can be aliphatic or aromatic)
- Classified primary/ secondary/ tertiary depending how many 'R' groups attached to N



Amines can form hydrogen bonds

Nitrogen: 1s2 2s2 2p3, 3 covalent bonds, leaving a lone pair, sp3 hybridised, with a lone pair in one orbital and Good at H-bonding

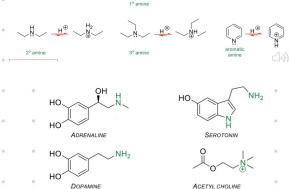
Amines are basic

Nitrogen: 1s2 2s2 2p3, covalent bonds, leaving a lone pair, sp3 hybridised, with lone pair in one orbital and Amines are basic

Amines as neurotransmitters

Amines are easily extracted from plants using dilute acid, among the earliest organic compounds studied. A number of important neurotransmitters and hormones contain amines

Amines as psychoactive drugs



Other N-containing Functional Groups

Amines are not the only functional groups that incorporate nitrogen.



NH attached directly to carbonyl group ($\text{C}=\text{O}$)

Common in this course: urea

Not covered in this course: uridylate, FAD

More about amides: [http://tiny.cc/meyarw](#)

More about aromatic amines: [http://tiny.cc/meyarw](#)

Cocaine: [http://tiny.cc/meyarw](#)

MDMA (Ecstasy): [http://tiny.cc/meyarw](#)

Nicotine: [http://tiny.cc/meyarw](#)

3° amine: [http://tiny.cc/meyarw](#)

2° amine: [http://tiny.cc/meyarw](#)

1° amine: [http://tiny.cc/meyarw](#)

amine: [http://tiny.cc/meyarw](#)

amine as donor and acceptor: [http://tiny.cc/meyarw](#)

amine as donor: [http://tiny.cc/meyarw](#)

amine as acceptor: [http://tiny.cc/meyarw](#)

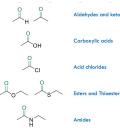
amine as both: [http://tiny.cc/meyarw](#)

amine as neither: [http://tiny.cc/meyarw</](#)

LECTURE 35: DERIVATIVES OF CARBOXYLIC ACIDS, HYDROLYSIS AND OXIDATION AND REDUCTION

LO: RECOGNISE CARBOXYLIC ACID DERIVATIVE FUNCTIONAL GROUPS (ACYL CHLORIDES, ESTERS, THIOESTERS AND AMIDES)

Carboxylic acid derivatives

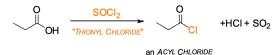


LO: UNDERSTAND THE DIFFERENT REACTIVITY OF THESE DERIVATIVES

Activating carboxylic acids for reaction

Carboxylic acids can be converted to acyl chlorides (or acid chlorides) with a specific chlorinating reagent, thionyl chloride (SOCl_2)

Acyl chlorides are very reactive and easily transformed into a range of other things, e.g. esters and amides.



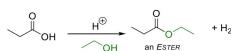
Making esters and amides from acyl chlorides

Acyl chlorides react with alcohols to make esters, and with amines to make amides. An amide can also be formed by reacting an ester with an amine, and heating it.

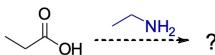


Making esters from carboxylic acids

It is also possible to make an ester by reacting a carboxylic acid and an alcohol directly. But this is a slower reaction, needs a catalyst (H^+) and sometimes heat.



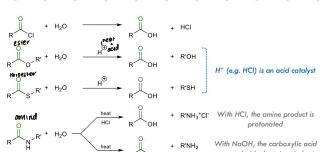
Making amides by reacting carboxylic acids directly with amines generally doesn't work.



LO: PREDICT CONDITIONS FOR HYDROLYSIS AND INTERCONVERSION OF CARBOXYLIC ACID DERIVATIVES

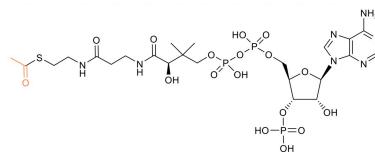
Hydrolysis

Hydro = water, lysis = breaking apart: all these derivatives can react with water



Thioesters in nature - acetyl coenzyme A

Thioesters play many roles in biology, most importantly in this cofactor. Coenzyme A is essentially a molecular crane for the delivery of acetate (CH_3CO , in orange) and other groups in biosynthetic processes (e.g. fatty acid biosynthesis).



LO: UNDERSTAND THE OXIDATION AND REDUCTION REACTIONS LEADING TO AND FROM CARBOXYLIC ACIDS

Oxidation

Oxidation of organic molecules increases their O content or decreases their H content. Reduction is the opposite process, which we come to later.

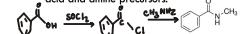


Typical oxidising agents: KMnO_4 , $\text{Na}_2\text{Cr}_2\text{O}_7$

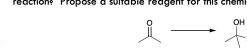


End of lecture problems

(1) Propose a synthesis of *N*-methylbenzamide using suitable carboxylic acid and amine precursors.



(2) Is the organic reaction shown below an oxidation or reduction reaction? Propose a suitable reagent for this chemical transformation.



The reagent, lithium aluminium hydride, supplies H^- .

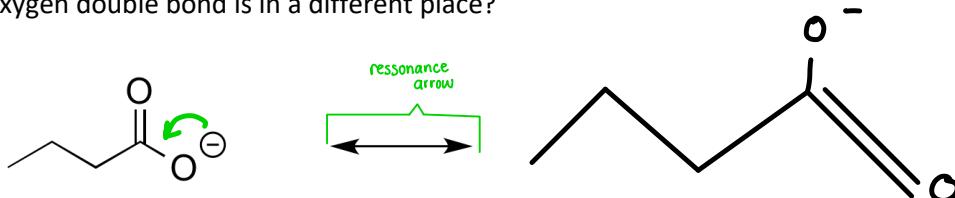
Reduction

Carboxylic acids are formed by oxidising 1° alcohols and aldehydes (slide 11). The reverse reaction is reduction of carboxylic acids. Ketones and aldehydes can be reduced to alcohols with LiAlH_4 although NaBH_4 is usually used as it is cheaper and easier to handle. It's not reactive enough to reduce carboxylic acids. LiAlH_4 is 'stronger' i.e. more reactive

CHEM1111 Worksheet – Lecture 33

- Carboxylic acids are more acidic than alcohols. This means that the conjugate base (the thing that is formed when a proton leaves) of a carboxylic acid, a *carboxylate*, is better stabilised than the conjugate base of the alcohol, the *alkoxide*.

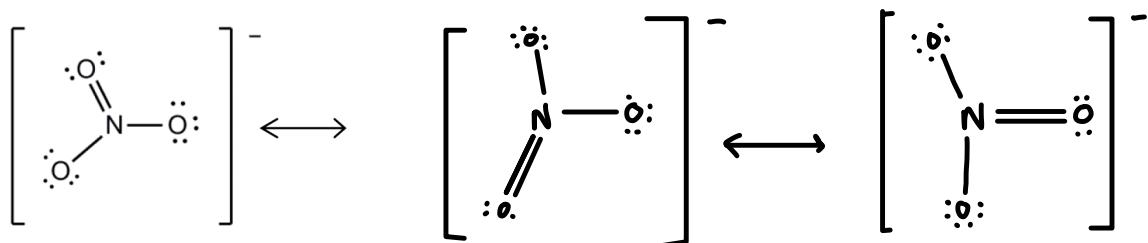
Can you draw another resonance structure for the carboxylate, in which the \ominus is on the other O, and the carbon-oxygen double bond is in a different place?



- The spreading out of negative charge onto electronegative oxygen atoms stabilizes the conjugate base. Nitric acid is even more acidic than carboxylic acids because its conjugate base, the nitrate ion, is better stabilized than the carboxylate anion.

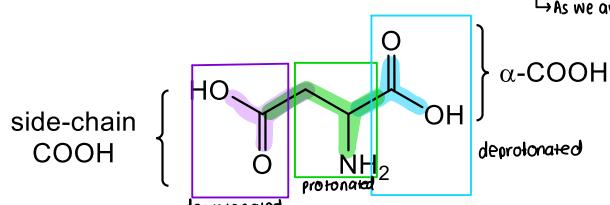
Can you draw other resonance structures for the nitrate ion? Why is the nitrate ion more stable than the carboxylate ion?

Because the negative charge is spread around more ions.



- Which functional groups in aspartic acid would be protonated or deprotonated at biological pH (pH~7.4)? (pKa of α -COOH: 2.1, pKa of COOH side-chain: 3.86, pKa of α -NH₃⁺: 9.82)

As the pKa of -COOH is 2.1 and the pKa of COOH is 3.86 both lower than 7.4, pH they will want to bring the pH close down to their dissociation number. This makes them deprotonated.
The pKa of -NH_3^+ = 9.82, which is higher than the pH of 7.4. This means it will not react and will stay protonated.

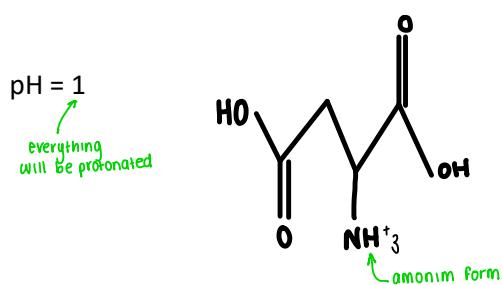


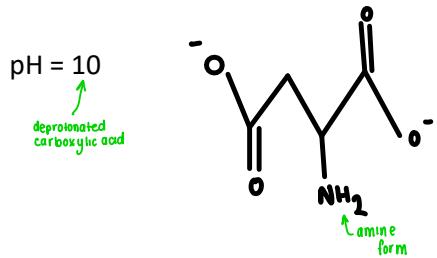
As we are looking at pKa we must look at conjugate base form

NOTE:

pKa = pH = equal parts protonated and deprotonated
pKa > pH = protonated
pKa < pH = deprotonated

- Draw the structural formulae for aspartic acid at pH 1 and pH 10.



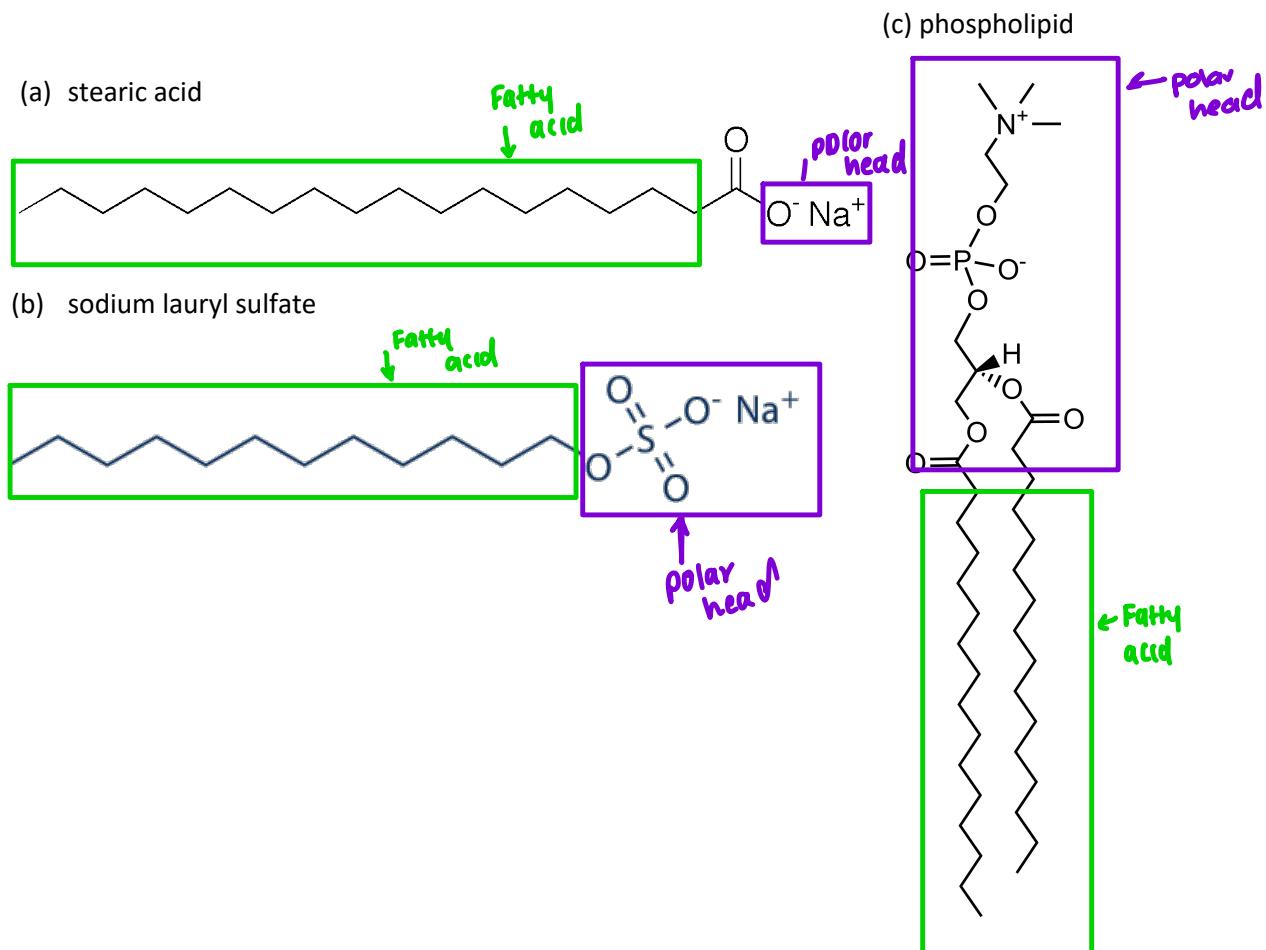


5. In lecture 29 (slide 4), we saw that amines are weak bases. Carboxylic acids are weak acids. What happens (instead of amide formation) when a carboxylic acid and an amine are combined?
you will get an acid - base reaction instead of substitution



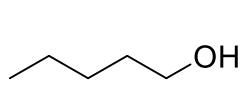
6. The structures of (a) a soap, (b) a detergent and (c) a phospholipid. Phospholipids make up the lipid bilayer that forms the envelope on the surface of viruses.

In each case, circle the fatty acid part and the polar head of the molecule.

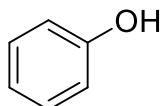


CHEM1111 worksheet – Lecture 34

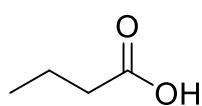
1. Consider molecules **A**, **B** and **C** below:



A
alcohol



B
alcohol
(phenol)

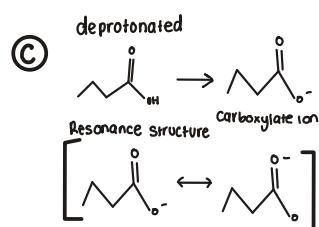
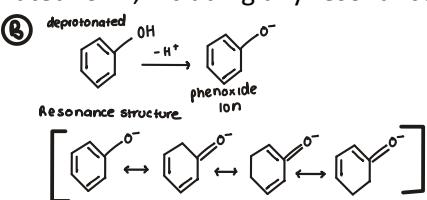
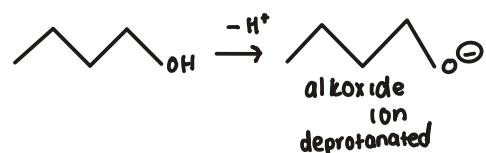


C
alcohol
(carboxylic
acid)

Name molecules **A** and **B**

Draw the deprotonated form, including any resonance structures, for molecules **A**, **B** and **C**.

Ⓐ



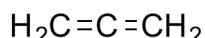
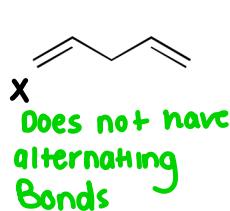
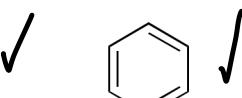
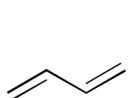
Rank molecules **A**, **B** and **C** in order of increasing acidity.

A < B < C

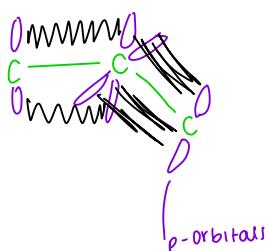
Justify your ranking.

A = Because it didn't need
↓ to be stabilised (resonance structure)
B = Because you can resonance stabilise
↓ more than an alcohol can
C = has a double bond
↓ highly favoured

2. Which of these molecules are conjugated?

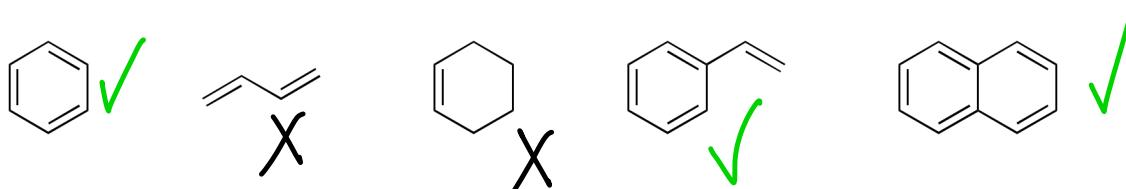


(Harder, if you have time)

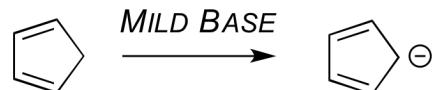


3. Which of these molecules are aromatic?

Aromaticity requires three things
 1. Aromatic systems are conjugated, but also
 2. the conjugated system is cyclic, and
 3. the conjugated system contains $4n+2$ p electrons (where $n = 0, 1, 2 \dots$, so 2, 6, 10... etc p electrons) > ('Hückel's Rule')



4. By thinking about aromaticity, can you explain the following difference in reactivity?

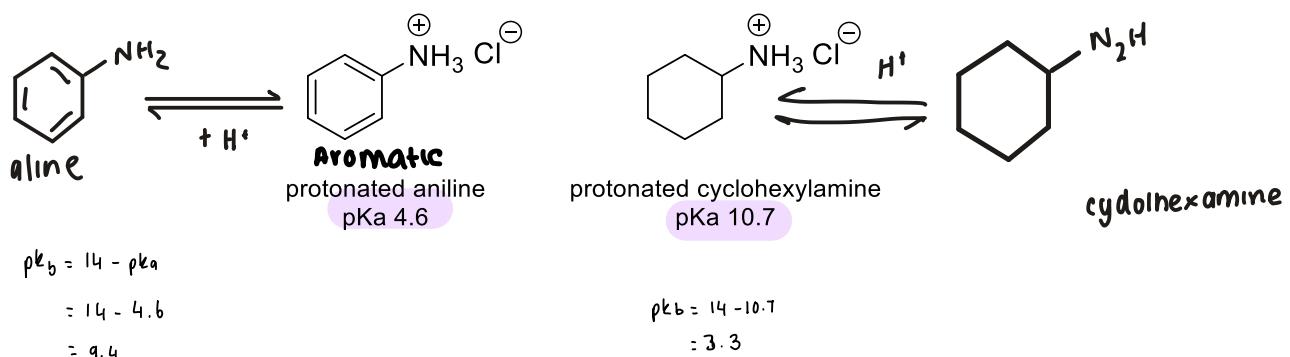


Product of the second reaction is aromatic, this stabilizes the negative charge through resonance.

5. Two protonated amines are shown below, which are formed from the reaction of aniline and cyclohexylamine with acid (HCl). The pK_a values are given.

(a) Draw the amine (^{↳ remove H⁺} the conjugate base) form and rank their basicity by calculating the pK_b values.

(b) What does this tell us about how the aromatic ring in aniline influences the basicity of the N?

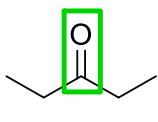


*Based on the pK_b values
 aniline is a stronger acid
 and cyclohexylamine is a stronger base.*

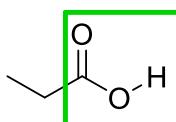
*Aromatic ring
 reduces the
 basicity.*

CHEM1111 Worksheet – Lecture 35

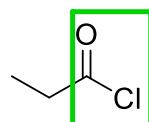
1. Highlight the functional group in each of the following:



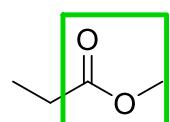
ketone



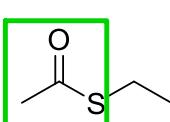
carboxylic acid



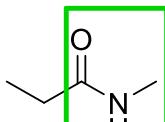
acid chloride



ester

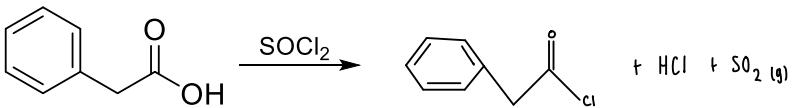
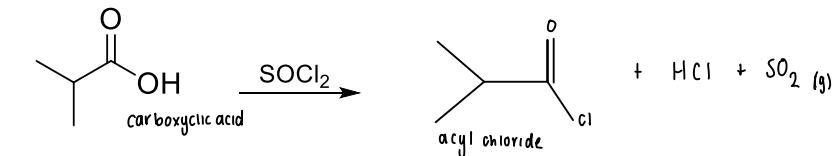


thioester

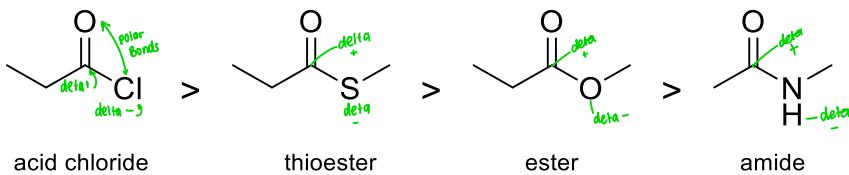


amide

2. Draw the products of the following reactions of carboxylic acids with thionyl chloride (SOCl_2).



3. The relative reactivity of these carboxylic acid derivatives in hydrolysis reactions is shown below.



Which carbon-heteroatom bonds are most polar (electronegativity: C 2.55, N 3.04, O 3.44, S 2.58, Cl 3.16)?

$\text{C} - \text{O}$ = polar

$\text{C} - \text{Cl}$ = polar

$\text{C} - \text{S}$ = less polar

$\text{C} - \text{N}$ = less polar
then above

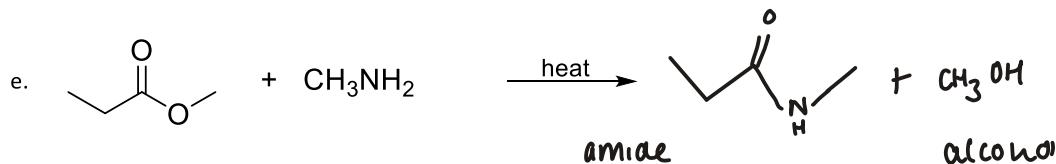
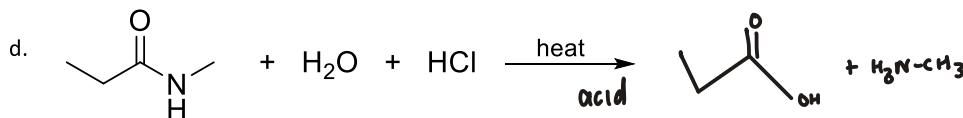
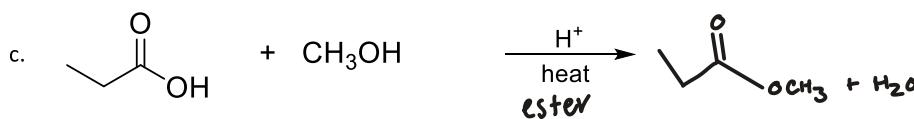
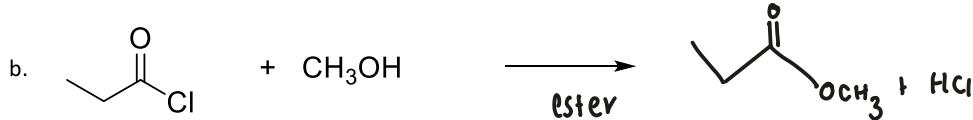
The bond Strength based on orbital overlap

Weaker the bond the more reactive

Stronger the bond the less reactive

Which of these heteroatoms (N, O, S, Cl) are in a different row of the Periodic Table to carbon? What effect might this have on orbital overlap, and so strength of the bond to carbon, and so on reactivity?

4. It is possible to interconvert carboxylic acid derivatives. What product(s) would you expect from the following reactions?



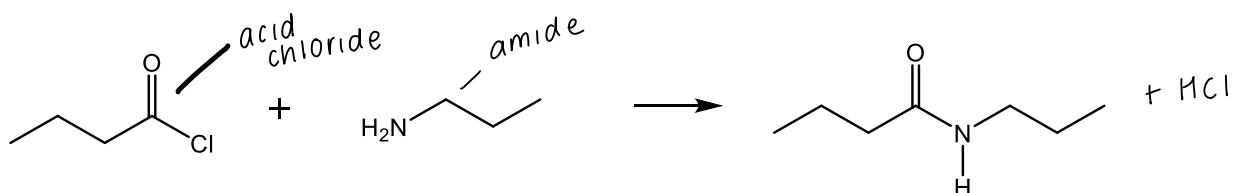
Why is heating required to drive the last two reactions? **There Reactivity is low and because they are stable.**

What is the role of H^+ in reaction (c)?

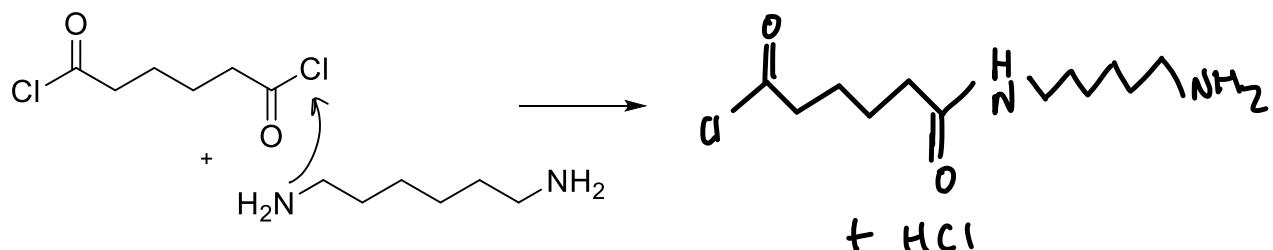
$\overset{\uparrow}{\text{Strong}} \quad \text{a catalyst for the reaction}$
acid

CHEM1111 Worksheet – Lecture 36

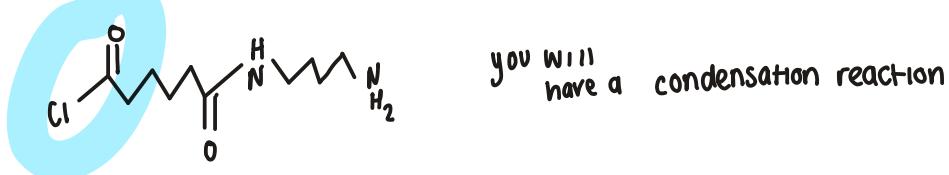
1. Remember from last time that an acid (acyl) chloride reacts with an amine to form an amide as shown below:



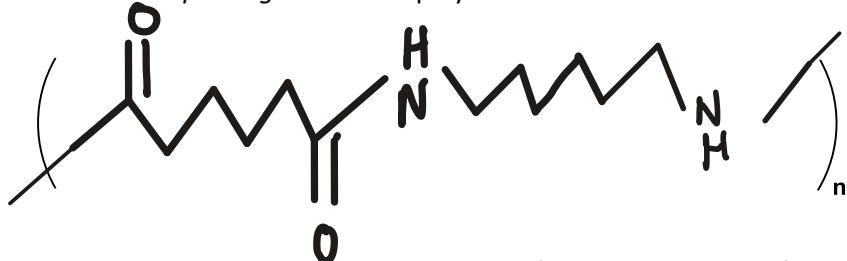
Now what do you think will happen when *this* acid chloride reacts with *this* amine? Draw the product that would form from the reaction of *one* of the acid chlorides with *one* of the amines.



Now what will happen if this initial product meets another molecule of the amine or acid chloride? And another ... and another ... and another ...?



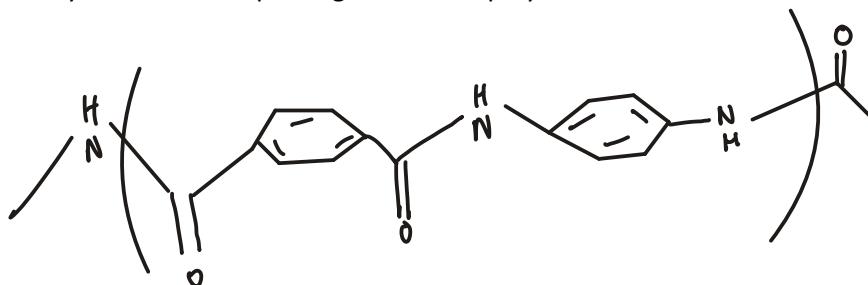
Can you draw the smallest *repeating unit* of this polymer between the brackets below?



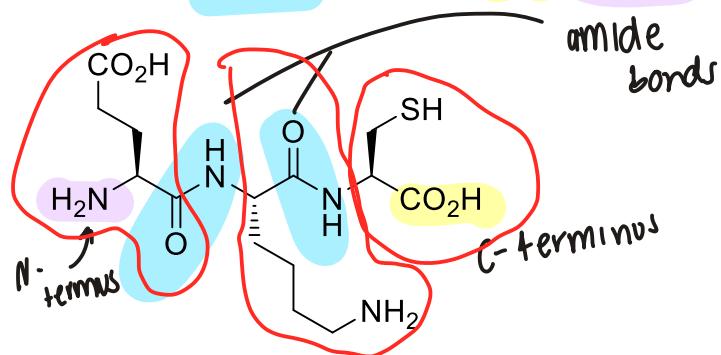
This polymer is called nylon-6,6. Why do you think this is? (Hint: count carbons.)

The length of the chain of carbon

2. Draw the two monomers that combine to make Kevlar (slide 7), where black = C, white = H, blue = N, red = O. Can you draw the repeating unit of this polymer?

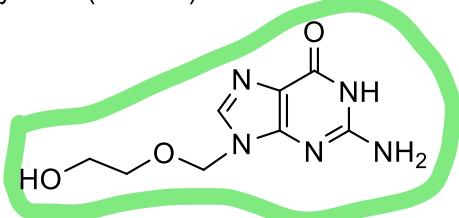


3. Highlight the peptide bonds in this tripeptide and label the C- and N-termini.



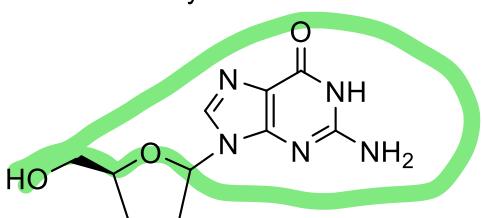
4. Using a coloured marker, highlight the structure of the molecule on the left hand side (acyclovir) *within* the molecule on the right hand side (guanine deoxyribonucleoside).

Acyclovir (Zovirax)



drug (tricks enzyme)

Guanine deoxyribonucleoside

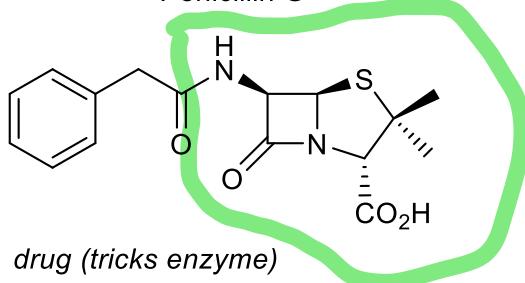


natural substrate for enzyme

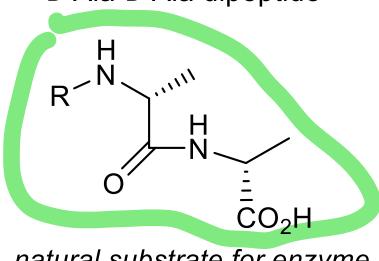
Can you see how acyclovir tricks the viral enzymes to beat Herpes simplex virus and treat cold sores?

5. Using a coloured marker, highlight the structure of the molecule on the right hand side (D-Ala-D-Ala dipeptide) *within* the molecule on the left hand side (penicillin G).

Penicillin G



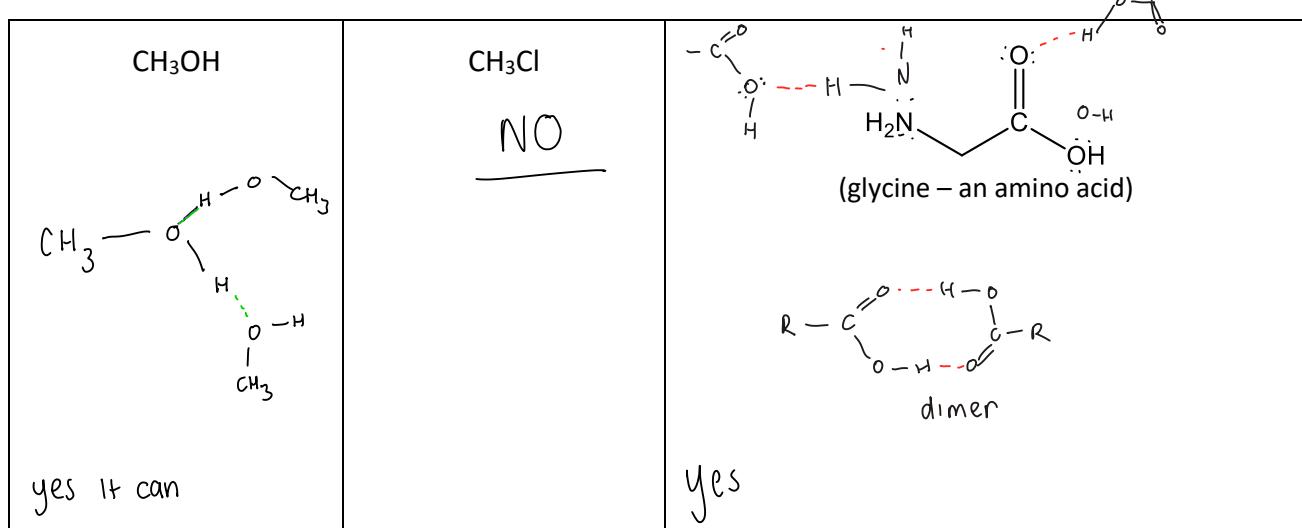
D-Ala-D-Ala dipeptide



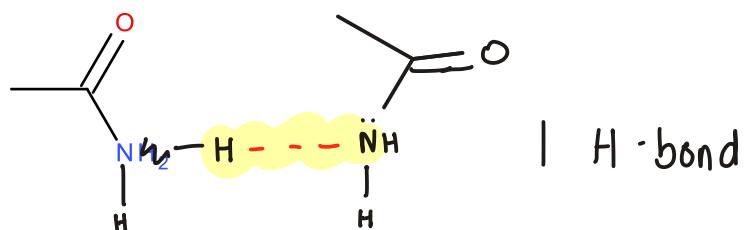
Can you see how penicillin tricks the transpeptidase enzyme to inhibit cell wall biosynthesis and kill bacteria?

CHEM1111 worksheet – Lecture 37

1. Which of the following molecules can be expected to show hydrogen-bonding with another molecule of the same substance? Draw the H-bonding interactions for those that will.

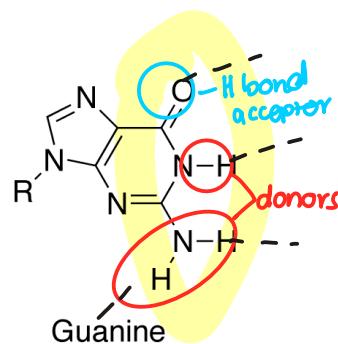


2. Acetamide can form pairs of H-bonds with another acetamide molecule. Draw in a second acetamide H-bonded to each one shown below. One should have two O - - H-N type H-bonds, and the other a single N - - H-N H-bond. Which of the two possibilities do you think is more favourable?



$$\begin{array}{c} \delta^- \\ X - H \\ \text{H-bond donor} \end{array} \cdots \cdots \begin{array}{c} \delta^- \\ y - Z \\ \text{H-bond acceptor} \end{array}$$

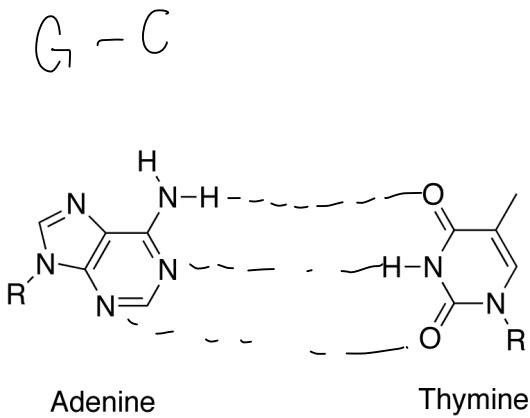
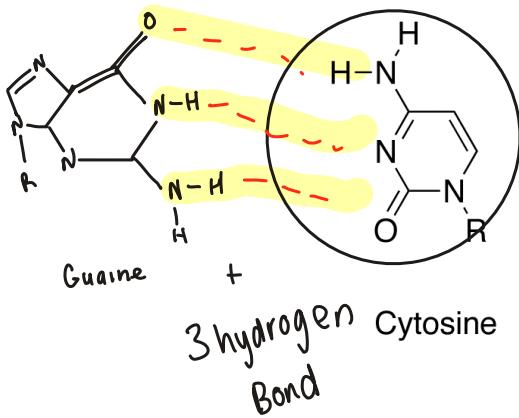
3. You've already seen that H-bonds can form between both like and unlike molecules, depending on each molecule's structure. H-bonding between unlike molecules is an important part of *molecular recognition*. The best-known example of this is DNA base pairing. When the guanine molecule is incorporated into a DNA strand it can only specifically H-bond to one of the three other available base pairs cytosine, adenine and thymine. Look at the three H-bonding sites on the **right hand side** of the guanine molecule shown (away from the R-group) and identify which are hydrogen donors (lone pair acceptors) and which are lone pair donors (hydrogen acceptors)



4. How many H-bonds can guanine form using the sites you identified in Q3?

3

5. Now look at the three other DNA nucleobases shown below and see if you can decide which **one** has complementary H-bonding ability and would therefore base pair with guanine. Re-draw it and guanine showing the H-bonds between them.



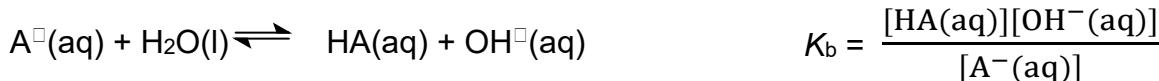
6. Are the remaining pair similarly compatible? Re-draw them, suitably orientated, showing the H-bonds between them.



Tutorial 13 (Week 13): Acids and bases (2)

Model 1: pH of a Weak Base

A **weak base** is significantly less than 100% associated in water and an equilibrium must be considered:



From the chemical equation:

$$[HA(aq)]_{\text{equilibrium}} = [OH^{\ominus}(aq)]_{\text{equilibrium}}$$

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

$$K_b = \frac{[OH^{\ominus}(aq)]^2}{[A^{\ominus}(aq)]_{\text{initial}}} \quad \text{and} \quad [OH^{\ominus}(aq)] = \sqrt{K_b \times [A^{\ominus}(aq)]_{\text{initial}}}$$

After working out $[OH^{\ominus}(aq)]$, the pOH can be calculated:

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

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

Critical thinking questions

1. Quinine is a natural product with antimalarial properties. It contains two basic N atoms, with pK_b values of 5.1 (tertiary amine) and 9.7 (pyridine).

- (a) Quinine is not very soluble in water. A saturated solution is only 1.6×10^{-3} M. What is the pH of this solution?

$$pK_b = 5.1 \text{ and } [\text{Base}] = 1.6 \times 10^{-3}$$

$$\text{Hence, } [OH^{\ominus}] = (10^{-5.1} \times 1.6 \times 10^{-3})^{0.5} = 1.13 \times 10^{-4}$$

$$pOH = -\log(1.13 \times 10^{-4}) = 3.95$$

$$pH = 14 - 3.95 = 10.05$$

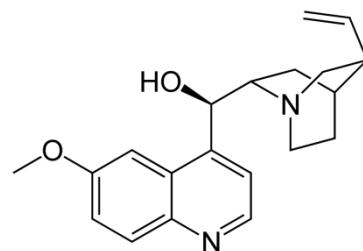
- (b) Show that the pyridine contributes negligibly to the pH.

$$pK_b = 9.7 \text{ and } [\text{Base}] = 1.6 \times 10^{-3}$$

$$\text{Hence, } [OH^{\ominus}] = (10^{-9.7} \times 1.6 \times 10^{-3})^{0.5} = 5.65 \times 10^{-7} \text{ M}$$

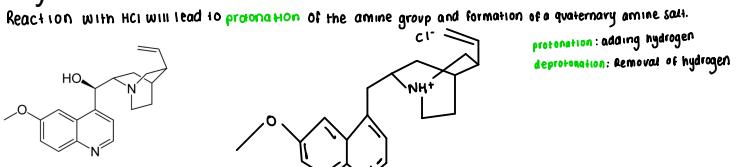
$$pOH = -\log(5.65 \times 10^{-7}) = 6.25$$

$$pH = 14 - 6.25 = 7.75$$



the concentration of
OH from pyridine is much
smaller than that from
amine

- (c) Because of its low solubility, quinine is normally given as an amine salt such as quinine hydrochloride. Draw the structure of this salt.



- (d) What is the pH of 0.53 M quinine hydrochloride?

$$pK_a = 14 - 5.1 = 8.9$$

$$pK_a = 8.9, [HCl] = 0.53 \text{ M}$$

$$K_a = 10^{-8.9}, \text{ so } [H^+] = (10^{-8.9} \times 0.53)^{0.5} = 2.58 \times 10^{-5}$$

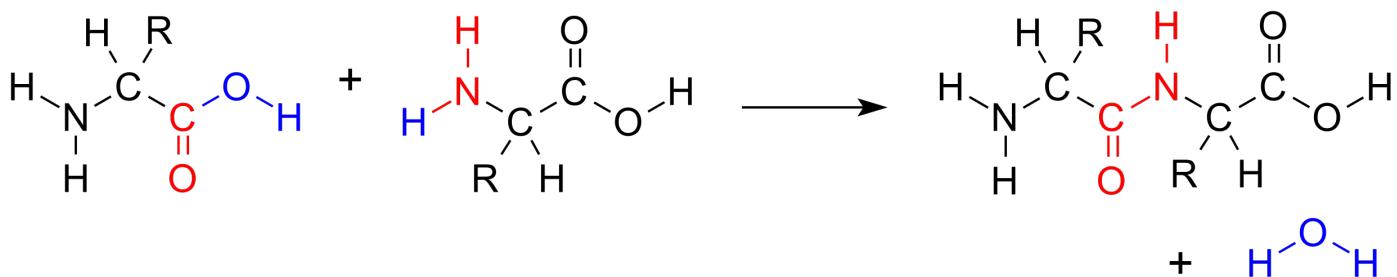
$$pH = -\log(2.58 \times 10^{-5}) = 4.59$$

pH = 4.59

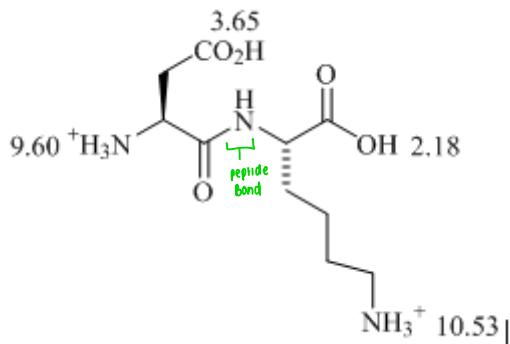
↳ The conjugate acid of the tertiary amine ($pK_a = 5.1$)
↳ page before

Model 2: Amino acids and peptides

Amino acids are bifunctional organic compounds containing carboxyl and amine groups. These two groups can react to form an amide, with what is known as a peptide bond:

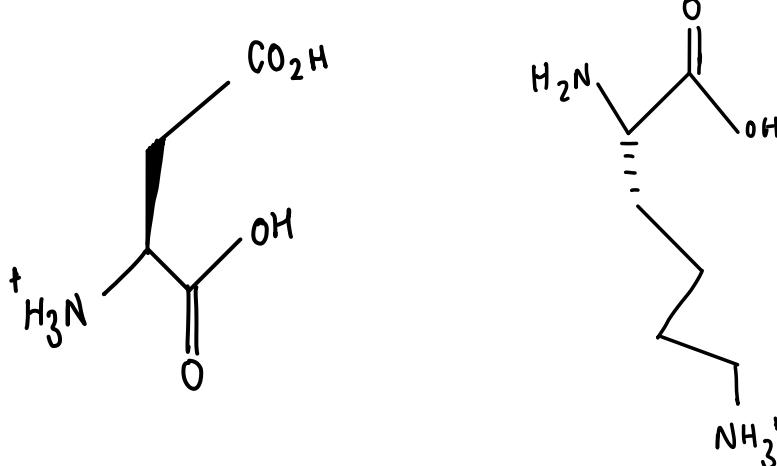


The dipeptide shown below has all of the ionisable groups in their conjugate acid forms, together with their pK_a values.

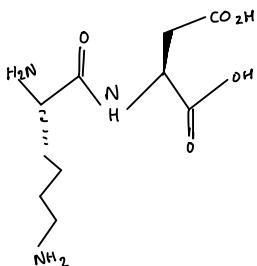


1. Draw the structure of the amino acids that formed this dipeptide:

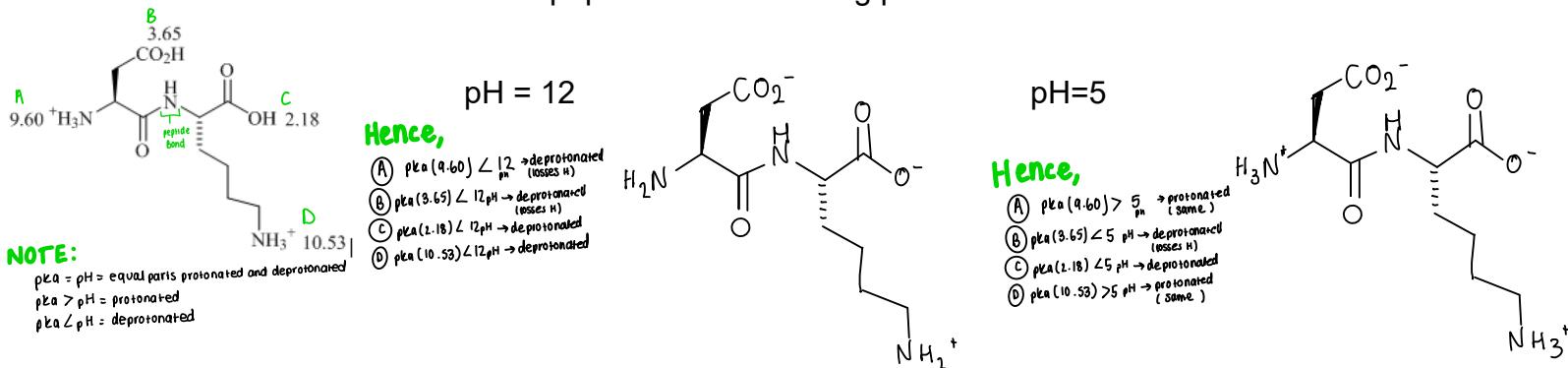
↳ a peptide composed of two amino-acids



2. Draw the structure of another dipeptide containing both of the amino acids in the dipeptide drawn above. Hint: rearrange the order of the amino acids – they can react at either end.

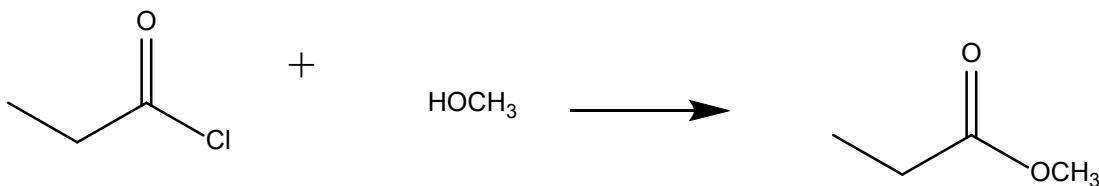


3. Draw the structure of the dipeptide at the following pH values:



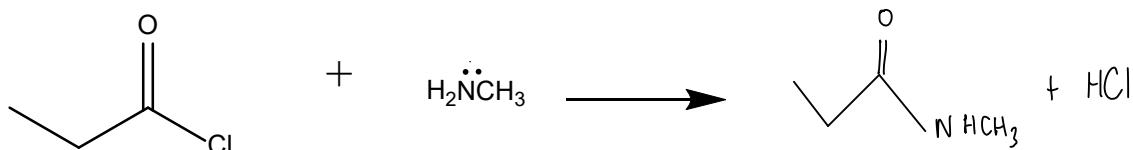
Model 3: Other Carboxylic Acid Derivatives

Following the example in model 2, other carboxylic acid derivatives are also formed from the condensation of a carboxylic acid with a second functional group, such as an alcohol or an amine. In some cases they can be formed directly. More often, the carboxylic acid must be converted to a more reactive intermediate, such as an acid chloride but the **process of condensation is essentially the same**:

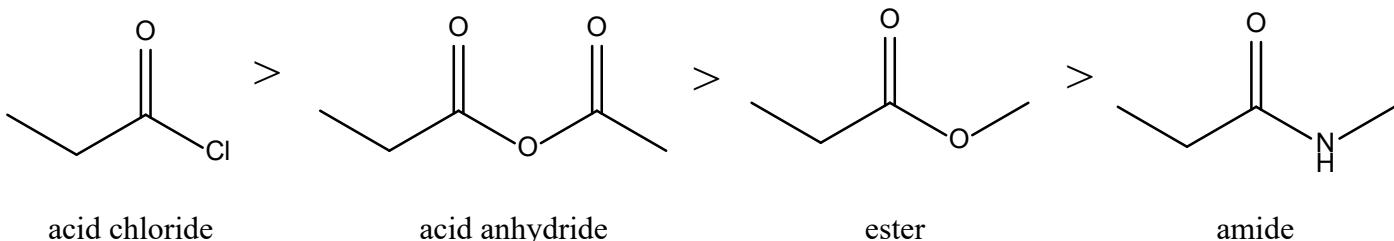


Critical thinking questions

1. Using the reaction above as a model, predict the products of the condensation of an acid chloride with an amine.



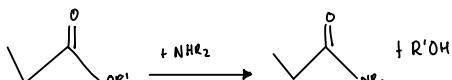
Here are the common carboxylic acid derivatives, arranged from most reactive to least reactive.



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

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

add an amine

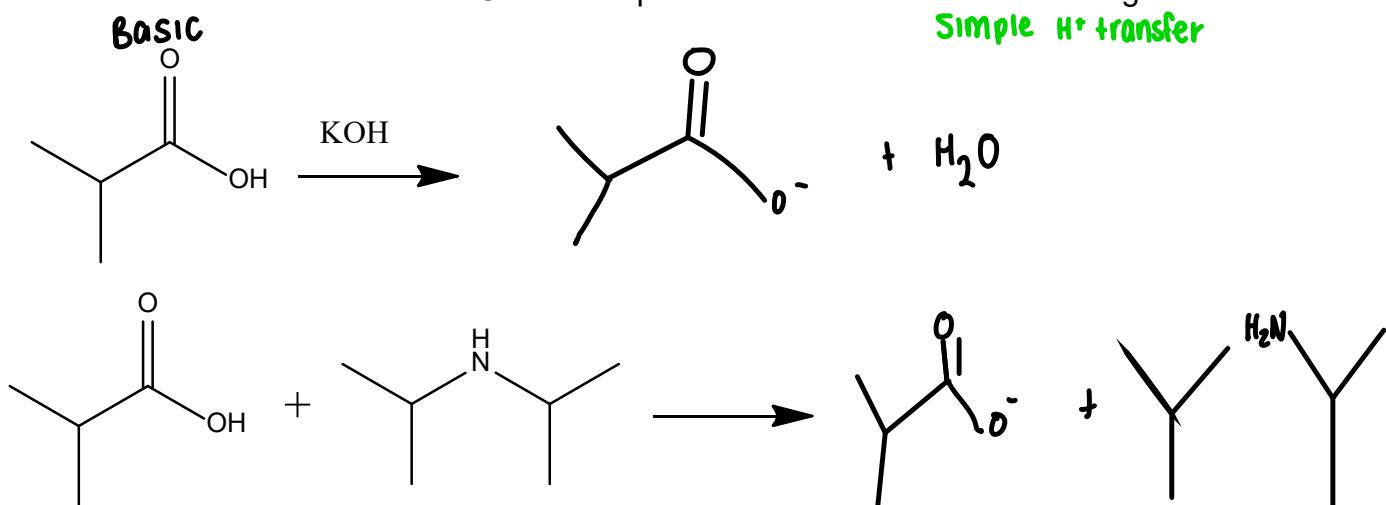


3. What is the by-product of this reaction?

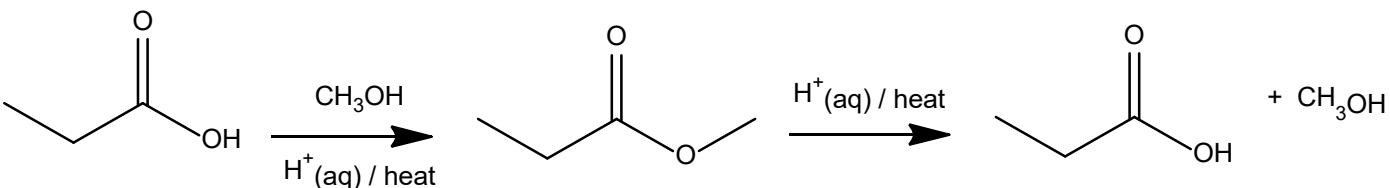
The alcohol

Extension:

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



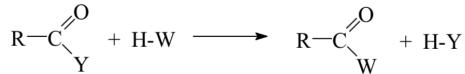
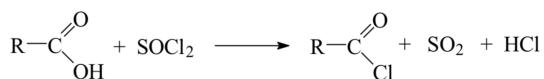
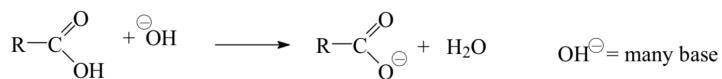
The scheme below shows the *condensation* of a carboxylic acid and an alcohol to give an ester, followed by *hydrolysis* of the ester back to the carboxylic acid and alcohol. Hydrolysis can be catalysed by acid or base.



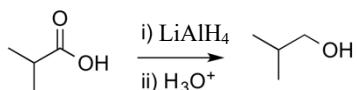
5. Overall, what is being removed or added in each step? How does this relate to the names we give these reactions (condensation and hydrolysis)?

Step 1: CH₃OH is added and H₂O is removed. The acid and alcohol combine to make an ester in the condensation reaction
Step 2: H₂O is added and CH₃OH is removed from this hydrolysis reaction.

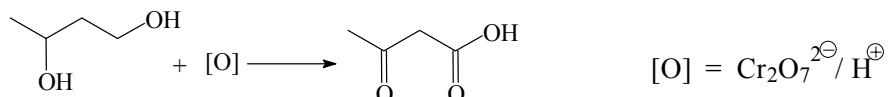
Carboxylic acids and derivatives – acid/base and substitution



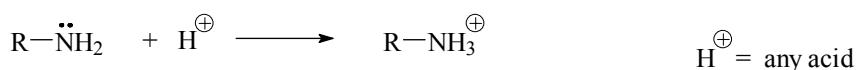
Y	W
Cl	OH, OR, NR ₂
OR	OH, NR ₂
NR ₂	OH



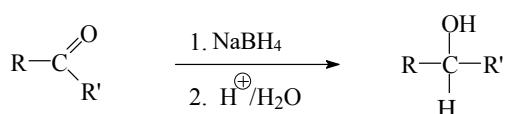
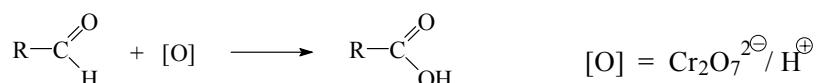
Alcohols – oxidation



Amines – acid/base



Aldehydes and ketones



Relative acidity

		pK _a	Very strong base (e.g. NaH)	Strong base (e.g. NaOH)	Weak base (e.g. NaHCO ₃)
Carboxylic acid	RCOOH	~5	✓	✓	✓
Phenol	C ₆ H ₅ OH	9.9	✓	✓	✗
Alcohol	ROH	~16	✓	✗	✗

Nuclear chemistry



Radio activity formula's

$$1. t_{1/2} = \frac{\ln 2}{k} \rightarrow t_{1/2} = \text{half life}, k = \text{radioactive constant}. (\text{Remember units must match e.g. S} \rightarrow \text{S}^{-1} \text{h}^{-1})$$

$$2. A = kN \rightarrow A = \text{Activity}, k = \text{radioactive constant}, N = \text{number of Nuclei}$$

$$3. \ln\left(\frac{N_0}{N_t}\right) = kt \xrightarrow{\text{from above equation}} \ln\left(\frac{N_0}{N_t}\right) = kt, N_0 = \text{initial number of nuclei}, N_t = \text{number of nuclei after Decay}$$

↳ making N_t the subject

$$4. {}^{14}\text{C age} = 8033 \ln\left(\frac{N_0}{N_t}\right) \text{ years}$$

$$\ln\left(\frac{N_0}{N_t}\right) = kt \rightarrow \frac{N_0}{N_t} = e^{kt} \xrightarrow{\text{FLIP}} \frac{N_t}{N_0} = e^{-kt} \rightarrow N_t = N_0 e^{-kt}$$

1. Technetium-99m has a decay constant of $3.2 \times 10^{-5} \text{ s}^{-1}$. What is its half-life in hours?

$$t_{1/2} = \frac{\ln 2}{\kappa} = \frac{\ln 2}{3.2 \times 10^{-5} \text{ s}^{-1}} = \frac{21660.84939 \text{ s}}{60 \times 60 \text{ sh}^{-1}} = 6.0 \text{ hrs}$$

2. What is the activity of 99 g of Tc-99m?

$$\kappa = 3.2 \times 10^{-5} \text{ s}^{-1}$$

$$A = \kappa N$$

$$\frac{99 \text{ g}}{99 \text{ g/mol}^{-1}} = 1 \text{ mole Tc}$$

$$1 \text{ mole Tc} \times 6.022 \times 10^{23} = 6.022 \times 10^{23} \text{ nuclei}$$

↑
Avogadro's number

$$A = 3.2 \times 10^{-5} \text{ s}^{-1} \times 6.022 \times 10^{23}$$

$$= 1.92704 \times 10^{19}$$

$$= 1.9 \times 10^{19} \text{ s}^{-1}$$

↑
or
6.02

3. A hospital is delivered with a sample of Tc-99m with an activity of $2.4 \times 10^{18} \text{ s}^{-1}$. What will be the activity after 2 days?

$$\begin{aligned}
 & A_t \quad t = 2 \text{ days} \\
 & 2 \text{ days} \times 24 \text{ hours} \times 60 \text{ mins} \times 60 \text{ sec} \\
 & t = 172800 \text{ s} \\
 \ln\left(\frac{A_0}{A_t}\right) &= k t \rightarrow e^{\ln \frac{A_0}{A_t}} = e^{k t} \rightarrow \frac{A_0}{A_t} = e^{k t} \rightarrow \frac{A_t}{A_0} = e^{-k t} \rightarrow A_t = A_0 e^{-k t} \\
 & \text{what we want to know} \\
 & = 2.4 \times 10^{18} \text{ s}^{-1} \times e^{-3.2 \times 10^{-5} \text{ s}^{-1} \times 172800 \text{ s}} \\
 & = 9.522181925 \times 10^{15} \\
 & = 9.5 \times 10^{15} \text{ s}^{-1} \\
 & \uparrow \text{Bq}
 \end{aligned}$$

4. An ancient wooden boat is discovered. A sample of the wood has a radiocarbon activity of 0.0058 Bq. A comparable modern standard piece of wood has a radiocarbon activity of 0.30 Bq.

What is the radiocarbon age of the wooden boat?

$$\begin{aligned}
 {}^{14}\text{C age} &= 8033 \ln\left(\frac{A_0}{A_t}\right) \text{ years} \\
 &= 8033 \ln\left(\frac{0.30}{0.0058}\right) \text{ years} \\
 &\approx 32000 \text{ years}
 \end{aligned}$$

Le Chatelier's Principles

"If change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change."

changes in concentration

consider the following reversible reaction:



If the reaction is at equilibrium, then

$$Q = K_c = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = 24.0$$

What would happen if we add more $\text{Cl}_2(\text{g})$?

Adding more Cl_2 will make Q get smaller. If $Q < K$ then reaction shifts to the right. This decreases $\text{Cl}_2(\text{g})$

- If the concentration **increases**, the system acts to **consume** some of it.
- If the concentration **decreases**, the system acts to **produce** some of it



Change in pressure

There are 3 ways in which the **pressure** of a system can be changed:

1. By adding (or removing) a gaseous reactant or product:
• This is the same effect as changing the concentration.
2. By adding a gas that is not involved in the reaction:
• This does **not** effect the concentrations of the reactants or products.
• Q is not changed and the reaction does **not** shift.
3. By changing the volume of the container.

Change in volume



If the reaction is at equilibrium, then

$$Q = K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

If the volume available is $1/2$ then $[\text{N}_2\text{O}_4]$ and $[\text{NO}_2]$ will both double

- Because we have $[\text{NO}_2]^2$, Q will decrease
- With $Q < K$, the reaction will shift to the right: the side with fewer moles of gas.



If the reaction is at equilibrium, then

$$Q = K_c = \frac{[\text{N}_2\text{O}_4]}{[\text{NO}_2]^2}$$

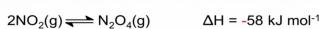
- If the volume available is **doubled**, then $[\text{N}_2\text{O}_4]$ and $[\text{NO}_2]$ will both **halve**
- Because we have $[\text{NO}_2]^2$, Q will **increase**
- With $Q > K$, the reaction will shift to the left: the side with **more** moles of gas

- If the volume **decreases**, the system acts to **decrease** the number of moles present
- If the volume **increases**, the system acts to **increase** the number of moles to fill it.

- Changing the volume alters **Q** and the reaction shifts so that **$Q \rightarrow K$**
- The value of **K** does not change!



Change in temperature



To see what happens when the temperature is changed, we treat the **heat** as a reactant.

- As this reaction is **exothermic**, heat is a product:



- By Le Chatelier's Principle, the reaction will move to minimise the change
- For an exothermic reaction, when the temperature is **raised** the reaction will move to the left to **remove** the heat.

- For **exothermic** reactions:
 - **Increasing** the temperature leads to a smaller value of **K** and the reaction shifts to the **left**.
 - **Decreasing** the temperature leads to a larger value of **K** and the reaction shifts to the **right**.

- For **endothermic** reactions:
 - **Increasing** the temperature leads to a larger value of **K** and the reaction shifts to the **right**.
 - **Decreasing** the temperature leads to a smaller value of **K** and the reaction shifts to the **left**.

Heat capacity

Heat and temperature are not the same

When an amount of heat is applied (q), the temperature (ΔT) rise depends on:

- the amount of substance: the more there is, the more smaller the temperature rise.
- The substance: when boiling water in a saucepan, the temperature rise for the metallic saucepan is greater than for the water

$$q = \text{constant} \times \Delta T$$

Where the constant depends on both the amount and on the identity of the substance being heated.

Heat capacity

$$q = \text{constant} \times \Delta T$$

→ Amount in grams → Specific heat capacity

$$q = m \times c \times \Delta T$$

m : mass of substance (g)

c : specific heat capacity. ($\text{J g}^{-1} \text{K}^{-1}$)

→ Amount in Moles → Molar heat capacity

$$q = n \times c \times \Delta T$$

n : moles of substance (mol)

c : molar heat capacity ($\text{J mol}^{-1} \text{K}^{-1}$)

Example.

How much energy (heat) does it take to heat an aluminium saucepan (200. g) containing 150 g of water from room temperature (20. °C) to boiling (100. °C)?

Find specific heat capacities:

$$c_{\text{Al(s)}} = 0.900 \text{ J g}^{-1} \text{K}^{-1}; c_{\text{H}_2\text{O(l)}} = 4.184 \text{ J g}^{-1} \text{K}^{-1}$$

With 20°C = 293 K and 100°C = 373 K

$$\Delta T = (373 - 293) \text{ K} = 80 \text{ K}$$

* NOTE: Temp diff in Kelvin is the same as temp diff in °C*

heat required for pan

$$q_{\text{Al(s)}} = m_{\text{Al(s)}} \times c_{\text{Al(s)}} \times \Delta T$$

$$(200 \text{ g}) \times (0.900 \text{ J g}^{-1} \text{K}^{-1})$$

$$\times (80 \text{ K}) = 14400 \text{ J}$$

heat required for water

$$q_{\text{H}_2\text{O(l)}} = m_{\text{H}_2\text{O(l)}} \times c_{\text{H}_2\text{O(l)}} \times \Delta T$$

$$(150 \text{ g}) \times (4.184 \text{ J g}^{-1} \text{K}^{-1})$$

$$\times (80 \text{ K}) = 50200 \text{ J}$$

$$q_{\text{total}} = q_{\text{Al(s)}} + q_{\text{H}_2\text{O(l)}} = (14400 + 50200) \text{ J} = 64000 \text{ J}$$

Bomb calorimeter

At constant volume, the 'bomb calorimeter' measures the internal energy change, ΔU_{int} .

Thermally insulated from the rest of the universe. The heat capacity of the calorimeter is known. Used to determine energy content of fuel and foods.

Coffee cup calorimeter

At constant pressure, the 'coffee cup calorimeter' measures the enthalpy change for a reaction, $\Delta r_{\text{rxn}} H$. Thermally insulated from the rest of universe. The heat capacity of the calorimeter is calibrated. Used for small scale reactions like dissolution and aqueous reactions.

Q: A manufacturer claims that their dessert has "fewer than 50 kJ per serving". The Consumer Affairs Department commissioned you to test the claim. You burn one serving in a bomb calorimeter and the temperature increased by 4.94 °C. Is the claim justified? The heat capacity of the bomb calorimeter is 8.15 kJ K⁻¹.

To find ΔT

We are given heat capacity of the whole instrument

$$m \times c = n \times c = 8.15 \text{ kJ K}^{-1}$$

$$q = (8.15 \text{ kJ K}^{-1}) \times (4.94 \text{ K}) = 40.3 \text{ kJ}$$

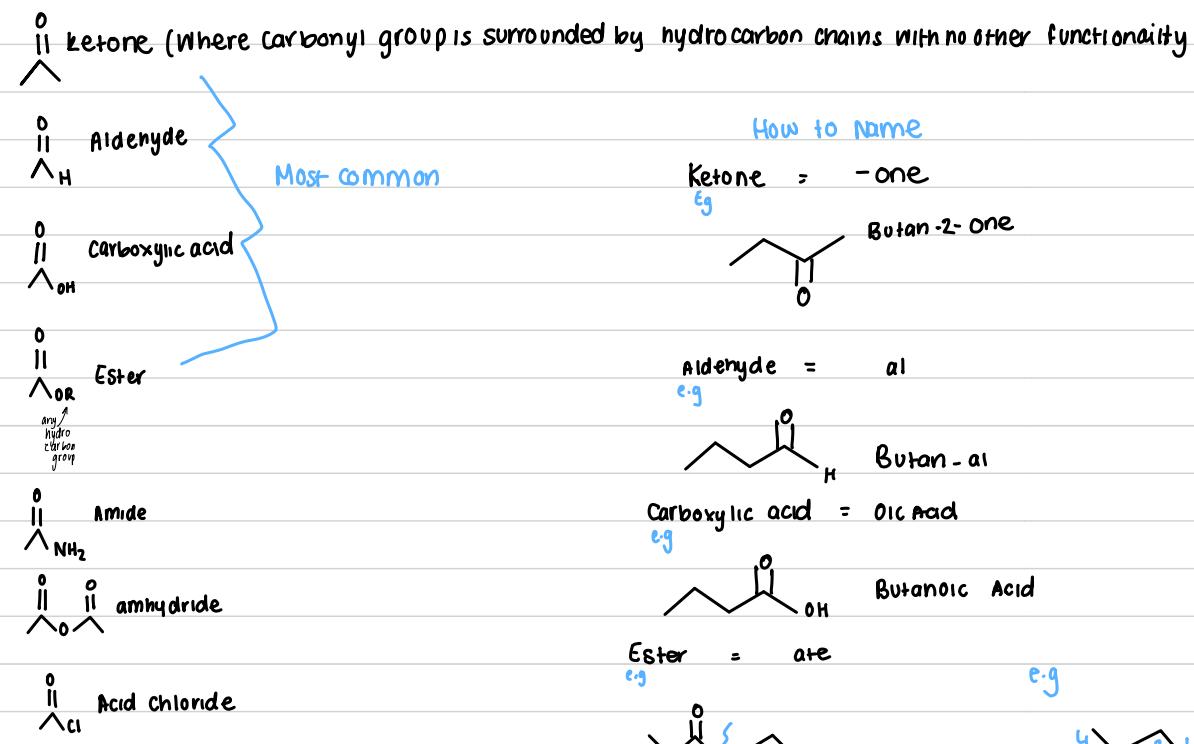
∴ Claim is upheld.

$$\Delta T = \frac{q}{m \times n}$$

Note: If cooling — neg number
as answer.

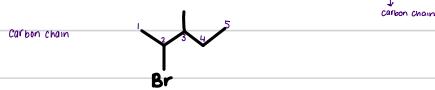
Carbonyl-containing Compounds

Different Functional Groups C=O

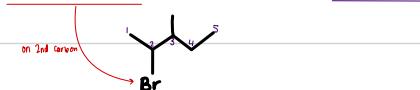


Naming Organic Compounds

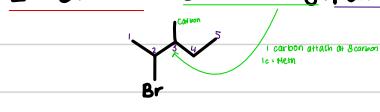
2-bromo - 3-methylpentane



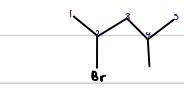
2-bromo - 3-methylpentane



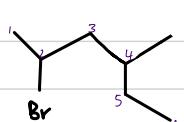
2-bromo - 3-methylpentane



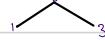
2-bromo - 4-methylpentane



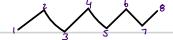
2-Bromo - 4-methylHexane



Compound: 3c = Propane



Compound: 8c Octane



Key for Carbon Names

1c = Meth

6 = Hex

2c = Eth

7c = Hept

3c = Prop

8c = Oct

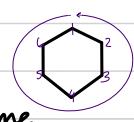
4c = But

9c = Non

5c = Pent

10c = Dec

Compound: 6c, Shape: ring

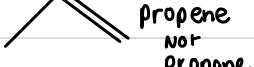


Name: cyclohexane

Name: cyclohexane

When a carbon double bond

is present. we change the name
at the end to ene



propene
not
propane

2-octene
(Oct-2-ene)

Key for Halogens

Br = Bromo

F = Fluoro

Cl = Chlоро

I = Iodo

Triple bonds the end become yne

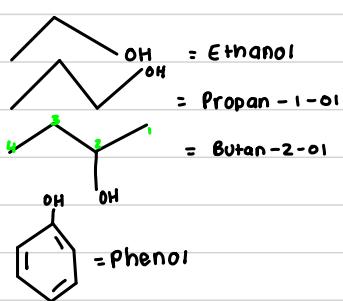
e.g. propyne



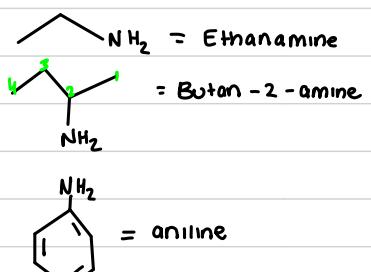
2-octyne
(Oct-2-yne)

Alcohol and Amine Nomenclature

Alcohols



Amine



Steps to naming
 1. - ol → an alcohol
 2. 1 - ol
 3. Butene ?? - 1 - ol
 4. But - 2 - ene - 1 - ol
 (double bond on 2nd)
 5. (E)-But - 2 - ene - 1 - ol

Steps to naming
 1. Amine (end) \leftarrow an amine
 2. Heptan (start) \leftarrow 7 carbon chain
 3. 4 - amine
 (amine in 4th position)
 4. 3 - Methyl
 (methyl in 3rd position)
 Name : 3 - Methyl - Heptan - 4 - amine

Primary Secondary Tertiary

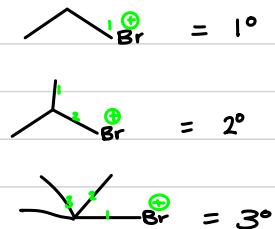
Cation

A cation charge with only one alkene attach = 1°

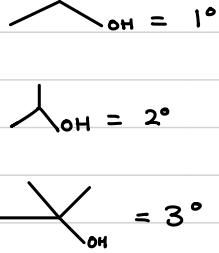
A cation charge with two alkynes attach is secondary = 2°

A cation charge with three alkynes attach is tertiary = 3°
Note
 Most stable

Examples



Alcohol



we are only concerned with the carbon that is attached to the OH

Carbonyl - containing Compound

Carbonyl group:

C=O

Ketones: when carbon group is surrounded by hydrocarbon chains

Aldehydes:

Carboxylic acid:

Amide:

Ester:

Acid hydride:

Acid chloride:

Naming

Ketone = -one

$\text{CH}_3\text{CH}_2\text{C=O}$ = Butan - 2 - one

Amines

