# Week 1

## CHEM1101 Worksheet 1: Atoms and Isotopes

### Model 1: Isotopes

Each element found in nature occurs as a mixture of isotopes. Isotopic abundances can vary appreciably on an astronomical scale – e.g. in the Sun versus the Earth. On Earth, however, natural abundance varies little from place to place.

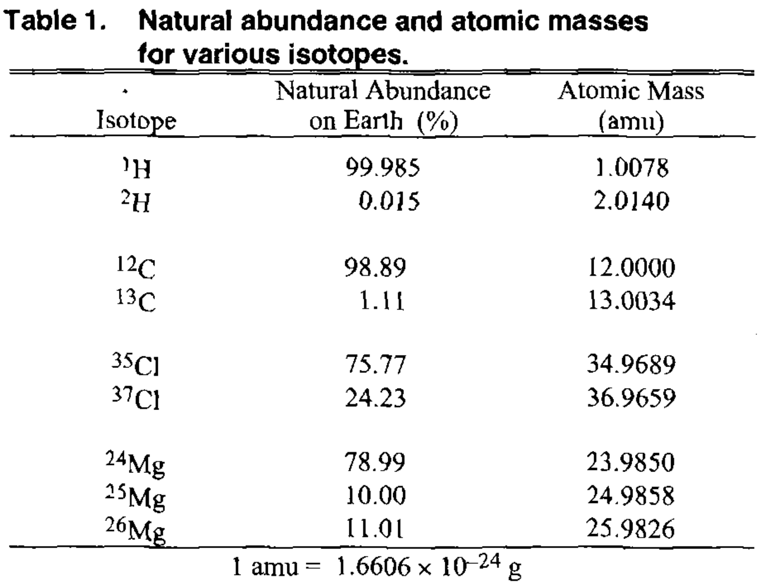


**Table 1. Natural abundance and atomic masses for various isotopes.**

| Isotope | Natural Abundance on Earth (%) | Atomic Mass (amu) |
|---|---|---|
| $^{1}H$ | 99.985 | 1.0078 |
| $^{2}H$ | 0.015 | 2.0140 |
| $^{12}C$ | 98.89 | 12.0000 |
| $^{13}C$ | 1.11 | 13.0034 |
| $^{35}Cl$ | 75.77 | 34.9689 |
| $^{37}Cl$ | 24.23 | 36.9659 |
| $^{24}Mg$ | 78.99 | 23.9850 |
| $^{25}Mg$ | 10.00 | 24.9858 |
| $^{26}Mg$ | 11.01 | 25.9826 |

1 amu = $1.6606 \times 10^{-24}$ g

### Critical thinking questions

1. How many isotopes of magnesium occur naturally on Earth?

2. Describe what all isotopes of magnesium have in common and also how they are different.

3. If you select one carbon atom at random, what is the mass of that atom is most likely to be (in amu)?

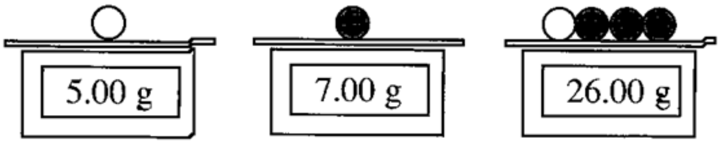
4. What is the mass (in amu) of 100 $^{12}C$ atoms? Of 100 $^{13}C$ atoms?

5. If you select one hundred carbon atoms at random, what will the total mass be?
   (a) 1200.00 amu, (b) slightly more than 1200.00 amu,
   (c) slightly less than 1200.00 amu, (d) 1300.34 amu or
   (e) slightly less than 1300.34 amu

Explain your reasoning.

## Model 2: Average Mass

In a collection of marbles, 25% of the marbles have a mass of 5.00 g and 75% of the marbles have a mass of 7.00 g. The average mass of a marble is 6.50 g.



The average mass of a marble can be determined by dividing the total mass of the marbles by the total number of marbles:

$$\text{average mass of a marble} = \frac{1 \times 5.00\text{ g} + 3 \times 7.00\text{ g}}{4} = 6.50\text{ g} \qquad (1)$$

Or, the average mass of a marble can be determined by (a) multiplying the fraction of marbles of a particular type by the mass of a marble of that type and (b) taking a sum over all types of marbles:

$$\text{average mass of a marble} = 0.2500 \times 5.00\text{ g} + 0.7500 \times 7.00\text{ g} = 6.50\text{ g} \qquad (2)$$

## Critical thinking questions

1. Show that equations (1) and (2) are equivalent.

2. Do any of the marbles in Model 2 have the average mass?

3. (a) Use the method of equation (2) and the data in Table 1 to calculate the average mass of a chlorine atom in amu.
   (b) Does any chlorine atom have this mass?
   (c) What is the average atomic mass of chlorine in any large collection of chlorine atoms?

(d) What is the average mass of a chlorine atom (in g)?

(e) Based on this answer, what is the mass of 6.022 x $10^{23}$ (randomly selected) chlorine atoms (in g)?

4. Naturally-occurring silver is composed of two isotopes. $^{107}$Ag with mass 106.9051 amu, and $^{109}$Ag with mass 108.9048 amu. The average atomic mass of silver is 107.8682. What are the percentages of $^{107}$Ag and $^{109}$Ag in naturally-occurring silver?

5. Suppose that on another planet the following stable isotopes and abundances of sulfur are found:

| | | |
|---|---|---|
| $^{32}$**S** | 31.972072 amu | *48.32 %* |
| $^{33}$**S** | 32.971459 amu | *17.78 %* |
| $^{34}$**S** | 33.967868 amu | *33.90 %* |

What would the average atomic mass of sulfur be on that planet?

# CHEM1101 Worksheet 2: The Nuclear Atom

## Model 1: The Atomic Symbol

The atomic symbol, $X$, is used to identify the element to which an atom belongs and the number of electrons, protons and neutrons it contains.

$$^{A}_{Z}X$$

A *neutral* atom of an element has the same number of electrons and protons:

number of protons = number of electrons = atomic number = $Z$

The mass number is equal to the number of protons plus the number of neutrons:

number of neutrons = mass number - number of protons = $A$ - $Z$

**Ions** have different numbers of protons and electrons and so have any overall charge. **Anions** have gained electrons so have a negative charge. **Cations** have lost electrons so have a positive charge. The overall charge is written as a superscript after the symbol:

$^{A}_{Z}X^{n-}$ is an anion: it has *n* more electrons than protons. $^{A}_{Z}X^{n+}$ is a cation: it has *n* fewer electrons than protons

## Critical thinking questions

1. How many electrons, protons and neutrons are there in each of the species below?

| | species | number of electrons | number of protons | number of neutrons |
|---|---|---|---|---|
| (a) | $^{24}_{12}\mathrm{Mg}$ | | | |
| (b) | $^{26}_{12}\mathrm{Mg}$ | | | |
| (c) | $^{24}_{12}\mathrm{Mg}^{2+}$ | | | |
| (d) | $^{79}_{35}\mathrm{Br}$ | | | |
| (e) | $^{81}_{35}\mathrm{Br}^{-}$ | | | |

2. Alpha and beta particles and gamma rays are important in radioactive decay. What are the charges and masses of the species below?

| | species | charge | mass |
|---|---|---|---|
| (a) | alpha particle: α or $^{4}_{2}\mathrm{He}^{2+}$ | | |
| (b) | high speed electron $\beta^{-}$ or $^{0}_{-1}\beta^{-}$ | | |
| (c) | positron $\beta^{+}$ or $^{0}_{+1}\beta^{+}$ | | |
| (d) | gamma rays: $^{0}_{0}\gamma$ | | |

3. The three subatomic particles (the electron, proton and neutron) contain only one type of particle so the overall charge is not added to the symbol. What are the masses and charges of these particles?

| | species | charge | mass |
|---|---|---|---|
| (a) | ${}_{-1}^{0}e$ (electron) | | |
| (b) | ${}_{1}^{1}p$ (proton) | | |
| (c) | ${}_{0}^{1}n$ (neutron) | | |

## Model 2: Radioactive Decay

A nuclide is a particular nuclear species with a specified number of protons and neutrons. The 6 most important ways in which radioactive nuclides decay are:

(a) α decay: the nucleus loses an α particle (${}_{2}^{4}\mathrm{He}^{2+}$)
(b) $\beta^-$ decay: a neutron in the nucleus is converted into a proton and an electron. The electron is ejected from the nucleus.
(c) Positron or $\beta^+$ 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

4. 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) | $\beta^-$ decay | | |
| (c) | $\beta^+$ emission | | |
| (d) | Electron capture | | |
| (e) | Neutron emission | | |
| (f) | γ decay | | |

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

(a) $^{238}_{92}\mathrm{U}$ undergoes α decay:

(b) $^{14}_{6}\mathrm{C}$ undergoes $\beta^-$ decay:

(c) $^{11}_{6}\mathrm{C}$ undergoes $\beta^+$ emission:

(d) $^{55}_{26}\mathrm{Fe}$ undergoes electron capture:

(e) $^{13}_{4}\mathrm{Be}$ emits a neutron:

(f) $^{99m}_{43}\mathrm{Tc}$ undergoes γ decay:

6. By first working out the number of neutrons (*N*) and the number of protons (*Z*) before and after the nuclear decays in question 5, 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 | | |
| (b) | $\beta^-$ decay | | |
| (c) | $\beta^+$ emission | | |
| (d) | electron capture | | |
| (e) | neutron emission | | |
| (f) | γ decay | | |

## Model 3: Predicting the Mode of Decay

The figure 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 ${}^{56}_{26}\mathrm{Fe}$, $N / Z = 1.28$ for ${}^{107}_{47}\mathrm{Ag}$ and $N / Z = 1.49$ for ${}^{184}_{74}\mathrm{W}$.
- 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

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

8. Nuclides *above* the band of stability in the figure have a *N* / *Z* ratio which is too high. Using your answer to question 6, which of the 6 modes of decay might such a nuclide undergo? Fill in your answer in the box on the figure overleaf.

9. Nuclides *below* the band of stability in the figure have a *N* / *Z* ratio which is too low. Using your answer to question 6, which of the 6 modes of decay might such a nuclide undergo? Fill in your answer in the box on the figure overleaf.

10. Nuclides with $Z > 83$ are beyond the band of stability and are unstable. Using your answer to question 6, which of the 6 modes of decay might such a nuclide undergo? Fill in your answer in the box on the figure overleaf.

11. For each of the following radioactive nuclides, calculate their *N* / *Z* ratios and hence predict the mode(s) of nuclear decay they are likely to undergo.

    (a) ${}^{12}_{5}\mathrm{B}$

    (b) ${}^{234}_{92}\mathrm{U}$

    (c) ${}^{127}_{57}\mathrm{La}$

12. Why is γ decay included in the modes of nuclear decay in Model 2?

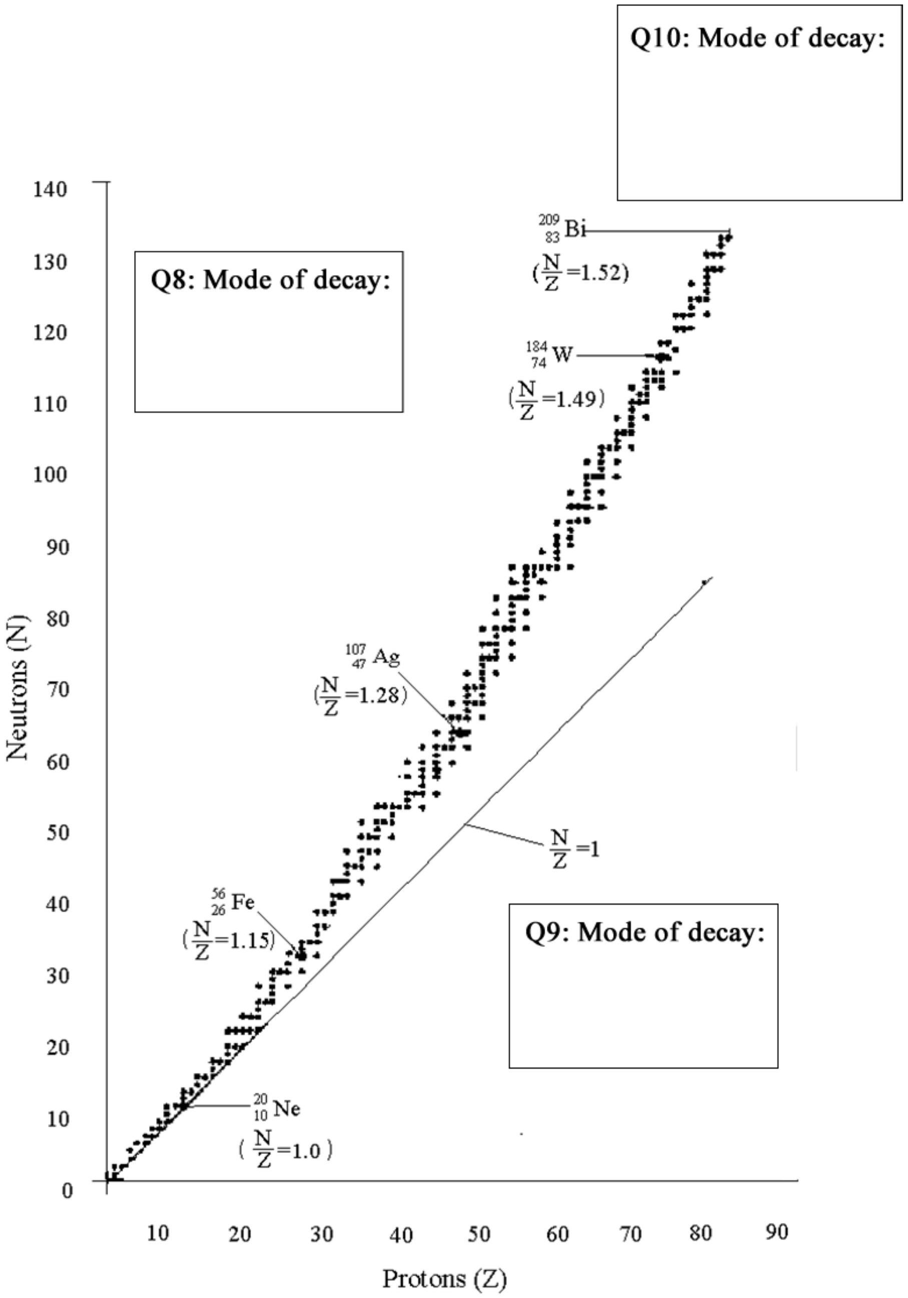


**Figure 1.** Plot of the number of neutrons (*N*) *vs* the number of protons (*Z*) for the stable nuclides.

# CHEM1101 Worksheet 3: Quantum Chemistry

## Model 1: 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.

We cannot see these waves. Instead, our eyes detect the *intensity* of the light which is given by the *square* of the wave.

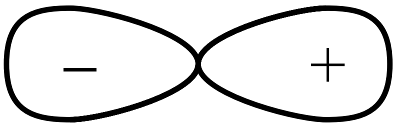
Squaring means multiplying the wave at each point by itself, remembering that positive × positive and negative × negative are both positive.

## Critical thinking questions

1. On the diagram, indicate the wavelength ($\lambda$) and the amplitude ($A$) of the wave.
2. Put an asterisk ('*") to mark the positions where the wave is zero. These are 'nodes'.
3. Peaks are where the wave is positive. Troughs are where the wave is negative. Labels these with "+" and "–" signs respectively. *Lightly* shade the "–" areas.
4. On top of the picture, draw a sketch of the *intensity* of the light.

## Model 2: Electron Waves

The picture below is a lobe representation of a 2-dimensional wave for an electron. The line encapsulates 90% of the electron density. We cannot see or measure the wave. Instead, the electron density can be measured and this is given by the *square* of the wave.



## Critical thinking questions

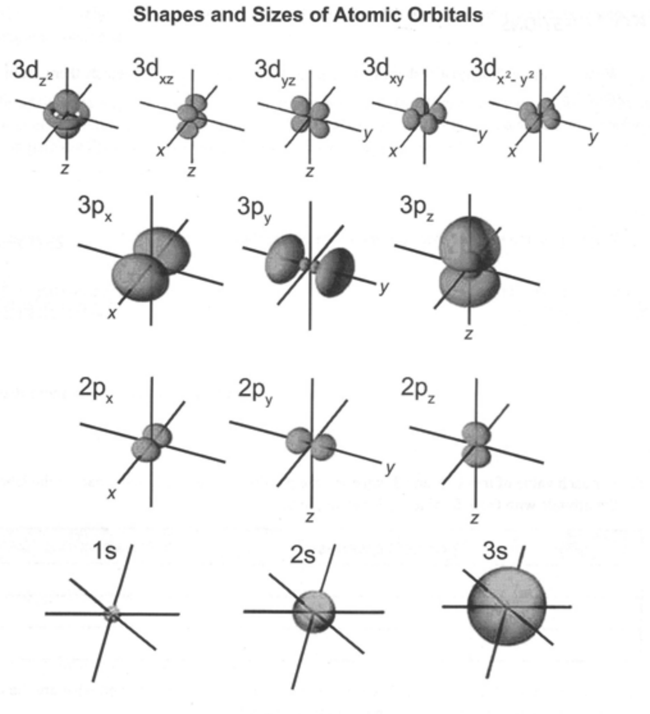
5. Mark the position of the node and *lightly* shade the "–" area.
6. Draw a sketch of the electron density for this electron.

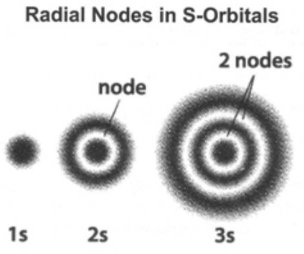
# Model 3: Atomic Orbitals and Quantum Numbers

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

As explored in Worksheet 3, 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, these are the *angular momentum quantum number, l,* and *magnetic quantum number,* $m_l$.

| Name | Characterizes | symbol | Allowed values |
|---|---|---|---|
| Principal | Size and Energy.<br>Total $n$ -1 nodes | $n$ | **$n$ = 1, 2, 3,…** |
| Angular Momentum | Shape<br>Energy in multi-electron atoms<br>$l$ planar nodes | $l$ | **$l$ = 0, 1, 2,… $n$-1** |
| Magnetic | Orientation | $m_l$ | **$m_l$ = -$l$, 1-l,…0… $l$-1, $l$** |


Shapes and Sizes of Atomic Orbitals


Radial Nodes in S-Orbitals

## Critical thinking questions

6. What are the characteristic shapes of *s*, *p*, and *d* orbitals?

7. Which quantum number identifies the shape of an orbital?

8. For each value of $n$ = 1, 2, and 3, what are the possible values for $l$, and what labels correspond to these orbitals?.

| ***n*** | **Possible *l* values** | **Orbital labels** |
|---|---|---|
| 1 | | |
| 2 | | |
| 3 | | |

9. 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 | | |
| 1 | | |
| 2 | | |

10. Which orbitals have a plane where the probability of finding the electron is zero (a *nodal plane*)?

11. What is the relationship between the value of the angular momentum quantum number and the number of such *nodal planes*?

12. Which orbitals in the model have *radial nodes*?

# Model 4: Electronic Configurations in Atoms

## Critical thinking questions

1. Discuss with your group and write down definitions of

   a. *The Aufbau Principle*

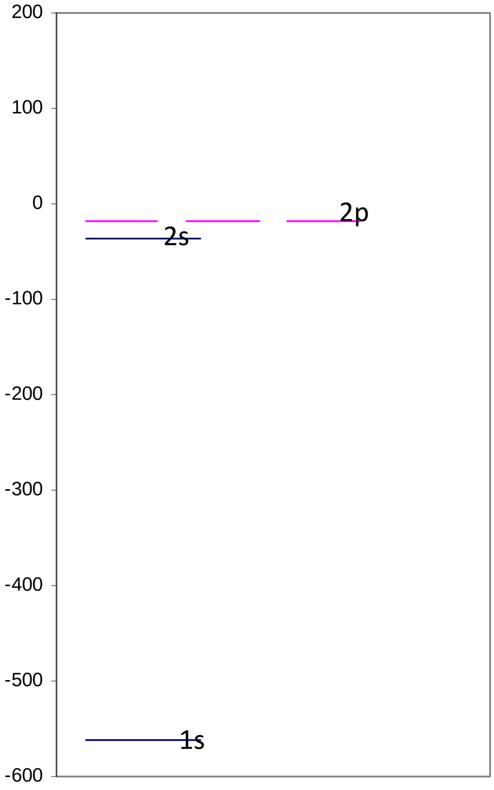
   b. *Pauli Exclusion Principle*

   c. *Hund's Rule*

2. Fill in the ground state electronic configuration for a carbon atom on the diagram below.

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

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



**Marks**
**5**

- Write two possible mechanisms for the radioactive decay of $^{83}$Rb to $^{83}$Kr.

The half-life of $^{83}$Rb is 86.2 days. Calculate the activity (in Bq) of an isotopically pure 1.000 g sample of $^{83}$Rb. (The molar mass of $^{83}$Rb is 82.915110 g mol$^{-1}$.)

Answer:

How many days will it take for this sample to diminish to 1 % of its initial activity?

Answer:

## Week 1 practice exam questions – answers on the web next week

**Marks**
**3**

- Explain the trends in electron affinities for the first 5 elements of the second row of the periodic table, in terms of their electronic configurations.
  *i.e.* Discuss the trend in Δ*H* for the following reaction: $A(g) + e^- \rightarrow A^-(g)$

| Element | Li | Be | B | C | N |
|---|---|---|---|---|---|
| Δ*H* (in kJ mol$^{-1}$) | –60 | +241 | –27 | –122 | +8 |

**Week 1 practice exam questions – answers on the web next week**

**Marks**
**4**

- Moseley discovered experimentally in 1913 that the atomic number, $Z$, of an element is inversely proportional to the square root of the wavelength, $\lambda$, of fluorescent X-rays emitted when an electron drops from the $n = 2$ to the $n = 1$ shell.

  $$i.e. \quad \frac{1}{\sqrt{\lambda}} = kZ$$

  If iron emits X-rays of 1.937 Å when a 2*s* electron drops back to the 1*s* shell, determine the identity of the elements contained in an alloy found to emit the same type of X-rays at 1.435 Å and 1.541 Å?

Answer:

**Week 1 practice exam questions – answers on the web next week**

**Marks**
**5**

- Sketch the following wavefunctions using lobe representations. Clearly mark all nodal surfaces, nuclear positions and the relative sign (+ or –) of the wavefunction within the lobes.

| | |
|---|---|
| a 2*s* atomic orbital | a 3*p* atomic orbital |

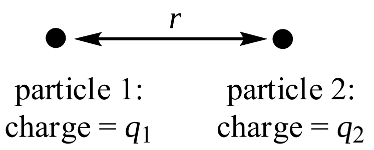
Explain the significance of (a) the lobes, (b) the nodes and (c) the sign of the wavefunction, in terms of the probability of finding an electron at a given point in space relative to the nucleus.

## Week 1 practice exam questions – answers on the web next week

# Week 2

## CHEM1101 Worksheet 4 – The Energy Levels of Electrons

### Model 1: Two charged Particles Separated by a Distance *r*



According to Coulomb, the potential energy of two stationary particles with charges $q_1$ and $q_2$ separated by a distance $r$ is:

$$V = k \times \frac{q_1 q_2}{r}$$

where $k$ is a positive-valued proportionality constant.

### Critical thinking questions

1. What happens to the magnitude of $V$ if $r$ is increased?

2. What is the value of $V$ if the particles are separated by an infinite distance (i.e. $r = \infty$)?

3. Is $V < 0$ or is $V > 0$ if the particles have the *same* charge?

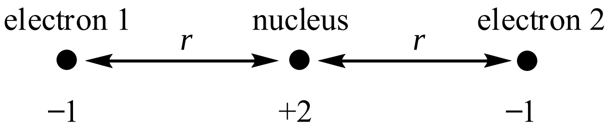
4. If $q = -1$ for an electron, what is $q$ for a proton?

5. A hydrogen atom consists of an electron orbiting around a proton. Is the potential energy of a hydrogen atom positive or negative?

6. Using your answers to questions 2 and 5, describe in *words* what happens to the potential energy of a hydrogen atom as its electron is removed (i.e. the atom is ionized)?

7. The picture opposite shows two electrons and a helium nucleus arranged in a straight line.

   Write down the total potential energy of this arrangement as a sum of *three* terms.



## Model 2: Electron Energy

For an atom, such as hydrogen, with one electron orbiting around a nucleus with charge $Z$, the energy of the electron is given by the equation below:

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

where $n$ = 1, 2, 3, 4.... 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 size of the electron's orbit are also controlled by the value of $n$:

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

## Critical thinking questions

8. The hydrogen atom has atomic number $Z = 1$. Using the equations above for the energy and average radius of electron's orbit, complete the table below for hydrogen.

| $n$ | $E_n$ (J) | $r_{\text{average}}$ (m) |
|---|---|---|
| 1 | $-218 \times 10^{-20}$ | $0.529 \times 10^{-10}$ |
| 2 | $-54.5 \times 10^{-20}$ | $2.12 \times 10^{-10}$ |
| 3 | $-24.2 \times 10^{-20}$ | |
| 4 | | |
| 5 | | |
| 6 | | |

9. The horizontal lines on the graph on the left hand side of last page of this worksheet 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 – 6.

10. Describe *in words* to your neighbour what happens to the energy levels and the average size of the orbit as $n$ increases. When you have agreed on this, write down your description in a grammatically correct sentence below.

11. What do you predict is the limiting behaviour of the energy and orbit of the electron when $n$ approaches infinity?

## Model 3: Atomic Spectroscopy

The electron in a H atom wandering around in space will be in the $n = 1$ level (the “ground state”). However, if a high voltage is passed through $H_2$ molecules, 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 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 as radiation 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 $194 \times 10^{-20}$ and (b) $n = 3$ to $n = 2$, the energy emitted is equal to $30 \times 10^{-20}$ J. These energies can be measured on the graph or calculated using the values in the table on question 8.

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

## Critical thinking questions

12. If the excited atom is formed with the electron in the $n = 4$ level, add dotted lines to the graph showing how the electron can relax.

13. For each of these jumps, work out the energy of the emitted radiation and mark it using a horizontal line on the right hand graph.

14. Repeat question 13 for an excited atom formed with the electron in the $n = 5$ level.

15. 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 $28 \times 10^{-20}$ is the infrared region. Light with energy *greater* than $50 \times 10^{-20}$ J is ultraviolet. Visible light lies between these values. Mark these regions on your spectrum.

16. (a) What wavelengths correspond to the upper and lower limits of visible light given in Q15?

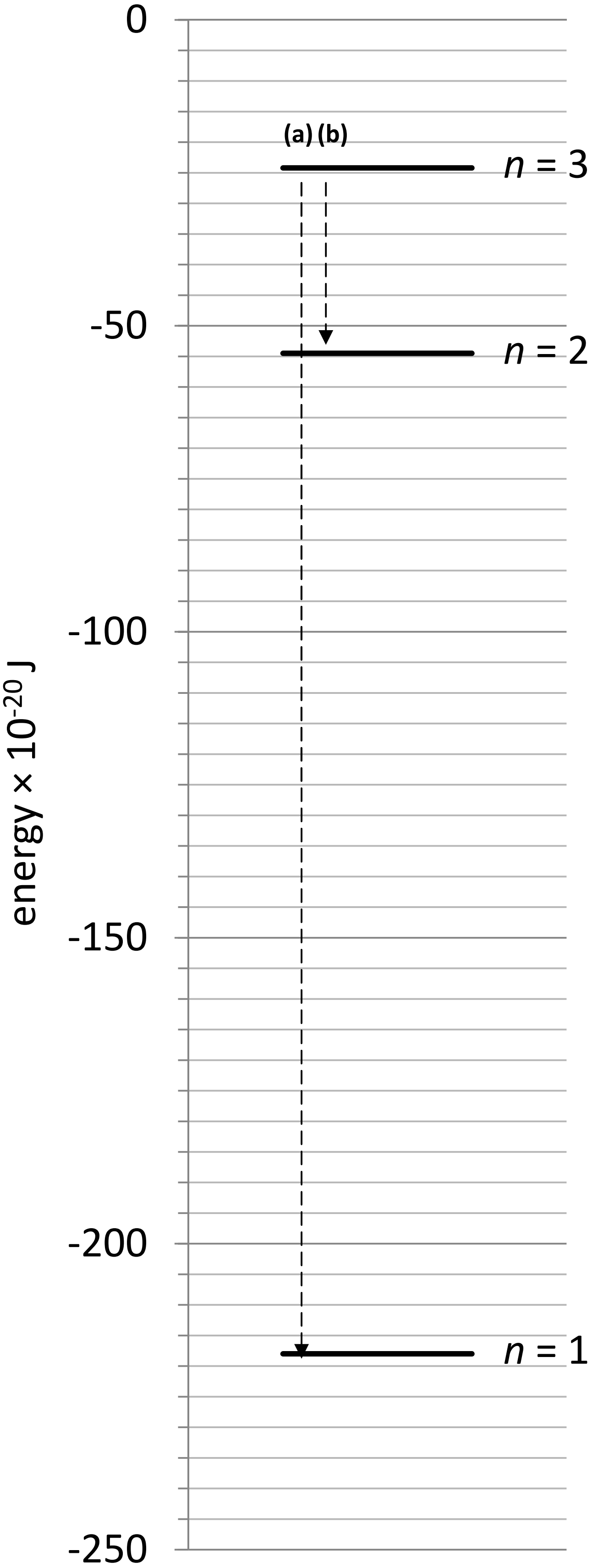
    (b) What colours correspond to these limits?

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

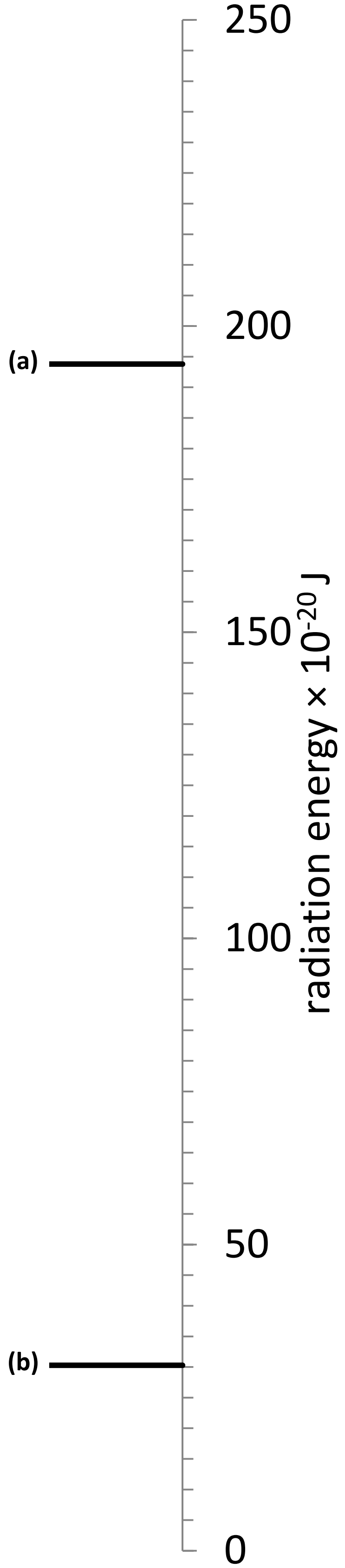
18. What do the lines in the ultraviolet part of the spectrum have in common?

| colour | red | orange | yellow | green | blue | indigo | violet |
|---|---|---|---|---|---|---|---|
| wavelength (nm) | 660 | 610 | 580 | 540 | 470 | 440 | 410 |

**Energy levels of the H atom**



**Atomic Spectrum of the H atom**

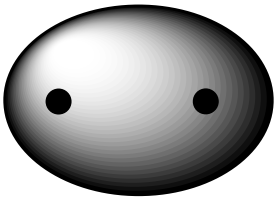


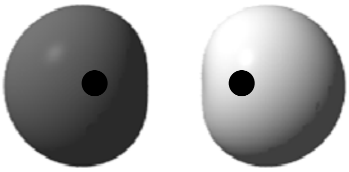
# CHEM1101 Worksheet 5: Molecular Orbitals

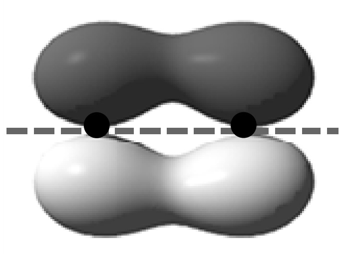
## Model 1: Molecular Orbitals

### σ 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 (●) show the position of the nuclei.


σ

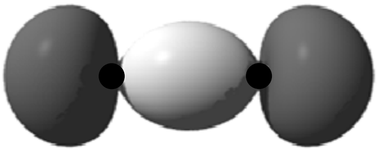

σ

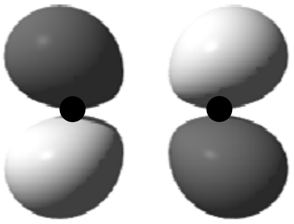

π

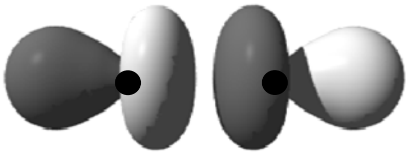
σ orbitals are symmetric around a line joining the two nuclei. π orbitals have a node along this line: they are zero along the *horizontal* dotted line shown above.

## Critical thinking questions

1. Label the orbitals below as σ or π.





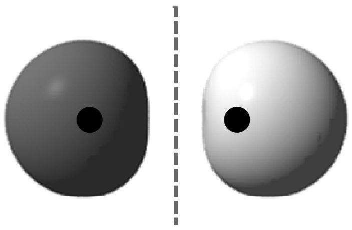


### Bonding and Anti-Bonding Molecular Orbitals

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

Anti-bonding orbitals, 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.


σ*

2. Identify the anti-bonding orbitals on this page and add an asterisk to their σ or π labels.

# Model 2: Molecular Orbital Diagrams

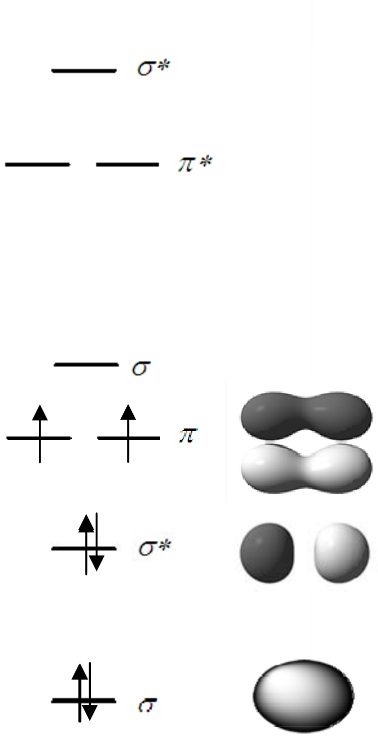
The figure opposite is a *molecular orbital diagram*, or MO diagram, for a diatomic molecule made of second row elements. Each orbital is represented by a line, showing its energy, and may hold a maximum of 2 electrons.

Note that there are 2 π orbitals and 2 π* 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:

bond order = ½ (number of bonding electrons – 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:

bond order = ½ (4 – 2) = 1

## Critical thinking questions

1. Using the labels as a guide, sketch the remaining orbitals from Model 1 on the diagram.

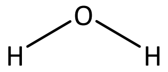
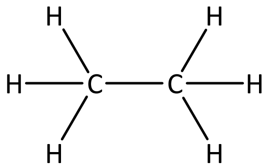
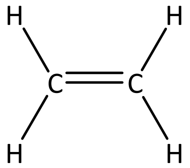
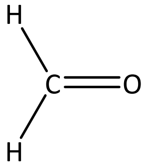
2. Add electrons to the diagram so that it shows the occupation for $N_2$. Calculate its bond order.

3. Add electrons to the diagram so that it shows the occupation for $O_2$. Calculate its bond order.

5. What would be the bond order in nitric oxide, NO?

## Model 3: Single, Double and Triple Bonds

The table below lists Lewis structures and bond orders and energies for selected molecules.

| Molecule | Structure | Bond | Bond Order | Bond Energy (kJ mol$^{-1}$) |
|---|---|---|---|---|
| $H_2O$ |  | O-H | 1 | 498 |
| ethane |  | C-C<br>C-H | 1<br>1 | 376<br>420 |
| ethene |  | C-C<br>C-H | 2<br>1 | 720<br>444 |
| ethyne | $H-C\equiv C-H$ | C-C<br>C-H | 3<br>1 | 962<br>552 |
| carbon dioxide | $O=C=O$ | C-O | 2 | 804 |
| methanal<br>(formaldehyde) |  | C-O<br>C-H | 2<br>1 | 782<br>364 |
| oxygen | $O=O$ | O-O | 2 | 498 |
| nitrogen | $N\equiv N$ | N-N | 3 | 945 |

## Critical thinking questions

1. The title of Model 1 identifies 3 types of bonds. Give an example of each type of bond from the molecules in the table.

2. What is the relationship between the *bond order* of a bond and the designation *single, double* and *triple* bonds?

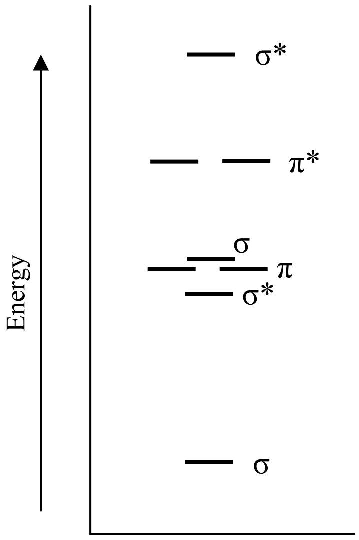
3. Rank the three types of bonds in Model 1 in order of increasing strength.

**Marks**
**5**

- The following relate to the electronic structure of the $N_2^-$ molecular ion.

How many valence electrons are in $N_2^-$?

The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in $N_2^-$. Indicate on this diagram the ground state electronic configuration of $N_2^-$ using the arrow notation for electron spins.



Calculate the bond order of $N_2^-$.

Is the bond strength in $N_2^-$ stronger or weaker than the bond strength in $N_2$? Why?

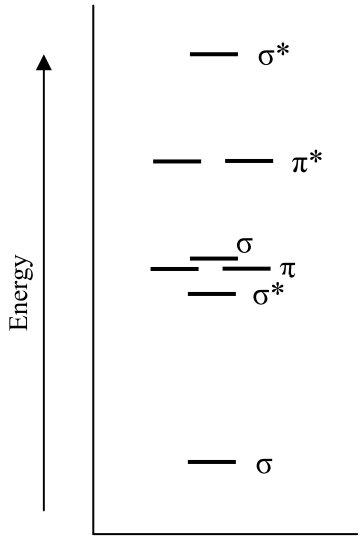
Do you expect $N_2^-$ to be paramagnetic? Explain your answer.

**Week 2 practice exam questions – answers on the web next week**

**Marks**
**6**

- Carbon and nitrogen can combine to form a cyanide ion or a neutral free radical.

  The molecular orbital energy level diagram provided shows the energies of the orbitals for the valence electrons in the free radical CN. Indicate on this diagram the ground state electronic configuration of CN using the arrow notation for electron spins.



How would you expect the magnetic properties of CN to differ from that of $CN^-$?

How would adding an electron to CN to form $CN^-$ affect the strength of the bond between the two atoms? Explain your answer.

Why do we only need to consider the valence electrons when discussing the bonding of CN?

**Week 2 practice exam questions – answers on the web next week**

# Week 3

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## CHEM1101 Worksheet 6 – Lone Pairs and Molecular Geometry

### Model 1: Lone Pairs

Lone pairs are pairs of electrons in a molecule which do not participate in the bonding. As described in Model 2, they play a key role in determining molecular shape and are also the source of the reactivity of many molecules.

For molecules and ions of the type $XY_n$ in which an atom X is surrounded by $n$ Y atoms, the number of lone pairs, $m$, can be easily worked out using the formula::

$$\text{number of lone pairs} = m = \tfrac{1}{2}\,(\text{number of valence electrons} - |\text{ oxidation number }|)^{*}$$

For an *s*-block element, the number of valence electrons is equal to the group number. For a *p*-block element, it is equal to the group number - 10.

The number of valence electrons gives the total number of electrons that an atom has available. The oxidation number reflects the number used to make bonds. The difference between them gives the number of unused electrons: this is halved to give the number of unused or lone pairs.

**Examples**

Cl and F are both in group 17 so both have (17 – 10) = 7 valence electrons.

(a) In $ClF_3$, F has an oxidation number of -1 and Cl has an oxidation number of +3:
number of lone pairs on F = ½ (7 – 1) = 3
number of lone pairs on Cl = ½ (7 – 3) = 2

(b) In $ClF_4^+$, F has an oxidation number of -1 and Cl has an oxidation number of +5:
number of lone pairs on F = ½ (7 – 1) = 3
number of lone pairs on Cl = ½ (7 – 5) = 1

(c) In $ClF_4^-$, F has an oxidation number of -1 and Cl has an oxidation number of +3:
number of lone pairs on F = ½ (7 – 1) = 3
number of lone pairs on Cl = ½ (7 – 3) = 2

### Critical thinking questions

1. How many lone pairs are there on the underlined atom in the molecules and ions below?

| System | Number of Lone Pairs | System | Number of Lone Pairs |
|---|---|---|---|
| $\underline{S}F_2$ | | $\underline{Xe}F_2$ | |
| $\underline{S}F_4$ | | $\underline{Xe}F_4$ | |
| $\underline{S}F_6$ | | $\underline{Xe}F_3^+$ | |
| $\underline{S}OF_4$ | | $\underline{Xe}O_2F_2$ | |

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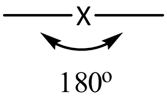
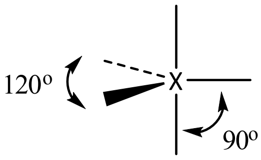
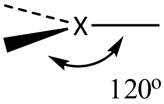
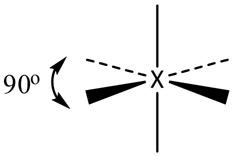
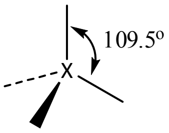
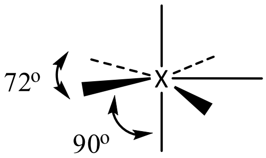
[**] Note that the *absolute* value of the oxidation number is used: the + or – sign is dropped.

## Model 2: Molecular Shape

The ‘Valence Shell Electron Pair Repulsion’ (VSEPR) model assumes that the because of the repulsion between electrons, the bonds and lone pairs surrounding an atom try to get as far from each other as possible. For molecules and ions of the type $XY_n$ in which the central atom X makes *n* bonds and has *m* lone pairs, **the shape is dictated by the total number of bonds and lone pairs: *n* + *m*.**

The 3D-arrangements of bonds and lone pair which maximize the distance between these bonds and lone pairs for common values of (*n* + *m*) are shown in the table below.

| *n* + *m* | Arrangement | | *n* + *m* | Arrangement | |
|---|---|---|---|---|---|
| 2 | linear |  | 5 | trigonal bipyramid |  |
| 3 | trigonal planar |  | 6 | octahedral |  |
| 4 | tetrahedral |  | 7 | pentagonal bipyramid |  |

### Examples

(a) There are 4H attached to the C atom in $CH_4$: $n = 4$. The C atom has an oxidation number of -4 so no lone pairs; $m = 0$. With $n + m = 4 + 0 = 4$, the arrangement is *tetrahedral*.

(b) There are 2O attached to the C atom in $CO_2$: $n = 2$. The C atom has an oxidation number of +4 no lone pairs: $m = 0$. With $n + m = 2 + 0 = 2$, the arrangement is *linear*.

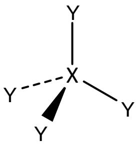
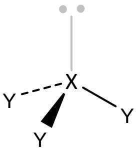
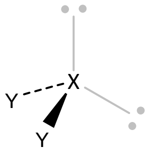
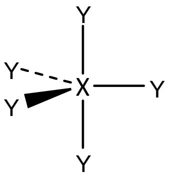
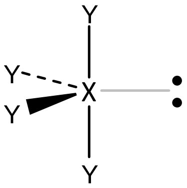
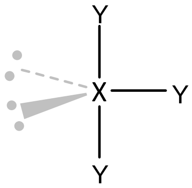
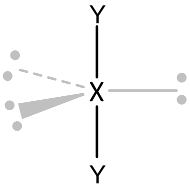
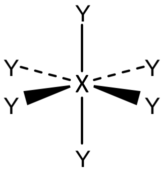
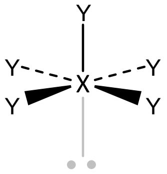
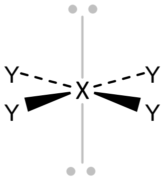
## Critical thinking questions

2. Complete the table below.

| System | *n* | *m* | *n* + *m* | Arrangement |
|---|---|---|---|---|
| $BeF_2$ | | | | |
| $BCl_3$ | | | | |
| $BCl_4^-$ | | | | |
| $PF_5$ | | | | |
| $SF_6$ | | | | |
| $IF_7$ | | | | |

## Model 3: Positioning the Lone 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. The table below shows the geometries possible when $n + m = 4$ and 6.

| $n + m$ | $m = 0$ | $m = 1$ | $m = 2$ | $m = 3$ |
|---|---|---|---|---|
| 4 | <br> <br>tetrahedral | <br> <br>trigonal pyramidal | <br> <br>bent or V shaped | |
| 5 | <br> <br>trigonal bipyramidal | <br> <br>see-saw | <br> <br>T-shaped | <br> <br>Linear |
| 6 | <br> <br>octahedral | <br> <br>square-based pyramid | <br> <br>square planar | |

Note that when $n = 5$, the lone pairs occupy the sites in the equatorial plane.

## Critical thinking questions

3. Sketch and describe the molecular geometries of the following systems.

(a) $H_2O$ (b) $XeO_3$ (c) $ClF_3$ (d) $ClF_4^-$

(e) $ClF_4^+$ (f) $XeF_2$ (g) $XeF_4$ (h) $XeO_2F_2$

# CHEM1101 Worksheet 7: Intermolecular Forces

## Information

Intermolecular forces are the interactions *between* rather than *inside* molecules. They are responsible for many of the physical properties of substances, including their melting and boiling points.

In pure substances, there are 3 important intermolecular forces which may be present:

- *Dipole – dipole forces*. The dipole moment in a molecule will tend to align with those in its neighbours. This type of interaction is only possible if the molecule possesses a dipole.
- *Hydrogen bonds*. This is a particularly strong dipole – dipole interaction involving the interaction between the δ+ H atoms in very polar bonds and lone pairs on very electronegative atoms. Hydrogen bonding therefore requires the presence of both δ+ H atoms *and* electronegative atoms.
- *Dispersion forces*. These forces are present in *all* molecules and atoms. At any moment in time, the electron density in a molecule or atom may not be symmetrical and this leads to a dipole moment. This momentary or *instantaneous* dipole moment *induces* a matching dipoles in neighbouring molecules or atoms by polarizing their electron density.

  Dispersion forces increase with the number of electrons in a molecule.

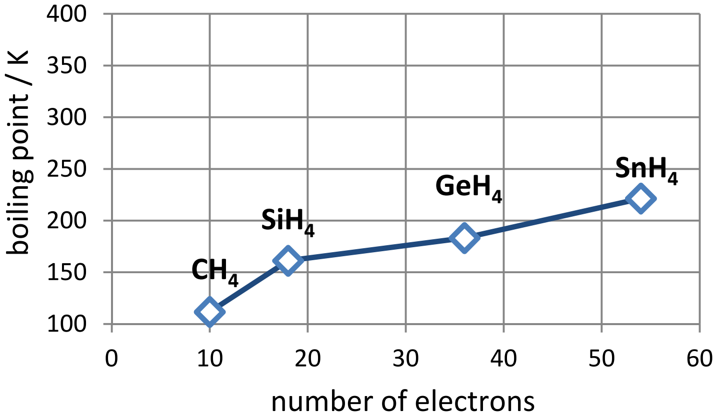
## Model 1: Boiling Points Change Down a Group of the Periodic Table

Molecules are held in the liquid phase due to intermolecular forces so that boiling points are a good guide to their strength.

The figure opposite shows the boiling points of the Group 14 hydrides. All have the same shape but differ in the total number of electrons.

For example:

- C has 6 electrons and each H has 1 electron so $CH_4$ has 6 + 4 × 1 = 10.
- Sn has 50 electrons so $SnH_4$ has 54 electrons.



## Critical thinking questions

1. What happens to the boiling point as the number of electrons increases?

2. What shape are the Group 14 hydrides?

3. Are dipole – dipole forces present in these molecules?

4. Is hydrogen bonding possible in these molecules?

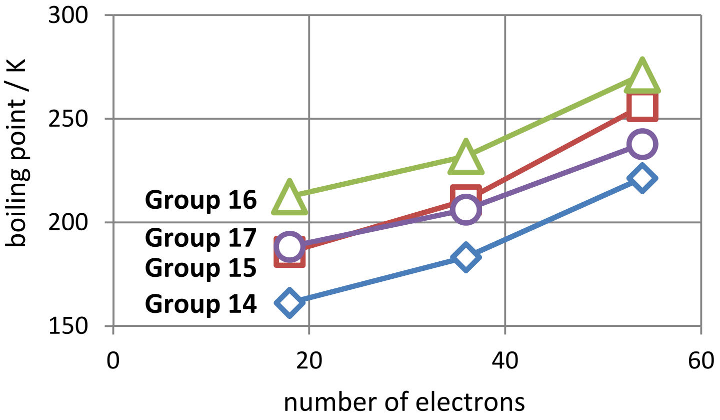
5. What intermolecular force is present in these molecules?

6. Explain why the boiling points vary in the way you described in answer to Q1.

## Model 2: Boiling Points Change Across a Row of the Periodic Table

On the graph to the right, the boiling points for the other hydrides have been added:

- Group 14 $SiH_4$, $GeH_4$ and $SnH_4$
- Group 15 $PH_3$, $AsH_3$ and $SbH_3$
- Group 16 $H_2S$, $H_2Se$ and $H_2Te$
- Group 17 HCl, HBr and HI



## Critical thinking questions

1. Use a Periodic Table to confirm that $SiH_4$, $PH_3$, $H_2S$ and HCl all have 18 electrons.

2. What happens to the boiling point as the number of electrons increases? Why?

3. What is the molecular shape of $PH_3$, $H_2S$ and HCl?

4. Do $PH_3$, $H_2S$ and HCl have dipole moments?

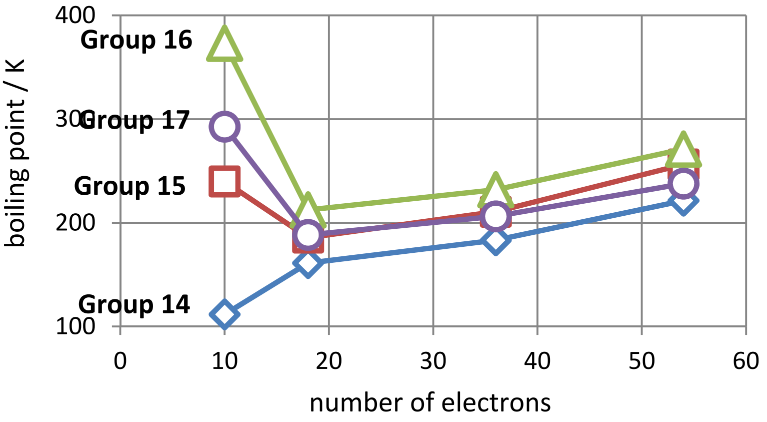
5. Why is the boiling point of $SiH_4$ *lower* than that of $PH_3$, $H_2S$ and HCl?

6. Is the boiling point of $SnH_4$ (54 electrons) higher or lower than the boiling point of $PH_3$ (18 electrons)?

7. Explain your answer to Q6, making sure that it is consistent with your answers to Q2 and Q5.

## Model 3: Anomalous Boiling Points of $NH_3$, $H_2O$ and HF

The graph to the right adds the boiling points of $CH_4$, $NH_3$, $H_2O$ and HF to Model 3. N, O and F are very electronegative and N-H, O-H and H-F bonds are very polar.



## Critical thinking questions

1. How do the boiling points of the Group 14 hydrides change down the group?

   Re-read your answers to Model 1.

2. How many δ+ H atoms are there on electronegative element in the molecules below?

   (a) $NH_3$ (b) $H_2O$ (c) HF

3. How many lone pairs are there on electronegative element in these molecules?

   (a) $NH_3$ (b) $H_2O$ (c) HF

4. Explain why the boiling points of $NH_3$, $H_2O$ and HF (10 electrons) are *higher* than those of $PH_3$, $H_2S$ and HCl (18 electrons) Refer to the **Information** if you are unsure.

5. Given your answer to Q4, suggest why the boiling point of $NH_3$ (10 electrons) is *lower* than that of $SbH_3$ (54 electrons).

6. Order the N-H, O-H and F-H bonds in terms of their polarity.

7. Predict the *relative* strength of the intermolecular forces between *two* $NH_3$ molecules, *two* $H_2O$ and *two* HF molecules.

8. How many hydrogen bonds can each $NH_3$ molecule make on average in $NH_3$(l)? (*Hint*: re-read your answers to Q2 and Q3).

9. How many hydrogen bonds can each HF molecule make on average in HF(l)? (*Hint*: re-read your answers to Q2 and Q3).

10. How many hydrogen bonds can each $H_2O$ molecule make on average in $H_2O$(l)? (*Hint*: re-read your answers to Q2 and Q3).

11. Use your answers to Q6 – Q10 to explain why the boiling points vary in the order $NH_3 < HF < H_2O$.

12. Many textbooks and websites state that dispersion forces are weaker than hydrogen bonding and dipole – dipole forces. Critically analyse this statement in the light of the evidence in Models 1 – 3.

# CHEM1101 Worksheet 8 – The Ideal Gas Law: *PV = nRT*

## Model 1: The Gas Laws

- $T$ (K) – Kelvin or absolute temperature = $T$ (°C) + 273°. $T$(K) is always ≥ 0 K
- Boyle's Law (1660). The volume of a gas varies inversely with pressure:

  $V = k_B \times \frac{1}{P}$ $k_B$ is Boyle's constant

- Charles' Law (1887). The volume of a gas varies linearly with temperture:

  $V = k_C \times T$ $k_C$ is Charles' constant

- Avogadros' Hypothesis (1812). The volume of a gas varies linearly with the number of moles:

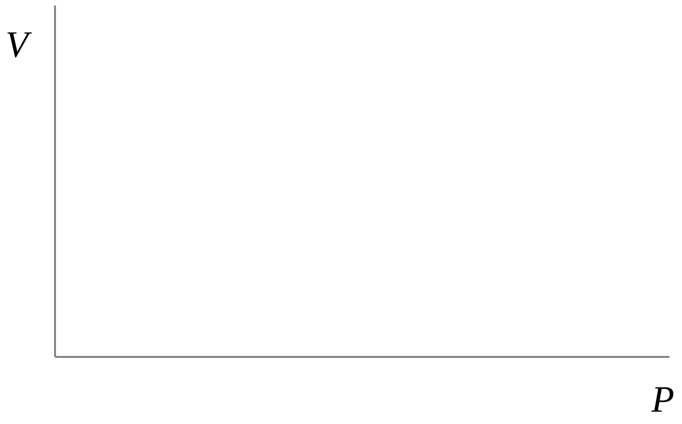
  $V = k_A \times n$ $k_C$ is Avogadro's gas constant

- These are unified in the ideal gas law:

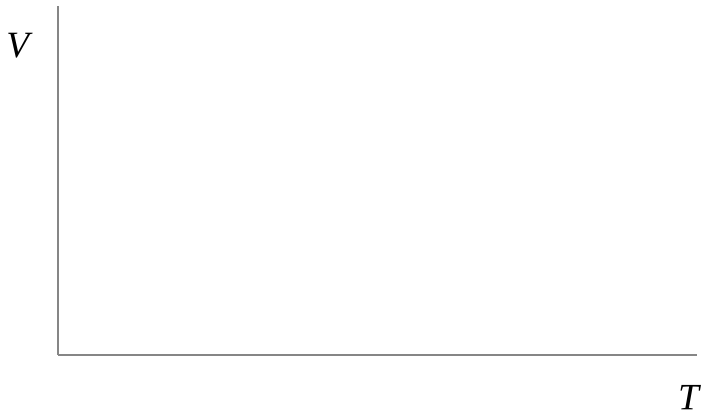
  $PV = nRT$ $R$ is the universal gas constant

## Critical thinking questions

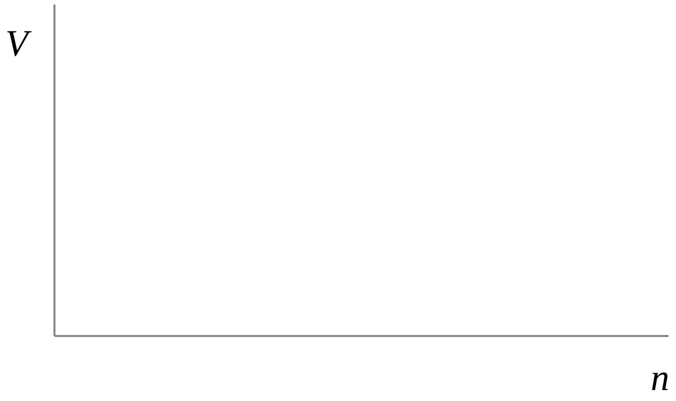
1. *Sketch* on the graph below how the volume of a gas changes as the pressure is increased.



2. *Sketch* on the graph below how the volume of a gas changes as the temperature is increased.



3. *Sketch* on the graph below how the volume of a gas changes as the number of moles of gas is increased.



4. For each case, rearrange the ideal gas law to show that it is consistent with the given law or hypothesis and obtain an expression for the corresponding constant.

   (a) Boyle's Law, $k_B$

   (b) Charles' Law, $k_C$

   (c) Avogadro's hypothesis, $k_A$

5. One mole of gas occupies 22.414 L at a pressure of 1.000 atm and a temperature of 0 °C (273.15 K). This is known as standard temperature and pressure or STP.

   Use the ideal gas law to work out the value of the universal gas constant, $R$, and its units.

6. The S.I. unit for volume is $m^3$ and for pressure is Pa where 1 $m^3$ = 1000 L and 1 atm = $1.01325 \times 10^5$ Pa.

   (a) What is the volume occupied by one mole of gas at STP in $m^3$?

   (b) Use the ideal gas law to work out the value of the universal gas constant, $R$, and its units when volume and pressure are given in S.I. units.

## Model 2: Partial Pressures

In a mixture of gases, the *partial pressure* of a gas is the pressure it would have if it alone occupied the volume. The total pressure of a gas mixture is the sum of the partial pressures of each ndividual gas in the mixture. The partial pressure of a gas A is given by:

$$P_A = n_A \frac{RT}{V}$$

The total pressure of the gases in a mixture is the sum of the partial pressures of each component:

$$P = P_A + P_B + P_C + P_D + .... = \sum_i P_i$$

## Critical thinking questions

7. The density of air at 1.000 atm and 25°C is 1.186 g $L^{-1}$.

   (a) Assuming that air is 80% nitrogen and 20% oxygen by volume, what are the partial pressures of the two gases?

   (b) Calculate the *average* molecular mass of air.

   (c) Assuming that air is only made up of nitrogen and oxygen, calculate the % by mass of $N_2$ and $O_2$ in air.

**Exercises**

These exercises are based on those used in the theory parts of scuba diving courses.

The density of salt water is 1.03 g $mL^{-1}$ which translates to an increase in pressure of 1.00 atm for every 10.0 m of depth below the surface. If the pressure at the surface is 1.00 atm, it will be 2.00 atm at 10.0 m, 3.00 atm at 20.0 m, 4.00 atm at 30.0 m etc. Scuba equipment controls the air flow to the lungs so that their *volume* is the same at depth as at the surface. It does this by providing air at a *pressure* equal to that of the water at that depth.

1. A balloon is inflated at the surface to 6.0 L, the approximate volume of the lungs. What volume would the balloon have at a depth of 15.0 m?

2. At a depth of 30.0 m, the balloon is filled from a cylinder to a volume of 5.0 L and sealed. What volume will the balloon be at the surface?

3. A ‘reverse block’ is a painful effect that occurs when air is trapped inside a cavity (such as in the ears or inside a tooth) during a diver’s ascent. Discuss with your group the cause of the pain.

4. A 12 L air cylinder is filled to a pressure of 200. atm in an air conditioned diving shop at 22 °C. What will be the pressure inside the tank once it has been left in the sun at 35 °C?

5. What happens to the *density* of the air in a diver’s lungs during descent?

6. What is the partial pressure of $O_2$ in a diver’s lungs at a depth of 10.0 m?

7. Oxygen toxicity occurs when its partial pressure reaches around 1.6 atm[†]. What depth of water does this correspond to?

---

[†] This figure is dependent on the time spent and the individual physiology and is used here for illustrative purposes only

**Marks**

- A helium balloon is filled on the ground, where the atmospheric pressure is 768 mmHg. The volume of the balloon is 8.00 $m^3$. When the balloon reaches an altitude of 4200 m, its volume is found to be 16.8 $m^3$. Assuming that the temperature remains constant, what is the air pressure at 4200 m in mmHg? **2**

Answer:

- The volume of a gas is 40.0 mL at –15 °C and 1.30 atm. At what temperature (°C) will the gas have a pressure of 1.00 atm and a volume of 65.0 mL? **2**

Answer:

## Week 3 practice exam questions – answers on the web next week

**Marks**
**5**

- A gaseous hydrocarbon is found to contain 85.6 % carbon and 17.4 % hydrogen by mass. A 10.0 L sample of this gas has a mass of 23.78 g at 1.00 atm and 298 K. Show, using the ideal gas law, that the hydrocarbon is butane, $C_4H_{10}$.

If heated air is injected into a balloon, it will rise. Use the ideal gas equation to explain why this happens.

## Week 3 practice exam questions – answers on the web next week

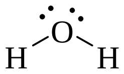
**Marks**
**2**

- Draw the major resonance contributors of nitryl chloride, $ClNO_2$.

What is the bond order of the N–O bonds?

**5**

- Complete the following table showing the number of valence electrons, a Lewis structure and the predicted shape of each of the following species.

| Molecule name | Chemical formula | Number of valence electrons | Lewis structure | Geometry of species |
|---|---|---|---|---|
| *e.g.* water | $H_2O$ | 8 |  | bent |
| beryllium difluoride | $BeF_2$ | | | |
| carbonate ion | | | | |
| chlorine trifluoride | | | | |

**Week 3 practice exam questions – answers on the web next week**

# Week 4

## CHEM1101 Worksheet 9: Introduction to Thermodynamics

### Model 1: Calorimetry

*Heat* is not the same thing as *temperature*, even though in common usage these concepts are often used interchangeable. *Heat* is the *energy transferred* from one object to another due to a difference in their temperature. Heat, therefore, has units of energy (joules, J). An object at a higher temperature will transfer energy to one at a lower temperature until they reach *thermal equilibrium* – until they are at the same temperature.

The amount of heat gained (to raise the temperature) or lost (to lower the temperature) by an object can be quantified with the following equations:

(1) $q = mC\Delta T$ or (2) $q = nc\Delta T$

where $q$ is the heat change (in J), $m$ is the mass (in g), $n$ is the number of moles (in mol), $C$ is the specific heat capacity (in J $g^{-1}$ $K^{-1}$) and $c$ is the molar heat capacity (J $mol^{-1}$ $K^{-1}$).

The change in temperature, $\Delta T$, is always:

$\Delta T = T_{\text{final}} - T_{\text{initial}}$

Hence, if the temperature increases, $\Delta T$ is positive and, if the temperature decreases, $\Delta T$ is negative.

The two equations (1) and (2) will give the same value for $q$ as long as the *specific heat capacity* is used when you know the mass and the *molar heat capacity* is used when you know the number of moles.

The specific and molar heat capacities are a measure of how much energy is needed to raise the temperature of 1 g or 1 mol, respectively, of an object by 1 K. Every object has a different heat capacity: some substances, like metals, are easier to heat than others, like rocks.

### Critical thinking questions

1. Under what circumstances would you get a negative value for the heat, $q$?

2. Provide an equation for converting between the specific heat capacity, $C$, and the molar heat capacity, $c$. (Hint: use the relationship between the number of moles and the mass of a substance).

3. If the temperature of a substance increases from 25 °C to 35 °C, what is ΔT (in Kelvin)?

4. Given your answer to Q3, explain to your group whether it is necessary to convert temperatures to Kelvin when working out ΔT.

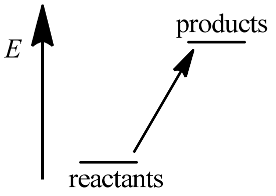
5. The specific heat capacity of olive oil is 2.0 J $g^{-1}$ $K^{-1}$. How much energy has to be transferred to 2.0 g of olive oil in a saucepan to heat it from room temperature to 130 °C? Assume that the room is at 25 °C.

6. The specific heat capacity of water is 4.18 J $g^{-1}$ $K^{-1}$. Is it easier or harder to heat water or olive oil?

7. The molar heat capacity of gold is 25.413 J $mol^{-1}$ $K^{-1}$. A necklace that weighs 1.2 g requires 0.426 J of energy to heat by 2.00 K. Is the necklace pure gold? (*Hint*: you will first need to either convert the molar heat capacity to the specific heat capacity using the equation you worked out in Q2 or convert the mass into the moles).

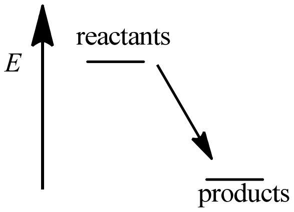
## Model 2: Energy

When a physical or chemical change occurs in a system, energy is either absorbed or released. Energy is required to break chemical bonds, and conversely, energy is released when bonds are made. Usually, a chemical reaction involves *both* breaking *and* making bonds so energy can either be released or absorbed, depending on whether the bonds that are made are stronger or weaker than the bonds broken. The energy change in a chemical reaction often leads to a change in *thermal energy*: heat.



If the products are *less* stable (*higher* in energy) than the reactants, the reaction involves an increase in the energy.

This energy must be supplied and so the reaction absorbs energy from the surroundings making it feel colder.



If the products are *more* stable (*lower* in energy) than the reactants, the reaction involves a decrease in the energy.

This energy is released to the surroundings making it feel hotter.

## Critical thinking questions

1. Which of the two figures above corresponds to the following reactions?

   (a) reactants → products + heat (b) reactants + heat → products

2. If *ex* is the Greek prefix for *out* and *endo* is the Greek prefix for *in*, which of the above reactions is exothermic and which is endothermic? What do you think *thermo* means?

3. Will a beaker containing an endothermic reaction get colder or hotter?

The amount of energy absorbed or released by a reaction at constant pressure is called the *enthalpy of reaction*, $\Delta H$. When energy, as heat, is *absorbed* in a reaction, ΔH is positive. This occurs when the bonds made in the products are weaker than those broken in the reactants.

4. If heat is released in a reaction, is $\Delta H$ positive or negative?

5. If heat is released in a reaction, are the bonds stronger or weaker in the products than in the reactants?

6. Is $\Delta H$ positive or negative for the two types of reaction:

   (a) exothermic (b) endothermic

# CHEM1101 Worksheet 10: 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?

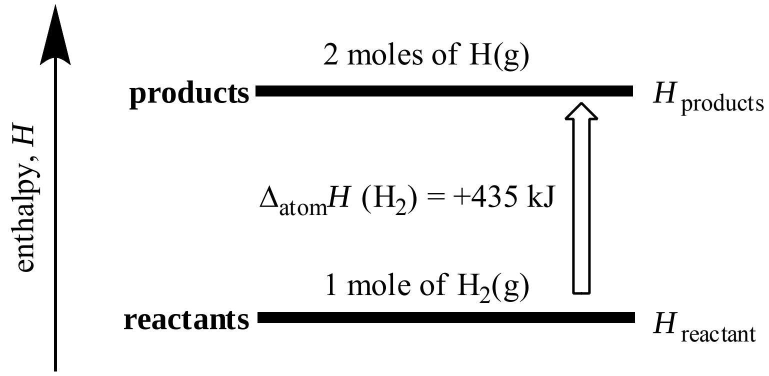
(a) $H_2(g) \rightarrow 2H(g)$ (b) $Cl_2(g) \rightarrow 2Cl(g)$

(c) $H(g) + Cl(g) \rightarrow HCl(g)$

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

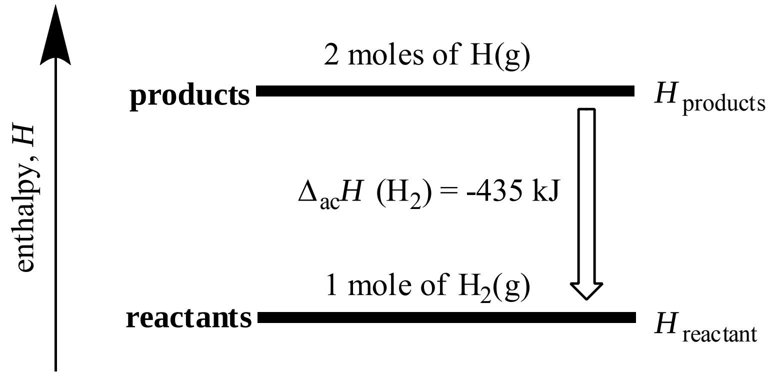
When a mole of a compound is broken apart into its constituent gas phase atoms, energy is consumed and the energy change is called the enthalpy of atomization ($\Delta_{atom}H$):

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



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 ($\Delta_{ac}H$):

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



## Critical thinking questions

1. What is the relationship between $\Delta_{atom}H$ and $\Delta_{ac}H$ for a *compound* like $H_2$?

2. What is the value of $\Delta H$ for the overall process of separating one mole of $H_2(g)$ into its constituent atoms and then reforming one mole of $H_2(g)$?

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

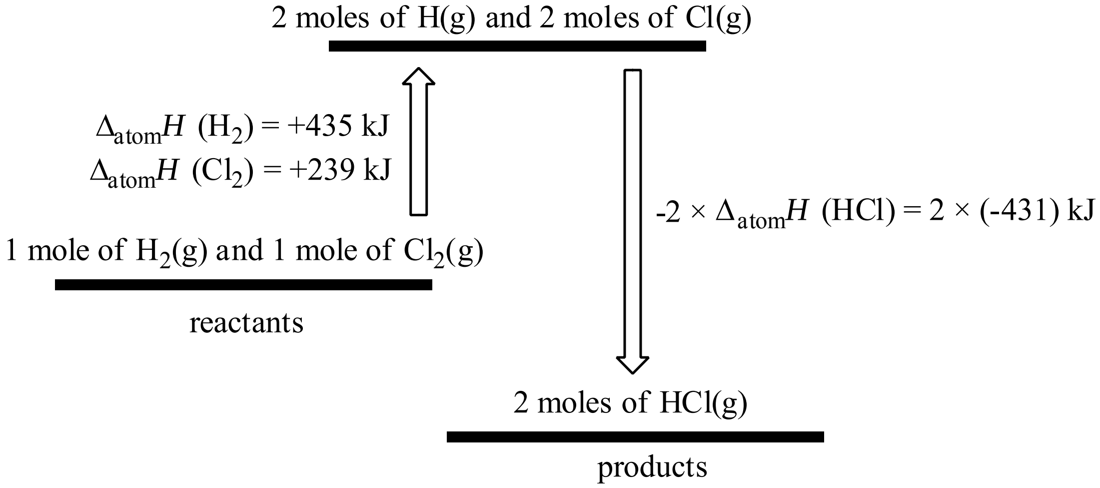
To determine the overall value of $\Delta H$ for a reaction, we can imagine the reaction taking place by:

(i) breaking apart all of the reactant molecules into their constituent atoms: $\Delta_{atom}H$ (reactants)

(ii) 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:

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



## Critical thinking questions

1. Why is the $\Delta H$ associated with the upward arrow in Model 3 a *positive* number?

2. Why is the $\Delta H$ associated with the downward arrow in Model 3 a *negative* number?

3. What is the value of $\Delta H$ for the overall reaction in Model 3?

4. Using your answer to Q2, rewrite the equation below so that it involves only $\Delta_{ac}H$ (reactants) and $\Delta_{ac}H$ (products).

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

5. Using your answer to Q2, rewrite the equation below so that it involves only $\Delta_{atom}H$ (reactants) and $\Delta_{atom}H$ (products).

   $\Delta_{rxn}H = \Delta_{atom}H$ (reactants) + $\Delta_{ac}H$ (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.

## Model 4: Enthalpy of Reaction using $\Delta_f H$

In Model 2, 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.

$$\Delta_{rxn}H = \Delta_{ac}H \text{ (products)} - \Delta_{ac}H \text{ (reactants)} \qquad (4)$$

An alternative is to use the enthalpy change of formation of a compound ($\Delta_f H$) 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 $O_2(g)$ for oxygen.

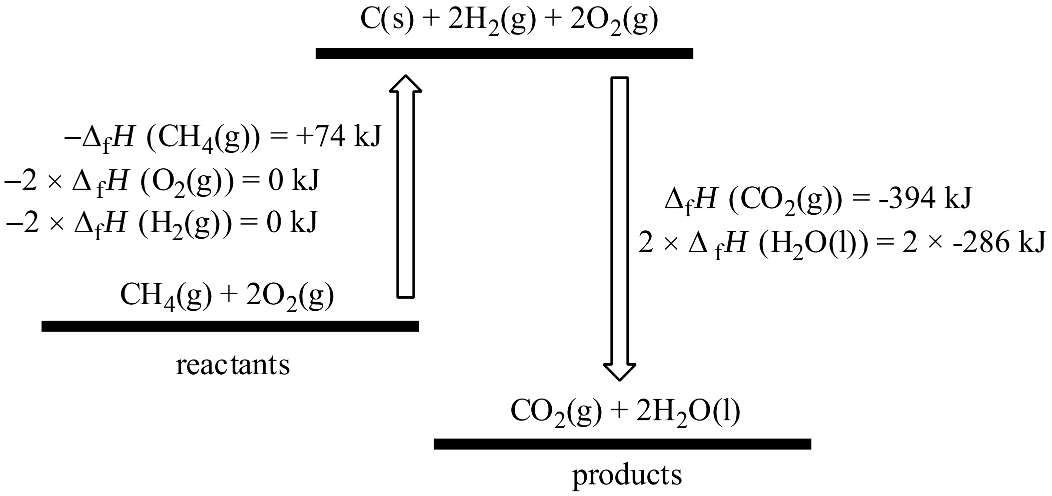
Using this method, the equation for the enthalpy of reaction becomes:

$$\Delta_{rxn}H° = \Delta_f H° \text{ (products)} - \Delta_f H° \text{ (reactants)} \qquad (5)$$

The enthalpy of formation of $CO_2(g)$ is then the energy change for its formation from graphite and $O_2(g)$:

$$C(s) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g)$$

The enthalpy change for the combustion of methane is represented on the energy level diagram below. On the left, $CH_4(g)$ and $O_2(g)$ are broken up into their elements in the standard states, graphite ($C(s)$), $H_2(g)$ and $O_2(g)$. This is the *reverse* of their formation so the energy required is $-\Delta_f H°$ (reactants). On the right, $CO_2(g)$ and $H_2O(g)$ are formed from the same elements in the same states so the energy change is $+ \Delta_f H°$ (products).



## Critical thinking questions

1. Why are $\Delta_f H°\ (O_2(g))$ and $\Delta_f H°\ (H_2(g))$ both equal to 0 kJ? (*Hint*: what is the reaction in each case?)

2. What is $\Delta_{rxn}H°$ for the reaction $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$?

3. Use equation (5) and the data below to calculate $\Delta_{rxn}H°$ for the reaction $MgO(s) + CO_2(g) \rightarrow MgCO_3(s)$.
$\Delta_f H°$: $MgO(s) = -602\ \text{kJ mol}^{-1}$, $CO_2(g) = -394\ \text{kJ mol}^{-1}$ and $MgCO_3(s) = -1096\ \text{kJ mol}^{-1}$

**Marks**
**3**

- Pentane, $CH_3CH_2CH_2CH_2CH_3$, burns completely in oxygen to form $CO_2(g)$ and $H_2O(g)$. Use the atomization enthalpies given below to calculate the enthalpy change for this process.

| | $\Delta_{atom}H$ (kJ mol$^{-1}$) | | $\Delta_{atom}H$ (kJ mol$^{-1}$) |
|---|---|---|---|
| pentane | 6352 | $CO_2$ | 1608 |
| $O_2$ | 498 | $H_2O$ | 926 |

Answer:

**Marks**
**5**

- The current "petrochemical economy" is based on the combustion of fossil fuels, of which octane is a typical example.

$$2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)$$

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$^{-1}$

Answer:

**Week 4 practice exam questions – answers on the web next week**

**Marks**
**6**

- The thermite reaction is written below. Show that the heat released in this reaction is sufficient for the iron to be produced as molten metal.

$$2Al(s) + Fe_2O_3(s) \rightarrow Al_2O_3(s) + 2Fe(l)$$

Assume that the values in the table are independent of temperature.

| Substance | Enthalpy of formation, $\Delta_f H^o$ kJ mol$^{-1}$ | Molar heat capacity, $C_p$ J K$^{-1}$ mol$^{-1}$ | Melting point $^o$C | Enthalpy of fusion kJ mol$^{-1}$ |
|---|---|---|---|---|
| Al | 0 | 24 | 660 | 11 |
| $Al_2O_3$ | –1676 | 79 | 2054 | 109 |
| Fe | 0 | 25 | 1535 | 14 |
| $Fe_2O_3$ | –824 | 104 | 1565 | 138 |

**Week 4 practice exam questions – answers on the web next week**

# Week 5

## CHEM1101 Worksheet 11: Free Energy And Equilibrium

### Model 1: Enthalpy ($\Delta_{rxn}H$) and Entropy ($\Delta_{rxn}S$) of Reaction

In Model 3 in week 10, 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:

$$\Delta_{rxn}H° = \Delta_f H° \text{ (products)} - \Delta_f H° \text{ (reactants)} \qquad (1)$$

The change in entropy in a reaction can similarly be calculated as the difference in the entropies of the reactants and products:

$$\Delta_{rxn}S° = S° \text{ (products)} - S° \text{ (reactants)} \qquad (2)$$

Nitrogen dioxide, $NO_2$, is a prominent air pollutant. At low temperatures, it is in equilibrium with its dimer, $N_2O_4$. Starting from $NO_2$, the formation of the dimer can be studied using one of the two equations below:

$$2NO_2(g) \rightleftharpoons N_2O_4(g) \qquad (A)$$

$$NO_2(g) \rightleftharpoons \tfrac{1}{2}\, N_2O_4(g) \qquad (B)$$

Starting from the dimer, the formation of $NO_2$ can be studied using one of the two equations below:

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \qquad (C)$$

$$\tfrac{1}{2}\, N_2O_4(g) \rightleftharpoons NO_2(g) \qquad (D)$$

### Critical thinking questions

1. Using the data below, calculate $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ for reaction A.

   $\Delta_f H°$: $NO_2(g)$, 33 kJ mol$^{-1}$, $N_2O_4(g)$ 9 kJ mol$^{-1}$. $S°$: $NO_2(g)$, 240 J K$^{-1}$ mol$^{-1}$, $N_2O_4(g)$ 304 J K$^{-1}$ mol$^{-1}$

2. Explain in *words* the origin of the *sign* of $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ in terms of the chemical changes in the reaction.

3. Calculate $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ for reaction B. How are these values related to your answer to Q1?

4. Calculate $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ for reaction C and explain in *words* the origin of the *sign* of $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ in terms of the chemical changes in the reaction.

5. What are the values of $\Delta_{rxn}H°$ and $\Delta_{rxn}S°$ for reaction D?

## Model 2: Free Energy of Reaction ($\Delta_{rxn}G$)

Reactions can be favoured if the products are more stable than the reactants. This occurs when the *enthalpy decreases*: $\Delta_{rxn}H < 0$. Reactions can also be favoured if the *entropy increases*: $\Delta_{rxn}S > 0$. Depending on the reaction, these factors can work together or in opposition. They are combined in the definition of the change in the *free energy*, $\Delta_{rxn}G$:

$$\Delta_{rxn}G° = \Delta_{rxn}H° - T\Delta_{rxn}S° \qquad (3)$$

Because a favourable reaction may have $\Delta_{rxn}H < 0$ and / or $\Delta_{rxn}S > 0$, a favourable reaction will have $\Delta_{rxn}G < 0$.

## Critical thinking questions

1. Is reaction A in Model 1 favourable or unfavourable with respect to the *enthalpy* factor?

2. Is reaction A in Model 1 favourable or unfavourable with respect to the *entropy* factor?

3. Is reaction C in Model 1 favourable or unfavourable with respect to the *enthalpy* factor?

4. Is reaction C in Model 1 favourable or unfavourable with respect to the *entropy* factor?

5. Given your answers to Q1 – 4 and the equation for $\Delta_{rxn}G°$ above, what additional factor needs to be considered to predict whether reaction A or C is favourable?

6. Calculate $\Delta_{rxn}G°$ for reaction A at the two temperatures below and predict whether the reaction is favourable.
   (a) $T = 298$ K
   (b) $T = 398$ K

7. Calculate $\Delta_{rxn}G°$ for reaction C at the two temperatures below and predict whether the reaction is favourable.
   (a) $T = 298$ K
   (b) $T = 398$ K

8. Using your answer to Q6, predict what happens to an *exothermic* reaction as the temperature is increased.

9. Using your answer to Q7, predict what happens to an *endothermic* reaction as the temperature is increased.

10. What combination of signs for $\Delta_{rxn}H$ and $\Delta_{rxn}S$ lead to a reaction that is *never* favourable?

## Model 3: The Equilibrium Constant

Many chemical reactions lead to a mixture of reactants and products. You will end up with a mixture of both $NO_2(g)$ and $N_2O_4(g)$ whether you start with pure $NO_2(g)$ or pure $N_2O_4(g)$. 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.

$$w\mathrm{W(g)} + x\mathrm{X(g)} \rightleftharpoons y\mathrm{Y(g)} + z\mathrm{Z(g)}$$

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:

$$K_c = \frac{[\mathrm{Y(g)}]^y[\mathrm{Z(g)}]^z}{[\mathrm{W(g)}]^w[\mathrm{X(g)}]^x}$$

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 Z) of the equation.

### Critical thinking questions

1. Write down the expression for $K_c$ for reactions A, B, C and D in Model 1.

$K_c$ (A) = ――――――  $K_c$ (B) = ――――――  $K_c$ (C) = ――――――  $K_c$ (D) = ――――――

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)  (b) $K_c$ (A) and $K_c$ (C)

3. At equilibrium at room temperature, $[NO_2(g)] = 1.60$ M and $[N_2O_4] = 0.20$ M. Calculate the values of $K_c$(A), $K_c$(B) and $K_c$(C) and hence confirm your analysis in Q2.

## Model 4: The Reaction Quotient

The reaction quotient, $Q_c$, for a reaction $w$W(g) + $x$X(g) $\rightleftharpoons$ $y$Y(g) + $z$Z(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.

From model 3, at equilibrium $[NO_2(g)] = 1.60$ M, $[N_2O_4] = 0.20$ M and $K_c = 0.078$.

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

## Critical thinking questions

1. Predict what will happen to this reaction if more $NO_2$ is added so that $[NO_2(g)] = 2.00$ M?

2. Predict what will happen to this reaction if instead $NO_2$ is removed so that $[NO_2(g)] = 1.00$ M?

3. Calculate the values for $Q_c$ for these two experiments.

   (a) $[NO_2(g)] = 2.00$ M and $[N_2O_4] = 0.20$ M: $Q_c$

   (b) $[NO_2(g)] = 1.00$ M and $[N_2O_4] = 0.20$ M: $Q_c$

4. Using your answers to Q1 - 3, what happens to a reaction if

   (a) $Q_c < K_c$

   (b) $Q_c > K_c$

**Marks**

- Explain the difference between an equilibrium constant and a reaction quotient. **2**

**2**

The following reactions have been demonstrated in mammalian liver at 37 °C and pH 7.5.

$\text{aspartate} + \text{citrulline} \rightleftharpoons \text{argininosuccinate} + H_2O \qquad K_{eq} = 13$

$\text{argininosuccinate} \rightleftharpoons \text{arginine} + \text{fumarate} \qquad K_{eq} = 4.5$

$\text{fumarate} + NH_4^+ \rightleftharpoons \text{aspartate} \qquad K_{eq} = 0.17$

Calculate the equilibrium constant at 37 °C and pH 7.5 for the following reaction.

$$\text{arginine} + H_2O \rightleftharpoons \text{citrulline} + NH_4^+$$

Answer:

## Week 5 practice exam questions – answers on the web next week

**Marks**
**5**

- Methanol, $CH_3OH$, is produced commercially by the catalysed reaction of carbon monoxide and hydrogen gas. $K_p$ for this reaction at 600 K is $1.13 \times 10^{-6}$.

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

The reaction is exothermic, yet the equilibrium favours the reactants. Explain why this is the case.

The reaction vessel at 600 K is filled with 20.0 atm of CO(g) and 20.0 atm $H_2(g)$. What is the final pressure of $CH_3OH(g)$ at equilibrium?

Answer:

Under what conditions of temperature and pressure do you think an industrial reactor would function to optimise the production of methanol? Explain.

**Week 5 practice exam questions – answers on the web next week**

**Marks**
**3**

- Solid $NH_4HS$ in placed in an evacuated container at 25 ºC and the following equilibrium is established.

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \qquad \Delta H^\circ = +93\ \text{kJ mol}^{-1}$$

At equilibrium, some solid $NH_4HS$ remains in the container. Predict and explain each of the following.

(a) The effect on the equilibrium partial pressure of $NH_3$ gas when additional solid $NH_4HS$ is introduced into the container.

(b) The effect on the amount of solid $NH_4HS$ present when the volume of the container is decreased.

(c) The effect on the amount of solid $NH_4HS$ present when the temperature is increased.

**Week 5 practice exam questions – answers on the web next week**

**Marks**
**2**

- $Fe_2O_3$ can be reduced by carbon monoxide according to the following equation.

$$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(s) + 3CO_2(g) \qquad K_p = 19.9 \text{ at } 1000 \text{ K}$$

At 1000 K, what are the equilibrium partial pressures of CO and $CO_2$ if the only gas initially present is CO at a partial pressure of 0.978 atm?

| | |
|---|---|
| $p$(CO) = | $p(CO_2)$ = |

**Week 5 practice exam questions – answers on the web next week**

# Week 6

## CHEM1101 Worksheet 12: Electrochemistry

### Model 1: Reduction Potentials

The **standard reduction potential**, $E^0_{\text{red}}$ has units of volts (V) and is a measure of a species ability to attract electrons. The *more positive* the reduction potential, the *stronger* is the attraction for electrons. Put another way, the *more positive* the reduction potential, the easier the reduction occurs. Some standard reduction potentials are given below.

| | Reduction reaction | $E^0_{\text{red}}$ (V) |
|---|---|---|
| (1) | $\mathrm{Ag^+(aq) + e^- \rightarrow Ag(s)}$ | +0.80 |
| (2) | $\mathrm{Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)}$ | +0.34 |
| (3) | $\mathrm{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)}$ | -0.14 |
| (4) | $\mathrm{Zn^{2+}(aq) + 2e^- \rightarrow Zn(s)}$ | -0.76 |

### Critical thinking questions

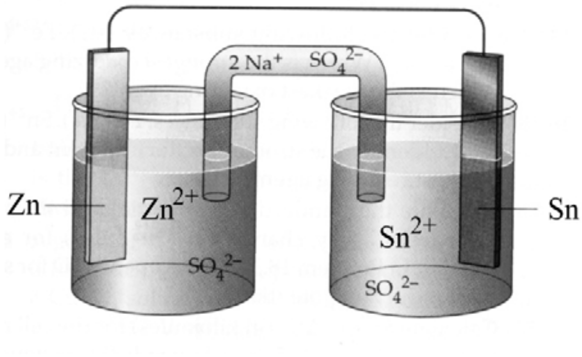
1. Which is a stronger **oxidising** agent: $Ag^+$ or $Cu^{2+}$? Explain how you can tell in terms of the reduction potentials.

2. If reactions (1) and (2) are added together as a redox reaction which do you think will proceed as a reduction and which as an oxidation? (*Hint*: which one will reverse?)

3. Apply the same logic to reactions (3) and (4). Does it matter that they both have negative reduction potentials?

### Model 2: Voltaic Cells

We can harness the electrical energy in a redox reaction, to make a battery, by setting up a **voltaic cell**. To do this, two half reactions are separated into compartments and electrodes are used to facilitate the electron transfer. The potentials for the two reactions are:



$\mathrm{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)}$ $\quad E^0_{\text{red}} = -0.14$ V
$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-}$ $\quad E^0_{\text{ox}} = +0.76$ V

This gives an overall voltmeter reading of:

$E^0_{\text{cell}} = E^0_{\text{ox}} + E^0_{\text{red}} = +0.62$ V.

### Critical thinking questions

1. Explain why the Zn half reaction is proceeding as an oxidation and why +0.76 V is used as the potential for its half cell instead of -0.76 V as in the table in Model 1?

2. Which electrode (Zn or Sn) will *lose* mass and which one will *gain* mass?

3. Does oxidation or reduction occur at the cathode?

4. Which of the following statements are correct?

   (a) Electrons flow through the wire, towards the zinc electrode.
   (b) Electrons flow through the wire, towards the tin electrode.
   (c) Electrons flow through the salt bridge, towards the zinc electrode.
   (d) Electrons flow through the salt bridge, towards the tin electrode.

5. Electrons flow from the *negative* electrode to the *positive* electrode. Which is positive, the anode or the cathode?

6. The salt bridge contains $Na^+(aq)$ and $SO_4^{2-}(aq)$. Do these ions *move* when the cell is operating and, if so, in which direction(s)?

7. If an electrochemical cell with Ag and Cu electrodes was setup, what would be the two half reactions, which would be the cathode and which would be the anode, and what would be the standard cell potential? (*Hint*: use the standard reduction potentials in Model 1.)

8. If an electrochemical cell with Sn and Cu electrodes was setup, what would be the two half reactions, which would be the cathode and which would be the anode, and what would be the standard cell potential?

9. If an electrochemical cell with Sn and Zn electrodes was setup, what would be thetwo half reactions, which would be the cathode and which would be the anode, and what would be the standard cell potential?

10. Which combination of the half cells in Table 1 would make the highest voltage battery?

11. Nicotine adenine dinucleotide (NAD) is involved in redox chemistry throughout the respiratory system. The reduced form of NAD is written as NADH and the oxidised form is written as $NAD^+$. The standard reduction reaction and potential of NAD is given by:

$$NAD^+ + H^+ + 2e^- \rightarrow NADH \quad E° = -0.105\ V$$

NAD is combined with each of the following reactions:

(a) $CO_2 + H^+ + 2e^- \rightarrow HCOO^- \quad E° = -0.20\ V$
(b) $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad E° = +0.69\ V$

Write the overall reaction for each of the cells in the direction of spontaneous change. Is the NAD reduced or oxidised in these reactions?

# CHEM1101 Worksheet 13: Concentration and Electrochemistry

## Model 1: The Effect of Concentration on the Cell Potential

In worksheet 12, you set up a **voltaic cell** to harness the electrical energy in a redox reaction, such as that below, to make a battery:

$$Zn(s) + Sn^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Sn(s) \qquad E^0_{cell} = +0.62\ V \qquad (1)$$

During the reaction, tin ions are consumed and zinc ions are produced. The driving force becomes weaker and the cell potential becomes smaller. Eventually, equilibrium is established and the battery is dead.

**The *standard* cell potential refers to the reaction in which the reactants are present at 1 M concentrations.**

In Model 2 of worksheet 12, you calculated the standard cell potential for the reduction of $O_2$ by nicotine adenine dinucleotide (NAD):

$$O_2 + H^+ + NADH \rightarrow H_2O_2 + NAD^+ \qquad E° = +0.80\ V \qquad (2)$$

## Critical thinking questions

1. What pH does the standard cell potential refer to?

2. If the reaction is performed at a pH of 7.4, will the cell potential be higher or lower?

## Model 2: The Nernst Equation

The actual cell potential, $E_{cell}$, can be calculated from the standard cell potential using the Nernst equation:

$$E_{cell} = E^0_{cell} - \frac{RT}{nF} \ln Q$$

where $R$ is the gas constant (8.314 J K$^{-1}$ mol$^{-1}$), $T$ is the temperature (in Kelvin), $n$ is the number of electrons transferred in the reaction, $F$ is Faraday's constant (96485 C mol$^{-1}$) and $Q$ is the reaction quotient. For the reactions in Model 1:

$$(1) \quad Q = \frac{[Zn^{2+}(aq)]}{[Sn^{2+}(aq)]} \qquad\qquad (2) \quad Q = \frac{[H_2O_2][NAD^+]}{[O_2][H^+][NADH]}$$

## Critical thinking questions

1. What is the value of $n$ in these reactions? (*Hint*: how many electrons in total are required to change the oxidation number of Zn in (1) and of the two O atoms in $O_2$ in (2)?)

2. In the biochemical literature, the biological standard state is used. This has all concentrations as 1 M, except [H$^+$] which is taken to be 10$^{-7}$ as this is closer to its value in the body. Use the Nernst equation to calculate the *biological* standard cell potential for the reduction of $O_2$ by NAD at the typical body temperature of 37 °C.

3. Is your numerical answer to Q2 in Model 2 consistent with your answer to Q2 in Model 1?

## Model 3: Concentration Cells

In Model 2, you investigated the effect of the concentrations of the chemicals in a redox reaction on the cell potential. It is also possible to generate a cell potential using differences in concentrations alone.

## Critical thinking questions

1. A pair of copper(II) sulfate solutions, one concentrated and dark blue and the other dilute and light blue, are separated by a removable barrier.

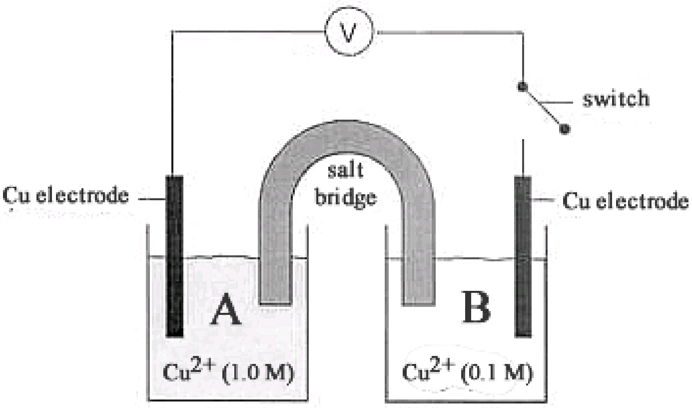
   (a) What will happen when the barrier is removed?

   (b) What will happen to the entropy of the system?

   (c) What will happen to the enthalpy of the system?

2. The cell opposite consists of two half cells connected together by a wire and a salt bridge. Each cell is made from a copper electrode in a solution of $Cu^{2+}$(aq) ions.

   - Cell A has [$Cu^{2+}$(aq)] = 1.0 M.
   - Cell B has [$Cu^{2+}$(aq)] = 0.1 M.



   (a) Is the system at equilibrium?

   (b) If not, what must happen to the concentrations in each cell to reach equilibrium?

   - Cell A:
   - Cell B:

   (c) Unlike the situation in Q1, equilibrium must be achieved *without* $Cu^{2+}$ ions being able to move.

   What *redox* processes can occur in each cell to change the concentrations in the required direction to achieve equilibrium?

   - Cell A:
   - Cell B:

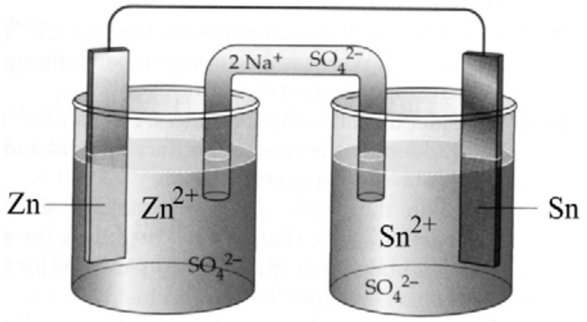
   (d) In which direction must electrons flow for these redox processes to occur?

   (e) Label the cathode and anode in the diagram.

   (f) What is the *standard* electrode potential for this cell?

   (g) Use the Nernst equation to work out the electrode potential of the cell when the switch is connected at 298 K. (*Hint*: remember that $E_{cell} > 0$ for a spontaneous process.)

## Model 4: Voltaic Cells



In worksheet 12, you saw how the electrical energy in a redox reaction can be harnessed to make a battery, by setting up the **voltaic cell** opposite. The potentials for the two reactions are:

$\mathrm{Sn^{2+}(aq) + 2e^- \rightarrow Sn(s)}$ $E^0_{\text{red}} = -0.14$ V
$\mathrm{Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-}$ $E^0_{\text{ox}} = +0.76$ V

The overall reaction is spontaneous as the reaction has a positive $E^0_{\text{cell}}$ value:

$$E^0_{\text{cell}} = E^0_{\text{ox}} + E^0_{\text{red}} = +0.62 \text{ V}.$$

## Critical thinking questions

1. Which electrode (Zn or Sn) will *lose* mass and which one will *gain* mass?

2. What is the overall reaction that occurs when the cells are connected?

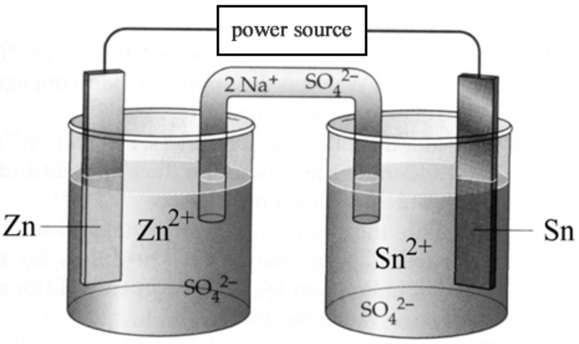
3. Oxidation always occurs at the anode. Label the anode and cathode on the cell.

4. Which way do the electrons flow? Draw an arrow on the diagram to show this.

5. Electrons flow from the *negative* electrode to the *positive* electrode. Which is positive, the anode or the cathode? Label the electrodes as positive or negative.

6. The salt bridge contains $\mathrm{Na^+(aq)}$ and $\mathrm{SO_4^{2-}(aq)}$. In which direction(s) do these ions move?

## Model 5: Electrolytic Cells



The *reverse* reaction can be made to happen if a power from an external source with potential *greater* than $E^0_{\text{cell}}$ is applied.

## Critical thinking questions

1. Which electrode (Zn or Sn) will now *lose* mass and which one will *gain* mass?

2. What is the overall reaction that now occurs when the cells are connected?

3. Oxidation always occurs at the anode. Label the anode and cathode on the cell.
4. Which way do the electrons flow? Draw an arrow on the diagram to show this.
5. The power source supplies electrons to the electrode where reduction occurs, so it becomes negative. The power sources removes electrons from the electrode where oxidation occurs, so it becomes positive. Which is positive, the anode or the cathode? Label the electrodes as positive or negative.

6. The salt bridge contains $\mathrm{Na^+(aq)}$ and $\mathrm{SO_4^{2-}(aq)}$. In which direction(s) do these ions move?

## Model 6: Electrolysis of Water

Electrolytic cells can be used to perform many useful tasks. A particular useful one is the electrolysis of water as this has the potential to convert electricity generated using solar energy into hydrogen gas, a combustible fuel. The reactions at the cathode and anode are:

Cathode: $2H_2O(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$ $E^0_{red} = -0.83$ V

Anode: $2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$ $E^0_{ox} = -1.23$ V

The amount of a substance produced in an electrolytic cell is directly proportional to the amount of electricity that passes through the cell. The number of moles of electrons that pass when a current $I$ is applied for a time $t$ is given by:

number of moles of electrons = $I \times t / F$

## Critical thinking questions

1. What is the overall reaction for the electrolysis of water?

2. $F$ is Faraday's constant. It is the charge of one mole of electrons. The charge of one electron is $1.602 \times 10^{-19}$ C. What is the charge of one mole?

3. If a current of 10.0 A is applied for 2.00 hours, how many moles of electrons are supplied? (*Hint*: remember to convert $t$ into seconds).

4. How many moles of $H_2(g)$ will be generated from this amount? (*Hint*: look at the stoichiometry of the reaction at the cathode.)

5. How many moles of $O_2(g)$ will be generated from this amount?

6. Water is a poor conductor so a salt is usually added to increase the conductivity. The salt must contain ions that are harder to reduce or oxidise than water. Using the standard reduction potentials, select a suitable salt.