Fundamentals of Atmospheric Chemistry and Astrochemistry

Lectures 1-3: an Introduction to Astrochemistry

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Some suggested reading:

This is by no means an exhaustive list, just a few suggestions to get you started. Many of the articles below go beyond the material covered directly in this course. There are many other review articles and research articles available on every different aspect of astrochemistry if you want to find out more about particular areas. Relevant literature is also cited throughout these lecture notes.

1.   *Astrochemistry,* by Andrew Shaw (textbook)

2.   *Ion chemistry and the interstellar medium*, Theodore P. Snow and Veronica M. Bierbaum, *Ann. Rev. Anal. Chem.*, **1** 229-259 (2008).

3.   *Laboratory Astrochemistry: Gas-phase processes*, Ian W. M. Smith, *Ann. Rev. Astron. Astrosphys.*, **49**, 29-6 (2011).

4.   *Frontiers of Astrochemistry*, David A. Williams, *Faraday Discuss.*, **109**, 1-13, (1998).

5.   *Laboratory astrochemistry: studying molecules under inter- and circumstellar conditions*, D. Gerlich and M. Smith, *Physica Scripta*, **73**, C25-C31 (2006).

6.   *Formation of complex chemical species in astrochemistry (a review)*, V. I. Shematovich, *Solar System Research*, **46(6),** 391-407 (2012).

7.   *Aromatic hydrocarbons, diamonds, and fullerenes in interstellar space: puzzles to be solved by laboratory and theoretical astrochemistry*, K. Sellgren, *Spectrochimica Acta Part A*, **57**, 627-642 (2001).

8.   *Quantum astrochemistry: prospects and examples*, G. Berthier, F. Pauzat and Tao Yuanqi, *J. Mol. Struct.*, **107**, 39-48 (1984).

9.   *Molecules, ices, and astronomy*, D. A. Williams, W. A. Brown, S. D. Price, J. M. C.Rawlings, and S. Viti, *Astronomy and Geophysics*, **48**, 1.25-1.34 (2007)

Contents

An Introduction to Astrochemistry

1. Introduction

> *"Far out in the uncharted backwaters of the unfashionable end of the Western Spiral arm of the Galaxy lies a small unregarded yellow sun. Orbiting this at a distance of roughly ninety-eight million miles is an utterly insignificant little blue-green planet whose ape-descended life forms are so amazingly primitive that they still think digital watches are a pretty neat idea."*
> – Douglas Adams, *Hitchhiker's Guide to the Galaxy*

So far in your degree studies, you have become very well acquainted with the chemistry occurring on the surface of the 'utterly insignificant little blue-green planet' referred to above. In this course, we shall extend our consideration of chemistry a little further to consider the rest of the universe. Much of what we know about the universe has been learnt through applying fundamental principles from physical chemistry to data acquired by earth-based and space telescopes, and we will highlight some of these principles as we proceed through the course. We will investigate the very early stages of the universe, and the events leading to synthesis of the chemical elements, and will take a tour of the interstellar medium (ISM), home to a rich chemistry of alien molecules that could not possibly survive on earth, yet can be understood using the same principles that allow us to understand terrestrial chemistry.

2. Studying the universe via spectroscopy

Unlike most other areas of chemistry and physics, we cannot carry out any active experiments to study the chemistry of the universe. Instead, all of the information we have comes from passive observations. The data from telescopes arrives in the form of spectroscopic signatures recorded in various portions of the electromagnetic spectrum (UV-vis, infrared, microwave etc) for different regions of space (stars, interstellar regions, and so on), and can be interpreted in order to establish the atomic and molecular composition of these regions. Ground-based telescopes are limited to studying regions of the electromagnetic spectrum in which the earth's atmosphere does not absorb. These include the visible-UV window spanning 300-900 nm, corresponding to electronic transitions; two infrared windows from 1-5 μm and 8-20 μm which can be used to probe vibrational transitions; a window in the microwave and millimetre wave region from 1.3-0.35 mm, which can be used to probe rotational transitions; and a radio wave window from 2-10 m which contains information on transitions between atomic hyperfine levels, such as the 21 cm line in atomic hydrogen. Space telescopes are not subject to such restrictions, and can observe in any region of the spectrum. In general, the microwave region is the most information rich, and therefore the most useful for studying small molecules in space, followed by the infrared and UV-vis regions.

Atoms and molecules may be identified through their absorption or emission frequencies and quantified by their absorption or emission intensities. There are one or two additional features of analysing spectral data from telescopes which differs from those encountered in more everyday spectroscopy. Firstly, most transitions will be Doppler shifted, and secondly, the lineshape can provide a great deal of information on the motion of the body under study.

3. Doppler shift

For velocities significantly less than the speed of light[1], the observed wavelength of light absorbed or emitted by a moving object is Doppler shifted by an amount

$$\frac{\Delta\lambda}{\lambda} = \frac{v_{source}}{c} \qquad (3.1)$$

Where λ is the transition wavelength, $\Delta\lambda$ is the Doppler shift, v_{source} is the velocity of the source relative to the observer, and c is the speed of light. The Doppler shift must be taken into account when identifying spectroscopic lines from telescope data; since the universe is expanding, such that all other astronomical objects are moving away from the earth, often the lines will appear at wavelengths that are significantly red-shifted from that expected for a stationary sample. If the velocity of the source is known then the wavelengths can be corrected for comparison with lab based or calculated spectroscopic data. If the velocity of the source is not known then lines must be identified through a process of 'pattern matching', and when a match is found they may be used to determine the velocity of the source.
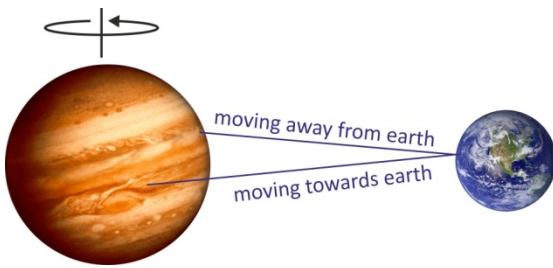
A nice example of velocity measurements via the Doppler shift is the determination of the rotational speed of Jupiter. During the rotation, one 'side' of the planet (as observed from earth) is moving towards the earth and will be blue-shifted, while the other side is moving away from the earth and will be red-shifted. By comparing the Doppler shift of the hydrogen Lyman α line from each side of the planet, we can determine both the speed of rotation and its direction.

4. Doppler lineshape

Within a sample there will usually be a distribution of velocities, meaning that each molecule will have a slightly different chemical shift. This leads to line broadening over and above the natural linewidth. For a sample of molecules of mass m with a Maxwell Boltzmann velocity distribution at temperature T, the Doppler linewidth is given by
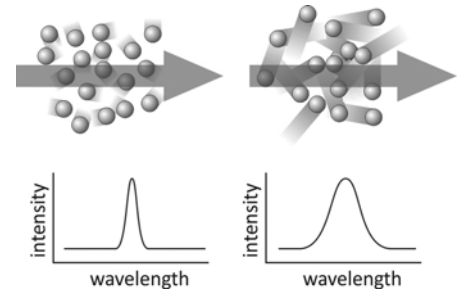
$$\delta\lambda = \frac{2\lambda}{c}\left(\frac{2k_{B}T\ln 2}{m}\right)^{1/2} \qquad (4.1)$$

The Doppler linewidth may therefore be used to determine the temperature of a sample.

5. The Hubble constant and the age of the universe

Hubble measured the Doppler red shift for a number of galaxies, and found that when red shift was plotted against distance for galaxies spanning a range of distances from earth, the plot gave a straight line. The result is summarised in the Hubble law:

$$v = Hd \qquad (5.1)$$

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[1] For velocities greater than around $0.7c$, a relativistic correction is required.

Here, v is the radial velocity, H is the Hubble constant, and d is the distance. The equation summarises the rate of recession of other galaxies, and therefore the rate at which the universe is expanding. The most recent determination of the Hubble constant yields a value of 23 km s^{-1} Mly^{-1}, with an error of around 10%. Other estimates give a value between 19 and 21 km s^{-1} Mly^{-1}. If we assume that the rate of expansion of the universe has remained constant (this could potentially be quite a large assumption), then the age of the universe is simply the inverse of the Hubble constant, giving an age of 13.8 billion years.

So how did chemistry originate, 13.8 billion years ago?

6. The very early universe: the building blocks of matter

Chemistry, like everything in the universe, began with the big bang. Immediately after the big bang, in what is known as the *inflationary epoch*, the universe underwent extremely rapid exponential expansion, increasing its volume by a factor of at least 10^{78} and expanding from subatomic dimensions to around the size of a grapefruit. The inflationary epoch lasted until around 10^{-32} seconds after the big bang, and this is the earliest meaningful 'time after the big bang'. The temperatures and pressures during this time were both unimaginably high, and from this point on the universe continued to expand[2] (non-exponentially) and cool rapidly.

Immediately after the inflationary epoch, the universe had cooled sufficiently for the first particles to form. These particles formed out of pure energy. Einstein first demonstrated the equivalence and interchangeability of matter and energy in his famous equation, $E = mc^2$. To put this equation into context, creation of 1 gram of mass requires an energy of 89 TeraJoules (8.9×10^{13} J), an almost incomprehensible amount of energy. However, fundamental particles weigh only a tiny fraction of a gram, and their equivalent energies, called their rest energies, are measured in MeV (mega electron volts, with 1 MeV = 1.602×10^{-13} J). The rest energies of electrons, protons, and neutrons, three particles you will be very familiar with, are 0.511 MeV, 938 MeV, and 950 MeV, respectively. At 10^{-32} s after the big bang, elementary particles began to form. These included quarks, gluons, electrons, and neutrinos. However, with the temperature still a toasty 10^{27} K, it was impossible for composite particles such as protons and neutrons to form. At this stage, the universe consisted of a unique phase of matter known as a *quark-gluon plasma*[3].

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2   When thinking about the big bang, most people picture matter expanding from a point in all directions in an infinite space. While this is a convenient mental picture, it is not really correct, as it is space itself that is expanding, not matter within space. A two dimensional analogy is to imagine living on the (two-dimensional) surface of an inflating balloon. The only directions you know are left, right, forwards, and backwards (up and down are meaningless on a two-dimensional surface). Over time, you observe that objects at rest with respect to the surface of the balloon are in fact moving apart from each other. This is despite the fact that you have explored your entire two-dimensional world and not found any edge or 'outside' for it to expand into. Similarly, we note that other galaxies appear to be receding from our galaxy. However, the galaxies are not really travelling through space away from us, like fragments from a 'big bang bomb'; instead, the space between the galaxies and us is expanding, and this expansion is happening simultaneously at every position in the universe. This analogy was taken from the excellent article 'Misconceptions about the big bang' from the March 2005 edition of Scientific American, available online for interested readers at http://space.mit.edu/~kcooksey/teaching/AY5/MisconceptionsabouttheBigBang_ScientificAmerican.pdf. Note that since the total energy in the universe is a constant, as the volume of the universe increases, the energy density, and therefore the temperature, must decrease as the universe expands.

3   Physicists are putting a great deal of effort into recreating this particularly fascinating state of matter, in which the strong interaction is overcome and free quarks and gluons are observed. As far as we know, this state of matter has only ever

Around 1 microsecond (10^{-6} s) after the big bang, the temperature had cooled to around 10^{13} K, a temperature low enough that quarks could combine to form protons and neutrons. There are six different varieties of quarks (up, down, top, bottom, charm, and strange), but only up and down quarks are involved in the formation of protons and neutrons. A proton is formed from two up quarks and a down quark, while a neutron contains two down quarks and an up quark. Up and down quarks have charges of +⅔ and −⅓ , respectively, giving protons and neutrons an overall charge of +1 and 0, respectively. Quarks also have a quantum number known as 'colour charge', which can take the values 'red', 'green', or 'blue' (yes, really). While charge determines how particles will interact via the electromagnetic interaction, colour charge is required to explain how particles interact via the strong interaction. In particular, to satisfy the Pauli principle that no two identical particles in a system can have the same set of quantum numbers, protons and neutrons must contain one quark of each colour. This also satisfies the principle that hadrons (composite particles made up of quarks) must be colourless (red+green+blue=colourless).
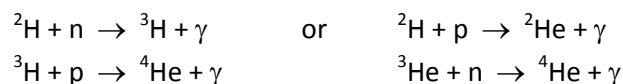
At this stage, a microsecond after the big bang, we have formed electrons, protons, and neutrons, and have all of the building blocks of matter.

7. Hydrogen and helium nuclei

Around 100 seconds after the big bang, at a temperature of around 1 billion K, the universe had cooled enough for the formation of the first composite atomic nuclei (note that we already had H nuclei with the formation of protons). Protons and neutrons reacted to form deuterium nuclei.

$$n + p \; \rightarrow \; {}^{2}H + \gamma$$
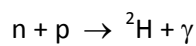
where γ is a high energy photon (gamma particle). Once we have deuterium nuclei, there are various pathways to ${}^{3}He$ and ${}^{4}He$.

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\begin{array}{lll}
{}^{2}H + n \; \rightarrow \; {}^{3}H + \gamma & \qquad \text{or} \qquad & {}^{2}H + p \; \rightarrow \; {}^{2}He + \gamma \\
{}^{3}H + p \; \rightarrow \; {}^{4}He + \gamma & & {}^{3}He + n \; \rightarrow \; {}^{4}He + \gamma
\end{array}
$$

8. The first atoms

We have gone from nothing to the first atomic nuclei in less than two minutes. From here on in the universe went through rather a quiet spell, with nothing remarkable happening for hundreds of thousands of years. During this time the universe consisted largely of a white hot opaque fog of hydrogen plasma, which was slowly cooling as it expanded. After around 370 000 years, the temperature had reduced to a balmy 10 000 K, sufficiently 'cool' that hydrogen and helium nuclei could capture electrons to form the first neutral atoms. These atoms could no longer absorb the thermal radiation, and the universe became transparent. The photons that existed in the universe at that time have gradually lost energy and become more dispersed as the universe has continued to expand and cool, but still exist today everywhere in the universe as the *cosmic microwave background radiation*. This radiation was first observed in 1964 by Arno Penzias and Robert Wilson, two American radio astronomers who received the Nobel prize for their work in 1978. The radiation takes the form of a black body spectrum with a temperature of 2.725 K.

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existed in nature in the instant after the big bang. However, it appears that it can be recreated in high energy collision experiments such as those being carried out at the Large Hadron Collider at CERN.
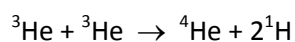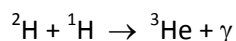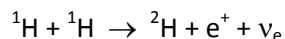
Up to this point our universe seems to be developing very nicely. However, we now run into a real problem, in that there are no further stable nuclei that can be formed by neutron capture. To synthesise further elements we need stars.

9. Star formation and nucleosynthesis of heavier elements

More hydrogen and helium formed as the universe continued to cool. By the time it had cooled to around 500 K, somewhere between 200 million and 1 billion years after the big bang, hydrogen and helium started to coalesce under the force of gravity into giant gas clouds[4]. Once the gas clouds became large enough (thousands to tens of thousands of solar masses), they started to collapse under the influence of gravity. Gravitational potential energy was converted to kinetic energy, and as the velocity of the particles increased, so did their temperature. In the early stages of star formation, energy can be lost from the gas particles by emission of infrared radiation. However, at some point the gas density increases to the point where the gas becomes opaque to radiation and the temperature increases, firstly to the point at which hydrogen atoms are ionized, and finally to temperatures at which the collisions between the resulting protons have sufficient energy to induce nuclear fusion. The star begins to shine. Two examples of star forming regions or 'stellar nurseries' within large gas clouds are shown in the image below.


The first stars, known as Population III stars, were huge, hundreds of times heavier than our sun, and burned out relatively quickly (compared to later stars), on a timescale of three to four million years[5]. For most of their lifetime they were fuelled largely by *hydrogen burning*, a multi-step process in which four ^{1}H nuclei are fused to form a single ^{4}He nuclei and various other elementary particles. There are two different mechanisms for hydrogen burning, but in young stars (including our sun) the *proton-proton cycle* dominates, and produces around 90% of the star's energy.

$$^1\text{H} + {}^1\text{H} \rightarrow {}^2\text{H} + e^+ + \nu_e$$

$$^2\text{H} + {}^1\text{H} \rightarrow {}^3\text{He} + \gamma$$

$$^3\text{He} + {}^3\text{He} \rightarrow {}^4\text{He} + 2{}^1\text{H}$$

Once the supply of ^{1}H in the core of a star was exhausted, near the end of its lifetime, the dominant process became *helium burning*, the fusion of two ^{4}He nuclei to form a ^{8}Be nucleus.

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[4]   It is thought that molecular hydrogen also formed at this stage via gas-phase reactions, and that the presence of H_2 was important in driving the gravitational collapse that led to formation of the first stars. In the modern universe, H_2 formation is dominated by chemistry occurring on the surface of interstellar dust grains, with gas-phase processes making only a very small contribution.
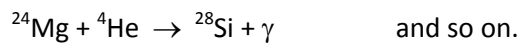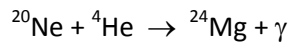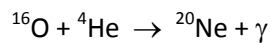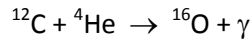
[5]   Somewhat counterintuitively, more massive stars have shorter lifetimes. Although the amount of fuel a star has increases with mass, the rate at which it consumes this fuel increases even faster with mass. It is found that a star's lifetime on the main sequence (the period while it is burning hydrogen as fuel) is proportional to $1/m^3$.

$$^4He + {}^4He \ \rightarrow \ {}^8Be + \gamma$$
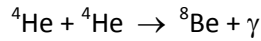
The ^8Be nucleus resulting from this process is not stable, and usually decays back to two ^4He nuclei, but can also undergo other reactions. For example,

$$^8Be + {}^4He \ \rightarrow \ {}^{12}C + \gamma$$
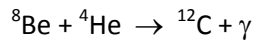
From ^{12}C it is possible to make all of the even numbered elements up to ^{56}Fe through analogous nuclear fusion process

$$^{12}C + {}^4He \ \rightarrow \ {}^{16}O + \gamma$$

$$^{16}O + {}^4He \ \rightarrow \ {}^{20}Ne + \gamma$$

$$^{20}Ne + {}^4He \ \rightarrow \ {}^{24}Mg + \gamma$$

$$^{24}Mg + {}^4He \ \rightarrow \ {}^{28}Si + \gamma \qquad \text{and so on.}$$

Odd numbered nuclei are formed in less efficient reactions involving proton capture. Many of the original Population III stars probably didn't get much further than helium burning before reaching the end of their lifetime, at which point they exploded in supernovae, scattering the elements they had formed through space. As far as we know, no Population III stars are still in existence. Over time, the cycle of giant gas cloud formation and star formation was repeated to form a generation of Population II stars. The presence of heavier elements in the gas clouds modified their cooling and contraction properties, with the result that Population II stars tend to be smaller than the first generation of stars, with much longer lifetimes. Many Population II stars are still in existence, and are thought to be between 10 and 13 billion years old (for comparison, remember that the universe is thought to be around 13.8 billion years old). These stars have a much higher fraction of 'heavy' (i.e. non hydrogen and helium) nuclei than the Population III stars. For some Population II stars that have reached the end of their lives, the star formation cycle has repeated itself to form Population I stars, with ages of less than 10 billion years, which contain even higher levels of heavy nuclei, having been given a 'head start' by their 'parent' Population II stars. Our sun is a Population I star. To keep things in perspective, even in so-called 'high metallicity'[6] star such as the sun, only around 1.8% of nuclei within the sun are heavy elements.

Nuclear fusion processes of the type described above are energetically favourable until we reach the ^{56}Fe nucleus. Iron has the most stable nucleus in terms of binding energy per nucleon, as shown in the plot below.
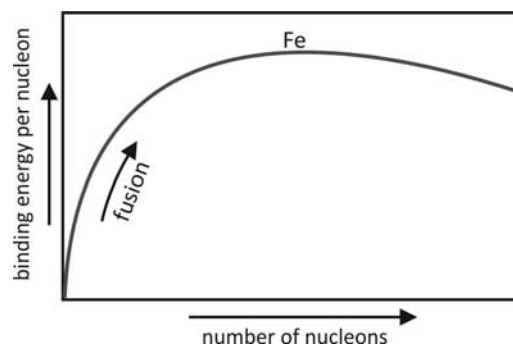
Beyond ^{56}Fe, fusion processes are no longer energetically favourable, and heavier elements are instead built up gradually through a combination of neutron capture and β decay (electron emission). In the example below, ^{98}Mo (atomic number 42) captures a neutron to form ^{99}Mo, which then emits an electron

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6   The *metallicity* of a star is the proportion of its matter made up from elements other than H and He.

to form ^{99}Tc, with atomic number 43, and a neutrino. Neutron capture followed by electron emission therefore has the overall effect of increasing the atomic number by one.

$$^{98}\text{Mo} + \text{n} \rightarrow {}^{99}\text{Mo} + \gamma$$

$$^{99}\text{Mo} \rightarrow {}^{99}\text{Tc} + \text{e} + \nu$$
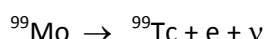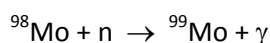
10. Dispersion of chemical elements

The dispersion of chemical elements from stars into the interstellar medium occurs at the end of a star's lifetime. The mechanism for the dispersion depends on the mass of the star.

During the time when a star is fuelled primarily by hydrogen burning it is known as a *main sequence star*. For a star similar in size to our sun, this period lasts around 10 billion years. Once all the hydrogen in the core has been converted to helium the hydrogen fusion reactions in the core stop. However, they continue in the shell around the core. The core begins to cool and contract under gravity. Eventually, in a sequence of processes similar to the formation of the original star, the core of the star has condensed and increased in temperature to the point where the density and temperature are high enough to initiate helium burning. The outer layers of the star begin to cool, expand, and shine less brightly, and the star is now a *red giant*. Eventually the helium within the star's core is converted to carbon, at which point the core becomes a *white dwarf*, and the outer layers of the star drift away to form a gaseous shell called a *planetary nebula*. The atomic species within the planetary nebula will eventually drift away into the interstellar medium. Once nuclear fusion reactions stop completely, the core of the now dead star is known as a *black dwarf*.

The sequence of events unfolds rather differently for massive stars (3-50 times heavier than our sun). Their main sequence lifetimes are much shorter, at millions rather than billions of years. Once a massive star has exhausted its supply of hydrogen and begins helium burning, it expands much more than a low mass star, forming a *red supergiant*. Over the next million years, many different nuclear reactions occur in the core, forming different elements in shells around an iron core. Eventually, the star runs out of fuel, leading to a spectacular gravitational collapse and subsequent explosion called a supernova. In contrast to the millions of years over which the star has evolved up to this point, the supernova event takes less than a second. The resulting shock wave blows off the outer layers of the star into the interstellar medium, but sometimes the core will survive the explosion. If the remaining core has a mass of between 1.5 and 3 solar masses it will contract to form a very dense *neutron star*, while a higher-mass core will contract to form a *black hole*.

11. Cosmic abundance of the elements

All of the chemical elements in the universe today formed through processes of the type described above. The cosmic abundances of each element are plotted below (note the log scale), and show some interesting features.

(i)   The universe consists of around 74% hydrogen, 24% helium, and only 2% heavier elements.

(ii)   The abundance falls off from light elements to heavier elements.

(iii)   Iron has the most stable nucleus, and consequently is one of the most abundant elements.

(iv)   Lithium, beryllium, and boron are extremely rare compared with other elements, since there is no straightforward way to make them through nuclear reactions.

(v)   Even elements are more abundant than odd since their nuclei are more stable and they are formed more efficiently.
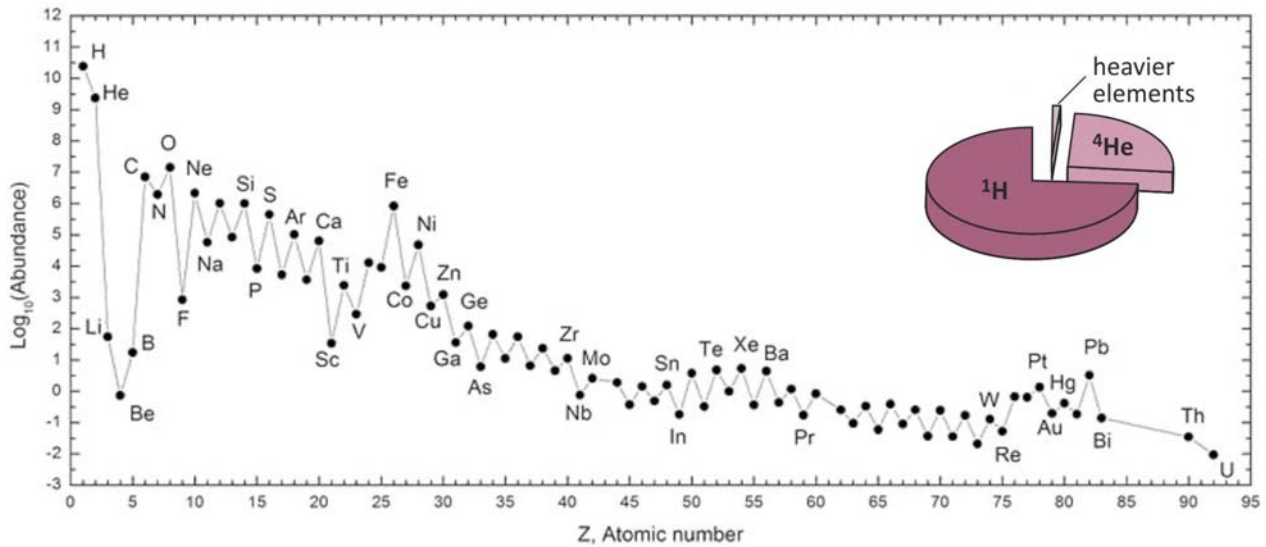
12. The interstellar medium

Now that we have spent some time looking at the synthesis of the chemical elements within stars, we turn our attention to the interstellar medium. The term 'interstellar medium' covers a number of different environments, listed below.

(i) Diffuse interstellar medium. These regions are effectively 'empty space'. Particle densities are around 1 to 100 cm^{-3}, and while the translational temperatures of atoms and molecules may be as high as 100 K, the concept of temperature is not really applicable with such low number densities. These regions of the interstellar medium contain mostly atomic hydrogen and atomic ions, with a small molecular fraction (defined by the ratio of H_2 to H) of between 0.0 and 0.1.

(ii) Giant molecular clouds. These are enormous collections of gas that can be tens of light years in diameter and contain most of the mass within the interstellar medium. They are also the regions of new star formation. The average density within a giant molecular cloud is around 100-1000 cm^{-3}, but the most dense regions may have densities of up to 10^6 cm^{-3}. Temperatures range from around 100 K near the edges of a cloud to around 10 K in the centre. As the name suggests, giant molecular clouds are home to a considerable amount of chemistry, and contain many different molecular species (over 160 at the last count – see table below). However, it should be noted that the average density within such a cloud is comparable to the best vacuum achievable on earth. Sometimes molecular clouds are classified into subcategories:

Diffuse molecular clouds: most matter is present in atomic, rather than molecular form. The molecular fraction (the ratio of the number of H_2 molecules to the total number of H atoms) lies between 0.1 and 0.5.

Translucent molecular clouds: most H is present in molecular form, but most carbon is present in atomic form as C or C^+, with some present in molecular form, predominantly as CO.

Dense molecular clouds: virtually all H is present as H_2, and most of the carbon is also present in molecular form. Dense clouds consist primarily of H_2, with CO the next most abundant molecule (at around 10^{-4} times the number density of H_2). Other simple molecules such as CH, OH, CN, and H_2O are present at considerably lower number densities, totalling around 10^{-7} of the H_2 density.

(iii) Circumstellar medium. These are the regions directly around a star, and the environment within these regions depends on the type and extent of evolution of the star. Regions around young stars experience high photon fluxes in the UV so that all molecules are photodissociated and photoionized (such regions are sometimes referred to as *photon-dominated regions*). Around older stars there may be significant dust, leading to surface chemistry as well as scattered starlight.

We will focus our attention on giant molecular clouds. The atomic composition of these regions is determined by the past history of nearby stars (see Sections 9 and 10), which eject processed nuclear material via stellar winds and supernova explosions. As we shall see, the molecular composition reflects the balance between chemical evolution via reactions, destruction of molecules by light from stars or by cosmic rays, and condensation and subsequent reaction on dust grains.

Table 1: Molecules detected in space. Unconfirmed detections are denoted with a ?. Taken from Molecules in Space, by J. Tennyson, Volume 3, Part 3, Chapter 14 of Handbook of Molecular Physics and Quantum Chemistry (John Wiley and Sons, 2003).

Diatomic molecules	AlF, AlCl, C2, CH, CN, CO, CP, CS, CSi, HCl, H_2, KCl, NH, NO, NS, NaCl, OH, PN, SO, SiN, SiO, SiS, HF, SH, SiH, CH^+, CD^+, CO^+, SO^+
Triatomic molecules	C_3, C_2H, C_2O, C_2S, CH_2, HCN, HCO, H_2O, H_2S, HNC, HNO, MgCN, MgNC, N_2O, NaCN, OCS, SO_2, c-SiC_2, CO_2, NH_2, SiCN, HCO^+, DCO^+, HCS^+, HOC^+, N_2H^+, H_3^+, H_2D^+
Four-atom molecules	c-C_3H, l-C_3H, C_3N, C_3O, C_3S, C_2H_2, HCCN, HNCO, HNCS, H_2CO, H_2CN, H_2CS, NH_3, SiC_3, CH_3, CH_2D^+?, $HCNH^+$, $HOCO^+$, H_3O^+
Five-atom molecules	C_5, C_4H, C_4Si, l-C_3H_2, c-C_3H_2, CH_2CN, CH_4, HC_3N, HC_2NC, HCOOH, H_2CHN, H_2C_2O, H_2NCN, HNC_3, SiH, H_2COH^+
Six-atom molecules	C_5H, C_5O, C_2H_4, CH_3CN, CH_3NC, CH_3OH, CH_3SH, HC_3NH+, HC_2CHO, $HCONH_2$, l-H_2C_4, C_5N, HC_3NH^+
Seven-atom molecules	C_6H, CH_2CHCN, CH_3C_2H, HC_5N, $HCOCH_3$, NH_2CH_3, c-C_2H_4O
Eight-atom molecules	CH_3C_3N, $HCOOCH_3$, CH_3COOH?, CH_2OHCHO, H_2C_6, C_7H
Nine-atom molecules	CH_3C_4N, CH_3CH_2CN, $(CH_3)_2O$, CH_3CH_2OH, HC_7N, C_8H
10-atom molecules	CH_3C_5N?, $(CH_3)_2CO$, NH_2CH_2COOH?
11-atom molecules	HC_9N
13-atom molecules	$HC_{11}N$

13. Chemistry in interstellar space

Molecular clouds are characterised by very low temperatures, on the order of 10 K. At these temperatures there is insufficient energy for collisions to overcome any activation barrier to reaction, and the only gas-phase chemical reactions that can proceed at such low temperatures are radical-radical reactions and ion-molecule reactions, both of which are barrierless. Interstellar gas clouds also have extremely low densities by terrestrial standards, which has drastic consequences for the collision frequency, and therefore the number of opportunities for chemistry to occur. The number of collisions within a unit volume each second (the collision frequency) is given by

$$z = \sigma_c \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} n_A n_B \tag{13.1}$$

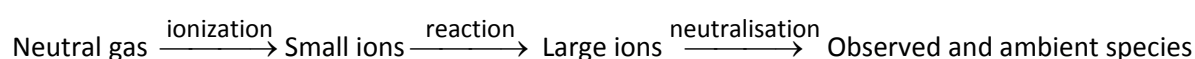Where σ_c is the collision cross section, T is the temperature, μ is the reduced mass, and n_A and n_B are the number densities of the species of interest. Even in the densest regions, with number densies of 10^6 cm^{-1},

collision rates are around 5×10^{-4} s^{-1}, approximately one collision every half an hour. In less dense regions, atoms and molecules may go for many weeks, or even longer, between collisions. Chemistry therefore occurs at a very slow rate in interstellar space compared to the timescales we are used to on earth. However, since giant molecular clouds last for around 10 to 100 million years before they are dissipated by heat and stellar winds from stars forming within them, there is plenty of time for some quite complex chemistry to occur, albeit at a rather leisurely rate. The very low collision frequency has important consequences for the types of molecules that may form in interstellar space. As we can see from the table of molecules above, terrestrial concepts of molecular stability simply do not apply in this extremely non-reactive environment. Carbon does not need to have four bonds; in fact, there are many subvalent species, radicals, molecular ions and energetic isomers amongst the molecules observed in interstellar gas clouds. Carbon-containing compounds tend to be highly unsaturated, with many double and triple bonds, and few branched chains. Polyynes are commonly observed, some with quite long chain lengths, for example H−C≡C−C≡C−C≡C−C≡C−C≡N. Many of the molecules observed in space would react almost instantly were they transported to earth.

As noted above, collisions between atoms and molecules in interstellar space are extremely infrequent, and as such, conventional chemical principles such as 'thermalisation' are not really relevant. It therefore makes more sense to consider chemistry in the interstellar medium in terms of individual collisions. We will return to this idea in detail when considering theoretical studies of astrochemical reactions later on in the course.

14. Molecular synthesis in interstellar gas clouds

Gas-phase molecular synthesis in interstellar clouds is believed to occur primarily via ion-molecule reactions, with some neutral reactions contributing. Since the molecular species identified from spectroscopic data are mostly neutral, the ionic species formed in these processes must become charge-neutral relatively quickly. The general scheme of molecular synthesis therefore looks something like the following:

$$\text{Neutral gas} \xrightarrow{\text{ionization}} \text{Small ions} \xrightarrow{\text{reaction}} \text{Large ions} \xrightarrow{\text{neutralisation}} \text{Observed and ambient species}$$

Chemistry can also occur on the surface of dust grains. Surface-catalyzed reactions of this type turn out to be very important in the interstellar medium, and we will look at these in some detail later.
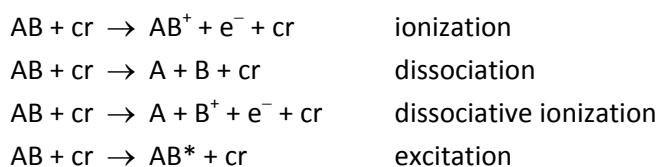
We will now consider the types of reaction contributing to each of the three stages involved in gas-phase interstellar chemistry i.e. ionization, reaction, and neutralisation, before moving on to look at dust-grain catalysed chemistry.

15. Ionization processes in the interstellar medium

Photoionization is a very common process near stars. However, the high density of hydrogen and dust grains in molecular clouds prevents visible and UV light from penetrating very far. For this reason, molecular clouds often appear dark when viewed through a telescope. An example is the Barnard 68 molecular cloud shown below.

Infrared light can penetrate molecular clouds, and indeed IR spectroscopy is a key method for identifying molecular species within these regions. However, infrared photons do not have sufficient energy to ionize neutral molecules. Instead, most ions within molecular clouds are formed through collisions with cosmic rays. Cosmic rays are extremely high kinetic energy particles emitted by stars, comprising around 84% protons, 14% alpha particles, and 2% electrons, heavier nuclei, and more exotic particles. Numerous chemical processes can result from a collision of a molecule with a cosmic ray (cr), as summarised below.

$$AB + cr \rightarrow AB^+ + e^- + cr \qquad \text{ionization}$$
$$AB + cr \rightarrow A + B + cr \qquad \text{dissociation}$$
$$AB + cr \rightarrow A + B^+ + e^- + cr \qquad \text{dissociative ionization}$$
$$AB + cr \rightarrow AB^* + cr \qquad \text{excitation}$$

Energy is of course conserved in all of these collisions; the cosmic rays appearing on the right hand side of the above equations are lower in energy than those on the left, having given up some of their energy to drive the chemical process of interest.

Electrons fairly commonly attach to large carbon-based molecules (e.g. PAHs), yielding a negative ion. Sometimes electron attachment is dissociative, in which case the rate can be extremely fast, with rate constants up to 10^{-7} cm^3 s^{-1}. In non-dissociative attachment, emission of a photon will generally be required in order to stabilise the ion. e.g.

$$e^- + PAH \rightarrow PAH^- + h\nu$$
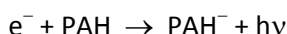
16. Gas-phase chemical reactions in the interstellar medium

A wide variety of reaction mechanisms operate within the interstellar medium. These can be categorised into bond formation, bond breaking, and rearrangement reactions, as follows:

Bond formation reactions:	Radiative association (neutral or ionic)	$A + B \rightarrow AB + h\nu$
	Associative detachment	$A^- + B \rightarrow AB + e^-$
	Dust-grain-catalysed reaction (neutral or ionic)	$A + B + grain \rightarrow AB + grain$
Bond breaking reactions:	Photodissociation (neutral or ion)	$AB + h\nu \rightarrow A + B$
	Collisional dissociation (neutral or ion)	$AB + M \rightarrow A + B + M$
	Dissociative recombination	$AB^+ + e^- \rightarrow A + B$
Rearrangement reactions:	Ion-molecule reaction	$A^+ + BC \rightarrow AB^+ + C$
	Charge transfer	$A^+ + B \rightarrow A + B^+$
	Neutral reaction	$A + BC \rightarrow AB + C$

Apart from photodissociation, these processes are all bimolecular, and usually diffusion controlled, with rate constants of around 10^{-9} cm^3 s^{-1}. The various types of reaction are considered in more detail and illustrated with examples in the following.

16.1   Bond formation reactions

16.1.1 Radiative association

Conservation of energy and momentum mean that the product of an association reaction, in which two reactants combine to form a single product, is usually highly internally excited. In terrestrial chemistry, such reactions normally rely on a subsequent collision with a 'third body' in order to carry away some of the energy of the excited product and thereby stabilize it. The low collision frequency in an interstellar gas cloud rules out this pathway to stabilization, and instead the highly energised product either decays back to reactants or is stabilised by emission of a photon. For example,

$$C^+ + H_2 \leftrightarrow CH_2^{+*} \rightarrow CH_2^+ + h\nu$$

$$CH_3^+ + H_2O \rightarrow CH_3^+.H_2O + h\nu \rightarrow CH_3OH_2^+$$
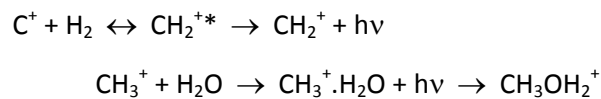
If the product has an allowed electronic transition back to the ground state, then radiative association can be very efficient; otherwise, it will be slow, relying on infrared emission to relax the excited molecule via vibrational relaxation. Rate constants for radiative association vary from 10^{-17} cm^3 s^{-1} for some diatomics up to 10^{-9} cm^3 s^{-1} for polyatomics.

Radiative association reactions can rapidly build large ions in a single step. They are difficult to study in the laboratory, and are often probed by studying the collisionally stabilised analogue.

16.1.2 Associative detachment

A negative ion and a neutral combine and the resulting negative ion detaches an electron. This type of reaction is fairly common for small species, and is also thought to occur for larger ones.

e.g. $$OH^- + H \rightarrow H_2O + e^-$$

### 16.1.3 Dust-grain-catalysed reactions

Around 1% of the mass of the interstellar medium consists of dust grains formed in the outflows of dying stars, particularly red supergiants (see Section 10). Molecules such as SiO and TiO form in the outer layers
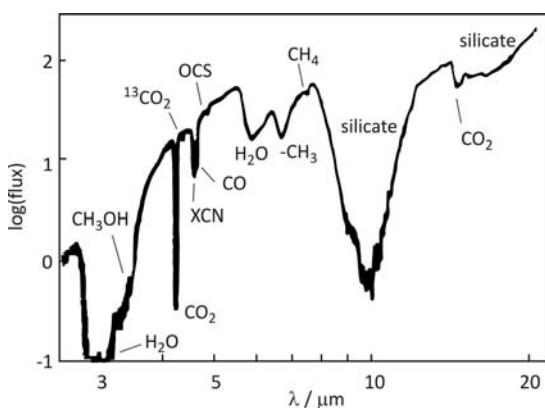

of these stars, and the large stellar winds that develop once the star ends its hydrogen burning phase blow these molecules out into the interstellar medium, where they form aggregation nuclei for dust particles. The dust aggregates into crystalline structures, forming a silicate core a few hundred nanometres in diameter through collection of oxygen atoms from the interstellar medium. Condensation of other molecules from within interstellar gas clouds leads to a layered mantle of ice on the surface, with inner layers containing organic molecules and outer

layers containing molecules such as H_2O, CO, CO_2, methanol, H_2CO, NH_3, and so on. A spectrum of interstellar dust (from the W33A dust-embedded massive young star), with some of the identifiable absorption features labelled, is shown on the left.

Dust grain chemistry is difficult to study, and is currently not well understood. However, the mechanisms available for dust grains to catalyse reactions in space must be similar to those involved in surface catalysis on earth. Dissociative adsorption to a surface yields highly reactive species and alternative reaction pathways, allowing reactions to proceed much more quickly than they would in the gas phase. A reaction of vital importance in the interstellar medium which is known to occur almost exclusively on the surface of dust grains is the formation of H_2 from two H atoms adsorbed to the surface.
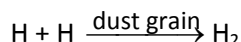
$$H + H \xrightarrow{\text{dust grain}} H_2$$

Organic synthesis is also thought to occur on the surface of dust grains. Adsorption of CO to the surface of a dust grain provides a carbon source to initiate such reactions. For example,
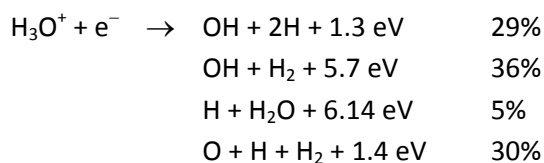
$$CO + H \rightarrow HCO$$
$$HCO + H \rightarrow H_2CO$$
$$H_2CO + H \rightarrow H_3CO$$
$$H_3CO + H \rightarrow CH_3OH$$
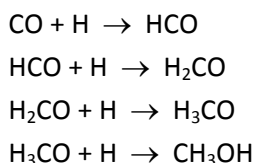
16.2 Bond breaking reactions

16.2.1 Photodissociation and collisional dissociation

Both of these processes should be familiar to you from earlier chemistry courses. Absorption of a photon or collision with a third body provides the energy required to break a chemical bond.

16.2.2 Dissociative recombination

As the name suggests, the ion combines with an electron to produce a high-energy neutral. Since a 'third body' collision to carry away the energy of the neutral is highly unlikely, the product fragments into smaller neutral species. For example,

$$
\begin{array}{lll}
H_3O^+ + e^- \rightarrow & OH + 2H + 1.3 \text{ eV} & 29\% \\
& OH + H_2 + 5.7 \text{ eV} & 36\% \\
& H + H_2O + 6.14 \text{ eV} & 5\% \\
& O + H + H_2 + 1.4 \text{ eV} & 30\%
\end{array}
$$

Such processes can be extremely fast, with rate constants of up to 10^{-6} cm^3 s^{-1}, significantly faster than ion-molecule reactions.

16.3 Rearrangement reactions

16.3.1 Charge transfer

Charge transfer involves the transfer of an electron from a neutral to an ion, and may lead to dissociation of the resulting ion. The charge transfer often occurs at large separations of up to 10 Å, and the process has a correspondingly large reaction cross section.

An example is the dissociative charge transfer from He^+ to CO (electron transfer from CO to He^+).

$$He^+ + CO \rightarrow C^+ + O + He + 2.2 \text{ eV}$$
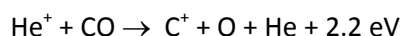
The large ionization energy of He (24.6 eV) is released during the charge transfer, leading to fragmentation of the product CO^+ back into its atomic constituents. This might seem like a backward step in terms of molecular synthesis, but the C+ ion formed in this reaction can go on to react further.

16.3.2 Neutral reactions

Fewer neutral reactions are involved in the interstellar medium than ion-molecule reactions, as they tend to have activation barriers, but even reactions with barriers can be important in higher temperature shocked regions; for example, when a supernova shock wave passes through a gas cloud then the gas is compressed and can heat up to over 1000 K.

16.3.3 Ion-molecule reactions

Ion-molecule reactions are usually barrierless (though there can often be a centrifugal barrier – see Section 42) and make up the majority of bimolecular reactions occurring in the ISM. The charge-transfer reactions described in Section 16.3.1 are a subset of ion-molecule reactions, but there are many other varieties. A few examples are given below.

Hydrogen atom abstraction

H atom abstraction reactions are important due to the high abundance of H atoms in the interstellar medium. One of the most common reactions is

$$H_2 + H_2^+ \rightarrow H_3^+ + H + 1.7 \text{ eV} \qquad \text{(fast)}$$
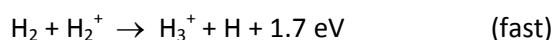
This is a fast reaction due to the high abundance of both reactants. The H_3^+ ion is extremely important in the ISM, being responsible for most of the proton transfer chemistry occurring.

Another example of a hydrogen atom abstraction is the reaction between NH_3^+ and H_2.

$$NH_3^+ + H_2 \rightarrow NH_4^+ + H + 0.9 \text{ eV} \qquad \text{(slow)}$$
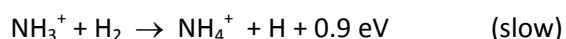
This reaction occurs much more slowly, and has an interesting temperature dependence. The reaction involves a barrier, such that the rate slows as the temperature is reduced from room temperature down to around 70 K. At lower temperatures the rate increases again as a quantum tunnelling mechanism takes over. Tunnelling becomes easier (and therefore faster) at lower temperatures since the collisions are slower and the reactants spend more time in close proximity. Within molecular clouds, the reaction goes almost entirely via the tunnelling mechanism.

Proton transfer

Proton transfer reactions are common from species of lower to higher proton affinity. The reaction exoergicity can be determined by the difference in proton affinities (PA) for the species involved. The H_3^+ ion is commonly involved in such reactions. For example,

$$H_3^+ + H_2O \rightarrow H_3O^+ + H_2 + 2.8 \text{ eV}$$
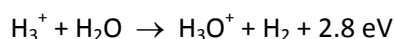
In this case the exoergicity is $\Delta E = PA(H_2O) - PA(H_2) = 2.8$ eV.

Carbon insertion

Carbon insertion reactions involve the insertion of a C^+ ion into a carbon chain. An atom or electron must be ejected during the process in order to conserve momentum e.g.

$$C^+ + C_2H_2 \rightarrow C_3H^+ + H + 2.2 \text{ eV}$$
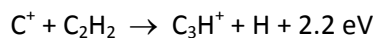
These reactions are important in synthesis of many of the carbon-containing molecules in the ISM. As an example, the C_3H^+ ion formed in the above reaction can go on to react further, eventually forming cyclic C_3H_2 via a sequence of steps involving hydrogen abstraction and electron ion recombination.

$$C_3H^+ + H_2 \rightarrow C_3H_2^+ + H$$
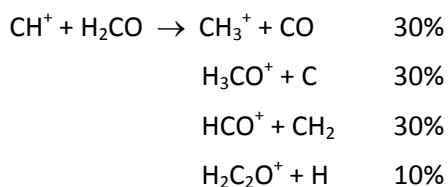$$C_3H_2^+ + e^- \rightarrow C_3H_2$$
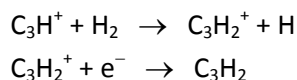
The carbon insertion process can lead to the formation of very large organic species known as polycyclic aromatic hydrocarbons, large aromatic ring structures of the type shown below.
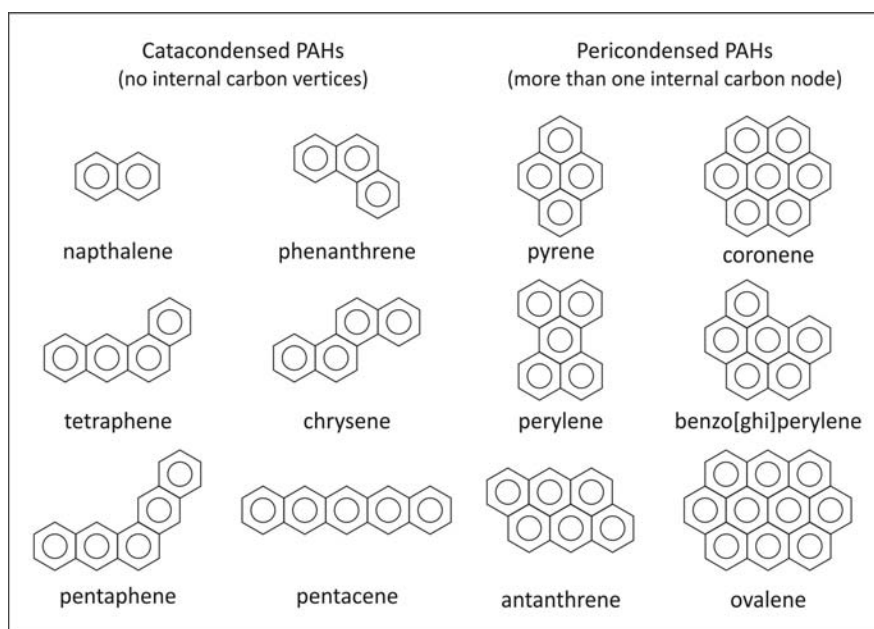
Carbon insertion reactions lead to the formation of carbon chains in a complex series of steps. Further radical-radical and dust-grain-catalysed chemistry then leads to ring formation and further chain propagation. The density of PAHs in the interstellar medium has not been quantified definitively, but may be comparable to that of other simple species such as OH, CH, CN and H_2O, and account for up to 20% of the carbon in the ISM.

Rearrangement reactions

These usually occur via a collision complex. A large amount of rearrangement can occur in the high energy complex, leading to fragmentation to various different sets of products. These products can then go on to react further, leading to a rich ion chemistry. Rearrangement reactions are often important for coupling different reaction sequences together. A simple example of a rearrangement reaction is the reaction between CH^+ and H_2CO.

$$\begin{aligned}
CH^+ + H_2CO \rightarrow\ & CH_3^+ + CO & 30\% \\
& H_3CO^+ + C & 30\% \\
& HCO^+ + CH_2 & 30\% \\
& H_2C_2O^+ + H & 10\%
\end{aligned}$$

17. Neutralisation processes in the interstellar medium

As noted in Section 14, most of the molecules observed in the interstellar medium are neutral, while the products of the ion-molecule reactions discussed in the previous section are ionic. There are a number of pathways by which an ion may be transformed into a neutral molecule within the interstellar medium. We have already covered one of these. In electron-ion dissociative recombination (Section 16.2.2), an ion and electron combine to form a neutral, which then fragments into two or more neutral products. Similarly, a negative ion and a positive ion may recombine to form a neutral complex, which dissociates into neutral products.

Examples:

|	
$CO^+ + e^- \rightarrow C + O$	electron-ion dissociative recombination
$HCCCNH^+ + e^- \rightarrow HCCCN + H / HCCNC + H$	electron-ion dissociative recombination
$O^- + O_2^+ \rightarrow O + O_2$	ion-ion dissociative recombination
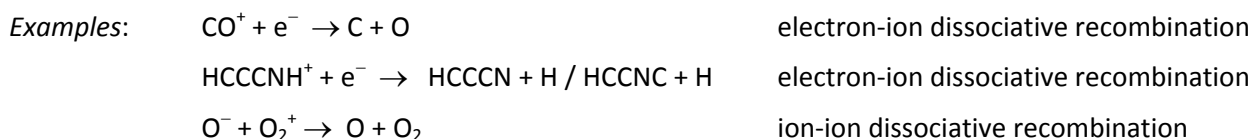
18. A simple model for calculating the rate of ion-molecule reactions

State-of-the-art QCT and quantum scattering calculations are capable of predicting reaction cross sections and rate constants for ion-molecule reactions. However, these calculations are only possible when a detailed potential energy surface is available for the reaction under study, which is often not the case. In the following, we will show how we can use basic principles of collision physics to understand the key factors determining the rates of ion-molecule reactions, and to develop a simple expression which can be used to calculate approximate rate constants. The model we will derive is known as the *Langevin model*, and is the simplest of a variety of *capture theories* that have been developed to describe the rates of ion-molecule reactions. Such models assume that reaction is governed by the long-range part of the interaction potential, a region that can be treated classically to a reasonable approximation. To develop the Langevin model, we need to introduce the concepts of *impact parameter*, *orbital angular momentum* and *centrifugal barriers*. These will already be familiar to anyone taking the Molecular Reaction Dynamics option.

The *impact parameter* quantifies the initial perpendicular separation of the paths of the collision partners. Essentially, this is the distance by which the colliding pair would miss each other if they did not interact in any way, and can be found by extrapolating the initial straight-line trajectories of the particles at large separations to the distance of closest approach.
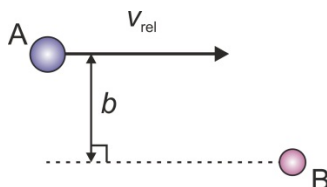
In the context of a collision, the *orbital angular momentum* is an angular momentum associated with the relative motion of the collision partners as they approach and collide. **It is not to be confused with the quantum mechanical orbital angular momentum of an electron in an atomic orbital.** Even for two particles travelling in completely straight lines, there is an associated orbital angular momentum when their relative motion is considered. We can illustrate this by looking at the line of centres of the two particles at various points in their trajectory.
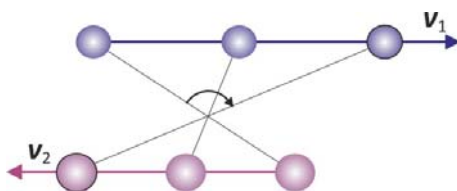
We see that even though the particles are travelling in straight lines, the line of centres of the particles rotates about their centre of mass. Only head on collisions with an impact parameter $b=0$ have no associated orbital angular momentum.

Mathematically, the orbital angular momentum for a colliding pair of particles is given by

$$\boldsymbol{L} = \boldsymbol{r} \times \boldsymbol{p} \tag{18.1}$$

where $\boldsymbol{r}$ is the (vector) separation of the particles and $\boldsymbol{p} = \mu \boldsymbol{v}_{rel}$ is their relative linear momentum (m is the reduced mass of the particles, and $\boldsymbol{v}_{rel} = \boldsymbol{v}_1 - \boldsymbol{v}_2$ is their relative velocity). We can therefore find the magnitude of $\boldsymbol{L}$ from

$$|\boldsymbol{L}| = |\boldsymbol{r} \times \boldsymbol{p}| = |\mu \boldsymbol{r} \times \boldsymbol{v}_{rel}| = \mu v_{rel} r \sin\theta \tag{18.2}$$

where θ is the angle between r and $\boldsymbol{v}_{rel}$. At large separations, $r\sin\theta$ is simply equal to the impact parameter, b, giving

$$|\boldsymbol{L}| = \mu v_{rel} b \tag{18.3}$$

Because the total angular momentum (the sum of the orbital angular momentum $\boldsymbol{L}$ and any rotational angular momentum $\boldsymbol{J}$ of the collision partners) must be conserved throughout the collision, this is true right up until the point that the particles collide, assuming the rotational states of the particles do not change.

The relative kinetic energy of the two particles can be written either as the sum of their individual kinetic energies relative to the centre of mass, or as the sum of the kinetic energy $\frac{1}{2} \mu v_{rad}^2$ associated with the 'radial' velocity component v_{rad} along their line of centres (the line joining the two particles) and the kinetic energy $L^2/2I$ (where $I = \mu r^2$ is the moment of inertia of the molecules) associated with their orbital motion. Since angular momentum must be conserved throughout the collision, the kinetic energy associated with the orbital motion is not available to help surmount an activation barrier, and because it has the effect of reducing the available energy, this term is often referred to as a *centrifugal barrier*. The centrifugal barrier term is often combined with the potential energy surface to give an effective potential. i.e.

$$V_{eff}(r) = V(r) + \frac{L^2}{2\mu r^2} \tag{18.4}$$

As shown in the figure below, the centrifugal barrier can give rise to an effective barrier to reaction, even when the potential energy surface itself has no barrier.
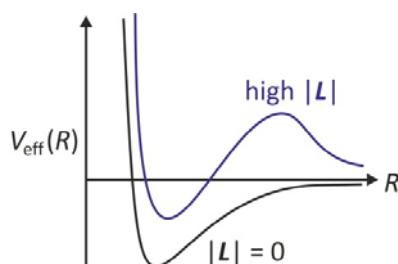
Using $L^2 = \mu^2 v_{rel}^2 b^2$ (see Equation 18.3), we can rewrite the effective potential as

$$V_{eff}(r) = V(r) + \frac{\mu v_{rel}^2 b^2}{2\,r^2} \tag{18.5}$$

We see that the barrier will be largest for heavy systems at large impact parameters. The centrifugal barrier often has the effect of reducing the maximum impact parameter that can lead to successful reaction, thereby reducing the reaction cross section.

Returning to our ion molecule reaction, we can now write down an effective potential for the long range attractive part of the potential. The effective potential in this region will contain contributions from ion-induced dipole interactions, ion-permanent dipole interactions (if the neutral molecule has a permanent dipole), ion quadrupole interactions, and so on, as well as a term representing the centrifugal barrier. We will consider only the simplest case, in which the molecule has no permanent dipole, and will therefier include only the contributions of the ion-induced dipole interaction and the centrifugal barrier to the effective potential. The long-range potential is then

$$V_{eff}(r) = -\frac{\alpha q^2}{8\pi\varepsilon_0 r^4} + \frac{\mu v_{rel}^2 b^2}{2\,r^2} \tag{18.6}$$

As the reactants approach, they initially have a kinetic energy of relative motion equal to $K_{rel} = \frac{1}{2}\mu v_{rel}^2$. As they experience the centrifugal barrier, some of this kinetic energy is converted into potential energy. In order for the reactants to surmount the barrier and for reaction to take place, the initial kinetic energy must be greater than the barrier height i.e. $K_{rel} > V_{eff}(r_{max})$, where r_{max} is the position of the barrier. This is shown schematically below for a number of different impact parameters, b. Because the height of the centrifugal barrier is determined by the impact parameter, there will be a maximum impact parameter b_{max} beyond which the particles do not have sufficient energy to react. We shall show in the following that by determining b_{max}, we can calculate a value for the rate constant.
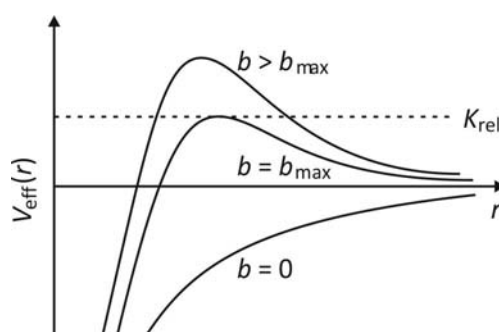
To find the value of r for which $V_{eff}(r)$ is a maximum, we solve

$$\frac{dV_{eff}(r)}{dr} = 0 \tag{18.7}$$

After some algebra (left as a straightforward exercise for the reader), we obtain

$$r_{max} = \left(\frac{\alpha q^2}{2\pi\varepsilon_0 \mu v_{rel}^2 b^2}\right)^{1/2} \tag{18.8}$$

The barrier height is therefore

$$V_{eff}(r_{max}) = -\frac{\alpha q^2}{8\pi\varepsilon_0 r_{max}^4} + \frac{\mu v_{rel}^2 b^2}{2r_{max}^2}$$

$$= \frac{\pi\varepsilon_0 \mu^2 v_{rel}^4 b^4}{2\alpha q^2} \tag{18.9}$$

For reaction to occur, we require $K_{rel} \geq V_{eff}(r_{max})$. i.e.

$$\frac{1}{2}\mu v_{rel}^2 \geq \frac{\pi\varepsilon_0 \mu^2 v_{rel}^4 b^4}{2\alpha q^2} \tag{18.10}$$

Rearranging, we find that the maximum impact parameter for which reaction can occur is given by

$$b^2 \leq \left(\frac{\alpha q^2}{\pi\varepsilon_0 \mu v_{rel}^2}\right)^{1/2} \tag{18.11}$$

The reaction cross section is then

$$\sigma_r(v_{rel}) = \pi b_{max}^2 = \pi\left(\frac{\alpha q^2}{\pi\varepsilon_0 \mu v_{rel}^2}\right)^{1/2} \tag{18.12}$$

According to this expression (sometimes referred to as the Langevin cross section), the reaction cross section has a $1/v_{rel}$ dependence on the reactant relative velocity, and takes the form shown below. Note that although the reactant kinetic energy increases with v_{rel}, so too does the centrifugal barrier, with the net effect being a dramatic decrease in cross section as the relative velocity increases.
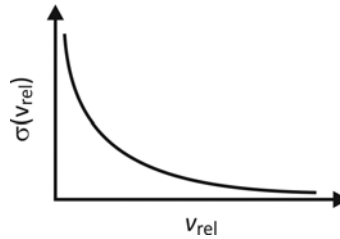
From simple collision theory, the rate constant for a given relative velocity is given by $k(v_{rel}) = \sigma_r(v_{rel})v_{rel}$, and the thermal rate constant can be found by integrating the rate constant over the Maxwell Boltzmann distribution $f(v_{rel})$ (assuming a thermal distribution of velocities), to give

$$k(T) = \int_0^\infty v_{rel}\,\sigma_r(v_{rel})\,f(v_{rel})\,dv_{rel}$$

$$= \int_0^\infty v_{rel}\,\pi\left(\frac{\alpha q^2}{\pi\varepsilon_0 \mu v_{rel}^2}\right)^{1/2} f(v_{rel})\,dv_{rel} \quad \text{(substituting for } \sigma_r(v_{rel})\text{)}$$

$$= \left(\frac{\pi\alpha q^2}{\varepsilon_0 \mu}\right)^{1/2}\int_0^\infty f(v_{rel})\,dv_{rel}$$

$$= \left(\frac{\pi\alpha q^2}{\varepsilon_0 \mu}\right)^{1/2} \quad \text{(since } f(v_{rel}) \text{ is normalised)} \tag{18.13}$$

Note that because we have only considered the possibility of a centrifugal barrier to reaction (i.e. we have ignored any true barriers that may be present on the potential energy surface), this expression represents an upper limit to the collisional rate coefficient for an ion-molecule reaction. A key point to note is that the thermal rate constant we have derived is *independent of temperature*, in line with our previous discussion of ion-molecule reactions.

There are many more sophisticated models available for modelling ion-molecule reaction rates. These include quantum mechanical models such as the catchily named adiabatic capture and centrifugal sudden approximation (ACCSA) theory, which takes into account the rotational states of the reactants, variational transition state theory, and trajectory calculations. The latter two approaches require a reasonably detailed knowledge of the potential energy surface for the reaction. Variational transition state theory is an improved version of transition state theory, which you have met in statistical mechanics courses. Trajectory calculations are covered in the Molecular Reaction Dynamics option.

19. Laboratory-based astrochemistry

While astronomical observations provide raw data on the physical conditions in various regions of space and the atomic and molecular species present, interpreting such data is only possible as a result of laboratory-based studies of a wide range of basic atomic and molecular processes. For example, molecular identification via the assignment of spectral lines recorded using a telescope can only be achieved through comparison with spectra recorded on earth (if the molecule of interest is sufficiently stable and can be generated in sufficiently high quantities to detect) or spectra simulated on the basis of electronic structure calculations. Kinetic models of interstellar chemistry require knowledge of rate constants for individual chemical steps, which again must either be measured in a laboratory or modelled theoretically. Understanding the complex chemistry occurring on the surface of interstellar dust grains requires the development of suitable laboratory-based analogues and methods for studying them. In many cases, the much higher number densities involved in laboratory experiments, combined with the extremely high detection sensitivities achievable for a wide range of molecules of interest, mean that it is often possible to simulate processes that occur over millions of years in space within a few minutes in the laboratory.

Laboratory-based astrochemistry is a growing field, and an ideal playground for physical chemists. In the following, we will outline a few of the current challenges in astrochemistry that laboratory-based studies can help to address.

19. The grand challenge: chemical modelling of giant molecular clouds

Perhaps the ultimate goal of the astrochemistry community is to develop a complete chemical model of an interstellar gas cloud. Amongst other things, such models would allow the age of a molecular cloud to be estimated based on measurements of its atomic composition.

The techniques used to model molecular clouds are very similar to those developed for modelling chemical processes in the earth's atmosphere. However, there are many more unknowns in modelling interstellar gas clouds than in atmospheric models. Many of the rate constants, particularly for reactions occurring on dust grains, are unknown, and measurements on gas clouds to establish parameters such as temperature and number density cannot be carried out directly in the same way as they can in the earth's atmosphere. Nonetheless, the process of setting up and solving a kinetic model follows the same general principles as for an atmospheric model, and similar parameters need to be quantified:

(i)   Data on the chemical composition of the cloud is taken from experimental observations. Ideally, we would have accurate number densities for all chemical species within the cloud, including electrons.

(ii)   The physical conditions within the cloud are needed, including temperature, number density, electron temperature, radiation field, and extinction coefficient (used to estimate the dust composition). These conditions will not generally be constant throughout the cloud. For example, the density will fluctuate due to stellar winds, stellar explosions such as supernovae, and random perturbations, while the temperature is determined by the balance of heat inputs from radiation and exothermic chemical reactions, and heat losses, primarily radiative losses accompanying relaxation of atomic and molecular species from excited states. The radiation field is determined by the proximity to nearby stars and extinction by interstellar dust.

(iii) Transport processes must be considered. These include diffusion and collisions, as well as more exotic phenomena such as shock fronts transiting the clouds, and magnetic turbulence.

(iv)   An estimate of the radiation field emanating from newly forming stars within the cloud is important in order to account for photochemical processes occurring in these regions.

(v)   Accurate reaction rates for all chemical processes occurring in the cloud are needed. Often these are not known, and must be estimated or modelled.

(vi)   The reactions to be included in the model must be decided upon, along with the target species that will be compared with available experimental data.

Once all of the required parameters have been quantified, we can set up the rate equations, a set of coupled differential equations, and propagate them numerically in time to predict the concentrations of the target species. Some parameters, for example the chemical composition of the cloud and sometimes the temperature in different regions, can be determined from astronomical observation data (see Sections 2 to 4) in combination with data from quantum chemistry calculations. Other parameters, such as rate constants, must be determined in laboratory-based studies, either through experimental measurement or theoretical modelling.

In addition to the 'grand challenge' of developing a complete chemical model of an interstellar gas cloud, a number of more specific problems in astrochemistry are currently attracting considerable attention from the research community. Two examples are given in the following.

20. The search for biological molecules

There is an enormous amount of interest in detecting biological molecules in interstellar space, as their presence would represent a significant step in the search for extraterrestrial life as well as potentially providing insight into the origins of life on earth. Laboratory-based studies appear to indicate that there are feasible mechanisms for generating simple amino acids under the conditions known to be present within interstellar gas clouds, and that glycine (the simplest amino acid) and perhaps other biogenic molecules should be abundant enough to be detected. However, to date there has only been one reported detection of glycine[7], and this has been contested rather than confirmed[8].

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[7]   Y-J Kuan, S. B. Charnley, H-C. Huang, W-0L. Tseng, and Z. Kisiel, Interstellar glycine, *Astrophys. J.*, **593**, 848-867 (2003).

21. The diffuse interstellar bands (DIBs)

The set of absorption features known as the diffuse interstellar bands represents perhaps the longest-standing mystery in astronomical spectroscopy. The first of these bands were reported in 1922[9], and now number more than 400, ranging across the UV, visible, and infrared parts of the spectrum. Despite general agreement that the absorptions are mostly likely due to large organic molecules in the ISM, there have been no definitive assignments to date. PAHs (see Section 16.3.3), carbon chains, and fullerenes have all been implicated as possible candidates for diffuse interstellar band absorptions. However, the spectroscopy of these species is difficult to study in the laboratory and challenging to model accurately via electronic structure calculations. It is known from solid-state studies that PAH cations comprising 30 or more carbon atoms absorb strongly in the visible, while the corresponding neutrals absorb in the UV, but such large species are very difficult to generate and maintain in the gas phase, a requirement if high-resolution spectroscopic studies are to be performed.

While the IR emission bands arising from vibrational transitions of PAHs are fairly similar, the electronic spectra are known to be highly characteristic for each molecule. If the problems outlined above are overcome and laboratory-based spectra for large PAHs become available, they are likely to allow specific molecules to be identified within the ISM.

22. Overview of astrochemistry

This course has provided a brief overview of the types of chemical processes occurring in interstellar space, beginning with the synthesis of chemical elements within stars and continuing with a summary of the various processes that lead to the formation of complex molecules within interstellar gas clouds. We have also considered a range of theoretical and experimental methods that may be employed to help identify molecules in space and to unravel the chemical processes by which they are formed.

There is a great deal more to the field of astrochemistry. We have not even touched upon the chemistry and physics of meteorites and comets, or the events leading to the formation of planets and their subsequent chemistry. Astrochemistry is a fascinating and rapidly evolving field, in which physical chemists have a great deal to offer, in the interpretation of observational data through our knowledge of spectroscopy, in the kinetic modelling of reaction cycles, and in laboratory measurements of rate constants and investigations into reaction mechanisms.

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[8] L. E. Snyder, F. J. Lovas, J. M. Hollis, D. N. Friedel, P. R. Jewell et al., A rigorous attempt to verify interstellar glycine, *Astrophys. J.*, **619**, 914-30 (2005).

[9] M. L. Heger, further study of the sodium lines in class B stars; the spectra of certain class B stars in the regions 5630 A – 6680 A and 3280 A to 3380 A; Note on the spectrum of g Cassiopeiae between 5860 A and 6600 A. *Lick Observatory Bull.,* **337**, 141-148, (1922).