1 What is Astrochemistry?

"To date, 241 individual molecular species, comprising 19 different elements, have been detected in the interstellar and circumstellar medium by astronomical observations. These molecules range in size from two atoms to seventy, and have been detected across the electromagnetic spectrum from centimetre wavelengths to the ultraviolet." (Brett A. McGuire)[1]

1.1 Astronomical Background

1.1.1 A Brief Historical Introduction

Astrochemistry is a fairly new and quite rapidly developing interdisciplinary subject, so it seems appropriate to begin with a brief account of how the subject began. Up to the 1930s, it was known that clouds of gas existed in the space between the stars in our galaxy, the Milky Way. Could the gas be partially molecular? It wasn't known. Careful theoretical studies, notably by the world famous astronomer, Sir Arthur Eddington, in 1926, concluded that no known processes in this gas could produce molecules at a sufficient rate that detectable abundances of molecules could be created.[2]

However, just over a decade later, in 1937, astronomers discovered for the first time that the optical signatures of a few simple molecular species were present in spectroscopic observations of the very low

Astrochemistry: Chemistry in Interstellar and Circumstellar Space
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Published by the Royal Society of Chemistry, www.rsc.org

density gas occupying the vast space between the stars in the Milky Way galaxy.[3,4] The first molecular species to be detected in interstellar gas were CH, CH^+, and CN, and their optical lines were seen in absorption along lines of sight towards several bright stars which acted as continuum sources of radiation. The molecular abundances were deduced to be very low. This first discovery of molecules in space was considered at the time to be interesting, but merely a backwater of contemporary astronomy, which at the time was mainly concerned with studying the evolution of stars. In fact, we now know that the first detections of these three interstellar molecular species were just the first steps in the discovery of a rich astronomical chemistry and in the development of what we now call *astrochemistry*. This new branch of science has provided a revolution in the way that astronomers understand the evolution of the Milky Way and all galaxies, and has brought new understanding of the formation of stars and planets: in fact, the role of molecules in astronomy is fundamental. At the time, however, it was recognised that – just as Eddington had found – the formation of molecules in the very low density interstellar gas where they are subjected to intense ultraviolet radiation from massive stars presented challenging chemical problems to which no convincing solutions could be offered. These and other problems are now largely resolved, and the special chemistry that has been discovered to operate under the physical conditions that astronomy provides is the main concern of this book.

In the years following the early molecular detections, astronomers began to use radio telescopes to explore the galaxy. The discovery in 1951 of interstellar emission from *atomic* hydrogen in the famous 21 cm line enabled maps of the Milky Way to be made, revealing its spiral structure. It became clear that the interstellar medium is almost entirely hydrogen, with helium being present with an abundance by number of atoms of about a tenth that of hydrogen; the main reactive elements are present merely in trace amounts.

A quarter-century after the first detections of the interstellar molecular species CH, CH^+, and CN, another molecular species, the hydroxyl radical, OH, was detected (in 1963) in interstellar space.[5] This detection was made using the new waveband for molecular detections: radio. The detection signature was absorption by foreground OH molecules of background radio emission, in a hyperfine transition in the molecule corresponding to a radio wavelength of 18 cm. This molecule was also detected in intense emission lines from material around an exploding star, a supernova. The emission intensity was found to be so great that it was attributed to stimulated emission: this was the first maser known in astronomy. Interstellar ammonia, NH_3, (in 1968) and water, H_2O, (in 1969) were also detected at radio wavelengths.

Another new waveband technique for molecular astronomy soon became available: ultraviolet spectroscopy carried out using rocket-borne spectrometers above the Earth's atmosphere (which is opaque in the far-ultraviolet). Later, ultraviolet spectrometers were carried on orbiting satellites. Rocket-borne observations of interstellar gas on lines of sight towards bright stars revealed for the first time in 1970 the presence of ultraviolet absorption lines of *molecular* hydrogen.[6] Together with the earlier discovery of interstellar atomic hydrogen by its emission at 21 cm, these observations of molecular hydrogen showed that a significant fraction of the total amount of interstellar hydrogen could be in molecular form. Later studies showed that on lines of sight where molecular hydrogen was abundant, other interstellar molecules were also more likely to be found. This association between the relatively abundant molecular hydrogen and other trace species suggested that molecular hydrogen played a fundamental role in interstellar chemistry.

Soon after the detection of interstellar molecular hydrogen, a flood of detections of new interstellar molecular species began. It continues to this day. Very many of these detections were made at millimetre and sub-millimetre wavelengths where molecular emissions or absorptions in rotational transitions often arise. One of the most important and abundant interstellar molecular species is carbon monoxide, CO. It was first detected in 1970, by its emission at a wavelength of 2.6 mm,[7] corresponding to the lowest energy and longest wavelength rotational transition of CO. This molecule is, after molecular hydrogen, the most abundant interstellar molecular species, and it has been used widely to trace the presence of interstellar gas and to show the structure of molecular gas in the Milky Way and other galaxies. CO traces interstellar gas that is denser than that in the low density clouds in which CH, CH^+, and CN were first detected. These CO observations mapped a population of cold, relatively dense, dark molecular clouds throughout the Milky Way galaxy; these clouds had been discovered earlier by their ammonia emissions.

The list of interstellar molecular species detected by their spectra over the electromagnetic spectrum from radio to far-ultraviolet has grown very significantly over the last half-century. It includes many molecular species that seem familiar from school chemistry (such as water, ammonia, methyl alcohol, *etc.*) but also many less familiar species. A few of these less familiar species were actually discovered to be present in interstellar space even *before* they had been synthesized and studied in the laboratory (*e.g.*, cyanotetraacetylene, HC_9N). Evidently, a rich and unusual chemistry is occurring in the interstellar gas in the Milky Way and other galaxies, in spite of what seem to be (see Table 1.3b, below) quite unfavourable physical conditions for an active chemistry. We'll discuss the chemistry that generates *interstellar molecules* in Chapters 3 and 4.

This astronomical chemistry is not limited to clouds of gas in interstellar space, far from stars. Molecules are also found in regions close to some types of stars. These circumstellar regions may have physical conditions, such as higher densities and warmer temperatures, which may be quite favourable to the operation of an effective chemistry. However, some special circumstellar regions appear to be quite hostile to chemistry (such as circumstellar gas around supernova explosions) but may be – rather surprisingly – fairly rich in molecules. We'll discuss in Chapter 6 the chemistries that produce these *circumstellar* molecules.

If molecular species found in circumstellar regions are included in the list of detected interstellar species, then the total number of all interstellar and circumstellar species is currently about 250. We'll show and discuss a complete (up to mid-2021) table of detected interstellar and circumstellar species in Section 1.3 of this chapter. If detected isotopologues (*i.e.*, molecules that differ only in their isotopic composition, such as $^{12}C^{16}O$, $^{12}C^{17}O$, $^{12}C^{18}O$, $^{13}C^{16}O$, $^{13}C^{17}O$, and $^{13}C^{18}O$) are also included, then the total number of detected species is probably several times larger than 250. The actual number of interstellar molecular species (detected and undetected) must be even larger; our studies in Chapter 4 will imply that many more species must be involved in the chemical networks that form the detected molecules, and these species must also be present. These additional species may be undetected because their abundance is too low for detection or they may be undetectable if they have no transitions in suitable regions of the electromagnetic spectrum.

For the astronomer, the molecules provide excellent probes of the physical conditions in interstellar and circumstellar regions. For the chemist, these regions provide an opportunity to explore gas phase, surface, and solid-state chemistry operating under physical conditions that are very different from those normally found on Earth and which are generally much more hostile to chemistry. To understand the chemistries that are functioning in space requires inputs from across a wide range of science: from astronomical observers who provide the fundamental data on molecular abundances and the physical conditions where the molecules are found, from computational modellers studying the networks of chemical processes that may give rise to the observed species, from astrophysicists who describe the remarkable role of molecules in the evolution of galaxies, and from laboratory and theoretical chemists who measure or compute essential data on reaction rate coefficients that are required in those computations. The interaction and cooperation between all these disciplines has created the new subject of astrochemistry. A gentle introduction to astrochemistry can be found in ref. 8.

In this book, we shall explore the chemistry that provides the rich array of molecular species that are found in interstellar and circumstellar regions, and describe the roles that these molecules play in the formation of stars and planets.

1.1.2 The Milky Way

The most detailed and complete observational information about astrochemistry is, of course, for our own galaxy, the Milky Way, so we'll summarize its main features first. But we note here that the Milky Way is merely one of very many galaxies that make up the observable Universe. We'll discuss very briefly in Section 1.1.5 the variety of galaxy types observed in the Universe. To a greater or lesser extent, depending on the physical conditions, the processes of astrochemistry that occur in the Milky Way also occur in external galaxies.

Our planet Earth orbits our star, the Sun, which is merely one of a huge number of stars in the Milky Way galaxy. In terms of its mass and intrinsic brightness, the Sun is a fairly typical member of this collection of stars; a few stars are much more massive and very much brighter, but many stars are fairly similar to the sun or less massive (down to about one tenth of a solar mass) and consequently fainter. There are believed to be a few times 10^{11} stars in the Milky Way and they are distributed approximately in a disc shape, roughly circular, with a spiral structure within the disc and a bar structure through the centre. The Sun is not located in the galactic Milky Way in a privileged position, but is located about one half of a radius from the galactic centre, and in the central plane of the disc. As seen from Earth on a moon-free night, the distribution of stars in the galaxy appears as a dense band of stars, many of which are too faint for the naked eye to distinguish. We see the light of unresolved stars as a diffuse (or milky) haziness, hence the name: the Milky Way.

The dimensions of the Milky Way are huge: the stellar disc's diameter is about 170 000 light years (roughly 50 kiloparsecs, or kpc; see tables in the preface for information on units used in astronomy) and the thickness of the stellar disc is about 0.6 kpc. On average, therefore, stars are separated by a few parsecs from each other, but in fact the distribution of stars in the galaxy is very far from uniform. The mass of the galaxy resides mainly in the stars, and is estimated to be about 10^{12} solar masses (or $M_{\odot}$). The whole structure, the barred spiral, is rotating. Some information about the Milky Way is summarized in Table 1.1. Of course, we can't obtain an image showing the large scale structure of the entire Milky Way as would be seen from outside the galaxy, since we are embedded within it. But we can examine images of galaxies that seem to be very similar in size and structure, and two such examples are shown in Figure 1.1. These images reveal the spiral

Table 1.1 Some approximate data for the Milky Way galaxy.

Diameter	27 kpc
Thickness of stellar disc	0.6 kpc
Number of stars	10^{11}
Total mass	10^{12} $M_{\odot}$
Interstellar mass	10^{11} $M_{\odot}$
Sun's distance from centre	8 kpc
Spiral pattern rotation period	3×10^{8} y
Galaxy type	Barred spiral

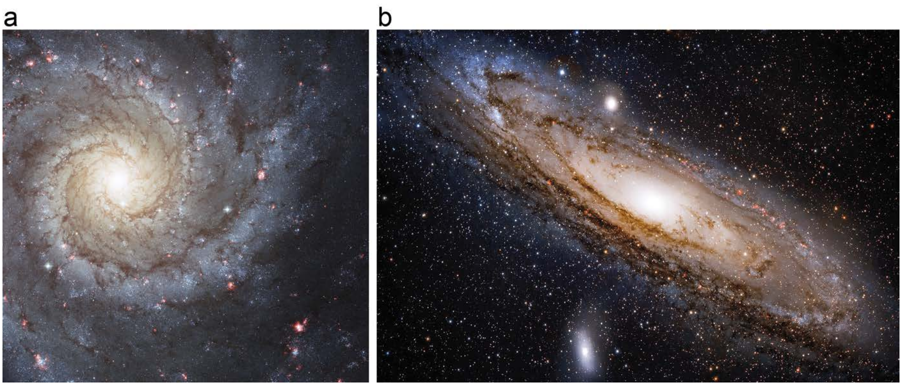

Figure 1.1 Images of two spiral galaxies believed to be similar to the Milky Way. (a) shows an optical image of galaxy M74 which we see nearly face-on (Credit: NASA, ESA, and the Hubble Heritage (STSC/AURA)-ESA/Hubble Collaboration; Acknowledgement: R. Chandler (University of Toledo) and J. Miller (University of Michigan)), and (b) shows the Andromeda galaxy which we see nearly edge-on. The spiral structure is evident in both images, and Andromeda shows a very thin disc. Reproduced from https://commons.wikipedia.org/w/index.php?curid=12654493 under the terms of the CC BY 2.0 license http://creativecommons.org/licenses/by/2.0/deed.en.

structure and the concentration of matter into a very thin disc in these galaxies. Both these features are present in the Milky Way.

We shall discuss in Chapter 6 the chemistry that occurs in cool stellar envelopes of stars of modest mass and also in the supernovae explosions that end the lives of more massive stars. These near-stellar regions are much denser than interstellar molecular clouds, and the temperatures within them are also much higher than the generally low temperatures of interstellar molecular clouds. It is not surprising, therefore, that a rich chemistry occurs so that these near-stellar regions can be largely molecular. Some of these stars eject gas and dust into interstellar space during a brief late stage of their evolution. Supernovae explosions from the relatively few stars of high mass (from about ten up to several tens of solar masses) also expel gas and dust into interstellar space. They also have a very significant large scale effect on gas in the galaxy, creating a very hot ($\sim 10^6$ K), very low density ($\sim 10^{-3}$ cm^{-3}) ionized gas that fills much of interstellar space (see Table 1.3a, below).

1.1.3 Interstellar Gas in the Milky Way

The space between the stars of the Milky Way is occupied by a very tenuous and dusty gas: *the interstellar medium*. This gas is almost entirely hydrogen, with traces of other elements (see Table 1.2). The mass of the interstellar medium is about one percent of the mass of the galaxy. If this large mass were spread over the entire volume of the galaxy it would amount to an average number density of about one hydrogen atom per cubic centimetre, an exceptionally low number density. As we can see from the elemental abundances in Table 1.2, these very low number densities would preclude the possibility of chemistry occurring on a reasonable timescale in the galaxy. Fortunately, the interstellar medium is far from uniform. The interstellar medium contains a variety of structures, with hydrogen number densities ranging from

Table 1.2 Approximate abundances by number, relative to hydrogen, of the most abundant elements in the Milky Way galaxy.

Element	Abundance	Element	Abundance
H	1	Si	3.16×10^{-5}
He	9.77×10^{-2}	Mg	3.63×10^{-5}
O	5.75×10^{-4}	Fe	3.31×10^{-5}
C	2.14×10^{-4}	S	1×10^{-5}
N	6.2×10^{-5}	Na, Ca	2×10^{-6}

Table 1.3 (a) Hot and (b) cool regions of the interstellar medium.

(a) Hot regions

Name	Filling factor in interstellar space	Typical dimension in interstellar space (pc)	Number density of H^+ ions (cm^{-3})	Temperature (K)
Coronal gas	~50%	1000	10^{-3}	10^6
Warm ionized gas	~40%	1000	0.3	8000
HII regions	<1%	1	10^2–10^4	8000
Warm neutral gas	~10%	100	0.3	8000

(b) Cool regions

Name	Typical size (pc)	Number density, H (cm^{-3})	Temperature (K)	State of hydrogen	Chemistry	Ice mantles on dust?	Dynamical age (My)
Cool neutral	10	30	100	H	No	No	10
Diffuse	10	10^2	100	H/H_2	Yes	No	3
Translucent	1	10^3	30	H_2/H	Yes	No	3
Molecular	0.1	10^4	10	H_2	Yes	Yes	1
IRDC[a]	0.1	10^5	25	H_2	Yes	Yes	0.01
"Hot" core	0.01	10^7	300	H_2	Yes	No	0.01

[a]Infrared dark cloud.

about ~10^{-3} cm^{-3} to ~10^{7} cm^{-3} (or even higher). Interstellar molecules are generally located in fairly cool interstellar gas with densities above about 10^{2} cm^{-3}. The gas in interstellar clouds is not uniform in density, but has a complex filamentary structure. Bright spots along these filaments are associated with the arrival of new stars forming from the interstellar gas.

The Milky Way (and probably the Universe, too) is flooded with *cosmic rays*. These "rays" are, in fact, fast-moving particles; they are atomic nuclei, and most of them are hydrogen nuclei (protons). They are probably accelerated to high velocities by extreme shocks arising from supernovae and active galactic nuclei. Energies for a single particle up to or larger than 10^{20} eV have been inferred. One of these very high energy atomic particles has kinetic energy comparable to that of an apple falling under Earth's gravity through several metres! In fact, cosmic rays with these extreme energies are very rare, and the much more numerous cosmic ray particles with much lower energies (about a few MeV per particle) are responsible for most of the influence of these particles on the gas. Cosmic rays ionize interstellar atoms and molecules, ejecting energetic electrons into the gas. The energy is shared through collisions, and so this amounts to an important heating effect in the interstellar medium. This heating may help to generate structures (such as clouds) in the interstellar gas. The ionization of molecules by cosmic rays creates molecular ions; however, these ions are short-lived (as we'll discuss in Chapter 3), and so cosmic ray ionization tends to suppress molecular abundances, affecting the cooling of molecular gas, its temperature and pressure, and hence its structure.

The electromagnetic radiation in the interstellar gas includes, of course, starlight from the many stars in the galaxy, especially in the optical and ultraviolet parts of the spectrum. Some of this radiation is absorbed by dust grains that are everywhere mixed with interstellar gas (we shall discuss the origin and properties of dust grains in Section 1.1.4, and also in the later chapters of this book) and re-radiated at longer wavelengths, so the Milky Way dust is also a source of infrared radiation. The Galaxy is also a source of radio waves emitted from ions moving through the tangled magnetic field lines that thread the Galaxy. Powerful events both inside the Galaxy and external to it generate X-rays and γ-rays. Thus, photons of the complete range of the electromagnetic spectrum pervade the interstellar medium and have a significant effect on the interstellar gas on both the local and large-scale interstellar structures. Some of these photon-driven processes are discussed in more detail in Chapter 3.

Table 1.3(a) and (b) summarize the approximate characteristics of the various types of interstellar region identified in the Milky Way. These structures are maintained by the impact of strong radiation fields, both particle radiation and electromagnetic radiation, on the interstellar gas. The numbers included in these tables are approximate and indicative rather than specific.

The data in Table 1.3(a) show that nearly all of the interstellar volume is occupied by gas that is either at very high temperatures (~10^6 K) and very low density (~10^{-3} cm^{-3}) or warm (~8000 K) and low density (~0.3 cm^{-3}). These structures are broadly maintained by heating caused by supernovae explosions. These gases are fully ionized. The very hot gas is called "coronal" gas because ultraviolet absorption lines from ionized oxygen, carbon, and nitrogen arise in this gas, and these lines were originally identified in the solar corona. Recombination in the warm ionized gas generates a warm neutral low density gas. The components called HII regions are the regions surrounding hot stars and ionized by ultraviolet starlight. These regions are roughly spherical, and can be seen in optical photographs (such as M51 shown in Figure 1.2) as regions of red emission at a wavelength of 656 nm corresponding to the Balmer transition 3→2 in the recombination spectrum of H^+ with electrons.

None of these "hot" components is capable of generating a significant chemistry as molecules are readily destroyed under these conditions. Their importance in the present context is that these "hot" components occupy nearly all of interstellar space but contain only a tiny fraction of interstellar mass; therefore, the remaining gas – which comprises nearly all of the interstellar mass – is confined to very small

Figure 1.2 Image of spiral galaxy NGC 2403, showing strings of near-spherical HII regions along the spiral arms. (Credit: Suburu Telescope (NAOJ), Hubble Legacy archive, processing by Robert Gendler.)

regions of space. This contrast may be illustrated by comparing the characteristic sizes of "hot" and "cold" regions in Tables 1.3(a) and (b).

Table 1.3(b) shows the types of interstellar region that have been observationally identified and which are relatively cool and dense. Note that the numerical values shown are merely indicative of typical rather than precise values. The *cool neutral regions* are of low density; they are pervaded by stellar ultraviolet radiation which dominates any chemistry occurring. However, the remaining regions are those in which molecules may be readily observed and an active chemistry is operating. *Diffuse* clouds are the type of cloud in which the first three detections of interstellar molecular species were made in 1937. The number of species detected in such clouds is now much greater and the chemistry is evidently fairly complex even in these rather low density clouds. There is some protection for the chemical processes against destruction by ultraviolet starlight provided by some extinction by interstellar dust. These diffuse clouds probably survive for millions of years until dynamical events associated with supernovae destroy them. *Translucent clouds* benefit from higher densities and increased extinction, and represent a transition region between diffuse clouds and molecular clouds.

Molecular clouds are denser regions that are almost entirely molecular. In them, ultraviolet radiation from nearby massive stars is largely excluded because of extinction caused by interstellar dust (see sub-section 1.1.4). The chemistry in molecular clouds is mainly determined by cosmic ray ionization. These molecular clouds may be dense enough to be gravitationally unstable, and if so they may not survive for more than a million years. In the process of collapse to higher densities, chemistry continues and becomes more complex. Ices are deposited on the surfaces of dust grains, and solid-state chemistry within these ices generates new molecular species. Regions like this are believed to be the sites where massive stars are formed; such regions are called *infrared dark clouds* (IRDCs). Eventually, the warming of the central regions by radiation from the protostar (the newly forming star) releases complex molecules from the ice mantles on dust grains. These late stages in the evolution have relatively short lifetimes, much less than a million years, and are known as *hot cores*.

1.1.4 Interstellar Dust in the Milky Way

We've referred several times already to the roles that interstellar dust may play in astrochemistry, and the catalytic activity of dust will be described in detail in the second part of this book. However, it will be useful in this rapid survey of the interstellar medium in the Milky Way to summarize in this section some of the main information about the origin and properties of interstellar dust.

The suggestion that there might be some material in interstellar space tending to obscure the light of background stars was made by William Herschel, who in 1784 was using a telescope to make simple sketches of rich star fields. He noticed in one such star field a small zone in which there appeared to be a complete absence of stars, and famously noted (in German) in his journal "Here indeed is a hole in the Heavens!" He may have believed that such a "hole" truly existed, or he may have considered that some localized material in front of the star field extinguished the light of the background stars, giving the appearance of a "hole". Later, more sensitive photographic techniques showed that some stars not detected by Herschel did exist in the putative "hole", confirming that the more likely explanation was of some obscuring material in the line of sight, rather than of a true absence of stars. Further observations showed that the obscuration was not just a local effect but a general phenomenon: there is a widespread interstellar "fog" – called *interstellar extinction* – along almost all lines of sight in the Galaxy (and, indeed, in external galaxies, too). This extinction causes a partial dimming of starlight everywhere; sometimes the dimming can be effectively total, just as a thick terrestrial fog can extinguish the light from a nearby streetlight. An example of extinction of a portion of a rich star field is shown in Figure 1.3.

Further, it was found that the amount of extinction caused by the interstellar fog varied with frequency in such a way that starlight in the blue part of the spectrum was more heavily extinguished than red light. Thus, distant stars were apparently "reddened" compared to closer similar stars. This was a useful phenomenon, allowing estimates of distances to stars to be made, since more reddened stars should be located at greater distances. Theoretical studies showed that this colour-dependent (*i.e.*, wavelength-dependent) behaviour in the visual spectrum could be accounted for if there was a population of spherical dust grains with a range of diameters comparable to the wavelengths of visible light, *i.e.*, around some hundreds of nanometres in diameter. Assuming that the amount of dust is proportional to the amount of gas along a line of sight, the fogginess can in principle be used to measure the amount of interstellar gas along that particular line of sight.

When studies of extinction were able to be extended into the infrared and ultraviolet, it was clear that extinction in the infrared continued to decrease as wavelength increased, whereas extinction in the

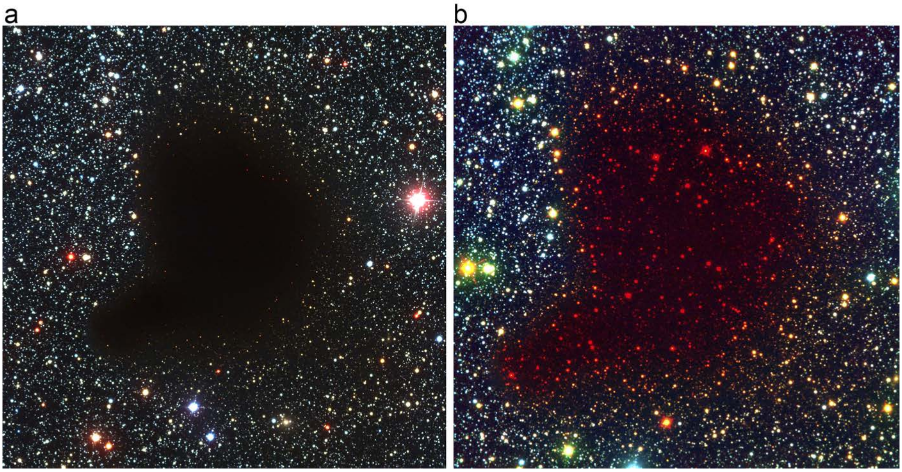

Figure 1.3 A rich star field photographed in the optical (a) and also in the infrared (b). An intervening dusty gas cloud extinguishes the optical light of the background stars (a), but the infrared image (b) reveals their presence. (Credit for both images: ESO.)

ultraviolet was more complicated. There is a localised peak in extinction in the near ultraviolet at a wavelength of about 220 nm, and then after a decline to a local minimum at a wavelength near 160 nm there is a strong rise in extinction in the far ultraviolet extinction (~100 nm). Astronomers measure extinction in magnitudes, a term reaching back to ancient astronomy when the brightest stars were said to be of first magnitude, the next brightest were said to be of second magnitude, *etc.* When numerical studies could eventually be made, it was found that a first magnitude star was about one hundred times brighter than a sixth magnitude star. This relationship could be expressed mathematically in the following way:

$$A_{\lambda} = 2.5\log_{10}(I_0/I_{\lambda}) \tag{1.1}$$

so a change in intensity caused by extinction from I_0 to I_{λ} by a factor of 100 corresponds to a change in extinction, A_{λ}, of 5 magnitudes. The variation of interstellar extinction with wavelength along a particular line of sight is generally measured relative to the extinction at a particular wavelength in the visual region of the spectrum, denoted by V; this reference wavelength is conventionally chosen to be 550 nm. The curve that shows how this normalized extinction varies with wavelength along a particular line of sight is called the *interstellar extinction curve*, and a typical example of a normalized interstellar extinction curve in the Milky Way is shown in Figure 1.4. This figure shows how the extinction caused by interstellar dust varies with wavelength along a typical line of sight in the Milky Way.

In Table 1.3(b), we list the cool regions of the interstellar medium; these are the regions which have the potential to be partly or largely molecular. Since the gas and dust are relatively well mixed, the density gives a measure of the extinction in a region. The cool neutral regions have little extinction and are freely pervaded by the mean interstellar radiation field. Diffuse clouds have a modest amount of extinction, up to about one magnitude of extinction in the visible, and more extinction in the ultraviolet (according to the curve shown in Figure 1.5). Translucent clouds may have about three magnitudes of visual extinction. The three remaining types, molecular clouds, the IRDCs, and Hot Cores, are denser and have so much extinction that one may assume that the external interstellar radiation field is almost entirely excluded by the extinction caused by interstellar dust.

On sufficiently long paths through the Milky Way galaxy, the amount of dust increases linearly with path length, at a rate of about 1.8 visual magnitudes per kiloparsec. On the large scale, assuming that dust and gas are well mixed, it is found that the average column density, N_H, of total hydrogen in both atoms H and molecules, H_2, and the average

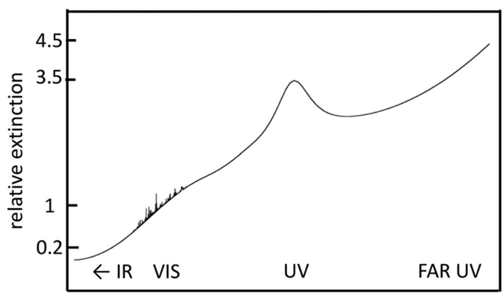

Figure 1.4 Characteristic interstellar extinction curve in the Milky Way. This diagram shows how the average extinction measured in the Milky Way galaxy varies with wavelength. In the infrared, extinction is small compared to that in the visible. Extinction increases almost linearly with inverse wavelength in the visible, and rises to a peak near 220 nm in the near ultraviolet. Further into the ultraviolet, extinction first decreases then rises strongly in the far ultraviolet, ~100 nm, where the amount of extinction is about three times that in the visible.

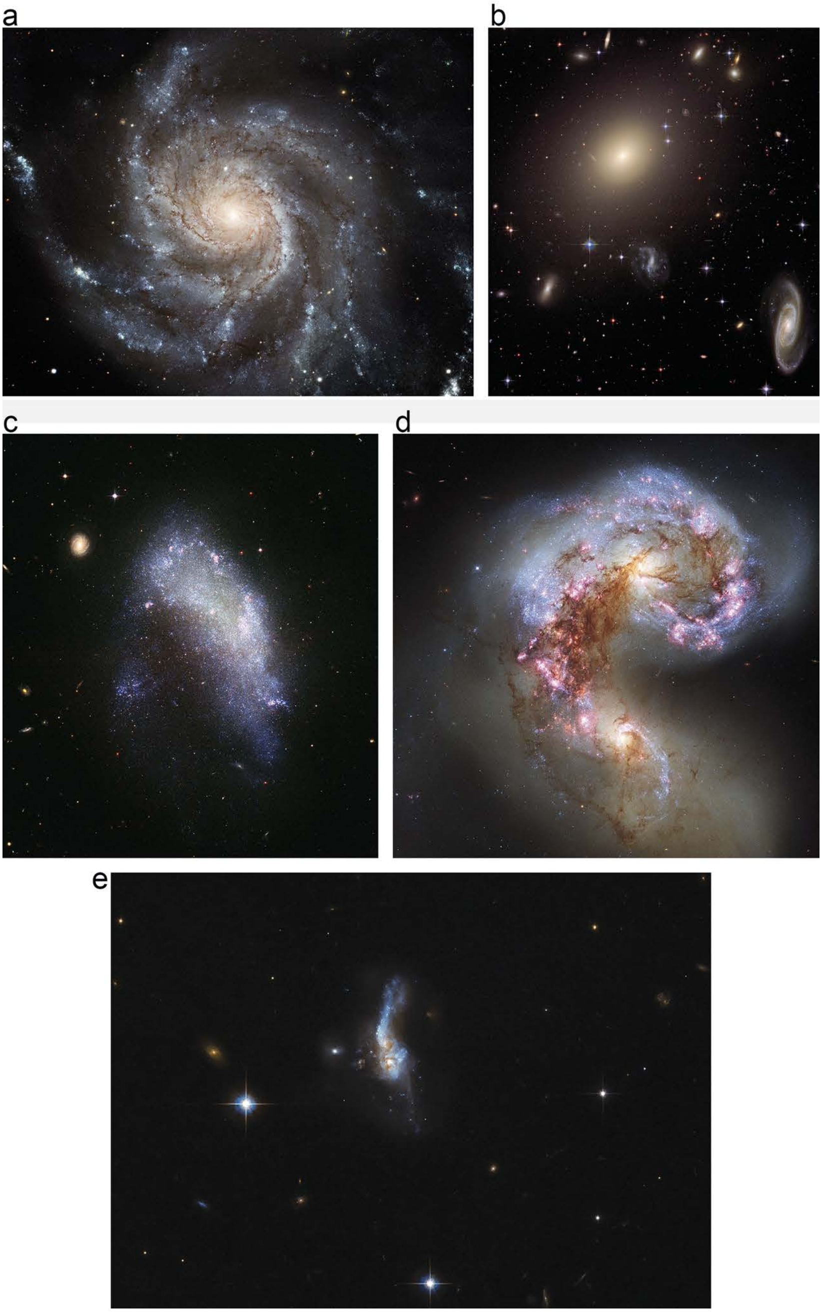

Figure 1.5 Some examples of images of various types of galaxy. (a) The Pinwheel galaxy (also called M101) is a spiral galaxy and from Earth is viewed face-on. (Credit: NASA, ESA, and the Hubble Space Telescope.) (b) The elliptical galaxy ESO-325-G004 has a

(continued)

visual extinction, A_V, taken over many lines of sight in the Milky Way are related in the following equation:

$$N_H/A_V = 1.9 \times 10^{21}\ \mathrm{cm}^2 \text{ per magnitude} \quad (1.2)$$

The idea that interstellar extinction is caused by a population of small particles in interstellar space is supported by other lines of evidence and is now accepted. This evidence includes

(i) the collection and identification of dust grains within the solar system; some of the collected grains clearly originate from outside the solar system;
(ii) detected interstellar absorption features in the infrared attributed to absorption in solid state material;
(iii) detected scattering and polarization of starlight; both of these phenomena are attributed to the interaction of starlight with solid particles; for polarization, at least some of the dust grains must be asymmetric and weakly aligned, probably by a magnetic field;
(iv) detected thermal emission (in the infrared) from solid particles heated by starlight;
(v) the observed absence (or the so-called *depletion*) of some gas phase atoms where dust grains are abundant. See Table 1.4 for information about interstellar depletions.

Table 1.4 shows the total relative abundances of the most abundant chemically active elements (consistent with Table 1.2), measured for hot stars in the Milky Way (relative to 10^6 hydrogen atoms). In these hot stars, the temperatures are so great that dust grains cannot exist. In the interstellar medium, however, elements may be either in the gas or in dust grains. The third column shows the measured relative elemental abundances in the diffuse interstellar gas. The difference between the second and third columns (the "missing" material)

Figure 1.5 *(continued)* smooth profile; none of the stars in this galaxy are resolved, and most of the stars are of relatively low mass. (Credit: NASA, ESA, and the Hubble Heritage Team and J. Blakeslee.) (c) Galaxy NGC 1427A is an irregular galaxy. These galaxies are small and their shapes are affected strongly by near-collisions with massive galaxies. (Credit: NASA, ESA, and the Hubble Heritage Team.) (d) The Antennae galaxies are galaxies (NGC 4038 and 4038) in collision, generating a high star formation rate. Such galaxies are called starburst galaxies. (Credit: ESA, Hubble, and NASA.) (e) This galaxy, IRAS 14348-1447, is an example of an Ultraluminous Infrared Galaxy (ULIRG). ULIRGs have very high star formation rates. (Credit: ESA, Hubble and NASA.)

Table 1.4 Interstellar depletions of elements in diffuse interstellar gas.

Element	Abundance	Interstellar gas	Interstellar dust
O	575	389	186
C	214	91	123
N	62	62	0
Mg	36.3	1.5	34.8
Fe	33.1	0.3	32.8
Si	31.6	2.2	29.4

shown in the fourth column is assumed to be in interstellar dust grains in diffuse interstellar gas.

The implication of Table 1.4 is that about one third of oxygen, more than half of carbon, and almost all of magnesium, iron and silicon are in dust grains, while all nitrogen is in the gas phase. The results suggest that the composition of interstellar dust could largely be made up of iron/magnesium silicates and carbons in solid form and in large hydrocarbons such as polycyclic aromatic hydrocarbons (PAHs). These conclusions are consistent with the results of modelling interstellar extinction curves. The models typically require a range of silicate dust grain radii from a few nm to a few hundred nm, for which the size distribution is very strongly skewed to the smallest sizes (typically, in these models, the number of grains with radii in the range a to $(a + \mathrm{d}a)$ is proportional to $a^{-3.5}\mathrm{d}a$. In such a distribution, there would be roughly three thousand times as many grains of radius 30 nm as 300 nm). A significant amount of carbon is required to be in interstellar PAHs, but solid interstellar carbon is also necessary, either as discrete grains or as a coating on silicate grains.

The conclusions of the previous paragraph depend on results of detailed calculations that describe the interaction of electromagnetic radiation with a sphere of specified refractive index. The calculation involves the application of Maxwell's equations of electromagnetism to a grain, and is simple in concept but complicated in practice. The calculation gives information about the scattering and absorption of radiation by the grain. For simplicity, let's consider the extinction caused by a population of spherical dust grains of radius a, all of the same material; the number density of the dust grains is n_d and the path length is l. Then, the intensity I_0 is reduced to

$$I_\lambda = I_0 \exp[-n_\mathrm{d}\pi a^2 Q_{\mathrm{ext}(\lambda)} l] = I_0 \exp(-\tau_\lambda) \tag{1.3}$$

where Q_ext is an efficiency factor for extinction, and is the main result from the calculation. Here, τ_v is the optical depth and equal to

$A_v/1.086$ (where A_v is in magnitudes). In fact, the extinction is a result of two separate processes: *scattering* of radiation out of the path by the dust grains, and *absorption* of radiation by the dust grains. The efficiencies of these two processes are Q_{sca} and Q_{abs}, respectively, and

$$Q_{ext} = Q_{sca} + Q_{abs} \tag{1.4}$$

The ratio $\omega = Q_{sca}/Q_{ext}$ measures the ability of the grains to reflect radiation, rather than absorb it, and is called the *albedo*. The calculation of these efficiencies is beyond the scope of this book. In general, the results show a near linear behaviour for $x = 2\pi a/\lambda$ on the order of unity, and approaching a constant value of 2 for large values of this same parameter, x. It is the linear behaviour that provided support for the idea that extinction is caused by dust grains, because it matches the near-linear behaviour of the interstellar extinction curve (Figure 1.4) in the visual part of the spectrum. This part of the interstellar extinction curve therefore requires the presence of some dust grains with sizes comparable to the wavelength of visual light. Similarly, the rise in extinction observed in the far ultraviolet suggests that dust grains are present with sizes much smaller than the wavelength of visible light.

We shall discuss some aspects of the formation of dust grains later in this book (see Chapter 6), but for now we shall simply note that the grains are formed (similar to the ways in which smoking candles create soot, or incomplete combustion in internal combustion engines makes sooty exhaust fumes) in cool stellar envelopes and in energetic stellar explosions, and ejected into interstellar space. These grains are not immutable and may change their sizes and physical and chemical nature after they leave the circumstellar environment and make their journey through interstellar space. They pervade the entire interstellar medium and are generally mixed uniformly with the interstellar gas. The total mass of dust in the Milky Way is about one percent of the mass of gas in the interstellar space of the Milky Way, or about 10^9 $M_\odot$. However, the dust-to-gas ratio may vary significantly from one galaxy to another, depending on stellar activity and the survivability of the dust. Although the dust is apparently a minor component of matter in the Milky Way, it has important consequences for interstellar chemistry. For our purposes in this book, the importance of dust lies mainly in its various roles in interstellar chemistry, and we shall discuss these in Chapters 7–9. The information that can be obtained about interstellar dust and its roles in chemistry are summarized in Table 1.5. A simple introduction to the properties and roles of interstellar dust can be found in ref. 9.

Table 1.5 A summary of information about interstellar dust and its roles in the Milky Way galaxy.

Origin	Circumstellar envelopes of cool, evolved stars Ejecta from supernovae
Signature	Extinction and polarization of starlight
Inferences from modelling interstellar extinction	Caused by small dielectric particles Typical range of grain radii: $a \sim 5$ nm–0.5 μm Typical size distribution: number in range $a \rightarrow a + \mathrm{d}a$ is $\mathrm{d}n \sim a^{-3.5}\mathrm{d}a$
Composition	Silicate and carbon solids, either distinct or combined; usually amorphous, plus PAH molecules
Role in interstellar chemistry	Surface reactions, especially H_2 formation
Role in solid-state chemistry	Accumulation of simple mixed ices on surfaces of dust particles Processing of mixed ices to more complex species
Role in evolution of the galaxy	Essential functions in star and planet formation

1.1.5 Galaxies Outside the Milky Way

The observable Universe is believed to contain a very large number of galaxies, possibly as many as 10^{12} galaxies, distributed throughout the Universe in a volume of radius around 15 gigaparsec (Gpc). On average, the separation between galaxies is typically measured in units of Gpc, very much greater than the dimensions of galaxies themselves (the Milky Way diameter being about 27 kpc). The galaxies are observed to be receding from each other, with velocities increasing (and apparently accelerating) with separation. Intergalactic space cannot be completely empty since galaxies are continually ejecting matter; however, no intergalactic gas has been detected so far.

Galaxies aren't all like the Milky Way and other spiral galaxies (discussed above, see subsections 1.1.2 and 1.1.3), but are found in various shapes and sizes, and the interstellar gas within them may have a variety of physical conditions, different from those of the Milky Way. Other types of galaxies include elliptical galaxies, starburst galaxies, and irregular galaxies.

Ellipticals have, as the name implies, an ellipsoidal shape, seen from any angle. The stars are in orbit about the common centre of mass but may not be resolved. Ellipticals have few high mass stars and little structure, generally appearing quite smooth. They usually have little interstellar gas; and the abundance of heavy elements is low so that a rich chemistry is unlikely in these objects. Giant ellipticals also form, and these are much larger than typical spirals.

Some galaxies are observed to be forming stars at a very high rate. They have large reserves of interstellar gas and are converting this gas rapidly into stars, so star formation in these galaxies – the so-called *starburst galaxies* – is intense. These galaxies are often associated with galaxies that are merging together. Mergers may also give rise to LIRGs (*luminous infrared galaxies*) and ULIRGs (*ultraluminous infrared galaxies*). These objects contain large amounts of gas and dust. They have a high star formation rate, but most of the optical and ultraviolet starlight is absorbed by the dust and re-emitted in the infrared.

Active galaxies are those galaxies that have an active nucleus. The source of radiation from these galaxies is dominated by the energy released as matter is accreted on to a supermassive black hole located at the centre of the galaxy. Very energetic processes at the centre of the disc carry matter away from the disc in two opposed high speed jets.

Many galaxies don't show the symmetry found in spirals or ellipticals, and are called *irregular galaxies*. They are often small, and the irregular shape may be caused by a near collision with a larger galaxy.

Table 1.6 lists characteristic data for some galaxy types and Figure 1.5 shows examples of these galaxy types.

1.2 Evolution in the Interstellar Medium

All the data presented for the Milky Way galaxy so far in this chapter are "snapshots": they represent the state in which we see the galaxy at present. However, it seems that everything in the Milky Way – and in other galaxies, too – is evolving. The data in Table 1.3 strongly suggest an evolving picture in which low density interstellar gas is swept up by supernova shock waves to form denser neutral gas clouds. These clouds develop an internal chemistry that provides molecules; by radiating energy away from the cloud, these molecules (particularly CO molecules) help to cool the cloud and maintain a low temperature, and the clouds become mainly molecular, and denser and colder. Gravity takes a stronger and stronger hold of the cloud – or on parts of it – and the gravitational collapse of a portion of the cloud results

Table 1.6 Data for some galaxy types.

	Description	Intrinsic luminosity, $L_\odot$	Mass range, $M_\odot$	Diameter, kpc
Spiral	Flat disc, spiral arms	10^8–10^{11}	10^9–10^{12}	10–100
Elliptical	Smooth ellipsoidal	10^6–10^9	10^6–10^{13}	1–200
Irregular	Irregular, dusty	10^6–10^9	10^6–10^{11}	1–10
Starburst	Intense star formation	10^9–10^{11}	10^6–10^{10}	10^2–10^3
ULIRG	Most emission in IR, very bright	$>10^9$	10^9 (?)	10^3 (?)

eventually in the formation of structures such as infrared dark clouds in which star formation may occur. The even denser gas around a newly-formed star (a hot core) is warmed by the radiation of that star, and the molecules released in the warming are a signature of the presence of the still deeply-embedded (and optically obscured) young star.

If sufficiently massive, a newly-formed star will – after a relatively short life of a few million years (in which it generates an *HII region*) – end its life as a supernova. The supernova explosion disrupts the star-forming cloud and sends shock waves into the surrounding interstellar medium, generating the very high temperature "*coronal*" gas that fills so much of space (see Table 1.3). The supernova also seeds the interstellar with the "ashes" of the thermonuclear burning that powered the star (these ashes consist mainly of the elements shown in Table 1.2) and of dust formed in the ejecta from the supernova. Less massive stars that are formed in the collapse of a molecular cloud evolve more slowly than more massive stars. Near the end of their lives, they pass through a phase in which they too eject the ashes of their nuclear burning into interstellar space (much more gently than in a supernova explosion), together with dust formed in their fairly cool envelopes. The roles of stars as sources of gas and dust for the interstellar medium will be discussed further in Chapter 6.

The very hot "*coronal*" gas takes a long time to cool, but eventually the gas reaches a lower temperature (the *warm ionized* gas) and begins to recombine (to form the *warm neutral* gas). Eventually, the cycle begins again: low density, mainly neutral, interstellar gas accumulates because of interstellar gas dynamical events and gravity, and ultimately forms new stars. Interstellar chemistry and dust both play crucial roles in this cycle of events. Together, chemistry and dust provide molecules that control the cooling processes in interstellar gas and allow gravity to take control. Dust is, of course, essential for planet formation (as we shall see in Chapter 9).

A schematic diagram of the evolution in a galaxy like the Milky Way is shown in Figure 1.6.

We can see from this model of galaxy evolution that the variety of galaxies that is observed isn't simply random. There are reasons why one galaxy differs from another. For example, the abundances of elements and of interstellar dust depend on the cumulative amount of star formation in a galaxy; star formation in a galaxy depends on gas density and temperature. These must obviously be crucial parameters in determining interstellar chemistry. As we'll see in Chapter 4, the flux of cosmic rays drives chemistry in dark clouds, and supernovae not only inject elements into interstellar space, they also are responsible

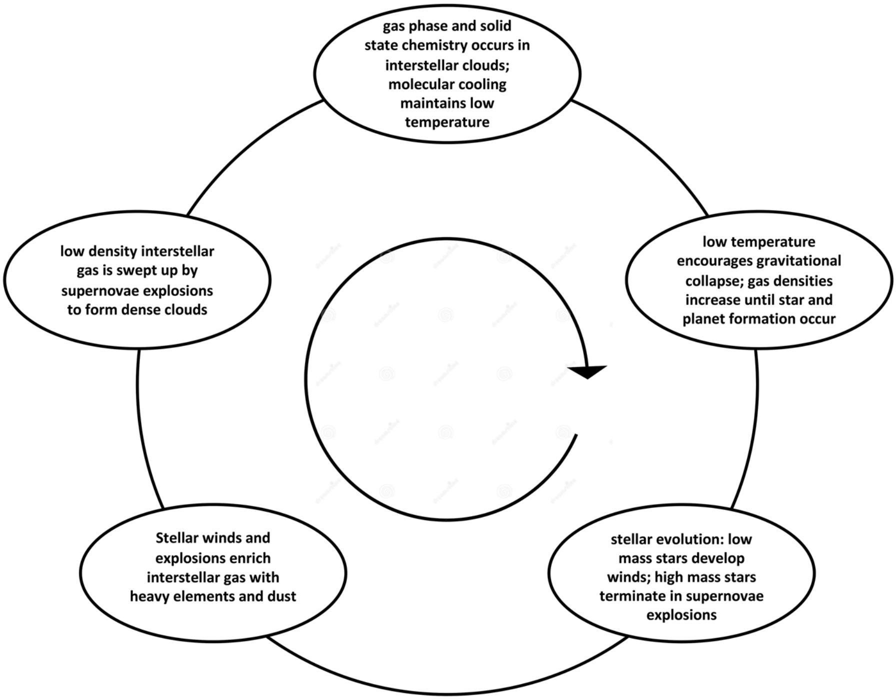

Figure 1.6 Evolution in a galaxy. The diagram indicates evolution in a galaxy like the Milky Way. Chemistry occurs in a molecular cloud, and radiation emitted by the molecules and dust maintains a low temperature, allowing gravity to dominate over pressure so the cloud collapses. Star and planet formation occurs. At the ends of their lives, low mass stars may develop winds while high mass stars may explode in supernovae. Winds and explosions enrich interstellar gas with heavy elements and dust. Low density interstellar gas is swept up by supernovae explosions into denser clouds, and the cycle repeats.

for generating cosmic rays. So, galaxies that are richer in massive stars should be richer in elements with greater atomic mass than hydrogen and also richer in interstellar dust. These galaxies should therefore be richer in interstellar molecules, and the effect of these molecules is to drive more star formation, generating more supernovae, and more cosmic rays, and so on – until the amount of interstellar gas used up in star formation begins significantly to deplete a galaxy of interstellar gas. Then the star formation rate declines. In general, spiral galaxies are rich in interstellar gas and have relatively high star formation rates (the star formation rate in the Milky Way is about one star per year for the entire galaxy, a substantial rate; but some spiral galaxies may have an even higher rate). Ellipticals, by contrast, have little interstellar gas, and a low star formation rate. On the other hand, starburst galaxies have a very high rate of star formation generated in the collisions of galaxies and the rapid compression of interstellar gas. ULIRGs have even higher star formation rates than starburst galaxies.

1.3 Detected Interstellar and Circumstellar Species

Now that we have set the astronomical scene and stated the appropriate physical parameters for various regions of interstellar and circumstellar space, we can focus more specifically on the chemistry occurring in these regions. One way to do this is to examine the list of detected molecular species and to consider the difficulties faced with understanding how this variety of molecules might be produced in the interstellar medium and in circumstellar regions including ejecta from stellar explosions. The list of new detections in interstellar and circumstellar sources, shown in Appendix, grows each year, and the discovery rate is very high at present. The list shown below is believed to be correct and complete as of mid-2021 and includes more than 250 species.

Many of the data contained in the table are taken from a recent very comprehensive review[1] and a constantly updated complete list may be found in ref. 10. Both sources give a reference to the discovery paper, for each of the species listed. Note that astronomers refer to all these species as molecules, whereas many of them should strictly be referred to as radicals. However, because of the tenuous conditions in interstellar and circumstellar space, radicals have a long lifetime in space and so may be reasonably classified as molecules. Under terrestrial conditions, these radical species could only have a fleeting existence.

Each entry in the table shows the chemical symbol, the conventional name, the date of detection, and the type of region (as defined in subsection 1.1.3) in which the molecular species exists, where *cse* denotes circumstellar envelope, *dc* denotes diffuse cloud, *mc* denotes molecular cloud, *sfr* denotes star forming region, and *snr* denotes supernova remnant. For each group of molecules (diatomics, triatomics, *etc.*), the molecules are listed in order of their date of discovery by astronomers. For brevity, isotopologues have not been included in the table (apart from one case); however, it should be noted that they are common in the interstellar medium – and often highly overabundant compared to the relative abundance of the main isotopologue.

The list is impressive in the number of species and in the range of the chemistry shown. Molecular species are found in a wide variety of objects not only in the Milky Way but also outside it, in external galaxies. Given the huge intergalactic distances and the consequent difficulties of making detections, it is remarkable that as many as one third of all known species detected in the Milky Way have also been identified in one or more external galaxies. Inside the Milky Way, molecular species are found not only in the gas phase but also in the solid state (*i.e.*, in molecular ices). Molecules are also detected in exotic regions such as the atmospheres of exoplanets, but planetary detections are not included in this table. As far as the relatively dense cold gas in the Milky Way is concerned (comprising almost all of the interstellar mass), we seem to be living in a largely chemical galaxy.

A few questions about the listed species may immediately come to mind, such as:

1. Galaxies are sources of powerful particle and electromagnetic radiations that are hostile to molecules, so can we devise chemical networks that successfully overcome these losses and produce species in the abundances observed?
2. Much of interstellar gas is at very low densities and temperatures, and chemistry is likely to be slow, so is there enough time available for molecular abundances to grow?
3. The interstellar gas is H-rich and other elements are present in trace values, so why are some (but not all) of the observed species H-poor (*i.e.*, chemically unsaturated)?
4. The list of detected species includes relatively large numbers of diatomic and triatomic species, and ends (with very few exceptions) with relatively small numbers of molecular species containing about a dozen atoms. Is this decline a real chemical effect or is it associated with observational difficulties detecting the larger species? Does the number and variety of interstellar species really decline with complexity?
5. Is the chemistry producing the fullerenes – and possibly the PAHs – simply an extension of the chemistry producing the simpler molecules listed in the appendix to this chapter, or are different processes likely to be required to form these more complex molecules?
6. Silicon and iron have quite similar relative elemental abundances in the interstellar medium of the Milky Way, so why does Si appear in 13 detected species while Fe appears in only one?
7. Why are some detected interstellar molecular species known to be in the solid state? How are they formed? Do these molecules ever appear in the gas phase?

8. Dust has a passive involvement in interstellar chemistry by locking up some elements that would otherwise be present in the gas. What are its active roles? How important are they in the evolution of a galaxy like the Milky Way? Are some environments in the Universe dust-free?
9. The list includes carbon species in the form of both rings and chains. Some recent detections are of PAH molecules and one 2021 detection is of indene (fused benzene and cyclopentene rings), while the chain $HC_{11}N$ (cyanopenta-acetylene) was also detected in 2021. Is it likely that both types of structure – rings and chains – are formed in similar ways?
10. In Section 1.1.1, we noted that isotopologues are present and may be relatively abundant in space. How are these isotopologues formed? Why are isotopologues involving minor isotopes often much more abundant than expected?

Many similar questions could be devised. Obviously, the major tasks are to identify the appropriate chemical mechanisms and to devise chemical networks that might operate under the physical conditions described earlier in this chapter, in the interstellar medium of the Milky Way and other galaxies. We may then see if they can provide suitable answers to these and other questions. That is the purpose of this book. We'll return to these issues in the final chapter of this book.

Appendix: Detected interstellar and circumstellar molecular species

Diatomic molecules

CH (methylidyne) 1937, dc; **CN** (cyanide) 1937, dc; **CH^+** (methylidyne cation) 1937, dc; **OH** (hydroxyl) 1963, snr; **CO** (carbon monoxide) 1970, sfr; **H_2** (molecular hydrogen) 1970, dc; **SiO** (silicon monoxide) 1971, sfr; **CS** (carbon monosulfide) 1971, sfr; **SO** (sulfur monoxide) 1973, sfr; **SiS** (silicon monosulfide) 1975, cse; **NS** (nitrogen sulfide) 1975, sfr; **C_2** (diatomic carbon) 1977, sfr; **NO** (nitric oxide) 1978, sfr; **HCl** (hydrogen chloride) 1985, sfr; **NaCl** (sodium chloride) 1987, cse; **AlCl** (aluminium monochloride) 1987, cse; **KCl** (potassium chloride) 1987, cse; **AlF** (aluminium monofluoride) 1987, cse; **PN** (phosphorus mononitride) 1987, sfr; **SiC** (silicon carbide) 1989, cse; **CP** (carbon monophosphide) 1989, cse; **NH** (nitrogen monohydride) 1991, dc; **SiN** (silicon mononitride) 1992, cse; **SO^+** (sulfur monoxide cation) 1992, mc; **CO^+** (carbon monoxide cation) 1993, cse; **HF** (hydrogen fluoride) 1997, mc; **LiH**

(lithium hydride)? 1998, mc; **FeO** (ferrous oxide) 2002, sfr; **N_2** (molecular nitrogen) 2004, mc; **CF^+** (fluoromethylidynium cation) 2006, sfr; **PO** (phosphorus monoxide) 2007, cse; **AlO** (aluminium monoxide) 2009, cse; **CN^-** (cyanogen anion) 2010, cse; **OH^+** (hydroxyl cation) 2010, sfr; **SH^+** (sulfur monohydride cation) 2010, sfr; **O_2** (molecular oxygen) 2011, dc; **HCl^+** (hydrogen chloride cation) 2012, sfr; **SH** (sulfur monohydride) 2012, cse; **TiO** (titanium oxide) 2013, cse; **ArH^+** (argonium cation) 2014, snr; **CrO** (chromium monoxide) 2015, cse; **NS^+** (nitrogen sulfide cation) 2018, mc, sfr; **HeH^+** (helium hydride ion) 2019, cse; **VO** (vanadium oxide) 2019, cse;

Triatomic molecules

H_2O (water) 1969, sfr; **HCO^+** (formylium cation) 1970, sfr; **HCN** (hydrogen cyanide) 1971, sfr; **OCS** (carbonyl sulfide) 1971, sfr; **HNC** (hydrogen isocyanide) 1972, sfr; **H_2S** (hydrogen sulfide) 1972, sfr; **N_2H^+** (protonated nitrogen) 1974, sfr; **C_2H** (ethynyl) 1974, sfr; **SO_2** (sulfur dioxide) 1975, sfr; **HCO** (formyl) 1976, sfr; **HNO** (nitroxyl) 1977, sfr; **OCN^-** (cyanate) 1979, cs; **HCS^+** (thioformyl cation) 1981, sfr; **HOC^+** (hydroxymethyliumidene cation) 1983, sfr; **SiC_2** (cylacyclopropynylidene) 1984, cs; **C_2S** (dicarbon sulfide) 1987, mc, cs; **C_3** (tricarbon)1988, cs; **CO_2** (carbon dioxide) 1989, mc; **CH_2** (methylene) 1989, sfr; **C_2O** (dicarbon monoxide) 1991, mc; **MgNC** (magnesium isocyanide) 1993, cs; **NH_2** (amidogen) 1993, sfr; **NaCN** (sodium cyanide) 1994, cs; **N_2O** (nitrous oxide) 1994, sfr; **MgCN** (magnesium cyanide) 1995, cs; **H_3^+** (protonated molecular hydrogen) 1996, sfr; **SiCN** (silicon monocyanide) 2000, cs; **AlNC** (aluminium isocyanide) 2002, cs; **SiNC** (silicon mono-isocyanide) 2004, cs; **HCP**(phospha-ethyne) 2007, cs; **CCP** (dicarbon phosphide) 2008, cs; **AlOH** (aluminium hydroxide) 2010, cs; **H_2O^+** (water cation) 2010, sfr; **H_2Cl^+** (chloronium cation) 2010, sfr; **KCN** (potassium cyanide) 2010, cs; **FeCN** (iron cyanide) 2011, cs; **HO_2** (hydroperoxyl) 2012, mc; **TiO_2** (titanium dioxide) 2013, cs; **CCN** (cyanomethylidine) 2014, cs; **Si_2C** (disilicon carbide) 2015, cs; **S_2H** (hydrogen disulfide) 2017, mc; **HCS** (thioformyl) 2018, mc; **HSC** (isothioformyl) 2018, mc; **NCO** (isocyanate) 2018, mc; **CaNC** (calcium isocyanide) 2019, cse; **NCS** (thiocyanogen) 2021, sfr;

Molecules containing 4 atoms

NH_3 (ammonia) 1968, sfr; **H_2CO** (formaldehyde) 1969, sfr; **HNCO** (isocyanic acid) 1972, sfr; **H_2CS** (thioformaldehyde) 1973, sfr; **C_2H_2** (acetylene) 1976, cs; **C_3N** (cyanoethynyl) 1977, cs; **HNCS** (isothiocyanic acid)

1979, sfr; **$HOCO^+$** (protonated carbon dioxide) 1981, sfr; **C_3O** (tricarbon monoxide) 1984, mc; ***l*-C_3H** (propynylidyne) 1985, mc, cs; **$HCNH^+$** (protonated hydrogen cyanide) 1986, sfr; **H_3O^+** (protonated water) 1986, sfr; **C_3S** (tricarbon monosulfide) 1987, mc; ***c*-C_3H** (cyclopropenylidyne) 1987, mc, cs; **HC_2N** (cyanocarbene) 1991, cs; **H_2CN** (methylene amidogen) 1991, cs; **SiC_3** (silicon tricarbide) 1999, cs; **CH_3** (methyl) 2000, sfr; **C_3N^-** (cyanoethynyl anion) 2008, cs; **PH_3** (phosphine) 2008, cs; **HCNO** (fulminic acid) 2009, mc; **HOCN** (cyanic acid) 2009, sfr; **HSCN** (thiocyanic acid) 2009, sfr; **HOOH** (hydrogen peroxide) 2011, mc; ***l*-C_3H^+** (propynylidyne cation) 2012, mc; **HMgNC** (hydromagnesium isocyanide) 2013, cs; **MgCCH** (magnesium monoacetylide) 2014, cs; **NCCP** (cyanophospha-ethyne) 2014, cs; **HCCO**(ketenyl) 2015, mc; **CNCN** (isocyanogen) 2018, mc; **HONO** (nitrous acid) 2019, sfr; **HCCS** (thioketenyl radical) 2021, sfr; **HNCN** (cyanomidyl radical) 2021, mc;

Molecules containing 5 atoms

HC_3N (cyanoacetylene) 1971, sfr; **HCOOH** (formic acid) 1971, sfr; **CH_2NH** (methanimine) 1973, sfr; **NH_2CN** (cyanamide) 1975, sfr; **H_2CCO** (ketene) 1977, sfr; **C_4H** (butadiynyl) 1978, cs; **SiH_4** (silane) 1984, cs; **c-C_3H_2** (cyclopropenylidene) 1987, sfr, mc; **CH_2CN** (cyanomethyl) 1988, sfr, mc; **C_5** (pentacarbon) 1989, cs; **SiC_4** (silicon tetracarbide) 1989, cs; **H_2CCC** (propadienylidene) 1991, mc; **CH_4** (methane) 1991, mc; **HCCNC** (isocyanoacetylene) 1992, mc; **HNCCC** 1992, mc; **H_2COH^+** (protonated formaldehyde) 1996, sfr; **C_4H^-** (butadiynyl anion) 2007, cs; **CNCHO** (cyanoformaldehyde) 2008, sfr; **HNCNH** (carbodiimide) 2012, sfr; **CH_3O** (methoxy) 2012, mc; **NH_3D^+** (deuterated ammonium cation) 2013, sfr; **H_2NCO^+** (protonated isocyanic acid) 2013, sfr; **$NCCNH^+$** (protonated cyanogen) 2015, mc; **CH_3Cl** (chloromethane) 2017, cs; **MgC_3N** (magnesium moncyanoacetylide) 2019, cse; **NH_2OH** (hydroxylamine) 2020, mc; **HC_3O^+** (protonated tricarbon monoxide) 2020, sfr; **HC_3S^+** (protonated tricarbon monosulfide) 2021, sfr; **H_2CCS** (thioketene) 2021, sfr; **C_4S** (tetracarbonsulfide) 2021, sfr; ***t*-HC(O)SH** (*trans*-thioformic acid) 2021, sfr; **HCSCN** (cyanothioformaldehyde) 2021, sfr;

Molecules containing 6 atoms

CH_3OH (methanol) 1970, sfr; **CH_3CN** (methyl cyanide) 1971, sfr; **NH_2CHO** (formamide) 1971, sfr; **CH_3SH** (methyl mercaptan) 1979, sfr; **C_2H_4** (ethylene) 1981, cse; **C_5H** (pentynylidyne) 1986, cs; **CH_3NC** (methyl isocyanide) 1988, sfr; **HC_2CHO** (propynal) 1988, mc; **H_2CCCC** (butatrienylidene) 1991, cse; **HC_3NH^+** (protonated cyanoacetylene)

1994, mc; **C_5N** (cyanobutadiynyl) 1998, mc; **HC_4H** (diacetylene) 2001, cs; **HC_4N** (no name for this radical) 2004, cs; ***c*-H_2C_3O** (cyclopropenone) 2006, sfr; **CH_2CNH** (ketenimine) 2006, sfr; **C_5N^-** (cyanobutadiynyl anion) 2008, cs; **HNCHCN** (*E*- and *Z*-cyanomethanimine) *E*-2013 and *Z*-2019, sfr; **SiH_3CN** (silyl-cyanide) 2014, cse; **C_5S** (pentacarbon monosulfide) 2014, cse; **MgC_4H** (magnesium monobuta diynide) 2019, cse; **CH_3CO^+** (acetyl cation) 2021, sfr; **CH_2CCH** (propargyl radical) 2021, sfr; **H_2CCCS** (thiopropadienone) 2021, sfr; **HCSCCH** (propynethial) 2021, sfr;

Molecules containing 7 atoms

CH_3CHO (acetaldehyde) 1973, sfr; **CH_3CCH** (methyl acetylene) 1973, sfr; **CH_3NH_2** (methylamine) 1974, sfr; **CH_2CHCN** (vinyl cyanide) 1975, sfr; **HC_5N** (cyanodiacetylene) 1976, sfr; **C_6H** (hexatriynyl) 1986, mc, **c-C_2H_4O** (ethylene oxide) 1997, sfr; **CH_2CHOH** (vinyl alcohol) 2001, sfr; **C_6H^-** (hexatriynyl anion) 2006, cs, mc; **CH_3NCO** (methyl isocyanate) 2015, sfr; **HC_5O** (butadiynylformyl) 2017, mc; **HNCHCCH** (propargylamine) 2020, mc; **HC_4NC** (isocyanodiacetylene) 2020, sfr; ***c*-C_3HCCH** (ethynyl cyclopropenylidene) 2021, sfr; **H_2C_5** (pentatetraenylidene) 2021, sfr; **MgC_5N** (magnesium cyanodiacetylide) 2021, cse;

Molecules containing 8 atoms

$HCOOCH_3$ (methyl formate) 1975, sfr; **CH_3C_3N** (methylcyanoacetylene) 1984, mc; **C_7H** (heptatriynylidyne) 1997, mc; **CH_3COOH** (acetic acid) 1997, sfr; **H_2C_6** (hexapenta-enylidene) 1997, mc; **C_7H** (heptatriynylidyne) 1997, cs; **CH_2OHCHO** (glycolaldehyde) 2000, sfr; **HC_6H** (triacetylene) 1997, cs; **CH_2CHCHO** (propenal) 2001, sfr; **CH_2CCHCN** (cyanoallene) 2006, mc; **NH_2CH_2CN** (aminoacetonitrile) 2008, sfr; **$HCOOCH_3$** (methyl formate) c-1975 and t-2012, sfr; **CH_3CHNH** (ethanimine) 2013, sfr; **CH_3SiH_3** (methyl silane) 2017, cs; **$(NH_2)_2CO$** (urea) 2019, sfr; **$HCCCH_2CN$** (propargyl cyanide), sfr; **HC_5NH^+** (protonated cyanodiacetylene), 2020, sfr; **CH_2CHCCH** (vinyl acetylene) 2021, sfr; **MgC_6H** (magnesium triacetylide) 2021, cse;

Molecules containing 9 atoms

CH_3OCH_3 (dimethyl ether) 1974, sfr; **CH_3CH_2OH** (ethanol) 1975, sfr; **CH_3CH_2CN** (ethyl cyanide) 1977, sfr; **HC_7N** (cyanotriacetylene) 1978, mc; **CH_3C_4H** (methyl diacetylene) 1984, mc; **C_8H** (octatriynyl) 1996, cs; **CH_3CONH_2** (acetamide) 2006, sfr; **C_8H^-** (octatriynyl anion) 2007, mc; **CH_2CHCH_3** (propylene) 2007, mc; **CH_3CH_2SH** (ethyl mercaptan)

2014, sfr; **HC_7O** (hexadiynylformyl) 2017, mc; **CH_3NHCHO** (*N*-methylformamide) 2017, sfr; **HC≡CCH=CHC≡N** (*trans*-cyanovinyl acetylene) 2021, sfr; **$H_2C{=}CHC_3N$** (vinylcyanoacetylene) 2021, sfr; **$H_2CCCHCCH$** (allenyl acetylene) 2021, sfr;

Molecules containing 10 atoms

$(CH_3)_2CO$ (acetone) 1987, sfr; **$HO(CH_2)_2OH$** (ethylene glycol) 2002, sfr; **CH_3CH_2CHO** (propanal) 2004, sfr; **CH_3C_5N** (methycyanodiacetylene) 2006, mc; **CH_3CHCH_2O** (propylene oxide) 2016, sfr; **CH_3OCH_2OH** (methoxymethanol) 2017, sfr; ***o*-C_6H_4** (*ortho*-benzyne) 2021, sfr; **H_2CCCHC_3N** (cyanoacetyleneallene) 2021, sfr;

Molecules containing 11 atoms

HC_9N (cyanotetraacetylene) 1978, mc; **CH_3C_6H** (methyltriacetylene) 2006, mc; **CH_3CH_2OCHO** (ethyl formate) 2009, sfr; **CH_3COOCH_3** (methyl acetate) 2013, sfr; **CH_3COCH_2OH** (hydroxyacetone) 2021, cse; **c-C_5H_6** (cyclopentadiene) 2021, sfr; **$NH_2CH_2CH_2OH$** (ethanolamine) 2021, mc;

Molecules containing 12 atoms

C_6H_6 (benzene) 2001, cs; **C_3H_7CN** (*n*- and i-propyl cyanide) *n*-2009, sfr, and i-2014, sfr; **$C_2H_5OCH_3$** (*trans* ethyl methyl ether) 2015, sfr; **c-C_5H_5CN** (1- and 2-cyanocyclopentadiene) 2021, sfr; **$C_2H_5CONH_2$** (propionamide) 2021, sfr;

Molecules containing 13 atoms

c-C_6H_5CN (benzonitrile) 2018, sfr; **$HC_{11}N$** (cyanopenta-acetylene) 2021, sfr;

Polycyclic aromatic hydrocarbon molecules (PAHs)

$C_{10}H_7CN$ (1- and 2-cyanonaphthalene) 2021, sfr; **c-C_9H_8** (indene [fused benzene and cyclopentene rings]) 2021, sfr;

Cage molecules (fullerenes)

C_{60} (buckminsterfullerene) 2010, cse; **C_{60}^+** (buckminsterfullerene cation) 2013, cse; and **C_{70}** (rugbyballene) 2010, cse.

References

1. B. A. McGuire, *Astrophys. J., Suppl.*, 2022, **259**, 30.
2. A. S. Eddington, *Proc. R. Soc. A*, 1926, **111**, 424–456.
3. T. Dunham, *Publ. Astron. Soc. Pac.*, 1937, **49**, 26.
4. P. Swings and L. Rosenfeld, *Astrophys. J.*, 1937, **86**, 483.
5. S. Weinreb, A. H. Barrett, M. L. Meeks and J. C. Henry, *Nature*, 1963, **200**, 829.
6. G. R. Carruthers, *Astrophys. J., Lett.*, 1970, **161**, L181.
7. R. W. Wilson, K. B. Jefferts and A. A. Penzias, *Astrophys. J., Lett.*, 1970, **161**, L43.
8. D. A. Williams and T. W. Hartquist, *The Cosmic-Chemical Bond*, Royal Society of Chemistry, 2013.
9. D. A. Williams and C. Cecchi-Pestellini, *Dust in Galaxies*, Royal Society of Chemistry, 2020.
10. www.astrochymist.org/astrochymist_ism.html.