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## International Reviews in Physical Chemistry

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713724383>

### Interstellar chemistry

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**To cite this Article** Flower, D. R.(1995) 'Interstellar chemistry', International Reviews in Physical Chemistry, 14: 2, 421 — 443

**To link to this Article:** DOI: 10.1080/01442359509353316

**URL:** <http://dx.doi.org/10.1080/01442359509353316>

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## Interstellar chemistry

by D. R. FLOWER

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In order to interpret spectral observations of interstellar clouds in terms of the physical and chemical conditions which prevail within them, a large body of atomic and molecular data is required. We consider both diffuse clouds, which are permeated by the background ultraviolet radiation field, and dense clouds, whose interiors are shielded from the external ultraviolet radiation by dust scattering and absorption in the outer layers. The categories of chemical reaction which are known or believed to be important are reviewed. The results of chemical models that attempt to simulate conditions in the clouds are summarized. The phenomenon of bistability of the steady-state solutions of the chemical rate equations is considered in detail. Interstellar clouds are perturbed from static equilibrium by shock waves, produced by a variety of mechanisms. The structure of shocks and their influence on the physical and chemical state of the medium are described. Processes intervening in the thermal balance of the medium and the exchange of energy with the environment are discussed.

### 1. Introduction

With our understanding of stellar evolution and its relationship with nuclear reactions in stellar interiors came the recognition that stars are born and die within the lifetime of a galaxy. It is now known that stars form in concentrations of molecular gas through a process of gravitational contraction. The gas is renewed and modified by stellar ejecta, notably in the late stages of stellar evolution (winds from Red Giants; planetary nebulae; supernovae). Studies of the interstellar medium lead ultimately to its symbiotic relationship with the evolution of stellar populations.

The interstellar medium is known, from observations, to consist of a mixture of gas and dust, with the gas comprising atoms, molecules and ions. The dust component is responsible for the obscuration of starlight and shields the interiors of sufficiently massive clouds of matter from the background ultraviolet radiation field. The principal source of energy in the interiors of such clouds is cosmic rays, which ionize and heat the gas. In a 'dense' cloud, the particle density may be of order  $10^4 \text{ cm}^{-3}$ , which is to be compared with  $10^{19} \text{ cm}^{-3}$  in the Earth's atmosphere, at ground level. The total mass of gas and dust in such clouds is, nonetheless, very large (hundreds or even thousands of solar masses) because their dimensions are measured in parsecs ( $1 \text{ pc} \approx 3 \times 10^{18} \text{ cm}$ ). The dust accounts for about one per cent of the total mass, and the gas consists predominantly of (molecular) hydrogen and helium. Solar-system abundances (table 1) are representative of the composition of the interstellar medium. Elements heavier than helium are divided between the gas and the dust, with certain elements (e.g. Mg, Si) being heavily depleted into the refractory cores of the grains. Only a small fraction ( $\approx 10^{-7}$  by number) of the gas is ionized, but the ions play a key role in the chemistry; they are also important because they interact directly with the magnetic field that pervades the medium. In dense clouds, the kinetic temperatures are very low, of order 10 K.

In the lower density, 'diffuse' medium which is exposed to the ultraviolet starlight,

Table 1. Solar-system abundances of the more important elements (from Anders and Grevesse (1989)). Numbers in parentheses are powers of 10.

H	1
He	0.10
C	3.6 (−4)
N	1.1 (−4)
O	8.5 (−4)
Mg	3.8 (−5)
Si	3.6 (−5)
S	1.8 (−5)
Fe	3.2 (−5)

the degree of ionization is much higher ( $\approx 10^{-4}$ ), as is the kinetic temperature ( $\approx 100$  K). Radiation shortwards of the H Lyman limit (91.2 nm) is absorbed, by hydrogen atoms close to the source. The remaining photons, of wavelength  $\lambda > 91.2$  nm, can travel further before being absorbed by a dust grain or in a photodissociation/ionization event. Some of these photons dissociate  $H_2$  and CO, the two most abundant interstellar molecules, and ionize atoms or molecules with ionization potentials less than 13.6 eV, notably C and S. Absorption of an ultraviolet photon, when followed by the emission of an electron leads to the heating of the gas.

The very low densities of interstellar clouds ensure that their physical conditions remain far from thermodynamic equilibrium. An exception is the translational energy distribution of the gas, which is maintained by elastic collisions between the particles. This distribution will often, though not always be Maxwellian and characterized by the kinetic temperature. Circumstances can arise in which the kinetic temperatures of the neutral and the ionized particles may differ, owing to the low fractional ionization of the gas and the relative infrequency of ion-neutral collisions. Level populations of the atoms, ions and molecules are generally non-thermal, with the lowest levels carrying a disproportionately large fraction of the total population. Thus, chemical reactions are highly initial state selective, and the intensities of emission lines are usually governed by the dominant collisional excitation processes.

In summary, physical conditions in the interstellar medium are determined by microscopic processes which are moderated by the electromagnetic interaction. The study of such a medium requires the expertise of the atomic physicist and the physical chemist. This medium is a singularly rich laboratory, as may be judged from the lists of species published (for example) in the reviews of Lequeux and Roueff (1991) or Dalgarno (1993), but one over which we have absolutely no control.

An understanding of the chemistry of the interstellar medium necessarily transits by a modelling process, in which an attempt is made to account for the dominant reaction mechanisms (Herbst and Leung 1989, Langer and Graedel 1989). Such models incorporate a library of reactions and associated rate coefficients. The UMIST ratefile (Millar *et al.* 1991) comprises almost 3000 gas-phase reactions, involving over 300 species and 12 elements. The rates of many important reactions have now been measured in the laboratory, although not always at the low temperatures at which they are required. Theory can be a useful guide to the temperature dependence of a reaction rate (see Clary 1994), although the existence of small barriers to reaction can be conclusively demonstrated only by low-temperature measurements. However, we are still far from a convincing interpretation of the observed composition of interstellar clouds. The mechanisms leading to the formation of polyatomic molecules are poorly appreciated;

the role of grain-surface reactions has yet to be established; the chemical and thermal history of interstellar clouds remains an enigma. Even if all the important reactions and their rate coefficients become known tomorrow, a lot of effort would still be required to couple this information correctly to the dynamics of the medium. Fortunately, the scientist's interest in a problem tends to be closely correlated with its complexity.

Chemical models of the interstellar medium may be broadly classified as steady-state or time-dependent. In the former case, the composition of the medium is calculated subject to the constraint that  $dn_j/dt = 0$ , where  $n_j$  is the number density of species  $j$ , and closure relations which ensure that the elemental abundances are conserved. A set of linear algebraic equations results, which may be solved by the Newton–Raphson method (Le Bourlot 1991). The alternative technique involves solving the time-dependent equations, starting from appropriate initial conditions (Watt 1983). This problem is non-trivial, because the first order differential equations which incorporate the rates of the chemical reactions are characterized by widely differing time constants. Such equations cannot be solved by conventional variable step algorithms, such as the Runge–Kutta method; their solution requires an algorithm which is specifically adapted to ‘stiff’ problems (Gear 1971, Hindmarsh 1974).

The composition predicted by the time-dependent model as  $t \rightarrow \infty$  may be compared with the steady-state solution. In practice, the two methods yield the same results, to within the numerical precision. It was generally believed that the steady-state solution was independent of the initial conditions. However, recent work, to be discussed below, has shown that the final state is not unique: two (perhaps more) stable solutions to the chemical rate equations are possible. Whilst this phenomenon of ‘bistability’ has been appreciated by chemical kineticists for some time (see Gray and Scott 1990), the recognition of its possible relevance to the interstellar medium is of more recent date.

In § 2, we shall briefly review the different types of chemical reaction which are known or believed to be important in the interstellar medium. The incorporation of these reactions into models of interstellar clouds is considered in § 3. The chemical significance of shock waves is discussed in § 4. Finally, processes influencing the thermal balance of the medium are reviewed in § 5.

## 2. Categories of reaction

The densities of interstellar clouds are so low that three-body reactions in the gas phase are completely negligible. Grains behave in some ways as a third body, by catalyzing reactions on their surfaces. Most gas-phase reactions are binary, and their rates vary quadratically with the density of the medium. Externally generated photons and cosmic rays ionize and dissociate the constituents of the gas, at a rate which increases linearly with its density. The rates of many reactions depend on the temperature, usually in a nonlinear way. The chemistry is driven by cosmic ray- or photoionization.

### 2.1. Photodissociation and -ionization

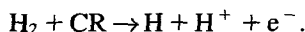
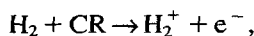
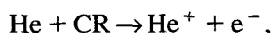
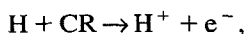
In diffuse clouds, photodissociation and photoionization are important processes, the motors of the chemistry; they are significant also in dense clouds (see § 2.2). The photodissociations of  $H_2$  and CO by the background ultraviolet radiation field are closely linked (see § 3.1). For other species, once the radiation field has been determined, the photodestruction rate may be calculated if the cross section is known in the relevant wavelength domain.

Information on dissociation and ionization rates of interstellar species has been

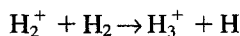
compiled by van Dishoeck (1988). The results derive partly from theoretical calculations, partly from experimental measurements. Much remains to be done, both in terms of extending the list of species studied and of improving the accuracy of the cross sections.

### 2.2. Cosmic ray-induced reactions

There is no reasonable doubt that ions play a key and perhaps a dominant role in interstellar chemistry. The most abundant elements—H and He—provide the most abundant species: atomic and molecular hydrogen and atomic helium. (Molecular hydrogen forms on grain surfaces: see § 2.8.) Cosmic rays (CR) with energies of a few MeV permeate the gas clouds, ionizing the atoms and ionizing or dissociatively ionizing  $H_2$ :



The formation of  $H_2^+$  is followed rapidly by

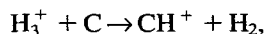


and then by protonation reactions (§ 2.3.). Alternatively,  $H^+$  production is followed by charge transfer (§ 2.4).

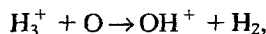
The electrons released by cosmic ray ionization have energies of typically 30 eV. Thermalization of these electrons in dense clouds is accompanied by collisional excitation of the Lyman, Werner and other bands of  $H_2$ . The subsequent fluorescence gives rise to a spectrum of ultraviolet radiation which can ionize and dissociate a number of species comprising elements heavier than helium. This process is much more efficient than direct cosmic ray ionization/dissociation of these same species. Detailed calculations show that the efficiency gain varies from a factor of about 10, for the dissociation of CO, to almost  $10^4$ , for the dissociation of CN (Gredel 1990). The reason is that the rate of cosmic ray ionization of  $H_2$  is proportional to the  $H_2$  number density,  $n(H_2)$ , whereas that of the heavy species  $X$  is proportional to  $n(X)$ . In dense clouds,  $n(H_2) \gg n(X)$ .

### 2.3. Ion-molecule reactions

Once  $H_3^+$  has formed, in the reaction  $H_2^+(H_2, H)H_3^+$ , molecular ions comprising heavy elements can be produced. In particular,



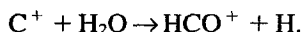
and



initiate sequences of hydrogen-abstraction reactions, of the type  $CH^+(H_2, H)CH_2^+$ , which terminate with  $CH_3^+$  and  $H_3O^+$ . Radiative association of  $CH_3^+$  and  $H_2$  may then occur. Although the rate coefficient for this process is small (see Bates and Herbst 1988), the rate of radiative association becomes comparable with the rate of dissociative recombination in dense clouds, where the fractional ionization is very low. The molecular ion formed at the end of the sequence undergoes dissociative recombination

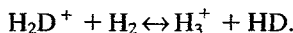
with electrons (§ 2.6); the net effect is the production of a molecule and the neutralization of the initial charge.

$C^+$  ions are formed, in dense clouds, by the indirect cosmic ray ionization process considered in § 2.2. These ions can then react with  $H_2O$ , a product of the dissociative recombination of  $H_3O^+$ :



Dissociative recombination of  $HCO^+$  then yields  $CO$ , which is predicted (and observed) to be the most abundant molecule in the interstellar medium, after  $H_2$ . Much of the elemental carbon available in the gas phase is locked into this stable species.

Another important ion–molecule reaction is



The reverse reaction is rapid, proceeding with a rate constant of order  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , typical of this category of reaction. However, the forwards reaction is slow at low temperatures (Smith *et al.* 1982), essentially because of the differences in the zero-point vibrational energies of the products and reactants. Thus, whilst the ratio  $n(HD)/n(H_2) \approx n_D/n_H \approx 10^{-5}$  (the value of the isotopic abundance ratio in the interstellar medium),  $n(H_2D^+)/n(H_3^+) \approx 0.1 \gg 10^{-5}$  in dense clouds. This enhancement is transmitted to other species through reactions initiated by  $H_2D^+$ , leading to anomalously large values of isotopic ratios such as  $n(OD)/n(OH)$  and  $n(HDO)/n(H_2O)$  (see Millar *et al.* 1989; Pineau des Forêts *et al.* 1989).

A lot of progress has been made in the measurement of the rates of relevant ion–molecule reactions (for a review of recent progress, see Gerlich 1994); these are required not only at room temperature but also at the very low temperatures which characterize dense clouds. Measurements can be made at low temperatures (see Rowe 1988), but they are expensive and difficult to carry out. Accordingly, theoretical predictions, which may be tested against experiment in a limited number of cases, have an important part to play.

Clary (1994) has reviewed progress in the theoretical determination of the rate coefficients for ion–molecule reactions. It is found that classical mechanics provides at least a qualitative understanding of the behaviour of the rate coefficients. Suppose that the ion and the molecule interact through a central potential  $V(R) = -C/R^n$ , where  $C$  is a positive constant,  $R$  is their separation and  $n$  is an integer. An effective potential may be defined by

$$V_{\text{eff}}(R) = V(R) + E\rho^2/R^2,$$

where  $\rho$  is the classical impact parameter for the collision and  $E$  the total energy in the centre-of-mass coordinate system; the second term on the right hand side of this equation is the centrifugal potential. A critical ('orbiting') impact parameter  $\rho_c$  is obtained by setting the maximum of the effective potential equal to  $E$ ; this gives

$$\rho_c^2 = n[(n-2)C/(2E)]^{2/n}/(n-2).$$

The corresponding collision cross section is

$$\sigma = P\pi\rho_c^2.$$

This expression incorporates the probability  $P$  that the reaction takes place when orbiting occurs. This probability should be determined from quantal calculations. For simplicity, we shall assume that  $P \approx 0.5$ , which is often true in practice.

Consider the important case where  $V(R) = -\alpha/(2R^4)$ , corresponding to the electrostatic potential between a singly-charged ion and a molecule of polarizability  $\alpha$ . (We employ atomic units.) It follows that

$$\sigma(E) = \pi[\alpha/(2E)]^{0.5}.$$

The rate coefficient as a function of kinetic temperature,  $q(T)$ , is obtained by integrating over a Maxwellian distribution,

$$q(T) = [8kT/(\pi\mu)]^{0.5} \int y\sigma(y) \exp(-y) dy,$$

where  $y = E/kT$ ,  $k$  is Boltzmann's constant,  $\mu$  the reduced mass and  $[8kT/(\pi\mu)]^{0.5}$  the mean thermal speed of the reactants. Thus, for a charge-induced dipole potential,

$$q(T) \approx \pi(\alpha/\mu)^{0.5}$$

and is independent of the temperature. If the molecule taking part in the reaction is  $H_2$  and the ion is much more massive, then  $\alpha \approx 5$  and  $\mu \approx 3700$ , whence  $q \approx 0.12$  a.u.  $\approx 10^{-9}$  cm<sup>3</sup> s<sup>-1</sup>.

This 'Langevin' value, derived from classical theory, is typical of an ion-molecule reaction at room temperature. At very low temperatures, on the other hand, interactions between the ionic charge and the multipole moments of the molecule come into play, as the relative orientation of the intra- and inter-molecular axes can lock into a minimum energy configuration. When the ion is singly charged and the molecule has a dipole moment  $d$ ,  $V(R) = -d/R^2$ . The orbiting impact parameter is then given by  $\rho_c^2 = d/E$  and the cross section by  $\sigma \approx \pi d/(2E)$ . The corresponding rate coefficient is

$$q(T) \approx [2\pi/(\mu kT)]^{0.5} d.$$

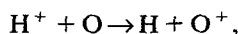
Dividing by the Langevin rate coefficient,  $q_L = \pi(\alpha/\mu)^{1/2}$ , we obtain

$$q(T)/q_L \approx [2/(\pi\alpha kT)]^{0.5} d.$$

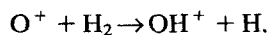
For HCl,  $\alpha \approx 18$  and  $d \approx 0.43$ , hence  $q(T)/q_L \approx 45/T^{1/2}$  and the charge-dipole interaction is dominant at low temperatures.

#### 2.4. Charge transfer reactions

An alternative mechanism for charge propagation in the interstellar gas is electron capture (charge transfer). Atomic ions, particularly  $H^+$ , recombine slowly (radiatively) with electrons; they are more likely to neutralize by electron capture from another species, where this is energetically possible. In diffuse clouds, which are permeated by the background stellar ultraviolet radiation field, ions such as  $C^+$ ,  $Si^+$  and  $S^+$  are produced by photoionization;  $H^+$  is one of the main ionic products of cosmic ray ionization. An alternative route to  $OH^+$  is then



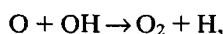
followed by



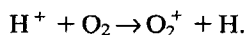
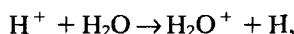
Although slightly endothermic (by 227 K; energies are expressed in K through division by Boltzmann's constant), the former reaction is still rapid at the higher temperatures ( $T \approx 100$  K) which prevail in translucent clouds. In general, charge transfer will proceed in the energetically favourable direction. It is believed that  $H^+$  undergoes charge

transfer with many molecules and radicals. The heavy atoms, C, Si and S, have lower ionization potentials and the corresponding ions tend to capture electrons less readily. Measurements and/or quantal calculations are necessary to establish the energy dependence of the cross section for any given charge transfer reaction.

We have seen in § 2.3 that ion–molecule (specifically protonation) reactions lead to the formation of oxygen-bearing species, such as OH and H<sub>2</sub>O. A further, neutral–neutral reaction,



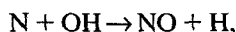
then yields O<sub>2</sub> (see § 2.5). Both H<sub>2</sub>O and O<sub>2</sub> remove H<sup>+</sup> through charge-transfer reactions:



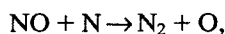
Because of the much faster rate of neutralization of the ionic products, through dissociative rather than radiative recombination, these reactions effectively lead to a reduction in the degree of ionization of the gas. The process is at least partly catalytic: H<sub>2</sub>O<sup>+</sup> reacts with H<sub>2</sub>, yielding H<sub>3</sub>O<sup>+</sup> which dissociatively recombines and forms OH or H<sub>2</sub>O; OH reacts with O to produce O<sub>2</sub>, as noted above. Consequently, in cold, dense clouds, the presence of stable species, such as H<sub>2</sub>O and O<sub>2</sub>, is associated with a very low fractional ionization.

### 2.5. Neutral–neutral reactions

Whilst ion–molecule reactions have been recognized as important for many years, neutral–neutral reactions have come to the fore only recently. Unlike the corresponding reactions with C and O, the protonation of N by H<sub>3</sub><sup>+</sup> is endothermic and unable to initiate the chain leading to one of the best observed interstellar species, NH<sub>3</sub>. Instead, the reactions



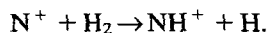
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are followed by



and then by the slightly endothermic reaction

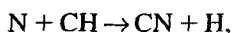


The initial neutral–neutral reactions are believed, on the basis of measurements at or around room temperature (see Smith 1988), to be sufficiently rapid at the much lower temperatures which prevail in dark clouds. However, caution is necessary, as a very small reaction barrier ( $\approx 10^{-2}$  eV) would probably not be detectable from the temperature variation of the rate coefficient in the vicinity of 300 K. On the other hand, such a barrier would significantly reduce the corresponding reaction rate at very low temperatures ( $\approx 10$  K). It is fortunate that results are beginning to flow from the technically-demanding experiments which have been mounted in order to study these reactions at such low temperatures (for a recent review, see Rowe *et al.* 1994).

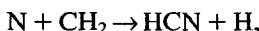
Once NH<sup>+</sup> is formed, hydrogen abstraction reactions with H<sub>2</sub> will proceed up to



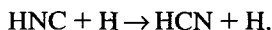
$\text{NH}_4^+$ , which yields  $\text{NH}_3$  through dissociative recombination with electrons. Other neutral–neutral reactions,



and

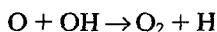


yield the important interstellar species CN and HCN (or its isomer, HNC). The relative abundance of these isomeric forms may be modified through the exothermic reaction



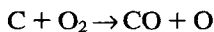
It has been postulated (Pineau des Forêts *et al.* 1990) that the apparent correlation of the ratio  $n(\text{HCN})/n(\text{HNC})$  with the temperature of the medium might be explained if this last reaction has a barrier which is sufficient to inhibit its rate at low temperatures.

We mentioned in § 2.4 that the reaction



may be a significant source of  $\text{O}_2$  in dense clouds. Its rate coefficient has been measured in the range  $250 \leq T \leq 515$  K (Howard and Smith 1981). Theoretical calculations (Clary and Werner 1984) are in good agreement with the measurements and indicate a rate coefficient of approximately  $10^{-10} \text{cm}^3 \text{s}^{-1}$  at  $T = 10$  K; this is only about an order of magnitude smaller than the ‘Langevin’ value which characterizes ion–molecule reactions (see § 2.3). Consequently, OH tends to react with O in dense clouds, rather than the less abundant ions.

Once  $\text{O}_2$  has formed, the reaction



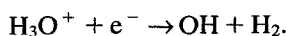
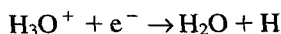
removes atomic carbon from the gas. Indeed, models generally predict that the ratio  $n(\text{C})/n(\text{CO}) \ll 1$  in dense clouds when steady state is attained. On the other hand, there is a growing body of observational evidence which indicates that  $n(\text{C}) \approx n(\text{CO})$ . The removal of atomic carbon is prejudicial to the formation of carbon-bearing species other than CO; the fractional abundances of these species, computed in steady state, fall far below the values observed in dense clouds (Herbst and Leung 1989, Langer and Graedel 1989).

Herbst (1988) suggested that, if the  $\text{C}(\text{O}_2, \text{CO})\text{O}$  reaction had a small activation energy, the abundances of atomic carbon and of complex carbon-bearing molecules might be significantly enhanced in dense clouds. However, the predictions of the models have since been driven further from the observations by the recognition of the importance of an additional group of neutral–neutral reactions, between atomic carbon and unsaturated organic species such as  $\text{C}_2\text{H}_2$ . Experimental work has shown these reactions to be rapid at room temperature (see Husain 1993), and it has been demonstrated and their incorporation into chemical models severely handicaps the production of the complex organic species which are observed in dense clouds (Herbst *et al.* 1994).

In summary, neutral–neutral reactions have long taken a back seat (to ion–molecule reactions) in theoretical studies of interstellar chemistry; in reality, they are about as important. The belated recognition of this fact has far-reaching consequences for studies of the interstellar medium.

### 2.6. Dissociative recombination

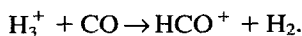
The mutual Coulomb attraction between a molecular ion and an electron, together with the high mobility of the latter, ensures that the rate coefficient for dissociative recombination is large, of the order of  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$  at room temperature; this is about 5 orders of magnitude greater than for radiative recombination of atomic ions. Nonetheless, the fractional ionization of dense clouds is so low ( $\approx 10^{-7}$ ) that molecular ions that can react with  $\text{H}_2$  will do so more rapidly than with electrons. The terminal ion in a chain of hydrogen abstraction reactions dissociatively recombines and hence is neutralized. The branching ratios to the various possible products of dissociative recombination are generally not known. A noteworthy exception is



for which the branching ratio has been measured to be 0.65 in favour of OH (Herd *et al.* 1990).

The value of the rate coefficient for dissociative recombination of  $\text{H}_3^+$  has been controversial. Believed for many years to have the canonical value of  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ , experimental and theoretical work in the 1980s indicated that, in fact, the rate coefficient was characteristically small ( $\approx 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at 300 K; Adams and Smith 1988). The implications of a very small value of the rate coefficient for dissociative recombination of  $\text{H}_3^+$  will be considered below. More recent experiments (Canosa *et al.* 1991, Sundstroem *et al.* 1994) have yielded values similar to that ( $10^{-7} \text{ cm}^3 \text{ s}^{-1}$ ) which is typical of this category of reaction.

We have already seen (§ 2.3) that  $\text{H}_3^+$  plays a pivotal role in the formation of interstellar molecules, especially in dense clouds, through protonation reactions.  $\text{H}_3^+$  reacts with many species, including the abundant CO,



This reaction proceeds with a rate coefficient of the order of  $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ , compared with  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$  for dissociative recombination (according to the more recent measurements cited above). It follows that the rate of removal of  $\text{H}_3^+$  by electrons becomes comparable with its rate of removal by CO when  $n_e/n(\text{CO}) \approx 10^{-2}$ . In dense clouds, where the fractional abundance of CO is  $n(\text{CO})/n_{\text{H}} \approx 10^{-4}$ , this condition becomes  $n_e/n_{\text{H}} \approx 10^{-6}$ . An initial study by Pineau des Forêts *et al.* (1992) (see also Graedel *et al.* 1982) suggested that, when this fractional ionization is attained, a sharp transition occurs between two distinct chemical phases. In the 'high ionization phase' (HIP),  $\text{H}_3^+$  is removed predominantly by electrons, in the 'low ionization phase' (LIP) by CO. More recent work has shown that, in fact, two different steady-state solutions can coexist (Le Bourlot *et al.* 1993 b, 1995 a, b, Flower *et al.* 1994). This phenomenon, known as 'bistability', will be discussed more fully in § 3.2. Here let it suffice to say that the rate of dissociative recombination of  $\text{H}_3^+$  is a key parameter of the problem.

### 2.7. Electron attachment to large molecules

There is ample observational evidence for the presence of small solid particles in interstellar space. In order to account for the wavelength dependence of the extinction of starlight, observed in the ultraviolet part of the spectrum, it is necessary for the size distribution of the grains to extend down to at least  $0.01 \mu\text{m}$  (10 nm). In reality, the size

distribution may be continuous down to atomic dimensions (0.1 nm) and include very small grains and large molecules.

Spectroscopic evidence, in the infrared, suggests that the large molecules comprise polycyclic aromatic hydrocarbons (PAH). Fullerenes have also been postulated as constituents of the interstellar medium, although no observational evidence yet exists to support this contention. Such molecules might have a significant effect on the chemistry of the interstellar gas by providing sites for the attachment of electrons. This process is non-radiative and exothermic and could lead, in dense clouds, to the large molecules carrying a substantial fraction of the negative charge. The fractional ionization of the medium would then be reduced, as atomic ions could neutralize *non-radiatively* in collisions with negatively-charged large molecules. However, recent experiments, using C<sub>60</sub> (Smith *et al.* 1993), have shown that an activation energy barrier of 0.26 eV (3000 K) exists to electron attachment. If similar barriers are common to other large molecules, then the influence of this family of particles on interstellar chemistry as a whole is much reduced.

Why is this question important? We have already seen in § 2.6 that the fractional ionization of the gas intervenes crucially in the bistability phenomenon. If electron attachment to large molecules is uninhibited by a reaction barrier, and if the fractional abundance of such molecules attains about 10<sup>-6</sup> (which is conceivable), then the LIP would predominate in dense clouds. A reduction in the degree of ionization also has implications for the structure of shock waves propagating in molecular clouds. In particular, the collisional coupling between the ions and the neutrals is reduced and large differences can develop between the flow velocities and kinetic temperatures of the ionized and neutral fluids.

### 2.8. Grain-surface reactions

Hydrogen is the most abundant interstellar molecule, as observations, initially in the ultraviolet but more recently in the infrared, have shown. However, no gas-phase process has been found which can produce molecular hydrogen at a rate which is compatible with these observations. Almost by default, one must conclude that grain-surface reactions predominate in the formation of H<sub>2</sub>.

If H atoms stick to the cold grains in interstellar clouds and then form molecules, it is reasonable to suppose that heavy species, such as C, N and O, do likewise. The rapid migration of H atoms makes it probable that saturated molecules (CH<sub>4</sub>, NH<sub>3</sub>, H<sub>2</sub>O) will form (see Watson 1975). The difficulty which remains is to subsequently desorb these species from the grain surface. Non-thermal evaporation processes have to be invoked, but their rates are uncertain. The alternative is the complete freeze-out of the heavy gas-phase species on to the grain surfaces on a timescale of 1–10 Myr, a scenario for which there is no observational evidence.

When discussing the hydrogenation of heavy species on the grain surfaces, the cases in which the number of layers in the grain mantle  $N \geq 1$  or  $< 1$  need to be considered separately (Le Boulot *et al.* 1995 b). Let us assume that  $N \geq 1$ . Then, the fraction  $F$  of the external sites occupied by the species  $X$  is

$$F = n(X^*) / \sum_X n(X^*),$$

where  $n(X^*)$  is the number of atoms/molecules of species  $X$  in grain mantles per unit volume of the medium. The mean number of sites explored by the migrating hydrogen

atom before reaching  $X$  is  $F^{-1}$ . If the hopping time of hydrogen atoms between adjacent sites is denoted by  $\tau$ , the rate (per unit volume) of hydrogenation of species  $X$  is

$$n(\text{H}^*)F/\tau = n(\text{H}^*)n(X^*) \left/ \left[ \tau \sum_X n(X^*) \right] \right.$$

Estimates of the hopping time for H atoms (Hasegawa *et al.* 1992) suggest that  $\tau \approx 10^{-11}$  s, owing to quantum tunneling between adjacent sites. Thus, a hydrogen atom will diffuse over the entire surface of a grain in about  $10^{-5}$  s, orders of magnitude faster than 'heavy' species (i.e. those containing atoms heavier than helium).

Once formed, saturated species may undergo photolysis by the ambient ultraviolet radiation or be ejected from the mantle. Calculations predict that the most abundant mantle species are  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CH}_4$  and  $\text{NH}_3$  (Hasegawa and Herbst 1993). The formation of  $\text{H}_2$  is governed essentially by the rate of sticking of hydrogen atoms to the cold grains. The rate per unit volume of collision of hydrogen atoms, of gas-phase number density  $n(\text{H})$ , with grains of number density  $n_g$  is  $n(\text{H}) < n_g \sigma > v_{\text{th}}$ , where  $\sigma = \pi a^2$  is the geometrical cross section of a grain (assumed spherical) and  $v_{\text{th}}$  is the mean thermal speed of a hydrogen atom. The total mass of grains, relative to the total mass of gas, averages about  $10^{-2}$  in the interstellar medium. The size distribution of the grains may be determined observationally (see Mathis 1993). Hence,  $\langle n_g \sigma \rangle \approx 10^{-21} n_{\text{H}} \text{ cm}^{-1}$ . At  $T = 10$  K, the mean thermal speed of a hydrogen atom is  $v_{\text{th}} = 0.5 \text{ km s}^{-1}$  and the probability of sticking to the grain on collision is believed to be of order unity. Thus, the rate at which hydrogen atoms stick to the grains is approximately  $n(\text{H}) < n_g \sigma > v_{\text{th}} \approx 5 \times 10^{-17} n(\text{H}) n_{\text{H}} \text{ cm}^{-3} \text{ s}^{-1}$  at  $T = 10$  K; this is also the approximate rate of formation of  $\text{H}_2$ , in equilibrium.

Once formed and returned to the gas phase, hydrogen molecules in dense clouds are destroyed principally by cosmic ray ionization (cf. § 2.2) at a rate  $n(\text{H}_2)\zeta \text{ cm}^{-3} \text{ s}^{-1}$ , where  $10^{-17} \leq \zeta \leq 10^{-16} \text{ s}^{-1}$  has been deduced (indirectly) from observations. Taking  $\zeta = 5 \times 10^{-17} \text{ s}^{-1}$ , and equating the rates of formation and destruction of  $\text{H}_2$ , we obtain  $n(\text{H}) \approx n(\text{H}_2)/n_{\text{H}} \text{ cm}^{-3}$ , where  $n_{\text{H}} = n(\text{H}) + 2n(\text{H}_2)$ . In dense clouds,  $n(\text{H}) \ll n(\text{H}_2)$ , and so  $n(\text{H}_2)/n_{\text{H}} = 0.5$ . It follows that the density of atomic hydrogen  $n(\text{H})$  is of order  $1 \text{ cm}^{-3}$ , independent of  $n_{\text{H}}$ , and that the fractional abundance,  $n(\text{H})/n_{\text{H}}$ , decreases as  $n_{\text{H}}$  increases.

### 3. Chemical models of interstellar clouds

#### 3.1. Diffuse clouds

Models of the chemical composition of diffuse interstellar clouds in steady state have had considerable success in accounting for the abundances of the observed atomic and diatomic species (see, for example, Black and Dalgarno (1977), van Dishoeck and Black (1986). These species are observed by means of their absorption of starlight in electronic transitions, either in the ultraviolet or visual regions of the spectrum. The quantity which is deduced from observations is the 'column density' of the species  $X$ ,

$$N(X) = \int n(X) dl,$$

the integral of the number density along the line of sight to the background star. Transitions in the Lyman and Werner bands of  $\text{H}_2$  were observed by the *Copernicus* satellite (Spitzer *et al.* 1973), arising from rotational levels  $J \leq 6$  of the vibrational ground state. These transitions are followed by fluorescence or by a radiative transition

Table 2. Observed and predicted column densities ( $\text{cm}^{-2}$ ) of atomic and molecular species along the line of sight to *o* Per. Where appropriate, upper limits to and ranges of the observed values are given. The computed results in column 3 are from van Dishoeck and Black (1986), and those in column 4 from Heck *et al.* (1993). The latter incorporated the production of  $\text{CH}^+$  in a shocked gaseous layer. Integers in parentheses are powers of 10.

	Observed	van Dishoeck & Black	Heck <i>et al.</i>
H	$(7.4 \pm 1.1)(20)$	6.9(20)	5.5(20)
H <sub>2</sub> (J = 0)	$(3.2 \pm 0.2)(20)$	3.2(20)	3.9(20)
H <sub>2</sub> (J = 1)	$(8.5 \pm 0.4)(19)$	8.8(19)	1.1(20)
H <sub>2</sub> (J = 2)	$(1.0 \pm 0.2)(18)$	5.9(17)	1.4(18)
H <sub>2</sub> (J = 3)	$(3.9 \pm 0.4)(17)$	2.7(16)	4.6(17)
H <sub>2</sub> (J = 4)	$(3.7 \pm 2.5)(16)$	2.5(15)	1.0(16)
H <sub>2</sub> (J = 5)	$(4.1 \pm 1.5)(14)$	4.0(14)	1.1(15)
H <sub>2</sub> (J = 6)	$\leq 1(14)$	5.3(13)	7.0(12)
H <sub>2</sub> (total)	$(4.1 \pm 0.2)(20)$	4.1(20)	5.0(20)
C	$(3.3-6.4)(15)$	3.3(15)	3.5(15)
C <sup>+</sup>	$(0.1-2.0)(17)$	6.7(17)	2.0(17)
CH <sup>+</sup>	$(6.0 \pm 0.5)(12)$	3.8(10)	7.6(12)
CH	$(1.9 \pm 0.1)(13)$	9.5(12)	7.2(13)
C <sub>2</sub>	$(1.3 \pm 0.2)(13)$	3.2(12)	4.3(12)
CO	$(4.9 \pm 0.5)(14)$	1.4(14)	1.4(14)
CO <sup>+</sup>	$< 8.0(13)$	1.6(10)	3.4(10)
N	$(7.9 \pm 3.3)(16)$	8.3(16)	7.7(16)
NH	$< 7.5(11)$	8.5(11)	7.6(10)
CN	$(1.6 \pm 0.1)(12)$	1.2(12)	5.4(11)
O	$(5.5 \pm 1.6)(17)$	6.9(17)	5.4(17)
OH	$(7.8 \pm 0.5)(13)$	7.2(13)	9.3(13)
H <sub>2</sub> O	$< 2.6(13)$	5.4(11)	1.0(13)
H <sub>2</sub> O <sup>+</sup>	$< 3.6(13)$	3.0(11)	1.1(12)

to the continuum of the vibrational ground state, and hence dissociation of the molecular hydrogen (Stecher and Williams 1967). In table 2 are listed the column densities (and upper limits) observed along the line of sight to the star *o* Per.

Absorption in the ultraviolet lines of H<sub>2</sub> occurs in the wavelength range from the Lyman limit of atomic hydrogen (91.2 nm), shortwards of which absorption in the H continuum dominates, to about 126 nm. The lifetimes and dissociation probabilities of the rovibrational levels of the B and C<sup>±</sup> electronic states of H<sub>2</sub> are known to high precision (Abgrall *et al.* 1992).

By a quirk of nature, the absorption bands of CO, which lead (via predissociation) to the photodestruction of this molecule, fall in the same wavelength domain as the Lyman and Werner bands of H<sub>2</sub>. The CO absorption lines have been extensively studied (spectroscopically) in the laboratory and have been catalogued (Eidelsberg *et al.* 1991). Thus, there exist the molecular data which are required for detailed numerical studies of the absorption by both H<sub>2</sub> and CO, allowing for the overlap of the absorption lines (Le Boulrot *et al.* 1993a). The latter effect is significant, as some of the H<sub>2</sub> absorption lines can become highly optically thick and hence very broad. Including the <sup>13</sup>CO and C<sup>18</sup>O isotopes of CO, several thousand absorption lines need to be taken into account.

In table 2 are also listed the column densities predicted by the chemical model of van Dishoeck and Black (1986) for the line of sight to *o* Per. The general level of agreement with the observations is quite good, given the difficulties of the enterprise. A striking exception is the CH<sup>+</sup> column density, which is over two orders of magnitude

below the observed value; this failing is common to all steady-state models of diffuse interstellar clouds. The problem was recognized over forty years ago by Bates and Spitzer (1951). Its solution may have been found in the dynamical effects leading to the production of  $\text{CH}^+$  in shock waves, as will be seen in § 4.

### 3.2. Dense clouds

For many years, studies of interstellar chemistry were conducted under the assumption that the composition of the gas in steady state was independent of the initial conditions. The first inkling that this statement might be incorrect is to be found in the work of Graedel *et al.* (1982), who uncovered the existence of two distinct chemical phases. This discovery remained neglected and unexploited for a decade, partly because of credence in a very low value for the coefficient of dissociative recombination of  $\text{H}_3^+$ . As we have seen in § 2,  $\text{H}_3^+$  plays a pivotal role in interstellar chemistry, and its rate of recombination with electrons is crucially important. The ‘two chemical phases’ were rediscovered by Pineau des Forêts *et al.* (1992), and subsequent work (Le Bourlot *et al.* 1993 b, 1995 a, b) demonstrated the existence of bistability in the chemistry of dark clouds.

Consider figure 1, which derives from the work of Le Bourlot *et al.* (1995a). In this figure, each point corresponds to a different steady-state solution of the chemical rate equations for a wide range of values of the density  $n_{\text{H}}$  of the medium. When obtaining the lower curve, the rate coefficient for dissociative recombination of  $\text{H}_3^+$  was taken to be  $10^{-10} \text{ cm}^3 \text{ s}^{-1}$  at room temperature, as measured by Adams and Smith (1988), and assumed to vary as  $T_e^{-0.5}$ , where  $T_e$  is the electron temperature. Under these conditions, to each value of  $n_{\text{H}}$  there corresponds a single steady-state solution, represented in figure 1 by the fractional ionization of the gas. On the other hand, when a more typical value of  $10^{-7} \text{ cm}^3 \text{ s}^{-1}$  at 300 K is adopted, in accord with more recent and independent measurements, the upper curve is obtained. In this case, the solutions display an unstable branch between the points A and B, and *two* stable branches, labelled ‘HIP’ (high ionization phase) and ‘LIP’ (low ionization phase). Thus, in the density range  $2 \times 10^3 \leq n_{\text{H}} \leq 2 \times 10^4 \text{ cm}^{-3}$ , bistability occurs. The degree of ionization is approximately an order of magnitude greater in the HIP than in the LIP.

The difference in the degree of ionization in the HIP and LIP is reflected in the abundances of many atomic and molecular species. In figure 2 are plotted the corresponding values of the ratio  $n(\text{C})/n(\text{CO})$ . It may be seen that this ratio is of order  $10^{-1}$  in the HIP but less than  $10^{-2}$  in the LIP. Observations have shown that  $n(\text{C})$  and  $n(\text{CO})$  can be comparable in dense clouds (cf. Keene 1994). Whilst other explanations of these observations have been advanced, the association of a high C:CO ratio with the HIP may yet prove to be the most compelling.

An alternative and instructive way of presenting these results is illustrated in figure 3, which shows  $n(\text{O}_2)$  plotted against  $n(\text{C})$  for models in which  $n_{\text{H}} = 2 \times 10^4 \text{ cm}^{-3}$  (Le Bourlot *et al.* 1993b). In steady state, the LIP solution yields a relatively high molecular oxygen and low atomic carbon abundance, and vice versa for the HIP solution. Very different initial conditions may lead to the same (HIP or LIP) solution. However, it is also possible for slightly different initial conditions to lead to *opposite* solutions. Indeed, it is this characteristic which makes the behaviour of the chemical rate equations so intriguing. Small variations in parameters such as the local gas density or cosmic ray flux might be responsible for the evolution of the chemical composition to one or other of the two distinct chemical phases.

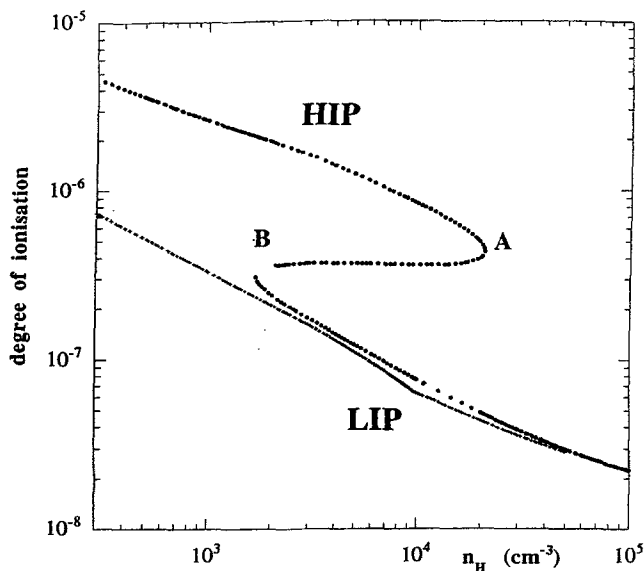


Figure 1. Degree of ionization of the gas, computed at steady state, for a range of values of the gas density  $n_H$ . The high and low ionization phases are indicated. The upper curve has an unstable branch between the points A and B, where it displays the phenomenon of bistability. The lower curve is obtained on using a very low value of the rate coefficient for dissociative recombination of  $H_3^+$  ( $10^{-10} (T_e/300)^{-0.5} \text{ cm}^3 \text{ s}^{-1}$ ).

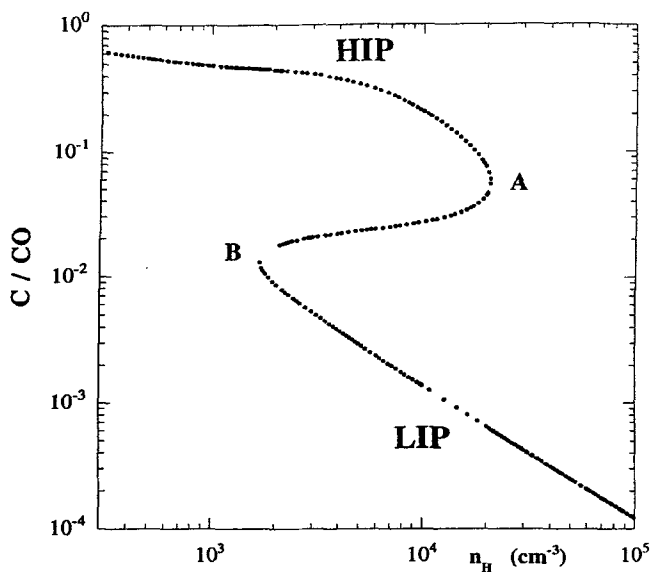


Figure 2. Bistability in the variation of  $n(C)/n(CO)$  with  $n_H$ .

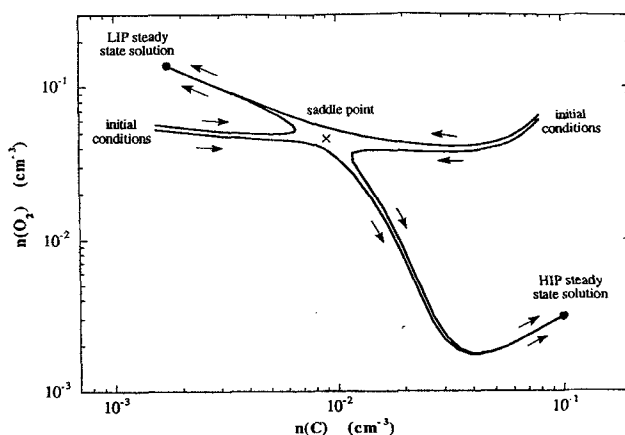


Figure 3. Evolutionary trajectories to steady state from various initial conditions. Very different initial conditions can lead to the *same* (HIP or LIP) solution. On the other hand, certain very similar initial conditions may lead to *different* solutions.

We have already seen, in § 2, that the reaction  $\text{H}_3^+(\text{O}, \text{H}_2)\text{OH}^+$  initiates the formation of oxygen-bearing species in dense clouds. Thus, a high equilibrium  $\text{H}_3^+$  abundance is associated with a low O abundance and high abundances of species such as  $\text{O}_2$  and  $\text{H}_2\text{O}$ . The latter are scavengers of atomic ions, particularly  $\text{H}^+$  and  $\text{C}^+$ , forming molecular ions which can *rapidly* neutralized by dissociative recombination with electrons. These conditions, in essence, are those of the LIP. As the fractional electron density increases, for whatever reason (e.g. a reduction in the gas density  $n_{\text{H}}$  or an increase in the cosmic ray ionization rate  $\zeta$ ), a point is reached where the rate of removal of  $\text{H}_3^+$  in recombination with electrons becomes equal to its rate of removal in protonation reactions. With the lower  $\text{H}_3^+$  abundance are associated a higher O abundance and lower abundances of  $\text{O}_2$  and  $\text{H}_2\text{O}$ . The consequent reduction in the rates of neutralization of  $\text{H}^+$  and  $\text{C}^+$  further enhances the electron density. A transition then occurs to the other phase (HIP).

#### 4. Interstellar shock waves

We have been concerned until now with the chemical composition of the gas in a steady state in which  $d/dt = 0$ . In general,  $d/dt = \partial/\partial t + \mathbf{v} \cdot \nabla$ , where  $\mathbf{v}$  is the velocity and  $\nabla = \mathbf{i}\partial/\partial x + \mathbf{j}\partial/\partial y + \mathbf{k}\partial/\partial z$  is the gradient operator; the abundances  $n = n(x, y, z, t)$ . In order to study dynamical perturbations of the gas from steady state, it is in general necessary to solve a set of coupled, partial differential equations in four dimensions. Such a problem has never been solved, at least in the context of the interstellar medium. However, meaningful information can be derived by studying more restricted problems. For example, if the explicit time dependence can be neglected, then  $\partial/\partial t = 0$  and  $n = n(x, y, z)$  are the corresponding steady-state abundances, functions of position in the cloud. Furthermore, if the dynamical perturbation has an associated direction, say the  $z$ -direction, it may be sufficient to determine  $n(z)$  assuming  $\partial/\partial x = \partial/\partial y = 0$ . Then,  $d/dt = v/dz$ , where  $v$  is the speed of flow, in the  $z$ -direction. Such a situation arises in the study of the propagation of planar shock waves.

Shock waves may be produced in the interstellar medium by a variety of mechanisms, including supernovae explosions, stellar winds, and collisions between



clouds. Their effect is similar to that of a piston, accelerating and compressing the gas in front of it. The adiabatic sound speed in the unperturbed gas is

$$c_s = (\gamma p / \rho)^{0.5},$$

where  $\gamma$  is the ratio of specific heats at constant pressure  $p$  and volume, and  $\rho$  is the mass density. If the velocity of the piston  $v_s > c_s$ , then a shock wave is driven into the gas, which induces a quasidiscontinuous change from the pre- to the post-shock conditions; these are connected through the Rankine–Hugoniot relations, which express the constancy of the mass flux,  $\rho u$ , the momentum flux,  $\rho u^2 + p$ , and the energy flux,  $\rho u \{u^2/2 + \gamma p / [(\gamma - 1)\rho]\}$  (where  $u$  is the flow speed of the gas relative to the shock front), across the discontinuity.

Shocks of this type may exist in the interstellar medium. In general, however, the situation is expected to be more complex. The medium is known to be permeated by a magnetic field, which has been amplified by the differential rotation of the Galaxy. This field is observed, for example, by means of the Zeeman effect and through the orientation of grains and the consequent polarization of starlight (see Heiles (1987)). The magnetic field acts (directly) on the ionized component of the gas and thence on the neutral component, owing to collisions between the ions and the neutrals. Because the gas density and the degree of ionization are very low, variations in the magnetic energy density, which are rapidly sensed by the ions, are transferred relatively slowly to the neutral gas, which comprises most of the mass of the medium. The net effect is a decoupling of the flows of the ionized and neutral fluids: the ions (and electrons) are accelerated by the shock wave prior to the neutrals. Detailed calculations (Mullan 1971, Draine 1980, Pineau des Forêts *et al.* 1986) have shown that, under the conditions that are believed to prevail in the interstellar medium, the transition from the pre- to the post-shock gas occurs smoothly, in a ‘C’ (for ‘continuous’) shock wave.

In figure 4 are shown the ion and neutral flow velocities for a shock of speed  $v_s = 10 \text{ km s}^{-1}$  propagating into a medium of density  $n_{\text{H}} = 10^4 \text{ cm}^{-3}$ ; the magnetic induction is  $B_0 = 100 \mu\text{G} = 10^{-8} \text{ T}$ , perpendicular to the direction of propagation of the shock wave (the component of the force  $\mathbf{v} \times \mathbf{B}$  is zero parallel to the flow direction). It may be seen that the maximum difference between the velocities of the ions and the neutrals,  $(v_i - v_n)_{\text{max}} \approx v_s/2$ , corresponding to several  $\text{km s}^{-1}$  for  $v_s = 10 \text{ km s}^{-1}$ ; this should be compared with a thermal speed of approximately  $0.3 \text{ km s}^{-1}$  in the preshock gas and a turbulent velocity of perhaps  $1 \text{ km s}^{-1}$ . Because the relative kinetic energy of the ions and the neutrals is proportional to  $(v_i - v_n)^2$ , such speeds might be expected to have implications for the rates of ion–molecule reactions.

This expectation has been fully confirmed by the results of calculations. Especially relevant are reactions with endothermicities or barriers which are sufficient to suppress their rates in the cold ambient medium but which may be surmounted by ion–neutral streaming in the shock. For example, it has been proposed that the long-standing problem of explaining the abundance of  $\text{CH}^+$ , observed in diffuse clouds, might be resolved by allowing for its formation through the reaction  $\text{C}^+(\text{H}_2, \text{H})\text{CH}^+$  in C-shocks. Laboratory studies (Gerlich *et al.* 1987) imply that this reaction, which is endothermic by  $0.4 \text{ eV}$ , will proceed rapidly under the conditions predicted for C-shocks. It is followed by further hydrogen-abstraction reactions, which are also rapid and lead to the production of  $\text{CH}_3^+$ , which dissociatively recombines, yielding  $\text{CH}$  or  $\text{CH}_2$ . Allowance for the production of  $\text{CH}^+$  in a shock wave leads to much improved agreement with the observations along the line of sight to  $\sigma \text{ Per}$  (see table 2).

Accompanying the compression of the gas in the shock wave is a rise in the kinetic

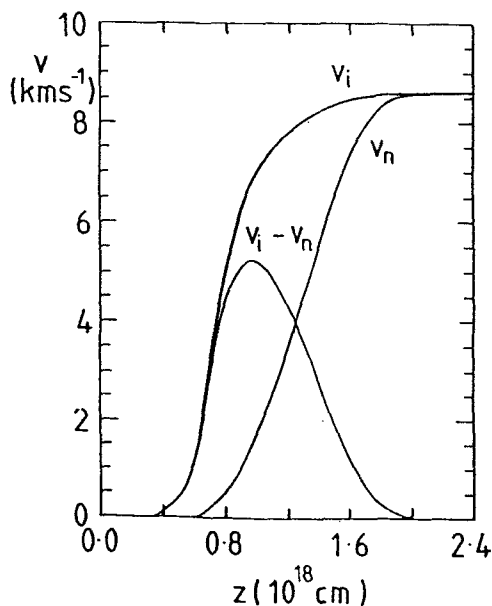
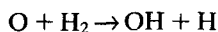
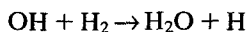


Figure 4. The velocity profiles of the ionized and neutral fluids for a shock wave propagating, from right to left, at  $10 \text{ km s}^{-1}$  into gas with a magnetic field strength of  $10^{-8} \text{ T}$ , transverse to the flow. The ions and electrons are accelerated first, dragging the neutrals behind them.

temperature. Not only the velocities, but also the kinetic temperatures of the ionized and neutral fluids decouple, with the ions attaining a much higher maximum temperature than the neutrals. Under conditions appropriate to diffuse clouds, and for a shock speed  $v_s \approx 10 \text{ km s}^{-1}$ , the maximum temperature of the neutral fluid is approximately  $10^3 \text{ K}$ . The reactions



and



have rate coefficients  $0.16 \times 10^{-12} (T_n/300)^{2.8} \exp(-2980/T_n) \text{ cm}^3 \text{ s}^{-1}$  and  $0.95 \times 10^{-12} (T_n/300)^{2.0} \exp(-1490/T_n) \text{ cm}^3 \text{ s}^{-1}$ , respectively (Cohen and Westberg 1983), where  $T_n$  is the temperature of the neutral gas. Negligible at the temperature of the ambient medium, these reactions become rapid in the shock-heated gas, converting atomic oxygen to OH and  $\text{H}_2\text{O}$ . The former (radical) is observed in the interstellar medium, notably in diffuse clouds, where its abundance may be locally enhanced by shock waves. Unfortunately, water is, as yet, unobservable in the interstellar gas owing to its presence in the intervening Earth's atmosphere. The forthcoming 'ISO' satellite, which will undertake spectroscopic measurements in the infrared, should make the first observations of this important interstellar species.

### 5. Thermal balance

The first law of thermodynamics states that, for a chemical system,

$$dQ = dU + p dV,$$

where  $U$  is the internal energy and  $p dV$  denotes the work done in the expansion of

volume  $V$  of the gas;  $dQ$  denotes the heat exchange with the environment. The first law may alternatively be written

$$dQ/dt = C_V dT/dt + p dV/dt,$$

where  $C_V$  is the heat capacity at constant volume. For a monatomic gas, the molar heat at constant volume is  $3R/2$ , where  $R$  is the universal gas constant, corresponding to  $R/2$  per translational degree of freedom. For a diatomic gas, the molar heat at constant volume is  $5R/2$  at room temperature, with additional contributions of  $R/2$  arising from the rotational degrees of freedom. In the interstellar gas, thermodynamic equilibrium (and hence a Maxwellian distribution) may hold for the translational motion, but the rotational (and vibrational) motions are far from being thermalized: most molecules spend most of their time in their rovibrational ground states. Thus,  $3R/2$  is a better approximation to the molar heat at constant volume than  $5R/2$ .

In steady state,  $d/dt = 0$  and so  $dQ/dt = 0$ . Then, the rates of heating and cooling of the gas, through energy exchange with its environment, are equal. These exchange processes involve the radiation field, cosmic rays, and collisions with grains. We shall consider each in turn.

### 5.1. Radiation field

Photo-ionization or -dissociation of atoms and molecules by the ultraviolet radiation field is a source of heating of the gas; the energy input on each event is the difference between the photon energy and the ionization potential/dissociation energy. If the intensity of the radiation and the ionization/dissociation cross-section are known as functions of the photon frequency, the corresponding heating rate can be evaluated. Absorption of ultraviolet photons by the grains results in heating, not only of the grains themselves, but also of the gas, through the photoelectric effect. Clearly, these heating processes are most important where the radiation field is most intense, namely at the edges of interstellar clouds. The background radiation intensity decreases exponentially with distance into the cloud owing to absorption and scattering, mainly by the grains.

Collisions between the most abundant species—H, He and  $H_2$ —and the constituents of the gas can lead to excitation of internal degrees of freedom, providing the corresponding levels are energetically accessible. At temperatures of a few hundred kelvin, rotational excitation of ortho- and para- $H_2$  occurs. Collisional excitation may be followed by the emission of an infrared photon which escapes from and thus cools the medium (the cross-sections for absorption and scattering of photons by grains decrease with increasing wavelength and are smaller in the infrared than in the ultraviolet; see Mathis (1993)). Pure rotational transitions in  $H_2$  occur through the electric quadrupole interaction, and the corresponding transition probabilities are very small, for example,  $2.94 \times 10^{-11} \text{ s}^{-1}$  for the  $J = 2$  level (Turner *et al.* 1977). However, the probabilities increase with the fifth power of the transition frequency and, as  $J$  increases, rapidly become comparable with the probabilities for transitions induced by collisions.

Cross-sections for the rotational excitation (and, by detailed balance, deexcitation) of  $H_2$  by He and  $H_2$  have been calculated (Danby *et al.* 1987). Calculations have also been performed for excitation of  $H_2$  by H, using both quasi-classical and quantum mechanical methods. In this case, uncertainties persist, regarding the accuracy of the quasi-classical method at low collision energies and of the available potential energy surfaces (see Lepp *et al.* 1995, Sun and Dalgarno 1995).

Other molecules, with permanent dipole moments and hence larger probabilities for

pure rotational transitions, may also contribute significantly to the cooling of the gas, depending on their abundances. Examples are CO, OH, H<sub>2</sub>O and NH<sub>3</sub>. Cross-sections and rate coefficients for the collisional excitation of these species have been computed by McKee *et al.* (1982), Schinke *et al.* (1985) and Flower and Launay (1985) for CO, by Dewangan *et al.* (1987) and Offer and van Dishoeck (1992) for OH, by Balasubramanian *et al.* (1993) for H<sub>2</sub>O, and by Offer and Flower (1990) and Rist *et al.* (1993) for NH<sub>3</sub>.

Also energetically accessible are the fine structure states of the <sup>2</sup>P and <sup>3</sup>P ground terms of various atoms and ions, including C<sup>+</sup>, C, O, and Si<sup>+</sup>. Quantum mechanical calculations have been performed for excitation by H (Launay and Roueff 1977 a, b, Roueff 1990), by He (Monteiro and Flower 1987, Lavendy *et al.* 1991, Staemmler and Flower 1991), and by H<sub>2</sub> (Flower and Launay 1977, Flower 1988, Schroeder *et al.* 1991, Jaquet *et al.* 1992).

### 5.2. Cosmic rays

The rate of heating of the gas owing to cosmic ray ionization has been evaluated by Spitzer and Scott (1969). Electrons produced by cosmic ray ionization of (predominantly) H, He and H<sub>2</sub> lose energy primarily in ionizing and collisionally exciting H or H<sub>2</sub>, until their kinetic energy falls below that required to attain the first electronically excited states (between about 10 and 11 eV). When the degree of ionization is low, as is the case in dense clouds, the mean heat energy supplied to the gas per cosmic ray ionization is 5.7 eV. Although this value was calculated for an atomic hydrogen gas, it holds approximately for molecular hydrogen also (Cravens *et al.* (1975)).

Excitation of H<sub>2</sub> or H by the secondary electrons is followed by the emission of ultraviolet photons which can give rise to further ionization and dissociation of the gas; this process somewhat enhances the overall heating rate.

### 5.3. Grains

At low temperatures, hydrogen atoms are believed to have a high probability of sticking when they collide with dust grains (cf. Tielens and Hollenbach 1985). Subsequent migration on the grain surface can lead to the formation of H<sub>2</sub> and the release of the binding energy (4.5 eV) of the molecule. This energy may be partly absorbed by the grain but may also be used to overcome the (relatively small) adsorption energy or to internally (rovibrationally) excite the molecule. It is often assumed that a third of the available energy, or 1.5 eV, appears as translational energy of the ejected H<sub>2</sub> molecule, i.e. as heat. The heating rate is then determined by the rate of formation of H<sub>2</sub> on grain surfaces, which is of order  $5 \times 10^{-17} n(\text{H})n_{\text{H}} \text{ cm}^{-3} \text{ s}^{-1}$  at low temperatures (see § 2.8). The rate of heating is greatest where the rate of H<sub>2</sub> formation, and hence the atomic hydrogen density, is highest, near the edges of molecular clouds.

In figure 5 are plotted the principal heating and cooling mechanisms for a model cloud of density  $n_{\text{H}} = 10^3 \text{ cm}^{-3}$ , illuminated by a background ultraviolet radiation field which is taken to be  $10^3$  times the mean of that in the solar vicinity (owing to the proximity of a putative hot star). The abscissa is  $A_{\text{v}} = 1.086 \tau_{\text{v}}$ , where  $\tau_{\text{v}} = 5.34 \times 10^{-22} \int n_{\text{H}} dz$  is the optical depth of the dust in the visual part of the spectrum and  $z$  (cm) is the distance into the cloud; the corresponding values of the gas kinetic temperature are displayed in figure 6. This figure encapsulates a wide range of physical and chemical processes and synthesizes a great deal of our current knowledge of interstellar clouds.

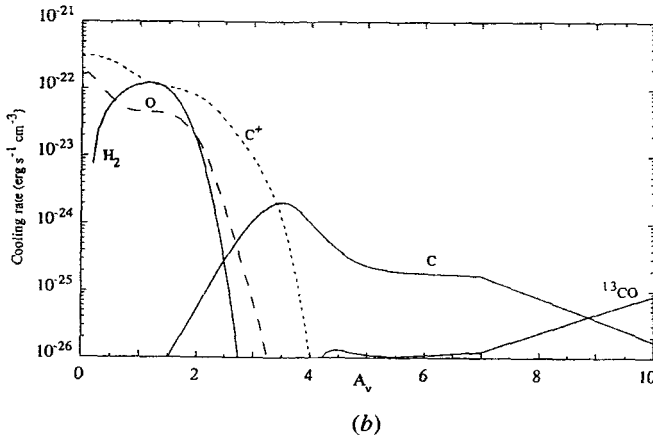
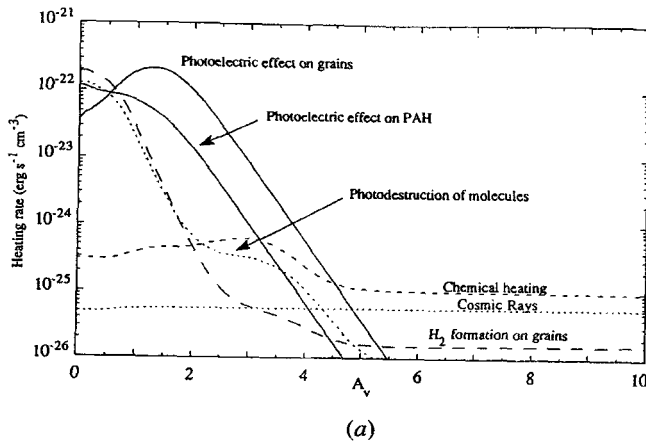


Figure 5. The principal rates of (a) heating and (b) cooling (in units of  $10^{-1} \text{ W m}^{-3}$ ) of a diffuse cloud, density  $n_H = 10^3 \text{ cm}^{-3}$ , exposed to an ultraviolet radiation field which is  $10^3$  times as intense as the stellar background field in the solar neighbourhood.  $A_v$  provides a measure of the extinction of the starlight towards the cloud interior (i.e. to the right); see the text, § 5.3. Note that heating due to exothermic chemical reactions dominates where the external radiation field fails to penetrate. Cooling is dominated by fine structure transitions of atoms and ions and by rotational transitions of molecules.

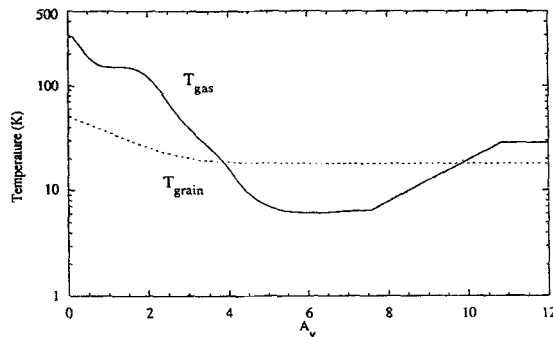


Figure 6. The gas temperature, computed for the same model as in figure 5, assuming thermal balance. The grain temperature, which determines the (black body) radiation of the dust grains, is shown for comparison.

## 6. Concluding remarks

I have not attempted in this review to provide a comprehensive summary of the current state of our knowledge of interstellar chemistry. Rather, the salient features have been identified, along with some of the major challenges. It is surely correct that we cannot hope to properly understand the formation and evolution of galaxies without first comprehending the formation and evolution of stars. The physical and chemical state of interstellar clouds preconditions the process of star formation. Sustained effort by physicists, chemists and astronomers is required in order to reveal the intricacies of this process, on which all life ultimately depends.

## Acknowledgements

I am indebted to Dr Evelyne Roueff for reading the typescript and making a number of valuable comments and corrections.

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