EPJ Web of Conferences **18**, 01001 (2011)
DOI: 10.1051/epjconf/20111801001

Introducing Cosmic Chemistry

L. Verstraete[a]

Institut d'Astrophysique Spatiale, UMR 8617, CNRS, Université Paris-sud XI, Bât. 121, 91405 Orsay Cedex, France

Abstract. The chemistry of cosmic diffuse gas as well as its astrophysical significance is discussed from the primordial gas to cold cores where stars can form.

1. INTRODUCTION

Chemistry develops in many astrophysical environments, from the tenuous primordial gas (containing 10^{-3} proton per cubic centimeter[1]) to the atmospheres of planets ($n_H \geq 10^{12}$ cm^{-3}). Diluted or diffuse gas at low to moderate densities ($n_H \leq 10^4$ cm^{-3}) fills up most of the volume of our Galaxy (the *interstellar medium* or ISM) and of the young Universe. The following presentation focuses on the chemistry of the diffuse cosmic gas. However, we note that this case shares many features with that of denser gas. The chemistry of denser environments such as protoplanetary disks or planetary atmospheres is discussed elsewhere in this volume (see contributions by Engrand, Guilloteau, Monod and Remusat).

In addition to gas temperature and density, ISM chemistry also depends on the composition of the gas as well as on the abundance and nature of small (1 to 100 nm in radius) solid particules called *dust grains*. We first give a brief overview of the composition and physical conditions of the ISM. We then discuss the dominant reaction schemes in the ISM and how they are probed with observations. The interesting case of chemistry in the young Universe is also briefly considered.

2. COMPOSITION AND PHYSICAL CONDITIONS IN THE ISM

In the ISM, evolved stars of mass comparable and up to a few times that of the Sun become red giants and expell a significant fraction of their mass in the form of dense winds ($n_H \sim 10^9$ cm^{-3}). As the temperature decreases in the stellar wind, dust grains form by condensation and the heavy elements synthesized by the star are thus depleted from the gas phase. In the Solar neighborhood (at distances below 1 kpc [2]), the mass flow from evolved stars accounts for a significant fraction of the elemental enrichment of the ISM. The elemental composition of the ISM is mostly derived from visible-UV spectroscopy. Observations of main sequence stars provide a census of all the elements in the gas and in the dust available in the ISM to form stars. This census provides the *interstellar* (IS) *abundances*. A reference set of abundances is given in [22] for the Solar nebula[3]. Depletions in gas phase abundances due to the presence of grains are estimated from absorption studies of IS clouds and a recent comprehensive review can be found in [17]

[a]e-mail: laurent.verstraete@ias.u-psud.fr

[1] The gas density n_H is always given in terms of protons because this is the most abundant species. In general one has $n_H = n(H^+) + n(H) + 2n(H_2)$.

[2] 1 parsec = 1 pc = 3.1 10^{18} cm or 3.3 lightyears.

[3] In the case of more massive B-stars, different abundances are found ([26]).

Table 1. Interstellar abundances of elements [22] and depletion factor δ_X for the $\zeta_{\rm oph}$ line of sight representative of the cold, diffuse ISM ($T\sim100$ K and $n_H\sim100\,\rm cm^{-3}$, see [17]).

Element	$[X/H]_{\rm IS}$ (ppm)	δ_X (%)
He	$7.8\ 10^4$	0
C	288.4	38.7
N	79.4	22.2
O	575.4	41.9
Mg	41.7	94.6
Si	40.7	95.6
S	18.2	80.7
Fe	34.7	99.4

for the Solar neighborhood. In Table 1, we present a summary of IS element abundances $[X/H]_{\rm IS}$ and depletion factors δ_X representative of the cold diffuse ISM. The abundance of element X in dust grains is $\delta_X\,[X/H]_{\rm IS}$: one sees that the major dust constituents are C, Si and O as expected from extinction and emission studies of dust indicating the presence of hydrogenated carbon and silicates grains (see Demyk this volume). Depletion of elements into dust grains is known to increase with the condensation temperature of the element (see [17] and references therein) as expected from dust formation in stellar winds. Depletion also tends to decrease with the first ionization potential of the element, suggesting that accretion of gas phase elements onto grains occurs in the ISM [29, 31]. This idea is further supported by the fact that depletion increases with the average density of the gas along the line of sight [17].

The physical conditions (gas density n_H and temperature T) in atomic IS clouds are derived from observations of the hyperfine HI transition (1.4 GHz) and of UV absorption lines. In molecular clouds, the CO rotational transitions (mostly $J=1\rightarrow0$ at 115 GHz) are used to derive physical conditions complemented by other far-infrared to submillimeter emission lines from species such as CS, NH_3, OH, HCO^+, H_2O, etc... which constrain the chemistry of these clouds. Another important physical quantity is the abundance of electrons or *ionized fraction* $x=n_e/n_H$ which is only indirectly constrained by observations of atomic or molecular ion lines (e.g., [6, 35]). In the neutral ISM, the main sources of electrons are (i) cosmic ray ionization of H and H_2 and, (ii) ionization by stellar UV photons of heavy elements with first ionization potential below 13.6 eV[4]. Cosmic ray ionization is the dominant source of electrons inside dense (UV-shielded) clouds whereas cloud interfaces are UV ionized (see Le Bourlot this volume). Conditions and mass fractions[5] for the neutral ISM where chemistry can develop are given in Table 2. The WNM and CNM are mostly atomic gas but significant fractions of H_2 may exist within CNM clouds, depending on their UV optical depth [11]. The numbers in Table 2 are average properties and it must not be forgotten that the ISM has a complex, scale invariant distribution of structures [24].

The ISM is an open system heated by the radiation of stars, cosmic rays and by local deposition of mechanical energy (stellar winds, shocks or turbulence). The ISM is a unique laboratory because it is highly rarefied (the pressure of the CNM is 10^{-15} mbar) and has long excitation timescales (1 UV photon absorbed per year and 1 cosmic ray per 100 Myr). The stellar radiation field is the dominant source of energy (0.5 eV/cm^3 in the Solar neighborhood [23]). On short timescales (less than a few years), a few percents of this energy is transfered to the gas via the photoelectric effect on dust grains. The IS gas is cooled by inelastic collisions of electrons, H (or H_2) with ions, atoms or molecules which then radiate

[4] Most abundant species in this case are C, S and Si.

[5] In our Galaxy the ISM mass is $\sim6\ 10^9$ solar masses, about 3% of the mass in stars.

Table 2. Typical conditions in neutral IS clouds with ionization fraction $x < 0.1$. CNM and WNM stand for Cold and Warm Neutral medium respectively, MC is for Molecular cloud. Estimates of x are from [36]. Mass fractions of the total ISM mass are also given.

Phase	n_H (cm^{-3})	T (K)	x	Mass (%)
WNM	0.1–1	$10^4 - 10^3$	$\sim$0.01	25
CNM	10–100	500-100	$\sim 10^{-4}$	25
MC	$>10^3$	<50	$<10^{-5}$	30

away spontaneously the energy stored. In the neutral gas, the typical cooling time[6] is short (<100 yrs) and the gas is often assumed to be in thermal balance on cloud evolution timescales (10^4 yrs or longer for the penetration of UV light or mechanical heating in a shock). Chemical timescales are longer and equilibrium is not generally warranted (see Le Bourlot this volume).

3. MAIN FEATURES OF INTERSTELLAR CHEMISTRY

In the ISM, chemistry starts with the formation of H_2 and develops in shielded regions where the UV opacity is high enough (corresponding to $A_V > 5$). The formation of H_2 is important in the ISM because H_2 absorbs dissociating photons and efficiently cools the gas [19]. It has been realized long ago that the main route for H_2 formation is by catalysis at the surface of dust grains. In spite of decades of research in this field, the H_2 formation mechanism and the excitation of the molecule formed are still poorly known, in particular because of our lack of knowledge on the relevant properties of dust grains (see Fillion this volume).

On the other hand, observations of UV absorption lines in IS clouds provide an estimate of the mean H_2 formation rate coefficient per proton R_0 along the line of sight. Early observations with *Copernicus* [18] and more recent *FUSE* data indicate that $R_0 \simeq 3\,10^{-17}$ cm^3 s^{-1} in the CNM (the formation rate per unit volume is then $n(\mathrm{H})\, n_H R_0$). Given the dust surface ($2\,10^{-21}$ cm^2 per H), this number amounts to a formation probability of $\sim 1/3$ for each H atom impinging on a grain. Furthermore, the rate coefficient for H_2 formation is observed to vary from a few tenths to a few times the standard value R_0 [1, 10, 12, 13, 32]. The rotational emission of H_2 observed in excited interfaces favors formation routes on small carbonaceous grains involving chemisorbed sites for H [3, 14] while formation in physisorbed sites may be dominant in the interiors of clouds.

Once H_2 is formed, gas phase chemistry can develop depending on the gas ionization and internal energy. Most important processes are ion-molecule reactions ($\sim 10^{-9}$ cm^3 s^{-1}, Langevin rate), dissociative recombination ($\sim 10^{-7}$ cm^3 s^{-1}, an important example is $H_3^+ + e^- \rightarrow H + H + H$), UV photodissociation (5 to 30 times $10^{-11} G_0$ s^{-1} per molecule for H_2 and CO respectively[7]), cosmic ray ionization ($\sim 10^{-16}$ s^{-1} per proton) and gas-grain interactions. Interstellar chemistry is a complex system involving a few 100 species with a few 1000 reactions (see Le Bourlot this volume) and a recent review of reaction networks can be found in [34]. In the ISM, two extreme cases can be distinguished. In dense molecular regions protected from UV radiation or *dark clouds* (with $n_H/G_0 \geq 10^4$ cm^{-3}), the primary source of energy is cosmic rays which destroys and ionizes H_2 leading to the formation of the key ion H_3^+ ($H_2^+ + H_2 \rightarrow H_3^+ + H$) . Reactions of H_3^+ with C or O then initiate the route to CO or H_2O. On the other hand, in regions where the gas is heated by stellar UV photons ($n_H/G_0 < 10^2$ cm^{-3}) or shocks

[6] The cooling time is defined as $\tau_C = 3 n_H k_B T/(2\Lambda)$ with Λ the gas cooling rate in erg/cm^3/s.

[7] G_0 is a scaling factor on the intensity of the standard interstellar 6-to-13.6 eV radiation field, $\nu I_\nu 4\pi \simeq 1.6\ 10^{-3}$ erg/cm^2/s.

(with velocities $>$20 km/s), H_2 is vibrationally excited allowing reactions with high activation barriers to occur, leading for instance to the formation of CH^+ and OH. UV heated gas is found at the surface of IS clouds in the so-called *photon-dominated regions* or PDR.

The case of diffuse IS clouds is intermediate in excitation ($n_H = 10^2 - 10^3\,cm^{-3}$ and $G_0 \sim 1$) but raises specific questions (see the review in [30]). For instance, the unexpected (because of the low H_2 abundance) detection of H_3^+ in diffuse molecular clouds suggests a cosmic ray ionization rate much higher than previously thought [20, 27], possibly the result of cosmic ray confinement by magnetohydrodynamic (MHD) waves [25]. The observed excitation of H_2 in PDRs could also be explained with an enhanced cosmic ray rate [28]. Other unexpected species are detected in the diffuse ISM like for instance CH^+, OH and HCO^+ which are formed by reactions with high activation barriers ($>$1000 K). Since the bulk of the diffuse molecular gas is at temperature below 100 K, this implies a strong and localized gas heating by processes such as MHD turbulence or shocks [5, 9].

Another key ingredient of interstellar chemistry are surface reactions and photochemistry occuring on dust grains (see Fillion and Demyk this volume). In addition to H_2, other molecules may form onto grains such as H_2O, CO_2, NH_3 and CH_4 [4]. In dark clouds, grains are cold ($\sim$10 to 15 K) and gas-phase species freeze out on their surface forming an ice mantle. On the other hand, cosmic rays and the UV flux they generate within clouds remove molecules off grain surfaces. Recent modeling suggests that these processes may explain the low O_2 and H_2O abundances observed [16]. IS chemistry is in fact sensitive to both surface and gas phase reactions [15]. The dust surface chemistry is also important in diffuse clouds where grains are warmer and bare [2]. Small grains like polycyclic aromatic hydrocarbons (PAHs) are abundant and easily polarizable: they may thus carry a significant fraction of the available electrons and affect the ion-molecule chemistry [6, 33]. Charge exchange reactions between grains and gas species may also affect the gas temperature and chemistry. For instance in diffuse clouds PAH anions may induce recombination of C^+ leading to warmer gas [37] and also quenching reactions with C^+. It must be noted however that rates for reactions involving dust grains are poorly known, in particular because the composition and structure of interstellar grains is not known in detail.

The field of interstellar and circumstellar chemistry is undergoing a significant leap forward thanks to the spectroscopic data of the *Herschel* satellite that covers the far-IR to submm wavelength range. Many interstellar molecules are detected, sometimes for the first time (e.g. H_2Cl^+ [21]) challenging our present best chemical schemes and probing the local physical conditions as well as the source of excitation of the gas, by radiation (PDRs) or dynamical motions (shocks, turbulence) (see Gerin this volume).

4. PRIMORDIAL CHEMISTRY

Chemistry also plays an important role in the young Universe because molecules are very efficient coolants for the gas and will help the collapse of density fluctuations to form stars or galaxies. In the standard cosmological model (also called Λ-CDM, that considers cold dark matter and a recent acceleration of the Universe's expansion), the first structures are formed by the collapse of baryonic matter ($\sim$5% of the mass) in the potential wells of dark matter ($\sim$25% of the mass). Simulations clearly indicate that the mass distribution of the structures thus formed depends on the ability of the baryonic gas to cool down[8].

Specifically, distorsions and anisotropies observed in the cosmic microwave background indicate that the Universe has been reionized at a redhift $z\sim40$ suggesting that stars have formed in primordial gas. At that time the cosmic gas is hot ($\sim10^4$ K) and diffuse ($\sim 7\,10^{-3}\,cm^{-3}$) and only contains the heavy elements synthesized during the big bang, namely He, D and Li (about $6\,10^5$, 500 and 10^{-4} ppm respectively) in addition to hydrogen. In such a poorly evolved gas, dust grains are absent and chemistry only occurs by gas-phase reactions. The chemical network involves some 20 species (e.g. H_2, HD, HeH,

[8] Simulations disregarding this aspect do not reproduce the mass distribution observed.

LiH, H_3^+, H_2D^+ and other ions) and about 100 reactions [7]. The time dependent reactions set is solved from epochs where H is fully ionized ($z \sim 10^4$) to present. Molecular hydrogen forms slowly[9] via the following routes:

$$H + e^- \rightarrow H^- + \gamma$$

$$H^- + H \rightarrow H_2 + e^-$$

with rate coefficients $1.4\,10^{-18} \times T \exp(-T/16,200)$ and 10^{-9} cm^3/s respectively or:

$$H + H^+ \rightarrow H_2 + +\gamma$$

$$H_2^+ + H \rightarrow H_2 + H^+$$

with rate coefficients 10^{-17} and $6.4\,10^{-10}$ cm^3/s respectively [7]. At $z = 40$, the H_2 abundance reaches a few ppm but H_2 efficiently cools the gas via excitation of its rotational lines by inelastic collisions with H or e^- followed by spontaneous emission. The abundances of certain molecules (HD, HeH^+) is very sensitive to the number of baryons per photon before recombination and may provide a valuable test of some cosmological parameters.

This chemical network can then be used to estimate the gas cooling function. This latter quantity incorporated into numerical simulations provides more realistic predictions for the mass distribution of structures collapsed at $z \sim 40$. However, some rates remain uncertain in particular those of $H^- + H \rightarrow H_2 + e^-$ and $H^- + H^+ \rightarrow H + H$ leading to a significant uncertainty on the density of the structures formed [8].

5. SUMMARY

The diffuse cosmic gas is a unique laboratory for the development of a complex chemistry in conditions of high isolation. In the interstellar medium, reactions involving dust grains are also important. Even when present in small amounts, molecules play an important role in the evolution of the gas because they are efficient coolants (e.g. H_2, CO, H_2O): thus they allow the formation and collapse of gravitationally bound structures to form stars or larger objects in the primordial gas. The chemical species observed in the interstellar medium are a powerful probe of the local physical conditions (gas density and temperature) and of excitation mechanisms (UV or X-ray radiation, shocks) in our Galaxy but also in external galaxies, as demonstrated by the scientific analysis of the *Herschel* data. Reactions involving dust grains remain poorly known in part because of our incomplete knowledge of the detailed nature of dust grains.

References

[1] Browning, M. K., Tumlinson, J., Shull, J. M., ApJ **582**, (2003) 810
[2] Cazaux, S., Cobut, V., Marseille, M., Spaans, M., Caselli, P., A&A **522** (2010) 74
[3] Cazaux, S., & Tielens, A. G. G. M., ApJ **604** (2004) 222
[4] Dartois, E., Space Science Rev. **119** (2005) 293
[5] Falgarone, E., Verstraete, L., Pineau Des Forêts, G., Hily-Blant, P., A&A **433** (2005) 997
[6] Flower, D. R., Pineau Des Forêts, G., Walmsley, C. M., A&A **474**, (2007) 923
[7] Galli, D., Palla, F., A&A **335** (1998) 403
[8] Glover, S. C., Savin, D. W., Jappsen, A.-K., ApJ **640** (2006) 553
[9] Godard, B., Falgarone, E., Pineau des Forêts, G., A&A **495** (2009) 847
[10] Gillmon, K., Shull, J. M., Tumlinson, J., & Danforth, C. ApJ **636**, (2006) 891
[11] Gillmon, K., Shull, J. M., ApJ **636**, (2006b) 908

[9] The abundances of H^+ and e^- are low, of the order of a few 100 ppm.

[12] Gry, C., Boulanger, F., Nehmé, C., Pineau des Forêts, G., Habart, E., Falgarone, E., A&A **391**, (2002) 675

[13] Habart, E., Boulanger, F., Verstraete, L., Pineau des Forêts, G., Falgarone, E., & Abergel, A., A&A **397**, (2003) 623

[14] Habart, E., Boulanger, F., Verstraete, L., Walmsley, C. M., & Pineau des Forêts, G. A&A **414**, (2004) 531

[15] Hincelin, U., Wakelam, V., Hersant, F., Guilloteau, S., Loison, J. C., Honvault, P., Troe, J., arXiv1104.1530 (2011)

[16] Hollenbach, D. J., Kaufman, M. J., Bergin, E. A., Melnick, G. J., ApJ **690** (2009) 1497

[17] Jenkins, ApJ **700**, (2009) 1299

[18] Jura, M. 1975, ApJ **197**, (1975) 575

[19] Le Bourlot, J., Pineau des Forêts, G., & Flower, D. R., MNRAS **305** (1999), 802

[20] Le Petit, F., Roueff, E., Herbst, E., A&A **417** (2004) 993

[21] Lis, D. C., Pearson, J. C., Neufeld, D. A. et al., A&A **521** (2010) 9

[22] Lodders, K., ApJ **591**, (2003) 1220

[23] Mathis, J. S., Mezger, P. G., Panagia, N., A&A **128**, (1983) 212

[24] Miville-Deschênes, M.-A. et al., A&A **518L**, (2010) 104M

[25] Padoan, P., Scalo, J., ApJ **624**, (2005) 97

[26] Przybilla, N., Butler, K., ApJ **688**, (2008) L103

[27] Shaw, G., Ferland, G. J., Srianand, R., Abel, N. P., van Hoof, P. A. M., Stancil, P. C., ApJ **675** (2008) 405

[28] Shaw, G., Ferland, G. J., Henney, W. J., Stancil, P. C., Abel, N. P., Pellegrini, E. W., Baldwin, J. A., van Hoof, P. A. M., ApJ **701** (2009) 677

[29] Snow, T.P., ApJ **202**, (1975) L87

[30] Snow, T. P., McCall, B. J., ARA&A **44** (2006) 367

[31] Tabak, R. G., Astrophysics and Space Science **66**, (1979) 161

[32] Thi, W.-F., van Dishoeck, E. F., Bell, T., Viti, S., & Black, J. 2009, MNRAS **400**, (2009) 622

[33] Wakelam, V., & Herbst, E. 2008, ApJ **680** (2008) 371

[34] Wakelam, V., Smith, I. W. M., Herbst, E., Troe, J., Geppert, W., Linnartz, H., ´Oberg, K., Roueff, E., Agúndez, M., Pernot, P., Cuppen, H. M., Loison, J. C., Talbi, D., Space Science Rev. **156** (2010) 13

[35] Williams, J. P., Bergin, E. A., Caselli, P., Myers, P. C., Plume, R., ApJ **503**, (1998), 689

[36] Wolfire, M. G., McKee, C. F. M., Hollenbach, D. J., Tielens, A. G. G. M., ApJ **587**, (2003) 278

[37] Wolfire, M. G., Tielens, A. G. G. M., Hollenbach, D. & Kaufman, M. J., ApJ **680** (2008) 384