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INTERSTELLAR MOLECULE FORMATION

BY

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ABSTRACT

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The formation of interstellar molecules is shown to be the result of chemical exchange reactions between atoms of the interstellar gas and atoms chemically bound to the interstellar grains. It is first shown that molecular formation by the physical absorption of the constituents on the grain with a subsequent three body reaction is of no consequence for graphite grains and Platt particles. Previous investigation has shown physical absorption is inoperative as a formation mechanism on ice grains. The theory of chemical exchange is then shown to apply to all types of grains and is then illustrated with graphite flakes. Production rates are given for H_2, CH, OH, NH, CN, CO, and N_2 as functions of temperature and pressure. Destruction of the molecules is due to photodissociation by starlight and also by other chemical exchange reactions. The varying conditions in the interstellar medium are considered. No molecules are formed when the gas is cold and quiescent. With the higher temperatures of cloud-cloud collisions H_2 is formed and it is shown that a minimum of 3/4 of all interstellar hydrogen atoms are in H_2 molecules. CH + CH^+, OH, and CN are produced by chemical exchange in the observed amount when graphite grains are driven at supersonic speeds through the gas by radiation pressure near early type stars. The process predicts the formation of H_2, CO, NH, N_2, from graphite flakes and possibly Platt particles.

Author

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I. INTRODUCTION

The formation of interstellar molecules was first discussed by Swings (1942), and by Kramers and ter Haar (1946), with two body recombinations as the mechanism. Following this, Bates and Spitzer (1951) suggested that molecules may be evaporated from the grains, whose constitution had been proposed by van de Hulst (1949). Since that time considerable progress has been made in the theory and application of chemical physics and in the description of the physical conditions in the interstellar medium. Recently a group of physicists working with van de Hulst (Knaap et al., 1965) has shown that the process of physical absorption of atoms on interstellar grains to form molecules in an atom-atom-grain three body process is inoperative. The existence of interstellar molecules such as CH, CH^+, CN, OH requires a formation mechanism since the lifetime of these molecules is on the order of a thousand years in the galactic radiation field. It is well known that the two and three body formation is negligible under the conditions existing in the interstellar medium.

A detailed theory should allow a prediction to be made on the observability of molecules whose transitions lie outside the spectral range that is now available but which may be observable in the future from above the Earth's atmosphere. The abundance of molecular hydrogen in the interstellar medium is of considerable interest because of its cooling efficiency. It is also of interest in the dynamics and structure of the spiral arms since it has been conjectured that it represents a significant portion of the mass of the galaxy.

We shall discuss the possible ways of forming and destroying molecules and the role of different types of interstellar grains in this process. In Section II we will adopt a simple model of the interstellar medium. The process of physical adsorption and the subsequent formation of molecules on the surface of grains

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will then be discussed and shown to be inadequate. In Section III a theory of chemical exchange will be presented in detail. Finally, in Section IV an application of the rate equations developed in Section III will be applied to each type of grain under a variety of physical conditions.

II. PHYSICAL ABSORPTION

The formation of molecules by two and three body collisional processes does not result in a significant density of molecules in the interstellar medium because of the low densities. Bates and Spitzer (1951) have shown for the CH molecule that the two body radiative association at a density of 10 hydrogen atoms per cm^3 fails to produce the observed CH density by a factor of 10^3 to 10^4. We will adopt a model where the hydrogen is concentrated in clouds with a density of 10 H atoms cm^{-3}, the clouds occupying five percent of the volume; between the clouds the density is assumed to be negligible for our purposes. The gas temperature in the clouds is assumed to be 100°K. This arrangement of the gas further reduces two body radiative association by a factor of more than ten.

To form molecular hydrogen by radiative association is almost impossible due to the very small f-value for the forbidden stabilizing transition. van de Hulst (1949) pointed out that molecules might form on the interstellar grains in a three body process where lattice vibrations in the grain absorbed the excess energy. This idea was developed as a mechanism for molecular hydrogen production by Gould and Salpeter (1963). The process is one of physical absorption of the atoms on the grains due to the weak van der Waals forces. A minimum condition for this to work is that an H atom must hit the grain and remain on it, at least until another H atom collides with the grains. Knaap et al., (1965) showed that for ice grains this can only occur when the grain temperature is below 7.5°K.

Interstellar grains composed of graphite have been proposed for a variety of reasons. Graphite grains are much better defined physically than dirty ice grains and we shall now use them to illustrate the calculation of Knaap et al., showing how the physical process may be generalized to other types of grains.

A. Physical Adsorption on Graphite Grains

The graphite grains are inherently very different from ice grains and Platt particles. They are chemically most unreactive on their basal planes but very reactive on the edges where there are many loose valencies. The carbon atoms in graphite arrange themselves in hexagons in which all the valencies are satisfied in the plane of the hexagon so that no chemical binding with this plane can take place. However, at the edge we have essentially cut the plane in two and so have unsatisfied valencies. The graphite flakes consist of many such layers of carbon rings all parallel to each other. The C-C distance is 1.415Å and the layer spacing is 3.35Å. The layers are bound only weakly together, and one can glide over another without much resistance. A complete physical description of graphite can be found in Ubbelohde and Lewis (1960), and a current bibliography on carbon appears in the journal "Carbon".

To facilitate the following discussion we shall consider a typical large graphite grain from extinction calculations. This is a rectangular block 10^{-5} cm × 10^{-5} cm × 10^{-6} cm. The basal planes are assumed parallel to the larger faces, and so there are about 300 planes stacked parallel, each plane containing 2×10^5 hexagon rings. There are a total of 10^7 carbon atoms in such an arrangement, and 5×10^5 free carbon valencies on the edge.

Defining T_{max} as the temperature above which molecular formation does not occur Knapp el al. showed:

$$T_{max} = \frac{q_a}{k} \left[\ln \frac{\nu_0}{\alpha N v Q} \right]^{-1} \tag{1}$$

where q_a is the binding energy, ν_0 is the frequency of oscillation in the van der Waals potential well, α is a numerical sticking factor, N is the hydrogen atom number density cm^{-3}, v is their velocity, and Q the cross section of the grain in cm^2. We have calculated T_{max} for H-H combination on graphite. We assume a Lennard-Jones (6-12) potential between the H-atom and the C-atoms in the grain. Of course, this will produce physical absorption on the basal plane surfaces, but on the edges the weak van der Waals attraction will be dominated by the chemical binding if there are free valencies. Following Young and Crowell (1962) we integrate this potential over all carbon atoms in the grain and obtain a binding energy E as a function of Z, the height of the H-atom from the grain, in the form

$$E(Z) = - \frac{\epsilon N \pi r_0^3}{3} \left[\left(\frac{r_0}{Z}\right)^3 - 1/15 \left(\frac{r_0}{Z}\right)^9 \right] \tag{2}$$

where ϵ is the strength parameter of the potential, N is the number density of carbon atoms cm^{-3}, and r_0 is the distance of the H atom from the nearest

C-atom. The binding energy at equilibrium can thus readily be obtained and put in terms of the coefficient of the r^{-6} term in the single atom-atom potential, i.e. the van der Waals coefficient. Experimental determinations of the binding energy of H_2 on graphite have been made (cf. Constabaris, Sams and Halsey, 1961) and thus the van der Waals attraction between H_2 and graphite is known. By the usual approximate relations between van der Waals coefficients (e.g. see Hirschfelder, Curtiss and Bird, 1954) using the H-H_2 coefficient calculated by Dalgarno and Williams (1965), we can find the H-graphite coefficient and hence the binding energy of H on graphite. As Knaap et al. have pointed out it is important to take account of the zero point energy of the H-atom in the binding energy. The result of the calculation is that T_{max} = 12°K, i.e. if the temperature of the grain is above this (as indeed it is) then an H-atom landing on the grain will in general (in 100°K clouds) have evaporated again before a second H-atom has arrived. As in the case of ice grains, therefore, H_2 formation is precluded on all the grains which contribute to the observed extinction curve. Although no measurements are available for physical adsorption of oxygen on graphite it seems unlikely that for our typical grain the T_{max} of oxygen atoms could exceed 45°K which is the expected temperature for our typical grain. Thus, the formation of OH and hence of ice mantles is most unlikely. Generalizing, it appears most unlikely that physical adsorption can be the method of formation of interstellar molecules.

B. Temperature and Charge of Graphite Grains

We examine the temperature of graphite grains under the dilute radiation field of interstellar space, which is taken to be that of a 10,000°K black body with various dilution factors. At the significant wavelengths the field pours energy into the grain, the cross section of the grain being enhanced by about 50% at these wavelengths. In equilibrium the grain must radiate this energy away at the same rate. Using Kirchhoff's law we calculate the rate of energy loss, $\int k_\nu B_\nu(T)\,d\nu$ for various temperatures T, until equality is obtained with the energy gain rate. k_ν is the absorption coefficient from the Mie calculations of Stecher (1966). For the grain considered the temperature is much greater than T_{max} calculated above. We plot the temperatures for graphite and for ice (Greenberg 1960) in Figure 1, calling attention to the large imaginary part of the refractive index for ices in the ultra-violet (Field 1965) which will probably raise these curves.

The processes affecting the charge on the grains are the photoelectric effect and ion collision, tending to make the grains positive, and electron collisions which tend to make the grains negative. The efficiency of this photoionization of graphite is unknown, but values of 10^{-4} electrons per photon are quoted for photoionization of similar systems (Spitzer 1948). Thus, the photoionization rate, is 2×10^{-6} sec^{-1}, whereas the electron collision rate is 4 × this value, and the ion collision rate is 5×10^{-8} sec^{-1} at 100°K gas temperature. In equilibrium, therefore, the electron collisions must be reduced by a factor of 4 due to accumulation of negative charge on the grain. If the distribution of energies is Maxwellian the potential on the grain is such that only electrons with energies 1.4 × the average get to the grain. The potential is thus 2.5×10^{-2} ev, which gives an average charge equivalent to less than one electron per grain.

Before leaving physical absorption, however, we must examine the effect of charge on these grains and on the processes involved. We shall assume that the typical charge on a graphite grain will be equivalent to less than that of one electron. This charge induces a polarization potential in the approaching H-atom essentially an r^{-4} potential which could thus dominate the van der Waals potential. Making a Born-Oppenheimer type approximation in saying that an electron moves much faster than the H-atom and thus appears spread out over the grain, and integrating over all the atoms in the grain it is easily seen that the induced potential due to this charge is quite negligible. This is also true when the charge might be that of ~10 electrons, which could occur at higher temperatures.

III. CHEMICAL EXCHANGE REACTION

As a result of the discussion in Section II we abandon physical absorption and assume the following new process as the significant one:

The mechanism of interstellar molecule formation is the capture by an incident atom of an atom chemically bound on the grain, to form a molecule by an exothermic chemical exchange reaction.

Chemical exchange reactions are those of the type

$$A + BC \rightarrow AB + C \tag{3}$$

While a full quantum mechanical treatment of this type of reaction has been carried out for only a few simple cases there are approximate methods of determining the rates of reaction.

The abundances of most diatomic molecules in interstellar space are known to be very low so that rates of the reaction (3) involving the diatomic molecule BC will usually be very slow. However, the advantage in a reaction of type (3) is that it is a three body reaction and will consequently be more favorable than a straight two body reaction except under extreme conditions. The problem is to have a sufficient density of the reactants at a sufficiently high temperature to provide an appreciable rate.

In this problem we have considered the diatomic molecules to be part of the interstellar grains. For whatever material these grains consist of, on part or all of their outer faces, there will be chemically bound atoms, bound into the grain itself. For instance, on the surface of an ice crystal there will be H atoms bound to 0 atoms which are part of an H_20 molecule attached to the lattice structure. We may consider a particular H atom to form a diatomic molecule with the rest of the grain thus: (grain) -H. Of course, there are many such H-atoms for one particular grain and so this may give a large increase in the effective number of diatomic molecules in space. With carbon grains the situation is only slightly different. We consider that these grains are probably graphite crystals of which the plane faces are chemically inert. The edges, however, are most reactive and will tend quickly to become filled with the atoms of interstellar space, mainly H-atoms. Thus again we have (grain) -H molecules. Alternatively, in the case of graphite we may regard these as CH molecules of which the C atom is bound into the grain. The situation with Platt particles, which are agglomerations of heavy hydrocarbons, is rather similar.

The theory used in the calculations of rates is simple Collision Theory, e.g. see Polanyi (1962). As in other treatments it is dependent on an activation energy A which may be regarded as the energy the incoming atom requires to overcome the repulsion of the initial molecule. A complex forms from the three atoms, dissociating into an atom and a new molecule with greater binding energy. The rate of reaction (3) is then

$$P\, n_A\, n_{BC}\, r_{AB}^2 \left(\frac{8\pi k T}{\mu}\right)^{½} \exp(-A/kT)\ \mathrm{cm}^{-3}\,\mathrm{sec}^{-1} \qquad (4)$$

where the steric factor P is an orientation parameter close to unity, n_A and n_{BC} are the number densities of the atoms A and the molecules BC in cm^{-3}, r_{AB} is the mean of the gas kinetic collision diameters r_{AA} and r_{BB} in the pure gases, μ is the reduced mass of atom A and molecule BC, and T is the gas temperature. The r^2 term specifies that the systems must come sufficiently close together to react. The conditions under which the reaction (3) will readily take place are (i) that the reaction is exothermic and (ii) that the activation energy is small compared to the binding energy.

The reaction that we must consider is, in general,

$$(\text{grain}) - X + Y \rightarrow (\text{grain}) + XY \tag{5}$$

To apply expression (4) to reaction (5) on grains we need to know N, the total number of diatomic molecules on the grain surface, f, the fraction of these available for chemical exchange, and the space density of grains, n_g. Then the rate is

$$\frac{1}{2} n_x r_{XY}^2 \left(\frac{8\pi k T}{\mu}\right)^{1/2} N f n_g \exp\left(-\frac{A}{kT}\right) \tag{6}$$

where we have given the steric factor P the value 1/2 since the atom x may approach the grain from only outside the grain.

We shall see in Section IV that grains close to hot stars may be moving very fast with velocity $V \sim 10^6$ cm sec^{-1}. In this event the random motions of the atoms in the gas are negligible compared to V. They have, relative to the grain, a velocity V, so the grain appears to be in a non-Maxwellian gas with temperature T_v such that

$$\frac{1}{2} m V^2 = 3/2 \, k T_v \tag{7}$$

and T_v will be large. m is the grain mass.

Because the grain is moving and not the gas the steric factor is unity (we assume the grain will rotate). The rate in this case is

$$n_x r_{XY}^2 \left(\frac{8\pi}{\mu}\right)^{1/2} \left(\frac{m}{3} X\right)^{1/2} V N f n_g \tag{8}$$

Note that the exponential factor may be dropped here as T_v is large. This implies that, for this case, the activation energy need not be known at all, and errors in A are not present in (8).

A. Molecular Production Rates for Graphite

To exemplify the rates described above we shall adopt as a model of a grain the graphite crystal discussed in II and evaluate rates of production by chemical exchange on its surface.

The 5×10^5 free valences of the graphite grain will tend to become saturated with atoms of interstellar space. Many of the vacancies will be filled with hydrogen. The binding energy of a C-C bond is ~5 ev and in the formation of a CH only ~3.5 ev is liberated, so that the grain is not destroyed (the kinetic energy being $\sim 10^{-2}$ ev). There are processes of destruction of this CH bond so that the number at any time is due to an equilibrium of production and destruction. C-N and C-C bonds will also tend to be formed, though in proportion to C-H, less than their relative abundances because of their lower velocities. A CO radical attached to the grain will not be formed in this way since the energy liberated in the formation of CO(~11 ev) is greater than the binding energy of 2C-C bands. It seems very likely to us that every collision of free H, C, N atoms on an empty valence on the edge of the grain will produce a reaction, as the incident atom has only to lose 10^{-2} ev to become bound. A system like a grain has many energy bands due to twisting, stretching and bending of C-H molecules each with energies less than 1 ev (Randic, 1960). A radiation-less free-bound transition is therefore most probable. The H-atom, the C-atom and the rest of the grain are the three bodies in the three body collision, the grain being a very convenient sink for the excess energy.

Reaction (5) for graphite may be written

$$> \text{C-X} + \text{Y} \rightarrow\ > \text{C} + \text{XY} \tag{9}$$

Under the conditions described above the fastest rates are obviously when X and/or Y is atomic hydrogen. The abundances of the elements are taken from Allen (1963) and we take $n_g = 6 \times 10^{-10}$ cm^{-3} in clouds.

Case I. X is atomic hydrogen

In this case we can form H_2, CH, OH, NH in exothermic reactions. In HI regions almost all carbon is ionized to C^+. We assume that the C^+ can react in the exchange mechanism with the negatively charged grains to form neutral CH. CH^+ must be formed by ionization. Following Glasstone, Laidler and Eyring (1941) we note that by ignoring the interaction between the two outer atoms, the activation energy is a definite fraction of the energy of the initial molecular bond, depending on the proportions of coulombic and resonance energies. Taking the coulombic energy to be 14% of the total, then the activation energy is 0.055 of the dissociation energy of the molecule (including the zero point energy). The binding energy in CH is of course altered by the situation of the carbon atom being part of the grain. Examining the change in the binding energy of this radical in large and small molecules leads to the conclusion that in large aggregates the binding energy is reduced by an appreciable factor. We adopt a new binding energy of 3.2 volts. (see, for example, Szwarc 1948, Szwarc and Roberts 1948, Gerö 1948, Honig 1948).

Letting Y be H, C^+, O, N in turn:

$$H_2 \text{ rate} = 7.0 \times 10^{-15} f(T) T^{1/2} \exp(-2040/T) P^2 \text{ cm}^{-3} \text{ sec}^{-1} \tag{10}$$

$$\text{CH rate} = \xi(T)\, 8.5 \times 10^{-19} f(T) T^{1/2} \exp(-2040/T) P^2 \tag{11}$$

$$\text{OH rate} = 1.7 \times 10^{-18} f(T) T^{1/2} \exp(-2040/T) P^2 \tag{12}$$

$$\text{NH rate} = 2.4 \times 10^{-19} f(T) T^{1/2} \exp(-2040/T) P^2 \tag{13}$$

where P is the pressure of the cloud measured in units of the pressure in a standard cloud in which $n_H = 10 \text{ cm}^{-3}$. $\xi(T)$ is a factor allowing for the interaction of the charge on the grain and that of the incident C^+.

Case II. Y is atomic hydrogen

By the same token that Case I does work, Case II does not, (except for H_2 production).

Case III. Y is C^+

The reaction we treat here is

$$[> C - X]^{-n} + C^{+} \rightarrow \; > C^{-(n-1)} + CX \tag{14}$$

where n is the number of electrons on the grain giving an exothermic method of production of CO and CN. The number of CX sites available is

$$\xi(T) \; 5 \times 10^{5} \; f(T) \frac{n_x}{n_H} \sqrt{\frac{M_H}{M_x}} \, n_g \; \mathrm{cm}^{-3} \tag{15}$$

so that the rate for the process is

$$\xi(T) \; r_{cx}^{2} \left[\frac{8\pi kT}{M_c}\right]^{1/2} 5 \times 10^{5} \; f(T) \frac{n_x}{n_H} \sqrt{\frac{M_H}{M_x}} \, n_g \, n_c \exp\left(\frac{-0.055}{kT} D'_{cx}\right) \tag{16}$$

where D' denotes dissociation energy of the relevant molecule when it is attached to the grain. We find:

$$\text{CN Rate} = 2.3 \times 10^{-23} \; f(T) T^{1/2} \exp(-4780/T) P^{2} \xi(T) \tag{17}$$

$$\text{CO Rate} = 1.4 \times 10^{-24} \; f(T) T^{1/2} \exp(-6500/T) P^{2} \xi(T) \tag{18}$$

using

$$D'_{CN} = 7.5 \text{ ev and } D'_{CO} = 10.2 \text{ ev.} \tag{19}$$

Case IV. X is C

This gives a second method of production of CO and CN using $D'_{C_2} = 4.5$ ev we obtain

$$\text{CN Rate} = 2.1 \times 10^{-23} f(T) T^{1/2} \exp(-2870/T) \qquad (20)$$

and

$$\text{CO Rate} = 1.5 \times 10^{-22} f(T) T^{1/2} \exp(-2870/T) P^2 \qquad (21)$$

Case V. Other reactions

The only case of importance not already considered which can proceed is N_2 production.

$$N_2 \text{ Rate} = \frac{1}{2} r^2_{N-N} \left[\frac{8\pi k T}{M_N}\right]^{1/2} 5 \times 10^5 f \frac{n_N}{n_H} \sqrt{\frac{M_H}{M_N}} n_g n_N \exp(-4780/T) P^2$$

$$= 6.0 \times 10^{-24} f(T) T^{1/2} \exp(-4780/T) P^2 \qquad (23)$$

Notably NO cannot be formed in this way.

B. Determination of f(T)

Suppose there are N sites on one grain, and that at a time t, n of these are available; i.e., not filled with H, so that (N-n) are filled with H.

When the H-atom hits an empty site, it stays, so a site is lost. If it hits a filled site, it may form H_2, freeing a site. The fraction of collisions doing this is $e^{-A/kT}$. Also we will assume that due to photodissociation filled sites empty at a rate $\beta \sim 10^{-11}$ sec^{-1}. (Bates and Spitzer 1951).

Suppose there are m H-atom collisions per second on the reactive face. The rate of increase in the number of sites available at time t is

$$\frac{dn}{dt} = (N-n)\,\beta + e^{-A/kT}\,(N-n)\,m' - m''\,n \tag{24}$$

where m' is the number of H-atom collisions on filled and m" on unfilled sites. We have $m' + m'' = m$

i.e. $m' = \frac{N-n}{N}\,m$ and $m'' = \frac{n}{N}\,M.$

At steady state (24) becomes $(N-n)\,\beta + e^{-A/kT}\,(N-n)\,m' = m''\,n$ i.e. substituting $f = (N-n)/N$,

$$f^2\left(1-e^{-A/kT}\right) - f\,(\beta/m + 2) + 1 = 0 \tag{25}$$

If the area of a reactive face is a cm^2 then

$$m = \frac{1}{2}\,a\sqrt{\frac{3kT}{m_H}}\,n_H\,.$$

For one grain $a = 4 \times 10^{-11}$ cm^2, so $m = 2 \times 10^{-6}\,PT^{1/2}$

Thus β/m is negligible, as long as β remains small.

Equation (25) becomes $f^2\left(1-e^{-A/kT}\right) - 2f + 1 = 0$ with solution

$$f = \left(1 + e^{-A/kT}\right)^{-1} \tag{26}$$

bearing in mind that $0 \leq f \leq 1$.

Thus f(T) is a monotonically decreasing function of temperature from f = 1 to f = ½.

C. Effect of Charge

It has been shown that a negatively charged grain which attracts to itself positively charged ions presents to an ion a cross section enhanced by a factor $\xi(T) = (1 - \xi/kT)$ where ξ is the negative potential, see, e.g. McNally (1962), van de Hulst (1949), Spitzer (1948). In this case, at cold cloud temperatures, the rates involving C^+ are thus enhanced by a factor of 3.9. At 2500°K this factor is 2.16, taking the average charge at these temperatures to be that of 10 electrons.

The seven most abundant elements which may be ionized in HI regions are C, Na, Mg, Si, S, Ca, Fe. For an exchange reaction to proceed it must be exothermic as noted previously. This appears to be so only in the case of carbon. Silicon (in the formation of SiH^+) is possible though undecided case.

D. Other Grains

If we try the same procedure with pure ice grains then the range of molecules which may be produced by this method is severely limited by the condition of exothermicity. Exothermic reactions are only to be expected in the case of H_2 and CO. Reactions producing NH, CH, and NO could proceed if about 3/4, 1 and 2 ev respectively, of energy could be given to the reactants to overcome the endothermicity. These endothermic reactions will be further inhibited by the fact that the most strongly bound molecule is the preferred end product. These are large amounts of energy, especially for ice, where the binding energy of an H_2O molecule in the structure is a few hundredths of 1 ev.

Platt particles should readily produce interstellar molecules by the process of chemical exchange.

E. Destruction Processes for Free Molecules

In the preceding sections we have shown how to calculate rates of production of diatomic molecules on the basis of chemical exchange. Chemical exchange may also be a destruction mechanism for some free molecules. For instance, the reaction

$$CH + H \rightarrow C + H_2 \tag{27}$$

is an exchange process which may be sufficiently rapid to destroy CH, while only adding an insignificant amount to the H_2 concentration. Using the collision theory we obtain for the rate of the above reaction per CH molecule

$$6.7 \times 10^{-11} T^{1/2} \exp(-2220/T) P \text{ sec}^{-1} \tag{28}$$

Comparing with the value given by Bates and Spitzer (1951) for the photodissociation rate of 1.5×10^{-11} sec^{-1} in a dilute radiation field we see that this destruction rate may easily be the dominant one for $T > 450°K$. We also have the following destruction rates by similar processes, per molecule

$$CH^+ : 6.7 \times 10^{-11} T^{1/2} \exp(-2300/T) P \text{ sec}^{-1} \tag{29}$$

$$OH : 4.4 \times 10^{-11} T^{1/2} \exp(-2870/T) P \text{ sec}^{-1} \tag{30}$$

$$OH^+ : 4.9 \times 10^{-11} T^{1/2} \exp(-2870/T) P \text{ sec}^{-1} \tag{31}$$

$$NH : 5.1 \times 10^{-11} T^{1/2} \exp(-2400/T) P \text{ sec}^{-1} \tag{32}$$

Polarization forces have been ignored in the calculation of the rates for ions.

If the temperature is such that chemical dissociation is inapplicable to these molecules, the destruction is controlled by photodissociation, and for this process we give the crude estimates, OH:3×10^{-12} sec^{-1}, NH:7×10^{-12} sec^{-1}, CO:10^{-14} sec^{-1}. under the Bates and Spitzer radiation field.

CN cannot be destroyed in an exothermic chemical exchange reaction. Following the methods of Bates and Spitzer we estimate a photodissociation rate $\sim 5 \times 10^{-14}$ sec^{-1}.

For the destruction of H_2 we adopt the arguments of Gould and Salpeter (1963). These authors point out that H_2 is a very stable molecule, which is shielded by neutral hydrogen and is unlikely to be dissociated except in the intense ultraviolet radiation field near a hot star. Assuming the arrangement of interstellar material into clouds and the random passage of these clouds near hot stars as described in Section IV then a reasonable dissociation rate for H_2 is 3×10^{-16} sec^{-1}. We also adopt this value for N_2.

IV. APPLICATION

The typical simplified model of a spiral arm will now be adopted to calculate the rates of molecular production involved in the different physical situations which may exist. This model is one in which the gas and interstellar grains are concentrated into clouds of mean density of 10 hydrogen atoms per cm^3 with the harmonic mean gas temperature of 100 degrees K. The cloud is assumed to have a diameter of 15 pc with an rms velocity of 7 km/sec. A collision with another cloud is assumed to occur every 10^7 years with a collision duration of 10^6 years. The temperature during a collision will rise to several thousand degrees. A density increase of a factor of 4 during the collision is assumed.

First we consider the production of molecules on graphite grains in the cold clouds. The destruction mechanism here is photodissociation, not chemical exchange. From equation (11) the concentration for ($CH + CH^+$) is

$$\xi(T)\ 8.5 \times 10^{-19}\ f(T) T^{1/2} \exp(-2040/T) P^2 / 1.5 \times 10^{-11} \sim 10^{-14}\ cm^{-3}.$$

The fastest rate of production is that of H_2; but in the time between two cloud/cloud collisions we have concentrations of $\sim 10^{-7}$ cm^{-3}, which we shall see is also negligible. The production of all other molecules considered on graphite is negligible at cold cloud temperatures. For ice grains, too, the molecular concentrations are much too low. However, when the clouds are in collision, the temperature is raised to several thousand degrees, and the atoms of the gas have sufficient energy to overcome the activation energy. We use equations (11), (28) for CH and similar equations for OH and NH. The resulting densities are given in Table 1. Here again the densities are lower than the observed ones (Allen 1963, and Robinson, et. al. 1964). However, the density of H_2 which we discuss in more detail in Section V, B is becoming significant during the course of a single cloud/cloud collision.

A third possibility exists for the production of molecules. When there is a sufficient velocity difference between the grains and the gas the activation energy for the reaction is overcome and molecules are formed. This velocity difference quickly disappears in collisions due to the drag exerted by the gas and would lead to little production unless the velocity difference is sustained through some force. We shall now show that radiation pressure in the neighborhood of early type stars is a sufficient force.

Table I

Densities in cm^{-3} Due to One Cloud/Cloud Collision

T = 1000°K	$\xi(T) = 2$		$f(T) = 0.8$	$P = 4$	
	$(CH+CH^+)$	OH	NH	CN	H_2^*
Density in clouds	8×10^{-8}	1.2×10^{-7}	4×10^{-9}	10^{-8}	2
Average in space and time	4×10^{-10}	6×10^{-10}	2×10^{-11}	5×10^{-11}	10^{-2}
Observed average	1.7×10^{-8}	2×10^{-7}	—	4×10^{-10}	—

*See Section VB.

A. Case of Moving Grains

Consider a grain at rest at a distance of R_0 pc from a star of equivalent black body temperature of 30,000°K. We take as dilution factor at this distance $W = 10^{-14} R_0^{-2}$. We will assume that all the energy occurs at around $\lambda = 2000$ Å, for which a photon has energy 10^{-11} ergs, and momentum h/λ. If the cross section of the grain is A then the force on the grain is $W\sigma T^4 \, A(h/\lambda)/10^{-11}$ dynes. Substituting, the acceleration due to this force is 10^{26} A/m R^{-2} cm sec^{-2} where R is the distance from the star in cm, m is the mass of the grain, and the dependence on R arises through the variation in W with R.

The effect of collisions of the grain with atoms is the retarding mechanism. The number of collisions the grain has per second is $\sim n_H A v$ in each of which it loses M_H/m of its momentum. Regarding this as a continuous process the retarding force is

$$n_H A v \left(M_H/m\right) m v = n_H A M_H v^2 .$$

The equation of motion is therefore

$$\frac{d}{dt}(mv) = \frac{10^{26} A}{R^2} - n_H A M_H v^2 \tag{33}$$

which may be written

$$v\frac{dv}{dR} = \frac{a_0}{R^2} - \alpha v^2 \qquad (34)$$

substituting a_0 for $10^{26}A/m$ and α for $n_H AM_H/m$

This has solution

$$v^2 = 2a_0 e^{-2\alpha R}\left[\frac{e^{2\alpha R_0}}{R_0} - \frac{e^{2\alpha R}}{R} + 2\alpha\left\{Ei(2\alpha R) - Ei\left(2\alpha R_0\right)\right\}\right] \qquad (35)$$

where R_0 is the initial point of the integration, in this case $R_0 = 1\text{pc}$, and Ei(x) is the exponential integral. A very good approximation to (35) is

$$v^2 = \frac{a_0}{\alpha}\left[\frac{1}{R^2} - \frac{1}{R_0^2}e^{-2\alpha(R-R_0)}\right]$$

so that for R not close to R_0: $v^2 = a_0/\alpha R^2$.

This reduces to

$$v = \frac{1}{R}\sqrt{\frac{10^{13}}{n_H}}\ \text{cm sec}^{-1}\ (R \text{ in pc}). \qquad (36)$$

Molecule Formation by Fast Grains

Combining equation (36) for the velocity of the grains and equation (6) for the rate of molecular production on fast particles, the rate for producing XH is

$$r^2 \frac{1}{R} \sqrt{\frac{10^{13}}{n_H}} \; 5 \times 10^5 \; f(T) \; n_g n_x \; \mathrm{cm}^{-3} \; \mathrm{sec}^{-1}$$

where n_x is the density in a standard cloud.

The destruction rate due to photodissociation is dependent on the dilution factor. Bates and Spitzer's calculation of the photodissociation rate of CH was based on a dilution factor (at intermediate energies) of 3×10^{-15}. Hence, photodissociation as a function of R is

$$\beta = \frac{\beta_0}{3 \times 10^{-15}} \times \frac{10^{-14}}{R^2} = \frac{3\beta_0}{R^2} \; \mathrm{sec}^{-1} \tag{38}$$

where β_0 is the dissociation rate for XH calculated for a dilution factor of 3×10^{-15}. For equation (38) β_0 should be the photodissociation rate for a 30,000°K star, which will be perhaps a factor of 5x larger than the value calculated under Bates and Spitzer's conditions. In the absence of known rates for the hotter star we use as β_0 5x the dissociation rates quoted in Section IIIE.

We must now consider the importance of the chemical destruction mechanism discussed in III. It is believed that near hot stars where the densities may be greater than the standard cloud, the temperature will certainly not be above 500°K, where the chemical begins to dominate the photodissociation. Thus, if the XH molecule which will after formation be traveling with the velocity of the grain, can become thermalized, its lifetime is controlled by photodissociation. We expect that half the XH molecules will survive the few collisions necessary to thermalize even in colliding with H-atoms only. But the dense clouds we are considering will also have an appreciable amount of H_2 and He. Collisions of XH with H_2 or He will serve to thermalize the XH molecules. Hence, we shall assume the destruction is controlled by photodissociation. Hence, the concentration expected is

$$\frac{4.3 \times 10^{-14} \; n_x \, f(T) \; P^{3/2}}{R} \times \frac{R^2}{3\beta_0} \; \mathrm{cm}^{-3} = 1.4 \times 10^{-14} \; n_x \frac{f(T)}{\beta_0} P^{3/2} R \; \mathrm{cm}^{-3} \tag{39}$$

Thus, from equations (38) and (39) the average density of XH surrounding a star will be

$$[XH] = \frac{1.4 \times 10^{-14}\ n_x\ f(T)\ P^{3/2}}{\left(R_{max} - R_{min}\right)\beta_0} \int_{R_{min}}^{R_{max}} R\ dR \qquad (40)$$

where R_{max} is the distance from the star at which the grain velocity becomes equivalent to a gas-atom temperature of say 1000°K, and R_{min} is the radius of the Strömgren sphere. Thus, R_{max} is given by

$$\frac{1}{R^2_{max}}\ \frac{10^{13}}{n_H} = \frac{3kT_{gas}}{m_x}$$

i.e.

$$R^2_{max} = \frac{10^{13}\, m_x}{3k\ T_{gas}\, n_H} \text{ in pc.} \qquad (41)$$

e.g. For C,

$$R_{max} = 7\ P^{-\frac{1}{2}}\ \text{pc.}$$

For type BO stars

$$R_{min} = 26\ n^{-2/3} = 5.5\ P^{-2/3}\ \text{pc.} \qquad (42)$$

We take

$$f(T) = 0.8,\ T_{gas} = 10^3\ ^\circ K,$$

and from Strömgren (1939)

$$R_{min} = 5.5 \times P^{-2/3} .$$

Table II shows the resulting concentrations for hydrides around the star.

Table II

Densities of Hydrides Around Star, in cm^{-3}

Molecule XH	CH	NH	OH
β_0(sec^{-1})	7.5×10^{-11}	3.5×10^{-4}	1.5×10^{-11}
n_x(cm^{-3})	3×10^{-3}	10^{-3}	7×10^{-3}
R_{max}(pc)	$6.7\ P^{-1/2}$	$7.4\ P^{-1/2}$	$7.9\ P^{-1/2}$
[XH], P = 1, cm^{-3}	2.7×10^{-6}	2.1×10^{-6}	3.5×10^{-5}
[XH], P = 10, cm^{-3}	2.4×10^{-5}	1.8×10^{-5}	3.1×10^{-4}

The values for CH concentrations have not included ξ (T), but since the effective temperature is very high, ξ (T) will only introduce a factor close to unity.

For reactions producing molecules which do not contain hydrogen, equation (39) for the density as a function of radius becomes

$$1.4 \times 10^{-14} \frac{n_x}{n_H} \sqrt{\frac{M_H}{M_x}}\, n_y \frac{f(T)}{\beta_0} P^{3/2} R \text{ cm}^{-3}$$

Thus the average density is

$$1.4 \times 10^{-14} \frac{n_x}{n_H} \sqrt{\frac{M_H}{M_x}}\, n_y \frac{f(T)}{\beta_0} P^{3/2} \frac{1}{2} \left(R^y_{max} + R_{min}\right) \text{ cm}^{-3} \qquad (43)$$

R_{max} is evaluated from equation (41) and f(T), T_{gas}, R_{min} are taken as above. We use the values of R_{max} for C, N, O as quoted in Table II. There are two ways of producing CN and CO, by writing the molecule as XY or YX. This is not so for N_2. The results are given in Table III.

Table III

Densities of Non-Hydride Molecules Around Stars, in cm^{-3}

Molecule XY	CN	CO	N_2
$\beta_0(sec^{-1})$	2.5×10^{-13}	5×10^{-14}	1.5×10^{-15}
[XY + YX], P = 1, cm^{-3}	4.7×10^{-8}	1.6×10^{-6}	6.5×10^{-9}
[XY + YX], P = 10, cm^{-3}	4.0×10^{-7}	1.4×10^{-5}	5.5×10^{-8}

B. Case of H_2

If we write equation (8) as

$$dn_{H_2}/dt = \alpha (T, P)\ n_H ,$$

then, since $dn_H/dt = -2dn_{H_2}/dt$ to a good approximation, we can express the number density of H_2 as a function of time t, temperature T, and pressure P.

$$n_{H_2} = \frac{1}{2} n_H^0 \left\{1 - e^{-2\alpha(T,P)t}\right\}. \quad (44)$$

We assume where n_H^0 is the initial density of H-atoms, a typical cloud undergoes 10 collisions each lasting 10^6 years in the average lifetime of 10^8 years, after which it enters an H II region and the molecules ionize and dissociate. Let us assume that T = 1000°K and P = 4 in a collision. Then from equation (8) $\alpha = 7 \times 10^{-16} f(T) T^{1/2} \exp(-2040/T) P = 8 \times 10^{-15}\ sec^{-1}$. So that after the first cloud/cloud collision $n_{H_2}/\frac{1}{2} n_H^0 = 0.38$. After the second collision 0.62 of the H-atoms will be in molecules. The molecular hydrogen concentration will thus appear as in Figure 2, with average value $\frac{2n_{H_2}}{n_H} = 0.74$, i.e., approximately three quarters of the hydrogen atoms are in molecules, on the average. Thus, if radio observations specify H-atom number densities, three times this number density of hydrogen atoms may be present as molecules. This is approaching the Oort limit (Gould, Gold and Salpeter, 1963). The number densities of other atoms may have to be increased by a proportionate factor. No H_2 will be produced by the "fast grain" mechanism, as R_{max} is always less than R_{min}, i.e. hydrogen atoms must move fastest of all atoms to overcome the activation energy, but the grain does not have this requisite velocity outside the Strömgren sphere. If all the H_2 is not destroyed after 10^8 years then three-fourths represents a lower limit to the H_2 abundance.

C. Results

Thus, we see that radiation pressure is sufficient to maintain the velocity difference necessary to overcome the activation energy. The densities produced around the early type star have been presented in Tables II and III. If we assume that this star is at a distance of $\sim 10^3$ pc it is seen in Table IV that the calculated mean densities are in reasonable agreement with observation. Also the mean observed velocity of approach of the molecules with respect to the star (Bates & Spitzer 1951) can easily be explained in terms of the motion of the gas in the presence of a hot star (Oort and Spitzer 1955).

Table IV

Space Densities in cm^{-3} for BO Stars, 1 kpc Distant

	CH	NH	OH	CN	CO	N_2
P = 1	3.2×10^{-9}	4.0×10^{-9}	8.4×10^{-8}	7.4×10^{-11}	3.1×10^{-9}	1.2×10^{-11}
P = 10	2.3×10^{-8}	2.1×10^{-8}	4.3×10^{-7}	4.3×10^{-10}	1.7×10^{-8}	6.5×10^{-11}
Observed	1.7×10^{-8}	--	2×10^{-7}	4×10^{-10}	--	--

Consider for instance the case where the gas has not been in an H II region for a long period of time. The ratio of H_2 to H has built up to the point where there is practically no atomic hydrogen. This might be expected to be the case in the cold gas near where stars are forming or at high galactic latitudes. The ratio of atomic hydrogen to the heavy elements becomes smaller. The unfilled sites on the grains will be more likely to fill up with heavier elements. In this way more CN, CO, N_2 will be formed. This is in apparent agreement with the observations reported by Münch (1964) where an anomalously large amount of CN is found around a young star.

V. SUMMARY AND DISCUSSION

We have presented a set of expressions which may be used to calculate the rate of formation and the concentration of molecules in interstellar space. These expressions are based on the theory of chemical exchange which, though an approximate theory, introduces an error in the rates and concentrations which is probably small when compared with the uncertainty in specifying the astrophysical conditions for which we wish to apply the theory. These expressions are generally applicable to any type of grain with very little modification. The physical specification of the various kinds of interstellar grains is of course necessary to predict the concentration and kinds of molecules. For graphite grains we have shown that it is possible to obtain CH, CH^+, CN, OH with amounts consistent with those which are observed. Graphite would also produce H_2, NH, N_2 and CO. Pure ice grains will produce only H_2, OH and CO since the other reactions are endothermic. In fitting extinction curves ice is generally assumed to be dirty ice to give it absorption properties. It would appear that the inclusion of enough other radicals to allow the production of CN, CH, OH, etc., by the process of chemical exchange would no longer leave it a dielectric. However, the Bates and Spitzer mechanism of evaporating and photodissociating parent molecules is not here ruled out. The problem of nucleating dirty ice and causing it to grow at the low temperatures involved seem insurmountable in view of the failure of physical absorption as a formation process. It is also difficult to understand how an ice particle could withstand the bombardment produced by the differential velocity between the ice and the gas even at great distances from the driving star because of the low crystal binding energy. Hoyle and Wickramasinghe (1962) suggested that graphite flakes would form in the atmospheres of carbon stars and subsequently be blown out by radiation pressure. Donn, Wickramasinghe, Stecher and Hudson (1965) have shown that graphite crystals would grow in the circumstellar cloud surrounding M-giants and Wickramasinghe, Donn and Stecher (1965) have suggested that graphite formation and subsequent radiation pressure on it in M-giants would lead to a possible explanation for mass loss in these stars through the coupling between the graphite and the gas. The ability of graphite to form and retain its properties at temperatures much higher than ice make it an attractive alternative.

Platt particles could conceivably produce the interstellar molecules in the required amount. However, a physical description of them would appear impossible. It might be pointed out that the end result of temperature annealing Platt type materials is graphite. The temperature of Platt particles should be considerably higher than graphite due to their smaller size and therefore processes involving physical absorption may be ruled out from the arguments for ice and graphite. Grains of sand could conceivably be present in interstellar space, formation occurring in a manner similar to the formation of graphite, i.e., nucleation and growth in the other atmospheres of late type stars where radiation pressure then blows them out of the star. The sand would be only useful for the production of silicon and oxygen molecules which have greater binding energies than SiO_2.

It may be pointed out that this theory does not produce the large molecules which have sometimes been sought as the explanation of the diffuse interstellar lines. With the graphite model of interstellar grains, the possible explanations for λ4430 are considerably limited: we see only three possible causes. The first is the absorption by the molecular end of the grain, i.e. the grain-CH molecule, which would shift the electronic transition $B^2\Sigma^- - X^2\Pi$ of the free CH radical to longer wavelengths and broaden it. The second is the inclusion of metals between the graphite planes, such as calcium, the resonant lines being shifted and broadened (Dressler 1965) by interaction with the crystal structure. This crystal compound of graphite would increase the infrared extinction (Hennig 1965) and could provide an explanation of the low calcium abundance in interstellar space (Spitzer 1954). The third possibility is the excitation of the lattice vibration by a photon. Many such phonons occur in radiation damaged crystals at optical frequencies.

On the basis of our theory of chemical exchange we suggest that the interstellar grains are graphite. If graphite grains do not exist, then this theory of chemical exchange will still apply to the actual grains, but may not supply all the known interstellar molecules.

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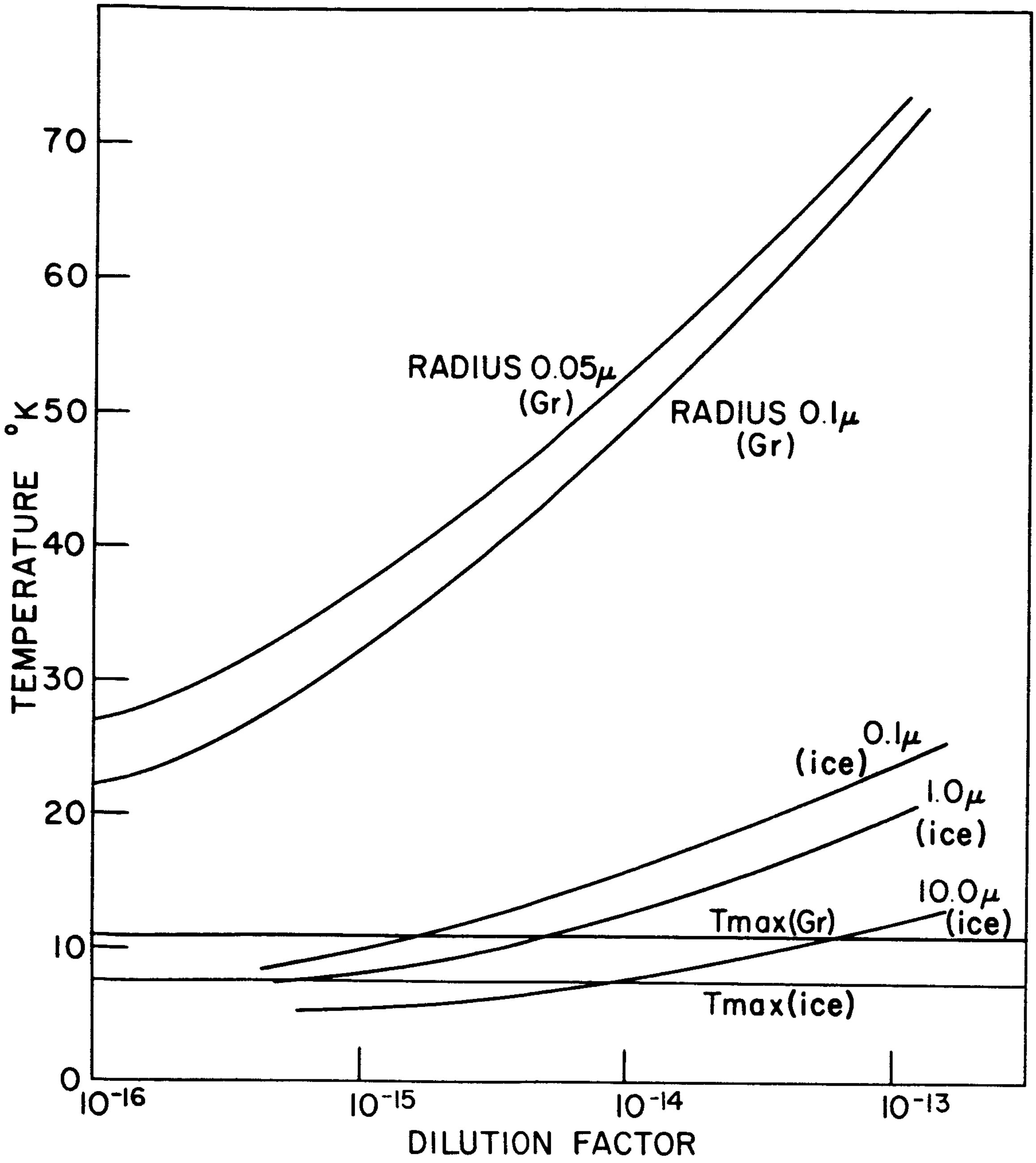

Figure 1. The temperature of interstellar grains as a function of the dilution factor. The curves are obtained from Mie calculations for a 10^4 °K black body radiation field. T_{max} is the maximum temperature for which molecular formation by the process of physical adsorption is possible.

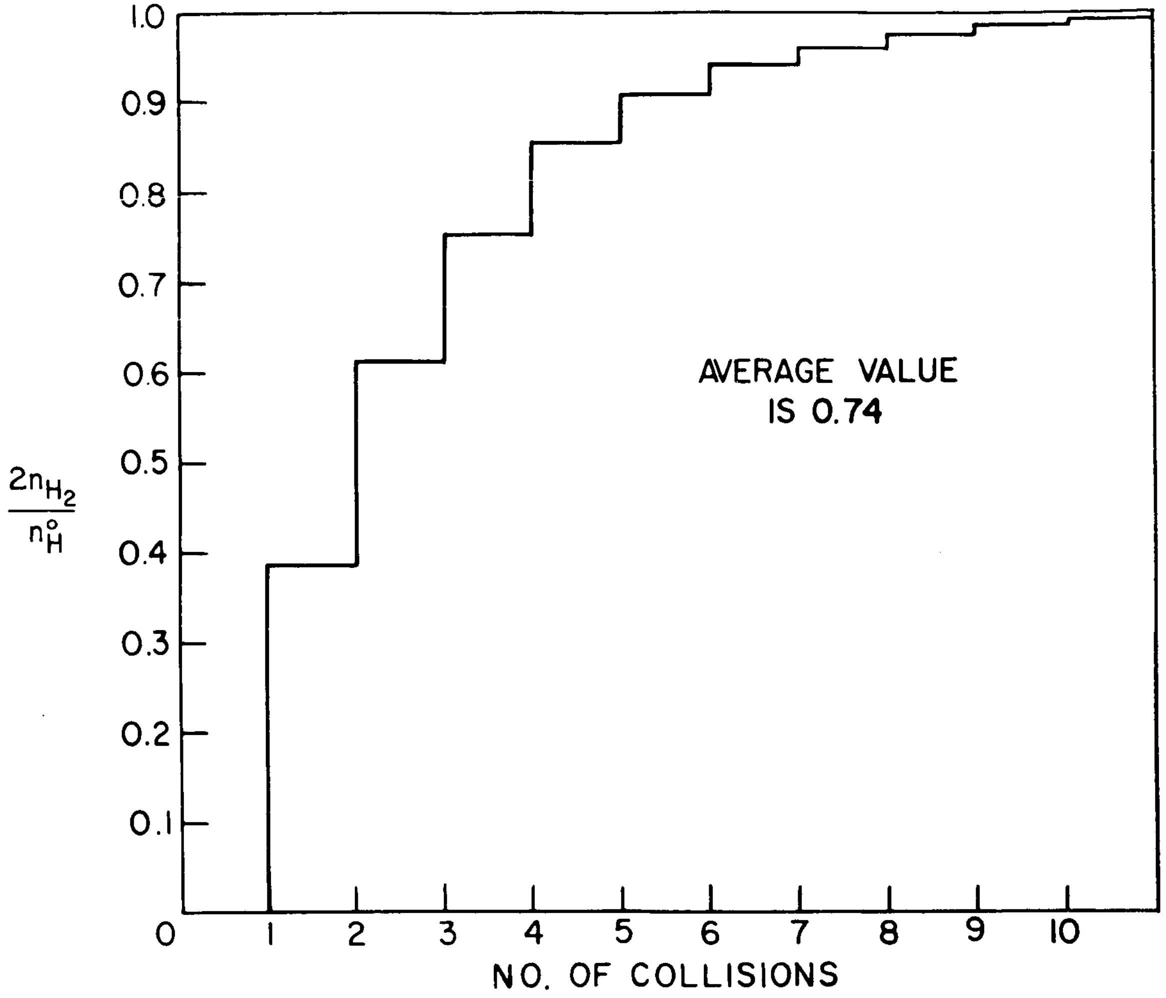

Figure 2. The ratios of hydrogen in molecular form to that in atomic form as a function of the number of cloud-cloud collisions.