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THE FORMATION AND DEPLETION OF MOLECULES IN DENSE INTERSTELLAR CLOUDS*

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ABSTRACT

The rates of a number of homogeneous gas phase chemical reactions likely to occur in dense interstellar clouds composed primarily of molecular hydrogen are considered. Over 100 reactions are included; of these, more than half have known rate constants. These reactions are sufficient to produce and destroy polyatomic species such as H_2O, HCN, NH_3, and H_2CO. Steady-state abundances of about 35 species are calculated for clouds of density $10^4 \leq n_{H_2} \leq 10^6\ cm^{-3}$. Calculations are performed for cosmic-ray–induced ionization rates $\zeta_{H_2} = 10^{-17}$ and $10^{-18}\ s^{-1}$. Typical times for reaching steady-state ($n_{H_2} = 10^5\ cm^{-3}$, $\zeta_{H_2} = 10^{-17}\ s^{-1}$) vary for different species; e.g., $H_2^+ \simeq 0.05$ day, $H_3^+ \simeq 0.3$ year, $H_2O \simeq 3 \times 10^3$ years. Comparisons of calculated and observed column densities are presented for a number of regions.

Subject headings: excitation and ionization — molecules, interstellar — nebulae

I. INTRODUCTION

In the past five years, radio and microwave observations have established the presence of a large number of polyatomic molecules in dense interstellar clouds. (For a recent review see Rank, Townes, and Welch 1971.) Several mechanisms have been proposed to explain the presence of these molecules. We intend to review the various mechanisms elsewhere (Herbst and Klemperer 1974). This paper presents a specific model for the formation and destruction of polyatomic molecules in dense clouds. The model, which we outline briefly, is quantitative and relies almost exclusively on gas phase reactions.

We shall be concerned primarily with the interiors of dense clouds. The optical extinction is assumed to be sufficiently high that interstellar radiation does not penetrate appreciably. The elemental composition of the gas is taken to follow cosmic abundance so that the density of each element is determined by the hydrogen density. Because of the high density and optical extinction, hydrogen exists almost entirely in its molecular form (Solomon and Werner 1971; Hollenbach, Werner, and Salpeter 1971). Similarly, carbon monoxide is the primary form of carbon. These two features shall be shown to be the primary origin of the differences in the chemistry of dense clouds as opposed to medium-density clouds studied in a similar manner by Solomon and Klemperer (1972).

The reactions considered in our model can involve only binary collisions since the densities are too low to permit efficient three-body encounters. (Three-body reactions become important at densities of $10^{11}\ cm^{-3}$.) Because the kinetic temperature is low, all reactions considered must be exothermic. In addition, in order for a reaction to occur at an appreciable rate, it must proceed without activation energy. Exothermic ion-molecule reactions obey these requirements (Gioumousis and Stevenson 1958) and, as a result, provide the major pathways for polyatomic molecule synthesis in the present model. Fortunately, the rate constants for many of the ion-molecule reactions used in our analysis are known from laboratory investigations.

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Ionization is produced in dense clouds by cosmic rays sufficiently energetic to penetrate the interior. Since H_2 and He are the dominant species, the major initial ions produced are H_2^+, H^+ (Solomon and Werner 1971), and He^+. The exothermic reaction $H_2^+ + H_2 \rightarrow H_3^+ + H$ is rapid (Bowers, Elleman, and King 1969), but the highly exothermic reaction of He^+ with H_2 does not occur for kinetic reasons (Fehsenfeld *et al.* 1966*b*). Thus He^+, unlike H_2^+, will exist in appreciable concentration. Having an electron affinity of 24 eV, He^+ ionizes most neutral species other than H_2 rapidly. The reactions of the primal ions—H^+, H_3^+, He^+—with abundant neutral species such as CO, O, N, O_2, and N_2 produce secondary ions such as C^+, N^+, O^+, N_2^+, O_2^+, HCO^+, and HN_2^+.

Since molecular hydrogen is the major component, polyatomic ions can be built up rapidly by exothermic ion-molecule reactions of the type

$$A^+ + H_2 \rightarrow AH^+ + H\,,$$

$$AH^+ + H_2 \rightarrow AH_2^+ + H\,, \qquad \text{etc.,}$$

where A^+ represents any ion. Another, albeit much less efficient, mode of synthesis is

$$A^+ + H_2 \rightleftharpoons (AH_2^+)^* \rightarrow AH_2^+ + h\nu\,,$$

where $(AH_2^+)^*$ is a short-lived collision complex that can stabilize itself by infrared emission.

Those polyatomic ions that do not react rapidly with either H_2 or CO are destroyed primarily by recombination with electrons. These reactions are very exothermic and usually lead to fragmented neutral products (Bardsley and Biondi 1970). Although laboratory measurement of rates of neutralization are frequently available, the neutral fragments have not been identified. We estimate the branching ratios leading to the formation of various sets of fragments in § II*c*. Among the neutral species formed by recombination reactions are CH, NH, OH, H_2O, NH_3, and H_2CO.

All neutral molecules are destroyed by gas phase reactions. At low temperatures, less reactive species such as NH_3 and H_2O can react efficiently only with ions. More reactive species such as OH and CH can react in some instances with neutral atoms as well as with ions. These neutral-neutral reactions produce a wider variety of neutral species, including O_2, N_2, NO, and CN. Condensation on the dust grains is an additional depletion mechanism for condensable neutrals, but this process is shown likely to be competitive for the less reactive species only.

Each polyatomic species is synthesized and destroyed rapidly and a stationary abundance reached within $\sim 10^5$ years. Because gas phase reactions both synthesize and deplete molecular species, molecular abundances are relatively stable with respect to changes in the total gaseous density and ionization rate. Our calculated results for clouds with $10^4 \leq n_{H_2} \leq 10^6$ cm^{-3} show that the most abundant polyatomic neutrals are H_2O, NH_3, and H_2CO, and that the major ionic species are C^+, H^+, He^+, HCO^+, and H_3O^+.

The present paper is divided into three major parts. Section II discusses the rates of relevant reactions and their functions in our model. The coupled simultaneous nonlinear kinetic equations are then solved as a function of H_2 density. Section III contains a discussion of our results and the validity of some of our assumptions. In § IV, calculated abundances are compared with observational values for several regions.

The chemistry of dense clouds is complex because of coupling among the many reactions that must be considered. By far the most serious difficulty in the present work is obtaining assurance that all relevant reactions have been included. The rates of the gas phase reactions in the present model are rapid compared with estimates of

grain reaction times. Thus, a model of molecule synthesis invoking grains must also include the reactions of the present article.

II. THEORY AND RESULTS

a) Elemental Abundances and Ionization

The relative cosmic abundances of the elements H, He, C, N, O used here are listed in table 1. Since dense clouds contain dust, it is possible that the gas phase abundances of some elements may be depleted below their average cosmic values. In the present work, we do not consider seriously depletion of heavy elements relative to hydrogen. As more information becomes available for interstellar elemental abundances, the calculations can be modified.

If, as assumed, ultraviolet photons do not penetrate the interior of dense clouds (Heiles 1971), the only external radiation that can influence the chemistry of these regions is cosmic-ray bombardment. Solomon and Werner (1971) have assumed an effective first-order rate constant of $\zeta = 10^{-15}\ s^{-1}$ for the cosmic-ray–induced ionization of molecular hydrogen, the dominant gas phase species. Their analysis assumes that 2-MeV cosmic-ray protons can penetrate the interiors of dense clouds. Utilizing the results of Dalgarno and Griffing (1958) and Bates and Griffing (1953), we estimate that a 2-MeV proton will penetrate an H_2 column density of at most $3 \times 10^{21}\ cm^{-2}$. For the clouds we consider that n_{H_2}, the density of molecular hydrogen, is at least $10^4\ cm^{-3}$, and N_{H_2}, the corresponding column density, is at least $5 \times 10^{22}\ cm^{-2}$ (Heiles 1971). Therefore, 2-MeV cosmic rays penetrate only the fringes of dense clouds.

Spitzer and Tomasko (1968) have calculated a value of $6 \times 10^{-18}\ s^{-1}$ for the cosmic-ray–induced ionization rate constant of atomic hydrogen assuming a cosmic-ray energy spectrum dominated by 100-MeV protons. Converting their result to an analogous one for molecular hydrogen, we obtain $\zeta_{H_2} \sim 10^{-17}\ s^{-1}$ (Solomon and Werner 1971). Utilizing the cross-section calculations of Bethe (1933) for ionization by high-energy protons, we calculate that 100-MeV protons penetrate a column density $N_{H_2} \sim 10^{24}\ cm^{-2}$. The very dense molecular cloud in Orion is thought to have a molecular-hydrogen column density of less than $10^{24}\ cm^{-2}$ (Thaddeus *et al.* 1971). Since few H_2 column densities are much larger than this, our tentative conclusion is that hard cosmic rays penetrate all but the most dense clouds and that $\zeta_{H_2} \simeq 10^{-17}\ s^{-1}$ is the correct parameter for the interiors of these regions.

TABLE 1

COSMIC ABUNDANCES

Element	Relative Abundance (by number)*
H	1
He	0.14†
C	3.75×10^{-4}
N	8.7×10^{-5}
O	4.4×10^{-4}
Ne	2.6×10^{-5}
Si	3.2×10^{-5}
S	1.4×10^{-5}
Fe	3.2×10^{-5}

* Dalgarno and McCray 1972.

† Heiles 1971.

The cosmic-ray–induced ionization of H_2 produces both H_2^+ and H^+ ions with branching ratio (Solomon and Werner 1971)

$$H_2 + \text{cosmic-ray proton} \begin{cases} \nearrow H_2^+ + e + p\ (95\%) \\ \searrow H^+ + H + e + p\ (5\%)\,. \end{cases}$$

H_2^+ is destroyed rapidly by reaction with molecular hydrogen (Bowers *et al.* 1969):

$$H_2^+ + H_2 \rightarrow H_3^+ + H\,.$$

In the present model, we also consider the cosmic-ray–induced ionization rate for helium. The experimental result that H_2 and He have approximately equal stopping power for high-energy protons (Allison and Warshaw 1953) leads us to conclude that $\zeta_{He} \sim \zeta_{H_2}$. Unlike H_2^+, He^+ does *not* react rapidly with H_2 (Fehsenfeld *et al.* 1966*b*). The resulting significant abundance of He^+ is important in the ion-controlled synthesis of several polyatomic species, notably ammonia. It is not necessary to consider the cosmic-ray–induced ionization of any species containing a heavy element. The reason is that ionization of H_2 and He followed by rapid ion-molecule reactions with abundant neutral species is much more efficient in producing heavy ions. This assertion is shown quantitatively in § III*b*.

b) Model

In this model, we assume that virtually all neutral hydrogen in the gas is present as H_2. There is observational evidence that the H concentration is small (Heiles 1971). In addition, Solomon and Werner (1971) have calculated a residual hydrogen atomic abundance of $\sim 1\ cm^{-3}$ for $\zeta_{H_2} \sim 10^{-17}\ s^{-1}$. It is almost certain that molecular hydrogen is formed by atomic recombination on the dust grains (Hollenbach *et al.* 1971).

Carbon is present chiefly as carbon monoxide. This assumption is not markedly different from observational result (Penzias, Jefferts, and Wilson 1971) and is indicated theoretically by the results of Solomon and Klemperer (1972) on clouds of medium density. These authors show that CO is formed by gas phase radiative association of CH and CH^+ followed by rapid exchange reactions with atomic oxygen.

If we include the grain-catalyzed reaction $H + H \rightarrow H_2$ in our analysis, we can demonstrate that our model is stable with respect to the two initial conditions above.

In this analysis, molecules are synthesized solely by gas phase reactions. Molecules are depleted by gas phase reactions as well, although condensation on the dust grains could be a competitive though not dominant depletion mechanism for polyatomic neutrals. The steady-state approximation is utilized to calculate abundances for the various atomic and molecular species; i.e., for all species considered, the rate of formation is set equal to the rate of depletion. This approximation is meaningful only if the time necessary for reaching steady-state is shorter than the cloud lifetime. For a cloud of $n_{H_2} = 10^5\ cm^{-3}$, arguments in § III*c* show that the steady-state condition is reached within 10^4 years from the time our model is "turned on," a time period much shorter than the gravitational collapse time of the cloud (Rank *et al.* 1971). Since condensation on the grains may be a competitive depletion mechanism for several neutral species, a more complete model should consider what happens to the species after condensation. Reactions on the surfaces of the dust grains may take place (Watson and Salpeter 1972; Aannestad 1973). Recent work, both experimental and theoretical (Greenberg 1972; Watson 1972) indicates that photo-desorption with

relatively nonenergetic and therefore relatively nonextinguished photons is an efficient process. It is presumably this process that prevents total condensation of dense clouds within a period of time only slightly longer than the time necessary for attaining steady-state gas phase molecular abundances. Photo-desorption and other desorption processes are not considered quantitatively in the present work because their inclusion in the model has little effect on the detailed numerical results.

The chemistry of the dense clouds is determined by a large number of reactions. In the following section, rate constants for these reactions are discussed.

c) *Reactions Considered*

Physical conditions in dense interstellar clouds place severe restrictions on the classes of gas phase reactions which must be considered. The diluteness of the gas rules out all reactions involving more than two bodies. The low kinetic temperatures ($T \leq 50°$ K) restrict the number of efficient reactions to those that are exothermic and possess no activation energy barriers. Since most reactions involving neutral species do proceed with activation energy (Kaufman 1969), these reactions are most likely unimportant in dense clouds. Neutral-neutral reactions involving an atom and a free radical are often exceptions to this rule, and we include such systems in our analysis. However, most of the reactions known to proceed efficiently at low collision energies involve at least one charged species. Cosmic-ray bombardment provides a source of positive ions. Consequently, positive ion-neutral reactions are of extreme importance in our model. Negative-ion reactions can be shown to be less important because of the low abundance of ions of negative charge (Dalgarno and McCray 1972).

In the following sections, we discuss the various types of reactions considered, the laboratory data available, and our estimates of the rate constants for those reactions not studied experimentally.

Thermodynamic information is taken from several works. The principal reference for positive ions is Franklin *et al.* (1969), and for neutral species the J.A.N.A.F. Thermochemical Tables. These are supplemented by Wagman *et al.* (1968). The above references are sometimes out-of-date for individual species. Table 2 presents a list of heats of formation obtained from more recent sources.

i) *Exothermic Positive Ion-Molecule Reactions*

These systems are described by the general reaction

$$A^+ + B \rightarrow C^+ + D\,, \qquad (1)$$

in which there is some mass transfer involved. Systems of this type have been investigated extensively in the laboratory, principally by the flowing afterglow technique. The experimentally determined rate constants are often observed to be independent

TABLE 2

ADDITIONAL HEATS OF FORMATION

Species	ΔH^0_f (kcal per mole)	Reference
H_3^+	266	Schwartz and Schaad 1967
HCO^+	196	Matthews and Warneck 1969
HCO_2^+	145	Haney and Franklin 1969
HN_2^+	< 266	Burt *et al.* 1970
H_3CO^+	170	Haney and Franklin 1969
NH_4^+	~150	Estimate

of temperature and to be approximated quite well by the simple Langevin relation (Gioumousis and Stevenson 1958).

$$k = 2\pi e(\alpha/\mu)^{1/2} \simeq 1\text{–}2 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}, \tag{2}$$

where e is the electronic charge, α the polarizability of the neutral reactant, and μ the reduced mass of the colliding species. Certain ion-molecule reactions proceed at a much slower rate than that given in equation (2). There is some recent evidence that these systems possess "negative activation energies"; i.e., their rate constants are enhanced somewhat at lower temperatures (Ferguson 1973). Consequently, there is no evidence to suggest that ion-molecule reactions are retarded at the low kinetic temperatures in dense clouds.

We have included more than 50 reactions of this type in our analysis. These reactions are listed in table 3. Most of the rate constants have been determined experimentally. Unless there is evidence to the contrary, we utilize equation (2) for those reactions not experimentally investigated.

In view of the large abundance of molecular hydrogen, systems of the type

$$A^+ + H_2 \rightarrow AH^+ + H, \tag{3a}$$

$$AH^+ + H_2 \rightarrow AH_2^+ + H, \tag{3b}$$

etc., constitute a most important subclass of ion-molecule reactions. If rapid, these reactions can synthesize large polyatomic ions quite efficiently. Several examples of such reactions with measured rate constants near the Langevin value are:

$$8.\quad O^+ + H_2 \rightarrow OH^+ + H,$$

$$10.\quad OH^+ + H_2 \rightarrow OH_2^+ + H,$$

$$12.\quad OH_2^+ + H_2 \rightarrow OH_3^+ + H,$$

$$9.\quad N^+ + H_2 \rightarrow NH^+ + H,$$

$$11.\quad NH^+ + H_2 \rightarrow NH_2^+ + H,$$

$$13.\quad NH_2^+ + H_2 \rightarrow NH_3^+ + H.$$

(The numbers to the left of each reaction are those utilized in tables 3–7.)

However, ion–H_2 systems are observed to show wide variations of rate constant. Two such very slow reactions are:

$$7.\quad He^+ + H_2 \rightarrow \text{products} \qquad (k < 10^{-13}\ \mathrm{cm^3\ s^{-1}}),$$

$$14.\quad NH_3^+ + H_2 \rightarrow NH_4^+ + H \qquad (k < 5 \times 10^{-13}\ \mathrm{cm^3\ s^{-1}}).$$

These systems are critical to our analysis. Because He^+ reacts very slowly with H_2, it is present in sizable amounts. With its high electron affinity, it is energetically capable of exothermic reaction with every neutral species. Table 3 shows a number of rapid He^+–molecule reactions. The importance of He^+ in our analysis lies in its ability to react with neutral species such as CO, N_2 that do not react with more abundant protons or C^+ ions.

In our model, NH_4^+ is a precursor of ammonia. We assume the $NH_3^+(H_2) \rightarrow NH_4^+(H)$ reaction to have a rate constant $k \sim 10^{-13}\ \mathrm{cm^3\ s^{-1}}$. If the true rate constant is much lower than this value, our calculated abundances of NH_4^+ and NH_3 are too high.

TABLE 3

ION-MOLECULE REACTIONS

	Reaction	$k(10^{-9}$ cm^3 s$^{-1})$	Reference/Remarks
	Ionization		
1.	H_2 + cosmic-ray proton → $H_2^+ + e$ + C.R.P.′	$(k_1 = 0.95\zeta_{H_2}$ s$^{-1})$	
2.	H_2 + cosmic-ray proton → $H + H^+ + e$ + C.R.P.′	$(k_2 = 0.05\zeta_{H_2})$	
3.	He + cosmic-ray proton → $He^+ + e$ + C.R.P.′	$(k_3 \sim \zeta_{H_2}$ s$^{-1})$	
4.	$H_2^+ + H_2 \rightarrow H_3^+ + H$	2.1	Bowers *et al.* 1969
5.	$CO^+ + H_2 \rightarrow HCO^+ + H$	2.0	Fehsenfeld *et al.* 1967
6.	$N_2^+ + H_2 \rightarrow HN_2^+ + H$	1.7	Fehsenfeld *et al.* 1967
7.	$He^+ + H_2 \rightarrow$ products	$< 10^{-4}$	Fehsenfeld *et al.* 1966*b*
8.	$O^+ + H_2 \rightarrow OH^+ + H$	2.0	Fehsenfeld *et al.* 1967
9.	$N^+ + H_2 \rightarrow NH^+ + H$	0.7	Fehsenfeld *et al.* 1967
10.	$OH^+ + H_2 \rightarrow OH_2^+ + H$	1.5	Fehsenfeld *et al.* 1967
11.	$NH^+ + H_2 \rightarrow NH_2^+ + H$	0.6	Ferguson 1973
12.	$OH_2^+ + H_2 \rightarrow OH_3^+ + H$	1.4	Fehsenfeld *et al.* 1967
13.	$NH_2^+ + H_2 \rightarrow NH_3^+ + H$	0.23	Ferguson 1973
14.	$NH_3^+ + H_2 \rightarrow NH_4^+ + H$	$< 5 \times 10^{-4}$	Ferguson 1973
15.	$CH^+ + H_2 \rightarrow CH_2^+ + H$	10^{-2}	
16.	$CH_2^+ + H_2 \rightarrow CH_3^+ + H$	10^{-2}	
17.	$HCN^+ + H_2 \rightarrow H_2CN^+ + H$	2.0	
18.	$He^+ + CO \rightarrow C^+ + O + He$	2.0	Laudenschlager *et al.* 1973
19.	$He^+ + N_2 \rightarrow N^+ + N + He$	0.72	Farragher 1970
20.	$\rightarrow N_2^+ + He$	0.48	Farragher 1970
21.	$He^+ + O_2 \rightarrow O^+ + O + He$	0.62	Farragher 1970
22.	$\rightarrow O_2^+ + He$	0.38	Farragher 1970
23.	$He^+ + CN \rightarrow C^+ + N + He$	2.0	
24.	$H_3^+ + O \rightarrow OH^+ + H_2$	2.0	
25.	$H_3^+ + C \rightarrow CH^+ + H_2$	2.0	
26.	$H_3^+ + CO \rightarrow HCO^+ + H_2$	1.4	Burt *et al.* 1970
27.	$H_3^+ + N_2 \rightarrow HN_2^+ + H_2$	1.5	Burt *et al.* 1970
28.	$H_3^+ + OH \rightarrow H_2O^+ + H_2$	2.0	
29.	$H_3^+ + CN \rightarrow HCN^+ + H_2$	2.0	
30.	$H_3^+ + H_2O \rightarrow H_3O^+ + H_2$	3.0	Burt *et al.* 1970
31.	$H_3^+ + CO_2 \rightarrow HCO_2^+ + H_2$	1.9	Burt *et al.* 1970
32.	$H_3^+ + NH_3 \rightarrow NH_4^+ + H_2$	3.6	Burt *et al.* 1970
33.	$H_3^+ + HCN \rightarrow H_2CN^+ + H_2$	2.0	
34.	$H_3^+ + H_2CO \rightarrow H_3CO^+ + H_2$	2.0	
35.	$HCO^+ + OH \rightarrow HCO_2^+ + H$	1.0	Only exothermic channel
36.	$HCO^+ + H_2O \rightarrow H_3O^+ + CO$	0.5	See analogous HN_2^+ reaction in Burt *et al.* 1970
37.	$HCO^+ + NH \rightarrow NH_2^+ + CO$	1.0	
38.	$HCO^+ + NH_2 \rightarrow NH_3^+ + CO$	1.0	
39.	$HCO^+ + NH_3 \rightarrow NH_4^+ + CO$	1.0	
40.	$HCO^+ + H_2CO \rightarrow H_3CO^+ + CO$	1.0	
41.	$C^+ + O_2 \rightarrow CO^+ + O$	1.1	Fehsenfeld *et al.* 1966*a*
42.	$C^+ + OH \rightarrow CO + H^+$	2.0	
43.	$C^+ + NH \rightarrow CN + H^+$	2.0	
44.	$C^+ + CH \rightarrow C_2^+ + H$	2.0	
45.	$C^+ + H_2O \rightarrow HCO^+ + H$	2.0	Bolden and Twiddy 1972
46.	$C^+ + NH_2 \rightarrow HCN + H^+$	2.0	
47.	$C^+ + CH_2 \rightarrow C_2H^+ + H$	2.0	
48.	$C^+ + HCN \rightarrow C_2N^+ + H$	2.0	
49.	$C^+ + CO_2 \rightarrow CO^+ + CO$	1.9	Fehsenfeld *et al.* 1966*b*
50.	$C^+ + NH_3 \rightarrow H_2CN^+ + H$	2.0	
51.	$C^+ + H_2CO \rightarrow HC_2O^+ + H$	2.0	
52.	$H^+ + CO_2 \rightarrow HCO^+ + O$	3.0	Fehsenfeld *et al.* 1971
53.	$O_2^+ + N \rightarrow NO^+ + O$	0.18	Goldan *et al.* 1966
54.	$HN_2^+ + CO \rightarrow HCO^+ + N_2$	1.0	See analogous CO_2 reaction in Burt *et al.* 1970
55.	$H_3O^+ + C \rightarrow HCO^+ + H_2$	2.0	
56.	$H_3O^+ + NH_3 \rightarrow NH_4^+ + H_2O$	2.0	

There are several ion–H_2 systems in our analysis that have not been studied in the laboratory:

$$15. \quad CH^+ + H_2 \rightarrow CH_2^+ + H\,,$$

$$16. \quad CH_2^+ + H_2 \rightarrow CH_3^+ + H\,,$$

$$17. \quad HCN^+ + H_2 \rightarrow H_2CN^+ + H\,.$$

Of these reactions, we assume that reactions 15 and 16 have slow rate constants of 10^{-11} cm^3 s^{-1} while reaction 17 proceeds at the Langevin rate. The exact value of k_{15} is not important in the present work on dense clouds. It is of considerable importance in low-density regions. It is quite possible that in those regions, reaction 15 followed by the fast reaction

$$CH_2^+ + e \rightarrow CH + H$$

is important in determining CH/CH^+ equilibria. These reactions were not considered by Solomon and Klemperer (1972). Reaction (15) is almost thermoneutral ($\Delta H^0 = -4$ kcal per mole) on the basis of present data. Since the uncertainty in these data is of the same magnitude, this reaction must be studied in greater detail. The species CH^+ is an unimportant species in dense clouds; thus, its reactions will not affect our present results.

Another important subclass of reactions are those involving H_3^+. This ion is produced by the well-studied reaction

$$4. \quad H_2 + H_2^+ \rightarrow H_3^+ + H\,,$$

and then reacts with many neutral species according to the general formula

$$H_3^+ + X \rightarrow XH^+ + H_2\,, \tag{4}$$

where X = CO, N_2, H_2O, NH_3, etc. These reactions have been studied by Burt *et al.* (1970), and all show Langevin-type behavior. We have assumed formula (4) to represent the dominant exit channel for the unstudied reactions

$$24. \quad O + H_3^+ \rightarrow OH^+ + H_2 \qquad (\text{and not} \rightarrow OH_2^+ + H)\,,$$

$$28. \quad OH + H_3^+ \rightarrow OH_2^+ + H_2 \qquad (\text{and not} \rightarrow OH_3^+ + H)\,,$$

$$29. \quad CN + H_3^+ \rightarrow HCN^+ + H_2 \qquad (\text{and not} \rightarrow H_2CN^+ + H)\,, \qquad \text{etc.,}$$

which are presumed to be Langevin in behavior. The choice of exit channel is not important in the above cases since the reaction

$$12. \quad H_2O^+ + H_2 \rightarrow H_3O^+ + H$$

is rapid, and the reaction

$$17. \quad HCN^+ + H_2 \rightarrow H_2CN^+ + H$$

is presumed rapid. The reactions

$$N + H_3^+ \rightarrow NH^+ + H_2\,,$$

$$O_2 + H_3^+ \rightarrow HO_2^+ + H_2$$

(Burt *et al.* 1970), are endothermic and therefore do not take place. No additional exit channel for the $N + H_3^+$ system is considered.

The important ion HCO^+ is assumed to react with many neutral species in a manner analogous to formula (4):

$$Y + HCO^+ \rightarrow YH^+ + CO\,, \tag{5}$$

where $Y = H_2O$, NH_3, H_2CO, etc. This mechanism is usually the only channel that is exothermic. Burt *et al.* (1970) have studied several reactions of the isoelectronic ion HN_2^+ which are approximately Langevin and follow a mechanism similar to formula (5).

It is uncertain in which direction the reaction

$$37.\quad HCN + HCO^+ \rightarrow H_2CN^+ + CO$$

proceeds because the thermodynamic information about H_2CN^+ is not precise. However, the system is assumed to proceed as in formula (5) and to be Langevin in behavior.

The last major subgroup of ion-molecule reactions is that involving C^+. Because C^+ is the most abundant ion in our analysis, its reactions are of considerable importance. In the present work we consider

$$42.\quad C^+ + OH \rightarrow CO + H^+\,,$$

$$43.\quad C^+ + NH \rightarrow CN + H^+\,,$$

$$44.\quad C^+ + CH \rightarrow C_2^+ + H\,,$$

$$45.\quad C^+ + H_2O \rightarrow HCO^+ + H\,,$$

$$46.\quad C^+ + NH_2 \rightarrow HCN + H^+\,,$$

$$47.\quad C^+ + CH_2 \rightarrow C_2H^+ + H\,,$$

$$48.\quad C^+ + HCN \rightarrow CCN^+ + H\,,$$

$$49.\quad C^+ + NH_3 \rightarrow H_2CN^+ + H\,,$$

$$50.\quad C^+ + H_2CO \rightarrow HC_2O^+ + H\,,\qquad \text{etc.}$$

Reaction with C^+ is the dominant destruction mechanism for stable polyatomic species such as H_2O, HCN, NH_3, and H_2CO. Reaction 49 is especially important because it leads to the formation of HCN. Except for 45, none of the above systems has been studied. They are presumed to proceed at the Langevin rate.

In the present work, we are not considering the formation of polyatomic molecules with several carbon atoms. Thus the detailed natures of the products of reactions 48 and 50 are not important. For the synthesis of multicarbon species, reactions of C^+ are likely to play a dominant role. It is of considerable importance that reactions of C^+ with molecules such as H_2CO, HCN, NH_3, CH_3CN, etc., be investigated.

ii) *Charge-Transfer Reactions*

These systems are described by the general relation

$$A^+ + B \rightarrow A + B^+\,. \tag{6}$$

In the present work, A^+ usually represents a proton. The charge-exchange reactions of interest are listed in table 4. Only one reaction has been studied at thermal energies.

TABLE 4

CHARGE-TRANSFER REACTIONS

	Reaction	$k(10^{-9}$ cm^3 s$^{-1})$	Reference
57.	$H^+ + NO \rightarrow NO^+ + H$	1.9	Fehsenfeld and Ferguson 1972
58.	$H^+ + O_2 \rightarrow O_2^+ + H$	1.0	
59.	$H^+ + OH \rightarrow OH^+ + H$	1.0	
60.	$H^+ + H_2O \rightarrow H_2O^+ + H$	1.0	
61.	$H^+ + NH_3 \rightarrow NH_3^+ + H$	1.0	
62.	$H^+ + H_2CO \rightarrow H_2CO^+ + H$	1.0	
63.	$C^+ + NO \rightarrow NO^+ + C$	1.0	
64.	$C + O_2^+ \rightarrow C^+ + O_2$	1.0	

It is assumed that the remainder of the reactions occur at one-half the collision frequency:

$$k_{\text{charge-transfer}} \simeq \tfrac{1}{2} k_{\text{Langevin}} \simeq 10^{-9}\ \text{cm}^3\ \text{s}^{-1}.$$

The reaction exothermicities are presumably taken up as internal energy in the molecular ions formed. For exothermic atom-atomic ion charge-transfer reactions, the extra energy can go only into translation or into excited electronic states of the products. If the latter are not nearly resonant, the reactions may be very slow due to Franck-Condon considerations.

In this category are

$$C + H^+ \rightarrow C^+ + H, \qquad N + He^+ \rightarrow N^+ + He,$$

which are excluded from table 4.

The reaction

$$O + H^+ \rightarrow O^+ + H$$

is very slightly endothermic. Field and Steigman (1971) have calculated the rate of this reaction as a function of temperature. The rate constant is highly temperature dependent between $T = 10°$–$50°$ K, increasing from 10^{-19} cm^3 s^{-1} at 10° K to 10^{-11} cm^3 s^{-1} at 50° K. In terms of our model, the reaction is important only for $T \geq 50°$ K. Except for the small central cores of certain dense molecular clouds, gas temperatures in the clouds we consider are expected to be less than 50° K (Heiles 1971; Solomon 1973). We therefore neglect this reaction in the present model.

Charge-exchange reactions between protons and neutral species are important in our model as depletion mechanisms for unreactive molecules such as H_2O and H_2CO which do not react with other neutrals at low temperatures.

iii) *Radiative Association*

The possibility of the association of two species is now considered. Reactions of the form

$$A^+ + H_2 \rightarrow AH_2^+$$

are known to occur under laboratory conditions via a two-step process (Ferguson 1973)

$$A^+ + H_2 \rightleftarrows (AH_2^+)^*. \qquad \text{Forward rate: } k_1\ (\text{cm}^3\ \text{s}^{-1}),\quad \text{Backward rate: } k_{-1}\ (\text{s}^{-1}),$$

$$(AH_2^+)^* + M \rightarrow AH_2^+ + M. \qquad \text{Rate: } k_M\ (\text{cm}^3\ \text{s}^{-1}), \qquad (7a)$$

where $(AH_2^+)^*$ is a collision complex with sufficient energy to dissociate into A^+ and H_2. Under laboratory conditions the excess energy is removed by a second collision during the lifetime of the complex. At gas densities below 10^{11} cm^{-3}, stabilization of the complex by infrared emission,

$$(AH_2^+)^* \rightarrow (AH_2^+) + h\nu. \qquad \text{Rate: } k_2\,(\text{s}^{-1}), \tag{7b}$$

can be shown to be more likely. This type of radiative capture process has been labeled "inverse vibrational predissociation" (Herzberg 1966). Since molecular hydrogen is the dominant species in our model, a mechanism of this sort may be competitive even if it possesses a small rate constant. In particular, we are interested in the reaction

$$HCO^+ + H_2 \rightarrow H_3CO^+ + h\nu, \tag{8}$$

since the product ion is a precursor of formaldehyde. The reactions

$$HCO^+ + H_2 \rightarrow H_2CO^+ + H$$
$$\rightarrow CO + H_3^+$$

are endothermic so that no rapid ion-molecule reactions are possible between HCO^+ and H_2. To the best of our knowledge, no reaction that proceeds by "inverse vibrational predissociation" has been investigated in the laboratory. Scattering-theory formalisms exist (Mies 1969) but the problem is difficult for large polyatomic ions. Instead, we utilize a crude model. We assume first that k_1 in reaction (7b) is equal to the Langevin value. Once the complex is formed, it can relax vibrationally via spontaneous emission and stabilize itself or it can dissociate back into the original reactants. The dissociation process is handled by the unimolecular rate theory of Kassel (1932). More recent approaches to this theory assume that vibrational energy can be treated as a continuous classical variable. These approaches break down under conditions of low energy.

An N-atom complex is assumed to possess $s = 3N - 6$ ($3N - 5$ if linear) harmonic oscillators of identical frequency ν; energy transfer among the oscillators is rapid. If the complex has j excited quanta and if dissociation occurs when m ($m \leq j$) quanta are transferred to any single oscillator, the statistical rate of dissociation is

$$k_{-1} = \nu \frac{(j - m + s - 1)!\, j!}{(j + s - 1)!\, (j - m)!}\, \text{s}^{-1}. \tag{9}$$

The H_3CO^+ complex is formed with an energy just at the minimum necessary for decomposition. Therefore, $m \simeq j$, and equation (9) simplifies to

$$k_{-1} \sim \nu \frac{j!\, (s - 1)!}{(j + s - 1)!}\, \text{s}^{-1}. \tag{10}$$

If any spontaneous emission occurs during the lifetime of the complex, it will no longer be capable of redissociation. To calculate k_2, the spontaneous emission rate constant, we assume that each infrared active mode relaxes at a rate of 10^2 s^{-1} (Herzberg 1966). Then

$$k_2 \sim n \times 10^2\, \text{s}^{-1}, \tag{11}$$

where n is the average number of excited infrared-active oscillators in the complex. To obtain the overall second-order rate constant k for radiative association via

"inverse vibrational predissociation," we apply the steady-state approximation to the $(AH_2^+)^*$ concentration in reaction (7b). Then,

$$k = \frac{k_1 k_2}{k_{-1} + k_2} \simeq \frac{k_1 k_2}{k_{-1}} . \tag{12a}$$

For reaction (8), k_1 is computed to be 1.5×10^{-9} cm^3 s^{-1}. The H_3CO^+ complex has nine normal modes which we assume to be harmonic oscillators of frequency 1800 cm^{-1} (5.4×10^{13} s^{-1}). The reaction exothermicity (table 2) of approximately 9100 cm^{-1} can be put into $j \simeq 9100/1800 \simeq 5$ excited quanta which, on the average, are all in different dipole-relaxable modes. We then obtain

$$k_{-1} \sim \nu \frac{5!\,8!}{13!} = 4 \times 10^{10} \text{ s}^{-1},$$

$$k_2 \sim 5 \times 10^2 \text{ s}^{-1},$$

and finally

$$k \sim \frac{(1.5 \times 10^{-9})(5 \times 10^2)}{4 \times 10^{10}} \sim 2 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}.$$

This result is presented in table 5. Note that k is eight orders of magnitude smaller than the Langevin rate constant. Nevertheless, reaction (8) is of prime importance in the synthesis of formaldehyde.

If the steady-state approximation is applied to $(AH_2^+)^*$ in the three-body process described by reaction (7a), an effective second-order rate constant can be derived:

$$k_{\text{eff}}^{(2)} = \frac{k_1 k_M [M]}{k_{-1} + k_M [M]} \simeq \frac{k_1 k_M [M]}{k_{-1}} . \tag{12b}$$

Comparison of equations (12a) and (12b) reveals that if $k_2 > k_M[M]$, radiative association is more rapid than three-body association. Since $k_2 \sim 10^2$ s^{-1} and $k_M \sim 10^{-9}$ cm^3 s^{-1}, gas densities below 10^{11} cm^{-3} are needed to favor the former mechanism.

It appears likely that radiative association reactions will be most important when one species is a molecular ion and the neutral species is H_2. The high density of H_2 compensates for the intrinsically low rate constant for this type of reaction. With increasing complexity of the molecular ion, the lifetime of the collision complex increases rapidly. Since the rate of photon emission remains roughly constant as does the collision frequency, the overall rate constant for radiative association should increase proportionally to the lifetime of the collision complex. In the present paper only the above $HCO^+ + H_2$ reaction is considered.

iv) *Ion-Electron Recombination Reactions*

Positive ions recombine rapidly with electrons to form neutral products. The large exothermicities of these reactions can be channeled into radiant energy or into bond rupture in the parent molecules. Diatomic ions containing two heavy atoms recombine

TABLE 5

RADIATIVE ASSOCIATION

65	$HCO^+ + H_2 \rightarrow H_3CO^+ + h\nu$	($k \simeq 2 \times 10^{-17}$ cm^3 s^{-1})

dissociatively (Bardsley and Biondi 1970) with large rate constants. Two examples in our analysis are (table 6)

$$O_2^+ + e \rightarrow O + O\,, \qquad k(300^\circ\,\mathrm{K}) = 2.1 \times 10^{-7}\,\mathrm{cm^3\,s^{-1}}\,;$$

$$NO^+ + e \rightarrow N + O\,, \qquad k(300^\circ\,\mathrm{K}) = 4.1 \times 10^{-7}\,\mathrm{cm^3\,s^{-1}}\,.$$

Atomic ion recombination is slow; e.g., the proton recombination rate is calculated to be $1.9 \times 10^{-10}T^{-0.7}$ cm^3 s^{-1} (Bates and Dalgarno 1962). The ions of interest in this study are predominantly polyatomic. Experimental data for polyatomic ion-electron reactions are sparse. Biondi *et al.* (1972) have measured several polyatomic ion recombination rate constants. Their values range from 10^{-6} to 10^{-7} cm^3 s^{-1} and have an inverse square-root dependence on temperature (Bardsley and Biondi 1970). We extrapolate their rates to $T \simeq 30^\circ$ K.

For most ions of interest it is necessary to estimate recombination rates. Since these rates appear to range over only one order of magnitude, there is probably no large error introduced by our crude methods. In analogy with the results of Biondi *et al.* (1972), we have assumed recombination rate constants of 6×10^{-7} cm^3 s^{-1} for all polyatomic ions except those consisting of a stable polyatomic molecule and a proton ($NH_4^+ = NH_3 + H^+$). These latter ions are assumed to recombine with a rate constant of 2×10^{-6} cm^3 s^{-1}. Table 6 lists all the recombination reactions used and their experimental or estimated rate constants.

The recombination reactions of polyatomic ions are certain to be dissociative in mechanism. The neutral product fragments of these reactions have never been experimentally determined. Theoretically, the problem involves detailed knowledge of repulsive potential curves of polyatomic species. For any particular reaction, there are several groups of products quite reasonable thermodynamically. In this treatment, we assume for simplicity that polyatomic ions containing a hydrogen atom can be thought

TABLE 6

ION-ELECTRON RECOMBINATION REACTIONS

	Reactants and Products	$k(10^{-7}$ cm^3 s$^{-1})$		Reference
66.	$H^+ + e \rightarrow H + h\nu$	$1.9 \times 10^{-3}T^{-0.7}$		Bates and Dalgarno 1962
67.	$O_2^+ + e \rightarrow O + O$	2.1		Mehr and Biondi 1969 ($T = 300^\circ$ K)
68.	$NO^+ + e \rightarrow N + O$	4.1		Weller and Biondi 1968 ($T = 300^\circ$ K)
69.	$H_3^+ + e \rightarrow H_2 + H$	1.5	3.0	Biondi *et al.* 1972 ($T = 200^\circ$ K)
70.	$H_3^+ + e \rightarrow 3H$	1.5		
71.	$HCO^+ + e \rightarrow CO + H$	3.0		Biondi *et al.* 1972 ($T = 200^\circ$ K)
72.	$HN_2^+ + e \rightarrow N_2 + H$	~6.0		
73.	$H_3O^+ + e \rightarrow H_2O + H$	6.5	13.0	Biondi *et al.* 1972 ($T = 300^\circ$ K)
74.	$H_3O^+ + e \rightarrow OH + H + H$	6.5		
75.	$NH_3^+ + e \rightarrow NH + H + H$	~6.0		
76.	$H_2CN^+ + e \rightarrow HCN + H$	~10.0	20.0	
77.	$H_2CN^+ + e \rightarrow CN + H + H$	~10.0		
78.	$NH_4^+ + e \rightarrow NH_3 + H$	18.0	20.0	
79.	$NH_4^+ + e \rightarrow NH_2 + H + H$	2.0		
80.	$CH_3^+ + e \rightarrow CH_2 + H$	~3.0	6.0	
81.	$CH_3^+ + e \rightarrow CH + H + H$	~3.0		
82.	$H_2CO^+ + e \rightarrow H + H + CO$	~6.0		
83.	$HCO_2^+ + e \rightarrow H + CO_2$	10.0	20.0	
84.	$HCO_2^+ + e \rightarrow H + O + CO$	10.0		
85.	$H_3CO^+ + e \rightarrow H_2CO + H$	10.0	20.0	
86.	$H_3CO^+ + e \rightarrow CO + 3H$	10.0		

of as pseudo-diatomic ions A—H^+. This is a reasonable assumption since the ions we deal with usually contain hydrogen–heavy-atom single bonds and much stronger heavy-atom–heavy-atom double and triple bonds. Upon recombination with electrons, the pseudo-diatomic ions dissociate:

$$AH^+ + e \rightarrow A^* + H\,. \tag{13}$$

Exothermicities are almost always insufficient to electronically excite atomic hydrogen. Therefore, the excess energy will be partitioned between translational energy of both products and internal energy of A*. If A* receives enough internal energy, it can dissociate into smaller fragments. Several of the recombination reactions listed in table 6 have exothermicities too small to further dissociate A*. These are:

$$HCO^+ + e \rightarrow CO + H\,, \qquad HN_2^+ + e \rightarrow N_2 + H\,.$$

No matter how large the exothermicities of recombination reactions, if most of the energy goes into translation, the A* fragments will not dissociate. We ignore this possibility which would have the effect of producing large polyatomic neutrals at a faster rate than our more conservative estimates. Below, we discuss individually important recombination reactions with exothermicities large enough to further dissociate A*. All spectroscopic information is taken from Herzberg (1966).

73. $H_3O^+ + e \rightarrow H_2O + H\,.$

The reaction exothermicity, $\sim 50{,}000\ cm^{-1}$, is sufficient to produce H_2O^* in the $\tilde{X}\,^1A_1$, $\tilde{a}\,^3B_1$, and $\tilde{A}\,^1B_1$ states. The $\tilde{A}\,^1B_1$ state is repulsive and presumably correlates with H and OH. Any H_2O^* formed in the ground $\tilde{X}\,^1A_1$ state may have enough energy to dissociate into H and OH since D(H—OH) = $41{,}300\ cm^{-1}$. Since H_2O $\tilde{a}\,^3B_1$ is presumably stable, this state will radiatively decay to stable vibrational levels of the ground state. We conclude that

$$H_2O^* \rightarrow H_2O \qquad \text{(branching ratio } \sim\tfrac{1}{2})\,;$$

$$H_2O^* \rightarrow H + OH \qquad \text{(branching ratio } \sim\tfrac{1}{2})\,;$$

78. $NH_4^+ + e \rightarrow NH_3^* + H\,.$

The estimated reaction exothermicity of $38{,}000\ cm^{-1}$ is slightly greater than the H—NH_2 bond dissociation energy of $36{,}000\ cm^{-1}$. Since some energy is partitioned into translation, we deem it unlikely that much NH_3^* will decompose:

$$NH_3^* \rightarrow NH_3 \qquad \text{(branching ratio } \sim 0.9)\,;$$

$$NH_3^* \rightarrow NH_2 + H \qquad \text{(branching ratio } \sim 0.1)\,;$$

85. $H_3CO^+ + e \rightarrow H_2CO^* + H\,.$

The reaction exothermicity of $51{,}000\ cm^{-1}$ is larger than the H—CHO bond dissociation energy of $29{,}000\ cm^{-1}$. H_2CO formed in its ground $\tilde{X}\,^1A_1$ state may dissociate. Other accessible discrete states of H_2CO are the $\tilde{a}\,^3A''$ and $A\,^1A''$ states. If formed in these states, H_2CO will probably relax to a stable vibrational level of the $\tilde{X}\,^1A_1$ state and survive. The dissociation

$$H_2CO^* \rightarrow HCO^* + H$$

leaves the HCO* radical with more than enough energy to dissociate to CO and H. Our conclusion is that

$$H_2CO^* \rightarrow H_2CO \qquad \text{(branching ratio } \sim\tfrac{1}{2})\,;$$

$$H_2CO^* \rightarrow CO + 2H \qquad \text{(branching ratio } \sim\tfrac{1}{2})\,.$$

The results of these and similar analyses are listed in table 6.

Polyatomic ion-electron recombination reactions are basic to our model. These reactions convert the rapidly synthesized polyatomic ions into neutral species.

v) *Neutral-Neutral Reactions*

These reactions are between atoms and free radicals; their major contribution to our model is in the destruction of radicals such as OH and CO and the formation of other diatomics such as O_2, N_2, CN, NO. The temperature dependence of neutral-neutral reactions without activation energy can be ignored ($k \propto T^{1/6}$). Consequently, we utilize rate constants determined at temperatures higher than those in interstellar clouds. Some examples are:

$$87.\quad N + OH \rightarrow NO + H \qquad (k = 7 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}})\,;$$

$$88.\quad O + OH \rightarrow O_2 + H \qquad (k = 5 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}})\,;$$

$$89.\quad N + NO \rightarrow N_2 + O \qquad (k = 2 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}})\,.$$

These reactions are listed in table 7. Reactions included in our analysis but not studied experimentally may possess activation energy. We adopt a rate constant of 4×10^{-11} $\mathrm{cm^3\ s^{-1}}$ for such systems; e.g.,

$$90.\quad O + NH \rightarrow NO + H\,,$$

$$93.\quad N + CH \rightarrow CN + H\,,$$

$$97.\quad C + OH \rightarrow CO + H\,, \qquad \text{etc.}$$

Two reactions deserve special attention. The first,

$$99.\quad CN + O \rightarrow CO + N\,,$$

has been studied in a complicated system at high temperature by Boden and Thrush (1968). Their rate constant is expressed by the relation $k \sim 10^{-10} \exp(-1200/T)$, but

TABLE 7

NEUTRAL-NEUTRAL REACTIONS

	Reaction	$k(10^{-11}\ \mathrm{cm^3\ s^{-1}})$	Reference
87.	$N + OH \rightarrow NO + H$	7.0	Campbell and Thrush 1968 ($T = 320°$ K)
88.	$O + OH \rightarrow O_2 + H$	5.0	Campbell and Thrush 1968 ($T = 300°$ K)
89.	$N + NO \rightarrow N_2 + O$	2.2	Phillips and Schiff 1962 ($T = 300°$ K)
90.	$O + NH \rightarrow NO + H$	~4.0	
91.	$O + CH \rightarrow CO + H$	~4.0	
92.	$C + NH \rightarrow CN + H$	~4.0	
93.	$N + CH \rightarrow CN + H$	~4.0	
94.	$N + NH \rightarrow N_2 + H$	~4.0	
95.	$O + CH_2 \rightarrow CH + OH$	~4.0	
96.	$O + NH_2 \rightarrow NH + OH$	~4.0	
97.	$C + OH \rightarrow CO + H$	~4.0	
98.	$C + NO \rightarrow CO + N$	~4.0	
99.	$O + CN \rightarrow CO + N$	$10 \exp(-1200/T)$	Boden and Thrush 1968
100.	$N + CN \rightarrow N_2 + C$	$\ll 10^{-2}$	Boden and Thrush 1968

this temperature coefficient may be inaccurate (Solomon and Klemperer 1972). Were the reaction rapid at low temperature, it would be the principal depletion mechanism for CN. However, we assume the above expression correct. The second reaction,

$$100. \quad CN + N \rightarrow C + N_2 ,$$

has also been studied by Boden and Thrush (1968) and its rate constant measured to be $\leq 10^{-13}$ cm^3 s^{-1}. We assume that this reaction possesses activation energy and is slow at low temperatures. Neither reaction is then important at temperatures below 100° K.

Since it is difficult to predict whether a given neutral-neutral reaction will possess activation energy, our estimates for the rate constants may be in error. The calculated abundance of CN in particular is subject to considerable uncertainty.

vi) *Condensation on Grains*

Assuming the customary grain parameters (Heiles 1971), we estimate that k, the frequency at which a gaseous species collides with dust grains, is

$$k \simeq \frac{1.53 \times 10^{-16}}{M^{1/2}} n_{H_2} \text{ s}^{-1}, \tag{14}$$

where M is the molecular weight in atomic mass units. Upon assumption of the maximum rate, namely, that polyatomic molecules condense upon every collision, the rate of condensation for several unreactive neutral species (H_2O, H_2CO, NH_3) becomes competitive with the rate of gas phase reactions. For $n_{H_2} = 10^4$ cm^{-3} and $M = 18$ amu, $k \sim 3.6 \times 10^{-13}$ s^{-1}. This rate is greater than the photodissociation rate for $A_v \geq 4$(mag) and a_λ(grain albedo) $\simeq 0.9$ (Herbst and Klemperer 1974). Condensation processes are included in the analysis to provide the framework for a more general theory of dust accretion and molecular development. In the present model, however, they rarely affect our calculated steady-state abundances to a significant extent.

d) Functions of Reactions

The chemistry of dense clouds is very complicated because of the coupling of many of the reactions utilized in the analysis. It is instructive, however, to roughly divide the reactions into several groups according to the functions they play in the model.

The formation of polyatomic molecules is driven by cosmic-ray–induced ionization processes. Although all neutral species experience ionizing bombardment, only the ionization of H_2 and He need be included (§ III*b*). The three "primal" ions H^+, H_3^+, He^+ can react rapidly with several of the more abundant neutral species (CO, O_2, N_2, O, N, etc.) to produce "secondary" ions such as C^+, O^+, N^+, HCO^+ (see reactions 18, 19, 20, 21, 22, 24, 26, 27, 29, 58). These ions are often precursors for larger ions. The major pathway for polyatomic ion buildup involves reactions of the type (§ II*c*)

$$A^+ + H_2 \rightarrow AH^+ + H ,$$

$$AH^+ + H_2 \rightarrow AH_2^+ + H , \qquad \text{etc.}$$

Ions synthesized in this manner include H_3O^+, NH_4^+, CH_3^+, and H_2CN^+. The ion H_3CO^+ is produced via the far less efficient mechanism of radiative association (§ II*c*).

Polyatomic neutrals are most often produced by the recombination of polyatomic ions and electrons. Electron abundances in our model are low enough that recombination reactions are orders of magnitude slower than ion-molecule reactions involving H_2 or CO. Thus, recombination reactions need be considered only for ions which react efficiently with neither H_2 nor CO; e.g., HCO^+, H_3O^+, NH_4^+, H_3CO^+. These

reactions are included in table 6 and lead to the production of H_2O, NH_3, H_2CO, CH, OH, NH_2, CH_2, etc. The more reactive neutral species formed can then react with atoms to produce a wider variety of neutral molecules (see reactions 87–100 in table 7).

Neutral species are depleted by gas phase reactions. They are also depleted by condensation on the dust grains if desorption processes are inefficient. At low temperatures, the more stable neutral species react rapidly with ions only, while the less stable species can in many instances react with neutral atoms as well. Radicals such as OH, NO, CH, CH_2 are destroyed primarily by reactions with abundant O and N atoms (§ III*c*). More stable neutrals are depleted by reactions with the abundant ions C^+, H^+, HCO^+, and H_3^+ (see especially reactions 30, 32, 36, 39, 40, 45, 48, 50, 51, 60, 61, 62). Ion abundances in the present model are low enough that ion-controlled depletion processes are usually slower than neutral atom-controlled processes (§ III*c*). This is one reason why our analysis predicts greater abundances for stable neutrals such as H_2O and NH_3, and lesser abundances for reactive radicals such as OH, NH, and CH. At its maximum possible rate, condensation on the grains is competitive with ion-controlled depletion processes (§ III*c*).

e) Solution to Equations

Kinetic equations for 31 species—C, H^+, He^+, C^+, OH, CH, NH, O_2, N_2, CN, NO, OH^+, O_2^+, NO^+, H_2O, NH_2, CH_2, HCN, CO_2, H_3^+, HCO^+, H_2O^+, HN_2^+, H_2CO, NH_3, H_3O^+, NH_3^+, H_2CN^+, HCO_2^+, NH_4^+, H_3CO^+—are written down utilizing the chemical reactions and rates presented in tables 3–7 and the condensation rates specified in equation (14). Of the six species for which kinetic equations are not set up, three (H_2, CO, He) are given by the H_2 density, two (O, N) are determined by conservation of elemental abundance, and one (the electron density) is determined by conservation of charge. The simultaneous coupled nonlinear equations are solved numerically by the method of iteration (Margenau and Murphy 1965) for several molecular-hydrogen concentrations from 10^4 cm^{-3} to 10^6 cm^{-3}. Only solutions with $\zeta_{H_2} = \zeta_{He} = 10^{-17}$ s^{-1} are presented, except for the highest H_2 density where an ionization rate of 10^{-18} s^{-1} is also utilized. The densities of the major neutral and ionic species are listed in tables 8 and 9.

TABLE 8

CALCULATED CONCENTRATIONS—MAJOR NEUTRALS (cm^{-3})

	ζ (s^{-1})					
SPECIES	10^{-17}	10^{-17}	10^{-17}	10^{-17}	10^{-17}	10^{-18}
H_2	1×10^4	3×10^4	1×10^5	3×10^5	1×10^6	1×10^6
CO	7.5	22.5	75	225	750	750
He	2.8×10^3	8.4×10^3	2.8×10^4	8.4×10^4	2.8×10^5	2.8×10^5
N	1	3	10	30	100	100
O	1	4	13	40	130	130
C	5×10^{-3}	0.01	0.02	0.02	0.09	0.08
OH	7×10^{-5}	7×10^{-5}	7×10^{-5}	7×10^{-5}	7×10^{-5}	7×10^{-6}
NH	3×10^{-6}	3×10^{-6}	2×10^{-6}	1×10^{-6}	1×10^{-6}	1×10^{-7}
CH	8×10^{-7}	6×10^{-7}	2×10^{-7}	1×10^{-7}	1×10^{-7}	1×10^{-8}
O_2	0.02	0.03	0.06	0.12	0.09	0.01
N_2	0.4	1.2	3.9	12.0	38	37
CN	5×10^{-4}	5×10^{-4}	4×10^{-4}	3×10^{-4}	4×10^{-4}	3×10^{-5}
NO	2×10^{-4}	2×10^{-4}	2×10^{-4}	2×10^{-4}	2×10^{-4}	2×10^{-5}
H_2O	4×10^{-3}	5×10^{-3}	8×10^{-3}	0.012	0.01	0.001
HCN	6×10^{-5}	7×10^{-5}	1×10^{-4}	1×10^{-4}	1×10^{-4}	1×10^{-5}
NH_3	1×10^{-4}	2×10^{-4}	3×10^{-4}	5×10^{-4}	4×10^{-4}	4×10^{-5}
H_2CO	1×10^{-5}	1×10^{-5}	5×10^{-5}	1×10^{-4}	1×10^{-4}	1×10^{-5}

TABLE 9

CALCULATED CONCENTRATIONS—MAJOR IONS (cm^{-3})

ION	ζ (s^{-1})					
	10^{-17}	10^{-17}	10^{-17}	10^{-17}	10^{-17}	10^{-18}
H_2	1×10^{4}	3×10^{4}	1×10^{5}	3×10^{5}	1×10^{6}	1×10^{6}
C^+	8×10^{-4}	2×10^{-3}	3×10^{-3}	5×10^{-3}	2×10^{-2}	2×10^{-2}
H^+	2×10^{-4}	5×10^{-4}	7×10^{-4}	1×10^{-3}	5×10^{-3}	4×10^{-3}
He^+	2×10^{-6}	2×10^{-6}	2×10^{-6}	2×10^{-6}	2×10^{-6}	2×10^{-7}
O_2^+	6×10^{-6}	7×10^{-6}	1×10^{-5}	2×10^{-5}	1×10^{-5}	1×10^{-6}
NO^+	1×10^{-6}	1×10^{-6}	5×10^{-6}	1×10^{-5}	9×10^{-6}	9×10^{-7}
H_3^+	7×10^{-6}	7×10^{-6}	7×10^{-6}	7×10^{-6}	7×10^{-6}	7×10^{-7}
HCO^+	1×10^{-4}	2×10^{-4}	4×10^{-4}	7×10^{-4}	6×10^{-4}	6×10^{-5}
HN_2^+	5×10^{-7}	5×10^{-7}	6×10^{-7}	6×10^{-7}	6×10^{-7}	5×10^{-8}
NH_3^+	3×10^{-7}	3×10^{-7}	4×10^{-7}	5×10^{-7}	4×10^{-7}	4×10^{-8}
H_3O^+	5×10^{-6}	6×10^{-6}	1×10^{-5}	3×10^{-5}	2×10^{-5}	2×10^{-6}
NH_4^+	1×10^{-7}	2×10^{-7}	5×10^{-7}	1×10^{-6}	8×10^{-7}	8×10^{-8}
H_3CO^+	1×10^{-8}	2×10^{-8}	9×10^{-8}	3×10^{-7}	2×10^{-7}	2×10^{-8}
e	0.001	0.003	0.004	0.007	0.03	0.03

III. DISCUSSION

a) Individual Species

i) C^+ *and* H^+

C^+ and H^+ do not react efficiently with H_2, CO, or electrons and are therefore the most abundant atomic ions in our model. C^+ is produced by the reaction of CO and He^+:

$$18.\quad CO + He^+ \rightarrow C^+ + O + He\,,$$

while H^+ is produced by direct cosmic-ray ionization of H_2. Both ions are destroyed principally by reaction with O_2. Their densities are predicted to be greater than 10^{-4} cm^{-3} under all conditions studied. Since these ions are so abundant, they are very important in depleting polyatomic neutrals such as H_2O, NH_3, and H_2CO.

ii) He^+

The helium ion is produced by direct cosmic-ray ionization and destroyed by reaction with CO. It is two to three orders of magnitude less abundant than C^+ and H^+ but plays a unique role in our analysis. He^+ is responsible for the production of C^+ (see above) and N^+:

$$19.\quad N_2 + He^+ \rightarrow N^+ + N + He\,.$$

N^+, rapidly depleted by reaction with H_2, is the precursor of ammonia. Since N_2 has a high ionization potential, neither H^+ nor C^+ can react with it.

iii) C, N, O

Our model predicts that only a small residual abundance (0.005–0.1 cm^{-3}) of atomic carbon is maintained. The initial assumption that "all" carbon is in the form of CO is therefore self-consistent. Almost all of the cosmic abundance of oxygen in excess of the CO abundance is predicted to remain in atomic form. Thus, reactions between O atoms and free radicals are expected to be of importance. About one-half of the cosmic abundance of nitrogen is predicted to remain in atomic form; the

remainder is primarily in the diatomic molecule. Reactions between N atoms and free radicals are just as important as the O analogs.

iv) OH, NH, CH

These free radicals are formed by dissociative recombination reactions:

$$73.\quad OH_3^+ + e \rightarrow OH + H + H\,,$$

$$75.\quad NH_3^+ + e \rightarrow NH + H + H\,,$$

$$80.\quad CH_3^+ + e \rightarrow CH + H + H\,.$$

They are destroyed by reaction with oxygen and nitrogen atoms:

$$87.\quad OH + N \rightarrow NO + H\,,$$

$$88.\quad OH + O \rightarrow O_2 + H\,,$$

$$89.\quad NH + O \rightarrow NO + H\,,$$

$$93.\quad CH + N \rightarrow CN + H\,, \qquad \text{etc.}$$

Of the three, we predict OH to be the most abundant, with a density of 7×10^{-5} cm^{-3} for all values of H_2 studied ($\zeta = 10^{-17}\ s^{-1}$).

v) NO, CN

These radicals are produced by reactions of atoms and other radicals (see above). NO is destroyed by reaction with abundant N atoms:

$$89.\quad N + NO \rightarrow N_2 + O\,.$$

For $\zeta = 10^{-17}\ s^{-1}$, we predict a constant NO density of 2×10^{-4} cm^{-3}. For a cloud of dimension 5×10^{18} cm, the predicted column density is 10^{15} cm^{-2}. NO has not been observed in the interstellar medium. Our prediction is below the upper limit obtained by Solomon (1973).

The cyano radical is produced by an additional important mechanism:

$$77.\quad H_2CN^+ + e \rightarrow CN + H + H\,.$$

CN does not react with atomic oxygen or nitrogen at low temperatures and is depleted much more slowly by reaction with ions:

$$23.\quad CN + He^+ \rightarrow C^+ + N + He\,,$$

$$29.\quad CN + H_3^+ \rightarrow HCN^+ + H_2\,,$$

and by condensation on the grains. CN is the only diatomic molecule for which this latter depletion mechanism is considered. Since it is a radical, it may well undergo chemisorption.

vi) N_2, O_2

These stable diatomic molecules are produced by atom-free radical reactions:

$$87.\quad NO + N \rightarrow N_2 + O\,,$$

$$88.\quad OH + O \rightarrow O_2 + H\,, \qquad \text{etc.}$$

Reactions of N_2 and O_2 with other neutral species possess considerable activation energy. Therefore, N_2 and O_2 are destroyed only by reaction with ions. O_2 has a low ionization potential and charge exchanges with protons:

$$58.\quad O_2 + H^+ \rightarrow O_2^+ + H\,,$$

as well as reacting with carbon ions:

$$41.\quad O_2 + C^+ \rightarrow CO^+ + O\,.$$

N_2 is less reactive and reacts only with the less abundant ions He^+ and H_3^+:

$$19.\quad N_2 + He^+ \rightarrow N^+ + N + He\,,$$

$$20.\quad \rightarrow N_2^+ + He\,,$$

$$27.\quad N_2 + H_3^+ \rightarrow HN_2^+ + H_2\,.$$

We predict that $[N_2] > [O_2]$ by at least one order of magnitude. N_2 represents a considerable fraction of the nitrogen abundance in our model.

vii) H_3^+

This ion is produced by the reactions

$$1.\quad H_2 + \text{cosmic-ray proton} \rightarrow H_2^+ + e + p\,,$$

$$4.\quad H_2^+ + H_2 \rightarrow H_3^+ + H\,,$$

and destroyed principally by reaction with CO:

$$26.\quad CO + H_3^+ \rightarrow HCO^+ + H_2\,.$$

We predict its concentration to be $\sim 10^{-5}$ cm^{-3} for $\zeta = 10^{-17}$ s^{-1} and $10^4 \leq n_{H_2} \leq 10^6$ cm^{-3}. Predicted column densities for H_3^+ would then be $\lesssim 10^{14}$ cm^{-2}. This ion possesses no microwave spectrum since it lacks a dipole moment or suitable hyperfine transition. However, H_2D^+ does possess a dipole moment. If the D/H ratio is 10^{-3}, we would predict column densities for DH_2^+ of $\lesssim 3 \times 10^{11}$ cm^{-2}. Predicted microwave transitions for this ion are given by Dalgarno *et al.* (1973).

viii) HCO^+

Our model predicts that HCO^+ is the most abundant polyatomic ion in the gas. It is produced by the reaction of CO and H_3^+ (see above) as well as by secondary mechanisms such as

$$45.\quad C^+ + H_2O \rightarrow HCO^+ + H\,,$$

$$52.\quad H^+ + CO_2 \rightarrow HCO^+ + O\,,\qquad \text{etc.}$$

HCO^+ is an exceedingly stable ion. Its major destruction pathway is dissociative recombination with electrons:

$$71.\quad HCO^+ + e \rightarrow CO + H\,.$$

Predicted densities lie in the range 10^{-3}–10^{-4} cm^{-3}. For clouds of dimension 1–2 pc, we would expect column densities of at least 10^{15} cm^{-2}. Klemperer (1970) has suggested that the X-ogen interstellar emission line at 89.190 GHz is the $J = 1 \rightarrow 0$

rotational transition of $H^{12}CO^+$. Confirmation of this speculation would be obtained by observation of the $J = 1 \rightarrow 0$ transition in $H^{13}CO^+$.

ix) H_2O, NH_3

Water and ammonia are predicted by our model to be very abundant. They are produced by dissociative recombination of the ions H_3O^+ and NH_4^+, respectively:

$$73.\quad OH_3^+ + e \rightarrow H_2O + H\,,$$

$$78.\quad NH_4^+ + e \rightarrow NH_3 + H\,.$$

Water is expected to be the more abundant of the two, with a concentration of approximately 10^{-2} cm^{-3}. H_2O and NH_3 are depleted by reaction with ions such as H^+, C^+, HCO^+ and to a lesser extent by condensation on the grains (§ III*c*).

x) HCN

Hydrogen cyanide is primarily produced as follows:

$$50.\quad C^+ + NH_3 \rightarrow H_2CN^+ + H\,,$$

$$76.\quad H_2CN^+ + e \rightarrow HCN + H\,.$$

It is destroyed by the reactions:

$$48.\quad C^+ + HCN \rightarrow CCN^+ + H\,,$$

$$33.\quad H_3^+ + HCN \rightarrow H_2CN^+ + H_2\,,$$

and by condensation on the grain. None of the above rate constants has been measured. We have assumed that reaction 76 yields HCN only. The interesting possibility that HNC could also be formed in this reaction is not considered.

Our calculated HCN densities are $\sim 10^{-4}$ cm^{-3}. These results are in good agreement with observational values.

xi) H_2CO

Formaldehyde is unique because of the fact that the reaction

$$H_2 + CO \rightarrow H_2CO$$

is endothermic at low temperatures. Thus it cannot be produced by a scheme, no matter how complex, whose net overall reaction is $H_2 + CO = H_2CO$. In our analysis, its production is possible only if we include a slow radiative association step:

$$65.\quad HCO^+ + H_2 \rightarrow H_3CO^+ + h\nu\,,$$

$$85.\quad (H_3CO^+ + e \rightarrow H_2CO + H)\,.$$

Formaldehyde is depleted by reaction with ions and condensation on the grain. Since H_2 is so abundant and HCO^+ moderately abundant, the production of H_2CO is relatively efficient even though it involves such a slow reaction. Our model predicts formaldehyde densities in the range 10^{-4}–10^{-5} cm^{-3}, and accounts quite well for observational results on dense clouds (§ IV).

xii) H_3O^+

This ion is predicted to be moderately abundant ($\sim 10^{-5}$ cm^{-3}) since its high stability allows depletion by electrons only:

$$73.\quad H_3O^+ + e \rightarrow H_2O + H\,,$$

$$74.\quad \rightarrow OH + H + H\,.$$

Calculations by Novick, Klemperer, and Stevens (1973) report an inversion frequency of 84 cm^{-1} for H_3O^+.

xiii) *Residual Atomic Hydrogen*

Atomic hydrogen is not included in our detailed numerical results. However, it is not difficult to estimate the residual H abundance predicted by our model. The formation of H is governed by a large number of processes with overall rate determined by the cosmic-ray–induced ionization of H_2. The depletion of H is caused by grain catalyzed surface recombination (Hollenbach *et al.* 1971). A steady-state treatment indicates that $n_H \sim 1$ cm^{-3} for $\zeta_{H_2} = 10^{-17}$ s^{-1} and $10^4 \leq n_{H_2} \leq 10^6$ cm^{-3}.

b) *Heavy-Element Ionization*

In this section, we demonstrate that the cosmic-ray–induced ionization of all species other than H_2 and He can be neglected. This is most readily seen by examples. Consider first the ionization of carbon monoxide. In our model, CO is ionized by reaction with helium ions:

$$CO + He^+ \rightarrow C^+ + O + He\,, \qquad k_{18} = 2.0 \times 10^{-9}\ \text{cm}^3\ \text{s}^{-1}\,,$$

$$C^+ + O_2 \rightarrow CO^+ + O\,, \qquad k_{41} = 1.1 \times 10^{-9}\ \text{cm}^3\ \text{s}^{-1}\,.$$

Assuming the C^+ concentration to be at steady-state, the formation rate of CO^+ is

$$\frac{dn_{CO^+}}{dt} = k_{18} n_{He^+} n_{CO} = 4 \times 10^{-15} n_{CO}\ \text{cm}^{-3}\ \text{s}^{-1} \tag{15}$$

for $\zeta_{H_2} = 10^{-17}$ s^{-1} (see table 9). If the cosmic-ray–induced ionization rate constant of CO is assumed to be $\sim 10^{-17}$ s^{-1} in analogy with ζ_{H_2}, then ionization by He^+ is more than *two* orders of magnitude more efficient.

Let us consider another example. O_2 is ionized by reaction with protons:

$$O_2 + H^+ \rightarrow O_2^+ + H\,, \qquad k_{58} \sim 10^{-9}\ \text{cm}^3\ \text{s}^{-1}\,.$$

Our calculations predict that with $\zeta_{H_2} = 10^{-17}$ s^{-1}, the H^+ abundance is $\geq 10^{-4}$ cm^{-3}. Consequently,

$$\frac{dn_{O_2^+}}{dt} \geq 10^{-13} n_{O_2}\ \text{cm}^{-3}\ \text{s}^{-1}\,. \tag{16}$$

This is over four orders of magnitude greater than the cosmic-ray–induced ionization rate if $\zeta_{O_2} \sim \zeta_{H_2}$.

Even if cosmic rays are somewhat more efficient in ionizing CO and O_2 than H_2, it is still clear that they do not provide the dominant ionization mechanism for these species in our model. A similar analysis can be performed for all other neutrals.

c) *Rates of Depletion*

This section presents a comparison of the rates of three depletion mechanisms—reaction with atoms, reaction with ions, and condensation on the dust grains. This analysis is necessary for neutral species only; ions are usually depleted by reaction with H_2, CO, or electrons.

Consider a hypothetical free radical such as OH that is able to react with atoms at low temperatures. OH is then depleted by three pathways:

$$\mathrm{OH} + \{\mathrm{O}, \mathrm{N}\} \rightarrow \text{products} \qquad (k \simeq 4 \times 10^{-11}\ \mathrm{cm^3\ s^{-1}}),$$

$$\mathrm{OH} + (\mathrm{C^+}, \mathrm{H^+}, \mathrm{HCO^+}, \mathrm{H_3^+}) \rightarrow \text{products} \qquad (k \simeq 2 \times 10^{-9}\ \mathrm{cm^3\ s^{-1}}),$$

$$\mathrm{OH} + \text{dust} \rightarrow \text{condensation} \qquad (k \simeq 1.53 \times 10^{-16} M^{-1/2} n_{\mathrm{H_2}}\ \mathrm{s^{-1}}).$$

The condensation rate constant is taken from equation (14). Consider $n_{\mathrm{H_2}} \sim 10^5$ $\mathrm{cm^{-3}}$. From table 8, $n_{\mathrm{O}} + n_{\mathrm{N}} \sim 25\ \mathrm{cm^{-3}}$. The effective first-order rate constant for depletion by reaction with atoms is then $25 \times [4 \times 10^{-11}] \sim 10^{-9}\ \mathrm{s^{-1}}$. The ion concentration is $\sim 4 \times 10^{-3}\ \mathrm{cm^{-3}}$ (table 9) so that the analogous rate constant for depletion by reaction with ions is $\sim (2 \times 10^{-9}) \times (4 \times 10^{-3}) = 8 \times 10^{-12}\ \mathrm{s^{-1}}$. The maximum condensation rate constant for a species with $M \sim 17$ is $\sim 4 \times 10^{-12}\ \mathrm{s^{-1}}$.

Reactive neutral species such as OH, CH_2, etc., are able to react rapidly with atoms at low temperatures. These species are then generally predicted to be less abundant than less reactive neutrals such as H_2O.

More stable neutrals are depleted by reaction with ions and by condensation. If we assume a 100 percent sticking probability, the condensation rate does become a competitive process. However, nonthermal mechanisms may remove adsorbed stable molecules from the grains (Greenberg 1972).

d) *Stability of Solutions*

In this section, we discuss the stability of our calculated results with respect to changes in several of the model parameters. Tables 8 and 9 show that the abundances of molecular species vary much more slowly than does the H_2 density. The general reason for this behavior is that species are both created and destroyed by gas phase reactions. A change in the H_2 density induces canceling changes in the rates of formation and depletion. Our model then predicts that given a constant rate of cosmic-ray–induced ionization, molecular abundances are relatively stable over several decades of H_2 density.

The dependence of our solutions on ζ is more complex. A slower rate of ionization results in calculated abundances that are sometimes decreased by somewhat smaller amounts than the change in ζ. This effect is shown in tables 8 and 9 for $n_{\mathrm{H_2}} = 10^6$ $\mathrm{cm^{-3}}$ and $\zeta = 10^{-17}$ and $10^{-18}\ \mathrm{s^{-1}}$. Ionization rates less than $10^{-17}\ \mathrm{s^{-1}}$ apply only to the interiors of clouds with H_2 column density much greater than $10^{24}\ \mathrm{cm^{-2}}$. On the other hand, higher ionization rates probably apply to the fringe regions of all dense clouds. For these regions, processes such as photodissociation cannot be neglected. In addition, as ions become more abundant, many additional ion-molecule reactions must be included. For smooth extrapolation to regions with $\zeta \sim 10^{-15}\ \mathrm{s^{-1}}$, a much more complex and general model is required, probably including atomic reactions (Solomon and Klemperer 1972) and detailed $2\mathrm{H} = \mathrm{H_2}$ equilibria (Solomon and Werner 1971; Hollenbach *et al.* 1971).

i) *Oxygen Abundance*

The cosmic abundance of oxygen is poorly known to within a factor of 2. The value used in this analysis, $\mathrm{O/H} \simeq 4.4 \times 10^{-4}$, is taken from Dalgarno and McCray (1972).

Allen (1964) lists a higher value, O/H $\sim 6.8 \times 10^{-4}$. If the higher oxygen abundance is used in our model, significant changes result. These changes are discussed in the Appendix.

e) Time Taken to Reach Steady State

The present model estimates all abundances as stationary in time. This assumption makes physical sense only if the chemical steady-state time constants are shorter than the cloud lifetimes. Free-fall gravitational collapse times for clouds of gas density 10^4–10^6 cm^{-3} range from $\sim 3 \times 10^5$ to 3×10^4 years (Rank *et al.* 1971). Cloud lifetimes may be considerably longer. In any case, we show that our model reaches steady-state within the free-fall collapse time.

Different species reach their steady-state concentrations at different times. The time dependence of the concentration of any species is given by a first-order differential equation. If we retain only the most important terms in these equations, it is possible to integrate them subject to one additional assumption. We assume that species that have already reached their steady-state values can be treated as constants in the differential equations of species that approach steady-state more slowly. When our model is "turned on," H_2 and CO have already reached their steady-state concentrations. The differential equation governing the $n_{H_2^+}$ dependence as a function of time,

$$\frac{dn_{H_2^+}}{dt} = k_1 n_{H_2} - k_4 n_{H_2} n_{H_2^+} \tag{18}$$

(table 3), is then easily integrated to yield

$$n_{H_2^+} = \frac{k_1}{k_4} [1 - \exp(-k_4 n_{H_2} t)] . \tag{19}$$

When a time $\tau_{H_2^+} = (k_4 n_{H_2})^{-1}$ elapses, $n_{H_2^+}$ reaches $1 - e^{-1} = 0.63$ of its steady-state value. For $n_{H_2} = 10^5$ cm^{-3}, $\tau_{H_2^+} \sim 4.8 \times 10^3$ s $= 0.05$ days. (The following calculations are all performed at this same value of n_{H_2}.) We are now able to compute the analogous quantity $\tau_{H_3^+}$ ($\tau_{H_3^+} \gg \tau_{H_2^+}$) assuming a steady-state value for the H_2^+ concentration. Integration of an approximate differential equation yields (table 3)

$$n_{H_3^+} \sim \frac{k_1 n_{H_2}}{k_{26} n_{CO}} [1 - \exp(-k_{26} n_{CO} t)] . \tag{20}$$

Then, $\tau_{H_3^+} = (k_{26} n_{CO})^{-1} = 9.5 \times 10^6$ s ~ 0.3 years. By similar considerations, we obtain $\tau_{He^+} \sim 0.2$ year, $\tau_{H^+} \sim 30$ years, and $\tau_{HCO^+} \sim 10^3$ years.

For a neutral molecule, the time constant for reaching steady-state is determined by its *depletion* rate. For an unreactive polyatomic neutral such as H_2O which is depleted by reaction with ions and condensation on the grains,

$$\tau_{H_2O} \sim \left(\sum_i k_i n_{M_i^+} + k_{cond} \right)^{-1} . \tag{21}$$

The $n_{M_i^+}$ are densities of the various ions that react with H_2O at rate constants k_i; k_{cond} is given in equation (14). Assuming $k_i \sim 2 \times 10^{-9}$ cm^3 s^{-1} and using the total ion abundance for $\sum_i n_{M_i^+}$, we obtain

$$\tau_{H_2O} \sim [(2 \times 10^{-9})(4 \times 10^{-3}) + 3.6 \times 10^{-12}]^{-1}$$
$$\sim 9 \times 10^{10} \text{ s} \sim 3 \times 10^3 \text{ years} . \tag{22}$$

Time constants for the other stable polyatomics are comparable; those for reactive species are shorter. These calculations have been performed on a cloud of $n_{H_2} \sim 10^5$ cm^{-3} whose free-fall collapse time is $\sim 10^5$ years (Rank *et al.* 1971). Thus, our model reaches steady-state well within the minimal lifetime of the cloud. This conclusion applies to clouds of lower and higher gas density as well.

IV. COMPARISON WITH OBSERVATION

At present, we are able to compare only a small percentage of our calculated results with observation. Polyatomic molecules have been observed in two types of regions—the dark clouds (Heiles 1971) and the molecular clouds near H II regions. We first consider the dark clouds. The physical conditions have been reviewed recently by Heiles and Gordon (1972). Molecular-hydrogen densities are thought to be $\sim 10^4$ cm^{-3} and cloud dimensions $\sim 5 \times 10^{18}$ cm, The clouds are believed to be relatively homogeneous. The expected H_2 column densities of $\sim 5 \times 10^{22}$ cm^{-2} are easily penetrated by 100-MeV cosmic rays. Table 10 compares observed and calculated column densities for CO, OH, NO, and H_2CO. Ammonia has also been observed but no column density reported (Zuckerman *et al.* 1971). Solomon (1973) has searched in vain for NO and reported an upper limit of

$$N_{NO} \leq 3 \times 10^{-3} N_{CO} .$$

This limit is assumed to apply to all regions considered in this section. Agreement between theory and observation is reasonable for NO and especially good for H_2CO. The OH abundance is underestimated by one order of magnitude.

Dense clouds near H II regions appear to be much richer in molecular species than dark clouds. Rank *et al.* (1971) have collated observational information for the clouds Orion A and Sgr B_2. These regions are quite inhomogeneous. Detailed structural information about the sizes and densities of the various molecular clouds in Orion A have been reported (Buhl and Snyder 1973). Orion A appears to possess a very dense central core with $n_{H_2} > 10^7$ cm^{-3}, but most molecular clouds extend over a much wider region. Table 11 presents observed and calculated column densities for CO, OH, CN, NO, HCN, HCO^+, and H_2CO in Orion A. For each molecule, the cloud size and approximate H_2 density are taken from Buhl and Snyder (1973). Agreement is well within one order of magnitude for all species considered if X-ogen is assumed to be HCO^+. Thus, a model that considers only gas phase reactions is able to account for much of the observational results in Orion A.

TABLE 10

COLUMN DENSITIES—DARK CLOUDS (cm^{-2})

Species	Observed*	Theoretical
H_2.....	5×10^{22}	5×10^{22}
[$[H_2] = 10^4$ cm^{-3}, dimension $\sim 5 \times 10^{18}$ cm]		
CO.....	$>10^{18}$†	4×10^{19}
OH.....	5×10^{15}	4×10^{14}
NO.....	$<3 \times 10^{15}$‡	10^{15}
NH_3.....	?§	5×10^{14}
H_2CO.....	1.5×10^{13}	5×10^{13}

* Heiles and Gordon 1972.
† Penzias *et al.* 1972.
§ Zuckerman *et al.* 1971.
‡ Solomon 1973.

TABLE 11

COLUMN DENSITIES—ORION A (cm^{-2})

Species	Cloud Size* (cm)	n_{H_2} (cm^{-3})*	Observed†	Theoretical
CO	$\sim 10^{19}$	10^4	$\geq 10^{18}$	8×10^{19}
OH	$\sim 5 \times 10^{17}$	$> 10^6$	3×10^{13}‡	4×10^{13}
NO	10^{18}(?)	10^5(?)	$< 3 \times 10^{15}$§	2×10^{14}
CN	3×10^{18}(?)	10^6(?)	10^{15}	1×10^{15}
HCN	3×10^{18}	10^6	10^{15}	3×10^{14}
HCO^+	3×10^{18}	10^6	$\sim 10^{15}$	2×10^{15}
H_2CO	10^{19}	10^4	$\sim 3 \times 10^{14}$	1×10^{14}

* Buhl and Snyder 1973. † Rank *et al.* 1971 unless otherwise indicated.
‡ Goss 1968. § Solomon 1973.

The last region considered is Sgr B_2. Hydrogen densities are not known very accurately, $n_{H_2} \gg 10^3$ cm^{-3} (Rank *et al.* 1971). If an average density $n_{H_2} \sim 10^6$ cm^{-3} and cloud size $\sim 5 \times 10^{18}$ are assumed, $N_{H_2} \sim 5 \times 10^{24}$ cm^{-2} and 100-MeV cosmic rays may experience some difficulty in penetrating the cloud interior if the region is spherically symmetric. Table 12 compares the observed column densities of OH, NH_3, and H_2CO with calculated values for $\zeta = 10^{-17}$ and 10^{-18} s^{-1}. Agreement is superior when the higher ionization rate is utilized.

In summation, our model provides quantitative results which are in reasonable agreement with observation.

V. CONCLUSIONS

We have considered a model for the formation and destruction of polyatomic species in dense clouds. Starting with significant abundances of H_2, He, and CO, we have demonstrated how cosmic-ray–induced ionization processes can initiate a series of gas phase chemical reactions that produces a wide variety of molecular species, both neutral and ionic. Sizable abundances of polyatomic species are achieved well within the minimal cloud lifetimes. Our quantitative results are in reasonable agreement with existing observational data. In addition, the model is capable of direct observational verification at several points as seen from the molecular abundances listed in tables 8 and 9. Since the present reactions are rapid compared with syntheses invoking grain-catalyzed reactions, it is necessary to include them in any general theory of molecular development in dense clouds.

It is important to note that the present paper is directed to regions where molecules (H_2, CO) dominate. The chemistry of these high-density regions is quite different from

TABLE 12

COLUMN DENSITIES—SAGITTARIUS B2 (cm^{-2})

Species	Observed*	Theoretical	
		$\zeta = 10^{-17}$ s^{-1}	$\zeta = 10^{-18}$ s^{-1}
H_2	$> 10^{22}$	5×10^{24}	5×10^{24}
	(dimension $\sim 5 \times 10^{18}$ cm)	($[H_2] \sim 10^6$ cm^{-3})	
CO	$\geq 10^{19}$	4×10^{21}	4×10^{21}
OH	10^{16}	4×10^{14}	4×10^{13}
NO	$< 3 \times 10^{16}$†	1×10^{15}	1×10^{14}
NH_3	10^{16}‡	2×10^{15}	2×10^{14}
H_2CO	2×10^{15}	5×10^{14}	5×10^{13}

* Rank *et al.* 1971. † Solomon 1973. ‡ Snyder 1972.

low-density regions where atoms dominate and photodissociation is important (Solomon and Klemperer 1972).

Superficially it might appear that the dust grains play no role in this model. This is quite incorrect. The conversion of atomic hydrogen to molecular hydrogen almost certainly occurs on grains (Hollenbach *et al.* 1971). The chemistry of the H_2 produced in this manner dominates our model. Second, the dust provides the shielding from the interstellar optical radiation field. Thus, the present model has a fundamental dependence upon the interstellar dust.

A more general model which includes both low-energy cosmic radiation and the interstellar optical radiation appears possible. This model would be quite elaborate in view of the large number of gas phase reactions. In addition, it would be necessary to specifically include $2H = H_2$ equilibria. It also appears possible to extend the general scheme of this paper to include formation and destruction of larger polyatomic species, especially molecules with several carbon atoms.

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APPENDIX

In this Appendix, the dependence of our calculated results on the cosmic abundance value of oxygen is discussed. Specifically, the kinetic equations are solved for $O/H \sim 6.8 \times 10^{-4}$ (Allen 1964) rather than $O/H \sim 4.4 \times 10^{-4}$ (table 1). Results for the two cases are significantly different.

Our model assumes that carbon is present as carbon monoxide. The excess oxygen is calculated to be primarily O and O_2. In table 1, the excess oxygen is 0.65×10^{-4} of the hydrogen density. With the higher O cosmic abundance, the excess oxygen becomes 3×10^{-4} of the hydrogen abundance, a significant change.

TABLE 13

CONCENTRATIONS OF MAJOR SPECIES USING HIGH O VALUE (cm^{-3})

ζ (s^{-1})	10^{-17}	10^{-17}	10^{-17}	10^{-17}	10^{-17}
H_2	1×10^4	3×10^4	1×10^5	3×10^5	1×10^6
O	1	5	20	50	180
N	1	2	8	20	80
O_2	2	7	20	60	200
N_2	0.5	1	5	10	50
OH	1×10^{-4}	1×10^{-4}	1×10^{-4}	9×10^{-5}	9×10^{-5}
NO	4×10^{-4}	4×10^{-4}	4×10^{-4}	3×10^{-4}	3×10^{-4}
CN	4×10^{-5}	1×10^{-5}	4×10^{-6}	1×10^{-6}	4×10^{-7}
H_2O	0.02	0.03	0.03	0.03	0.03
HCN	2×10^{-5}	8×10^{-6}	3×10^{-6}	1×10^{-6}	4×10^{-7}
NH_3	8×10^{-4}	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}
H_2CO	7×10^{-5}	2×10^{-4}	3×10^{-4}	7×10^{-4}	1×10^{-3}
H^+	2×10^{-6}	2×10^{-6}	2×10^{-6}	2×10^{-6}	2×10^{-6}
C^+	9×10^{-6}	9×10^{-6}	1×10^{-5}	1×10^{-5}	1×10^{-5}
He^+	2×10^{-6}	2×10^{-6}	2×10^{-6}	2×10^{-6}	2×10^{-6}
O_2^+	2×10^{-5}	3×10^{-5}	3×10^{-5}	3×10^{-5}	4×10^{-5}
NO^+	6×10^{-6}	1×10^{-5}	3×10^{-5}	6×10^{-5}	1×10^{-4}
H_3^+	7×10^{-6}	7×10^{-6}	7×10^{-6}	7×10^{-6}	7×10^{-6}
HCO^+	4×10^{-4}	6×10^{-4}	1×10^{-3}	2×10^{-3}	4×10^{-3}
H_3O^+	2×10^{-5}	4×10^{-5}	6×10^{-5}	1×10^{-4}	2×10^{-4}
e	4×10^{-4}	7×10^{-4}	1×10^{-3}	2×10^{-3}	4×10^{-3}

TABLE 14

COLUMN DENSITIES IN ORION A (cm^{-2})

Species	Observed*	Theoretical (High O Value Used)
CO	$\geq 10^{18}$	8×10^{19}
OH	3×10^{13}	5×10^{13}
NO	$< 3 \times 10^{15}$	3×10^{14}
CN	10^{15}	1×10^{12}
HCN	10^{15}	3×10^{12}
HCO^+	10^{15}	6×10^{15}
H_2CO	3×10^{14}	7×10^{14}

* See table 11 for observational references and physical information.

Calculations indicate that the additional oxygen results in O_2 densities that are greater than the previously calculated values by one or more orders of magnitude. This increase has important consequences for H^+ and C^+ since these ions are destroyed primarily by reaction with O_2:

$$41. \quad C^+ + O_2 \rightarrow CO^+ + O,$$

$$5. \quad CO^+ + H_2 \rightarrow HCO^+ + H,$$

$$58. \quad H^+ + O_2 \rightarrow O_2^+ + H,$$

$$67. \quad O_2^+ + e \rightarrow O + O.$$

The net result is a drastic decrease in the abundances of C^+ and H^+ and an increase in the HCO^+ abundance. The total ion densities are decreased by a factor of ~ 3. A consequence of the decrease in ion densities is that condensation on the grains becomes a slightly more rapid depletion mechanism than reaction with ions for certain polyatomic neutrals. If these polyatomic species—H_2O, NH_3, etc.—do not stick to the grains on every collision or if nonthermal grain desorption mechanisms exist, then the calculated polyatomic abundances are too low. Table 13 presents calculated densities for the major species using the high value for the oxygen cosmic abundance. In table 14, a comparison of calculated and observational results for species in Orion A is presented. It is found that theory and observation are once more in reasonable agreement, with the exception of CN and HCN for which the calculated densities are too low by more than two orders of magnitude. Abundances of these two species may be very sensitive to the oxygen abundance in the cloud.

The consequences of utilizing the higher value for the cosmic abundance of oxygen can be summarized. Ions such as H^+ and C^+ are reduced in abundance significantly whereas O_2 densities are greatly increased. The densities of polyatomic ions such as HCO^+ and H_3O^+ are increased somewhat, as are the abundances of the major polyatomic neutrals with the exception of HCN.

The apparent sensitivity of our calculated results with respect to changes in the oxygen abundance may be an artifact of our analysis. Alternatively, it may account at least partially for the differences in chemical composition observed among the various dense clouds.

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