

Three-phase chemical models of dense interstellar clouds: gas, dust particle mantles and dust particle surfaces

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ABSTRACT

Gas–grain models of the chemistry of dense interstellar clouds are presented in which two grain phases surrounding refractory cores are included. In addition to the actual grain surfaces, on which chemistry occurs, grain mantles, which are formed as adsorbed material trapped below new layers of such material, are considered. Material in grain mantles is assumed to be chemically inert, and therefore protected against destruction. The dust grain and gas temperatures are fixed at 10 K and the gas density $n = n(\text{H}) + 2n(\text{H}_2)$ remains at approximately $2 \times 10^4 \text{ cm}^{-3}$ in these models. Differences between the current three-phase (gas–mantle–surface) model results and those of previous two-phase (gas–surface) models for the overall grain abundances of individual species are small for inert species, but can be substantial for chemically reactive species, especially at late times ($\geq 10^6 \text{ yr}$) after non-reactive, protected mantles have been built up. It is possible to obtain molecular abundances for different mantle layers deposited at different times; we find that all layers are dominated by water ice. The calculated condensed phase abundance of CO depends strongly on the surface abundance of atomic hydrogen.

Key words: molecular processes – ISM: abundances – ISM: clouds – dust, extinction – ISM: molecules.

1 INTRODUCTION

There is ample evidence that both gas-phase and surface chemistries occur in dense interstellar clouds (Williams & Millar 1993). Although until recently most detailed models of cool interstellar regions emphasized gas-phase chemistry, models of surface chemistry have been formulated by Pickles & Williams (1977a,b), Allen & Robinson (1977), Tielens & Hagen (1982), d'Hendecourt, Allamandola & Greenberg (1985), Brown & Charnley (1990) and Willacy & Williams (1993), among others. In addition, the role of dust surface chemistry in star formation regions has been investigated by Brown, Charnley & Millar (1988), Brown & Millar (1989a,b), Millar, Herbst & Charnley (1991) and Charnley, Tielens & Millar (1992), who studied high-mass star formation regions in Orion; by Nejad, Williams & Charnley (1990) and Williams & Hartquist (1991), who studied cyclical models; and by Rawlings et al. (1992), who studied low-mass star formation regions.

Recently, we have formulated a series of gas–grain chemical models of dense interstellar clouds that have incorporated our previous large gas-phase network (Herbst & Leung 1989, 1990), which involves molecules up to more than 10 atoms in size. In our first paper (Hasegawa, Herbst & Leung 1992; hereinafter HHL), we investigated the combined gas and surface chemistry of cool clouds with density $n = n(\text{H}) + 2n(\text{H}_2) = 2 \times 10^4 \text{ cm}^{-3}$ and temperature 10 K, without consideration of non-thermal desorption processes. At so-called early times (10^5 – 10^6 yr), reasonable agreement with both gas-phase observations and surface observations of CO, H_2O and possibly CH_4 was found for models in which the initial form of hydrogen is molecular. Models with this initial condition show the synthesis of complex molecules to occur on grain surfaces as well as in the gas. At times later than 10^6 yr , the gas phase was found to be significantly depleted of all species heavier than He. In a second paper (Hasegawa & Herbst 1993; hereinafter HH), we developed a simple approach to the computation of rate coefficients for the cosmic ray induced non-thermal desorption of different surface molecules, and incorporated the rates into our previous model. With the inclusion of this process, we found that

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significant abundances of a few of the lighter molecules heavier than He (e.g. NH_3) can be maintained in the gas phase at times as late as 10^8 yr, although a true steady state is never achieved. The best agreement with observations was still obtained at early times. In the second paper, we also included a variety of tunnelling reactions on grain surfaces involving radicals and H_2 . Although not studied in the laboratory, the activation energies of these reactions can be reasonably estimated. Radical- H_2 reactions (considered for the first time in HH) render the production of large molecules on grain surfaces impossible, even under H_2 -rich conditions. In a third paper (Caselli, Hasegawa & Herbst 1993), we used our large gas-grain chemical model at temperatures up to 40 K to study the chemistry of high-mass star-forming regions, such as the Orion Hot Core and Compact Ridge. It was found that differences in temperature between these two sources during a previous cooler era could account for much of their current chemical differences because of the sensitivity of surface chemistry to temperature.

In our previous work, we considered grains to be composed of surfaces and refractory cores. Here we refer to these models as two-phase models: the two phases can either be regarded as the cores and surfaces of grains, or as the two reactive phases included – the gas and grain surfaces. The two-phase approach is not very physical because large numbers (≈ 100) of monolayers are built up during the evolution of grains, suggesting that the grains really consist of cores, mantles and surfaces, with the term ‘mantle’ referring to adsorbed material which lies beneath the current surface and which is presumably more inert to chemical reaction. It is more reasonable to consider three-phase models, in which a chemical distinction is made between mantle and surface. Even three-phase models represent a simplification, because the different layers of the mantle can be quite different chemically. Observations of condensed-phase CO (Whittet & Walker 1991; Tielens et al. 1991) show two distinct environments; one interpretation of these results is that these distinct environments have their origins in different layers in individual grain mantles.

In this paper, we present our first results with a new three-phase model in which the chemistries of grain mantles and surfaces are distinct. Cool quiescent sources are studied, and our results are compared with previous two-phase models of such regions. Although our model was not designed to monitor the chemical environment of individual layers in mantles, we find that we can obtain such information from our results during periods when net deposition from the gas is occurring. A comparison with the condensed-phase CO results that show two distinct environments can then be made.

2 MODEL

In the three-phase model, we make a distinction between mantle and surface abundances. The distinction is shown in Fig. 1, from which it can be seen that the surface now represents only the outermost monolayer of adsorbed material. All layers of adsorbed material inside the outermost layer are considered to be the mantle. In previous models, all layers of adsorbed material were dubbed the surface and assumed to be indistinguishable regarding reactivity. In the current model, the mantle species are completely unreactive; i.e. it is assumed that once species are covered by an outer mono-

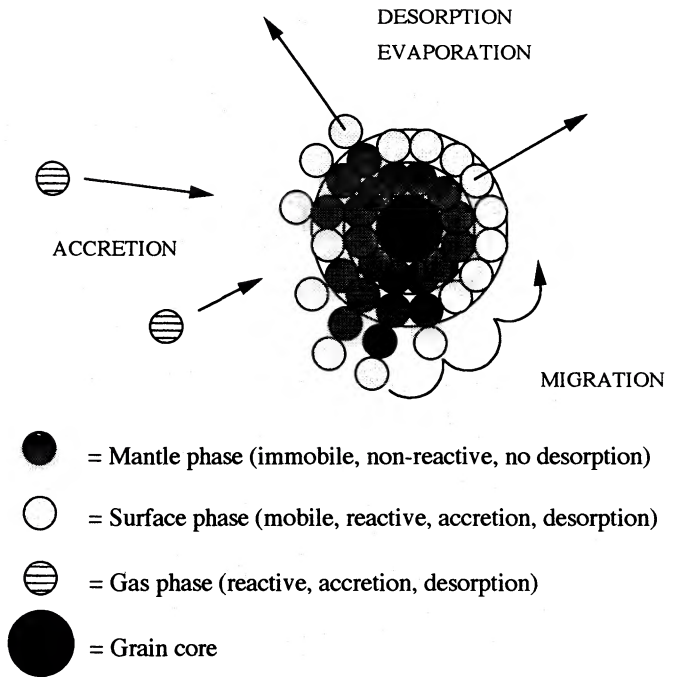


Figure 1. The three-phase model is depicted. Gas-phase species accrete on to and desorb from dust particles. The outermost layer of adsorbed material is known as the surface; all adsorbed material inside the surface, but above the core, is labelled ‘the mantle’ and is chemically inert.

layer they are essentially inert. In addition, it is assumed that both accretion and desorption only occur between the gas and the outermost layer (the surface).

The differential equations governing gaseous, mantle and surface abundances are derived from the equations we used for our previous two-phase models (HHL; HH). In the two-phase approach (gas + surface), the differential equations governing gaseous and surface abundances are

$$\begin{aligned} \frac{dn(i)}{dt} = & \sum_l \sum_j K_{lj} n(l) n(j) - n(i) \sum_j K_{ij} n(j) - k_{\text{acc}}(i) n(i) \\ & + [k_{\text{evap}}(i) + k_{\text{crd}}(i)] n_s(i), \end{aligned} \quad (1)$$

$$\begin{aligned} \frac{dn_s(i)}{dt} = & \sum_l \sum_j k_{lj} n_s(l) n_s(j) - n_s(i) \sum_j k_{ij} n_s(j) + k_{\text{acc}}(i) n(i) \\ & - [k_{\text{evap}}(i) + k_{\text{crd}}(i)] n_s(i), \end{aligned} \quad (2)$$

where $n(i)$ and $n_s(i)$ represent the gaseous and surface concentrations, respectively, of species i ; K_{lj} and k_{ij} represent the gaseous and surface rate coefficients, respectively, for reactions between species l and j ; and $k_{\text{acc}}(i)$, $k_{\text{evap}}(i)$ and $k_{\text{crd}}(i)$ are the grain accretion, thermal evaporation and cosmic ray desorption rates (s^{-1}), respectively, for species i . The surface concentration of species i is defined via the relation

$$n_s(i) = N_s(i) n_d, \quad (3)$$

where $N_s(i)$ is the average number of molecules of i on the grain surface, and n_d is the dust concentration. All rate coefficients involving surface species are defined and listed in HHL or HH.

We now divide the molecules previously considered to be on grain surfaces into mantle and surface species. Let $n_m(i)$

be the concentration (cm^{-3}) of species i in grain mantles, $n_s(i)$ be the concentration (cm^{-3}) of species i on grain surfaces (outermost layers), n_m be the total concentration of molecules in grain mantles [$n_m = \sum_i n_m(i)$], and n_s be the total concentration of molecules on grain surfaces [$n_s = \sum_i n_s(i)$]. Now define a core coverage factor α ($0 \leq \alpha \leq 1$) by the equation

$$\alpha = n_s / (N_{\text{site}} n_d) = N_s / N_{\text{site}}, \quad (4)$$

where $N_{\text{site}} = 1 \times 10^6$ is the number of sites adopted for adsorption on an average grain, and $N_s = \sum_i N_s(i)$. In order to replace equation (2) for the old two-phase model with appropriate equations for the surface and mantle species in our new model, it is necessary to monitor the overall rate of gain or loss of surface molecules $dn_s/dt = \sum_i dn_s(i)/dt$. This permits a determination of the core coverage factor α as a function of time. In the models discussed below, this factor is initially set to zero, increases to near unity in $\approx 10^4$ yr when the first monolayer is formed, and remains near unity thereafter. The actual determination of α is discussed below.

In the subsequent equations, we label the derivative in equation (2) $[dn_s(i)/dt]_0$; it now determines the rate of change of surface species i in the absence of surface-mantle transitions. In the event of a positive net accretion from gas to surface [$(dn_s/dt)_0 > 0$], the rate of change of the concentration of species i on the surface is given by the equation

$$dn_s(i)/dt = [dn_s(i)/dt]_0 - \alpha (dn_s/dt)_0 [n_s(i)/n_s], \quad (5)$$

in which the loss of surface species i to the mantle is related to the product of the core coverage factor, the net accretion rate and the fraction of the surface molecules that consists of species i . Thus the relative concentrations of various surface species are transferred to the mantle as new material accretes to form a changing outer monolayer, or surface. Equation (5) is consistent with a picture of molecules landing randomly on to grain surfaces. By conservation of mass, the rate of change of the concentration of species i in the mantle is given by the relation

$$dn_m(i)/dt = \alpha (dn_s/dt)_0 [n_s(i)/n_s]. \quad (6)$$

Note that, if net accretion is occurring, we only consider the possibility that material from the surface is transferred to the mantle.

The differential equation for n_s , the overall surface concentration as a function of time, can be obtained by summation over all species i in equation (5) as

$$dn_s/dt = (1 - \alpha)(dn_s/dt)_0, \quad (7)$$

while the corresponding equation for n_m is

$$dn_m/dt = \alpha (dn_s/dt)_0. \quad (8)$$

Given that $\alpha(0) = 0$, subsequent values of α can be determined by integration of (7), to obtain n_s , followed by use of equation (4). For $\alpha = 1$, there is no net addition to the surface layer; all surface deposition is compensated for by mantle addition.

In the event of net desorption from the surface to the gas [$(dn_s/dt)_0 < 0$], the rate of change of the concentration of species i on the surface is given by the equation

$$dn_s(i)/dt = [dn_s(i)/dt]_0 - \alpha (dn_s/dt)_0 [n_m(i)/n_m]. \quad (9)$$

The distinction between equations (5) and (9) is that, in the latter equation, surface material is returning to the gas, and

material which previously was part of the mantle is returning to the surface to compensate for this lost material. The new surface material reflects the relative concentrations of the mantle. By conservation of mass, the rate of change of the concentration of mantle species i in this instance is given by

$$dn_m(i)/dt = \alpha (dn_s/dt)_0 [n_m(i)/n_m]. \quad (10)$$

Equations (7) and (8) remain unchanged. In practice, equations (9) and (10), and equations (7) and (8) in the case of net desorption, must be modified to account for possible numerical instabilities in the solutions of the coupled differential equations. In particular, if the core coverage factor α becomes slightly greater than unity while net desorption to the gas is occurring, equation (7) indicates that the surface layer will increase in concentration. This will increase α further and lead to a numerical instability. To avoid this problem, we replace α with $\beta = 2 - \alpha$ if net desorption into the gas is occurring. This has the effect of replacing $1 - \alpha$ with $\alpha - 1$ in equation (7). The modification is nonsensical unless $\alpha \approx 1$; fortunately, net desorption in our model can only occur at late times, for which this condition is met. In fact, in the actual models discussed below, net desorption never occurs, and this contingency does not arise. Because the non-reactive mantles are continually growing, it is possible to determine abundances of species in individual layers, or spherical shells, in the mantles. Specifically, the differences in mantle concentrations between times t_1 and t_2 can be regarded as the abundances of a shell formed during the time interval $t_2 - t_1$.

The species H, H₂ and He are treated as exceptional. They are included in surface chemistry, but they are not considered surface molecules in the estimation of the surface-to-mantle transition rate. In other words, these light species are not allowed to become part of the grain mantles. One justification for this omission is that the binding energy of H₂ on top of H₂ is quite small, approaching the sublimation energy for H₂ ice (Govers, Mattera & Scoles 1980), so that H₂ cannot bury itself easily in mantles. Another justification is that very light species can diffuse outwards more readily than heavier species. If H₂ mantles were allowed to form, as would occur if our standard value for the H₂ grain binding energy was used, unphysically large grains dominated by trapped H₂ would grow. Under the physical conditions adopted here, the exceptional treatment of H₂ leads to a surface abundance of 1.5×10^6 molecules per grain, while there are 1×10^6 heavy molecules per grain surface once $\alpha \approx 1$.

The gas-mantle-surface equations have been solved via a Gear algorithm using the so-called 'low metal' elemental abundances (Graedel, Langer & Frerking 1982; Leung, Herbst & Huebner 1984). Reactions in the gas and on grain surfaces are assumed to take place at a temperature of 10 K. At this temperature, thermal desorption is unimportant, except for the light species H, He and H₂, so that, in the absence of cosmic ray desorption, heavy molecules disappear from the gas phase entirely by a time of 10^7 yr. All models reported here include cosmic ray induced desorption, with the rates given previously (HH). Sticking coefficients are assumed to be unity for neutral species and zero for ions. The initial gas density $n = n(\text{H}) + 2n(\text{H}_2)$ is $2 \times 10^4 \text{ cm}^{-3}$ and remains effectively constant. The initial dust density n_d is set at $1.32 \times 10^{-12} n$, based on a 1 per cent dust-to-gas ratio by mass. The visual extinction is set at a sufficiently large value that photodestructive processes can be safely

ignored. The gas-phase and surface reaction networks are essentially unchanged from our previous work (HH), in which two sets of activation energies were used for surface reactions that involve H-atom transfer between the unsaturated hydrocarbons C_n or C_nH and H_2 . We have here chosen the lower of the two sets of activation energies used previously (2100 K) because these energies are the more reasonable physically. As before, two sets of initial abundances have been used, in which grain mantles and surfaces have not yet been formed. In the first set, labelled normal or N, hydrogen is assumed to be molecular and all other elements to be in atomic form and in the state of ionization found in diffuse clouds. In the second set, labelled atomic or A, all elements are assumed to be in neutral atomic form. The normal initial abundances are so named because they have been chosen in most previous gas-phase calculations. The three-phase models reported here can be compared with our previous models, N(2100 K, CR) and A(2100 K, CR), the names of which refer to the chosen initial conditions, the use of the low activation energy, and the inclusion of cosmic ray desorption (HH).

One surface reaction in our previous models that has become questionable is



because current theoretical treatments (Koizumi, Schatz & Bowman 1992) show that, although HN_2 has a minimum energy in the potential energy surface for the system, this minimum lies above the energy of the reactants $H + N_2$, from which it is separated by a transition state barrier. The nature of the potential surface implies that reaction (11), which is slightly endothermic, cannot occur at 10 K, and that if HN_2 is formed by another (exothermic) reaction, such as



then the newly formed HN_2 will rapidly dissociate via tunnelling to $H + N_2$. The theoretical treatments refer, however, to gas-phase HN_2 , not to this species adsorbed on the surfaces of dust particles. It is still arguable that HN_2 is sufficiently stable on dust surfaces that it is both formed exothermically in reaction (11) and stable against dissociation. Unfortunately, the HN_2 radical is of some importance in dust surface chemistry because it catalytically converts H into H_2 via the reaction sequence



(Tielens & Hagen 1982), which is the dominant loss mechanism for surface H at intermediate and advanced cloud ages. Elimination of this mechanism has the effect of increasing the surface H abundance substantially. In most of the model results reported here, this catalytic mechanism is retained to facilitate comparison with our previous two-phase results.

2.1 Mantle protection

Before discussing individual results in detail, it is useful to consider the question of how the existence of mantles can protect species that are reactive on grain surfaces. The issue of protection is related to the time-scale for formation of a monolayer of heavy species (anything other than H, H_2 and He). This time-scale is easily obtained from the formula for

the accretion rate τ^{-1} (species/unit time) per grain in the absence of competing processes:

$$\tau^{-1} = k'_{acc} n_h, \quad (15)$$

where n_h is the gaseous concentration of heavy species, and k'_{acc} , the average accretion rate coefficient ($cm^3 s^{-1}$) for a heavy species accreting on to a given dust particle, is given by the relation

$$k'_{acc} = \sigma_d v_s, \quad (16)$$

where $\sigma_d \approx 3 \times 10^{-10} cm^2$ is a typical geometrical dust cross-section, and $v_s \approx 1 \times 10^4 cm s^{-1}$ is a typical molecular velocity. Until late stages of evolution, when heavy molecules are depleted from the gas, $n_h \approx 1 cm^{-3}$. For this concentration, the rate of accretion of heavy species, τ^{-1} , on to an average grain is $\approx 10^2$ species per year, and it requires 10^4 yr to cover 10^6 surface sites. Given the relative inefficiency of desorption in our calculations, one can regard 10^4 yr as the time needed to deposit an additional layer of heavy species on grains. By 10^6 yr, 100 monolayers have been deposited. After this time, further adsorption is insignificant. The increased grain radius and surface area lead to an effective increase in the number of grain surface sites N_s of up to 40 per cent, which is neglected in our calculations.

The protection of heavy atoms and molecules via incorporation into dust mantles is also related to surface reaction times. For surface species that are not totally inert, but which have surface reaction times greater than 10^4 yr, the three-phase model should produce significantly larger condensed-phase (surface + mantle) abundances for $t \geq 10^4$ yr due to incorporation in the non-reactive mantle. However, even for species that react quickly on grain surfaces, a small mantle-protection efficiency can lead to large mantle abundances over time. To demonstrate the effect of mantle protection in a simple, semiquantitative manner, one can consider the steady-state grain abundance of a representative heavy species X that accretes from the gas and is depleted via hydrogenation with surface atomic hydrogen. (An extension of this approach to species depleted via H-atom transfer reactions with surface H_2 is considered below.) If other processes are neglected, the steady-state surface abundance of X, $n_s^{(0)}(X)$, in the two-phase model is given by the equation

$$n_s^{(0)}(X) = [k_{acc}(X) n^{(0)}(X)] / [k_H n_s^{(0)}(H)] \quad (17)$$

(see equation 2), where the superscript (0) refers to the two-phase model, k_H is the surface rate coefficient for hydrogenation, and $n^{(0)}(X)$ is the gas-phase abundance. In the three-phase model, the steady-state surface abundance of X becomes

$$n_s(X) = [k_{acc}(X) n(X)] / [k_H n_s(H) + k_m], \quad (18)$$

where k_m is the rate coefficient ($10^{-4} yr^{-1}$) for mantle layer deposition (see above), and it is assumed that the mantle is continually increasing in size. To obtain equation (18) from the more general equation (5), the constant k_m can be regarded as the heavy molecule accretion rate divided by the number of surface species n_s when $\alpha \approx 1$. The mantle abundance of X as a function of time is then obtainable via integration of equation (6) as

$$n_m(X, t) = \int_0^t k_m n_s(X) dt'. \quad (19)$$

From the division of equation (19) by equation (17) (using the result of equation 18, and assuming that the gas-phase abundance of X is constant and the same in the two models, and that the surface abundance of hydrogen atoms is independent of time), we obtain that

$$n_m(X, t)/n_s^{(0)}(X) = [tk_m k_H n_s^{(0)}(H)]/[k_m + k_H n_s(H)], \quad (20)$$

and it can be seen that the abundance ratio $[n_m(X, t)/n_s^{(0)}(X)]$ grows linearly with time at this level of approximation. If $n_m(X, t) \gg n_s(X)$, then the ratio in equation (20) relates the total condensed-phase abundance in the three-phase model to the surface abundance in the two-phase model, and can be thought of as the enhancement factor due to mantle protection. If the enhancement factor is regarded as a function of hydrogenation rate, the maximum enhancement due to mantle protection occurs if the hydrogenation rate exceeds the mantle deposition rate. Then

$$[n_m(X, t)/n_s^{(0)}(X)] = [tk_m n_s^{(0)}(H)]/[n_s(H)], \quad (21)$$

and the abundance ratio simply reflects the abundance ratio of surface hydrogen. Although equation (21) was derived for species that are accreted from the gas, the same formula holds under steady-state conditions for species produced by hydrogenation on grain surfaces. In the models with normal initial conditions discussed below, the ratio $[n_s^{(0)}(H)]/[n_s(H)] \approx 1/30$ for $t < 10^6$ yr, and significant enhancements are not expected until $t > 10^5$ yr, because at 10^5 yr the product $k_m t = 10$ so that the estimated ‘enhancement’ is not even unity. Unlike the case of surface H, the surface abundance of H_2 is the same in the two models. If the main destruction of surface species X is via reaction with molecular hydrogen (as is the case for the radicals C_n and C_nH), the expected enhancement is greater by a factor of ≈ 30 . The approximation given in equation (21) for the enhancement due to mantle protection breaks down for $t > 10^6$ yr because of the heavy depletion of species X from the gas phase, which lowers its surface abundance due to reduced accretion. The result is that the enhancement increases dramatically, because the current surface abundance becomes much lower than the stored-up mantle abundance.

The existence of separate mantle and surface phases also affects the rate of desorption into the gas. In particular, cosmic ray induced desorption time-scales are likely to be longer in the three-phase model than in the two-phase model for several reasons. First, mantle molecules cannot desorb into the gas directly, but must first replace lost surface molecules. As a result, the desorption rate equations do not contain the total grain (surface + mantle) concentrations of species. For chemically inert (e.g. saturated) surface molecules with similar overall grain abundances in the different models, the result will clearly be a slower desorption rate in the three-phase model compared with the two-phase model. One might expect mitigation of this effect for chemically reactive species that can be protected against surface destruction only in the three-phase model. Since the mantle abundances of these species can be large, especially at late times, indirect desorption via the mantle–surface transition, followed by desorption from the surface, might be expected to be competitive. However, in our model results, net accretion is always occurring, so the mantle $\rightarrow$ surface transition is not considered at all. We therefore expect that a smaller residual gas of heavy species will exist at late times than in

our two-phase models. Even if net desorption occurs, as will be the case in models with warmer grains in which thermal desorption plays a role, the presence of large abundances of water ice on the surface acts as a deterrent against desorption because of the large binding energy of water molecules to the dust surfaces and their resultant slow desorption.

3 SELECTED RESULTS

Gaseous, mantle and surface abundances for a wide variety of species are listed in Tables 1 (normal initial conditions) and 2 (atomic initial conditions) at times of 1.0×10^5 , 3.2×10^5 , 1.0×10^6 , 1.0×10^7 and 1.0×10^8 yr. The abundances are expressed relative to $n/2$. For a small number of solid and gaseous species, the ratios of the abundances for the three-phase model with normal initial conditions to the abundances for the analogous two-phase model N(2100 K, CR) are shown in Table 3 as functions of time. In general, for both the condensed-phase abundances of reactive molecules and the gaseous abundances of all molecules, the ratios between the new models and the two-phase models of HH move further from unity with increasing time. For condensed-phase species, the results in Table 3 illustrate that saturated (inert) species generally show small differences, whereas unsaturated species tend to have larger abundances at late times in the three-phase models due to protection in the mantle, as discussed in the previous section. Equation (21), or its equivalent for surface molecules depleted by H_2 , is of semiquantitative use in predicting selected enhancements of reactive species due to mantle protection through 10^6 yr. Use of this equation correctly leads, for example, to very large enhancements for C_9 , which is depleted via reaction with H_2 . Smaller enhancements are achieved for species that are destroyed by surface reactions with atomic hydrogen, due to the relatively high abundance of H in the three-phase models. This high abundance (see Table 3) derives from protection of the major surface scavengers of H, including HN_2 , in the mantle.

The surface + mantle abundances of unsaturated molecules reach steady-state values at moderate times in the three-phase models, as can be seen in Tables 1 and 2, whereas the surface abundances decrease strongly after 10^6 yr in the two-phase models due to continuing hydrogenation to saturated forms (HHL; HH). Indeed, the surface + mantle abundances of complex unsaturated species can reach considerable values at steady state in the three-phase model with normal initial conditions. For example, the fractional abundances of the condensed-phase unsaturated polyynes HC_3N , HC_5N , HC_7N and HC_9N reach 1.2×10^{-8} , 8.1×10^{-10} , 1.3×10^{-10} and 1.4×10^{-11} respectively. Fig. 2 shows the time dependence of the fractional abundances for condensed-phase CO, HC_3N and C_7H_2 in the three-phase model with normal initial conditions, along with analogous abundances from the two-phase model N(2100 K, CR). The strong divergence at times greater than 10^6 yr of the condensed-phase abundances of these unsaturated species for the three-phase model from those for the two-phase model is apparent. The respective condensed-phase steady-state fractional abundances in the three-phase model with atomic initial conditions generally take longer to achieve and are significantly lower than in the model with normal initial conditions, due mainly to more rapid surface hydrogenation, but also to less

Table 1. Gas, surface and mantle abundances for the model with normal initial conditions expressed as a fraction of $n/2$.

t (yr)	1.0E+05	3.2E+05	1.0E+06	1.0E+07	1.0E+08							
Species	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle			
H	2.0E-04	8.1E-22	0.0E+00	1.2E-04	2.2E-22	0.0E+00	1.2E-04	4.5E-21	0.0E+00	1.2E-04	3.1E-20	0.0E+00
HE	2.8E-01	1.5E-21	0.0E+00	2.8E-01	1.5E-21	0.0E+00	2.8E-01	1.5E-21	0.0E+00	2.8E-01	1.5E-21	0.0E+00
C	3.7E-05	7.4E-14	4.5E-12	1.8E-06	1.1E-18	5.8E-12	5.9E-08	6.5E-21	5.8E-12	2.7E-11	4.9E-21	5.8E-12
N	3.1E-05	9.7E-14	3.0E-12	1.5E-05	1.2E-13	8.7E-12	1.5E-06	1.4E-14	1.2E-11	1.1E-08	1.8E-18	1.2E-11
O	1.9E-04	1.7E-13	8.7E-12	7.6E-05	4.4E-17	1.2E-11	5.9E-06	6.3E-19	1.2E-11	2.9E-12	1.3E-23	1.2E-11
NA	9.5E-10	4.8E-18	8.0E-17	8.7E-10	1.8E-17	6.1E-16	5.0E-10	9.1E-18	1.4E-15	1.9E-11	1.7E-20	1.4E-15
MG	3.9E-09	1.9E-17	3.2E-16	3.3E-09	6.6E-17	2.4E-15	1.8E-09	3.3E-17	5.0E-15	4.8E-11	4.3E-20	5.2E-15
SI	1.2E-08	5.6E-17	1.4E-15	7.5E-09	1.4E-16	6.1E-15	1.4E-09	2.3E-17	1.0E-14	2.9E-17	2.4E-26	1.1E-14
S	7.8E-08	5.7E-16	1.6E-14	6.4E-08	6.4E-15	1.2E-13	2.0E-08	1.1E-15	3.3E-13	1.1E-13	4.4E-20	3.4E-13
FE	1.1E-09	3.4E-18	5.5E-17	8.5E-10	1.1E-17	4.1E-16	4.0E-10	4.7E-18	8.5E-16	4.6E-11	2.7E-20	8.8E-16
H2	1.0E+00	4.0E-06	0.0E+00	1.0E+00	4.0E-06	0.0E+00	1.0E+00	4.0E-06	0.0E+00	1.0E+00	4.0E-06	0.0E+00
CH	4.2E-09	1.5E-16	2.1E-14	9.5E-10	7.7E-24	2.2E-14	1.1E-09	1.6E-24	2.2E-14	6.0E-11	5.3E-24	2.2E-14
NH	4.9E-10	7.4E-16	3.0E-14	1.7E-10	7.1E-16	6.4E-14	1.2E-10	7.8E-16	9.9E-14	1.2E-09	1.4E-17	1.1E-13
OH	2.1E-08	2.3E-16	1.1E-14	3.5E-08	1.0E-16	1.9E-14	1.2E-07	1.0E-17	2.1E-14	1.6E-11	2.6E-23	2.1E-14
C2	2.5E-08	2.2E-18	2.3E-16	1.0E-08	1.7E-20	2.6E-16	1.5E-08	2.5E-20	2.6E-16	1.0E-12	1.6E-24	2.6E-16
NAH	2.3E-13	7.6E-12	1.5E-10	1.3E-13	1.4E-11	6.7E-10	4.7E-14	4.8E-11	1.8E-09	7.6E-16	9.6E-10	2.8E-09
MGH	8.3E-13	1.9E-17	3.2E-16	1.8E-13	6.6E-17	2.4E-15	2.0E-14	3.3E-17	5.0E-15	2.7E-18	4.3E-20	5.2E-15
FEH	8.6E-34	5.4E-12	1.0E-10	5.0E-33	8.7E-12	4.5E-10	2.5E-32	2.5E-11	1.1E-09	1.3E-30	7.2E-10	1.6E-09
CN	7.2E-08	6.6E-18	3.1E-16	2.2E-08	3.1E-20	4.4E-16	3.8E-09	5.4E-21	4.4E-16	1.1E-11	1.5E-23	4.4E-16
N2	3.1E-08	6.4E-09	1.2E-07	1.3E-07	3.7E-08	1.1E-06	1.4E-07	4.4E-09	2.1E-06	3.3E-10	3.5E-15	2.1E-06
CO	6.7E-05	9.4E-08	2.1E-06	6.0E-05	2.5E-07	1.0E-05	1.3E-05	6.2E-08	1.9E-05	4.1E-12	1.0E-15	2.0E-05
SiH	2.8E-11	5.7E-17	1.4E-15	1.2E-10	1.4E-16	6.2E-15	2.6E-10	2.8E-17	1.1E-14	7.2E-18	3.0E-26	1.1E-14
NO	6.4E-09	7.9E-13	2.4E-11	2.7E-08	9.6E-14	8.3E-11	3.8E-06	5.4E-08	3.4E-06	3.0E-17	2.6E-20	3.6E-06
O2	1.2E-06	3.6E-13	1.2E-11	5.0E-06	9.9E-09	1.3E-08	2.8E-11	1.5E-14	8.2E-13	1.6E-16	1.8E-14	9.9E-13
HS	2.3E-11	2.2E-15	7.7E-14	5.5E-11	9.9E-15	2.7E-13	5.2E-12	4.0E-13	4.1E-11	2.8E-21	7.8E-14	4.5E-11
SIC	2.8E-11	1.7E-13	2.5E-11	9.5E-12	1.2E-13	3.3E-11	2.3E-10	1.8E-12	4.3E-10	1.9E-22	5.3E-13	4.4E-10
SIO	5.2E-10	3.1E-12	1.5E-10	2.7E-10	3.1E-12	2.9E-10	5.1E-10	1.2E-12	8.4E-11	4.4E-16	4.3E-17	8.9E-11
CS	6.8E-09	1.5E-15	5.8E-14	3.1E-09	2.5E-13	5.3E-13	2.5E-12	3.5E-14	1.9E-12	8.6E-21	1.8E-14	2.3E-12
NS	1.3E-10	1.2E-15	2.7E-14	7.0E-11	2.8E-14	3.9E-13	1.1E-10	5.8E-13	3.7E-11	1.1E-21	5.4E-18	3.9E-11
SO	1.1E-09	1.9E-15	5.9E-14	9.0E-10	8.3E-14	3.9E-13	7.1E-14	5.3E-15	6.8E-12	7.6E-26	1.9E-16	6.8E-12
SIS	1.2E-11	5.9E-14	1.9E-12	1.3E-15	1.2E-17	1.7E-16	1.4E-15	8.6E-17	2.4E-15	2.0E-25	6.7E-18	2.9E-15
S2	7.5E-17	3.4E-19	3.6E-18	4.8E-08	3.0E-17	1.0E-12	5.1E-09	1.0E-18	1.0E-12	2.6E-10	9.4E-20	1.0E-12
CH2	3.0E-07	1.0E-14	9.1E-13	4.8E-08	3.0E-17	1.0E-12	4.0E-09	8.2E-16	7.5E-14	9.4E-09	2.4E-17	8.2E-14
NH2	7.6E-09	5.4E-16	2.3E-14	2.6E-09	4.7E-16	4.6E-14	1.7E-07	1.5E-06	2.0E-04	1.9E-11	1.5E-06	2.1E-04
H2O	1.0E-06	1.7E-06	6.3E-05	3.5E-07	1.5E-06	1.4E-04	7.0E-30	2.8E-17	1.1E-14	5.5E-38	3.0E-26	1.1E-14
SiH2	8.8E-31	5.7E-17	1.4E-15	5.3E-30	1.4E-16	6.2E-15	7.0E-40	5.2E-11	2.6E-09	1.0E-39	1.7E-10	6.6E-09
MGH2	3.7E-41	3.0E-11	6.1E-10	2.0E-40	5.2E-11	2.1E-06	3.0E-09	3.1E-20	3.6E-16	1.3E-13	1.9E-24	3.6E-16
C2H	6.2E-08	2.7E-18	3.3E-16	8.3E-09	3.2E-20	3.6E-16	8.5E-15	4.1E-12	4.3E-10	5.3E-16	2.5E-26	4.6E-10
N2H	5.6E-16	1.9E-12	4.8E-11	3.2E-15	4.7E-12	2.0E-10	1.1E-16	5.2E-14	2.6E-12	1.8E-24	2.3E-13	2.9E-12
O2H	1.4E-20	3.2E-17	1.3E-15	2.4E-19	6.3E-15	1.0E-14	1.3E-					

Table 1 – continued

t (yr)	1.0E+05			3.2E+05			1.0E+06			1.0E+07			1.0E+08		
Species	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle
O3	5.4E-20	3.2E-10	8.5E-09	6.7E-19	9.0E-09	5.8E-08	2.9E-18	6.3E-10	2.7E-07	5.5E-25	2.8E-28	2.8E-07	1.1E-38	7.6E-30	2.8E-07
C2N	2.5E-08	9.0E-17	6.7E-15	5.6E-09	8.9E-17	6.7E-15	7.4E-11	1.0E-18	8.2E-15	1.7E-16	8.5E-26	8.2E-15	1.2E-16	1.2E-26	8.2E-15
C2O	2.1E-25	3.5E-19	2.7E-17	1.8E-25	3.1E-24	3.1E-17	4.9E-26	5.7E-26	3.1E-17	1.7E-33	3.8E-36	3.1E-17	1.1E-42	6.3E-37	3.1E-17
C2S	9.8E-10	3.6E-17	1.0E-15	3.7E-10	6.9E-13	9.1E-13	1.6E-11	9.1E-13	8.7E-11	1.3E-20	1.1E-21	9.3E-11	7.9E-21	4.4E-21	9.3E-11
NAOH	4.1E-14	2.6E-16	6.1E-15	4.7E-15	5.8E-17	1.2E-14	6.5E-16	5.1E-17	1.5E-14	3.2E-22	9.0E-17	1.5E-14	5.2E-29	9.0E-17	1.5E-14
OCN	1.6E-07	6.3E-14	1.6E-12	1.3E-09	2.0E-17	4.3E-12	1.5E-09	2.0E-18	4.3E-12	1.8E-24	1.9E-24	4.3E-12	1.8E-24	2.6E-26	4.3E-12
CO2	2.6E-07	4.3E-08	1.1E-06	1.9E-07	2.4E-09	2.9E-06	4.5E-09	3.7E-10	2.9E-06	6.1E-21	5.2E-11	2.9E-06	6.5E-21	5.1E-11	2.9E-06
OCs	4.3E-08	4.0E-16	1.0E-14	1.7E-08	2.5E-16	3.2E-14	5.4E-10	8.9E-18	3.7E-14	7.6E-23	9.9E-29	3.7E-14	5.5E-23	3.9E-31	3.7E-14
SO2	2.6E-10	5.4E-10	1.7E-08	6.6E-11	1.7E-11	4.0E-08	2.2E-12	8.1E-12	4.0E-08	4.1E-26	3.3E-12	4.0E-08	4.1E-26	3.3E-12	4.0E-08
CH3	1.4E-08	1.0E-09	5.4E-08	3.6E-09	4.4E-09	8.5E-08	4.8E-09	4.4E-09	1.4E-07	3.0E-09	3.8E-18	2.6E-12	3.0E-09	5.8E-19	2.6E-12
NH3	2.5E-32	5.7E-17	1.4E-15	1.5E-31	1.4E-16	6.2E-15	2.0E-31	2.8E-17	1.1E-14	2.0E-39	3.0E-26	1.1E-14	2.8E-52	8.3E-38	1.1E-14
C2H2	2.6E-07	6.4E-09	4.3E-07	1.5E-07	1.4E-09	5.6E-07	3.7E-08	8.4E-10	6.1E-07	1.1E-12	2.0E-15	6.2E-07	1.0E-12	2.7E-16	6.2E-07
N2H2	8.4E-10	4.9E-08	1.2E-06	4.0E-09	1.2E-07	5.2E-06	2.3E-09	1.1E-07	1.1E-05	1.1E-11	6.2E-09	1.2E-05	4.2E-13	2.4E-10	1.2E-05
H2O2	1.1E-20	3.4E-11	1.6E-09	6.7E-20	2.6E-09	5.2E-09	1.0E-16	1.0E-07	2.8E-06	3.4E-24	7.3E-20	3.3E-06	1.5E-29	1.1E-20	3.3E-06
H2S2	4.0E-16	1.8E-18	1.8E-17	7.2E-15	6.5E-17	9.0E-16	7.8E-15	4.9E-16	1.4E-14	8.3E-26	2.5E-17	1.7E-14	8.0E-26	2.5E-17	1.7E-14
CH2N	1.2E-19	1.1E-15	4.3E-14	1.6E-19	1.6E-17	6.9E-14	3.4E-20	5.8E-20	6.9E-14	1.8E-28	2.4E-25	6.9E-14	1.1E-30	2.1E-27	6.9E-14
CHNH	4.1E-19	1.5E-17	1.2E-15	3.3E-19	3.1E-24	1.4E-15	7.0E-20	6.2E-25	1.4E-15	2.3E-28	1.9E-27	1.4E-15	3.7E-30	5.5E-29	1.4E-15
H2CO	1.8E-07	2.3E-07	7.4E-06	3.9E-08	3.3E-07	2.0E-05	7.8E-09	5.8E-07	4.0E-05	1.9E-14	3.5E-07	4.6E-05	2.0E-14	3.5E-07	4.6E-05
CHOH	1.5E-19	1.6E-13	3.5E-12	1.0E-18	4.2E-13	1.7E-11	1.6E-18	1.0E-13	3.2E-11	2.1E-26	1.7E-21	3.2E-11	1.8E-27	2.4E-22	3.2E-11
HCCN	4.2E-25	9.0E-17	1.7E-15	2.1E-24	8.9E-17	6.7E-15	9.9E-25	1.0E-18	8.2E-15	3.4E-32	8.5E-26	8.2E-15	5.9E-34	1.2E-26	8.2E-15
HC2O	2.1E-25	3.5E-19	2.7E-17	1.8E-25	3.1E-24	3.1E-17	5.0E-26	5.7E-26	3.1E-17	2.4E-33	3.8E-36	3.1E-17	1.2E-42	6.3E-37	3.1E-17
HNC	7.5E-16	1.0E-07	3.3E-06	1.4E-15	1.2E-10	6.5E-06	4.1E-16	1.2E-11	6.5E-06	5.9E-20	1.2E-12	6.5E-06	6.3E-20	1.3E-12	6.5E-06
C3H	3.9E-08	1.1E-19	1.0E-17	5.4E-09	2.5E-20	1.3E-17	1.2E-09	3.2E-20	1.4E-17	2.6E-16	8.0E-27	1.4E-17	2.3E-16	6.9E-27	1.4E-17
H2CS	9.2E-10	1.7E-11	8.8E-10	3.0E-10	3.9E-12	1.3E-09	9.7E-12	2.2E-11	1.8E-09	4.0E-18	1.1E-11	2.0E-09	2.5E-18	1.7E-11	2.0E-09
C4	1.7E-08	3.2E-20	2.8E-18	5.3E-09	1.0E-20	3.7E-18	1.1E-08	2.1E-20	4.1E-18	3.0E-17	5.7E-29	4.4E-18	2.3E-17	4.2E-29	4.4E-18
C3N	2.2E-08	8.4E-17	1.5E-15	5.4E-09	7.4E-17	5.9E-15	2.9E-10	3.6E-18	7.3E-15	3.9E-18	2.4E-27	7.3E-15	3.7E-18	3.3E-28	7.3E-15
C3O	3.0E-11	1.4E-19	4.7E-18	5.2E-11	7.1E-19	2.2E-17	3.7E-12	4.5E-20	4.0E-17	1.9E-23	1.1E-32	4.1E-17	1.5E-23	1.4E-33	4.1E-17
C3S	4.0E-10	7.1E-12	2.5E-10	1.3E-10	4.3E-12	5.2E-10	5.6E-12	4.6E-13	5.9E-10	4.4E-23	3.0E-13	5.9E-10	2.3E-23	3.0E-13	5.9E-10
CH4	1.8E-06	7.0E-08	4.9E-06	1.3E-06	2.7E-08	6.9E-06	1.4E-07	1.8E-08	7.7E-06	2.8E-09	3.8E-07	8.4E-06	2.8E-09	3.7E-07	8.4E-06
SiH4	1.4E-27	9.1E-11	2.9E-09	4.5E-27	1.1E-10	7.6E-09	1.2E-26	1.5E-10	1.4E-08	1.5E-26	1.6E-10	1.5E-08	1.5E-26	1.6E-10	1.5E-08

Table 1 – *continued*

t (yr)	1.0E+05			3.2E+05			1.0E+06			1.0E+07			1.0E+08		
Species	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle
CH3NH	1.3E-19	1.1E-14	4.1E-13	2.2E-19	7.8E-16	7.2E-13	6.3E-20	3.5E-16	7.4E-13	2.5E-25	3.2E-21	7.4E-13	6.6E-28	1.0E-23	7.4E-13
CH3OH	2.7E-09	2.6E-07	7.6E-06	9.6E-11	3.3E-07	2.2E-05	7.2E-12	5.8E-07	4.2E-05	3.3E-16	3.5E-07	4.8E-05	3.4E-16	3.5E-07	4.8E-05
C3H3	1.8E-10	9.2E-16	5.1E-14	6.8E-11	1.4E-16	7.0E-14	2.0E-12	2.2E-16	7.6E-14	4.8E-19	3.3E-24	7.8E-14	4.6E-19	4.3E-25	7.8E-14
CH3CN	3.7E-09	3.4E-10	7.6E-09	2.1E-11	8.6E-11	1.7E-08	8.1E-13	7.4E-12	1.9E-08	4.2E-17	7.6E-13	1.9E-08	4.0E-17	8.1E-13	1.9E-08
H2C3N	2.1E-29	1.6E-16	3.7E-15	5.4E-29	6.1E-17	9.0E-15	7.4E-29	4.9E-18	1.0E-14	1.0E-35	3.2E-27	1.0E-14	5.7E-40	4.5E-28	1.0E-14
H2C3O	9.9E-26	2.3E-13	1.0E-11	3.5E-25	5.5E-13	2.7E-11	7.4E-25	2.6E-13	4.8E-11	1.6E-25	6.4E-14	5.0E-11	1.6E-25	6.4E-14	5.0E-11
C4H2	2.0E-08	3.7E-10	1.2E-08	3.5E-09	1.3E-10	2.3E-08	1.9E-10	1.6E-10	2.8E-08	1.4E-19	2.4E-20	2.9E-08	1.2E-19	2.7E-21	2.9E-08
C5H	4.2E-09	2.5E-20	2.5E-18	1.7E-10	3.2E-21	3.0E-18	1.2E-11	3.6E-21	3.1E-18	1.1E-23	1.1E-32	3.1E-18	8.7E-24	7.6E-33	3.1E-18
C6	3.4E-09	6.2E-21	7.6E-19	3.6E-10	6.6E-22	8.7E-19	2.2E-10	4.1E-22	8.9E-19	2.2E-24	4.1E-36	9.0E-19	1.6E-24	2.9E-36	9.0E-19
C5N	2.9E-09	8.2E-18	1.5E-16	3.7E-10	4.2E-18	5.0E-16	6.7E-12	6.8E-20	5.6E-16	1.7E-24	8.6E-34	5.6E-16	1.5E-24	1.1E-34	5.6E-16
CH3NH2	6.4E-10	1.8E-08	8.8E-07	1.9E-11	6.5E-10	1.3E-06	4.1E-12	1.7E-09	1.3E-06	9.3E-14	7.3E-29	1.4E-06	1.0E-13	7.4E-09	1.4E-06
C2H5	1.3E-21	8.4E-15	5.7E-13	1.3E-21	1.5E-15	7.2E-13	6.4E-22	8.7E-16	7.8E-13	7.2E-27	1.5E-20	7.9E-13	6.4E-27	1.4E-20	7.9E-13
C3H4	2.3E-10	1.7E-09	1.5E-07	2.5E-10	1.1E-10	1.7E-07	4.8E-12	1.1E-09	1.8E-07	1.2E-18	6.0E-09	2.3E-07	1.1E-18	6.0E-09	2.3E-07
C4H3	1.1E-28	3.1E-16	1.0E-14	2.2E-28	1.1E-16	1.9E-14	2.4E-28	1.3E-16	2.3E-14	3.9E-34	2.0E-26	2.5E-14	5.9E-39	2.3E-27	2.5E-14
CH3CHO	1.4E-11	2.7E-13	7.8E-12	2.5E-12	4.9E-14	1.6E-11	1.9E-13	3.4E-14	1.8E-11	1.2E-22	8.7E-14	1.8E-11	1.2E-22	9.8E-14	1.8E-11
H3C3N	2.0E-10	9.6E-12	2.2E-10	2.0E-11	3.5E-12	5.3E-10	4.6E-14	3.0E-13	6.0E-10	1.6E-21	1.9E-22	6.0E-10	1.6E-21	2.8E-23	6.0E-10
C5H2	4.3E-09	3.8E-11	1.8E-09	4.1E-10	1.3E-11	2.9E-09	1.2E-11	2.1E-11	3.5E-09	3.4E-23	3.9E-24	3.7E-09	2.7E-23	4.1E-25	3.7E-09
C6H	2.0E-09	1.0E-20	1.0E-18	6.7E-11	7.8E-22	1.2E-18	3.5E-12	4.2E-22	1.2E-18	1.5E-26	4.1E-36	1.2E-18	1.2E-26	3.0E-36	1.2E-18
HC5N	5.1E-09	1.6E-11	3.3E-10	1.8E-10	3.1E-12	7.6E-10	9.6E-13	8.1E-14	8.1E-10	7.7E-26	1.1E-27	8.1E-10	7.3E-26	1.5E-28	8.1E-10
C7	1.5E-09	2.7E-21	3.1E-19	1.2E-10	2.2E-22	3.6E-19	5.6E-11	1.0E-22	3.6E-19	4.4E-27	8.0E-39	3.6E-19	3.0E-27	5.3E-39	3.6E-19
H4C3N	3.3E-32	1.6E-16	3.6E-15	8.5E-32	5.7E-17	8.7E-15	4.9E-32	4.9E-18	9.9E-15	2.2E-38	3.2E-27	7.9E-15	9.6E-43	4.5E-28	9.9E-15
CH3C3N	3.7E-10	1.9E-12	4.5E-11	8.4E-12	8.7E-14	7.8E-11	3.3E-14	2.1E-15	7.9E-11	1.9E-24	1.9E-16	7.9E-11	1.9E-24	1.9E-16	7.9E-11
H2C5N	4.6E-38	1.3E-17	2.7E-16	1.1E-37	2.5E-18	6.1E-16	5.5E-38	6.5E-20	6.5E-16	2.2E-43	9.0E-34	6.6E-16	5.5E-54	1.2E-34	6.6E-16
C2H6	1.5E-16	1.4E-08	1.3E-06	1.3E-16	1.2E-09	1.5E-06	7.3E-17	4.3E-09	1.6E-06	4.3E-16	1.8E-08	1.7E-06	4.4E-16	1.8E-08	1.7E-06
C4H4	6.5E-24	5.2E-10	2.1E-08	9.1E-24	8.5E-11	3.2E-08	1.6E-23	6.3E-10	3.9E-08	2.2E-22	3.0E-09	6.7E-08	2.2E-22	3.0E-09	6.7E-08
C5H3	3.4E-35	3.1E-17	1.5E-15	9.9E-35	1.1E-17	2.4E-15	7.0E-35	1.8E-17	2.9E-15	3.5E-40	3.2E-30	3.0E-15	2.2E-48	3.4E-31	3.0E-15
C6H2	4.5E-09	2.0E-11	8.0E-10	6.8E-10	1.6E-12	1.4E-09	3.9E-11	2.7E-12	1.5E-09	4.1E-25	1.7E-27	1.6E-09	3.1E-25	1.8E-28	1.6E-09
C7H	1.1E-09	4.7E-21	4.3E-19	1.8E-11	2.5E-22	5.0E-19	7.5E-13	1.0E-22	5.1E-19	3.6E-29	8.1E-39	5.1E-19	2.5E-29	5.4E-39	5.1E-19
C8	7.8E-10	1.4E-21	9.2E-20	4.1E-11	7.2E-23	1.1E-19	1.9E-11	3.3E-23	1.1E-19	1.3E-29	2.3E-41	1.2E-19	8.5E-30	1.5E-41	1.2E-19
C7N	5.4E-10	1.3E-18	2.6E-17	2.6E-11	2.5E-19	6.5E-17	2.7E-13	2.4E-21	6.8E-17	1.4E-30	6.3E-40				

Table 1 - continued

t (yr)	1.0E+05			3.2E+05			1.0E+06			1.0E+07			1.0E+08		
Species	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle
C8H3	3.3E-46	3.5E-18	1.3E-16	4.9E-46	3.8E-19	2.0E-16	2.7E-46	1.4E-19	2.1E-16	9.9E-51	6.0E-39	2.1E-16	4.5E-67	5.6E-40	2.1E-16
C9H2	2.1E-10	9.5E-13	3.4E-11	1.9E-12	5.9E-14	5.1E-11	1.3E-14	2.6E-14	5.2E-11	6.4E-36	1.2E-36	5.3E-11	4.3E-36	1.1E-37	5.3E-11
HC9N	1.3E-10	3.2E-13	7.4E-12	1.3E-12	1.3E-14	1.3E-11	1.7E-15	3.8E-17	1.4E-11	3.6E-38	6.5E-41	1.4E-11	2.8E-38	7.1E-42	1.4E-11
H3C7N	1.5E-41	3.7E-12	9.6E-11	2.3E-41	1.6E-13	1.6E-10	1.1E-41	1.8E-14	1.6E-10	1.6E-43	3.3E-15	1.6E-10	1.6E-43	3.3E-15	1.6E-10
HC3C7N	5.3E-12	2.0E-14	4.6E-13	1.3E-14	1.1E-16	7.2E-13	1.9E-17	8.8E-19	7.2E-13	6.6E-37	6.6E-20	7.2E-13	5.2E-37	6.6E-20	7.2E-13
H2C9N	1.1E-54	2.5E-19	5.8E-18	1.9E-54	9.9E-21	1.0E-17	9.5E-55	3.0E-23	1.1E-17	5.6E-59	5.1E-47	1.1E-17	3.6E-82	5.6E-48	1.1E-17
C8H4	8.2E-41	5.8E-12	2.8E-10	9.8E-41	3.1E-13	3.7E-10	5.7E-41	6.5E-13	3.8E-10	2.2E-40	2.3E-12	4.2E-10	2.2E-40	2.3E-12	4.2E-10
C9H3	7.3E-52	7.5E-19	2.7E-17	1.0E-51	4.7E-20	4.0E-17	5.7E-52	2.0E-20	4.1E-17	2.8E-56	9.7E-43	4.1E-17	7.9E-76	8.4E-44	4.1E-17
C9H4	1.8E-46	1.3E-12	5.6E-11	2.1E-46	3.9E-14	7.4E-11	1.2E-46	9.4E-14	7.6E-11	1.4E-46	1.3E-13	7.9E-11	1.4E-46	1.2E-13	7.9E-11
H3C9N	5.2E-50	4.1E-13	1.1E-11	7.7E-50	8.5E-15	1.8E-11	3.7E-50	1.6E-16	1.8E-11	3.0E-53	1.7E-17	1.8E-11	2.8E-53	1.7E-17	1.8E-11
E	3.6E-08			4.1E-08			5.2E-08			2.7E-07			2.6E-07		
H+	3.0E-10			8.4E-10			1.5E-09			8.7E-08			7.7E-08		
HE+	6.4E-10			8.3E-10			2.7E-09			1.4E-08			1.4E-08		
C+	2.9E-09			8.0E-09			8.4E-09			5.2E-11			4.6E-11		
N+	5.6E-12			2.6E-12			4.4E-12			9.9E-12			1.1E-11		
O+	2.3E-15			1.4E-14			2.4E-14			6.5E-18			6.4E-18		
NA+	2.9E-09			2.4E-09			1.7E-09			2.6E-10			4.0E-17		
MG+	9.5E-09			8.0E-09			5.4E-09			4.6E-10			2.7E-19		
SI+	1.4E-11			3.6E-11			9.3E-12			9.2E-18			1.6E-28		
S+	1.2E-10			5.0E-10			1.1E-10			9.5E-14			5.4E-14		
FE+	4.8E-09			4.7E-09			4.5E-09			3.7E-09			5.8E-10		
O2+	9.1E-12			1.0E-10			1.2E-10			1.1E-20			9.5E-21		
CH+	1.8E-13			1.6E-14			3.0E-15			6.8E-16			5.5E-16		
SO+	1.1E-11			2.0E-11			6.7E-12			1.3E-19			7.6E-20		
H3+	2.2E-09			4.0E-09			1.9E-08			1.7E-07			1.7E-07		
CH2+	2.7E-13			3.9E-14			1.7E-14			2.0E-15			1.7E-15		
NH2+	1.9E-14			7.0E-15			1.4E-14			4.4E-13			4.6E-13		
HCO+	5.2E-09			8.1E-09			6.5E-09			3.5E-15			3.6E-15		
HOC+	5.0E-10			5.8E-10			4.5E-10			2.1E-16			2.1E-16		
N2H+	5.8E-13			5.2E-12			2.3E-11			1.0E-13			6.8E-15		
C2N+	3.4E-10			6.1E-11			1.2E-11			6.4E-17			5.8E-17		
HCS+	2.0E-11			3.8E-11			2.4E-11			4.9E-17			2.5E-17		
OCS+	2.0E-10			1.4E-10			5.2E-12			8.6E-25			4.1E-25		
H3O+	2.0E-09			1.3E-09			1.1E-09			2.2E-13			2.2E-13		
HCO2+	4.5E-12			6.7E-12			7.3E-13			2.0E-24			2.2E-24		
H2CN+	4.1E-10			5.6E-11			3.4E-11			1.9E-13			2.0E-13		
H3CO+	2.3E-10			7.0E-11			3.0E-11			1.1E-16			1.2E-16		
CH3+	3.4E-10			7.0E-11			2.9E-11			4.0E-12			3.6E-12		
NH3+	1.5E-12			6.5E-13			1.7E-12			3.5E-11			3.8E-11		
CH4+	9.0E-16			1.8E-15			1.5E-15			1.4E-15			1.4E-15		
NH4+	4.7E-11			1.6E-11			3.7E-11			1.3E-10			1.5E-10		
CH5+	4.0E-10			2.0E-10			1.1E-10			5.0E-12			5.0E-12		
C2H2+	6.5E-11			1.8E-11			7.7E-12			2.0E-15			1.7E-15		
C2H3+	1.3E-10			1.6E-10			4.6E-11			2.1E-15			2.0E-15		
C2H4+	2.6E-10			1.1E-10			6.0E-11			2.7E-15			2.5E-15		
C3H3+	2.4E-10			1.2E-10			5.3E-11			2.4E-17			2.0E-17		
C3H2N+	6.8E-10			1.3E-10			1.1E-11			1.6E-19			1.6E-19		

Table 2. Gas, surface and mantle abundances for the model with atomic initial conditions expressed as a fraction of $n/2$.

t (yr)	1.0E+05			3.2E+05			1.0E+06			1.0E+07			1.0E+08		
Species	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle
H	6.0E-01	5.3E-16	0.0E+00	4.4E-02	8.6E-18	0.0E+00	1.2E-04	2.4E-22	0.0E+00	1.2E-04	4.1E-21	0.0E+00	1.2E-04	3.0E-20	0.0E+00
HE	2.8E-01	1.5E-21	0.0E+00	2.8E-01	1.5E-21	0.0E+00	2.8E-01	1.5E-21	0.0E+00	2.8E-01	1.5E-21	0.0E+00	2.8E-01	1.5E-21	0.0E+00
C	6.1E-05	6.6E-19	2.0E-17	4.5E-06	3.0E-18	1.1E-16	5.4E-08	6.1E-21	2.2E-16	2.7E-11	3.6E-20	2.2E-16	2.5E-11	4.7E-21	2.2E-16
N	3.1E-05	3.1E-19	7.3E-18	1.5E-05	9.4E-18	1.3E-16	1.6E-06	1.4E-14	1.8E-13	1.1E-08	1.4E-17	2.4E-13	1.1E-08	1.9E-18	2.4E-13
O	2.2E-04	2.0E-18	5.1E-17	8.3E-05	4.6E-17	7.2E-16	5.5E-06	6.0E-19	4.8E-15	2.8E-12	1.1E-23	4.8E-15	2.5E-12	1.5E-23	4.8E-15
NA	3.9E-10	3.0E-24	5.3E-23	8.2E-10	3.9E-22	4.1E-21	5.4E-10	9.1E-18	6.5E-17	2.1E-11	2.1E-20	1.2E-16	2.7E-18	3.6E-28	1.2E-16
MG	1.7E-08	1.3E-23	2.3E-22	3.2E-09	1.5E-21	1.6E-20	2.0E-09	3.3E-17	2.4E-16	5.3E-11	5.1E-20	4.2E-16	2.5E-20	3.4E-30	4.4E-16
SI	1.2E-08	8.7E-23	1.5E-21	8.1E-09	3.5E-21	4.5E-20	1.5E-09	2.3E-17	2.2E-16	3.1E-17	2.8E-26	3.2E-16	6.1E-28	7.5E-38	3.2E-16
S	1.3E-07	8.3E-22	1.6E-20	7.2E-08	2.9E-20	3.8E-19	2.0E-08	1.1E-15	8.0E-15	1.1E-13	5.6E-20	1.3E-14	8.2E-14	1.0E-21	1.3E-14
FE	1.6E-10	8.0E-25	1.6E-23	6.2E-10	1.9E-22	1.8E-21	4.2E-10	4.5E-18	3.3E-17	5.0E-11	3.2E-20	6.0E-17	7.9E-12	6.8E-22	6.0E-17
H2	7.0E-01	4.5E-06	0.0E+00	9.8E-01	4.0E-06	0.0E+00	1.0E+00	4.0E-06	0.0E+00	1.0E+00	4.0E-06	0.0E+00	1.0E+00	4.0E-06	0.0E+00
CH	1.3E-08	6.6E-19	2.0E-17	1.4E-09	1.1E-18	9.0E-17	1.0E-09	1.5E-24	9.8E-17	5.6E-11	4.6E-24	9.8E-17	4.9E-11	6.2E-24	9.8E-17
NH	1.0E-10	3.1E-19	7.3E-18	2.9E-10	9.4E-18	1.3E-16	1.3E-10	8.3E-16	2.8E-14	1.2E-09	1.6E-17	3.4E-14	1.4E-09	2.1E-18	3.4E-14
OH	1.1E-08	2.0E-18	5.1E-17	3.4E-08	3.4E-17	6.4E-16	1.3E-07	9.9E-18	2.6E-15	1.7E-11	2.6E-23	2.6E-15	1.6E-11	2.5E-23	2.6E-15
C2	5.2E-08	3.9E-22	8.9E-21	1.5E-08	5.3E-21	1.1E-19	1.4E-08	2.3E-20	7.9E-19	8.8E-13	1.4E-24	1.0E-18	7.7E-13	1.2E-24	1.0E-18
NAH	2.5E-14	2.3E-12	9.1E-11	1.2E-13	1.2E-11	4.6E-10	5.1E-14	5.4E-11	1.6E-09	8.4E-16	1.1E-09	2.6E-09	1.1E-22	1.4E-09	2.6E-09
MGH	8.0E-15	1.3E-23	2.3E-22	1.5E-13	1.5E-21	1.6E-20	2.4E-14	3.3E-17	2.4E-16	3.3E-18	5.1E-20	4.4E-16	2.2E-34	3.4E-30	4.4E-16
FEH	1.5E-34	6.1E-13	3.0E-11	1.8E-33	5.6E-12	1.7E-10	2.3E-32	2.7E-11	7.5E-10	1.4E-30	7.8E-10	1.3E-09	8.1E-30	4.1E-09	1.3E-09
CN	4.0E-09	3.2E-22	5.8E-21	3.0E-08	1.0E-20	1.6E-19	3.9E-09	5.5E-21	8.6E-19	1.0E-11	1.5E-23	8.9E-19	1.0E-11	1.4E-23	8.9E-19
N2	5.4E-09	3.6E-17	3.5E-16	6.4E-08	2.8E-14	2.1E-13	1.2E-07	3.9E-09	2.9E-08	3.7E-10	3.9E-13	4.5E-08	2.2E-11	3.7E-15	4.5E-08
CO	4.3E-05	9.2E-14	1.3E-12	5.4E-05	7.1E-12	8.1E-11	1.2E-05	5.4E-08	5.0E-07	4.0E-12	1.1E-15	7.4E-07	3.9E-12	1.4E-16	7.4E-07
SiH	9.6E-11	8.8E-23	1.5E-21	1.1E-10	3.6E-21	4.6E-20	2.9E-10	2.7E-17	2.5E-16	7.7E-18	3.4E-26	3.8E-16	1.6E-28	9.5E-38	3.8E-16
NO	1.7E-09	1.6E-18	2.1E-17	1.9E-08	4.6E-17	7.6E-16	3.3E-08	7.4E-15	1.1E-13	1.4E-14	2.8E-16	1.7E-13	1.2E-14	1.9E-16	1.7E-13
O2	3.5E-07	2.4E-15	2.2E-14	3.2E-06	1.3E-12	1.0E-11	4.0E-06	5.2E-08	4.5E-07	3.1E-17	2.7E-20	7.0E-07	3.1E-17	3.6E-21	7.0E-07
HS	5.9E-11	5.6E-15	1.9E-13	6.9E-11	8.0E-15	5.6E-13	2.8E-11	1.5E-14	1.1E-12	1.7E-16	1.8E-14	1.2E-12	1.5E-16	1.9E-14	1.2E-12
SIC	1.0E-10	5.0E-13	2.5E-11	1.7E-11	1.9E-13	4.3E-11	5.3E-12	4.2E-13	5.3E-11	2.7E-21	8.4E-14	5.6E-11	1.2E-31	8.4E-14	5.6E-11
SiO	1.7E-10	7.4E-13	1.3E-11	2.6E-10	2.7E-12	1.1E-10	2.4E-11	2.0E-12	2.5E-10	2.0E-22	5.9E-13	2.6E-10	3.3E-31	5.9E-13	2.6E-10
CS	1.3E-09	2.5E-18	7.5E-17	2.1E-09	2.4E-16	2.4E-15	5.0E-10	1.2E-12	1.1E-11	3.8E-16	5.1E-17	1.5E-11	2.0E-16	9.1E-19	1.5E-11
NS	1.1E-11	1.0E-14	1.8E-13	5.7E-11	4.7E-15	8.2E-13	2.6E-12	3.5E-14	1.4E-12	9.2E-21	1.8E-14	1.7E-12	8.6E-21	1.9E-14	1.7E-12
SO	1.0E-10	9.8E-14	1.7E-12	6.0E-10	4.8E-14	7.9E-12	1.2E-10	6.5E-13	1.5E-11	1.2E-21	5.0E-18	1.8E-11	9.9E-22	5.0E	

Table 2 – continued

t (yr)	1.0E+05			3.2E+05			1.0E+06			1.0E+07			1.0E+08		
Species	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle
O3	1.3E-33	3.8E-23	2.3E-22	1.3E-27	3.0E-17	9.5E-17	3.3E-19	5.4E-10	5.6E-09	1.4E-25	3.1E-28	7.8E-09	1.1E-38	7.4E-30	7.8E-09
C2N	2.2E-09	1.3E-23	1.1E-22	5.3E-09	2.0E-21	2.6E-20	6.8E-11	8.9E-19	1.3E-17	1.1E-16	8.4E-26	1.6E-17	1.0E-16	1.1E-26	1.6E-17
C2O	8.8E-41	1.3E-33	1.2E-32	1.8E-36	2.4E-29	1.0E-28	4.8E-32	4.7E-26	8.6E-25	9.9E-39	3.3E-36	1.2E-24	9.1E-43	5.0E-37	1.2E-24
C2S	3.4E-10	6.8E-13	1.6E-11	3.1E-10	2.6E-13	4.9E-11	1.4E-11	8.5E-13	6.5E-11	1.1E-20	8.4E-22	7.1E-11	7.0E-21	4.1E-21	7.1E-11
NAOH	4.6E-17	1.9E-19	1.2E-18	3.2E-15	3.4E-17	6.3E-16	7.3E-16	5.9E-17	3.1E-15	3.6E-22	1.0E-16	3.8E-15	4.9E-29	1.0E-16	3.8E-15
OCN	3.1E-11	1.8E-25	1.1E-24	7.9E-10	2.8E-22	2.2E-21	1.7E-10	2.1E-18	3.1E-17	1.8E-24	2.4E-24	3.8E-17	1.7E-24	2.8E-26	3.8E-17
CO2	8.6E-11	3.5E-13	2.4E-12	5.7E-09	5.8E-11	8.7E-10	2.9E-09	2.2E-10	7.9E-09	6.2E-21	5.1E-11	9.7E-09	6.6E-21	5.0E-11	9.7E-09
OCs	2.4E-09	1.2E-23	9.9E-23	1.2E-08	3.6E-21	3.8E-20	5.1E-10	7.7E-18	1.1E-16	7.6E-23	1.2E-28	1.3E-16	5.8E-23	3.7E-31	1.3E-16
SO2	2.4E-12	2.4E-13	2.6E-12	3.2E-11	6.6E-12	1.3E-10	2.6E-12	9.2E-12	7.9E-10	4.2E-26	3.4E-12	8.5E-10	4.2E-26	3.4E-12	8.5E-10
CH3	4.3E-09	6.9E-19	2.2E-17	7.2E-09	3.0E-18	1.1E-16	3.0E-08	3.2E-16	1.9E-15	2.9E-09	4.0E-18	7.2E-15	2.9E-09	5.6E-19	7.2E-15
NH3	1.9E-09	2.4E-07	1.1E-05	1.2E-08	2.8E-07	2.7E-05	5.5E-09	5.7E-09	3.8E-05	9.8E-09	6.1E-08	3.8E-05	1.1E-08	6.8E-08	3.8E-05
SiH3	2.2E-38	8.8E-23	1.5E-21	1.4E-36	3.6E-21	4.6E-20	4.1E-32	2.7E-17	2.5E-16	1.6E-39	3.4E-26	3.8E-16	3.2E-52	9.5E-38	3.8E-16
C2H2	1.4E-07	1.8E-15	2.5E-14	1.4E-07	7.6E-14	1.1E-12	3.5E-08	7.4E-10	4.7E-09	9.5E-13	1.9E-15	1.1E-08	8.9E-13	2.4E-16	1.1E-08
N2H2	1.2E-13	2.6E-11	3.7E-10	1.3E-11	8.1E-10	1.4E-08	2.2E-09	1.1E-07	1.5E-06	1.2E-11	6.9E-09	2.3E-06	4.3E-13	2.4E-10	2.3E-06
H2O2	4.5E-25	7.3E-15	6.9E-14	4.4E-22	4.1E-12	3.1E-11	6.0E-17	1.0E-07	9.0E-07	3.2E-24	8.3E-20	1.5E-06	1.6E-29	1.1E-20	1.5E-06
H2S2	7.0E-16	2.2E-18	1.2E-17	2.7E-14	2.2E-16	4.3E-15	7.7E-15	5.1E-16	2.4E-14	9.1E-26	2.7E-17	2.7E-14	9.0E-26	2.6E-17	2.7E-14
CH2N	8.8E-36	3.4E-31	3.5E-30	8.2E-32	2.9E-27	1.4E-26	1.1E-23	4.3E-20	4.1E-19	1.5E-28	2.6E-25	5.6E-19	1.0E-30	2.0E-27	5.6E-19
CHNH	1.5E-31	4.3E-29	4.4E-28	7.1E-28	1.3E-25	9.5E-25	3.2E-26	5.9E-25	2.9E-23	1.5E-28	2.0E-27	3.8E-23	3.3E-30	4.9E-29	3.8E-23
H2CO	1.1E-08	1.2E-07	2.6E-06	4.3E-08	3.5E-07	1.6E-05	7.3E-09	5.6E-07	3.8E-05	1.9E-14	3.5E-07	4.4E-05	2.0E-14	3.4E-07	4.4E-05
CHOH	7.7E-26	1.5E-19	2.2E-18	9.7E-24	1.2E-17	1.3E-16	3.1E-19	8.9E-14	8.3E-13	1.8E-26	1.8E-21	1.2E-12	1.8E-27	2.4E-22	1.2E-12
HCCN	2.2E-32	1.3E-23	1.1E-22	1.1E-29	2.0E-21	2.6E-20	2.5E-26	8.9E-19	1.3E-17	9.9E-33	8.4E-26	1.6E-17	5.4E-34	1.1E-26	1.6E-17
HNCO	8.8E-41	1.3E-33	9.8E-13	5.3E-20	8.1E-12	1.4E-10	4.8E-32	4.7E-26	8.6E-25	1.2E-38	3.3E-36	1.2E-24	9.2E-43	5.0E-37	1.2E-24
C3H	7.9E-09	2.8E-22	4.9E-21	5.9E-09	5.1E-21	9.3E-20	1.1E-09	2.9E-20	8.2E-19	2.2E-16	6.6E-17	1.2E-18	1.8E-16	5.7E-27	1.2E-18
H2CS	3.9E-11	6.2E-12	3.9E-10	2.0E-10	2.4E-11	1.1E-09	9.5E-12	2.3E-11	2.4E-09	3.7E-18	1.1E-11	2.6E-09	2.3E-18	1.8E-11	2.6E-09
C3N	6.2E-09	3.3E-23	3.2E-22	6.4E-09	2.1E-21	3.0E-20	2.8E-10	3.2E-18	3.6E-17	3.3E-18	2.2E-27	5.0E-17	3.1E-18	2.8E-28	5.0E-17
C3O	1.2E-11	6.1E-26	6.3E-25	3.6E-11	1.1E-23	1.2E-22	3.1E-12	3.5E-20	3.7E-19	1.6E-23	1.0E-32	5.1E-19	1.3E-23	1.1E-33	5.1E-19
C3S	1.5E-10	1.2E-12	2.2E-11	1.1E-10	3.6E-12	1.7E-10	5.0E-12	4.3E-13	2.8E-10	3.5E-23	2.7E-13	2.9E-10	1.9E-23	2.7E-13	2.9E-10
CH4	1.5E-07	5.3E-07	3.4E-05	8.8E-07	1.1E-10	5.2E-05	1.3E-07	1.8E-08	5.4E-05	2.6E-09	3.6E-07	5.5E-05	2.6E-09	3.5E-07	5.5E-05
SiH4	7.8E-28	6.9E-11	2.0E-09	3.8E-27	1.1E-10	7.2E-09	1.2E-26	1.7E-10	1.4E-08	1.7E-26	1.7E-10	1.6E-08	1.7E-26	1.7E-10	1.6E-08
C2H3	9.4E-09	1.8E-21	2.4E-20	1.4E-08	7.9E-										

Table 2 – continued

t (yr)	1.0E+05			3.2E+05			1.0E+06			1.0E+07			1.0E+08		
Species	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle
CH3OH	8.7E-12	1.2E-07	2.6E-06	1.2E-10	3.5E-07	1.6E-05	7.0E-12	5.6E-07	3.8E-05	3.3E-16	3.4E-07	4.4E-05	3.4E-16	3.4E-07	4.4E-05
C3H3	3.3E-12	3.4E-22	5.7E-21	3.4E-11	9.0E-21	1.4E-19	1.8E-12	1.9E-16	1.0E-15	4.1E-19	3.0E-24	2.9E-15	3.9E-19	3.6E-25	2.9E-15
CH3CN	1.5E-11	1.1E-11	1.1E-10	4.5E-11	7.0E-11	3.0E-09	8.0E-13	7.2E-12	4.8E-09	3.8E-17	7.1E-13	4.8E-09	3.6E-17	7.6E-13	4.8E-09
H2C3N	1.7E-36	3.9E-23	3.7E-22	4.8E-34	3.8E-21	5.2E-20	2.4E-30	4.5E-18	5.1E-17	2.1E-36	3.0E-27	7.1E-17	5.0E-40	3.9E-28	7.1E-17
H2C3O	5.7E-27	4.6E-14	6.6E-13	1.6E-25	3.4E-13	1.1E-11	5.4E-25	2.3E-13	2.8E-11	1.4E-25	5.7E-14	2.9E-11	1.4E-25	5.7E-14	2.9E-11
C4H2	7.4E-10	4.1E-16	6.3E-15	2.4E-09	8.6E-15	1.5E-13	1.7E-10	1.3E-10	6.7E-10	1.1E-19	2.0E-20	2.0E-09	9.7E-20	2.0E-21	2.0E-09
C5H	2.9E-10	6.3E-23	1.1E-21	1.5E-10	5.6E-22	1.4E-20	9.6E-12	3.0E-21	8.4E-20	7.9E-24	7.7E-33	1.1E-19	6.2E-24	5.1E-33	1.1E-19
C6	1.8E-09	7.8E-24	1.1E-22	3.9E-10	9.3E-23	2.1E-21	1.8E-10	3.3E-22	1.1E-20	1.5E-24	2.7E-36	1.5E-20	1.1E-24	1.9E-36	1.5E-20
C5N	5.0E-10	2.2E-24	2.3E-23	3.4E-10	9.2E-23	1.5E-21	5.8E-12	5.5E-20	6.9E-19	1.3E-24	7.1E-34	9.1E-19	1.2E-24	8.7E-35	9.1E-19
CH3NH2	4.0E-12	1.9E-14	1.5E-13	7.0E-11	9.1E-13	2.3E-11	4.3E-12	7.6E-16	4.9E-15	6.5E-27	1.4E-20	1.1E-14	5.8E-27	1.3E-20	1.1E-14
C2H5	9.8E-29	2.8E-21	4.7E-20	5.0E-27	8.1E-20	1.2E-18	1.2E-22	7.6E-16	4.3E-08	9.8E-19	5.2E-09	8.2E-08	9.3E-19	5.2E-09	8.2E-08
C3H4	6.6E-12	2.7E-10	7.5E-09	9.9E-11	2.8E-10	2.6E-08	4.3E-12	1.0E-09	4.3E-08	2.9E-34	1.7E-26	1.7E-15	4.4E-39	1.7E-27	1.7E-15
C4H3	4.9E-35	3.5E-22	5.4E-21	2.3E-33	7.3E-21	1.3E-19	6.6E-29	1.1E-16	5.7E-16	1.1E-22	8.5E-14	1.7E-12	1.1E-22	9.6E-14	1.7E-12
CH3CHO	6.8E-14	2.7E-16	1.6E-15	1.5E-12	1.6E-14	3.9E-13	1.8E-13	2.9E-14	1.1E-12	1.1E-22	1.8E-22	4.3E-12	1.4E-21	2.4E-23	4.3E-12
H3C3N	2.3E-13	2.4E-18	2.2E-17	1.2E-11	2.3E-16	3.2E-15	4.2E-14	2.7E-13	3.1E-12	1.4E-21	1.8E-22	4.3E-10	2.0E-23	2.8E-25	2.3E-10
C5H2	5.1E-11	7.7E-17	1.4E-15	2.8E-10	8.8E-16	1.8E-14	1.0E-11	1.6E-11	8.3E-11	2.5E-23	3.0E-24	2.3E-10	7.8E-27	1.9E-36	1.6E-20
C6H	5.7E-11	8.1E-24	1.1E-22	6.1E-11	1.1E-22	2.4E-21	2.8E-12	3.4E-22	1.2E-20	1.1E-26	2.8E-26	1.6E-20	7.0E-27	1.9E-36	1.6E-20
HC5N	4.4E-11	2.9E-18	3.0E-17	1.4E-10	1.6E-16	2.5E-15	8.3E-13	6.6E-14	8.6E-13	5.9E-26	9.2E-28	1.1E-12	5.5E-26	1.1E-28	1.1E-12
C7	3.8E-10	1.5E-24	1.7E-23	1.4E-10	3.1E-23	6.6E-22	4.4E-11	8.0E-23	3.4E-21	2.8E-27	5.0E-39	4.3E-21	1.8E-27	3.2E-39	4.3E-21
H4C3N	2.8E-39	3.9E-23	3.7E-22	7.9E-37	3.8E-21	5.2E-20	3.8E-33	4.4E-18	5.0E-17	4.4E-39	3.0E-27	7.0E-17	8.3E-43	3.9E-28	7.0E-17
CH3C3N	4.7E-13	1.5E-15	8.5E-15	7.2E-12	6.5E-14	2.4E-12	2.9E-14	2.0E-15	3.4E-12	1.8E-24	1.6E-16	3.4E-12	1.5E-24	1.6E-16	3.4E-12
H2C5N	3.4E-45	2.4E-24	2.4E-23	5.4E-43	1.3E-22	2.0E-21	9.7E-40	5.3E-20	7.0E-19	8.8E-45	7.5E-34	9.2E-19	4.2E-54	9.1E-35	9.2E-19
C2H6	3.2E-18	1.4E-09	3.0E-08	2.3E-17	2.4E-09	1.6E-07	5.9E-17	4.3E-09	2.8E-07	3.9E-16	1.6E-08	4.0E-07	4.0E-16	1.7E-08	4.0E-07
C4H4	1.7E-24	2.7E-10	6.7E-09	8.1E-24	2.3E-10	2.5E-08	1.7E-23	5.9E-10	3.5E-08	1.9E-22	2.5E-09	5.8E-08	1.9E-22	2.5E-09	5.8E-08
C5H3	2.3E-41	6.4E-23	1.1E-21	5.8E-40	7.3E-22	1.5E-20	1.9E-35	1.4E-17	6.8E-17	2.4E-40	2.5E-30	1.9E-16	1.5E-48	2.3E-31	1.9E-16
C6H2	2.7E-10	1.1E-17	1.5E-16	6.1E-10	3.5E-16	6.0E-15	3.2E-11	2.1E-12	1.1E-11	2.8E-25	1.2E-27	3.1E-11	2.1E-25	1.2E-28	3.1E-11
C7H	1.4E-11	1.6E-24	1.7E-23	1.9E-11	3.5E-23	7.4E-22	5.8E-13	8.1E-23	3.6E-21	2.3E-29	5.1E-39	4.5E-21	1.5E-29	3.2E-39	4.5E-21
C8	1.2E-10	4.7E-25	3.9E-24	4.8E-11	9.9E-24	2.3E-22	1.4E-11	2.5E-23	9.9E-22	7.8E-30	1.4E-41	1.4E-21	4.7E-30	8.0E-42	1.4E-21
C7N	1.8E-11	6.7E-26	4.5E-25	3.1E-11	7.1E-24	1.2E-22	2.3E-13	1.9E-21	2.3E-20	9.4E-31	4.5E-40	3.2E-20	7.0E-31	4.6E-41	3.2E-20
CH3OCH3	3.0E-16	1.1E-18	5.8E-												

Table 2 – continued

t (yr)	1.0E+05			3.2E+05			1.0E+06			1.0E+07			1.0E+08		
Species	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle	Gas	Surface	Mantle
C9H2	1.9E-13	1.3E-19	1.1E-18	1.3E-12	3.5E-18	7.4E-17	9.5E-15	1.7E-14	8.5E-14	3.6E-36	7.4E-37	2.6E-13	2.3E-36	5.6E-38	2.6E-13
HC9N	8.8E-14	4.4E-21	2.7E-20	6.8E-13	4.6E-19	8.3E-18	1.3E-15	2.7E-17	4.1E-16	2.2E-38	4.2E-41	5.3E-16	1.6E-38	4.1E-42	5.3E-16
H3C7N	5.6E-44	5.5E-14	4.4E-13	4.4E-42	3.9E-13	2.1E-11	3.7E-42	1.6E-14	2.8E-11	1.2E-43	2.6E-15	2.8E-11	1.2E-43	2.6E-15	2.8E-11
H3C37N	6.5E-16	1.5E-18	6.6E-18	1.7E-14	1.2E-16	5.5E-15	1.5E-17	7.5E-19	6.8E-15	4.1E-37	4.9E-20	6.8E-15	3.1E-37	4.8E-20	6.8E-15
H2C9N	3.3E-63	3.4E-27	2.1E-26	1.9E-60	3.5E-25	6.5E-24	4.7E-58	2.1E-23	3.2E-22	5.8E-62	3.3E-47	4.1E-22	2.0E-82	3.2E-48	4.1E-22
C8H4	1.1E-42	4.1E-13	4.2E-12	2.1E-41	5.9E-13	5.5E-11	2.5E-41	5.2E-13	7.0E-11	1.6E-40	1.6E-12	9.4E-11	1.6E-40	1.6E-12	9.4E-11
C9H3	2.0E-59	1.0E-25	8.4E-25	2.5E-57	2.7E-24	5.8E-23	2.0E-53	1.4E-20	6.6E-20	6.8E-57	5.8E-43	2.1E-19	4.1E-76	4.4E-44	2.1E-19
C9H4	2.2E-48	7.6E-14	7.9E-13	3.6E-47	8.7E-14	9.2E-12	4.0E-47	7.1E-14	1.1E-11	9.2E-47	8.3E-14	1.4E-11	9.1E-47	8.3E-14	1.4E-11
H3C9N	6.9E-53	2.4E-15	1.8E-14	4.7E-51	1.1E-14	7.5E-13	3.4E-51	1.3E-16	9.1E-13	2.0E-53	1.2E-17	9.1E-13	2.0E-53	1.2E-17	9.1E-13
E	1.2E-07			4.5E-08			5.3E-08			2.7E-07			2.6E-07		
H+	3.5E-08			2.2E-09			1.5E-09			8.3E-08			7.3E-08		
HE+	1.2E-09			9.2E-10			2.8E-09			1.4E-08			1.4E-08		
C+	4.9E-08			9.7E-09			7.7E-09			4.8E-11			4.1E-11		
N+	7.2E-12			3.5E-12			4.6E-12			1.0E-11			1.2E-11		
O+	5.7E-15			1.1E-14			2.5E-14			6.6E-18			6.5E-18		
NA+	3.5E-09			2.7E-09			1.8E-09			2.8E-10			3.6E-17		
MG+	1.2E-08			9.0E-09			5.9E-09			5.0E-10			2.4E-19		
SI+	1.1E-09			5.4E-11			9.3E-12			9.4E-18			1.7E-28		
S+	6.2E-09			6.2E-10			9.8E-11			8.9E-14			5.1E-14		
FE+	5.8E-09			5.2E-09			4.8E-09			3.9E-09			6.1E-10		
O2+	1.0E-10			1.6E-10			1.2E-10			1.1E-20			9.4E-21		
CH+	1.5E-13			3.8E-14			2.9E-15			6.0E-16			4.8E-16		
SO+	2.1E-11			2.3E-11			6.4E-12			1.3E-19			7.5E-20		
H3+	1.5E-09			4.0E-09			2.0E-08			1.7E-07			1.7E-07		
CH2+	4.5E-13			7.6E-14			1.6E-14			1.8E-15			1.6E-15		
NH2+	3.7E-14			1.5E-14			1.5E-14			4.5E-13			4.6E-13		
HCO+	1.2E-09			6.8E-09			6.2E-09			3.4E-15			3.5E-15		
HOC+	1.3E-10			5.3E-10			4.3E-10			2.1E-16			2.1E-16		
N2H+	2.8E-14			2.3E-12			2.1E-11			1.2E-13			7.2E-15		
C2N+	1.4E-10			1.0E-10			1.1E-11			5.6E-17			5.0E-17		
HCS+	5.9E-11			3.2E-11			2.4E-11			4.2E-17			2.2E-17		
OCS+	1.8E-10			1.2E-10			4.7E-12			7.3E-25			3.6E-25		
H3O+	4.5E-10			1.2E-09			1.1E-09			2.2E-13			2.2E-13		
HCO2+	1.1E-14			3.6E-13			4.9E-13			2.0E-24			2.3E-24		
H2CN+	1.2E-11			7.6E-11			3.6E-11			1.8E-13			2.0E-13		
H3CO+	2.3E-12			6.6E-11			2.9E-11			1.1E-16			1.2E-16		
CH3+	3.4E-10			1.3E-10			2.7E-11			3.7E-12			3.3E-12		
NH3+	2.8E-12			1.8E-12			1.9E-12			3.6E-11			4.0E-11		
CH4+	1.1E-14			3.1E-15			1.5E-15			1.4E-15			1.3E-15		
NH4+	1.3E-11			4.2E-11			4.1E-11			1.4E-10			1.6E-10		
CH5+	1.6E-10			2.7E-10			1.0E-10			4.7E-12			4.7E-12		
C2H2+	1.8E-10			2.4E-11			7.2E-12			1.7E-15			1.5E-15		
C2H3+	6.8E-11			1.3E-10			4.3E-11			1.8E-15			1.7E-15		
C2H4+	1.8E-10			1.3E-10			5.6E-11			2.4E-15			2.2E-15		
C3H3+	3.9E-10			1.5E-10			4.8E-11			1.9E-17			1.6E-17		

Table 3. Abundances in the three-phase model with normal initial conditions divided by abundances in the two-phase model N(2100K,CR).

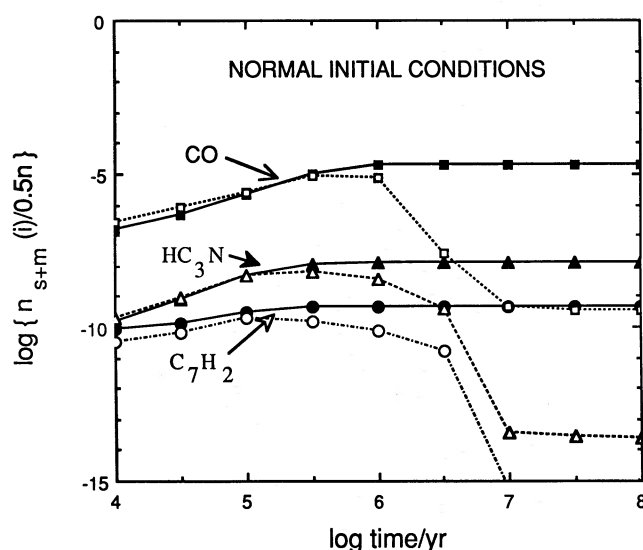
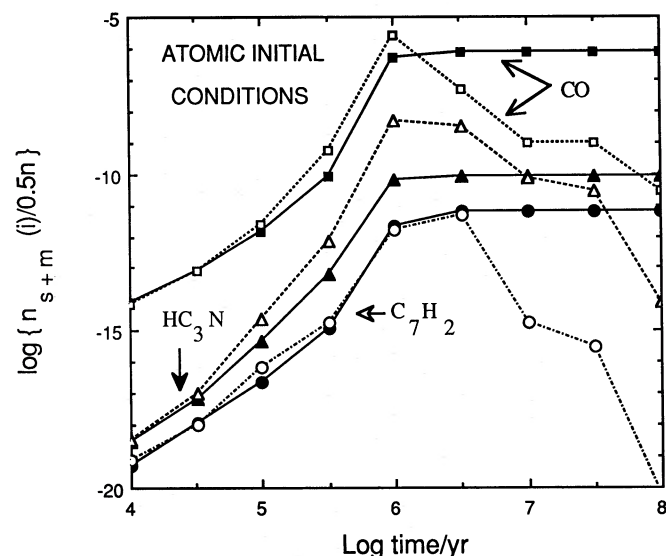
Species	Time (yr)			
	1(5)	3(5)	1(6)	1(7)
A. [Surface + Mantle] / Surface				
H	21.	31.	83.	1400.
H ₂	1.0	1.0	1.0	1.0
CO*	0.9	1.2	2.6	4.2(+4)
N ₂ *	0.3	0.4	0.6	1.9
H ₂ O	1.3	1.3	1.2	1.1
NH ₃	8.5	9.5	7.2	0.1
C ₂ H ₂ *	6.2	8.1	7.4	1.7(+4)
C ₃ N*	0.7	2.6	9.5	4.9(+5)
CH ₄	8.0	3.6	3.0	2.3
CH ₂ CN*	1.1	3.8	65.0	2.1(+5)
HC ₃ N*	0.9	1.6	3.4	3.4(+5)
C ₂ H ₆	2.7	2.5	2.2	1.7
H ₅ C ₃ N	0.9	0.7	0.6	0.5
C ₉ *	79.	2.0(+3)	5.6(+3)	4.3(+19)
B. Gas / Gas				
H	1.0	1.0	1.0	0.9
H ₂	1.0	1.0	1.0	1.0
CO	1.0	1.0	0.9	3.7(-3)
N ₂	0.8	0.5	0.1	3.5(-4)
H ₂ O	1.0	1.0	1.0	9.0(-3)
NH ₃	0.9	0.9	0.3	0.01
CH ₄	1.0	1.0	0.9	0.08

Notes: $a(b)$ refers to $a \times 10^b$; * refers to reactive species with abundance ratios that might be expected to be reproduced by equation (21).

efficient and slower gas-phase synthesis. Fig. 3 contains a comparison of the condensed-phase fractional abundances of CO, HC₃N and C₇H₂ for the three-phase and two-phase models with atomic initial conditions.

For gaseous species, the three-phase models tend to show smaller abundances at late times compared with previous two-phase models that include cosmic ray induced desorption (HH), due to the hampering of cosmic ray induced desorption in the former models. The gaseous chemistry at the so-called early times of $1-3 \times 10^5$ yr, during which complex molecules reach their peak abundances, is hardly affected by adding the mantle phase. In general, the good agreement between observations of gaseous molecules in cold sources and purely gas-phase model results at early times is not changed by the inclusion of condensed-phase chemistry in either two-phase or three-phase gas-grain models.

In Tables 4 and 5, we compare percentage abundances of the dominant surface + mantle species in our new models at a variety of times with the dominant surface species calculated in our previous two-phase models (HH). Table 4 contains results for the models with normal initial abundances and Table 5 contains results for the models with atomic initial abundances. The species are listed roughly in order of decreasing percentage abundance for the models with normal initial abundances. In addition, we list new results for

**Figure 2.** The total condensed-phase (surface + mantle) fractional abundances of the representative unsaturated molecules CO, HC₃N and C₇H₂ are plotted versus time for the three-phase (solid lines) and older two-phase (dotted lines) models with normal initial conditions. The three-phase model abundances reach steady-state values within a reasonably short period of time.**Figure 3.** The total condensed-phase (surface + mantle) fractional abundances of the representative unsaturated molecules CO, HC₃N and C₇H₂ are plotted versus time for the three-phase (solid lines) and older two-phase (dotted lines) models with atomic initial conditions. The three-phase model abundances reach steady-state values within a reasonably short period of time despite the fact that the formation of complex molecules is significantly slower than in the model with normal initial conditions.

four layers of the mantle formed during the time intervals $0-1 \times 10^5$, $1-3 \times 10^5$, $3-10 \times 10^5$ and $1-10 \times 10^6$ yr. These layers contain approximately 26(30), 34(34), 32(30) and 8(6) of the 100 individual monolayers of material, respectively, for the models with normal (and atomic) initial abundances.

Comparison between old and new total condensed-phase results indicates that in general little has changed regarding

Table 4. Composition of surface and mantle layers for normal initial conditions by percentage.

Time (yr)	Old N(2100K,CR)		Three-phase		Three-phase			
	Surface (Cumulative)		Surface + Mantle (Cumulative)		Mantle Layers (Differential)			
	3(+5)	1(+7)	3(+5)	1(+7)	0 - 1(+5)	1-3(+5)	3-10(+5)	1-10(+6)
% of final mantle	57	100	60	100	26	34	32	8
Species								
H ₂ O	55	55	61	56	64	61	47	47
H ₂ CO	3.4	12	8.7	12	7.5	9.9	17	21
CH ₃ OH	13	17	9.5	13	7.8	11	17	21
CO ₂	10	5.8	1.2	0.8	1.1	1.4	0.05	0.007
CO	4.2	1(-4)	4.7	5.1	2.1	6.7	7.3	0.9
HNCO	3.5	2.0	2.8	1.7	3.4	2.6	8(-4)	0.0
N ₂ H ₂	1.8	2.7	2.3	3.1	1.3	3.2	4.8	2.9
H ₂	2.0	1.1	1.7	1.0	0.0	0.0	0.0	0.0
HCN	2.9	1.6	1.6	1.0	2.6	1.0	0.01	0.02
HNC	0.1	0.08	0.9	0.6	1.5	0.5	0.002	0.007
CH ₄	0.9	1.1	3.0	2.3	5.0	1.6	0.7	2.4
NH ₃	0.004	0.8	0.04	0.1	0.06	0.02	0.05	0.6
CH ₃ NH ₂	0.08	0.05	0.6	0.4	0.9	0.3	0.02	0.2
C ₂ H ₆	0.3	0.3	0.6	0.5	1.3	0.2	0.07	0.5
O ₂	0.005	4(-7)	0.01	1.0	1(-5)	0.01	2.8	0.9
H ₂ O ₂	1(-4)	0.03	0.003	0.9	0.002	0.003	2.3	2.0
N ₂	1.4	0.3	0.5	0.6	0.1	0.8	0.8	0.06

Note: $a(b)$ refers to $a \times 10^b$.**Table 5.** Composition of surface and mantle layers for atomic initial conditions by percentage.

Time (yr)	Old A(2100K,CR)		Three-phase		Three-phase			
	Surface (Cumulative)		Surface + Mantle (Cumulative)		Mantle Layers (Differential)			
	3(+5)	1(+7)	3(+5)	1(+7)	0 - 1(+5)	1-3(+5)	3-10(+5)	1-10(+6)
% of final mantle	67	100	64	100	30	34	30	6
Species								
H ₂ O	61	61	60	57	62	60	53	48
H ₂ CO	5.8	10	5.6	9.8	2.0	8.7	17	20
CH ₃ OH	5.8	10	5.6	9.8	2.0	8.7	17	20
CO ₂	0.002	0.006	3(-4)	2(-3)	2(-6)	6(-4)	0.005	0.007
CO	2(-4)	2(-4)	3(-5)	0.2	1(-6)	5(-5)	0.4	0.9
HNCO	2(-4)	0.02	5(-5)	2(-4)	7(-7)	9(-5)	7(-4)	3(-4)
N ₂ H ₂	0.03	3.0	5(-3)	0.5	3(-4)	9(-3)	1.1	3.1
H ₂	1.4	0.9	1.4	0.9	0.0	0.0	0.0	0.0
HCN	0.04	0.3	0.01	0.01	0.006	0.02	0.02	0.02
HNC	0.008	0.07	7(-4)	0.002	3(-5)	0.001	0.003	0.005
CH ₄	18	12	18	12	25	12	1.4	2.3
NH ₃	7.7	1.1	9.3	8.4	8.6	10	8.2	0.6
CH ₃ NH ₂	0.001	0.3	8(-6)	0.02	1(-7)	2(-5)	0.007	0.2
C ₂ H ₆	0.04	0.1	0.05	0.09	0.02	0.08	0.09	0.4
O ₂	2(-5)	5(-8)	4(-6)	0.2	2(-8)	7(-6)	0.3	0.9
H ₂ O ₂	5(-5)	0.03	1(-5)	0.3	5(-8)	2(-5)	0.7	2.1
N ₂	5(-6)	0.4	8(-8)	0.01	3(-10)	1(-7)	0.02	0.06

Note: $a(b)$ refers to $a \times 10^b$.

the dominant species, although the CO abundance at late times in the new models is appreciably greater than in the old models, because of limited protection by the mantle against hydrogenation in the former. Outside the core, it is predicted that the dust particles will be dominated by water ice, with large abundances of other species such as methanol and formaldehyde. Although these predictions are independent of initial abundances (atomic or normal), other molecules possess abundances strongly dependent on initial abundances. For example, as expected, condensed-phase methane and ammonia are far more abundant in the model that com-

mences with atomic hydrogen, whereas condensed-phase CO is far more abundant until late times for the model that commences with molecular hydrogen. The sensitivity of abundances to initial conditions has been discussed in detail in our earlier papers (HHL; HH).

The layer-by-layer results indicate that water ice dominates in all layers, although other species can show sharp variations. Other than the actual dust particle surfaces, in which molecular hydrogen has a high abundance, the layers provide a polar environment.

3.1 Three-phase model without HN_2

As discussed in Section 2, HN_2 may have only a fleeting existence. We have run one model with normal initial conditions in which this important molecule was effectively removed by exclusion of reaction (11) and insertion of a rapid rate, $3 \times 10^8 \text{ s}^{-1}$, for the unimolecular decomposition of HN_2 into H and N_2 . The results show that, with the effective removal of HN_2 as a surface scavenger of H, the surface atomic hydrogen abundance increases strongly, specifically by 2 orders of magnitude through 10^6 yr . The condensed-phase molecular abundances move closer, on the whole, to the abundances obtained in the model with atomic initial conditions, which contains large surface abundances of H at early times. This result is similar to that obtainable in two-phase models when HN_2 is effectively removed from the reaction network. Surface species that are depleted principally by reaction with atomic hydrogen have lowered abundances in all models without HN_2 . The enhancement in abundance due to mantle protection is the same as in models with surface HN_2 , but the overall condensed-phase abundances are still lower by roughly 2 orders of magnitude than in our previous model with normal initial conditions. An important example is condensed-phase CO. Other examples are unsaturated condensed-phase complex molecules, which are produced in the gas and depleted via reaction with atomic hydrogen. Surface molecules, such as C_n and C_nH , that are depleted principally by hydrogenation with H_2 are unaffected by the increased surface atomic hydrogen. Saturated condensed-phase molecules, such as NH_3 and CH_4 , have increased abundances. Finally, the gas-phase

Table 6. Surface+mantle abundances in the three-phase model with normal initial conditions but without HN_2 divided by analogous abundances in the previous three-phase models containing HN_2 .

Species	Time (yr)-----			
	1(5)	3(5)	1(6)	1(7)
A. Normal Initial Conditions Without HN_2 / Normal Initial Conditions With HN_2				
H	9(+1)	2(+2)	1(+2)	9.
CO	1(-2)	1(-2)	1(-2)	1(-2)
NH_3	2(+2)	3(+2)	3(+2)	1(+2)
HC_3N	2(-2)	2(-2)	2(-2)	2(-2)
C_4H_2	2(-2)	2(-2)	2(-2)	2(-2)
C_2H_6	1(-1)	2(-1)	3(-1)	3(-1)
HC_7N	3(-2)	2(-2)	2(-2)	2(-2)
$\text{C}_2\text{H}_5\text{CN}$	2.	2.	2.	2.
C_9	1.	1.	1.	1.
B. Normal Initial Conditions Without HN_2 / Atomic Initial Conditions With HN_2				
H	1(-4)	4(-3)	1(+2)	1(+1)
CO	2(+4)	1(+3)	3(-1)	3(-1)
NH_3	1.	9(-1)	1.	1.
HC_3N	2(+5)	3(+3)	4.	3.
C_4H_2	5(+4)	3(+3)	7(-1)	3(-1)
C_2H_6	5.	2.	1.	1.
HC_7N	2(+6)	1(+4)	6(+1)	5(+1)
$\text{C}_2\text{H}_5\text{CN}$	3(+1)	4.	3.	3.
C_9	3(+4)	8(+2)	2(+2)	2(+2)

Note: $a(b)$ refers to $a \times 10^b$.

abundances are mainly unaffected. Table 6 contains a comparison of condensed-phase abundances for selected molecules in the model without HN_2 and analogous abundances in the HN_2 -containing previous model with normal initial conditions. A comparison with condensed-phase abundances in the HN_2 -containing previous model with atomic initial conditions is also provided, and shows that the abundances of unsaturated molecules are still significantly larger in the present model, especially at early times.

At higher temperatures than 10 K, hydrogen atoms desorb more rapidly from grain surfaces and, if other rate processes such as rapid reactions can be ignored, this should lower the surface atomic hydrogen abundance. We have run models at temperatures up to 15 K in order to determine whether slightly higher temperatures moderate the effective removal of HN_2 in the 10 K model by reducing the surface atomic hydrogen abundance. We have found, however, that surface hydrogen tends to increase slightly in abundance as the temperature is increased at times of $3 \times 10^4 \text{ yr}$ and later.

4 CONCLUSIONS

As discussed in LHH and HH, our gas-grain model results for non-star-forming regions can best be compared with condensed-phase observations of foreground sources where temperatures are not raised by the influence of the background infrared continuum. This restriction effectively limits the comparison to the strongly absorbing condensed-phase molecules CO, H_2O and possibly CH_4 (HHL; HH). However, in order to consider a wider variety of condensed-phase observations, we have also compared our condensed-phase abundances with so-called ‘typical’ interstellar condensed-phase abundances from a variety of sources, both warm and cold (Tielens 1989). In these comparisons, we have restricted attention to times before 10^6 yr , because, even with cosmic ray induced desorption, we are not able to maintain significant gas-phase abundances for many species in our models past this time. In general, condensed-phase abundances are satisfactorily reproduced by 10-K two-phase models with normal initial conditions and surface HN_2 at early times, although there are some glaring exceptions (HHL; HH). The three-phase model results do not show significant changes from past results at early times. Table 7 compares observed condensed-phase abundances of CO, H_2O and CH_4 for the Taurus complex, in which background stars are used as the infrared continua, and for 7538 IRS9, with results of the three-phase models, both including and removing surface HN_2 . Total condensed-phase model abundances are obtained by summing $n_s(i)$ and $n_m(i)$ values. Specifically, the comparison is made for the ratios of the abundances of condensed-phase CO to gaseous CO, condensed-phase CO to gaseous H_2 , condensed-phase CO to condensed-phase H_2O , and condensed-phase CH_4 to condensed-phase CO. Once again, the model with normal initial conditions and surface HN_2 provides a reasonable fit to the data at early times. The model with atomic initial conditions produces orders of magnitude too little condensed-phase CO at early times and perhaps 1 order of magnitude too much CH_4 , due to the dominance of hydrogenation reactions on grain surfaces. The model with normal initial conditions and no surface HN_2 , while somewhat better than the model with atomic initial conditions at

Table 7. Comparison with condensed-phase observations of quiescent regions.

	$\frac{[n_s(\text{CO}) + n_m(\text{CO})]}{n(\text{CO})}$	$\frac{[n_s(\text{CO}) + n_m(\text{CO})]}{n(\text{H}_2)}$	$\frac{[n_s(\text{CO}) + n_m(\text{CO})]}{[n_s(\text{H}_2\text{O}) + n_m(\text{H}_2\text{O})]}$	$\frac{[n_s(\text{CH}_4) + n_m(\text{CH}_4)]}{[n_s(\text{CO}) + n_m(\text{CO})]}$
Observations				
Taurus ^a	0.25	2.9(-5)	0.2	---
7538IRS9 ^b	0.10	---	0.24	0.13
Normal Initial Conditions				
1(+5) yr	0.033	2.2(-6)	0.034	2.27
3(+5) yr	0.18	1.1(-5)	0.076	0.65
1(+6) yr	1.47	1.9(-5)	0.095	0.40
1(+7) yr	4.9(+6)	2.0(-5)	0.095	0.44
Normal Initial Conditions without N₂H				
1(+5) yr	4.2(-4)	2.8(-8)	3.7(-4)	8.7(+2)
3(+5) yr	2.0(-3)	1.2(-7)	7.6(-4)	2.8(+2)
1(+6) yr	0.015	1.9(-7)	8.2(-4)	1.8(+2)
1(+7) yr	5.4(+4)	1.9(-7)	7.9(-4)	1.9(+2)
Atomic Initial Conditions				
1(+5) yr	3.2(-8)	1.4(-12)	1.6(-8)	2.5(+7)
3(+5) yr	1.6(-6)	8.8(-11)	5.1(-7)	5.9(+5)
1(+6) yr	0.046	5.5(-7)	2.3(-3)	9.8(+1)
1(+7) yr	1.9(+5)	7.4(-7)	2.8(-3)	7.5(+1)

Note: $a(b)$ refers to $a \times 10^b$. ^aWhittet & Duley (1991); see discussion in HHL. ^bLacy et al. (1991); Mitchell et al. (1990).

$t < 10^6$ yr, still shows far too little CO and somewhat too much CH₄. All models correctly produce copious amounts of condensed-phase water. The CO problem is serious, since condensed-phase CO is a prominent and widespread interstellar molecule. Assuming the basic validity of our surface chemical network, there are two possible explanations of the divergence between observed CO abundances and our results in the absence of HN₂. First and most simply, HN₂ may well exist on grain surfaces and within grain mantles. Secondly, the activation energy of the hydrogenation reaction



currently set at 1000 K based on rather old gas-phase measurements (Wang, Eyre & Derfman 1973), may be somewhat low; a new determination would be helpful. Of course, too large an activation energy would interfere with the surface synthesis of methanol, which is known to be abundant in the condensed phase (Skinner et al. 1992), and which is produced efficiently in all of our 10-K models as well as in our model of the Orion Compact Ridge (Caselli et al. 1993).

Detailed observations of condensed-phase CO (Tielens et al. 1991; Whittet & Walker 1991) show that the CO feature splits into two components – a narrow line, indicating a non-polar environment, and a broad line, indicating a polar environment. Our model results for both atomic and normal initial conditions cannot reproduce this effect. In essence, as depicted in Tables 4 and 5, all layers investigated show a high abundance (≥ 50 per cent) of polar water ice. (The actual surface, with a large abundance of H₂, represents the only exception, but it is a trivial one since it contains so little material.) The theoretical result stems from the existence of several surface pathways for water production, one that proceeds via standard H-atom hydrogenation, and others that

proceed via ozone and HNO production, so that water is produced efficiently under both H-rich and H₂-rich conditions. If the second set of pathways was eliminated, the production of condensed-phase water would show the same strong dependence on H/H₂ abundances as shown by ammonia and methane.

The low-temperature (10-K) thermal grain chemistry studied here is in general strongly dependent on the atomic hydrogen surface abundance, so that the initial conditions, as well as the abundances of surface hydrogen scavengers such as HN₂, play key roles in the determination of the abundances of heavy species. The chemistry is also strongly dependent on the molecular hydrogen surface abundance. Is this view of surface chemistry at 10 K obviously the correct one? It appears to rely on significant sticking rates for H and H₂ on cold grains, followed by the ability of both H and H₂ to migrate rapidly. Both of these assumptions can be attacked (Brown 1990). We have shown, however, that a reduction of the H₂ sticking efficiency must be dramatic to have even a limited effect (HH). This is also true for atomic hydrogen, mainly because the lowered sticking efficiency leads to larger gas-phase abundances, which tend to maintain the actual deposition rate. The idea of reduced H and H₂ surface mobilities seems more promising (Smoluchowski 1983; Brown 1990), but a reduced mobility for surface H will lead to a smaller destruction rate, increasing the overall surface abundance and tending to maintain the same overall hydrogenation rate. The inclusion of chemisorption traps or ‘active sites’, especially for H atoms (Hollenbach & Salpeter 1971; Mendoza & Ruetten 1989), can be an efficient way to reduce the role played by hydrogenation. Traps can be included in our models by allowing only a fraction of the surface H atoms to be fully mobile, although all H atoms would still be considered reactive. Another idea for reducing the relative

importance of surface H and H₂ is the suggestion (Brown 1990) that the exothermic products of surface reactions can use at least some of the energy to migrate non-thermally, thus increasing their reactivity. We hope to test some of these ideas in the future.

At present, our model does not allow us to vary the temperature of the dust grains while the chemistry is occurring. We are presently working to incorporate such temperature variation into our gas-grain code. This capability will enable us to study gas and surface chemistry under conditions of changing temperature which pertain, for example, to expanding circumstellar shells and evolutionary interstellar clouds.

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