Ch/Ge128 – Problem Set #2
Due May 15th, 2003

(1) Can the reaction sequence

\[
C^+ + H \rightarrow CH^+ + h\nu \quad k = 10^{-16} \text{ cm}^3\text{s}^{-1}
\]

\[
CH^+ + H \rightarrow C^+ + H_2 \quad k = 10^{-12} \text{ cm}^3\text{s}^{-1}
\]

compete with grain synthesis as a production mechanism for H\textsubscript{2}? What are the relative rates for the above process and grain formation?

(3) Derive an expression for the relative rates of formation of OH by the two mechanisms below at T=100 K. Which mechanism is faster?

\[
H + \text{cosmic ray} \rightarrow H^+ + e^- \quad \Gamma_1 = 10^{-17} \text{ s}^{-1}
\]

\[
H^+ + O \rightarrow O^+ + H \quad k_1 = 10^{-9} e^{-232/T} \text{ cm}^3\text{s}^{-1}
\]

\[
O^+ + H_2 \rightarrow OH^+ + H \quad k_2 = 10^{-9} \text{ cm}^3\text{s}^{-1}
\]

\[
OH^+ + H_2 \rightarrow H_2O^+ + H \quad k_3 = 10^{-9} \text{ cm}^3\text{s}^{-1}
\]

\[
H_2O^+ + H_2 \rightarrow H_3O^+ + H \quad k_4 = 10^{-9} \text{ cm}^3\text{s}^{-1}
\]

\[
H_3O^+ + e^- \rightarrow OH + 2H \quad k_5 = 10^{-6} \text{ cm}^3\text{s}^{-1}
\]

\[
H + e^- \rightarrow H^- + h\nu \quad k_6 = 10^{-18} T \text{ cm}^3\text{s}^{-1}
\]

\[
H^- + O \rightarrow OH + e^- \quad k_7 = 1 \times 10^{-9} \text{ cm}^3\text{s}^{-1}
\]

\[
H^- + h\nu \rightarrow H + e^- \quad \Gamma_2 = 10^{-7} \text{ s}^{-1}
\]

Assume \(n(H_2) = n(H), n(e^-) = 10^{-4} n(H)\) and that the reactions in mechanism 1 are the only production and loss mechanisms for the species involved. Prove that \(H^+ + O\) is faster than \(H^+ + e^-\) and that the major loss process for \(H^-\) is photodetachment (vs. reaction with O atoms). When evaluating such steady state expressions numerically, it’s always helpful to compare orders of magnitude in the individual rates first, as a single process is often rate limiting.

(4) Using the expression

\[
(D/H)_{\text{molecule}} = \frac{g k_x n(\text{HD})}{k_x n(H_2)b + k_M n(M) + k_e n(e)}
\]

(see p. 179 of Duley and Williams), where \(g=\)the statistical factor, \(k_x=\)the deuterium exchange rate (p. 177 Duley and Williams), \(k_M=\)the reaction rate of deuterated ions with neutrals, and \(b = e^{-\Delta E/kT}\) where \(\Delta E=\)the deuterium exchange reaction exothermicity, calculate \(n(\text{CH}_3\text{D})/n(\text{CH}_4)\) in dark clouds – assuming that these molecules are formed by the reaction

\[
\text{CH}_3^+ + \text{HD} \rightarrow \text{CH}_2\text{D}^+ + \text{H}_2 + \Delta E,
\]

that \(g=1/5\), and that the other parameters are as in Figure 8.5 of Duley and Williams. Show also that this ratio is independent of temperature for \(T < 25 \text{ K}\).
(5) Solve the time-dependent rate equation for the number density $n(AB)$ of the molecule AB formed and destroyed by

$$A + B \rightarrow AB \quad k_1 \text{cm}^3s^{-1}$$

$$AB \rightarrow A + B \quad k_2 s^{-1} \quad \text{(rate)}$$

$$AB + C \rightarrow A + B + C \quad k_3 \text{cm}^3s^{-1}$$

Assume that $n(AB)$ is small, that $n(A)$, $n(B)$, and $n(C)$ are constant, and that $n(AB)$ is initially zero.

Show that the time scale for $n(AB)$ to approach the equilibrium value is on the order of $t_{eq}$, where

$$t_{eq} = [k_2 + k_3n(C)]^{-1}$$

Evaluate $t_{eq}$ for

(i) Diffuse cloud: $k_2=10^{-10}, k_3=10^{-9}, n(C)=10^{-2} \text{cm}^{-3}$,

(ii) Dense cloud: $k_2=0, k_3=10^{-9}, n(C)=10^{-5} \text{cm}^{-3}$

(6) As you know, NH$_3$ is difficult to produce via gas-phase reactions. Grain surface chemistry is often invoked to explain the observed ammonia abundance in dark clouds. The following reaction sequence is an abbreviated description of nitrogen chemistry on grains:

$$N + \text{ grain} \rightarrow N - \text{ grain} \quad \text{(physisorption)}$$

Catalyzed by the grain:

$$N + N \rightarrow N_2$$

$$N + C \rightarrow CN$$

$$N + H \rightarrow NH$$

$$NH + H \rightarrow NH_2$$

$$NH_2 + H \rightarrow NH_3$$

$$N + NH \rightarrow N_2H$$

$$N + NH_2 \rightarrow N_2H_2$$

(a) Assume that the nitrogen chemistry is completely described by the above reactions. Plot the total gas plus grain abundances of N, N$_2$, and NH$_3$ versus time, using sticking coefficients of unity and no desorption. You may assume that at $t = 0$, all N is atomic and in the gas phase. Also, $n(N)_c \sim 10^{-4}n_{\text{total}}$, and $n_{\text{grain}} \sim 10^{-12}n_{\text{total}}$. Start by writing an equation for the abundance of atomic N on grains as a function of time.

(b) Qualitatively, how could you boost the proportional amount of N$_2$ produced?