Ch/Ge128 – Problem Set #2
Due May 5th, 2005

(1) Can the reaction sequence
\[
\begin{align*}
C^+ + H &\rightarrow CH^+ + h\nu \quad k = 10^{-16} \text{ cm}^3\text{s}^{-1} \\
CH^+ + H &\rightarrow C^+ + H_2 \quad k = 10^{-12} \text{ cm}^3\text{s}^{-1}
\end{align*}
\]
compete with grain synthesis as a production mechanism for H\(_2\)? 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?
\[
\begin{align*}
\text{H} + \text{cosmic ray} &\rightarrow \text{H}^+ + e^- \quad \Gamma_1 = 10^{-17} \text{ s}^{-1} \\
\text{H}^+ + \text{O} &\rightarrow \text{O}^+ + \text{H} \quad k_1 = 10^{-9} e^{-232/T} \text{ cm}^3\text{s}^{-1} \\
\text{O}^+ + \text{H}_2 &\rightarrow \text{OH}^+ + \text{H} \quad k_2 = 10^{-9} \text{ cm}^3\text{s}^{-1} \\
\text{OH}^+ + \text{H}_2 &\rightarrow \text{H}_2\text{O}^+ + \text{H} \quad k_3 = 10^{-9} \text{ cm}^3\text{s}^{-1} \\
\text{H}_2\text{O}^+ + \text{H}_2 &\rightarrow \text{H}_3\text{O}^+ + \text{H} \quad k_4 = 10^{-9} \text{ cm}^3\text{s}^{-1} \\
\text{H}_3\text{O}^+ + e^- &\rightarrow \text{OH} + 2\text{H} \quad k_5 = 10^{-6} \text{ cm}^3\text{s}^{-1} \\
\text{H} + e^- &\rightarrow \text{H}^- + h\nu \quad k_6 = 10^{-18}T \text{ cm}^3\text{s}^{-1} \\
\text{H}^- + \text{O} &\rightarrow \text{OH} + e^- \quad k_7 = 1 \times 10^{-9} \text{ cm}^3\text{s}^{-1} \\
\text{H}^- + h\nu &\rightarrow \text{H} + e^- \quad \Gamma_2 = 10^{-7} \text{ s}^{-1}
\end{align*}
\]

Assume \(n(\text{H}_2) = n(\text{H}), n(e^-) = 10^{-4} n(\text{H})\) and that the reactions in mechanism 1 are the only production and loss mechanisms for the species involved. Prove that \(\text{H}^+ + \text{O}\) is faster than \(\text{H}^+ + e^-\) and that the major loss process for \(\text{H}^-\) 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
\[
(D/H)_{\text{molecule}} = \frac{g k_x n(\text{HD})}{k_x n(\text{H}_2)b + k_M n(M) + k_e n(e)}
\]
(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 \(T <25\) K.
(5) Solve the time-dependent rate equation for the number density \( n(AB) \) of the molecule AB formed and destroyed by

\[
A + B \rightarrow AB \quad k_1 \text{ cm}^3\text{s}^{-1} \\
AB \rightarrow A + B \quad k_2 \text{ s}^{-1} \quad \text{(rate)} \\
AB + C \rightarrow A + B + C \quad k_3 \text{ cm}^3\text{s}^{-1}
\]

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

\[
t_{eq} = [k_2 + k_3 n(C)]^{-1}
\]

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:

\[
\begin{align*}
N + N &\rightarrow N_2 \\
N + C &\rightarrow CN \\
N + H &\rightarrow NH \\
NH + H &\rightarrow NH_2 \\
NH_2 + H &\rightarrow NH_3 \\
N + NH &\rightarrow N_2H \\
N + NH_2 &\rightarrow N_2H_2
\end{align*}
\]

(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, \( n(N)_{\text{g}} \sim 10^{-4} n_{\text{total}} \), 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?