1. The species we're trying to make is H₂:

\[
\frac{d[H_2]}{dt} = 10^{-12} [CH^+] [H]
\]

- and

\[
\frac{d[CH^+]}{dt} = 10^{-14} [C^-] [H] - 10^{-12} [CH^+] [H]
\]

If we assume steady state for CH⁺ \( \Rightarrow \) \( \frac{d[CH^+]}{dt} = 0 \)

\[ [CH^+] = 10^6 [C^-] \]

\[
\frac{d[H_2]}{dt} = 10^{-16} [C^-] [H]
\]

You showed in problem #1 that almost all carbon is ionized, so:

\[
\frac{[C^-]}{[H]} = \frac{[C^-]}{[H]} \approx 10^{-4}
\]

\[
\frac{d[H_2]}{dt} = 10^{-20} [H_2] \text{ cm}^3 \text{ s}^{-1}
\]

From class, grain formation of H₂ is

\[
(\frac{d[H_2]}{dt})_{\text{grain}} = \text{Rate (gas)}
\]

and

\[
\text{Rate (gas)} = 3 \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}
\]

so,

\[
\frac{\text{Rate (gas)}}{\text{Rate (grain)}} = \frac{10^{-20}}{3 \times 10^{-17}} = 3 \times 10^4
\]

grain formation of H₂ is much more efficient
2. We are interested in the rate of formation of OH:

Mechanism (1):

\[ \frac{d[OH]}{dt} = k_1 [H_3O^+] [e^-] \]

\[ \rightarrow \quad \frac{d[H_3O^+]}{dt} = 0 = k_5 [H_3O^+] [H_2] - k_3 [H_3O^+] [e^-] \]

(assume steady state for all species except OH)

\[ \Rightarrow [H_3O^+] = \frac{k_3 [H_3O^+] [H_2]}{k_5 [e^-]} \]

\[ \frac{d[OH]}{dt} = k_4 [H_2O^+] [H_2] \]

If you continue this substitution procedure assuming steady state, you end up with

\[ \frac{d[OH]}{dt} = [H] \]

(Actually, since the reactions given are the only production/loss mechanisms for the species, and in steady state, you know that all the intermediate steps will cancel.)

Mechanism (2):

\[ \frac{d[OH]}{dt} = k_2 [H] [O] \]

\[ \rightarrow \quad \frac{d[H]}{dt} = k_6 [H] [e^-] - k_7 [H] [O] - [H] \]

\[ [H] = \frac{k_6 [H] [e^-]}{k_7 [O]} \]

so:

\[ \frac{d[OH]}{dt} = \frac{k_6 [H] [e^-] * k_7 [O]}{k_7 [O]} \]

Before we evaluate these expressions, let's do the next part of the problem 1°. (It will make the 2nd expression a little simpler.)

Loss of H:

a) \[ \frac{d[H]}{dt} = [H] = 10-7 [H] \]
b) \( \frac{d[H]}{dt} = k[H][O] \)

So the relative rates are

\[
\frac{\text{photodetachment}}{\text{reaction with O}} = \frac{10^7}{k_7[O]} \sim \frac{10^7}{10^{29}10^{10}} \sim 10^4
\]

So photodetachment is much more important as a loss mechanism for H.

So, Mechanism(1): \( \frac{d[OH]}{dt} = [H] \)

Mechanism(2): \( \frac{d[OH]}{dt} = \frac{k_6k_7[O][H][e^-]}{k_7[O]} \sim \frac{k_6k_7[O][H][e^-]}{k_7[O]} \)

\[
(2) \quad k_6k_7[O][e^-] \quad 10^{15} \times 10^{16} \times 10^{16} \times (10^{15} \times 10^{15}) \times (10^{15} \times 10^{12})
\]

So mechanism (1) is \( \sim 10^5 \) times more efficient at producing OH.

Finally,

\[
\begin{align*}
\text{H}^+ + O & \rightarrow O^+ + H & k = 10^4 \times e^{-222000} = 9.8 \times 10^{11} \sim 10^{36} \\
\text{H}^+ + e^- & \rightarrow H + h & k = 10^{12} \text{ (same as He}^+ + e^- \text{ in notes)}
\end{align*}
\]

Since \( \text{H}^+ \) will react with O faster than \( e^- \), and \( [O]/[e^-] \sim 1 \), mechanism (1) will go on once \( \text{H} + \text{C.R.} \) happens.
3. The fractionation equation is:

\[
\frac{[\text{CH}_3\text{D}]}{[\text{CH}_4]} = \frac{g \lambda e_{[\text{HD}]}}{[\text{H}_2] k_i e^{-T/k} + k_a [\text{M}] + k_e [e]}
\]

Typical values for some of the variables above are, from Duley & Williams:

- \(k_i - k_a \sim 10^9 \text{ cm}^3 \text{ s}^{-1}\)
- \(k_e \sim 10^6 \text{ cm}^3 \text{ s}^{-1}\)
- \([\text{H}_2] \sim \frac{1}{2} n_{\text{total}}\)
- \([\text{M}] \sim 10^{-1} n_{\text{total}}\)
- \([\text{HD}] \sim 2 \times 10^{-5} n_{\text{total}}\)
- \(E \sim 100 \text{ K}\)

We are given \(g \sim 1/5\) and \([e]\) for dense clouds is \(\sim 10^{-7} [\text{H}_2]\)

\[
\Rightarrow \frac{[\text{CH}_3\text{D}]}{[\text{CH}_4]} = \frac{1/5 \times 10^9 \times 2 \times 10^5 n_{\text{total}}}{0.5 n_{\text{total}} + 10^{-7} e^{-7 + 10^9 \times 10^5 n_{\text{total}} + 10^5 \times 10^7 n_{\text{total}}} e^-}
\]

at 10 K:

\[
\frac{[\text{CH}_3\text{D}]}{[\text{CH}_4]} \sim 0.02
\]

The only temperature dependant term is the 1st one in the denominator, and if \(T \cdot 12\text{K}\), it is relatively small compared to the other terms.

Note that the amount of fractionation is independent of total number density here.

\(\text{CH}_3\text{D}\) has a small dipole moment (\(\sim 0.026\) Debye), and thus it has a rotational spectrum and can be observed.
4. Time rate-of-change of $[AB]$

$$\frac{d[AB]}{dt} = k_1[AB] - [AB] (k_2 + k_3[C])$$

$\frac{d[AB]}{[AB] (k_2 + k_3[C]) - k_1[AB]} = dt$  \hspace{1cm} (in the form $dx/(Ax+B) = dt$)

$$\ln \left[ \frac{[AB] (k_2 + k_3[C]) - k_1[AB]}{(k_2 + k_3[C])} \right] = t + \text{const.}$$

And with $[AB]_{t=0} = 0$ :

$$\frac{\ln(-k_1[AB])}{(k_2 + k_3[C])} = \text{const.}$$

So:

$$\ln \left[ \frac{[AB] (k_2 + k_3[C]) - k_1[AB]}{(k_2 + k_3[C])} \right] = -t + \ln(-k_1[AB])$$

$\ln \left[ \frac{[AB] (k_2 + k_3[C]) - k_1[AB]}{(k_2 + k_3[C])} \right] = -t^*$

set $(k_2 + k_3[C]) = t_{eq}$, then:

$$[AB] (k_2 + k_3[C]) - k_1[AB] \cdot (-k_1[AB])^t = e^{t_{eq}}$$

$$[AB] = \frac{k_1[AB] \cdot (-1 \cdot e^{t_{eq}})}{(k_2 + k_3[C])}$$

i) Diffuse cloud:  \hspace{1cm} $t_{eq} = (10^{-10} + 10^{*10^{-2}})^t = 9.09 \times 10^9$ sec = 290 yrs

ii) Dense cloud: \hspace{1cm} $t_{eq} = (0 + 10^{*10^{-5}})^t = 10^{14}$ sec = 3.2x10^5 yrs

In diffuse clouds, there is lots of light, which leads to fast destruction and quick
equilibrium.
5. We said to ignore a few reactions to make the problem simpler. The important reactions and their rate coefficients (from the notes) are:

\[
\begin{align*}
N + N &\rightarrow N_2, \quad k_1 = 3.43 \times 10^3 \text{ cm}^3/\text{s} \\
N + H &\rightarrow NH, \quad k_2 = 1.94 \times 10^{12} \text{ cm}^3/\text{s} \\
NH + H &\rightarrow NH_2, \quad k_3 = 1.94 \times 10^{12} \text{ cm}^3/\text{s} \\
NH_2 + H &\rightarrow NH_3, \quad k_4 = 1.94 \times 10^{12} \text{ cm}^3/\text{s}
\end{align*}
\]

Qualitatively, once N is adsorbed on the grain surface, it will eventually either go into \( N_2 \) or \( NH_3 \). (NH and \( NH_2 \) are not sinks for large amounts of \( N \). If there is enough H on a grain for \( N \) to go to \( NH \), then since \( k_2 = k_3 = k_4 \), \( NH_2 \) will quickly be made.) What governs the final nitrogen budget of either \( N_2 \) or \( NH_3 \) is the amount of H on a grain surface. If H is lower than a certain amount, \( N_2 \) is the favored product. If H is higher, then \( NH_3 \) is dominant. The amount of H on grains will be considered constant here, which isn't correct, but makes things easier. In dark clouds, where this chemistry is happening, atomic H is small compared to \( H_2 \), and since it is so volatile, its abundance on grain surfaces will be even less.

Now let's get more quantitative. \( N \) starts as atomic and in the gas phase. So, the amount of \( N \) in the gas phase is:

\[
d[\text{[N]_{gas}}]/dt = -S \sigma v \text{[grains]} [\text{[N]_{gas}}]
\]

\[
[\text{[N]_{gas}}] = [\text{[N]_{gas}}]_0 \exp\{ -S \sigma v \text{[grains]} t \}
\]

where

\[
S = \text{sticking coefficient of } [\text{[N]_{gas}}] = 1 \\
\sigma = \text{cross section of grains} \sim 10^{-6} \text{ cm}^2 \\
v = \text{velocity of } [\text{[N]_{gas}}] \sim 3 \times 10^4 \text{ cm/sec} \\
\text{[grains]} = \text{grain # density} = 10^{11} \text{H}_{\text{total}} \sim 10^{-8} \text{ cm}^3
\]

\[
[\text{[N]_{gas}}]_0 = 10^4 \text{H}_{\text{total}} \sim 1 \text{ cm}^3
\]

So:

\[
[\text{[N]_{gas}}] \sim \exp\{-3 \times 10^{-14} t\} \text{ due to depletion on grains}
\]

Since \( N \) must get onto grains before it produces molecules (in this problem at least), the next equation we need is the time rate of change of \( [\text{[N]_{gas}}] \):

\[
d[\text{[N]_{gas}}]/dt = S \sigma v \text{[grains]} [\text{[N]_{gas}}] - 2k_1 [\text{[N]_{gas}}]^2 - k_2 [\text{[N]_{gas}}][\text{[H]_{gas}}]
\]

= \text{gas-phase depletion} - \text{loss to } N_2 - \text{loss to } NH (NH_2 \text{ eventually})

Specifically:

\[
d[\text{[N]_{gas}}]/dt = (1 \times 10^{39} + 3 \times 10^8) 10^4 \exp\{-3 \times 10^{-14} t\} - 2 \times 3.43 \times 10^3 [\text{[N]_{gas}}]^2 \\
- 1.94 \times 10^{12} [\text{[N]_{gas}}][\text{[H]_{gas}}]
\]
\[
\frac{d[N_{\text{grain}}]}{dt} = (3\times10^{-14}) \exp[-3\times10^{-14}t] - 2\times3.43\times10^5 [N_{\text{grain}}]^2 - 1.94\times10^{12} [N_{\text{grain}}] [H_{\text{grain}}]
\]

This equation doesn’t lend itself to a quick analytical solution, but we can simplify the problem. Note that if \([N]/[H]\) is much larger than some value, the second term is much greater than the third term and vice versa if \([N]/[H]\) is small. A more quantitative comparison:

2\text{nd} and 3\text{rd} terms equal if

\[
2\times3.43\times10^5 [N_{\text{grain}}]^2 = 1.94\times10^{12} [N_{\text{grain}}] [H_{\text{grain}}]
\]

\[
[N_{\text{grain}}] / [H_{\text{grain}}] = 2.9\times10^6
\]

So if \([N_{\text{grain}}] / [H_{\text{grain}}] >> 2.9\times10^6\), expect only \(N_2\) to be produced

and if \([N_{\text{grain}}] / [H_{\text{grain}}] << 2.9\times10^6\), only \(NH_3\) will be produced

This number is much greater than unity because \(H\) migrates much faster than \(N\) on a grain surface.

But if we can solve the problem more completely by realizing that individual reactions (adsorption + reaction) take place on much faster timescales than cloud lifetimes. This means that \(d[N_{\text{grain}}] / dt\) at any given time is very small and the system is almost in steady state. Thus we can approximate by saying at any given time \(d[N_{\text{grain}}] / dt \approx 0\), and then find \(N_{\text{grain}}\) at that particular time:

\[
0 = d[N_{\text{grain}}]/dt = -(3\times10^{-14})\exp[-3\times10^{-14}t] + 2\times3.43\times10^5[N_{\text{grain}}]^2 + 1.94\times10^{12}[N_{\text{grain}}][H_{\text{grain}}]
\]

and plug in different times and solve for \(N_{\text{grain}}\) (given a constant \(H_{\text{grain}}\)).

Once we know \(N_{\text{grain}}\), we know the rate of production of \(N_2\) and \(NH_3\):

\[
\frac{d[N_2]}{dt} = 2\times3.43\times10^5[N_{\text{grain}}]^2
\]

\[
\frac{d[NH_3]}{dt} = k_4 [N_{\text{grain}}] [H] - 1.94\times10^{12}[N_{\text{grain}}][H_{\text{grain}}]
\]

Plots of these for \([H] = 10^{-16} \text{ cm}^{-3}\) and \([H] = 10^{-20} \text{ cm}^{-3}\) are attached.

b) I find that at \([H_{\text{grain}}] \approx 3.7\times10^{-16}, N_2\) and \(NH_3\) are produced at about the same rate. So if \([H_{\text{grain}}] >> 3.7\times10^{-16}, NH_3\) will be strongly favored, if \([H_{\text{grain}}] << 3.7\times10^{-16}, N_2\) will be the dominant product.