Cosmochemistry
Problem Set #2 Solutions

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

$$d[H_2]/ dt = 10^{-12} [CH^+] [H]$$

-and $$d[CH^+] / dt = 10^{-16} [C^+] [H] - 10^{-12} [CH^+] [H]$$

If we assume steady state for CH^+ ==> $d[CH^+] / dt = 0$

$$[CH^+] = 10^{-4} [C^+]$$

$$d[H_2]/ dt = 10^{-16} [C^+] [H]$$

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

$$[C^+] / [H] = [C^+] / [H] \sim 10^{-4}$$

$$d[H_2]/ dt = 10^{-20} [H]2 \text{ cm}^3 \text{ s}^{-1}$$

From class, grain formation of is $(d[H_2]/ dt)\text{grain} = R [H]^2$

and $R = 3\text{x}10^{-17} \text{ cm}^3 \text{ s}^{-1}$

so, $$\frac{\text{Rate(gas)}}{\text{Rate(grain)}} = \frac{10^{-20}}{3\text{x}10^{-17}} = 3\text{x}10^{-4}$$

grain formation of H2 is much more efficient

2. We are interested in the rate of formation of OH:

Mechanism (1) :

$$d[OH] / dt = k_5 [H_30^+] [e^-]$$

--> $d[H_30^+] / dt = 0 = k_4 [H_20^+] [H_2] - k_5 [H_30^+] [e^-]$

(assume steady state for all species except OH)

==> $[H_30^+] = \frac{k_4 [H_20^+] [H_2]}{k_5 [e^-]}$

$d[OH] / dt = k_4 [H_20^+] [H_2]$

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

$$d[OH] / dt = \quad [H]$$

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

Mechanism (2) :

$$d[OH] / dt = k_7 [H^-] [O]$$

--> $d [H^-] / dt = k_6 [H^-] [e^-] - k_7 [H^-] [O] - \quad [H^-]$

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

so:

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

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

Loss of H^- :

a) $d [H^-] / dt = \quad [H^-] = 10\text{-}7 [H^-]$

b) $d[H^-]/dt = k_7 [H^-][O]$

So the relative rates are

$$\frac{\text{photodetatchment}}{\text{reaction with O}} = \frac{10^{-7}}{k_7 [O]} \sim \frac{10^{-7}}{10^{-9}*10^{-4}*10^{-2}} \sim 10^4$$

So photodetatchment is much more inportant as a loss mechanism for H^-

So, Mechanism(1) : $d[OH]/dt =$ [H]

Mechanism(2) : $\frac{d[OH]}{dt} = \frac{k_6 k_7 [O][H][e^-]}{k_7 [O]} \sim k_6 k_7 [O][H][e^-]$

(2) $k_6 k_7 [O][e^-]$ $10^{-18} * 10^2 * 10^{-9} * (10^{-4} * 10^2) * (10^{-4} * 10^2)$

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

Finally,

$H^+ + O \rightarrow O^+ + H$ $k = 10^{-9} * e^{-232/100} = 9.8 \times 10^{-11} \sim 10^{-10}$
$H^+ + e^- \rightarrow H + h$ $k \sim 10^{-12}$ (same as $He^+ + e^-$ in notes)

Since H^+ will react with O faster than e^-, and $[O]/[e^-] \sim 1$, mechanism (1) will go on once H + C.R. happens.

3. The fractionation equation is:

$$\frac{[CH_3D]}{[CH_4]} = \frac{g\, le_x\, [HD]}{[H_2]\, k_x\, e^{-E/kT} + k_m\, [M] + k_e\, [e]}$$

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

$k_x \sim k_m \sim 10^{-9}$ cm^3 s^{-1}
$k_e \sim 10^{-6}$ cm^3 s^{-1}
$[H_2] \sim ½\, n_{total}$
$[M] \sim 10^{-1}\, n_{total}$
$[HD] \sim 2x10^{-5}\, n_{total}$
$E \sim 100$ K

We are given $g \sim 1/5$ and $[e^-]$ for dense clouds is $\sim 10^{-7}\, [H_2]$

$$==> \quad \frac{[CH_3D]}{[CH_4]} = \frac{1/5 * 10^{-9} * 2x10^{-5}\, n_{total}}{0.5\, n_{total} * + 10^{-9} e^{- /T} + 10^{-9} * 10^{-4} n_{total} + 10^{-6} * 10^{-7}\, n_{total}}$$

at 10 K :

$$\frac{[CH_3D]}{[CH_4]} \sim 0.02$$

The only temperature dependant term is the 1st one in the denominator, and if T • 12K, it is relatively small compared to the other terms.

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

CH_3D has a small dipole moment (~0.026 Debye), and thus it has a rotational spectrum and can be observed.

4. Time rate-of-change of [AB]

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

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

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

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

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

So:

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

$$(k_2 + k_3 [C])\text{-}1 * \ln \{[AB] (k_2 + k_3 [C]) - k_1 [A][B]) * (- k_1 [A][B])^{-1} \} = -t$$

$$\ln \{[AB] (k_2 + k_3 [C]) - k_1 [A][B]) * (- k_1 [A][B])^{-1} \} = -t * (k_2 + k_3 [C])$$

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

$$[AB] (k_2 + k_3 [C]) - k_1 [A][B]) * (- k_1 [A][B])^{-1} = e^{-t / teq}$$

$$[AB] = \frac{k_1 [A][B]) * [1 - e^{-t / teq}]}{(k_2 + k_3 [C])}$$

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

ii) Dense cloud: $t_{eq} = (0 + 10^{-9}*10^{-5})^{-1} = 10^{14}$ sec = $3.2\text{x}10^{6}$ 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:

$N + N \rightarrow N_2$ $k_1 = 3.43\text{x}10^{3}\ cm^3/s$
$N + H \rightarrow NH$ $k_2 = 1.94\text{x}10^{12}\ cm^3/s$
$NH + H \rightarrow NH_2$ $k_3 = 1.94\text{x}10^{12}\ cm^3/s$
$NH_2 + H \rightarrow NH_3$ $k_4 = 1.94\text{x}10^{12}\ cm^3/s$

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_3 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:

$$d[N_{gas}]/dt = - S\ \sigma\ v\ [grains]\ [N_{gas}]$$

$$[N_{gas}] = [N_{gas}]_o\ \exp\{- S\ \sigma\ v\ [grains]\ t\}$$

where
S = sticking coefficient of $N_{gas} = 1$
σ = cross section of grains ~ $10^{-10}\ cm^2$
v = velocity of N_{gas} ~ $3\text{x}10^{4}$ cm/sec
[grains] = grain # density = $10^{-12}\ n_{total}$ ~ $10^{-8}\ cm^{-3}$
$[N_{gas}]_o = 10^{-4}\ n_{total}$ ~ $1 cm^{-3}$

So: $[N_{gas}]$ ~ $\exp\{-3\text{x}10^{-14}\ t\}$ 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 N_{grain}:

$$d[N_{grain}]/dt = S\ \sigma\ v\ [grains]\ [N_{gas}] - 2\ k_1\ [N_{grain}]^2 - k_2\ [N_{grain}]\ [H_{grain}]$$
= gas-phase depletion - loss to N_2 - loss to NH (NH_3 eventually)

Specifically:

$$d[N_{grain}]/dt = (1*10^{-10}*3\text{x}10^{4})\ 10^{-8}\ \exp\{-3\text{x}10^{-14}\ t\} - 2*3.43\text{x}10^{3}\ [N_{grain}]^2 - 1.94\text{x}10^{12}\ [N_{grain}]\ [H_{grain}]$$

$$d[N_{grain}]/dt = (3x10^{-14}) \exp\{-3x10^{-14} t\} - 2*3.43x10^{3} [N_{grain}]^2 - 1.94x10^{12} [N_{grain}] [H_{grain}]$$

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

2nd and 3rd terms equal if $2*3.43x10^{3} [N_{grain}]^2 = 1.94x10^{12} [N_{grain}] [H_{grain}]$

$$[N_{grain}] / [H_{grain}] = 2.9x10^{8}$$

So if $[N_{grain}] / [H_{grain}] >> 2.9x10^{8}$, expect only N_2 to be produced

and if $[N_{grain}] / [H_{grain}] << 2.9x10^{8}$, 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 $d[N_{grain}] / dt$ 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 $d[N_{grain}] / dt \sim 0$, and then find $[N_{grain}]$ at that particular time:

$$0= d[N_{grain}]/dt = -(3x10^{-14})\exp\{-3x10^{-14}t\}+ 2*3.43x10^{3}[N_{grain}]^2+ 1.94x10^{12}[N_{grain}][H_{grain}]$$

and plug in different times and solve for $[N_{grain}]$ (given a constant specified $[H_{grain}]$)

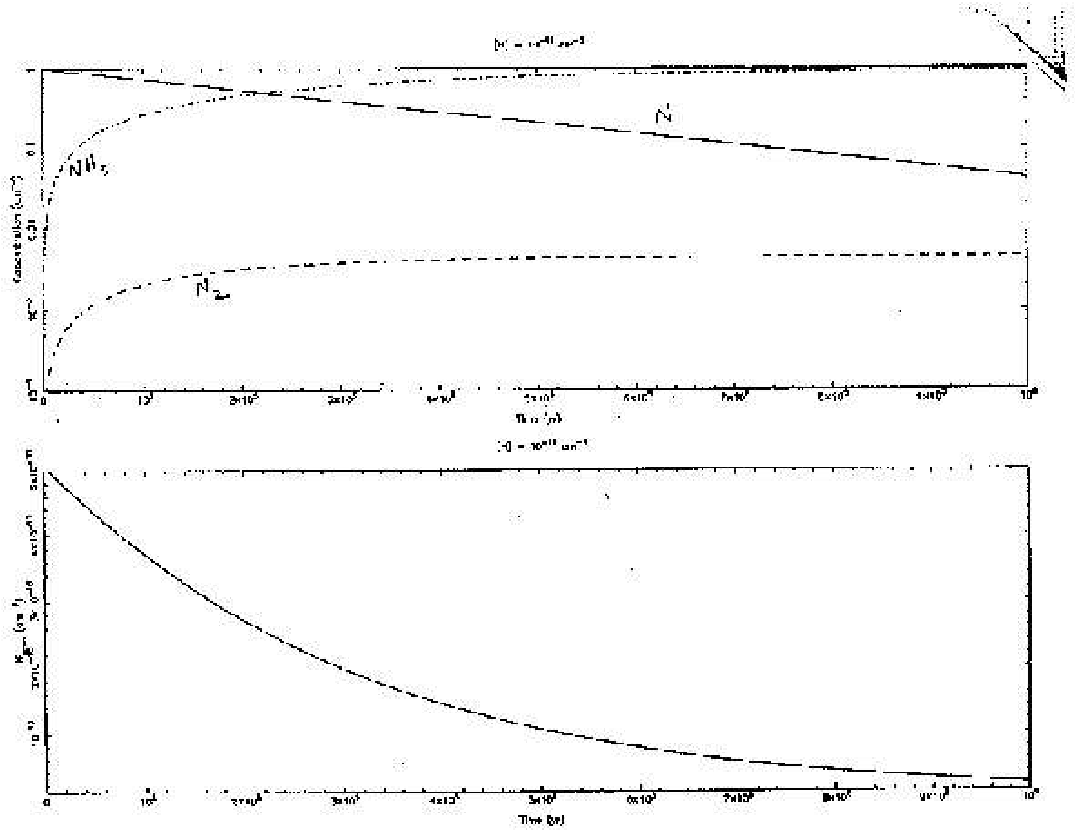
Once we know $[N_{grain}]$, we know the rate of production of N_2 and NH_3

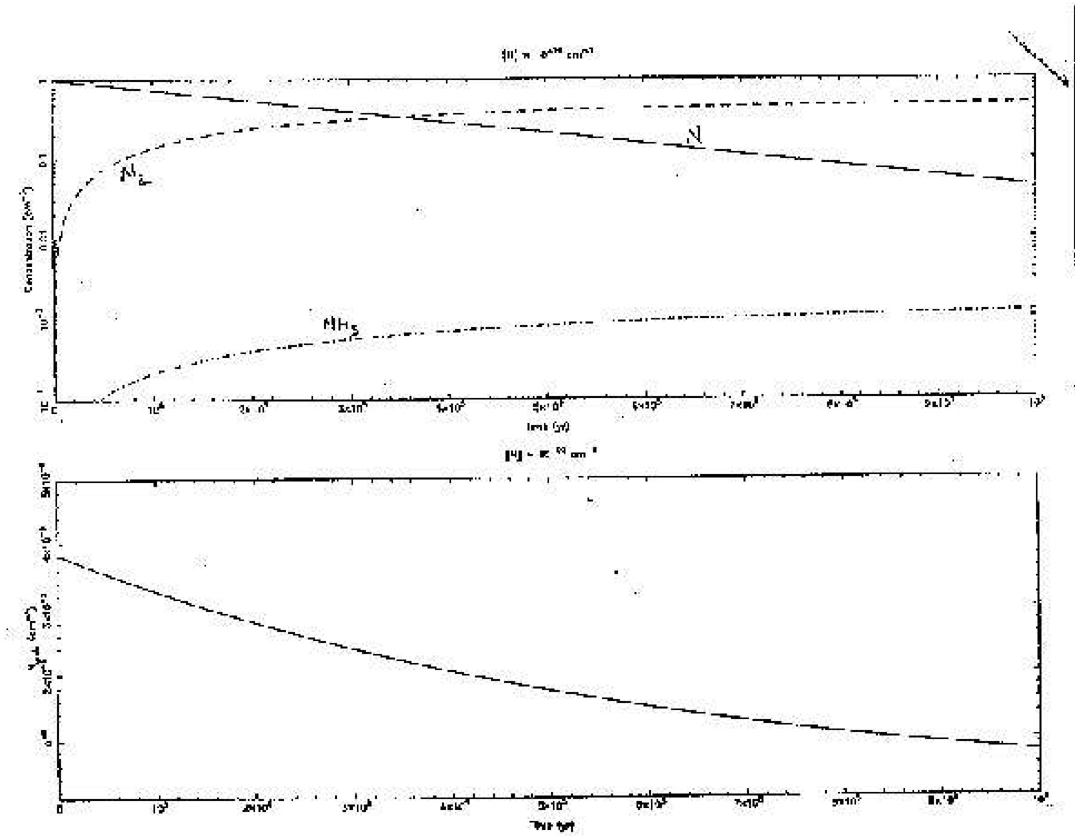
$$d[N_2]/dt = 2*3.43x10^{3}[N_{grain}]^2$$

$$d[NH_3]/dt = k_4 [NH_2] [H] \sim 1.94x10^{12}[N_{grain}][H_{grain}]$$

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

b) I find that at [Hgrain] ~ $3.7x10^{-18}$, N_2 nd NH_3 are produced at about the same rate. So if $[H_{grain}] >> 3.7x10^{-18}$, NH_3 will be strongly favored, if $[H_{grain}] << 3.7x10^{-18}$, N_2 will be the dominant product.


N
NH3
N2
Time (s)


N
0.1
0.01