Lecture 5: "Gas-phase Processes and First Molecules"
## I. Chemical Processes in Space

<table>
<thead>
<tr>
<th>Name</th>
<th>Representation</th>
<th>Example</th>
<th>Rate*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiative association</td>
<td>A + B → AB + ν</td>
<td>C⁺ + H₂ → CH₂⁺</td>
<td>~10⁻¹⁰⁻¹⁰⁻¹⁷ cm³ s⁻¹</td>
</tr>
<tr>
<td>Ion-molecule</td>
<td>A⁺ + B → C⁺ + D</td>
<td>CO + H₃⁺ → HCO⁺ + H₂</td>
<td>~10⁻⁷⁻¹⁰⁻¹⁰ cm³ s⁻¹</td>
</tr>
<tr>
<td>Neutral-neutral</td>
<td>A + B → C + D</td>
<td>O + CH₃ → H₂CO + H</td>
<td>~10⁻¹⁰⁻¹⁰⁻¹⁰⁻¹⁰⁻¹⁶ cm³ s⁻¹</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>A⁺ + B → B⁺ + C</td>
<td>C⁺ + Mg → C + Mg⁺</td>
<td>~10⁻⁹ cm³ s⁻¹</td>
</tr>
<tr>
<td>Radiative recombination</td>
<td>A⁺ + e⁻ → A + ν</td>
<td>Mg⁺ + e⁻ → Mg + ν</td>
<td>~10⁻¹² cm³ s⁻¹</td>
</tr>
<tr>
<td>Dissociative recombination</td>
<td>AB⁺ + e⁻ → A + B</td>
<td>HCO⁺ + e⁻ → CO + H</td>
<td>~10⁻⁷ cm³ s⁻¹</td>
</tr>
<tr>
<td>Ionization</td>
<td>A + hν → A⁺ + e⁻</td>
<td>C + hν → C⁺ + e⁻</td>
<td>~10⁻¹⁰ x RF** cm³ s⁻¹</td>
</tr>
<tr>
<td>Dissociation</td>
<td>AB + hν → A + B</td>
<td>CO + hν → C + O</td>
<td>~10⁻¹⁰ x RF cm³ s⁻¹</td>
</tr>
</tbody>
</table>

**Arrhenius rate:** $k = \alpha \left( \frac{T}{300} \right)^\beta \exp \left( -\gamma/T \right)$
Radiative Association: bond formation

\[ H + C \Rightarrow CH^* \]

Formation of a excited collisional complex

\[ CH^* \Rightarrow CH + hv \]

Energy conservation $\Rightarrow$ emission of photon

or (more likely)

\[ CH^* \Rightarrow C + H \]

A key process to form first molecules & chemical bonds (early Universe)

\[ k \approx 10^{-17} - 10^{-12} \text{ cm}^3\text{s}^{-1} \]

(Courtesy of Tom Millar, David Williams, Eric Herbst)
Radiative Association: bond formation

Timescales:
$10^{-2}$ s - vibrational transition,
$10^{-8}$ s - electronic transition,
$10^{-13}$ s - collisional timescale (or lifetime of collisional complex)

=> molecule formation only after $\sim 10^{11}$ collisions ($10^5$ if electronic transitions are available)!

Slow for small reactants, but can be rapid for complex radicals

Hard to measure in laboratory (3-body processes dominate)

Hard to calculate for complex species
Photodissociation: bond destruction

Bonding energies: 5-10 eV => FUV

Direct dissociation: transition to a continuum of excited electronic state

Predissociation: excited electronic state is mixed with dissociative state

Spontaneous radiative dissociation: sometimes electronic excited states decay into continuum of the ground-state
Photodissociation: bond destruction

Examples:
H$_2$O, OH, ...

CO

Only H$_2$
Photodissociation: bond destruction

\[ \text{CO} + h\nu \Rightarrow \text{C} + \text{O} \]
\[ \text{HCO}^+ + h\nu \Rightarrow \text{no} \]

Line dissociation: \( \text{H}_2, \text{CO} \)

Lyman\(\alpha\) dissociation: \( \text{OH}, \text{CN}, \text{NH}_3 \)

Continuum dissociation: \( \text{CH}_4 \)

Calculated only for a few tens species

Strongly depends on radiation energy distribution

van Dishoeck et al. (2006)
Cosmic Ray & UV Ionization

\[ \text{H}_2 + \text{CRP/UV} \Rightarrow \text{H}_2^+ + \text{e}^- \]

\[ \text{H}_2^+ + \text{H}_2 \Rightarrow \text{H}_3^+ + \text{H} \]

\[ \text{He} + \text{CRP} \Rightarrow \text{He}^+ + \text{e}^- \]

From observations:

\[ k_{\text{CRP}} \approx 10^{-17} \text{ s}^{-1} \]

Relativistic energy particles (89% protons, 10% \(^4\text{He}\), 1% heavy elements)

⇒ penetrate a large gas columns ⇒ energy source even in “dark” regions

Key process to form \( \text{H}_3^+ \)

⇒ enables proton transfer reactions

⇒ rich molecular chemistry

I.P. of He is 24.6 eV ⇒

\( \text{He}^+ \) breaks chemical bonds ⇒

destruction of molecules (CO!)
Ion-Molecule Reactions: bond rearrangement

H$_3^+$ + CO $\Rightarrow$ Ion induces dipole moment $\Rightarrow$ long-range strong attraction $\Rightarrow$ no activation barriers

H$_2$ + HCO$^+$ Rates increase at low T if a molecule is polar due to a long-distance Coloumb attraction

H$_2^+$ + H$_2$ $\Rightarrow$ H$_3^+$ + H Langevin rate: $k_L = 2\pi e \left( \frac{\alpha}{\mu} \right)^{1/2}$

$\mu$ - reduced mass, $\alpha$ - polarizability

$k \approx 10^{-9}$-$10^{-7}$ cm$^3$s$^{-1}$ A key process to form complex ions and complex neutrals (after DR)

$\Rightarrow$ $\sim$50% of all processes in astrochemical models
Neutral-Neutral Reactions: bond rearrangement

\[ N + CH \Rightarrow CN + H \]

Long-range attraction is weak

\[ N + CH_3 \Rightarrow HCN + H_2 \]

Usually have barriers due to bond breaking for molecular rearrangement

Some are rapid reactions even at \( \sim 10 \text{ K} \) (radical-radical, radical-neutral)

Particularly competitive at high temperatures, \( >100 \text{ K} \)

\[ k \approx <10^{-11}-10^{-9} \text{ cm}^3\text{s}^{-1} \]

Many barriers are ‘guessed’ values, \( \sim 100-1000 \text{ K} \)
**Disassociative Recombination: bond destruction**

\[
\text{HCO}^+ + e^- \Rightarrow \text{CO} + \text{H}
\]

Capture of e- by an ion => formation of neutral in excited electronic state => dissociation

\[
\text{H}_3\text{O}^+ + e^- \Rightarrow \text{H}_2\text{O} + \text{H} \quad \text{OH} + 2\text{H}
\]

Rapid processes, increased rates at low T

If radiative (no break-up), then usually slow

\[k \approx 10^{-7} \text{ cm}^3\text{s}^{-1}\]

A final step in formation of neutral species

Branching ratios and products are not well known
Radiative Attachment

\[ \text{C}_6\text{H} + e^- \rightarrow \text{C}_6\text{H}^- + \text{hv} \]

Effective for molecules with large e-affinities

\[ k \approx <10^{-7} \text{ cm}^3\text{s}^{-1} \]

Excess of energy is re-radiated => less efficient for small molecules

<10% of anion/neutral for hydrocarbons (predicted by Herbst 1981)

Discovered in ISM with predicted abundances (McCarthy et al. 2006, Bruencken et al. 2007, etc.)

Important in chemistry of the early Universe
Chemical Reaction Databases

- Ohio State University (OSU), now Kinetic Database for Astrochemistry (KIDA):
  5000 reactions, 500 species, 12 elements

- Manchester University (UMIST):
  Rate06: 4600 reactions, 420 species, 12 elements

- NIST Chemical Kinetics Database: ~30,000 neutral-neutral reactions (T>300K)

- JPL (Anicich): Compilation of all ion-molecule reactions with references

- Only ~10-20% of accurate rates!

Courtesy of Eric Herbst
Gas-phase Formation of Water

\[
\begin{align*}
H_2 & \quad + \quad \text{CRP} \quad \Rightarrow \quad H_2^+ \quad + \quad e^- \\
H_2^+ & \quad + \quad H_2 \quad \Rightarrow \quad H_3^+ \quad + \quad H \\
H_3^+ & \quad + \quad O \quad \Rightarrow \quad OH^+ \quad + \quad H_2 \\
OH_n^+ & \quad + \quad H_2 \quad \Rightarrow \quad OH_{n+1}^+ \quad + \quad H \\
H_3O^+ & \quad + \quad e^- \quad \Rightarrow \quad H_2O \quad + \quad H; \quad OH \quad + \quad 2H, \quad \text{etc}
\end{align*}
\]
Gas-phase formation of complex molecules

\[
\begin{align*}
C^+ + H_2 & \Rightarrow CH_2^+ \\
CH_2^+ + H_2 & \Rightarrow CH_3^+ + H \\
CH_3^+ + H_2/O & \Rightarrow CH_5^+/HCO^+ + H_2 \\
CH_5^+ + e^- & \Rightarrow CH_3 + H_2 \\
CH_3 + O & \Rightarrow H_2CO \\
CH_3^+ + H_2O & \nless CH_3OH_2^+ \quad \text{(too low rate, Luca et al. 2002)} \\
CH_3OH_2^+ + e^- & \Rightarrow CH_3OH + H \quad (3 \pm 2\%, Geppert et al. 2006)
\end{align*}
\]
Chemical Kinetics

\[
\frac{\partial n_i}{\partial t} = \sum_{j,k \neq i} k_{jk} n_j n_k - n_i \sum_l k_l n_l + \nabla D n \nabla n_i / n - \nabla U n_i
\]

- Physical conditions
- (For last 2 terms): dynamical parameters (wind, turbulence, advection)
- Initial abundances
- A chemical network
- A numerical solver

- Steady-state: \( n_i(t) = \text{const} \) (derivative is 0) => algebraic equations
Chemical codes

- ALCHEMIC (MPIA Heidelberg): gas-grain
- GADGET (ITA Heidelberg): gas-phase, early Universe
- NAHOON (Bordeaux Obs.): gas-grain, uncertainties
- MONACO (Univ. of Virginia): gas-grain, Monte Carlo stochastic chemistry
- ASTROCHEM (Grenoble): gas-grain
- OSU codes (now at Univ. of Virginia): gas-grain, warm-up
- Many codes for photon-dominated chemistry (CLOUDY, Meudon, Leiden, etc., see Roellig et al. 2007)
Computed abundances have error bars

- Chemistry of planetary atmospheres: Dobrijevic et al. (1998, 2001)

Modeled abundances are uncertain by factor of $>3$
Pause
II. Chemistry in the Early Universe

- Simple chemistry, only light elements: H, D, He, Li
- Almost isotropic physical conditions (no structures)
- First molecules: cooling of gas \Rightarrow \text{formation of first stars (Pop III)}
- High-z molecules are detected \((z \sim 7)\)!
# The Universe after Big Bang

<table>
<thead>
<tr>
<th>Epoch</th>
<th>Time, s</th>
<th>$T_R$, K</th>
<th>$n_H$, cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lepton</td>
<td>$10^{-4}$</td>
<td>$10^{12}$</td>
<td>–</td>
</tr>
<tr>
<td>Radiation-dominated</td>
<td>2</td>
<td>$10^{10}$</td>
<td>–</td>
</tr>
<tr>
<td>Matter-dominated</td>
<td>$10^{11}-10^{12}$</td>
<td>4000</td>
<td>500</td>
</tr>
<tr>
<td>Present</td>
<td>$10^{18}$</td>
<td>2.73</td>
<td>$2 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Radiative temperature: \[ T_R = 2.73K (1 + z) \]

Density: \[ n_H = 200 \left( \frac{1+z}{1000} \right)^3 \left( \frac{\Omega}{0.1} \right)^4 \left( \frac{H}{50} \right)^8 \text{ cm}^{-3} \]
Standard Cosmological Model

Composition at the beginning of the matter-dominated era:
\[ \text{H : D : }^4\text{He : }^3\text{He : }^7\text{Li} \]
\[ 1 : 4 \times 10^{-5} : 8 \times 10^{-2} : 10^{-5} : 2 \times 10^{-10} \]
(all atoms fully ionized)

(1) \( \text{H} + \text{hv} \rightarrow \text{H}^+ + \text{e}, \text{rate} \sim \text{ambient radiation field} \)
(2) \( \text{H}^+ + \text{e} \rightarrow \text{H}, \text{rate} \sim T^{-0.61} \)

Temperature of matter \( T_M = T_R \) due to Thompson scattering of photons on electrons

As Universe cools, recombination becomes more important:
\( n(\text{H}^+) = n(\text{H}) \) at \( z=1340, T_R = T_M = 3630 \text{ K} \)

After that no thermodynamical equilibrium \( \Rightarrow \) chemical kinetics has to be considered to predict molecular abundances
**First neutral & molecule: He and He$_2^+$**

Ionization potentials [in eV]

<table>
<thead>
<tr>
<th></th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>13.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>He</td>
<td>24.6</td>
<td>54.4</td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>5.4</td>
<td>75.6</td>
<td>122.5</td>
</tr>
</tbody>
</table>
First Molecules

Figure 2. Fractional abundances of molecules and molecular ions in the early Universe at high redshift $z$. The cosmological parameters correspond to the standard cosmology model III of Stancil et al (1996, 1998): $\Omega_0 = 1$, $\Omega_b = 0.0367$, $h = 0.67$. Variation in spacing is proportional to $\alpha$. The measurements were all consistent with no time dependence and the best limit was $\delta\alpha/\alpha = 3.5 (\pm 5.5) \times 10^{-6}$ (Cowie and Songaila 1995) back to $z = 2.811$. More recently a new technique, the many-multiplet method, has been used which simultaneously compares the wavelengths of many multiplets to get a more sensitive determination (Webb et al 1999). The alkaline doublet method compares two lines with the same ground state, whereas the many-multiplet method compares many lines with different ground states. Using this method, Webb et al (2001) suggest that the fine structure constant is varying with time, with $\delta\alpha/\alpha = -0.72 (\pm 0.18) \times 10^{-5}$ over the redshift range $0.5 < z < 3.5$.

The result is provocative, but the analysis to get it is complicated and errors which could result in such a small effect are many including: unresolved velocity structures, uncertainties in wavelength calibrations or laboratory wavelengths, and, since their lines come from different levels, sensitivity to variations in temperature or excitation within the cloud.

4. Standard chemistry in the early Universe

The chemistry of the early Universe was investigated by Lepp and Shull (1984), Dalgarno and Lepp (1987), Latter and Black (1991), Puy et al (1993), and Palla et al (1995). All of these examined one or more of the molecules which might be formed in the early Universe. More recently, Galli and Palla (1998) and Stancil et al (1996, 1998) attempted a comprehensive review of all the reactions involved in the study of the early Universe. In particular, Stancil et al (1998) included 23 atomic and molecular species and 144 chemical processes. Figure 2 is adapted from Stancil et al (1998) and shows the abundance of molecular ions and molecules with redshift.

In table 1, we list 41 reactions which we have considered since Stancil et al (1998). They can be added to the lists given in table 1 of Stancil et al (1996, 1998) for a more complete set. Most of these reactions are new to our models, but some are improved rate coefficient fits which supersede those previously given. We will discuss some of these reactions below.

Chemistry of He

He$^+$ recombines earlier than H$^+$:
He$^{2+}$ + e → He$^+$ + hν
He$^+$ + e → He + hν

First molecules were He$_2^+$ and HeH$^+$:
He$^+$ + He → He$_2^+$ + hν (radiative association)
He + H$^+$ → HeH$^+$ + hν (radiative association)

They were removed by photodissociation & dissociative recombination:
He$_2^+$ + hν → He$^+$ + He
He$_2^+$ + e → He + He
Reaction rates of He-chemistry

Table 3. Reaction rates for Helium species

<table>
<thead>
<tr>
<th>reaction</th>
<th>rate (cm$^3$ s$^{-1}$ or s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He1)  $\text{He}^{++} + e \rightarrow \text{He}^+ + \gamma$</td>
<td>$1.891 \times 10^{-10} \left[ \sqrt{\frac{T_g}{9.37}} \left( 1 + \sqrt{\frac{T_g}{9.37}} \right)^{0.2476} \times \left( 1 + \sqrt{\frac{T_g}{2.774 \times 10^6}} \right)^{-1} \right]$</td>
</tr>
<tr>
<td>He2)  $\text{He}^+ + \gamma \rightarrow \text{He}^{++} + e$</td>
<td>$5.0 \times 10^1 T_r^{1.63} \exp \left( -\frac{590000}{T_r} \right)$</td>
</tr>
<tr>
<td>He3)  $\text{He}^+ + e \rightarrow \text{He} + \gamma$</td>
<td>$3.294 \times 10^{-11} \left[ \sqrt{\frac{T_g}{15.54}} \left( 1 + \sqrt{\frac{T_g}{15.54}} \right)^{0.309} \times \right.$ $\left. \left( 1 + \sqrt{\frac{T_g}{3.676 \times 10^7}} \right)^{-1} \right]$</td>
</tr>
<tr>
<td>He4)  $\text{He} + \gamma \rightarrow \text{He}^+ + e$</td>
<td>$1.0 \times 10^4 T_r^{1.23} \exp \left( -\frac{280000}{T_r} \right)$</td>
</tr>
<tr>
<td>He5)  $\text{He} + \text{H}^+ \rightarrow \text{He}^+ + \text{H}$</td>
<td>$4.0 \times 10^{-37} T_g^{4.74} \times$ $3.7 \times 10^{-25} T_g^{2.06} \times$ $\left[ 1 + 9.9 \exp \left( -\frac{T_g}{2570} \right) \right]$</td>
</tr>
<tr>
<td>He6)  $\text{He}^+ + \text{H} \rightarrow \text{He} + \text{H}^+$</td>
<td>$7.6 \times 10^{-18} T_g^{-0.5}$ $3.45 \times 10^{-16} T_g^{-1.06}$</td>
</tr>
<tr>
<td>He7)  $\text{He} + \text{H}^+ \rightarrow \text{HeH}^+ + \gamma$</td>
<td>$5.0 \times 10^{-21}$</td>
</tr>
<tr>
<td>He8)  $\text{He} + \text{H}^+ \rightarrow \text{HeH}^+ + \gamma$</td>
<td>$7.6 \times 10^{-18} T_g^{-0.5}$ $3.45 \times 10^{-16} T_g^{-1.06}$</td>
</tr>
<tr>
<td>He9)  $\text{He} + \text{H}_2^+ \rightarrow \text{HeH}^+ + \text{H}$</td>
<td>$3.0 \times 10^{-10} \exp \left( -\frac{6717}{T_g} \right)$</td>
</tr>
<tr>
<td>He10) $\text{He}^+ + \text{H} \rightarrow \text{HeH}^+ + \gamma$</td>
<td>$1.6 \times 10^{-14} T_g^{-0.33}$ $1.0 \times 10^{-15}$</td>
</tr>
<tr>
<td>He11) $\text{HeH}^+ + \text{H} \rightarrow \text{He} + \text{H}_2^+$</td>
<td>$9.1 \times 10^{-10}$</td>
</tr>
<tr>
<td>He12) $\text{HeH}^+ + e \rightarrow \text{He} + \text{H} + e$</td>
<td>$1.7 \times 10^{-7} T_g^{-0.5}$</td>
</tr>
<tr>
<td>He13) $\text{HeH}^+ + \text{H}_2 \rightarrow \text{H}_3^+ + \text{He}$</td>
<td>$1.3 \times 10^{-9}$</td>
</tr>
<tr>
<td>He14) $\text{HeH}^+ + \gamma \rightarrow \text{He} + \text{H}^+$</td>
<td>$6.8 \times 10^{-1} T_r^{1.5} \exp \left( -\frac{22750}{T_r} \right)$</td>
</tr>
<tr>
<td>He15) $\text{HeH}^+ + \gamma \rightarrow \text{He}^+ + \text{H}$</td>
<td>$7.8 \times 10^3 T_r^{1.2} \exp \left( -\frac{240000}{T_r} \right)$</td>
</tr>
</tbody>
</table>
Chemistry of H

Molecular hydrogen cannot form on dust grains as at present time => slow gas-phase reactions

Direct formation by radiative association:
H + H → H₂ + hν is too slow

(H₂ does not have a dipole moment => difficult to get rid of excess of energy via radiation)
Formation of H$_2$ from HeH$^+$

First H$_2$ were formed via ion-molecule reactions with HeH$^+$:
He + H$^+$ → HeH$^+$ + hν
HeH$^+$ + H → H$_2^+$ + He
H$_2^+$ + H → H$_2$ + H$^+$

(here He and H are catalysts!)

At that time, H$_2$ is quickly destroyed by background radiation (photodissociation)
Formation of $\text{H}_2$ from $\text{H}^+$

Later, formation $\text{H}_2$ involves RA & ion-molecule reaction:
$\text{H} + \text{H}^+ \rightarrow \text{H}_2^+ + \text{h}\nu$
$\text{H}_2^+ + \text{H} \rightarrow \text{H}_2 + \text{H}^+$

$\text{H}_2^+$ is destroyed by photodissociation and DR:
$\text{H}_2^+ + \text{h}\nu \rightarrow \text{H} + \text{H}^+$
$\text{H}_2^+ + \text{e} \rightarrow \text{H} + \text{H}$

Photodissociation of $\text{H}_2^+$ is efficient when $T_R > 4000 \text{ K}$ => no $\text{H}_2$ at earlier times!
Formation of H$_2$ from H$^-$

At $z \approx 100$, H$_2$ can be formed through H$^-$:

H + e $\rightarrow$ H$^-$ + hν (radiative attachment)

H$^-$ + H $\rightarrow$ H$_2$ + e (associative detachment)

H$^-$ is destroyed by photodetachment reaction:

H$^-$ + hν $\rightarrow$ H + e (barrier is 0.75 eV)

=>$T_R < 1000$ K are needed to slow down this process
New experiments on $\text{H}^- + \text{H}$

Kreckel et al. (2010), Science
**Destruction of H₂**

H₂ is efficiently destroyed by photodissociation, ion-molecule reactions with H⁺, and collisional dissociation:

\[ H₂ + H^+ \rightarrow H₂^+ + H \]
\[ H₂ + e \rightarrow H + H^- \]

\[ \Rightarrow \text{small molecular fraction in the early Universe: } X(H₂) \sim 10^{-6} \]
### Reaction rates of H-chemistry

**Table 1. Reaction rates for Hydrogen species**

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate (cm$^3$ s$^{-1}$ or s$^{-1}$)</th>
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<tbody>
<tr>
<td><strong>H1)</strong> $\text{H}^+ + \text{e} \rightarrow \text{H} + \gamma$</td>
<td>$R_{c2}$</td>
</tr>
<tr>
<td><strong>H2)</strong> $\text{H} + \gamma \rightarrow \text{H}^+ + \text{e}$</td>
<td>$R_{2c}$</td>
</tr>
<tr>
<td><strong>H3)</strong> $\text{H} + \text{e} \rightarrow \text{H}^- + \gamma$</td>
<td>$1.4 \times 10^{-18} T_g^{-0.928} \exp \left( - \frac{T_g}{16200} \right)$</td>
</tr>
<tr>
<td><strong>H4)</strong> $\text{H}^- + \gamma \rightarrow \text{H} + \text{e}$</td>
<td>$1.1 \times 10^{-1} T_r^{2.13} \exp \left( - \frac{8823}{T_r} \right)$</td>
</tr>
<tr>
<td><strong>H5)</strong> $\text{H}^- + \text{H} \rightarrow \text{H}_2^+ + \text{e}$</td>
<td>$1.5 \times 10^{-9}$</td>
</tr>
<tr>
<td><strong>H6)</strong> $\text{H}^- + \text{H}^+ \rightarrow \text{H}_2^+ + \text{e}$</td>
<td>$4.0 \times 10^{-9} T_g^{0.17}$</td>
</tr>
<tr>
<td><strong>H7)</strong> $\text{H}^- + \text{H}^+ \rightarrow 2\text{H}$</td>
<td>$5.7 \times 10^{-6} T_g^{0.5} + 6.3 \times 10^{-8} - 9.2 \times 10^{-11} T_g^{0.5} + 4.4 \times 10^{-13} T_g$</td>
</tr>
<tr>
<td><strong>H8)</strong> $\text{H} + \text{H}^+ \rightarrow \text{H}_2^+ + \gamma$</td>
<td>$\text{dex}\left[ -19.38 - 1.523 \log T_g + 1.118 \left( \log T_g \right)^2 - 0.1269 \left( \log T_g \right)^3 \right]$</td>
</tr>
<tr>
<td><strong>H9)</strong> $\text{H}_2^+ + \gamma \rightarrow \text{H} + \text{H}^+$</td>
<td>$2.0 \times 10^{1} T_r^{1.59} \exp \left( - \frac{82000}{T_r} \right)$</td>
</tr>
<tr>
<td><strong>H10)</strong> $\text{H}_3^+ + \text{H} \rightarrow \text{H}_2 + \text{H}^+$</td>
<td>$1.63 \times 10^7 \exp \left( - \frac{32400}{T_r} \right)$</td>
</tr>
<tr>
<td><strong>H11)</strong> $\text{H}_3^+ + \text{e} \rightarrow 2\text{H}$</td>
<td>$2.0 \times 10^{-7} T_g^{0.5}$</td>
</tr>
<tr>
<td><strong>H12)</strong> $\text{H}_2^+ + \gamma \rightarrow 2\text{H}^+ + \text{e}$</td>
<td>$9.0 \times 10^{1} T_r^{1.48} \exp \left( - \frac{335000}{T_r} \right)$</td>
</tr>
<tr>
<td><strong>H13)</strong> $\text{H}_3^+ + \text{H}_2 \rightarrow \text{H}_4^+ + \text{H}$</td>
<td>$2.0 \times 10^{-9}$</td>
</tr>
<tr>
<td><strong>H14)</strong> $\text{H}_2^+ + \text{H} \rightarrow \text{H}_3^+ + \gamma$</td>
<td>irrelevant</td>
</tr>
<tr>
<td><strong>H15)</strong> $\text{H}_2 + \text{H}^+ \rightarrow \text{H}_2^+ + \text{H}$</td>
<td>$3.0 \times 10^{-10} \exp \left( - \frac{21050}{T_g} \right)$</td>
</tr>
<tr>
<td><strong>H16)</strong> $\text{H}_2 + \text{e} \rightarrow \text{H} + \text{H}^-$</td>
<td>$1.5 \times 10^{-10} \exp \left( - \frac{14000}{T_g} \right)$</td>
</tr>
<tr>
<td><strong>H17)</strong> $\text{H}_2 + \text{e} \rightarrow 2\text{H} + \text{e}$</td>
<td>$2.7 \times 10^{-8} T_g^{1.27} \exp \left( - \frac{43000}{T_g} \right)$</td>
</tr>
<tr>
<td><strong>H18)</strong> $\text{H}_2 + \gamma \rightarrow \text{H}_2^+ + \text{e}$</td>
<td>$4.4 \times 10^{-10} T_g^{0.35} \exp \left( - \frac{102000}{T_g} \right)$</td>
</tr>
<tr>
<td><strong>H19)</strong> $\text{H}_3^+ + \text{H} \rightarrow \text{H}_2^+ + \text{H}_2$</td>
<td>$2.9 \times 10^{2} T_r^{1.56} \exp \left( - \frac{178500}{T_r} \right)$</td>
</tr>
<tr>
<td><strong>H20)</strong> $\text{H}_3^+ + \text{e} \rightarrow \text{H}_2 + \text{H}$</td>
<td>$7.7 \times 10^{-9} \exp \left( - \frac{17560}{T_r} \right)$</td>
</tr>
<tr>
<td><strong>H21)</strong> $\text{H}_2 + \text{H}^+ + \gamma \rightarrow \text{H}_3^+ + \gamma$</td>
<td>$4.6 \times 10^{-6} T_g^{0.65}$</td>
</tr>
<tr>
<td><strong>H22)</strong> $\text{H}_3^+ + \gamma \rightarrow \text{H}_3^+ + \text{H}$</td>
<td>irrelevant</td>
</tr>
</tbody>
</table>
Chemistry of D

Formation of HD is dominated by ion-molecule and charge transfer processes:

\[ \text{H}^+ + \text{D} \rightarrow \text{H} + \text{D}^+ \]
\[ \text{D}^+ + \text{H}_2 \rightarrow \text{HD} + \text{H}^+ \]

and minor processes:

\[ \text{H} + \text{D} \rightarrow \text{HD} + \text{h} \nu \text{ (RA)} \]
\[ \text{H}^+ + \text{D} \rightarrow \text{HD}^+ + \text{h} \nu \text{ (RA)} \]
\[ \text{H} + \text{D}^+ \rightarrow \text{HD}^+ + \text{h} \nu \text{ (RA)} \]
\[ \text{HD}^+ + \text{H} \rightarrow \text{HD} + \text{H}^+ \text{ (charge transfer)} \]

HD is destroyed by similar processes as \( \text{H}_2 \)

\[ \Rightarrow X(\text{HD}) \sim (\text{D}/\text{H}) * X(\text{H}_2) \sim 10^{-10} - 10^{-9} \]
Reaction rates of D-chemistry

Table 2. Reaction rates for Deuterium species

<table>
<thead>
<tr>
<th>reaction</th>
<th>rate (cm$^3$ s$^{-1}$ or s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D1) $D^+ + e \rightarrow D + \gamma$</td>
<td>$3.7 \times 10^{-10} T_g^{0.28} \exp \left( -\frac{43}{T_g} \right)$</td>
</tr>
<tr>
<td>D2) $D + \gamma \rightarrow D^+ + e$</td>
<td>$3.7 \times 10^{-10} T_g^{0.28}$</td>
</tr>
<tr>
<td>D3) $D + H^+ \rightarrow D^+ + H$</td>
<td>$1.0 \times 10^{-25}$</td>
</tr>
<tr>
<td>D4) $D + H \rightarrow HD + \gamma$</td>
<td>$9.0 \times 10^{-11} \exp \left( -\frac{3876}{T_g} \right)$</td>
</tr>
<tr>
<td>D5) $HD + H \rightarrow H_2 + HD$</td>
<td>$2.1 \times 10^{-9}$</td>
</tr>
<tr>
<td>D6) $D + H_2 \rightarrow H + HD$</td>
<td>$3.2 \times 10^{-11} \exp \left( -\frac{3624}{T_g} \right)$</td>
</tr>
<tr>
<td>D7) $HD^+ + H \rightarrow H^+ + HD$</td>
<td>$7.2 \times 10^{-8} T_g^{-1/2}$</td>
</tr>
<tr>
<td>D8) $D^+ + H_2 \rightarrow H^+ + HD$</td>
<td>$(2.1 - 0.4 \log T_g) \times 10^{-9}$</td>
</tr>
<tr>
<td>D9) $HD + H \rightarrow H_2 + D$</td>
<td>$2.0 \times 10^{-8} T_g^{-1}$</td>
</tr>
<tr>
<td>D10) $H_2D^+ + e \rightarrow H + D$</td>
<td>$1.0 \times 10^{-6} T_g^{-1/2} \times 0.73$</td>
</tr>
<tr>
<td>D11) $H_2D^+ + e \rightarrow H_2 + D$</td>
<td>$1.0 \times 10^{-6} T_g^{-1/2} \times 0.07$</td>
</tr>
<tr>
<td>D12) $H_2D^+ + e \rightarrow H + H$</td>
<td>$1.0 \times 10^{-6} T_g^{-1/2} \times 0.20$</td>
</tr>
<tr>
<td>D13) $H_3D^+ + e \rightarrow H_3^+ + D$</td>
<td>$4.7 \times 10^{-9} \exp \left( -\frac{215}{T_g} \right)$</td>
</tr>
<tr>
<td>D14) $H_3D^+ + e \rightarrow HD + H$</td>
<td>$5.5 \times 10^{-10}$</td>
</tr>
<tr>
<td>D15) $H_3D^+ \rightarrow H_3^+ + HD$</td>
<td>$2.0 \times 10^{-8} T_g^{-1} \exp \left( -\frac{632}{T_g} \right)$</td>
</tr>
</tbody>
</table>
Chemistry of Li

I.P. of Li is 5.4 eV => relevant chemistry begins at z<450:

Major species are LiH and LiH⁺:

LiH⁺ chemistry:
\[ \text{Li}^+ + H \rightarrow \text{LiH}^+ + h\nu \text{ (RA)} \]
\[ \text{LiH}^+ + e \rightarrow \text{Li} + H \text{ (DR)} \]
\[ \text{LiH}^+ + h\nu \rightarrow \text{Li}^+ + H \text{ (photodissociation)} \]

LiH chemistry:
\[ \text{Li} + H \rightarrow \text{LiH} + h\nu \text{ (RA)} \]
\[ \text{Li} + \text{H}^- \rightarrow \text{LiH} + e \text{ (associative detachment)} \]
\[ \text{Li}^- + H \rightarrow \text{LiH} + e \text{ (AD)} \]
\[ \text{LiH} + h\nu \rightarrow \text{Li} + H \text{ (PD)} \]
\[ \text{LiH} + H \rightarrow \text{Li} + H_2 \text{ (PD)} \]

Minor species: \( X(\text{LiH}) \sim 1\% \text{ of } X(\text{LiH}^+) \sim 10^{-18} \)
Summary: abundances of early molecules


Fig. 4. The evolution of all the chemical species considered in the standard model as a function of redshift. The four panels show the results for H (upper left), D (upper right), He (lower left), and Li (lower right).

As for deuterium, Fig. 4 shows that the evolution of D is very sensitive to the charge exchange reactions (D3)–(D4). At z < 40, the abundance of D drops precipitously due to the exponential factor in the reaction rate (D3). The only molecule formed in significant amount is HD, whose evolution with redshift follows closely that of H2. However, its abundance at freeze-out is [HD/H2] ≃ 10⁻³. More important, the asymptotic value of [HD/H2] becomes about 10⁻³ with an enhancement factor of ∼30 from the initial [D/H] abundance. This is due to the large fractionation implied by reaction (D8). The behaviour of HD⁺ follows that of H₂⁺ up to z ≃ 100, while at lower redshifts its evolution is dominated by reaction (D12). The flattening at z < 10 reflects the behaviour of the reaction rate at temperatures below ∼20 K.

The case of H₂D⁺ is of interest after the suggestion by Dubrovich (1993) and Dubrovich & Lipovka (1995) that in the early universe this molecule could reach significant abundances (up to [H₂D⁺/H₂] = 10⁻⁵) and that spectral features associated with the rovibrational transitions might be detectable in the spectrum of the CBR. Such a high abundance would result from the complete conversion of H₂⁺ into H₂D⁺ because of deuterium fractionation at low temperatures (T < 50 K). However, it is very unlikely that this mechanism could work in the conditions of the primordial gas, since the abundance of H₂⁺ ions is quite low due to the absence of ionizing sources (see Fig. 4). In present-day molecular clouds, searches for the rotational transitions of H₂D⁺ have yielded a fractional abundance of 3 × 10⁻¹¹ (Boreiko & Betz 1993). The results shown in Fig. 4 indicate that the final abundance of H₂D⁺ is extremely small [H₂D⁺/H] ≃ 5 × 10⁻¹⁴ and [H₂D⁺/H⁺][H⁺] ≃ 10⁻². It is clear from our models that the presence of H₂D⁺ molecules can hardly affect the shape of the CBR (in order to see detectable effects on the CBR, Dubrovich & Lipovka (1993) assume an abundance of 10⁻⁸). On the other hand, the isotopic ratio is greatly enhanced with respect to the primordial abundance [D/H] = 4 × 10⁻⁵, due to fractionation effects.

According to the results shown in Fig. 4, the main molecular species containing helium is HeH⁺, formed by the radiative association of He and H⁺. As emphasized by Lepp & Shull (1984), this reaction is slower than the usual formation mode via association of He⁺ and H, but since the abundance of He⁺ is quite small, reaction (He8) takes over. The HeH⁺ ions are removed by CBR photons and at z < ∼250 also by collisions with H atoms to reform H₂⁺ (reaction He11). This explains the...
Scheme: chemistry in the early Universe

Sensitivity to cosmological parameters

Hatched area covers range of variation of $\Omega_0 = 0.1 - 1$, $h = H_0/100 = 0.3 - 1$ and $\eta_{10} = \text{baryon/photon} = 1 - 10$. 

E. van Dishoeck, "Master course in Astrochemistry" (2011)
Homework

1) Calculate the value of $T_R$ and average density in the Universe, assuming the standard cosmological model with $\Omega = 0.1$ and Hubble constant $H_0=50$ km/s Mpc$^{-1}$:

   a) At $z = 6.4$
   b) At $z = 0$

2) Get the frequencies of HeH$^+$ transitions in the CDMS (http://www.astro.uni-koeln.de/cdms/) and find out if there are transitions detectable at (sub-)mm wavelength region from a high-z redshift objects ($z \sim 10–100$)

3) How large could be the fraction of HeD$^+$ molecule compared to HeH$^+$ in the early Universe?
Suggested literature

• Galli, Palla (1998), A&A, 335, 403


• Master course in Astrochemistry, Ewine van Dischoek (2011): http://www.strw.leidenuniv.nl/~sanjose/astrochem

• D. Semenov "Chemistry in protoplanetary disks" in "Encyclopedia of Astrobiology" (2010), Springer
The End
Observations vs Theory

About 75% agreement for 50 observed molecules in TMC1