We start with an assumption — that \( \text{H}_2 \) is the primordial molecule and the H-H bond is the primordial bond.

We will be required to prove this assumption at some point. The rationale for the assumption is:

- H atoms are by far the most abundant in the universe.
- \( \text{H}_2 \) is the simplest molecule.
- Observations show \( \text{H}_2 \) is abundant in diffuse clouds.

Now we need a mechanism; but first we need to determine the required formation rate. To do this we will find the loss rate, then require formation to balance the loss.

We will also make the second assumption that the major loss process for \( \text{H}_2 \) is photodissociation, and will later show this to be true.

A simplified energy level diagram for \( \text{H}_2 \) looks like:

{ see Ch. 6, Duley & Williams }
There are no allowed transitions to repulsive states from the ground state at energies less than the Lyman limit (13.595 eV).

However, there are transitions to excited levels

\[ \text{H}_2 (X^1\Sigma_g^+ , v=0) + h\nu \rightarrow \text{H}_2 (B^1\Sigma_u^+ , v') \lambda < 110\text{\AA} \]
\[ \rightarrow \text{H}_2 (C^1\Pi_u , v') \lambda < 1009 \text{\AA} \]

at energies < 13.6 eV, followed by fluorescence back to excited levels of the ground state and to repulsive continuum levels of the ground state:

\[ \text{H}_2 (B^1\Sigma_u^+ , v') \rightarrow \text{H}_2 (X^1\Sigma_g^+ , v'') + h\nu \rightarrow \text{H} + \text{H} + h\nu \]

\[ \text{H}_2 (C^1\Pi_u , v') \rightarrow \text{H}_2 (X^1\Sigma_g^+ , v'') + h\nu \rightarrow \text{H} + \text{H} + h\nu \]

From quantum mechanical calculations, the fraction leading to dissociation is

\[ f_D (X \rightarrow B) \approx 0.23 \]
\[ f_D (X \rightarrow C) \approx 0.01 \]

The relative strength of fluorescent emission in non-dissociative vs. dissociative processes is illustrated on the following page.
Fig. 6.6 Relative emission spectrum in the Lyman bands (sharp lines), and continuum in the wavelength range $0.14 \leq \lambda \leq 0.17 \, \mu m$, in the fluorescence spectrum of hydrogen.

One must now calculate the dissociation rate using the interstellar radiation field and the cross sections for $\text{H}_2$ photodissociation:

$$
\Gamma_{\text{H}_2} = \int_{912\text{Å}}^{\infty} \sigma_\text{D}(\lambda) \ F(\lambda) \ d\lambda.
$$

The interstellar radiation field has the form

![Graph: Interstellar Radiation Flux F(λ) in Photons cm$^{-2}$ s$^{-1}$ E-V$^{-1}$ ster$^{-1}$ for different values of τ.]

Fig. 4.4 The interstellar radiation flux $F(\lambda)$ photons cm$^{-2}$ s$^{-1}$ eV$^{-1}$ ster$^{-1}$ in unobscured regions of the interstellar medium, in a typical diffuse cloud with $\tau \approx 0.5$, and in a denser cloud with $\tau \approx 2$.

The cross section calculated is then

$$
\Gamma_{\text{H}_2} = 5.2 \times 10^{-11} \ \text{s}^{-1}
$$

in the unattenuated interstellar radiation field.

Ch. 4 of Duley & Williams outlines similar calculations dealing with the photophysics and photochemistry of a variety of interstellar species.
Further, the $\text{H}_2$ molecule has the interesting property in the ISM that it is efficient at self-shielding.

Since photodissociation occurs via a line spectrum (albeit broad), once these photons are absorbed, the molecule can no longer be photodissociated. The figure below shows the self-shielding effect for photodissociation & fluorescence in $\text{H}_2$.

![Graph showing self-shielding effect]

**Fig. 4.7** Dependence of $\beta$ on $N(\text{H}_2)$ ($\text{H}_2$ column density) for $\text{H}_2$ and HD. Note that $\beta$(HD) is not reduced by self-shielding. The effect of $\text{H}_2$ absorption on the photoionization rate of C is also shown. (J. H. Black and A. Dalgarno, *Astrophysical Journal Supplement Series*, 1977, 34, 405.)

Simply put, this means that $\text{H}_2$ can effectively protect itself in clouds with sufficient column density.

A cloud of radius 1 pc = $3 \times 10^{18}$ cm and a density of 100 cm$^{-3}$ has a column density of

$$N = 3 \times 10^{20} \text{ cm}^{-2}$$

and is effectively self-shielded.
Assuming a uniform distribution along the line of sight:

Table 6.1 Column densities $N(H)$ and $N(H_2)$ for several paths through the interstellar medium; $\langle n \rangle = n(H) + 2n(H_2)$ is the total space density of H, assuming a uniform distribution along the entire line of sight, $r$; $r_\tau$ is the total visual extinction due to dust over the path $r$.

<table>
<thead>
<tr>
<th>Star</th>
<th>$r$ (pc)*</th>
<th>$r_\tau$</th>
<th>$N(H)$ (cm$^{-3}$)</th>
<th>$N(H_2)$ (cm$^{-3}$)</th>
<th>$\langle n \rangle$ (cm$^{-3}$)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>λSco</td>
<td>102</td>
<td>0.08</td>
<td>$2.4 \times 10^{19}$</td>
<td>$5.0 \times 10^{12}$</td>
<td>0.076</td>
<td>4.2 $\times 10^{-7}$</td>
</tr>
<tr>
<td>ζPup</td>
<td>668</td>
<td>0.14</td>
<td>$1.0 \times 10^{20}$</td>
<td>$2.8 \times 10^{14}$</td>
<td>0.047</td>
<td>6.0 $\times 10^{-6}$</td>
</tr>
<tr>
<td>τSco</td>
<td>236</td>
<td>0.165</td>
<td>$3.1 \times 10^{20}$</td>
<td>$3.2 \times 10^{14}$</td>
<td>0.42</td>
<td>2.0 $\times 10^{-6}$</td>
</tr>
<tr>
<td>ζOri</td>
<td>409</td>
<td>0.22</td>
<td>$2.8 \times 10^{20}$</td>
<td>$3.7 \times 10^{16}$</td>
<td>0.22</td>
<td>2.6 $\times 10^{-4}$</td>
</tr>
<tr>
<td>ηLac</td>
<td>589</td>
<td>0.30</td>
<td>$5.0 \times 10^{19}$</td>
<td>$1.6 \times 10^{19}$</td>
<td>0.29</td>
<td>6.0 $\times 10^{-2}$</td>
</tr>
<tr>
<td>ζPer</td>
<td>538</td>
<td>0.91</td>
<td>$1.3 \times 10^{21}$</td>
<td>$3.4 \times 10^{20}$</td>
<td>1.2</td>
<td>3.5 $\times 10^{-1}$</td>
</tr>
<tr>
<td>ηPer</td>
<td>394</td>
<td>0.91</td>
<td>$6.5 \times 10^{20}$</td>
<td>$4.7 \times 10^{20}$</td>
<td>1.3</td>
<td>5.9 $\times 10^{-1}$</td>
</tr>
<tr>
<td>ζOph</td>
<td>138</td>
<td>0.88</td>
<td>$5.2 \times 10^{20}$</td>
<td>$4.5 \times 10^{20}$</td>
<td>3.3</td>
<td>6.3 $\times 10^{-1}$</td>
</tr>
</tbody>
</table>

Column densities of H and H$_2$, $N(H)$ and $N(H_2)$, show the rapid transition from atomic to molecular hydrogen as $r$ increases.

In this table,

$$f = \frac{2n(H_2)}{n(H) + 2n(H_2)} \approx \frac{2N(H_2)}{N(H) + 2N(H_2)}$$

We now use the maximum calculated loss rate to derive the most stringent requirement on the formation rate on grains:

$$\frac{d}{dt} n(H_2) = k_{g\tau} n_g n(H) n(H) - \Gamma_{H_2} n(H_2) = 0$$

in steady state.

$$k_{g\tau} n_g n(H) n(H) = \Gamma_{H_2} n(H_2)$$

The rate of formation of H$_2$ is $k_{g\tau} n_g n(H)$ s$^{-1}$, and the effective rate constant is $k_{g\tau} = R$ cm$^3$ s$^{-1}$

$$\Rightarrow R n(H) n(H) = \Gamma n(H_2)$$

and for a diffuse cloud where $f = \frac{2n(H_2)}{2n(H_2) + n(H)} < 1$

$$R = \frac{\Gamma f}{2n}$$
For some "typical" lines-of-sight \( \Rightarrow \)

The canonical value is usually taken to be

\[ R = 3 \times 10^{-17} \text{ cm}^3 \text{s}^{-1} \]

How does this stack up against grain formation?

**Molecule formation on grains**

There are several steps (here for H\(_2\)):

1. An H atom must collide with a grain.
2. The colliding atom must be accommodated (adsorbed).
3. The H atom must be retained until another H atom is absorbed.
4. The H atoms must be mobile in order to find each other.
5. H\(_2\) must be formed in the collision and ejected from the surface.

1. The formation rate for H\(_2\) on grains is

\[
k_c P n_g n(\text{H}) = \sigma v_H P n(\text{H}) \text{ s}^{-1}
\]

\[
\sigma = 3 \times 10^{-22} \text{ cm}^2 \text{s}^{-1}
\]

\[
\sigma = 3 \times 10^{-17} \text{ cm}^2 \text{s}^{-1}
\]

for \( v_H = 1 \times 10^5 \text{ cm/s} \)

<table>
<thead>
<tr>
<th>Star</th>
<th>( n (\text{cm}^{-3}) )</th>
<th>( F_\parallel (\text{s}^{-1}) )</th>
<th>( f )</th>
<th>( R (\text{cm}^3\text{s}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>δOri</td>
<td>10–30</td>
<td>5.5 \times 10^{-11}</td>
<td>5.6 \times 10^{-6}</td>
<td>1.5 \times 10^{-17}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>to 5.2 \times 10^{-18}</td>
</tr>
<tr>
<td>rSco</td>
<td>10–100</td>
<td>4.4 \times 10^{-10}</td>
<td>2.0 \times 10^{-6}</td>
<td>4.4 \times 10^{-17}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>to 4.4 \times 10^{-18}</td>
</tr>
<tr>
<td>ζPup</td>
<td>100</td>
<td>1.8 \times 10^{-9}</td>
<td>6.0 \times 10^{-6}</td>
<td>5.3 \times 10^{-17}</td>
</tr>
</tbody>
</table>

The "effective two body" rate constant is \( k_c \text{Pn} \text{ cm}^3 \text{s}^{-1} = 83 \times 10^{-17} \text{ Pn cm}^3 \text{s}^{-1} \),

and to meet the required ("observed") \( R = 3 \times 10^{-17} \text{ cm}^3 \text{s}^{-1} \) we need the product Pn to be large.

2. To determine the absorption times, use a classical expression:

\[
t_a = \frac{1}{\nu} e^{D/kT}
\]

which says that the probability for overcoming a barrier of height D at a temperature T is \( \sim e^{-D/kT} \), and that there are \( \nu \) opportunities/second to overcome the barrier.

\( \nu \) is the vibrational frequency for H in the absorption potential. For a particle-in-a-box potential

\[
\nu \approx \frac{D}{\hbar} \approx 10^{12} \text{ s}^{-1}.
\]

If the H is physi-sorbed we take

\[D_p \sim 400 \text{K},\]

and if chemi-sorbed we use \( 2eV \) as an extreme value,

\[D_c \approx 2eV = 20,000 \text{ K}.
\]

Thus,

\[
t_a = \begin{cases} 3 \times 10^5 \text{ s} & \text{ at } 10 \text{K} \\ 2 \times 10^{-8} \text{ s} & \text{ at } 40 \text{K} \\ \infty & \text{ at } 100 \text{K} \end{cases}
\]

Thus, absorption physical

\[ \Rightarrow \text{H atoms will evaporate above 40K (perhaps less) before forming H}_2, \text{ unless there are strong binding sites!} \]
3. The time between collisions of H-atoms & grains is

$$t_c = \frac{1}{k_e n(H)} = \frac{1}{\pi a^2 v_n n(H)} = \frac{1}{\pi (10^{-5} \text{cm})^2 (10^5 \text{cm/s}) n(H)}$$

or

$$t_c = 3 \times 10^4 \text{ s} \quad \text{for } n(H) = 1$$
$$t_c = 300 \text{ s} \quad \text{for } n(H) = 2.00$$

At low T, physical absorption will retain H atoms long enough, but chemisorption is required at "high" T. The breakpoint is about T~15 K.

4. If we postulate that chemisorption sites are present to accomodate H₂ formation at higher temperature, the H atoms must be able to find them. Note: The H atoms are not mobile at a chemisorption site. What is the physisorption mobility?

Use the standard quantum solution for barrier penetraton:

$$P = 1 + \left[ \frac{D^2 \sinh^2 \beta \Delta}{4E (D-E)} \right]^{-1}, \quad \beta = \sqrt{2m (D-E) \hbar^2}$$

For D=400 K, E=\nu, \nu = 10^{12} \text{s}^{-1}, m=\text{m}_\text{H}, \Delta = 1 \text{Å}

$$P = 10^{-3}$$

and the time required to penetrate the barrier is
\[ t_h = \frac{1}{\rho_v} = 10^{-9} \text{ s} \quad \text{"hopping" time for an individual hop}\]

Thus, H atoms are very mobile if held by physical adsorption.

The time to find another site on the grain, for a random, 2D walk, is:

\[ t_m = \lambda^2 t_h \quad \lambda = \# \text{ of "hops" needed} \]

Assume, as a worst case, there is only one chemisorption site on a 0.1\,\mu m grain.

\[ \Rightarrow \lambda = \frac{\sqrt{\text{rad.12}}}{r} \{ \frac{\text{distance between sites}}{\text{spacing of sites}} \} \]

If \( d = 1 \times 10^{-5} \text{ cm} \) and \( r = 1.5 \text{ Å} = 1.5 \times 10^{-10} \text{ cm} \)

\[ \Rightarrow \lambda \approx 10^3 \quad \text{and} \quad t_m = \lambda^2 t_h = 10^{-3} \text{ s} \]

\[ \text{so } t_m \approx t_c, \text{ so that the H atom can find the chemisorption site before the next collision.} \]

\[ \text{and } t_m \approx t_a \text{ for } T \approx 20K \]

so when \( T \approx 20K \) the H-atom can find the chemisorption site(s) before evaporating.

To be able to raise the temperature for H\(_2\) formation on grains, we need increasing \( t_m \) of chemisorption sites. We postulate that the grains have large \( t_m \) of chemisorption sites so that H\(_2\) can be formed at \( T \approx 100K \).
The consequence is that a grain is saturated with H atoms and the rate of formation of H$_2$ is controlled by the rate of arrival of H atoms at the surface.

5. Assume H$_2$ is formed out of every H-H encounter.

In essence, trade a grain-H chemical bond for an H-H molecular bond. There are now no strong grain-H$_2$ bonds, the H$_2$ can only be physically adsorbed, and

$$t_{\text{evaporation}} = \frac{1}{v_{\text{H}_2}} \exp \left( \frac{D_{\text{H}_2} k T}{E_a} \right) \leq t_a (H).$$

Under these conditions, \( P = 1 \) and

$$k_g \approx 3 \times 10^{-17} \, \text{n cm}^3 \text{s}^{-1}$$

which is just what is observed in the diffuse ISM!

What about the gas phase?

1. The simplest way is just to shake two H-atoms together:

$$H + H \rightarrow H_2 + h\nu$$

**Problem:**

There are no low-lying states that are available in the H$_2$ molecule.

---

**Fig. 6.4** Potential energy curves for two ground state H atoms. $X^1\Sigma_g^+$ is the normal ground state of H$_2$. Stabilizing collisions that lead to radiative association are shown. (1) is a transition between $v'' = \text{continuum}$ and $v'' = 14$ of the $X^1\Sigma_g^+$ state. (2) is a spin forbidden $3\Sigma_u^+ \rightarrow X^1\Sigma_g^+$ electronic transition.
You could try \( \Sigma^+ \rightarrow \Sigma^+ \) at large separations, or emission from the continuum to high lying vibrational states [1] in figure 1, but both are very slow. Essentially will not work...

2. Try it with a proton:

\[
\begin{align*}
h^+ + H & \xrightarrow{k_1} H_2^+ + hV \quad k_1 \approx 10^{-17} \text{ cm}^3 \text{s}^{-1} \\
H_2^+ + H & \xrightarrow{k_2} H_2 + H^+ \quad k_2 \approx 10^{-9} \text{ cm}^3 \text{s}^{-1}
\end{align*}
\]

\[
R = k_2 n(H_2^+) \quad n(H_2^+) = \frac{k_1 n(h^+) n(H)}{k_2 n(H)}
\]

\[
0 \leq k_2 n(H_2^+) \leq k_1 n(h^+) \leq 10^{-17} n(H^+)
\]

Further, \( n(h^+) \ll n(H) \) and \( k_2 \approx 10^{-17} n(H) \)

3. Try it with a negative ion:

\[
\begin{align*}
h + e^- & \xrightarrow{k_1} H^- \quad k_1 = 10^{-18} T \quad \text{cm}^3 \text{s}^{-1} \\
H^- + H & \xrightarrow{k_2} H_2 + e^- \quad k_2 = 1.3 \times 10^{-9} \text{ cm}^3 \text{s}^{-1} \\
" + hV & \xrightarrow{\Gamma} H + e^- \quad \Gamma = 5 \times 10^{-7} \text{ s}^{-1} \\
" + C^+ & \xrightarrow{k_3} C + H \quad k_3 \approx 10^{-6} \text{ cm}^3 \text{s}^{-1}
\end{align*}
\]

We want \( k_2 n(H^-) \);

Use steadystate

\[
\Rightarrow n(H^-) = \frac{k_1 n(H) n(e^-)}{k_2 n(H) + k_3 n(C^+) + \Gamma}
\]
What is the fastest loss process?

\[
\frac{k_2 \, n(H)}{\Gamma} = \frac{1.3 \times 10^{-9} \, n(H)}{5 \times 10^{-7}} = 3 \times 10^{-3} \, n(H)
\]

so for \( n < 300 \), photodetachment wins.

\[
\frac{k_3 \, n(C^+)}{\Gamma} = \frac{10^{-6} \cdot 10^{-4} \, n(H)}{5 \times 10^{-7}} = 2 \times 10^{-4} \, n(H)
\]

so photodetachment wins again.

\[
k_2 \, n(H^-) = \frac{k_1 \, k_2 \, n(c^-) \, n(H)}{\Gamma}
\]

\[
= \frac{(10^{-18}) \, (1.3 \times 10^{-9}) \, [10^{-4} \, n(H)] \, n(H)}{5 \times 10^{-7}}
\]

\[
= 3 \times 10^{-25} \, n^2 \, \Gamma
\]

For \( n \leq 100 \) and \( T = 100 \),

\[
k_2 \, n(H^-) = 10^{-20} \, \text{cm}^3 \, \text{s}^{-1}
\]

\[
\ll k_g
\]

| Grain synthesis of \( H_2 \) "wins" |

But recall that the process has to be nearly "perfect"!

Note: In the early universe, there are no grains. There is also no \( C^+ \) and less visible UV radiation. Mechanism #3 above therefore becomes quite important to the chemistry of the early universe & the first generation of star formation.