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ON THE REACTION RATES AND CHEMICAL KINETICS OF MOLECULAR HYDROGEN FORMATION

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RESUMEN

Se presentan las tasas de las reacciones $H^- + H \leftrightarrows H_2 + e$, $H + e \rightarrow H^- + h\nu$, $H^- + e \rightarrow H + 2e$ y $H_2 + H \rightarrow 3H$ como funciones de la temperatura. Estas tasas se han obtenido de los datos más recientes. Empleando estas tasas se estudia la evolución química de una nube transparente de hidrógeno con temperatura $T \leq 8\,000°K$. A temperaturas $T \geq 3\,000°K$ la producción de H_2 nunca es significativa. A temperaturas $T \leq 2\,000°K$ prácticamente todo el hidrógeno inicial se liga en forma molecular con una escala de tiempo $\tau = 1/2\alpha(He)N(e^0)$. En el caso de que $\alpha(H_2H)$ esté sobreestimada (y $T \leq 8\,000°K$) el hidrógeno inicial siempre se liga casi totalmente en moléculas con la escala de tiempo τ.

ABSTRACT

The reaction rates of the reactions $H^- + H \leftrightarrows H_2 + e$, $H + e \rightarrow H^- + h\nu$, $H^- + e \rightarrow H + 2e$ and $H_2 + H \rightarrow 3H$ are given as functions of temperature. These rates are obtained from the best data available and are used to study the chemical evolution of a transparent cloud of neutral hydrogen for temperatures $T \leq 8\,000°K$. For temperatures $T \geq 3\,000°K$ H_2 production is never significant. For temperatures $T \leq 2\,000°K$ practically all the initial hydrogen bounds into H_2 with a scaletime $\tau = 1/2\alpha(He)N(e^0)$. If $\alpha(H_2H)$ is actually overestimated (and $T \leq 8\,000°K$) then the initial hydrogen always bounds into molecules with the scaletime τ.

Key Words: **INTERSTELLAR MATTER — MOLECULAR FORMATION — REACTION RATE.**

I. INTRODUCTION

In recent years the problem of dust formation in the interstellar medium has become increasingly important. One reason is that some discrepancies between theory and observations are attributed to the presence of dust. Another one is, of course, its intrinsic interest. The overall problem is to find the rate of dust formation given the chemical composition and the physical conditions of the medium. Since this problem is quite complicated, the first step must be to consider the formation of simple molecules. It has been shown (Gould and Salpeter 1963) that this process achieves great efficiency if the individual componentes of the molecule are adsorbed at the surface of dust grains. This mechanism has been quite exhaustively studied in the last years, (see for instance Hollenbach *et al.* 1971). Nevertheless there remains the obvious problem of the origin of the "primeval" dust grains, which are, in turn, made up of molecules or aggregates of atoms. Also, there may be situations where molecules are formed in the absence of dust grains. Some work has been done on the subject (De Jong 1972) for steady state conditions, a work that yields the equilibrium abundances of the various components under that restriction. In these calculations the temperature dependence of the rate coefficients has not been accurately taken into account. Clearly the time-scale of the process is also of primordial importance. It is our purpose to study the problem of molecule formation without the influence of dust or other external factors. In this paper we will study the problem in its simplest form, that is, we study the evolution towards equilibrium of an isolated, transparent cloud of atomic hydrogen, containing some free electrons, under different initial physical conditions. We will consider only two-body processes, the only important ones at usual astronomical densities, making an accurate estimate of the temperature dependence of the rate coefficients.

II. THE REACTION RATES

a) *The Processes*

There are many two-body processes which may appear in our problem, so we have to select the relevant ones. We will always start with an atomic hydrogen cloud, with a small fraction of impurities which will be considered only as a source of free electrons, since we will consider conditions at which H is neutral but C may be ionized. Under these conditions, the only important process which may produce H_2 molecules is associative detachment:

$$H^- + H \rightarrow H_2 + e. \qquad (1)$$

The negative ion of hydrogen is formed in the recombination of a hydrogen atom with a free electron through the reduction

$$H + e \rightarrow H^- + h\nu. \qquad (2)$$

We will require that hydrogen be completely neutral at the beginning. This restriction will guarantee maximum efficiency in H^- formation during the first stages of evolution, and will also avoid the extra contribution to the free electron density due to ionized hydrogen. In order to be sure that this condition is always fulfilled we will restrict ourselves to the temperature range $T \leq 8000°K$. At these temperatures most of the usual binary reactions are very slow. Under these assumptions the only relevant processes are those mentioned above (see for instance De Jong 1972). Hence we will not consider processes involving more complicated molecules (H_2^+, H_3^+, etc.) whose creation requires higher energies. Nevertheless, since the ionization potential of H^- is very low ($I = .75$ ev) we will have to consider collisional ionization of H^-, that is

$$H^- + e \rightarrow H + 2e. \qquad (3)$$

Due to all the conditions we have mentioned, the only destruction mechanisms of the H_2 molecule that we will consider are: dissociative attachment

$$H_2 + e \rightarrow H + H, \qquad (4a)$$

and collisional dissociation with hydrogen atoms

$$H_2 + H \rightarrow H + H + H. \qquad (4b)$$

b) *The Rate Coefficients*

The rate coefficient for the reaction $A + B$ is defined, as usual, by the relation

$$\alpha(AB) \equiv \int_0^\infty \sigma(AB) \;\; v \;\; f(v)\,dv,$$

where $\sigma(AB)$ is the cross section for the process, v the relative velocity of the reactants and $f(v)dv$ the relative velocity distribution probability function. Then $\alpha(AB)\ N(A)\ N(B)$ gives the number of reactions that take place per unit time and per unit volume, $N(A)$ and $N(B)$ being the number densities of reactants A and B respectively.

Usually the rates are taken to be constant or at most, use is made of Arrenhius' formula which assumes a constant cross section. Since, eventually, we would like to study the evolution of a gas cloud including cooling mechanisms, we will first of all derive the temperature-dependent rate-coefficients for the processes mentioned above. We use the most recent available data so that the expressions we obtain are the best possible at this time.

i) *α(He)*

The cross section for the photoionization of H^- was calculated theoretically by Chandrasekhar (1958). A more sophisticated approach and experimental measurements give the "best known values"

TABLE 1

CROSS SECTION FOR THE PHOTOIONIZATION OF H- AS A FUNCTION OF λ (MEENA AND KWONG 1975)

λ Å	σ (10^{-17} cm²)
1311	0.5838
1672	0.7690
2196	1.0941
4241	2.4631
5065	2.9549
5883	3.3640
6289	3.5332
6755	3.6950
7296	3.8375
7931	3.9400
8687	3.9677
9603	3.8625
10734	3.5246
12167	2.8096
14042	1.5314

given in Table 1 (Meena and Kwong 1975). From these values we find the cross section for the inverse process (the one we are interested in) by means of Milne's relation. Let $\sigma(H^- \gamma)$ be the cross section for the reaction $H^- + h\nu \rightarrow H + e$, and let $\sigma(He)$ be the cross section for the inverse reaction. Then we have

$$\sigma(He) = (g_i/g_f)(k_i^2/k_f^2)\ \sigma(H^- \gamma), \qquad (5)$$

where g_i and g_f are the statistical weights of the initial and final states of the hydrogen atom, and k_i and k_f are the momenta of the photon and the electron, respectively. Since $\frac{1}{2}\,mv^2 + I = h\nu$, where m is the electron mass, v the electron velocity, ν the frequency of the emitted photon and $I \equiv hc/\lambda_0 = .753$ ev, the ionization potential of H^-, we have from (5):

$$\sigma(He) = (1/4)(I/mc^2)\ [(1 + x)^2/x]\ \sigma(H^- \gamma), \qquad (6)$$

where $x = (mv^2/2I)$.

We may always write

$$\sigma(H^- \gamma) = \frac{\sigma_0}{(1 + x)^2}\ f(x) \text{ with}$$

$$\sigma_0 \equiv \sigma(H^- \gamma)_{\max} = 3.9677 \times 10^{-17}\ \text{cm}^2$$

and f(x) determined from Table 1. Then, assuming a Maxwellian velocity distribution

$$\alpha(He) = (c\sigma_0/\sqrt{2\pi})\,(I/mc^2)^{3/2}\ (I/kT)^{3/2} \times \int_0^\infty f(x)\ \exp\ (-Ix/kT)\ dx. \qquad (7)$$

The values of f(x) may be approximated by three straight lines. The best fit is:

$$f(x) = \begin{cases} f_1(x) = fo_1 x^\alpha,\ 0 \leq x \leq .7547 = x_1, \\ f_2(x) = fo_2 x^\beta,\ x_1 \leqslant x \leqslant 1.95034 = x_2, \\ f_3(x) = fo_3 x^\delta,\ x_2 \leqslant x \leqslant \infty; \end{cases} \qquad (8)$$

with $fo_1 = 4.3697$, $\alpha = 1.1983$, $fo_2 = 3.9976$, $\beta = .88209$, $fo_3 = 4.6758$ and $\delta = .6475$;

which is compared in Table 2 with the exact values of f(x). Putting (8) in (7) we finally have:

$$\alpha(He) = K\{x_1^{\beta+1}[H(\alpha, y_1) - H(\beta, y_1)] + x_2^{\beta+1}[H(\beta, y_2) - H(\delta, y_2) + \Gamma(\delta + 1)/y_2^{\delta+1}]\}, \qquad (9)$$

with

$$K = (c\sigma_0/\sqrt{2\pi})\ (I/mc^2)^{3/2}\ (I/kT)^{3/2}\, fo_2,$$

and $H(p, q) = \gamma(p + 1, q)/q^{p+1}$. $\gamma(a, x)$ is the incomplete gamma function $\gamma(a, x) = \int_0^x x^{a-1}\ e^{-x}\ dx$,

TABLE 2

COMPARISON OF VALUES OF f(x) OBTAINED FROM TABLE 1 AND THE POWER LAW FITS

x	f(x)	f(x) fit
11.5858	23.3070	22.8432
8.8684	18.8747	19.2129
6.5137	15.5677	15.7332
2.8906	9.3967	9.2972
2.2576	7.9031	7.9222
1.8047	6.6694	6.7295
1.6236	6.1295	6.1301
1.4426	5.5562	5.5232
1.2615	4.9465	4.9068
1.0804	4.2978	4.2799
.8994	3.6077	3.6407
.7182	2.8739	2.9391
.5372	2.0991	2.0754
.3561	1.3022	1.2680
.1750	.5329	.5413

$\Gamma(x)$ is the gamma function $\Gamma(x) = \int_0^\infty e^{-t}t^{x-1}\,dt$, and $y_i = x_i\, I/kT$.

Equation (9) goes to zero if $T \mapsto 0$, but it diverges at high temperatures. This behaviour is not important since we will work at relatively low temperatures but, for the sake of completeness, we may try to solve this problem. Using Chandrasekhar's work (1958) where, for high energies, $\sigma(H^-\gamma) \sim \nu^{-4}$ and remembering also that the usual behaviour is $\sigma \sim \nu^{-3}$, we see that σ goes at least as ν^{-3} for high energies. Then

$$f(x) = \begin{cases} f_1(x), & 0 < x < x_1, \\ f_2(x), & x_1 < x < x_2, \\ f_3(x), & x_2 < x < 16 = x_3, \\ f_{04}/x, & x_3 < x < \infty; \end{cases} \qquad (10)$$

with $f_{04} = 450.45$.

Introducing this correction we find:

$$\begin{aligned} \alpha(\mathrm{He}) = K\{&x_1^{\beta+1}[H(\alpha, y_1) - H(\beta, y_1)] \\ &+ x_2^{\beta+1}[H(\beta, y_2) - H(\delta, y_2)] + x_2^{\beta-\delta}x_3^{\delta+1} \\ &\times [H(\delta, y_3) + E_1(y_3)]\}. \end{aligned} \qquad (11)$$

This expression does indeed go to zero as $T \mapsto \infty$. A plot of $\alpha(\mathrm{He})$ versus T is given in Figure 1.

ii) $\alpha(H_2e)$

The cross section for this process has been measured both for low energies (Schulz and Asundi 1967) and for high energies (Rapp *et al.* 1965). We fitted these measurements with a sum of gaussians and a straight line, with reasonable accuracy. We found

$$\sigma(H_2e) = \begin{cases} \sigma_{01}\exp[-a_1(E - b_1)^2] \\ \quad +\sigma_{02}\exp[-a_2(E - b_2)^2];\ E \leq 8.6\ \text{ev.} \\ a + bE + \sigma_{02}\exp[-a_2(E - b_2)^2] \\ \quad +\sigma_{03}\exp[-a_3(E - b_3)^2];\ E \geq 8.6\ \text{ev.} \end{cases} \qquad (12)$$

$\sigma_{01} = 1.8 \times 10^{-21}\,\mathrm{cm}^2$, $\sigma_{02} = 1.15 \times 10^{-20}\,\mathrm{cm}^2$, $\sigma_{03} = 1.42 \times 10^{-20}\,\mathrm{cm}^2$, $a = -.9736 \times 10^{-20}\,\mathrm{cm}^2$,

$b = .113 \times 10^{-20}\,\dfrac{\mathrm{cm}^2}{\mathrm{ev}}$,

$a_1 = 4\ \mathrm{ev}^{-2}$, $b_1 = 3.8117$ ev,

$a_2 = 0.23\ \mathrm{ev}^{-2}$, $b_2 = 10.03$ ev,

$a_3 = 3.2556\ \mathrm{ev}^{-2}$ and $b_3 = 13.9276$ ev.

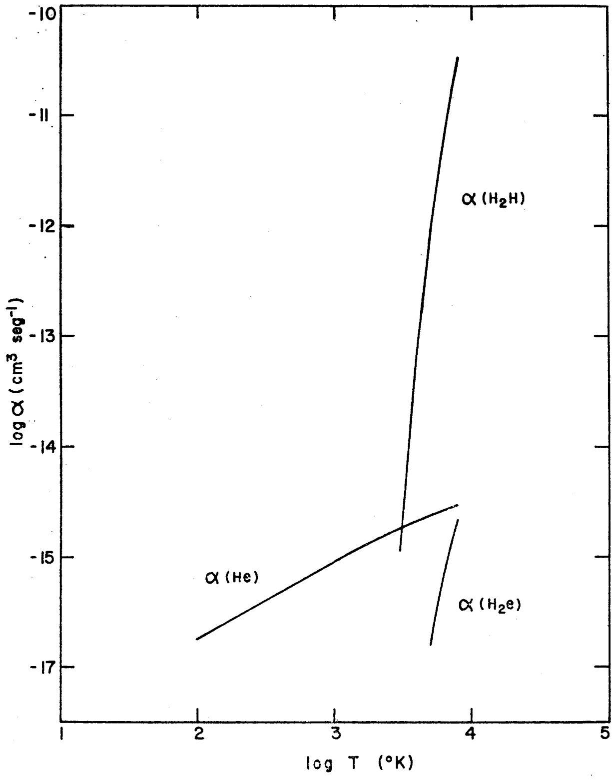

Fig. 1. Rate coefficients for the reactions $H + e \rightarrow H^- + \gamma$, $H_2 + H \rightarrow 3H$ and $H_2 + e \rightarrow H + H^-$ as a function of temperature for $100°K \leqslant T \leqslant 8000°K$.

A comparison of this function with the experimental values is given in Table 3.

Then

$$\alpha(H_2e) = \alpha_0 + \alpha_1 + \alpha_2 + \alpha_3 \qquad (13)$$

with

$$\begin{aligned} \alpha_0 = {} & 6.208 \times 10^{-15}T^{1/2} \\ & \times \left\{\frac{T}{102604}\left[\left(\left(1 + \frac{T_0}{T}\right)^2 + 1\right)\right] - .9736\left(1 + \frac{T_0}{T}\right)\right\} \\ & \times \exp(T_0/T) \qquad \mathrm{cm}^3\ \mathrm{sec}^{-1}, \end{aligned} \qquad (14a)$$

$$\begin{aligned} \alpha_1 = {} & 1.88 \times 10^{-8}T^{-3/2} \\ & \times \{.678\exp(-E_0/kT) - \\ & - \sqrt{\pi}\,x_1\,\mathrm{erfc}(x_1 + 7) \\ & \times \exp(x_1^2 - \beta_1)\} \qquad \mathrm{cm}^3\ \mathrm{sec}^{-1}, \end{aligned} \qquad (14b)$$

$$\begin{aligned} \alpha_2 = {} & 2.08 \times 10^{-6}T^{-3/2} \\ & \times \{5.5 \times 10^{-5}\exp(-E_0/kT) - \\ & - \sqrt{\pi}\,x_2\,\mathrm{erfc}(x_2 + 1.68) \\ & \times \exp(x_2^2 - \beta_2)\} \qquad \mathrm{cm}^3\ \mathrm{sec}^{-1}, \end{aligned} \qquad (14c)$$

TABLE 3

COMPARISON OF MEASURED AND FITTED VALUES OF σ (H_2e)

E (ev)	σ_m (10^{-20} cm^2)	σ_{fit} (10^{-20} cm^2)
3.2	.005	.040
3.5	.050	.122
4.0	.127	.156
4.3	.06	.07
5.0	.020	.004
5.3	.016	.007
7.5	.15	.264
8.0	.35	.446
8.5	.65	.671
9.0	.9	.944
9.5	1.16	1.178
10.0	1.28	1.306
11.0	1.13	1.196
12.0	.77	.853
13.0	.55	.733
14.0	2.0	2.034
15.0	.88	.759
16.0	.82	.835
17.0	.92	.947
18.0	1.05	1.06

$$\begin{aligned}\alpha_3 = {} & 1.82 \times 10^{-7} T^{3/2} \\ & \times \{1.82 \times 10^{-154} \exp(-E_0/kT) - \\ & - \sqrt{\pi}\, x_3 \operatorname{erfc}(x_3 + 6.315) \\ & \times \exp(x_3^2 - \beta_3)\} \qquad \text{cm}^3\ \text{sec}^{-1},\end{aligned} \tag{14d}$$

where

$$T_0 = 99894.8°\text{K}, \quad \frac{E_0}{k} = 40580°\text{K},$$

$$x_1 = -7.623\left(1 - \frac{381°\text{K}}{T}\right)$$

$$\beta_1 = 58.11,$$

$$x_2 = -4.81\left(1 - \frac{2522°\text{K}}{T}\right)$$

$$\beta_2 = 23.14,$$

$$x_3 = -25.13\left(1 - \frac{128°\text{K}}{T}\right)$$

$$\beta_3 = 631.51.$$

T is in °K and

$$\operatorname{erfc} x \equiv \frac{2}{\sqrt{\pi}} \int_x^\infty e^{-t^2} dt.$$

A plot of $\alpha(H_2e)$ versus T is given in Figure 1.

iii) $\alpha(H^-e)$

For this process we have the cross section as a function of energy (Peart *et al.* 1970). We fitted these values with

$$\sigma = \sigma_m \{4(E - I)(E_m - I)/(E + E_m - 2I)^2\} \tag{15}$$

using the method given by Cantó and Daltabuit (1974). We know that $I = 3/4$ ev. and used $\sigma_m = 3.42 \times 10^{-15}$ cm^2, $E_m = 21$ ev. The fit is quite good for low energies, where we will work, as can be seen in Table 4. From Cantó and Daltabuit (1974) we immediately have

TABLE 4

COMPARISON OF MEASURED AND FITTED VALUES OF σ (H^-e)

E (ev)	σ_m (10^{-15} cm^2)	σ_{fit} (10^{-15} cm^2)
12.4	3.1	3.17
15.9	3.76	3.35
19.4	3.46	3.41
22.4	3.4	3.42
27.4	3.42	3.36
32.4	3.3	3.25

$$\alpha(H^-e) = 16\sigma_m (kT/2\pi m)^{1/2}\, g(\beta, Z)\ \text{erp}\ (-I/kT) \tag{16}$$

where

$$\begin{aligned} g(\beta, Z) = {} & (\beta^2 - 3\beta + 2)Z^2 + (\beta - 1)Z \\ & - (\beta - 1)Z \exp((\beta - 1)Z)\ E_1((\beta - 1)Z) \\ & \times [(\beta^2 - 3\beta + 2)Z^2 + (2\beta - 3)Z] \end{aligned}$$

with

$$\beta = Em/I, \quad Z = I/kT.$$

A plot of $\alpha(H^-e)$ versus T is given in Figure 2.

iv) $\alpha(H^-H)$

To find $\alpha(H^- H)$ as a function of temperature, we used the values of $\alpha(H^-H)$ measured by Browne and Dalgarno (1969). We found that they can be fitted by

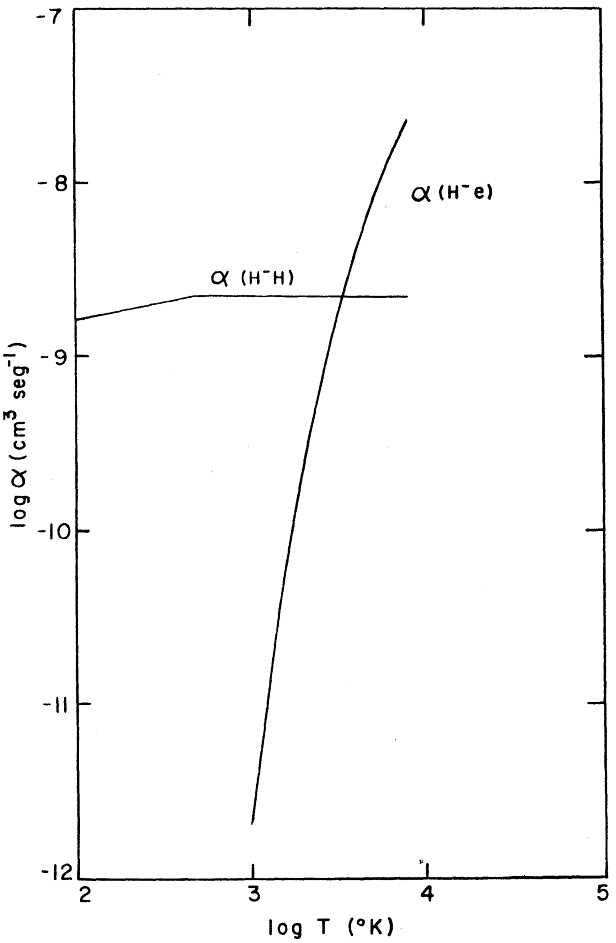

FIG. 2. Rate coefficients of the reactions $H^- + e \rightarrow H + 2e$ and $H^- + H \rightarrow H_2 + e$ as a function of temperature for 100°K $\leqslant T \leqslant$ 8000°K.

$$\alpha(H^-H) = \begin{cases} 6.28 \times 10^{-10} T^{0.203} \mathrm{cm}^3/\mathrm{s}, \quad T \leq 470°K, & (17) \\ 2.19 \times 10^{-9} \ \mathrm{cm}^3/\mathrm{s}, \quad 470 \leq T \leq 8000°K. \end{cases}$$

A plot of $\alpha(H^-H)$ versus T appears in Figure 2.

v) *$\alpha(H_2H)$*

It looks like the only known values of this rate are the ones obtained by Gardiner *et al* (1961). They give

$$\alpha(H_2H) = 2 \times 10^{-6} \ T^{-1/2} \exp\,(-51906/T). \quad (18)$$

A plot of this rate as a function of T is given in Figure 1.

All rates that we have obtained may be compared with the order of magnitude values that Watson (1976) obtains using physical considerations. They may also be compared with those used by Hutchins (1976) to study the collapse of a protostar. It may be worth to note that, although Hutchins also follows the evolution in time of a cloud of gas, the physical conditions under which he works are so different that, unfortunately, his results may not be compared with ours.

c) *Analytical Approximations*

As we mentioned before, we will work only at temperatures $T \leq 8000°K$. In this temperature range formulae (11), (13) and (16) may be approximated by simple analytical functions. We find that

$$\alpha(He) = \begin{cases} 7.19 \times 10^{-18} \ T^{0.6983} \ \mathrm{cm}^3 \ \mathrm{s}^{-1}, \ T \leq 2000°K, & (19a) \\ 7.19 \times 10^{-18} \ T^{0.6983} \ (1 - T/34000) \ \mathrm{cm}^3 \ \mathrm{s}^{-1}, \end{cases}$$

$$2000°K \leq T \leq 8000°K;$$

$$\alpha(H^-e) = 3.3 \times 10^{-10} \ T^{1/2} \exp\left(\frac{-8695.65}{T}\right) \times \left(1 + \frac{T}{5990}\right) \mathrm{cm}^3 \ \mathrm{s}^{-1}, \quad (19b)$$

$$\alpha(H_2e) = 5.37 \times 10^{-11} \ T^{-1/2} \exp\left(-\frac{41000}{T}\right) \times \left(1 - \frac{T}{20000}\right) \mathrm{cm}^3 \ \mathrm{s}^{-1} \quad (19c)$$

where T is in °K.

These relations together with (17) and (18) will be used in this paper. A comparison among "exact" values and equations (19) is given in Tables 5-7.

TABLE 5

COMPARISON OF α (He) AS COMPUTED WITH FORMULAE 11 AND 19 (*a*)

T (°K)	α(He) (10^{-15} cm³ s⁻¹)	α_{fit}(He) (10^{-15} cm³ s⁻¹)
500	.551	.551
1000	.894	.895
2000	1.43	1.45
4000	2.13	2.08
6000	2.58	2.57
8000	2.90	2.92

TABLE 6

COMPARISON OF α (H⁻e) AS COMPUTED USING FORMULAE 16 AND 19(*b*)

T (°K)	$\alpha(H^-e)$ ($cm^3 s^{-1}$)	$\alpha_{fit}(H^-e)$ ($cm^3 s^{-1}$)
100	3.51(−47)	5.77(−47)
500	2.06(−16)	2.24(−16)
1000	1.97(−12)	2.04(−12)
2000	2.55(−10)	2.55(−10)
4000	4.01(−9)	3.96(−9)
6000	1.2 (−8)	1.2 (−8)
8000	2.29(−8)	2.32(−8)

TABLE 7

COMPARISON OF $\alpha(H_2e)$ AS COMPUTED USING FORMULAE 13 AND 19(*c*)

T (°K)	$\alpha(H_2e)$ ($cm^3 s^{-1}$)	$\alpha_{fit}(H_2e)$ ($cm^3 s^{-1}$)
100	0	0
500	8.37(−48)	5.73(−48)
1000	2.65(−30)	2.52(−30)
2000	1.33(−21)	1.35(−21)
4000	2.32(−17)	2.41(−17)
6000	5.07(−16)	5.24(−16)
8000	2.22(−15)	2.15(−15)

III. THE CHEMICAL EVOLUTION

a) *The Population Equations*

Let N(H), N(e), N(H⁻), N(H_2) be the number densities of H, electrons, H^- and H_2 respectively. Then (from the definition of rate coefficient) their time rate of change is given by:

$$\begin{aligned}
\frac{dN(H)}{dt} &= \alpha(H^-e)N(H^-)N(e) + \\
&+ 2\alpha(H_2e)N(H_2)N(e) \\
&+ 2\alpha(H_2H)N(H_2)N(H) - \\
&- \alpha(He)N(H)N(e) \\
&- \alpha(H^-H)N(H^-)N(H), \\
\frac{dN(e)}{dt} &= \alpha(H^-e)N(H^-)N(e) + \\
&+ \alpha(H^-H)N(H^-)N(H) \\
&- \alpha(He)N(H)N(e) - \alpha(H_2e)N(H_2)N(e), \qquad (20) \\
\frac{dN(H^-)}{dt} &= \alpha(He)N(H)N(e) + \alpha(H_2e)N(H_2)N(e) \\
&- \alpha(H^-e)N(H^-)N(e) - \\
&- \alpha(H^-H)N(H^-)N(H), \\
\frac{dN(H_2)}{dt} &= \alpha(H^-H)N(H^-)N(H) - \\
&- \alpha(H_2e)N(H_2)N(e) \\
&- \alpha(H_2H)N(H_2)N(H).
\end{aligned}$$

These equations fulfill the laws of charge and mass conservation which can be stated respectively as $N(H^-) + N(e) = N(e^0) + N(H^{-0})$, $2N(H_2) + N(H) + N(H^-) = 2N(H_2{}^0) + N(H^0) + N(H^{-0})$ where the superscript "0" refers to a certain instant of time. Since we will start with a cloud containing only neutral hydrogen and some free electrons we have at $t = 0 : N(H^{-0}) = N(H_2{}^0) = 0$ where the superscript now refers to the initial time. The conservation laws now become $N(H^-) + N(e) = N(e^0)$ and $2N(H_2) + N(H) + N(H^-) = N(H^0)$. Using these relations the original set of four equations reduces to two equations.

Let $N(H^0) = \beta N(e^0)$, $x = N(H^-)/N(e^0)$, $y = 2N(H_2)/(\beta - 1)N(e^0)$. (Note that these new variables have values such that $0 \leq x \leq 1$, $0 \leq y \leq \beta/(\beta - 1)$ and that at $t = 0$, $x = 0$ and $y = 0$. Substituting in (20) we obtain

$$\begin{aligned}
\dot{x} &= a_1x^2 - a_2x - a_3y + a_4xy + a_5 \\
&\qquad\qquad\qquad\qquad (21) \\
\dot{y} &= -b_1x^2 + b_2x - b_3y - b_4xy + b_5y^2
\end{aligned}$$

with

$$a_1 = [\alpha(He) + \alpha(H^-e) + \alpha(H^-H)]N(e^0),$$

$$a_2 = [(\beta + 1)\alpha(He) + \alpha(H^-e) + \beta\alpha(H^-H)]N(e^0),$$

$$a_3 = \frac{\beta - 1}{2}[2\alpha(He) - \alpha(H_2e)]N(e^0),$$

$$a_4 = \frac{\beta - 1}{2}[2\alpha(He) + 2\alpha(H^-H) - \alpha(H_2e)]N(e^0),$$

$$a_5 = \beta\alpha(He)N(e^0),$$

$$b_1 = \frac{2\alpha(H^-H)}{\beta - 1}N(e^0),$$

$$b_2 = \frac{2\beta\alpha(H^-H)}{\beta - 1}N(e^0),$$

$$b_3 = [\alpha(H_2e) + \beta\alpha(H_2H)]N(e^0),$$

$$b_4 = [2\alpha(H^-H) - \alpha(H_2e) - \alpha(H_2H)]N(e^0),$$

and

$$b_5 = (\beta - 1)\alpha(H_2H)N(e^0).$$

b) *Solution for Small Values of the Variables*

Equations (21) can be written as

$$\begin{aligned} \dot{x} &= (1 - x)(-a_1x + a_5 - a_3) + (1 - y) \times \\ &\qquad \times (a_3 - a_4x) \\ \dot{y} &= (1 - x)(b_1x + b_5 - b_3) + (1 - y) \times \\ &\qquad \times (b_3 - b_5 - b_5y + b_4x) \end{aligned} \tag{22}$$

Hence x = 1, y = 1 is a steady state solution of the system. Nevertheless it can be shown by means of Liapunov's stability criterion that this solution is unstable.

If x, y $\ll 1$ equation (22) becomes

$$\dot{x} = -(a_1 + a_4)x + a_5$$
$$\dot{y} = (b_1 + b_4)x - b_5y,$$

which give directly:

$$\begin{aligned} x &= x_p(1 - e^{-\alpha t}), \\ y &= y_p\left[1 - e^{-b_5t} - \frac{b_5}{b_5 - \alpha}(e^{-\alpha t} - e^{-b_5t})\right], \end{aligned} \tag{23}$$

where

$$\alpha = a_1 + a_4,\ x_p = a_5/(a_1 + a_4)$$

and

$$y_p = x_p(b_1 + b_4)/b_5.$$

Note that x_p and y_p would be the equilibrium values in this particular case.

This solution is valid as long as x and y remain $\ll 1$. We will use it only to check that the general method behaves as it should.

c) *General Solution*

Since a general method for obtaining analytic solutions of equation (21) is not available, and usual numerical methods are not sufficiently accurate for such a stiff system, a particular method had to be found. We solved the problem in the following way: we integrated analytically equation (21*a*) from t to t + Δt assuming a constant y, and did the same with equation (21*b*) assuming a constant x. In this way we obtained

$$\begin{aligned} x &= \frac{(B_1x_0 - 2C_1)(1 - E_1) - D_1x_0(1 + E_1)}{(2A_1x_0 - B_1)(1 - E_1) - D_1(1 + E_1)} \\ y &= \frac{(B_2y_0 - 2C_2)(1 - E_2) - D_2y_0(1 + E_2)}{(2A_2y_0 - B_2)(1 - E_2) - D_2(1 + E_2)} \end{aligned} \tag{24}$$

where

$$A_1 = a_1,\ B_1 = a_2 - a_4y_0,\ C_1 = a_5 - a_3y_0,$$
$$D_1 = \sqrt{B_1^2 - 4A_1C_1},\ E_1 = \exp(-D_1\Delta t)$$
$$A_2 = b_5,\quad B_2 = b_3 + b_4x_0,\quad C_2 = b_2x_0 - b_1x_0^2,$$
$$D_2 = \sqrt{(B_2^2 - 4A_2C_2)},\ E_2 = \exp(-D_2\Delta),$$
$$x = x(t + \Delta t),\ x_0 = x(t),$$
$$y = y(t + \Delta t),\ y_0 = y(t).$$

We performed the integration by means of equation (24b) checking continuously the values of x and y. While x and y remained $\ll 1$ we compared the results of the numerical integration with equation (23) and, since accuracy was always better than 1% we are confident that subsequent integration steps are very close to the real solution. Integration was stopped when subsequent integration steps produced no change in the values of the variables. At this point it always happened that $|\dot{x}| \ll x$ and $|\dot{y}| \ll y$ so that we are confident that we reached equilibrium.

The present technique it not appropriate for temperatures below ~ 500°K, because of numerical problems.

At these temperatures the H_2 destruction rates become practically zero. (For instance, at T = 100°K $\alpha(H_2e) = 4.64 \times 10^{-190}$ cm³/s, $\alpha(H_2H) = 7.52 \times 10^{-233}$ cm³/s). We may then work with the simplified equations obtained from equation (21) by making $\alpha(H_2e) = \alpha(H_2H) = 0$. In this case it is easy to show that equilibrium is attained when $x = x_{eq} = 0$, $y = y_{eq} = \beta/(\beta - 1)$. The numerical integration of this system was made by changing variables to $\varepsilon = x_{eq} - x$, $\delta = y_{eq} - y$ and then applying the method we described in the last paragraph.

IV. RESULTS

For the actual numerical integration of the system we took β to be the normal cosmic ratio of hydrogen to carbon abundances. From Allen (Allen 1964) we have $\beta = 3311$.

Results are plotted in Figures 3 and 4. In Figure 3 we have plotted the numerical results for x/x_{eq} and y/y_{eq} as a function of $(a_1 + a_1)t \equiv t/\tau_x$ and $b_5 t$ respectively, for T = 3000°K and T = 8000°K. As can be seen in the figure, in this "high temperature" case the numerical solution behaves exactly as the analytical solution we found for small values of "x" and "y" (equation 23). Furthermore, the numerically obtained equilibrium values come out to be exactly x_p and y_p. We conclude that in this case the evolution of the system is described by equation (23). In this case H_2 production is never significant.

In Figure 4 we note that for "low" temperatures the behaviour of y is almost exponential if we define a timescale $\tau_y \equiv 1/2\alpha(\text{He})N(e^0)$. Furthermore, in all these cases practically all the initial neutral hydrogen is transformed into molecular hydrogen, and this is done, as mentioned before in a timescale τ_y.

At low temperatures the behaviour of x is not as simple as that of y. It always rises to x_p (timescale $= 1/a_1 + a_4$) where it remains until y becomes comparable to 1. Then it decreases towards its equilibrium value. Since at very low temperatures this equilibrium value is zero, x only decreases monotonically after reaching x_p. We found it unnecessary to plot this case.

V. CONCLUSIONS

We can summarize the most important results as follows:

1) A stable equilibrium situation is always achieved without oscillations for any initial conditions.

2) At temperatures $T \geq 3000°K$ H_2 production is never significant. At temperatures $T \leq 2000°K$ practically all the initial H is transformed to H_2.

3) During the evolution of the system the abundance of H^- is never significant.

4) At $T \leq 2000°K$ the timescale of H_2 formation is given by $\tau_y = 1/2\alpha(\text{He})N(e^0)$.

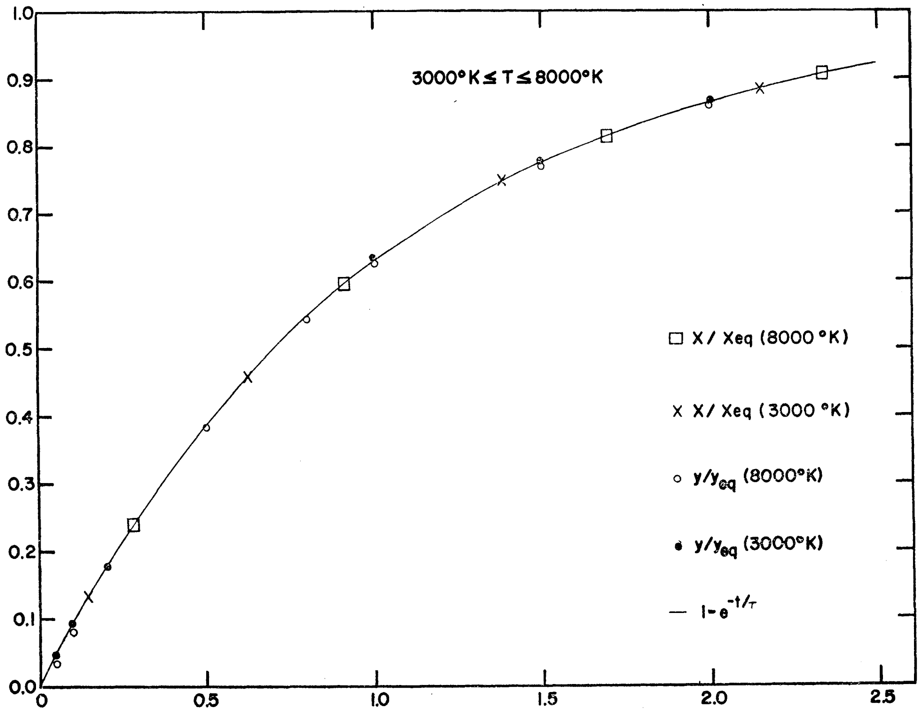

FIG. 3. x/x_{eq} as a function of t/τ_x and y/y_{eq} as a function of t/τ_y for T = 3000°K and T = 8000°K.

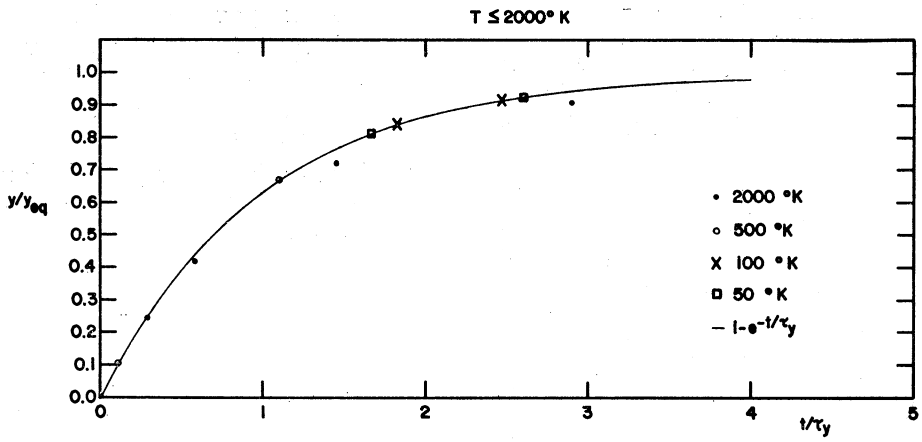

Fig. 4. y/y_{eq} as a function of t/τ_y for $T \leqslant 2000°K$.

APPENDIX

The reason of poor H_2 production at "high" temperatures is the relatively high value that the destruction rate $\alpha(H_2H)$ attains. There are reasons to believe that this rate is overestimated by several orders of magnitude.

If this were true and the main destruction mechanism of H_2 were due to dissociative attachment with electrons one can show that the equilibrium values of x and y are

$$x_{eq} \simeq \sqrt{\frac{\beta\alpha(He)\alpha(H_2e)}{2\alpha(H^-e)\,\alpha(H^-H)}} - \frac{\alpha(H_2e)}{4\alpha(H^-H)},$$

$$y_{eq} = \frac{\beta}{\beta-1}\left(1 - \frac{\alpha(He) + \alpha(H^-e)}{\beta\alpha(He)}\,x_{eq}\right).$$

As can be seen this means that even at T = 8000°K there would be significant H_2 production. Furthermore, the timescale of this process would always be given by τ_y. As an example we give in Table 8 the whole evolution in time for a cloud at T = 8000°K and with $N(H^0) = 10^{12}$ cm^{-3}.

TABLE 8

THE CHEMICAL EVOLUTION OF A CLOUD OF NEUTRAL HYDROGEN AT 8000°K WITH $N(H^0) = 10^{12}$ cm^{-3}, $\beta = 3311$, IF $\alpha(H_2H) = 0$

t (s)	$N(H^-)$ (cm^{-3})	$N(H_2)$ (cm^{-3})
0	0	0
3.31(−7)	2.92(−1)	1.05(−4)
3.31(−5)	2.82(1)	1.02
3.31(−3)	4.01(2)	2.51(3)
3.31(−1)	4.02(2)	2.91(5)
3.31(1)	4.02(2)	2.91(7)
3.31(3)	4.03(2)	2.90(9)
1.66(5)	4.50(2)	1.26(11)
1.66(6)	1.88(3)	4.58(11)
1.66(7)	4.23(3)	4.83(11)
∞	4.23(3)	4.83(11)

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