The Influence of Excited States on the Reactive Thermal Conductivity of an L.T.E. Hydrogen Plasma

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The influence of excited states on the reactive thermal conductivity of an L.T.E. hydrogen plasma has been studied by making realistic assumptions on the cross sections of these species.

The influence of excited states on the reactive thermal conductivity λ_R of an L.T.E. hydrogen plasma has been recently discussed [1] under several assumptions on the cross sections of these species.

The results showed a strong dependence of λ_R on the magnitude of the cross sections relative to the interaction $H(1) - H(n)$, where $H(n)$ denotes a hydrogen atom in the nth principal quantum number. In this note we reconsider the problem in the light of the recent calculations of the cross sections $H(1) - H(n)$ [2].

The reactive thermal conductivity has been calculated by means of the Butler-Brokaw equation [3, 4]

$$\lambda_R = -1/RT^2 \begin{vmatrix} A_{11} \dots A_{1\mu} & \Delta H_1 \\ A_{\mu 1} \dots A_{\mu\mu} & \Delta H_\mu \\ \Delta H_1 \quad \Delta H_\mu & 0 \end{vmatrix} \Bigg/ \begin{vmatrix} A_{11} \dots A_{1\mu} \\ \\ A_{\mu 1} \quad A_{\mu\mu} \end{vmatrix} \quad (1)$$

where

$$A_{ij} = \sum_{K=1}^{\nu-1} \sum_{l=K+1}^{\nu} \frac{RT}{D_{kl}\, p}\, x_k\, x_l \left(\frac{n_{ik}}{x_k} - \frac{n_{1l}}{x_l}\right)\left(\frac{n_{ik}}{x_k} - \frac{n_{jl}}{x_l}\right).$$

The order of determinants in Eq. (1) depends on the number of the independent reactions present in the plasma.

To a first degree of approximation (model I) we consider that the only reaction contributing to λ_R is

$$H(1) = H^+ + e\,.$$

This means that the excited hydrogen atoms are considered as inert species. In this case Eq. (1) reduces after dropping the terms due to the electrons to the following form

$$\lambda_R = (\Delta H^2/RT^2)/A_{11}\,,$$

$$A_{11} = \frac{RT}{p}\left[\frac{(x+x_2)^2}{x_1 x_2}\frac{1}{D_{12}} + \frac{x_4}{x_1}\frac{1}{D_{14}} + \frac{x_4}{x_2}\frac{1}{D_{34}}\right] \quad (2)$$

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where ΔH is the difference of enthalpy of the ionization reaction, x_i is the molar fraction of the ith species, and D_{ij} is the binary diffusion coefficient for species i and j [$i=1=H(1)$; $i=2=H^+$; $i=3=e$; $i=4=H(n)$].

To a second degree of approximation (model II) we consider the following ionization reactions:

$$H(1) = H^+ + e;\ H(2) = H^+ + e;\ H(3) = H^+ + e;$$

$$H(4) = H^+ + e;\ H(5) = H^+ + e;$$

$$H(6-12) = H^+ + e\,.$$

[$H(6-12)$ includes excited states, the principal quantum numbers of which range from 6 to 12.]

In this case Eq. (1) cannot be reduced to the simple form of Equation (2). Values of λ_R corresponding to the models I and II can be evaluated once the diffusion coefficients of the interactions $H(1) - H(n)$ and $H(n) - H^+$ are known.

Table 1. Binary diffusion coefficients (cm^2/sec) of excited states.

	$H(n) - H^+$					
T	$n=1$	$n=2$	$n=3$	$n=4$	$n=5$	$n=6-12$
14000	165.	26.9	9.08	3.79	1.61	0.16
20000	295.	48.3	16.3	6.82	2.89	0.28

	$H(1) - H(n)$		
	$n=2$	$n=3$	$n>3$
14000	48.5	219.	165.
20000	98.	396.	295.

These coefficients have been reported in Table 1 for various temperatures and principal quantums number n; they are based on recent calculations of collision integrals of the diffusion type [1, 2]. The calculations have shown that these integrals for the interactions $H(n) - H^+$ increase as n^3; on the contrary, those for the interactions $H(1) - H(n)$ seem to converge at high values of n to the $H(1) - H^+$ value. These considerations are useful for estimating the diffusion coefficients of highly excited hydrogen atoms. As for the molar fractions which enter in the calculation of λ_R, they have been calculated by considering an L.T.E. plasma; the Griem's criterion has been used for the cut-off of the electronic partition function [5]. It can be noted that according to this method the principal quantum numbers of excited states inserted in the partition function approximately range from 2 to 12 (at one atmosphere). Finally, the differences of enthalpy of the ionization reactions have been calculated by adding to the ionization potential of each particular state the translational energy of the electrons.

Values of λ_R corresponding to models I and II have been reported in Table 2(b) and compared with the values obtained by imposing to all excited states the diffusion coefficients relative to the ground state interactions (a) i. e.

$$D_{H(n)-H^+} = D_{H(1)-H^+}\,; \quad D_{H(1)-H(n)} = D_{H(1)-H(1)}\,. \quad (3)$$

The last procedure is commonly adopted in the literature. The results show a strong dependence of λ_R on the adopted model. In the model I in fact the values of λ_R calculated according to the ground state cross sections (column a of Table 2) are enormously greater than the corresponding λ_R values calculated by means of the more realistic hypothesis made on the cross sections of excited states (column b).

This behaviour disappears in the model II, where the maximum deviation in the two sets of λ_R values is of the order of 12%.

It might be instructive as a conclusion to see how the present results may alter the data of λ_R up to date calculated. In this connection we note that the equation commonly used for λ_R is practically given by Eq. (2) under the hypothesis of Equations (3). These data (column I a of Table 2) must be compared with the corresponding values obtained by using the rigorous Eq. (1) and the realistic cross sections of Table 1 (column II b of Table 2). The comparison shows a very good agreement, despite the completely different methods adopted for obtaining the two sets of λ_R values.

This can be probably attributed to compensation effects operating in the two models, rather than to the insensitivity of λ_R to the cross sections of excited states.

Table 2. Values of λ_R (10^3 cal/°K cm) at different temperatures.

	Model I		Model II	
T K	*a*	*b*	*a*	*b*
10,000	7.97	7.19	8.0	8.0
12,000	24.4	11.0	24.6	24.6
14,000	47.6	8.55	48.0	48.0
15,000	51.8	7.52	52.0	51.9
16,000	46.3	6.93	46.4	46.2
18,000	23.3	6.12	23.3	23.1
20,000	9.14	4.58	9.25	9.07
22,000	3.61	2.68	3.74	3.58
24,000	1.73	1.49	1.87	1.72
25,000	1.19	1.08	1.33	1.19

[1] M. Capitelli, XI Int. Conf. Phen. Ionized Gases, Prague 1973.
[2] M. Capitelli and U. Lamanna, J. Plasma Phys., in press.
[3] N. Butler and R. S. Brokaw, J. Chem. Phys. **26**, 1636 [1957]; **32**, 1005 [1960].
[4] W. E. Meador and L. D. Staton, Phys. Fluids **8**, 1694 [1965].
[5] M. Capitelli and E. Molinari, J. Plasma Phys **4**, 335 [1970]; Z. Naturforsch. **26 a**, 672 [1971].