Local Thermodynamic Equilibrium Study
of H⁻ Abundance
in Negative-Ion Source Discharges

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ABSTRACT

A local thermal equilibrium study of a hydrogen gas has been carried out for temperatures and densities relevant to the expected conditions in the Penning SAS source, which is a negative-ion source presently under investigation by AT-2 at Los Alamos National Laboratory. For the pure hydrogen mixture, it was found that the relative abundance of H⁻ ions peaks at about 10 000 K but is extremely low. The inclusion of cesium does improve the H⁻ abundance significantly only at low temperatures ($\leq$5000 K), raising it to about several parts per million, which should be considered low in view of estimates from the sheath physics which is not based on the local thermodynamic equilibrium assumption. Incorporation of the enhancement of dissociative attachment from contributions by higher rotational-vibrational states associated with a nonthermal hot electron component has not been attempted, being an intrinsically nonthermal effect. The higher rotational-vibrational states themselves are, however, fully included.

I. DESCRIPTION OF THE METHOD AND THE PARAMETER RANGE

A mixture of atomic and molecular hydrogen with the inclusion of H^+, H^-, and H_2^+ ions is considered, both with and without cesium atoms. In the case when cesium is included, Cs^+ and CsH are also incorporated in the most interesting regime with regard to the enhancement of the H^- abundance by cesium, namely from 2000 up to and including 5000 K. Temperatures ranging from 2000 to 20 000 K are considered. The pressure is varied between 100 dyne/cm^2 and $10^{3.5}$ dyne/cm^2, bracketing the estimated value of $n = 3 \times 10^{14}$/cm^3 for the particle number density. Inherent in the model is the existence of only one canonical temperature, shared by electrons, atoms, molecules, and ions. Spatial inhomogeneities are only allowed through the spatial dependence of the

lowest-order moments (i.e., density, velocity, temperature), and the abundances are local estimates in this sense. We call this the LTE (Local Thermodynamic Equilibrium) model.

For a system at a (locally) constant temperature T and pressure P, the state of local thermodynamic equilibrium is the state in which the Gibbs free energy F is minimal.

In a mixture of ideal gases, the numbers of moles of the individual molecular species are variable, subject to the constraints of constant pressure P and temperature T and constant number of gram-atoms of constituent chemical elements. The equilibrium state is the state of minimal free energy F, subject to these constraints. The needed thermochemical data are obtained from the JANAF[1] tables (heat capacities, enthalpies, free energy functions, etc.). A system of nonlinear equations results and is solved by means of the Newton-Raphson technique, using a modified version of the Los Alamos MES (i.e, Molecular Equation of State) code.[2] External influences, such as magnetic fields and nonequilibrium radiation, are ignored. As we strictly adhere to thermal equilibrium, the inclusion of nonthermal plasma components (such as hot electrons) is not attempted. The influence of a nonthermal hot electron species on the dissociative attachment rate of molecular hydrogen may in itself well be a very important effect and deserves scrutiny in the future. However, its importance mainly resides in the possibility of equilibration between the hot electrons and the molecular vibrational quanta, bringing about occupational levels of the vibrational states that are high enough to influence the order of magnitude of the reaction rate for dissociative attachment. This effect strictly is outside the realm of the present LTE model, in which one canonical temperature is shared by all species. Its importance would a fortiori cast serious doubt on the validity of the Chapman-Enskog expansion method that underlies any internally consistent fluid-dynamical treatment.

II. RESULTS AND CONCLUSIONS

From Table I-a, I-b, and I-c, listing the abundances of H atoms, H^+ ions, H_2 molecules, H_2^+ ions, and H^- ions (the log of the concentrations in cm^{-3}) as a function of temperature (kelvin) for log P_g =3.5, 2.5, and 1.5, respectively, it follows that the gas mixture undergoes a transition from weakly ionized to strongly ionized between 5000 and 15 000 K. Furthermore, it is clear that the concentration of H^- ions is down by at least six orders of magnitude from the most abundant species in the pure hydrogen mixture. The relative concentration of H^- ions increases with increasing density and is optimal as a function of temperature for about 10 000 K in the pure hydrogen mixture.

The inclusion of Cs, Cs^+, and Cs^{++} was considered in the highest density case for two values of the concentration of cesium relative to hydrogen, namely 0.01 and 0.1 (ratio of number of nuclei). The addition of cesium was found to be important only below 10 000 K, increasing the H^- ion concentration by almost two orders of magnitude for one cesium nucleus per 100 hydrogen nuclei and by almost three orders of magnitude for one

TABLE I-a

log $P_g = 3.5$

T (K):	2000	5000	10 000	15 000	20 000
H	14.5	15.6	15.2	13.2	11.67
H$^+$	0.3	11.1	14.8	15.1	15.0
	(−11.9,−12.4)	(9.2,8.2)			
A H$_2$	16.0	11.5	8.3	3.7	0.313
H$_2^+$	−1.8	5.4	6.9	4.6	2.4900
H$^-$	−4.2	6.6	8.5	6.5	4.76
	(7.9,8.3)	(8.5,9.5)			

TABLE I-b

log $P_g = 2.5$

T (K):	2000	5000	10 000	15 000	20 000
H	14.8	14.7	13.8	11.2	9.7
H$^+$	0.03	10.9	14.1	14.1	14.0
	(−11.9,−12.4)	(9.2,8.2)			
H$_2$	15.0	9.5	5.6	−0.2	−3.68
H$_2^+$	−2.5	4.1	4.9	1.6	−0.511
H$^-$	−5.0	4.8	6.4	3.6	1.76
	(6.9,7.3)	(6.5,7.5)			

TABLE I-c

log $P_g = 1.5$

T (K):	2000	5000	10 000	15 000	20 000
H	13.5	13.7	12.6	09.2	7.67
H$^+$	−0.2	10.4	13.3	13.1	13.0
	(−11.9,−12.4)	(9.2,8.2)		.	
H$_2$	13.9	7.5	2.2	−4.2	−7.70
H$_2^+$	−3.4	3.7	2.3	−1.4	−3.500
H$^-$	−5.8	3.3	3.8	0.6	−1.2
	(5.8,6.2)	(4.5,5.5)			

cesium nucleus per 10 hydrogen nuclei (see the two abundances given in parentheses in Table I-a). Still, the relative abundance of H^- ions does not rise above three parts per million hydrogen nuclei, which is extremely low compared with its value in the experiment as estimated from a sheath-physics modeling[3] that incorporates a widely used[4] value of the secondary emission coefficient of H^-.

As evidenced from Figs. 1–3, the H^- abundance in the pure hydrogen mixture is a monotonically increasing function of temperature for fixed gas pressure. The inclusion of cesium provides an alternative source of electrons for hydrogen atoms, independent of the ionization process of hydrogen itself. As a significant fraction of the temperature corresponding to the ionization potential of cesium is reached, a dramatic increase in the H^- abundance results (Figs. 4–9). An increase in temperature in the state in which cesium is fully ionized leads to a decrease in the H^- abundance due to ionization of hydrogen itself. Therefore, a maximum in the H^- abundance as a function of the temperature exists (Figs. 4–9). The value of this maximum increases with increasing cesium concentration (C) and gas pressure (P) roughly like $(CP)^{0.7}$ and shifts towards slightly higher temperature for increasing gas pressure.

Taking into account the mean-free-path estimate of 0.1 cm for the annihilation of the surface-generated H^- ions in the Penning SAS source studied in AT-2,* we arrive at a relative abundance of H^- with respect to H^+ of about 1%. This estimate is arrived at by means of a generalization of the Bohm model of a cathode sheath which incorporates a secondary emission coefficient of $K^- = 0.7$ for the production of H^- by H^+ bombardment of a cesiated cathode surface. Based on the fill pressure of $4 \times 10^{15}/cm^3$ of the hydrogen gas and the spectroscopically measured electron density of $3 \times 10^{14}/cm^3$* the relative abundance of H^- with respect to the quiescent neutral hydrogen gas then is found to be roughly between 0.04% and 0.08%, depending on the dissociation degree of hydrogen, which is not well-known empirically.* This percentage range is an operational figure of merit to be compared with the prediction of about 0.0001% according to the LTE model.

In conclusion, the Penning SAS source studied by AT-2 contains a gas mixture that is far from local thermodynamic equilibrium. This observation is highly relevant to future modeling attempts. In particular, fluid-dynamical modeling, reliant as it is on the Chapman-Enskog expansion based on the assumption of the proximity of a local thermodynamic equilibrium, cannot be justified on the basis of the present LTE results. For completeness, it is noted here that for the present range of temperature and density, the number of particles within a Debye sphere is insufficiently large to justify the Chapman-Enskog approximation for the interactions between and within plasma constituents. Therefore, under these conditions the plasma is strongly coupled, resembling no longer a gaseous system. This fact all by itself invalidates the use of the fluid-dynamical

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* P. Allison, Los Alamos National Laboratory, AT-2, personal communication, June 1986.

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approach for the plasma constituents implicit in the Chapman-Enskog approximation for the present regime, for which present theory does not offer a satisfactory kinetic model at the present time, typical as it is of a system for which the BBGKY (Born-Bogolyubov-Green-Kirkwood-Yvon) hierarchy does not contain a small parameter.[5,6] In this regard, it is noted that the truncation error in the derivation of the plasma kinetic equation is of order $\lambda^{-1/2} \ell n \lambda$, where λ is the number of particles within a Debye sphere.[7] This number is of order unity over almost the entire regime studied in the present work.

The purpose of any future modeling might be to focus on a single non-LTE feature, e.g., the effect of a distinct electron temperature; other non-LTE features such as steep spatial gradients or strong coupling then still could be suppressed, for simplicity.

ACKNOWLEDGMENTS

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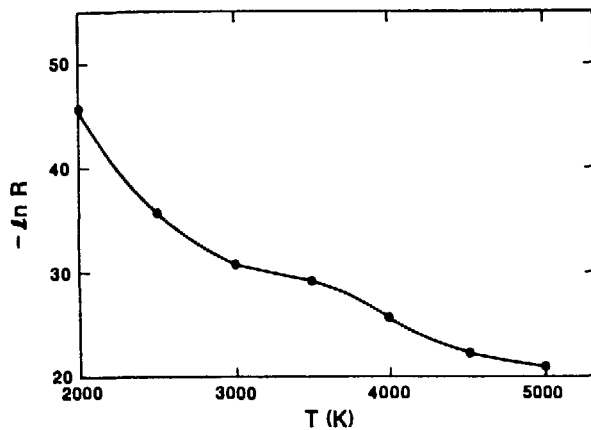7. J. P. Mondt, "Binary Correlation and Convergent Collision Integral for a Plasma," Ann. Phys. 117, 195 (1979).

Fig. 1. -1nR, where $R \equiv [H^-]/[H_{nuclei}]$, as a function of temperature (kelvin) for the pure hydrogen mixture, at a gas pressure of 100 dyne/cm^2.
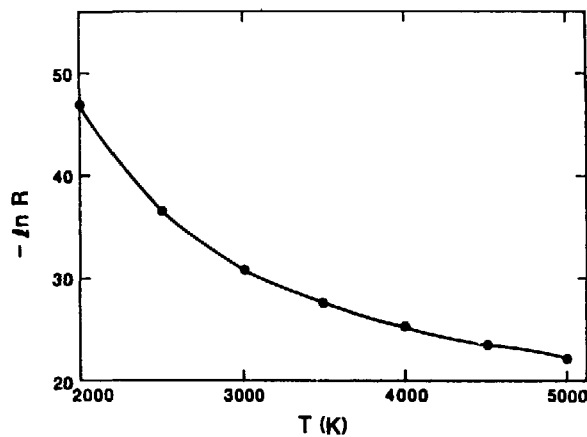

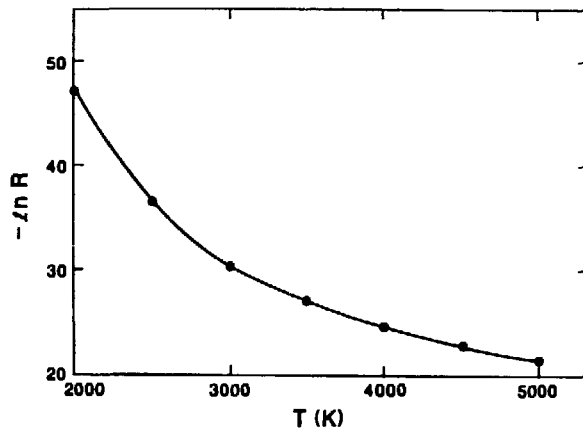Fig. 2. Idem as in Fig. 1, but at a gas pressure of 800 dyne/cm^2.

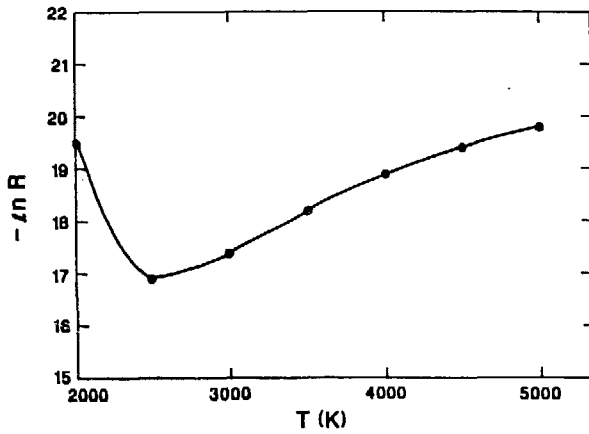Fig. 3. Idem as Fig. 1, but at a gas pressure of 3162 dyne/cm^2.

Fig. 4. Idem as Fig. 1, but with 1% cesium added (percentage of nuclei). Maximum R of 4.6×10^{-8} achieved at roughly 2500 K.
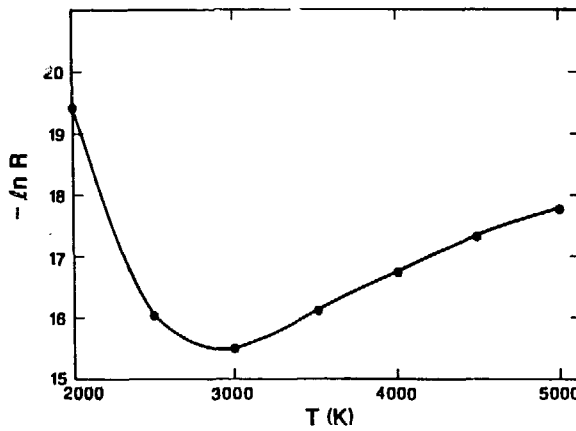

Fig. 5. Idem as in Fig. 2, but with 1% cesium added. Maximum R of 1.8×10^{-7} achieved at approximately 3000 K.
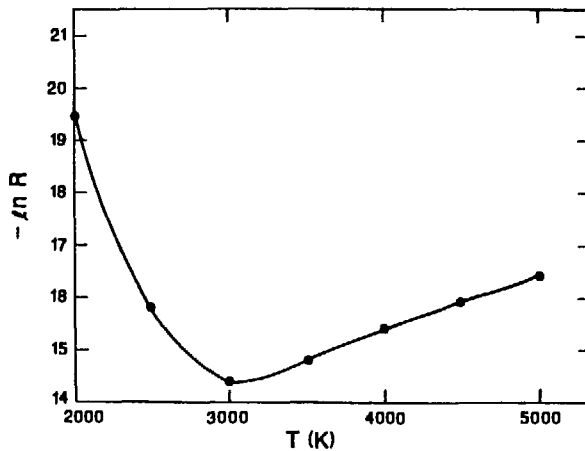

Fig. 6. Idem as Fig. 3, but for 1% cesium added. Maximum R of 5.6×10^{-7} achieved at 3000 K.
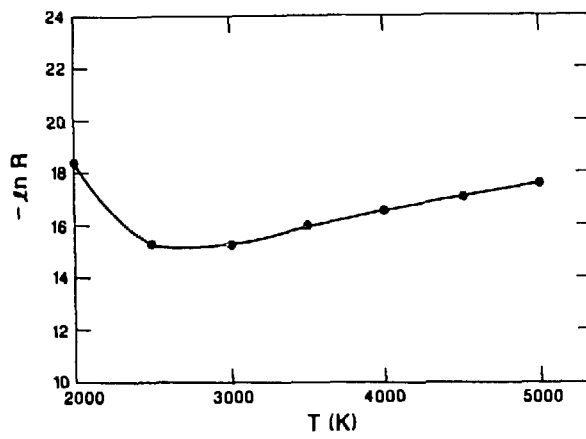
Fig. 7. Idem as Fig. 1, but for 10% cesium added. Maximum R of 2.2×10^{-7} achieved at about 2700 K.
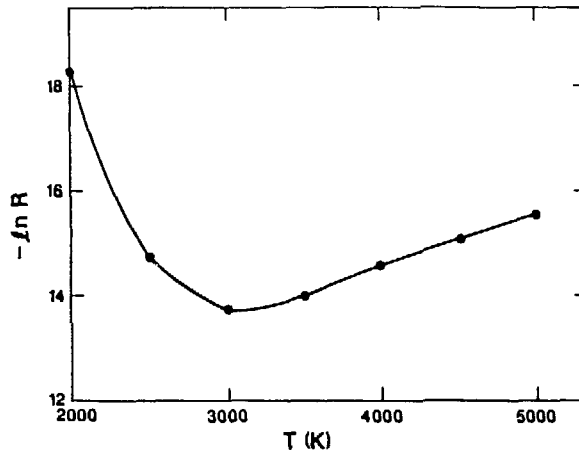

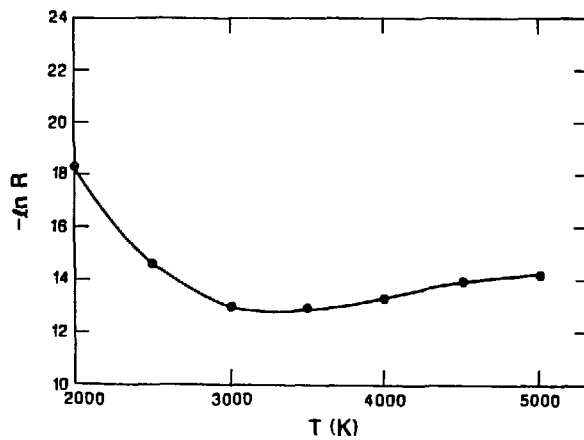Fig. 8. Idem as Fig. 2, but with 10% cesium added. Maximum R of 1.08×10^{-6} achieved at 3000 K.

Fig. 9. Idem as Fig. 3, but with 10% cesium added. Maximum R of 2.6×10^{-6} achieved at 3500 K.

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