Each point on the top curve represents the average of eight observations, while those of the lower curve are for four.

It is apparent from the top curve that the addition of CCl_2F_2 increases the power level at which breakdown occurs. Since the electrons will suffer many collisions while acquiring sufficient energy for impact ionization from the radiation field, they have many opportunities to be captured by the electron-acceptor molecules. Thus, a higher power level is required to supply the additional electrons required to replace those lost via this process. Also, at the higher power levels, the acceleration process will give the electrons appreciable energy during fewer atomic collisions, thus reducing their probability of capture.

The results (lower curve, Fig. 2) are quite different for a more rapidly rising laser pulse. The effect of the CCl_2F_2 was to reduce the breakdown threshold in this case. Evidently, the electron-acceleration process occurred during sufficiently few collisions that electron capture was not such an important factor. Another process, that of the production of more free electrons by the ionization and/or breakup of CCl_2F_2 molecules probably also contributed to the actual decrease of the threshold power.

It was also noted in the course of this work that the *pressure threshold* for breakdown of pure argon for laser power (1.7 MW) was less than for pure CCl_2F_2 while at the higher power (4.5 MW), the opposite was true.

These results give further evidence of the inverse bremsstrahlung process for electron acceleration in laser-production sparks.

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Analog to the Saha Equation for Recombining High-Pressure Plasmas in Which the Electron Temperature Exceeds the Gas Temperature*

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The question of steady-state populations produced by a balance of heavy-particle collisional ionization against its inverse is considered. An analog to the Saha equation is derived which is useful in estimating the populations of excited states with high quantum numbers expected in plasmas recombining at high neutral pressures and electron temperatures in excess of the heavy-particle temperature.

INTRODUCTION

Recently Bates and Khare[1] discussed a type of electron-ion recombination which could occur in high-pressure plasmas in which the primary capture occurs according to the scheme

$$X^+ + e + X \rightarrow X^*(p) + X\,, \qquad (1)$$

where $X^*(p)$ denotes the pth excited state of the X atom. The recombination is considered to be stabilized by subsequent superelastic collisions with heavy particles

$$X^*(p) + X \rightarrow X^*(q) + X\,, \quad p>q\,, \qquad (2)$$

as well as by spontaneous radiation. Subsequently Collins[2] suggested that such processes might be considerably more important in laboratory plasmas in the Torr pressure range than had been previously suspected. Further it was suggested that contributions to the X^* population from such a process could conceivably explain the serious discrepancies between the intensity of radiation from the X^* population observed in certain experiments and that predicted by the otherwise successful theory of collisional-radiative recombination.[3]

Although the method used by Bates and Khare to calculate the recombination rates neither depended on nor yielded excited state populations one can immediately infer that in the limit of high quantum numbers the excited state populations would be given by the Saha equation

$$N_n = N^+ N_e \frac{g_n}{g^+ g_e}\left(\frac{h^2}{2\pi m K T_g}\right)^{3/2} e^{U_n/KT_g}\,, \qquad (3)$$

where: N_n, N^+, and N_e are the populations of the nth bound level, ion, and free electrons, respectively, g_n, g^+, and g_e are the degeneracies of the nth bound level, ion, and free electron, respectively, U_n is the ionization potential of the nth bound level, T_g is the heavy-particle

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[1] D. R. Bates and S. P. Khare, Proc. Phys. Soc. (London) **85**, 231 (1965).

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[3] D. R. Bates, A. E. Kingston, and R. W. P. McWhirter, Proc. Roy. Soc. (London) **A267**, 297 (1962).

temperature, m is the electron mass, and other symbols have conventional meanings.

However, in many cases of possible interest such as early afterglows or active discharges the experimental plasma is nonthermalized, the electrons possessing a somewhat higher temperature than that of the heavy particles. Although Eq. (3) will no longer apply in these cases, it can still be expected that in the limit of high quantum numbers the population of bound states will be in collisional equilibrium with the free electrons. For such a quantum number i,

$$dN_i/dt=0, \tag{4}$$

or considering the detailed collisional populating and depopulating mechanisms

$$[\sum_{j\neq i} Q_{ij}N_j - N_i \sum_{j\neq i} Q_{ji}] + [Q_{ic}N_c - Q_{ci}N_i] = 0, \tag{5}$$

where Q_{ij} is the collision-induced transition rate from the jth to the ith level, Q_{ci} is the collision-induced ionization rate, Q_{ic} is the collision-induced recombination rate, and N_c is the concentration of free electrons. Unlike thermalized plasmas for which each bracketed expression equals zero independently, nonthermalized plasmas do not necessarily require equilibrium between ionization and recombination to satisfy Eq. (4).

This paper concerns the calculation of the excited state populations resulting from recombination of the Bates-Khare type, first in the limiting case of a balance between collision-induced ionization and recombination and subsequently in the limiting case satisfying Eq. (4) for plasmas in which the electron temperature exceeds the gas temperature. It is found that the first case yields an analog of the Saha equation which is convenient to relate the gross rate of collision-induced recombination to the inverse process of ionization but which does not in general satisfy Eq. (4). However, it is shown subsequently that except for cryogenic plasmas the exact solutions to Eq. (4) are sufficiently approximated by those predicted by the analog Saha equation for most applications.

IONIZATION-RECOMBINATION BALANCE PER STATE

In terms of Eq. (5), a balance between ionization and recombination requires

$$Q_{ic}N_c - Q_{ci}N_i = 0, \tag{6}$$

This is essentially equivalent to the equilibrium problem considered by Dewan[4] in which ionization and recombination of idealized one-state atoms were balanced for the general case of particle concentrations with arbitrary velocity distribution functions. Modifying Dewan's[4] results by neglecting radiation, allowing only collisions with heavy particles to induce ionization or recombination, and assuming Maxwellian distributions for both the free electrons and heavy particles at characteristic temperatures of T_e and T_g, respectively, yields the following equation:

$$N_n = N^+ N_e \frac{g_n}{g^+ g_e}\left(\frac{h^2}{2\pi m K T_e}\right)^{3/2} e^{U_n/KT_g} f_n, \tag{7}$$

where the terms are as defined in Eq. (3) and f_n is a function given by

$$f_n = \left[\int_{U_n}^{\infty} K(U_n,\epsilon)d\epsilon\right]^{-1} \int_{U_n}^{\infty} e^{\alpha(\epsilon-U_n)} K(U_n,\epsilon)d\epsilon, \tag{8}$$

where

$$\alpha = (1/KT_g - 1/KT_e), \tag{9}$$

and $K(U_n,\epsilon)$ is the rate coefficient per unit energy for the ionization of the nth level with the emission of an electron of energy between $(\epsilon - U_n)$ and $(\epsilon - U_n)+d\epsilon$, i.e.,

$$K(U_n,\epsilon) = \int_{\epsilon}^{\infty} V_{\text{rel}}\sigma_{\text{ex}}(\epsilon,e)dN(e). \tag{10}$$

V_{rel} being the relative velocity between X and X^*, $\sigma_{\text{ex}}(\epsilon,e)$ the cross section per unit energy for transfer of energy between ϵ and $\epsilon+d\epsilon$ to X^* from an X atom having kinetic energy of $e/2$ relative to the center of mass of X^* and X, and $N(e)$ represents the distribution function for X as a function of e.

To solve for f_n exactly requires detailed knowledge, which is generally unavailable, of the ionization rate coefficient as a function of the ejected electron energy for the inverse of the process described in Eq. (1). Classically, however, one would expect that the difficulty of transferring large amounts of heavy-particle energy e to the ejected electron would require $K(U_n,\epsilon)$ to be a rapidly decreasing function of ϵ. Further, since $K(U_n,\epsilon)$ is not a function of T_e, for a particular quantum level n an electron temperature $T_{\max}$ sufficiently close to T_g can always be found such that $e^{\alpha(\epsilon-U_n)} \simeq 1$ over the range of ϵ for which $K(U_n,\epsilon)$ contributes significantly to the integrals in (8). Consequently, for this particular n and electron temperature less than $T_{\max}$, f_n is approximately unity and the excited-state population is closely approximated by Eq. (7) with $f_n=1$.

The question now remains as to whether or not $T_{\max}$ is sufficiently larger than T_g to permit the simplified form of (7) with $f_n=1$ to be used in relating the gross rate of collision-induced recombination to the inverse process in real plasmas of interest. Figure 1 compares the results of substituting into Eq. (7) the approximation $f_n=1$ with the explicit calculations of f_n using the classical ionization rate coefficients $K(U_n,\epsilon)$, given by Bates and Khare[1] for helium. In the particular case presented, $T_g=300$°K and the electron temperature is

[4] E. M. Dewan, Phys. Fluids 4, 759 (1961).

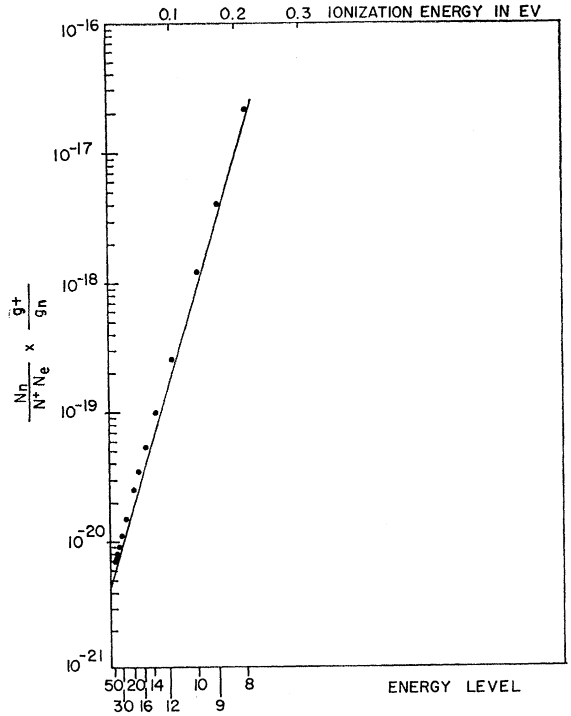

FIG. 1. A graph of rationalized population per state of excited helium levels as a function of principal quantum number and ionization energy. The solid curve represents values obtained from the analog to the Saha equation, Eq. (15). Points represent values obtained from Eq. (7) showing the results of including the explicit value of f_n. $T_g=300°\text{K}$, $T_e=1200°\text{K}$.

1200°K. Lower electron temperatures were found to give even better agreement while higher electron temperatures gave agreement almost as good, as would be expected from the fact that at a gas temperature of 300°K, α varies from zero to 38.7 eV^{-1} as T_e varies from 300°K to infinity, whereas the example presented for $T_e=1200°\text{K}$ corresponds to an α of 29.0 eV^{-1}. Higher values of gas temperature were examined up to $T_g=1000°\text{K}$, and agreement was found to improve with increasing T_g in all cases in which $T_e>T_g$.

STEADY-STATE POPULATIONS

For the set of N_j's, defined by (7), to be a solution of Eq. (4) would require that in addition to relation (6),

$$\sum_{j\neq i} Q_{ij}N_j - N_i \sum_{j\neq i} Q_{ji}=0, \tag{11}$$

for each quantum number i.

These relations have the immediate general solution

$$N_j=Ce^{(U_j/KT_g+\gamma)}, \tag{12}$$

where C and γ are arbitrary constants which are not functions of j. Equation (7) cannot be placed in this form unless the f_n's of Eq. (8) are constants, independent of n. Since this is not the case for the classical cross sections used to calculate the N_j's presented in Fig. 1, these N_j's cannot be steady-state populations.

Nevertheless, the set N'_j of true steady-state populations, satisfying Eq. (4) but not (6), can be shown to be reasonably approximated by the N_j's provided cryogenic temperatures are avoided. This can best be considered in terms of a set of f'_j's analogous to the f_j's but derived from the N'_j's by the relation

$$f'_j=f_jN'_j/N_j. \tag{13}$$

Proceeding from the principle of detailed balancing, the sets of Eqs. (5), (13), and (7), and provided that only finitely many bound quantum levels exist, as in the case in real plasmas, it can be rigorously shown that if f'_p and f'_q are, respectively, the largest and smallest of the f'_j's then

$$f_p>f'_p \quad\text{and}\quad f_q<f'_q. \tag{14}$$

Since (8) requires all f's to be greater than unity, the set of f'_j's is bounded by f_p and unity. Consequently, use of Eq. (7) with $f_n=1$ is an even better approximation to the steady-state populations N'_n than to the populations N_n, obtained by balancing ionization and recombination.

CONCLUSIONS

Although little experimental evidence is available on the detailed form of the ionization rate coefficient $K(U_i,\epsilon)$ as a function of the ejected electron energy $(\epsilon-U_i)$, under the not particularly restrictive conditions discussed above it appears that the analog to the Saha equation,

$$N_n\simeq N^+N_e\frac{g_n}{g^+g_e}\left(\frac{h^2}{2\pi mKT_e}\right)^{3/2}e^{U_n/KT_g}, \tag{15}$$

is an approximation, sufficiently accurate for most purposes, of both the excited state populations produced by an equilibrium between process (1) and its inverse and the steady state population for which Eq. (4) is satisfied under conditions in which the electron temperature is greater than the gas temperature and collisions with heavy particles dominate.