THE

PHYSICAL REVIEW

Ionization Processes in Decaying Plasmas. I. Helium

HOWARD MYERS

Aerospace Corporation, El Segundo, California

(Received 3 December 1962; revised manuscript received 20 February 1963)

The current theories of the helium afterglow are shown not to be substantiated by published experimental results. The experimental data are reanalyzed to obtain a more consistent interpretation of the ionization mechanisms. The primary conclusion of this analysis is that the enhancement of ionization in the afterglow occurs by the conversion of metastable helium atoms to *molecular ions*: $He^* + He^* \rightarrow He_2^+ + e$. The analysis yields specific rate constants for the important reactions in the plasma.

THE study of decaying plasmas in microwave cavities[1,2] has greatly enhanced our understanding of the mechanisms of ionization processes. However, in spite of these advances, the behavior of one of the most extensively studied plasmas, helium, has not been completely unravelled.[3] The difficulty arises from the presence of the several ionic species in the plasma, and the persistence of ambipolar diffusion as the dominant electron loss process throughout the pressure range.

Two sets of experimental results are of particular significance in the study of helium afterglow. The first is a direct measurement of the rates of production and loss of positive ions in helium (see Fig. 1), obtained by Phelps and Brown[4] by attaching a mass spectrometer into their microwave apparatus. The second is a study performed by Biondi[5] of the variation of the decay rate of metastable helium atoms with pressure.

In the interpretation of his experimental results (Fig. 2) Biondi assumes that the helium plasma consists of atomic ions over the entire pressure range of his experiments. However, Biondi's assumption is contradicted by Brown's mass spectrographic results (Fig. 1) obtained at the same pressure. In addition, the

helium ion ambipolar diffusion coefficient derived from the slope of Biondi's electron density decay curve in Fig. 2 yields a value the product of diffusion coefficient times pressure $(D_a p)$ of 645 cm^2/mm Hg-sec, very close to the value of $D_a p = 665$ obtained by Oskam[6] for the helium molecular ion at higher pressures. Therefore, the experimental results of Biondi should be reinterpreted in such a manner that a more significant role to the molecular ion. It is the intention of this paper to present a more consistent picture of the ionization processes in the helium afterglow.

IONIZATION PROCESSES

Any analysis of reaction rate data is strongly influenced by the assumptions that are made regarding the mechanisms governing the reaction; therefore, it is necessary to discuss first the processes that possibly occur in a helium plasma.

At the instant the microwave discharge is switched off, the helium plasma consists of helium metastable atoms, helium atomic ions, helium molecular ions, electrons, and, predominantly, un-ionized helium atoms. Consider, first, the fate of the metastable atoms. Before they are destroyed, the metastable atoms will undergo a number of collisions with the other constituents of the gas phase. Three factors influence the collisional excitation and ionization of atoms: the relative velocity of the collision, the electronic excitation of the atoms, and the probability that the colliding atoms transfer from their original potential energy curve to one

[1] M. A. Biondi and S. C. Brown, Phys. Rev. **75**, 1700 (1949); M. A. Biondi, Rev. Sci. Instr. **22**, 500 (1951).

[2] D. R. Bates, Phys. Rev. **77**, 718 (1950); **78**, 492 (1950).

[3] An excellent review of the current state of confusion is to be found in L. B. Loeb, *Basic Processes of Gaseous Electronics* (University of California Press, Berkeley, California, 1960), 2nd ed., revised, Appendix I, pp. 971–976.

[4] A. V. Phelps and S. C. Brown, Phys. Rev. **86**, 102 (1952).

[5] M. A. Biondi, Phys. Rev. **88**, 660 (1952).

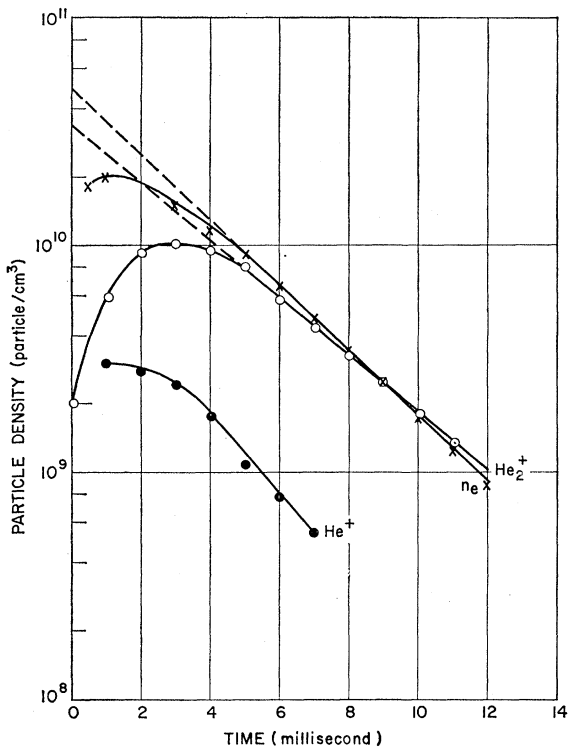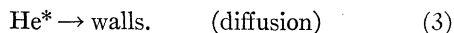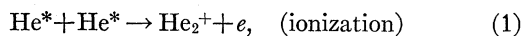[6] H. J. Oskam, Philips Res. Rept. **13**, 335, 401 (1958).

1639

FIG. 1. Measured electron, He_2^+, and He^+ densities in helium afterglow at 3 mm Hg pressure (Phelps and Brown).

representative of an ionized state.[7] The third condition would indicate that in a collision between two metastable atoms leading to ionization, $He^*+He^* \rightarrow He^+ +He+e$, or $He^*+He^* \rightarrow He_2^*+e$, the electronic energy of the second atom may have small influence on the ionization of the first. By far the greatest number of collisions of metastables will be with ground-state helium atoms; however, only a very small fraction of unexcited helium atoms of room temperature have sufficient translational energy (at least 1.8 eV) to ionize metastable helium atoms. Therefore, collisions of metastable atoms will lead to the ionization or the de-excitation of the metastable atom, or leave the metastable atom unchanged. The ionizing collisions will lead to the formation of *molecular ions* in preference to *atomic ions*, because the ionization potential of molecular helium is lower than that of the atomic helium by the value of the binding energy of the molecular ion, 2.16 eV. The metastable atoms which are unaffected by collisions diffuse through the plasma and collide with the walls of the vessel. These various alternatives may be represented as follows:
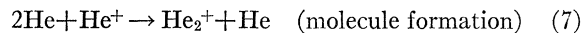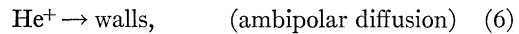
$$He^*+He^* \rightarrow He_2^++e, \quad \text{(ionization)} \qquad (1)$$

$$He^*+He \rightarrow 2 He, \quad \text{(de-excitation)} \qquad (2)$$

$$He^* \rightarrow walls. \quad \text{(diffusion)} \qquad (3)$$

[7] D. R. Bates and H. S. W. Massey, Phil. Mag. 45, 111 (1954).

He_2^+, the critical ion in the plasma, may be removed by dissociative recombination or by ambipolar diffusion to the walls:

$$He_2^++e \rightarrow He^*+He, \quad \text{(recombination)} \qquad (4)$$

$$He_2^+ \rightarrow walls. \quad \text{(ambipolar diffusion)} \qquad (5)$$
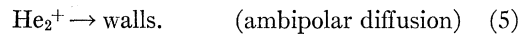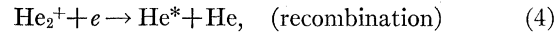
He^+ may be removed by ambipolar diffusion or by conversion to He_2^+:

$$He^+ \rightarrow walls, \quad \text{(ambipolar diffusion)} \qquad (6)$$

$$2He+He^+ \rightarrow He_2^++He \quad \text{(molecule formation)} \qquad (7)$$

The electrons disappear by ambipolar diffusion or by recombination with He_2^+:

$$e \rightarrow walls, \qquad (8)$$

$$e+He_2^+ \rightarrow He^*+He. \qquad (4)$$
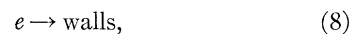
(The argument against direct recombination advanced by Bates, *et al.*,[8] that the reaction $He^++e \rightarrow He+h\nu$ is too slow, is accepted.)

To recapitulate, theoretical considerations suggest a reaction scheme in which the ionization of metastable
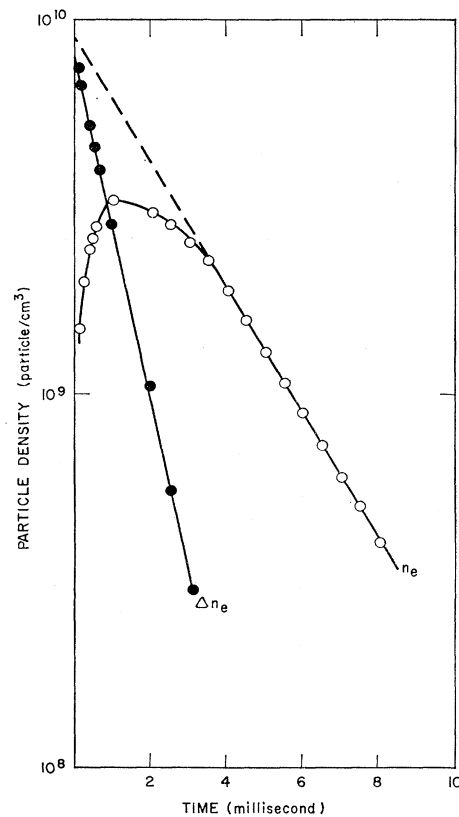

FIG. 2. Electron density and electron density differences in helium afterflow at 3.1 mm Hg pressure (Biondi).

[8] D. R. Bates, R. A. Buckingham, H. S. W. Massey, and J. J. Union, Proc. Roy. Soc. (London) A170, 322 (1939).

helium occurs by mutual collisions, forming molecular ions, He_2^+. The decay of ionization in the plasma occurs by a combination of ambipolar diffusion and dissociative recombination. The analysis of the experimental data in the next section provides strong supporting evidence for these mechanisms.

ANALYSIS OF EXPERIMENTAL DATA

It is evident from Fig. 1 that in the later stages of the afterglow both the He_2^+ and electron densities follow an exponential decay law. The data may be analyzed in the manner suggested by Biondi.[9] The final slopes of the He_2^+ and electron density curves are extrapolated back to zero time, and the differences between the extrapolated lines and the experimental values are determined. Semilogarithmic plots of these differences, ΔHe_2^+ and Δn_e, versus time again yield straight lines. In the experiment represented in Fig. 1, the slopes λ of these two lines as almost identical (Fig. 3), and $\lambda(\Delta He_2^+) = 833$ sec^{-1} and $\lambda(\Delta n_e) = 823$ sec^{-1}. If the ionization of metastables had occurred by

$$He^* + He^* \rightarrow He^+ + He + e, \qquad (9)$$
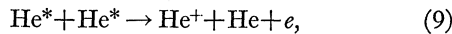
and the formation of He_2^+ by

$$He^+ + He \rightarrow He_2^+,$$
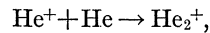
one would not expect the rates of electron enhancement and He_2^+ enhancement to be so similar because different processes would be involved. A second argument against the mechanism of reaction (9) is that no increase in He^+ corresponding to the increase in electron density is seen in Fig. 1. If, therefore, the enhancement in He_2^+ and electron densities is attributed to the ionization of metastable atoms, the near identity of the slopes suggests that the additional He_2^+ and electrons are produced at the same rate and by the same mechanism; namely,

$$He^* + He^* \rightarrow He_2^+ + e.$$
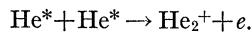
Assuming that metastable ionization proceeds by reaction (1), it is possible to reinterpret Biondi's measurements. Considering reactions (1) through (8) altogether, the time rate of change of He^* may be expressed by

$$-d(He^*)dt = k_1(He^*)^2 + k_2(He^*)(He) \\ + k_3(He^*) - k_4(He_2^+)n_e, \qquad (10)$$

and the time rate of change of electrons by

$$-dn_e/dt = -k_1(He^*)^2 + k_4(He_2^+)n_e - k_8 n_e. \qquad (11)$$

As noted above, Oskam[6] found that ambipolar diffusion to be the primary loss mechanism for electrons in helium; Gray and Kerr[10] report that the rate constant

[9] M. A. Biondi, Phys. Rev. **82**, 453 (1951).
[10] E. P. Gray and D. E. Kerr, in *Proceedings of the Fourth International Conference on Ionization Phenomena in Gases* (North-Holland Publishing Company, Amsterdam, 1960), p. 48.
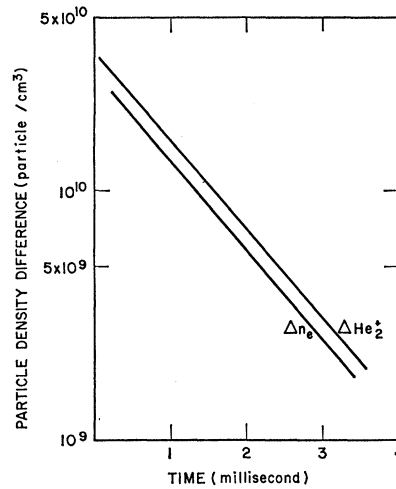
FIG. 3. Electron and He_2^+ density differences in helium at 3 mm Hg pressure.

for dissociative recombination, k_4, in helium must be less than 2×10^{-9} cm^3/ion-sec. Therefore, the term $k_4 n_e(He_2^+)$ is neglected at present:

$$-d(He^*)/dt = k_1(He^*)^2 + k_2(He^*)(He) + k_3(He^*),$$

$$\frac{d(He^*)}{(He^*)[(He^*) + K_{21}(He) + K_{31}]} = -k_1 dt;$$

$$[K_{12} = k_2/k_1, \quad K_{31} = k_3/k_1] \qquad (12)$$

$$\frac{(He^*)/[(He^*) + K_{21}(He) + K_{31}]}{(He^*)_0/[(He^*)_0 + K_{21}(He) + K_{31}]}$$

$$= \exp\{-[k_2(He) + k_3]t\}.$$

The degree of ionization is sufficiently low that the helium atom concentration is taken to be constant and equated to the total pressure, p. $(He^*)_0$ is the initial value of (He^*) at the beginning of the afterglow. Since the behavior of a helium plasma contained in a microwave cavity is dominated by diffusion processes, $(He^*) \ll K_{21}(He) + K_{31}$. Therefore, solution of Eq. (12) reduces to

$$(He^*) = (He^*)_0 \exp\{-[k_2(He) + k_3]t\}. \qquad (13)$$

Substituting the expression for He^* into Eq. (11) and solving,

$$n_e = A \exp(-k_8 t) + B \exp\{-2[k_2(He) + k_3]t\}, \qquad (14)$$

where

$$A = (n_e)_0 - \frac{k_1(He^*)^2_0}{k_8 - 2[k_2(He) + k_3]},$$

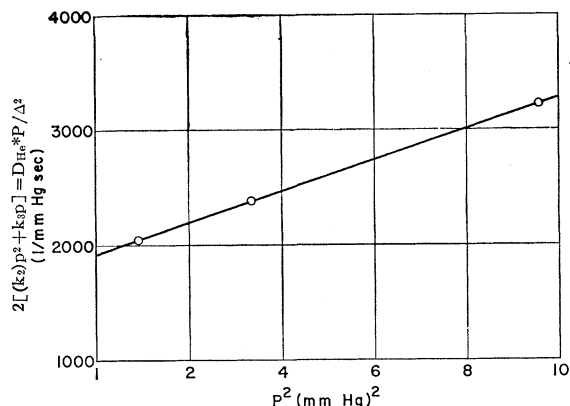$$B = \frac{k_1(He^*)^2_0}{k_8 - 2[k_2(He) + k_3]}.$$

FIG. 4. Variation of He* decay rate with gas pressure.

It is clear from Eq. (14) that the slope of the curve obtained by plotting the difference between the measured and extrapolated electron densities versus time is identified as the second exponential term of Eq. (14):

$$2[k_2(\text{He})+k_3]=\lambda(\Delta n_e).$$

When values of $\lambda(\Delta n_e)$ are obtained over a range of pressures and the values multiplied by the pressure $[p=(\text{He})]$,

$$\lambda(\Delta n_e)\cdot p=2[k_2(\text{He})+k_3].$$

A plot of $\lambda(\Delta n_e)\cdot p$ versus p^2 yields a line with an intercept equal to k_3p (Fig. 4). The intercept at $p=0$ is identified with the diffusion coefficient of He*:

$$2k_3p=D_{\text{He}*}p/\Lambda^2,$$

where Λ is the characteristic diffusion length of the microwave cavity. In Biondi's experiments $\Lambda^2=0.54$ cm^2. As shown in Fig. 4, the intercept is 1920 mm Hg/sec; accordingly, $D_{\text{He}*}p=1037$ cm^2 mm Hg/sec. The value for unexcited Helium atoms, calculated from the kinetic theory self-diffusion coefficient, is 1092 cm^2 mm Hg/sec.[11] The value for the diffusion coefficient of He* permits us to estimate k_2 and k_3. For example, in

TABLE I. Experimental reaction rate coefficient.

Pressure (p, mm Hg)	Characteristic diffusion length (Λ^2, cm^2)	Slope of electron density ($k_g=D_a/\Lambda^2$)	Diffusion coefficient (D_ap, cm^2/mm Hg-sec)	Slope of electron density difference [$\lambda(\Delta n_e)$, sec^{-1}]
0.98	0.540	932	494	2080
1.85	0.540	580	578	1292
3.0	0.85	268	684	823
3.1	0.540	383	645	1040

[11] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), p. 15.

Biondi's experiment at 3.1 mm Hg,

$$\lambda(\Delta n_e)=1040=2[k_2p+k_3].$$

Therefore, $k_2p=210$/sec and $k_2=67.8$/mm Hg sec.

For the Phelps and Brown experiment at 3 mm Hg where $\Lambda^2=0.85$ cm^2 and $D_{\text{He}*}p=1037$,

$$2k_3=D_{\text{He}*}p/\Lambda^2p=407$$

and

$$\lambda(\Delta n_e)=412=k_2p+k_3.$$

Accordingly, $k_2=69.2$/mm Hg sec. The results of this analysis for the four experiments for which sufficient data exists are presented in Tables I and II.

If the initial concentrations of metastable helium, $(\text{He}*)_0$, were known, k_1 could be determined directly from Eq. (14). However, $(\text{He}*)_0$ can be estimated only indirectly. The initial electron density difference, $(\Delta n_e)_0$, represents that portion of He* which is ionized during the afterglow. The remainder of the He*, by far the larger amount, is either de-excited in the gas phase or drifts to the walls of the container. At higher levels of ionization the conversion of metastables becomes more

TABLE II. Derived reaction rate constants.

| Pressure (mm Hg)	$(k_2)p+k_3$ (sec^{-1})	k_3 (sec^{-1})	$(k_2)p$ (sec^{-1})	k_2 (mm Hg sec)$^{-1}$	k_2 (10^{-15} cm^3/ part.-sec)
0.98	1040	980	60	61.3	1.97
1.85	646	518	128	68.9	2.21
3.0	412	204	208	69.2	2.22
3.1	520	310	210	67.8	2.18

competitive with the other processes. When experimental results at higher ionization become available, a comparison with the present data may provide an analytical estimate of $(\text{He}*)_0$. A more satisfactory approach would be a spectrographic determination of the initial metastable concentration.
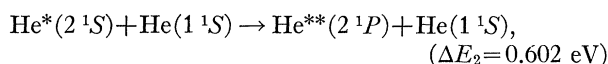
DISCUSSION

The reaction scheme that is advanced to describe a decaying helium plasma accounts for the details of the ionization processes in a consistent manner. By this scheme ionization of metastable helium atoms occurs with the formation of the molecular ion, He_2^+. The predominant process for the decay of electron density is ambipolar diffusion. On the basis of these mechanisms, a value for the diffusion constant for helium metastables is deduced which is in close agreement with the helium atom self-diffusion constant. Furthermore, the rate constant for de-activation of helium metastables, $k_2\sim 2\times 10^{-15}$, corresponds to a collision efficiency for deactivation of 10^{-5} and a lifetime of 1.6×10^{-2} sec at 1 mm Hg pressure.

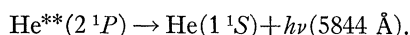The specific values of k_1 and k_2 can be derived

from energy considerations if the identity of the metastable species is established. Biondi[5] observed that irradiation of the helium afterglow with 20 580 Å light reduced the initial rise in electron density; irradiation with 10 830 Å light had no such effect. This observation would indicate that the metastable helium is in the $2\,^1S$ state and not the $2\,^3S$ state, the assumption being that the absorption of 20 580 Å raises the $2\,^1S$ state to the $2\,^1P$ resonance state, which may be de-cited by spontaneous emission. If metastable population consists primarily of $2\,^1S$ helium, the reaction (1) may be interpreted as

$$\mathrm{He}^*(2\,^1S)+\mathrm{He}^*(2\,^1S)\rightarrow\mathrm{He_2}^++e, \quad (\Delta E_1\leqslant 1.81\ \mathrm{eV})$$
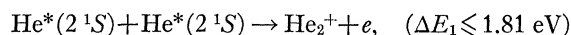
(the activation energy, ΔE_1, depending on the efficiency of converting electronic energy to ionization), and reaction (2) as

$$\mathrm{He}^*(2\,^1S)+\mathrm{He}(1\,^1S)\rightarrow\mathrm{He}^{**}(2\,^1P)+\mathrm{He}(1\,^1S),$$
$$(\Delta E_2=0.602\ \mathrm{eV})$$

followed by

$$\mathrm{He}^{**}(2\,^1P)\rightarrow\mathrm{He}(1\,^1S)+h\nu(5844\ \text{Å}).$$

On this basis

$$k_1/k_2\sim\exp(-\Delta E_1)/\exp(-\Delta E_2)\leqslant 4\times 10^{-21},$$

depending on the precise value of ΔE_1. However, the identification of the helium metastables is far from conclusive. The radiative de-excitation of the $1\,^1S$ state has not been detected, probably because the line lies in the vacuum ultraviolet. In addition, Biondi and Rogers[12] have observed the 5876 Å line in microwave-produced plasmas. This radiation corresponds to the $3\,^3D$ to $2\,^3P$ transition of the orthohelium system, and therefore,

weakens the argument outlined above that the meta-stables consist exclusively of the para, $2\,^1S$, system. Furthermore, Anderson[13] reports measurements of the $3\,^1P\rightarrow 2\,^3S$ (ortho) transition in the helium afterglow, together with molecular band emission. It is clear that the identity of the reactive metastable species in the helium afterglow is as yet uncertain.

A second problem in regard to the optical observa-tions in the helium plasmas concerns the location within the gas of the emitting processes. The radiation emitted by the neutralization of ions at the walls must be distinguished from the various radiative processes that occur within the gas phase. The broadening of the 5876 Å in the late afterglow observed by Rogers and Biondi[12] is reasonably attributed by the investigators to excited helium atoms formed in dissociative recom-bination within the gas. On the other hand, the helium molecular bands observed by Anderson[13] may be due to radiative processes occurring during neutralization of molecular ions at the walls. These questions may be resolved by measuring the intensities of the various radiations at specific locations within the container.

The validity of the reaction scheme may receive further verification with the publication of additional time-resolved mass spectrographic data. A simultaneous measurement of the rate of change of ion concentration and radiative intensity (to correlate the ionization processes with the specific chemical species) is required for complete verification of the ionization mechanism.

ACKNOWLEDGMENT

[12] W. A. Rogers, Ph. D. thesis, University of Pittsburgh (1958) (unpublished), quoted by M. A. Biondi in *Chemical Reactions in the Lower and Upper Atmosphere* (Stanford Research Institute Symposium, San Francisco, 1961).

[13] J. M. Anderson, *Proceedings of the Fifth International Con-ference on Ionization Phenomena in Gases* (North-Holland Publish-ing Company, Amsterdam, 1962), p. 621.