THE INFLUENCE OF FOREIGN GASES ON THE INTENSITIES OF THE MAGNESIUM RESONANCE LINES 4571 AND 2852

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Abstract

The Mg line 4571, $3^1S-3^3P_1$, is very weak in the arc while 2852, 3^1S-3^1P, is very intense. The life of the 3^3P_1 state is calculated to be 4×10^{-3} sec., while 3^1P has a life of 3×10^{-9} sec. Collisions of second kind between excited Mg atoms reduce intensity of 4571 in the arc. At a vapor pressure of 10^{-4} mm, the time between collisions of the Mg atoms is 10^{-3} sec. The 4571 line should appear strong at this or lower vapor pressures. Vapor from solid Mg metal at 500°C was excited in an evacuated tube by an electrodeless short-wave discharge. The 4571 line appeared in the discharge as a fairly prominent line.

Effect of foreign gases on 4571. The noble gases enhanced this line, the intensity relative to the triplet 3838 increasing up to about 20 mm in argon and 10 mm in neon and helium and then remaining practically constant. At these pressures, argon increased the line 100 times, Ne about 70 times, and He about 40 times. N_2 and CO increased 4571 up to the limit of pressure, about 2 mm, at which the discharge could be operated. H_2 caused a *slight* increase at a pressure of about 2 mm.

Intensity-pressure curves for noble gases have been reproduced theoretically, proving the assumption that excited Mg atoms suffer collisions of the second kind with the walls, and that action of a noble gas in enhancing the 4571 line is due entirely to the slowing up of diffusion of Mg atoms in 2^3P_1 state to the walls, and to its inefficiency in causing collisions of the second kind with excited Mg atoms.

Effect of foreign gases on 2852. All gases reduce 2852 and all singlets terminating on the 3^1P level. Increasing pressure of H_2 reduces 2852 faster than the singlets. Dissociation of the H_2 molecules by Mg atoms in 3^1P state reduces radiation from that state.

THE Mg line 4571, 3^1S–3^3P_1, is either very weak or entirely absent in the ordinary arc in air. On the other hand, the line 2852, 3^1S–3^1P, is exceptionally strong in the arc. 4571 is found in the flame spectrum and King[1] reports it as a fairly strong line in the low-temperature-furnace spectrum. Foote and Mohler[2] have produced it with considerable intensity in a controlled electron discharge, it being the first line to appear at an accelerating potential of 2.7 volts. Since the transition from the 3^1S to the 3^3P_1 state requires the minimum energy, this line should ordinarily be the strongest line in the spectrum. Its anomalous behavior is therefore of interest. The fact that it appears fairly strong wherever the excited vapor is of low pressure has been explained by Bowen[3] on the same basis as his explanation of nebular lines that arise from metastable states in nitrogen and oxygen.

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[1] A. S. King, Astrophys. J. **48,** 13 (1918).

[2] Foote and Mohler, Phil. Mag. **37,** 33 (1919).

[3] Bowen, Proc. Nat. Acad. Sci. **14,** 30 (1928).

In a recent paper Houston[4] has shown how the transition probabilities of singlet and triplet systems may be calculated. From these calculations the natural life of an excited state may be determined. In Mg the life of the 3^3P_1 state approximates 4×10^{-3} sec. whereas the 3^1P state has a life of 3×10^{-9} sec. These figures show at once, in accordance with Bowen's theory, that the long life of the 3^3P_1 state accounts for the behavior of the 4571 line, collisions of the second kind returning most of the excited atoms to the normal state when the vapor pressure is sufficiently high. Now if the vapor pressure were low enough so that the time between collisions of the excited atoms is of the order of magnitude of the free life of the excited state, transition to the normal state should more likely give rise to radiation. Kinetic theory considerations show that at a vapor pressure of 10^{-4} mm, the time between collisions of Mg atoms is of the order of 10^{-3} sec. At this or lower vapor pressures, the 4571 should be a prominent line. There is one limitation, however, to obtaining the full intensity of the line at these low pressures. The vapor is confined to a vessel, and since the mean free path of the Mg atoms at 10^{-3} mm is several cm, collisions with the walls will be very frequent. Cario and Franck[5] and other observers have suggested that impacts of excited atoms with the walls of a discharge tube are collisions of the second kind. Recently, Pool[6] has found direct experimental evidence for this kind of impact of excited Hg atoms with the walls of the tube. If, then, we wish to obtain the full intensity of the Mg 4571 line at low pressures, we must reduce the frequency of collisions with the walls. This can be done, as we shall see later, by introducing a noble gas to prevent diffusion to the walls.

This experiment was primarily undertaken, at the suggestion of Professor I. S. Bowen, to compare the intensity of the 4571 line excited at low pressure with the intensity of the corresponding line in the arc. This comparison did not prove feasible because of the weakness of the line in the arc. A study of the variation of intensity of the line with vapor pressure was not undertaken on account of the experimental difficulties involved. It is necessary, for example, to heat the discharge tube to 500°C or higher to secure enough vapor for a discharge. It was decided, therefore, to make a study of the line with the vapor at 500°C, and particularly, the effect of foreign gases and vapors on it at this temperature. With the technique developed in this work, it is hoped to carry on a further investigation of the effect of pressure on the line.

Experimental Procedure

A short-wave oscillator supplied the energy for an electrodeless discharge in the Mg vapor at 500°C. According to International Critical Table data, the vapor pressure at this temperature is approximately 10^{-4} mm. A short stick of carefully scraped Mg metal was inserted in a tube 30 cm long, and 4 cm diameter. The presence of vapor from this stick was always indicated

[4] Houston, Phys. Rev. **33**, 297 (1929).

[5] Cario and Franck, Zeits. f. Physik **37**, 619 (1926).

[6] M. L. Pool, Phys. Rev. **33**, 22, (1929).

by the appearance of a brilliant green glow which filled the entire tube. A quartz window was sealed to the Pyrex tube by a graded seal. The spectra were photographed on a E-1 Hilger spectrograph. Intensity measurements were made in the manner described by Frayne and Montgomery.[7]

Experimental Results

Hydrogen. With hydrogen in the tube, it was possible to excite a discharge only between pressures of about 2 mm and 10^{-2}mm. The Mg combined with the H_2 to form MgH_2. This made it necessary to pass in H_2 through a capillary during the excitation of the discharge. The intensity of the 4571 line relative to the triplet 3838 increased slightly with pressure.

Carbon monoxide. CO apparently had an oxidizing effect on the Mg vapor, as it was difficult to keep the discharge going. This gas caused a decided increase in the 4571 line.

Nitrogen. N_2 was studied between 2 and 10^{-2} mm, no discharge being possible above 2 mm. The 4571 line showed a strong increase at 2 mm, while the 2852 line showed a decided decrease. The singlet series also showed a falling off in intensity at the higher N_2 pressures.

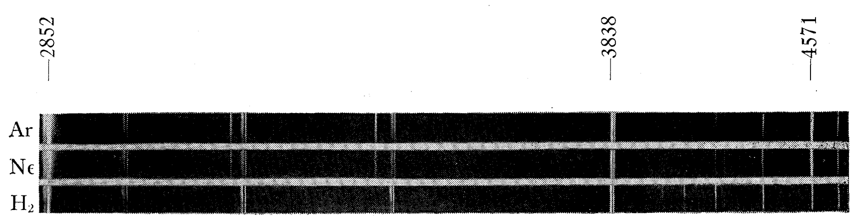

Fig. 1. Spectrum of Mg vapor in presence of foreign gases.

Argon. The argon used in this work was not entirely free from nitrogen and oxygen. It was partly purified by operating the discharge in it for a couple of hours. The 4571 line shows an increase at 1 mm, see Fig. 1, and increases rapidly with pressure up to 10 or 20 millimeters. The intensity seems to remain practically constant at higher pressures. The 2852 line as well as all the singlet lines diminish rapidly with pressure.

Neon. Neon behaves similarly to argon. It was very pure and no difficulty was encountered in getting a strong discharge at a pressure of 200 mm. The 4571 line is again enhanced, reaching its saturation value at 10 mm or lower. The increase is not as great as in the case of argon. The diminution of the 2852 line is not very pronounced.

Helium. The helium used in this work was very pure. Its behavior is quite similar to neon.

All the noble gases, argon particularly, diminished the intensity of the singlet series. With an argon pressure of 6 cm, the singlets only appear as very faint lines, and the 2852 line has become so reduced in intensity that

[7] Frayne and Montgomery, Phys. Rev. **33**, 549 (1929).

it is actually weaker on the plate than 4571. This is remarkable when one considers the intensities of these two lines in the arc. The results of observa-

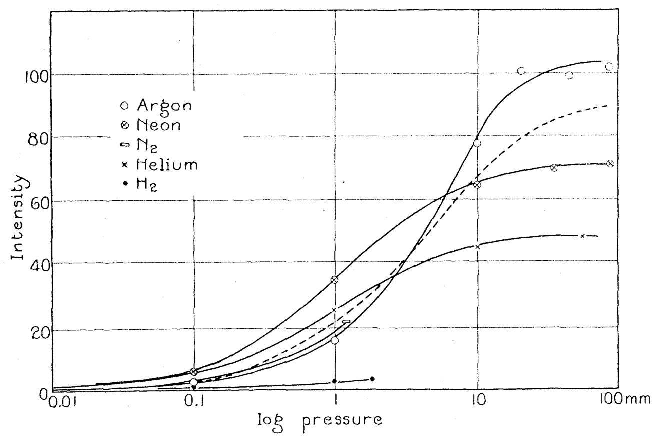

Fig. 2. Relation of intensity of Mg 4571 line to the pressure of foreign gas.

tions on the 4571 line are shown in Fig. 2 and those on the 2852 line are shown in Fig. 3.

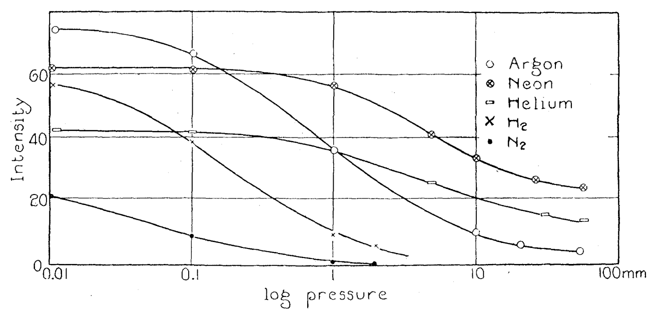

Fig. 3. Relation of intensity of Mg 2852 line to the pressure of foreign gas.

Discussion of Results on 4571.

The curves of Fig. 2 show clearly that of all the permanent gases studied, H_2 alone fails to cause any appreciable increase in the intensity of the 4571 line. Figure 3, however, shows that all the gases bring about a quenching of the 2852 resonance line. The behavior of the 4571 line may be explained as follows. The Mg vapor pressure in the discharge was about 10^{-4} mm and at this low pressure collisions of the second kind of the excited Mg atoms with the walls are very frequent. The introduction of any gas will slow up diffusion to the walls, thus diminishing collision with the walls and increasing the possibilities of radiation from the excited 3^3P_1 state. Since the velocity of diffusion varies inversely as the pressure, one would expect the intensity of the line to increase with pressure up to a certain point above which the intensity of the line should remain constant, if there were no collisions of the second kind between the excited Mg atoms and the gas. On the other hand, the line should show a decrease of intensity if such collisions take place. In this research, it was only possible to attain the "saturation" value of the 4571 line with noble gases in the tube. It was not possible to excite any discharge with N_2, H_2, or CO above a few mm, and consequently, the conditions for obtaining the maximum value of the 4571 line could not be attained. Now Stuart[8] has found that the noble gases are very inefficient in effecting collisions of the second kind with excited atoms. In this research, a slight decrease in intensity of the 4571 line was found in argon above 40 mm, while the intensity appeared to remain constant above 1 cm for neon and helium. This suggests that N_2 impurities are responsible for the slight decrease in argon. Of course, the accuracy of measurement in this type of work is not sufficiently great to detect a small decline in the intensity. The fact that H_2 has little effect on 4571 is probably due to collisions of the second kind between H_2 molecules and the excited Mg atoms. These collisions offset the effect of reduced diffusion to the walls.

Mathematical Theory

The curves in Fig. 2 lend themselves readily to mathematical analysis. Let us consider the tube containing Mg excited atoms distributed across any cross section. We will assume, as above, that these excited atoms undergo collisions of the second kind with the walls of the tube. We will further assume that collisions between Mg excited atoms may be neglected at a pressure of 10^{-4} mm and that there are no collisions of the second kind with the foreign gas present in the tube.

The equation for the steady state in the tube is:

$$\frac{kd^2n}{dr^2}+\frac{k}{r}\,\frac{dn}{dr}+(c-\tau n)=0$$

where n is the number of excited Mg atoms per cc at a point distant r from the center; k the diffusion coefficient; c the rate at which the excited atoms are being produced; $\tau=$ the transition probability of the excited atoms. The boundary condition is that at the periphery of the tube n shall be zero. On making the substitutions $y=c-\tau n$ and $x=(\tau/k)^{1/2}r=\alpha r$, the equation reduces to

$$\frac{d^2y}{dx^2}+\frac{1}{x}\,\frac{dy}{dx}-y=0$$

a solution of this equation is:

$$y=a_0\left\{1+\frac{x^2}{2^2}+\frac{x^4}{2^2\cdot 4^2}+\frac{x^6}{2^2\cdot 4^2\cdot 6^2}+\cdots\right\}$$

or

$$n=\frac{c}{\tau}-\frac{a_0}{\tau}\left\{1+\frac{\alpha^2r^2}{2^2}+\frac{\alpha^4r^4}{2^2\cdot 4^2}+\frac{\alpha^6r^6}{2^2\cdot 4^2\cdot 6^2}+\cdots\right\}.$$

[8] Stuart, Zeits. f. Physik **32**, 262 (1925).

If we now let $n=0$ when $r=R$, we may evaluate a_0 and we have

$$n=\frac{c}{\tau}\ \frac{\dfrac{\alpha^2(R^2-r^2)}{2^2}+\dfrac{\alpha^4(R^4-r^4)}{2^2\cdot4^2}+\dfrac{\alpha^6(R^6-r^6)}{2^2\cdot4^2\cdot6^2}+\cdots}{1+\dfrac{\alpha^2R^2}{2^2}+\dfrac{\alpha^4R^4}{2^2\cdot4^2}+\dfrac{\alpha^6R^6}{2^2\cdot4^2\cdot6^2}\cdots}$$

Now the intensity of the 4571 line will be proportional to the number of atoms in a cross-section of the tube, the number being given by

$$N=2\pi\int_0^R rndr.$$

If we multiply the right hand side of Eq. (1) by $2\pi r\ dr$, and integrate term by term with respect to r, we will have an expression that will be proportional to the intensity of the 4571 line for the given experimental conditions. We obtain

$$N=2\pi c/\tau\left\{\frac{\dfrac{\alpha^2}{2^2}\,\dfrac{R^4}{4}+\dfrac{\alpha^4}{2^2\cdot4^2}\cdot\dfrac{R^6}{3}+\dfrac{\alpha^6}{2^2\cdot4^2\cdot6^2}\,\dfrac{3R^8}{8}+\cdots}{1+\dfrac{\alpha^2R^2}{2^2}+\dfrac{\alpha^4R^4}{2^2\cdot4^2}+\dfrac{\alpha^6R^6}{2^2\cdot4^2\cdot6^2}}\right\}$$

Since c is unknown we need only evaluate the expression inside the brackets. If we let $R=2$ cm, we obtain the following values

$\alpha^2=0.01$	0.1	1	10	0.100
$N\propto 0.01$	0.094	0.606	1.52	1.75
$p=0.0155$	0.155	1.55	15.5	155

Now $\alpha^2=\tau/k$ and τ is the reciprocal of the natural life of the excited state or $\tau=0.25\times10^3$. The constant k is rather uncertain as it really is the diffusion constant for excited Mg atoms in a foreign gas atmosphere. We may assume, however, that k is $\lambda c/3$ and for argon under standard conditions this has the value 0.112. When c, the mean molecular velocity, and λ, the mean free path, are corrected for the temperature of 500°C used in the experiment, λ and hence the pressure p may be determined for any of the values of α^2 listed above. When the values of N are plotted against log p, we obtain the broken curve shown in Fig. 2. The scale chosen for N is quite abitrary, but it will be noticed that the curve as drawn is in general agreement with the experimental curves. While the slope of the curve at 1 mm pressure is more nearly like that of neon, than argon, its saturation value is reached around 50 mm which is in fair agreement with the experimental curve for argon. The argon used in this experiment was not very pure and this may account in part for the discrepancy between experimental and theoretical curves. There is also considerable error in experimental values of the intensities. The remarkably close agreement, however, indicates that the life of the Mg 2^3P_1 state must be very nearly 4×10^{-3} sec. If the value were reduced to 2×10^{-3}, the saturation value would occur about 25 mm which would agree very well with experimental data.

This remarkably close fit of the theoretical and experimental curves undoubtedly proves that the general conditions proposed to explain the curves of Fig. 2 are correct. *It proves that collisions of excited metastable atoms with the walls are collisions of the second kind*, and furthermore, proves without any doubt that the *action of a noble gas* particularly argon or neon, *in enhancing lines from metastable states, is one of reducing diffusion to the walls.* Finally, the life of the Mg 2^3P_1 state is proved to be approximately 4×10^{-3} sec.

Discussion of Results on 2852.

It has already been pointed out that the intensity of the 2852 line diminishes with pressure of the foreign gas. Neon and He show the least diminution over the pressure range. Argon and N_2 have a very pronounced effect while H_2 appears to cause the greatest diminution. The same conditions that reduce 2852 also diminish the singlet lines terminating on the 3^1P state. Referred to the triplet line 3838, the 2852 line is diminished to the same extent as the singlet lines. H_2, however, is an exception. Here, the 2852 line shows a diminution of one-thirtieth in the pressure range that reduces the singlets only one fifth. This quenching of the 2852 line must be similar to the quenching of Hg resonance radiation found by Wood,[9] Cario[10] and Stuart. The quenching action of H_2 is attributed to the action of the excited Hg atom in dissociating the H_2 molecule. Since the Mg 3^1P state has an energy of 4.4 equivalent volts, an atom in that state can readily dissociate the H_2 molecule. Mg atoms would then return to the normal state without radiation. This process should in no way involve the intensity of the 4571 line.

In the case of gases other than H_2, the diminution of the singlet lines and the 2852 line cannot be explained as any result of collisions of the second kind. The life of the 3^1P state is one millionth that of the 3^3P_1 state and collisions of the second kind should be far more effective for the state with the longer life. We have already seen, in the case of the noble gases, that collisions of the second kind are ineffective with the 3^3P_1 state, and, accordingly, we can hardly expect them to account for the decrease observed in the intensity of the singlet members. Since the intensities of these singlets are measured with reference to a triplet, it would seem that the higher pressures favor the triplet series rather than the singlets. Similar effects were found by Frayne and Montgomery[7] in Hg vapor in which increased vapor pressure reduced all the singlets relative to the triplets. Professor Ornstein[11] has recently offered an explanation of this differentiation between singlet and triplet lines at high pressures. It appears that higher pressure of the emitting vapor or a foreign gas give similar results.

In conclusion the author desires to thank Professor I. S. Bowen for his many suggestions and advice in interpreting the experimental results. He also wishes to thank Dr. W. V. Houston for assistance in the mathematical work and Dr. M. Muscat for assistance in the experimental work.

[9] R. W. Wood, Phys. Zeits. **13,** 353 (1912) and numerous later papers.
[10] G. Cario, Zeits. f. Physik **10,** 185 (1922).
[11] L. S. Ornstein. Zeits. f. Physik **51,** 34(1928).

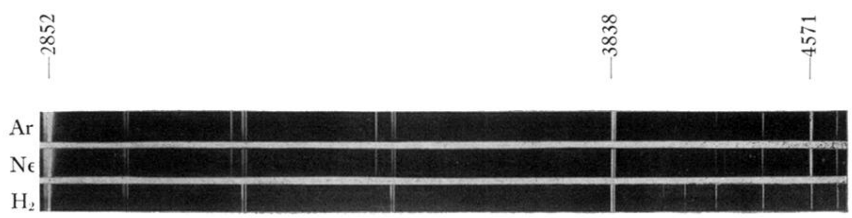

Fig. 1. Spectrum of Mg vapor in presence of foreign gases.