ON THE ELECTRICAL DISCHARGE IN MIXED GASES

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Abstract

Spectra of argon, hydrogen and oxygen in the negative glow and positive column of a discharge tube containing A $-H_2$ and A $-O_2$ mixtures.—The following mixtures were used: (1) H_2 90% $-$A 10%, (2) H_2 50% $-$A 50%, (3) O_2 90%$-$A 10%, (4) O_2 50%–A 50%. Tables are given showing the principal lines in each region, and their estimated relative intensities. In all four cases the change in concentration was found to make little difference in the distribution of electronic energy. In (1) the argon red spectrum is very strongly excited in the positive column and the blue spectrum appears most intensely in the negative glow. A considerable number of electrons in the positive column possess energies of about 16 volts, while their energy in the negative glow reaches as much as 38 and 40 volts. In (3) and (4) the electrons on the whole possess energies of a higher order in both regions. The argon blue spectrum, the hydrogen Balmer series, and the oxygen series and elementary spectra predominate in the negative glow, whereas the argon red spectrum is most intense in the positive column. The behavior of the Balmer lines in hydrogen and argon is the opposite of its behavior in hydrogen and helium. The *striated state* was produced in every mixture, and abrupt changes in the discharge occurred, when the pressure was reduced to critical values. *The rotation of inclined striae* is connected with the intermittency of the discharge.

Introduction

An examination of the spectra emitted by different regions of the discharge, in mixtures of hydrogen and nitrogen and of hydrogen and helium was recently carried out by Keys and Home.[1] The present paper deals with a similar investigation in mixtures of argon and hydrogen, and of argon and oxygen. Different proportions of the gases were tried and their effect was recorded.

The spectrographic examination of the discharge possesses the following advantages; (1) it introduces no foreign element into the discharge, (2) it is applicable to any region of any type of discharge with equal facility, and (3) it provides data whereby the average energy of the moving electrons and the states of excitation of the atoms and molecules may be determined. This method is only limited by our power to interpret the spectra in terms of atomic states and energy distributions, whether electronic or quantum.

This method is not of recent inspiration, for De La Rue and Müller[2] found some fifty years ago, that in hydrogen, the Balmer lines were more strongly excited in the negative glow than elsewhere. The same discharge

[1]Keys and Home, Phys. Rev. **27**, 709 (1926).
[2]De La Rue and Müller, Phil. Trans. **178**, 155 (1878).

was examined by Crookes[3] who proved that the bluish sheath occasionally found on the convex side of striae was due to mercury vapour. More recently we have the work of Whiddington[4] on hydrogen and argon, and of Banerji[5] on argon. The spectrum of the mercury vapour and hydrogen discharge has been studied by Turner and Compton,[6] and of the striated hydrogen discharge by Keys.[7]

In the present work the spectra of the negative glow and of the striated positive column were obtained and interpreted as far as possible.

Apparatus

The discharge tube was of quartz; 2.3 cm in diameter and 90 cm long, fitted with aluminium disc electrodes, 2.2 cm in diameter, placed 62 cm apart. One of the electrodes was water cooled. A Cenco "Hyvac" pump and a charcoal bulb in liquid air were used in exhausting the tube, which was excited by the direct current from a 300–6000 volt motor generator by Evershed. The spectra were obtained with a Hilger E2 quartz spectrograph, and in addition a constant deviation glass spectrograph was frequently employed. The iron arc was used for comparison purposes. The gases were mixed and carefully dried before being admitted to the tube, which was washed thoroughly before an exposure was attempted. Wratten and Wainwright, and Ilford Rapid Process, Panchromatic plates were used throughout.

Observations

The conditions under which the four principal plates were obtained are shown in Table I.

Table I

No.	Mixture	Pressure	Current	Potential	Exposure	Plate
I	A 90%–H 10%	.18 mm	8 m.a.	1100 volts	6 hrs.	Ilf.
II	A 50%–H 50%	.09 mm	4 m.a.	1500 volts	3.7 hrs.	W & W.
III	A 10%–O 90%	.01 mm	1 m.a.	1800 volts	4.5 hrs.	W & W.
IV	A 50%–O 50%	.07 mm	2 m.a.	1500 volts	7 hrs.	Ilf.

Only the principal lines on these plates were considered and they are given in the following Tables II, III, IV. The columns under N.g. and P.c. give the estimated relative intensities of the lines in the negative glow and positive column respectively.

[3]Crookes, Proc. Roy. Soc. **69**, 399 (1902).
[4]Whiddington, Nature **116**, 506 (1925).
[5]Banerji, Nature **116**, 429 (1925).
[6]Turner and Compton, Phys. Rev. **25**, 606 (1925).
[7]Keys, Trans. R. S. C. **19**, 143 (1925).

TABLE II

The spectrum of argon in the negative glow and positive column of a discharge tube.
Plate I = A 90 %–H_2 10 %. Plate III = A 10 %–O_2 90 %. Plate IV = 50 %–O^2 50 %

Wave-length	Plate I. N. g	Plate I. P. c	Plate III. N. g	Plate III. P. c	Plate IV. N. g	Plate IV. P. c
	Blue spectrum					
4848	3	0				
4765			3	1		
4727			5	1		
4675	7	0				
4658			3	1		
4610	8	0	3	1	3	0
4590	7	0				
4579	7	0				
4545	8	0				
4491			1	1		
4482	6	0			1	0
4432	5	0				
4426	6	0			1	0
4401	5	0			2	0
4379	5	0				
4371					3	0
4348	7	1				
4331	7	0				
4283					9	0
4277	9	0	8	4		
4237	5	0	6	0		
4223	3	0				
4156			2	2	4	4
4132	9	0	2	0	3	0
4113			2	0		
4104	5	0				
4082	4	0				
4073	8	0	3	0	3	0
4053	6	0	2	0	3	0
4043	7	0			3	0
4014	3	0				
3996	4	0				
3968	3	0	3	0		
3961					4	0
3944					3	0
3919	10	0				
3915					9	0
3908			3	2		
3851	6	0	3	0		
3803	7	0	7	9		
3754			7	9	6	1
3729	7	0				
3582	7	0	6	1		
3577	8	1	7	10	10	9
3560	6	0				
3546	9	0	2	0		
3535	6	1	6	1	8	8
3509	6	0	2	0		
3491	9	0				
3392			2	0		
3286			5	4		
3282					4	4
3264			4	1	2	3
3093	8	0	5	0	6	1
3034			2	0	1	0
2979	8	0			4	0
2943	10	0	4	0	7	2
2879					6	1
2754	7	0			3	0
2708	2	0			1	0
2479			4	2		
2439			4	3		
2421					3	0
2338					3	0
	Red spectrum					
6416	1	6				
6032	0	5				
6026			1	1		
5912	1	4				
5607	1	4				
5559	1	4				
5506	0	2				
5496	1	4				
5452	1	3				
5253	1	3				
5222	1	3				
5163	1	4				
4868	1	4				
4629	1	4				
4596	1	4				
4522	0	4				
4511	4	10	3	4	2	5
4345	2	6	3	5		
4335	0	9	3	4	0	4
4300	3	10				
4272	3	10	1	4		
4266	2	8				
4259	5	10			5	6
4201	5	10	4	7	6	6
4198	3	10				
4182	3	9				
4164	3	8				
4159	5	10			4	6
4044	3	10			3	6
3949	3	9	3	6		
3894					0	3
3835	2	6				
3670	0	3	2	3		
3650	0	8				
3635	1	5				
3554	0	5				
3460	0	3				
3374	7	8			9	10
3305			2	5		
3022	0	2				
2967	0	2			0	3
2834	0	1				
2802					0	1

Discussion

Plate I. Argon 90 percent—Hydrogen 10 percent. In the positive column we find the argon red spectrum very strongly developed, whereas in the negative glow it is comparatively weak. On the other hand the blue spectrum, which is intense in the negative glow, is represented by three feeble lines in the positive column. The primary hydrogen spectrum is quite strong in the negative glow, and weak in the positive column. The secondary hydrogen spectrum is distributed with more impartiality in both regions.

Table III

The spectrum of hydrogen in the negative glow and positive column of a discharge tube.
Plate I = A 90%–H_2 10%. Plate II = A 50%–H_2 50%

Hydrogen primary spectrum Wave-length	Plate I. N.g	Plate I. P.c	Plate II. N.g	Plate II. P.c	Hydrogen secondary spectrum Wave-length	Plate I N.g	Plate I P.c
6563 Hα	10	4	10	1	6299	0	3
4861 Hβ	7	2	8	1	6135	1	3
					5888	0	4
					5505	0	3
4340 Hγ	6	1	6	1	4474	5	0
					4171	1	1
4101	7	1	5	0	4070	1	1
3970	2	1	3	0	4063	0	3
3835	5	4	3	0	3998	5	5
3791	1	1	0	0	3993	2	1
3771	1	1	0	0	3990	3	1
3712	1	1	0	0	3872	1	1
					3805	5	6
					3797	1	1
					3684	1	0
					3674	1	1

From the work of Dejardin,[8] Horton and Davies,[9] Shaver,[10] and Barton,[11] it appears that the argon atom is ionised at about 15.2 volts, and furthermore that at this potential the whole red spectrum is emitted. It is evident therefore, that a large number of argon ions are present in the positive column, and that the "velocity" of a great number of electrons in this region is close to 15.2 volts. Were it less, the red spectrum could not be so intense. On the other hand, the comparative weakness of the Balmer lines; which, according to Horton and Davies,[12] Smyth,[13] and Duffendack,[11] correspond to a potential of about 16 volts, indicates that it can hardly be in excess of the above value.

[8] Dejardin, C. R. **172,** 1482 (1921); Ann. d. Physique **10,** 241 (1924).
[9] Horton and Davies, Proc. Roy. Soc. **97,** 1 (1920) and **102,** 131 (1922).
[10] Shaver, Trans. R. S. C. **16,** 135 (1922).
[11] Barton, Phys. Rev. **25,** 469 (1925).
[12] Horton and Davies, Phil. Mag. **46,** 872 (1923).
[13] Smyth, Phys. Rev. **25,** 452 (1925).
[14] Duffendack, Phys. Rev. **20,** 665 (1922).

The relative weakness of the red spectrum in the negative glow is perhaps due to the average energy of the electrons being greatly in excess of the first ionising potential. The great intensity of the blue lines requires potentials of a much higher order.

A number of authorities are of the opinion that at 34 volts, when the blue spectrum appears, the argon atom is doubly ionised. (At high

TABLE IV

The spectrum of oxygen in the negative glow and positive column of a discharge ube. Plate III = A 10%–O_2 90%. Plate IV = A 50%–O_2 50%.

Oxygen "series" spectrum	Plate				Oxygen "elementary" line spectrum	Plate			
Wave-length	III.		IV.		Wave-length	III.		IV.	
	N. g	P. c	N. g	P. c		N. g	P. c	N. g	P. c
1*S–mP*					4662	4	1		
4368 (2)	3	1	3	0	4609	3	0	3	0
3692 (3)	3	0			4590			3	0
1*s–mp*					4415	4	3		
3947 (2)	3	6	3	0	4369			3	0
1*p–ms*					4367	3	1		
4674 (7)	4	0			4345	3	4		
4588 (8)	3	0			4337	3	3	4	4
1*p–md*					4276	8	4		
4773 (6)	1	0			4156	2	3	4	5
4654 (7)	3	1	2	0	4154	2	0		
4233	6	0	3	0	4143	2	2		
2897	9	3	6	1	4122	2	0		
2895	9	3	6	1	4114	2	0		
2884	9	3	6	1	4070			3	0
2882	9	3	6	1	4060	4	7	3	0
2753			3	0	3998	4	7	5	6
2708			1	0	3962	3	0	4	0
2474	3	1			3952	3	0		
2446	4	3			3912	10	5	4	4
2420	3	0			3907	3	2		
2325	3	0			3896	3	2	0	3
2299	3	0			3883	3	2	5	0
					3805	7	9	7	8
					3755	7	9	6	7
					3712	4	7	5	6
					3390	2	0		
					3135	6	8	7	8

current densities, a 19 volt impact, doubtless with an ion, will produce the 34 volt blue spectrum; thus 15+19=34 volts.) In their experiments, Lowe and Rose,[15] were unable to produce any blue lines below 39 volts, and Barton,[11] by positive ray analysis found no double ions below 45 volts. Stark[16] classifies a number of lines of the blue spectrum as "bivalent" or "trivalent," and associates these with the formation of double or triple ions respectively. Horton and Davies[9] accept the formation of double ions at 34 volts, and in their 1922 paper give tables showing

[15]Lowe and Rose, Trans. R. S. C. **18,** 313 (1924).
[16]Stark, Ann. d. Physik. **42,** 241 (1913).

the electron energies (in volts) necessary to excite a number of blue lines, as well as the variation of intensity with voltage. Using these data, which appear reliable, we can form an estimate of electron energies in the negative glow. The occurrence, as well as the intensity, of the blue lines in this region (cf Table II) points to the presence of electrons having "velocities" of as high as 38 and 42 volts. A number of double argon ions are doubtless formed in this region. It is known that line intensity depends also upon other factors, such as current density and the presence of other gases. The strong excitation of the Balmer lines may result from 29.4 volt collisions which, according to Horton and Davies,[12] can dissociate the hydrogen molecule and ionise both atoms.

Plate II. Argon 50 percent—Hydrogen 50 percent. The argon spectra on this plate were distributed in exactly the same manner, and point to the same distribution of energy as in the last plate. True, the number of argon lines is somewhat less, but this may be accounted for by the smaller number of argon atoms present. Even though more hydrogen was present in this case, the Balmer lines are both fewer and weaker than in the preceding case. This may be accounted for in two ways: first, that the velocity of most electrons in the positive column was lower than in the previous case, or second, that the Balmer lines were enhanced in the previous case by the presence of a great excess of argon atoms. Indeed both causes may have co-existed. In the negative glow, the Balmer lines are as intense but no more so than in the first Plate.

Spectra taken of both sides of striae in this mixture show only this difference, that the lines are more intense on the cathode side, indicating an excess of excited atoms on this surface, as is to be expected. It was also found that the spectra of striae were more intense than of the uniform positive column in the same mixture.

Plate III. Argon 10 percent—Oxygen 90 percent. With regard to the argon spectrum, two facts are to be noted; First, that much fewer lines are present than in Plates I and II, and second, that the contrast between the lines in the two regions is less marked. The scarcity of lines is attributed to the small proportion of argon atoms present.

In this case, the pressure is low, the potential across the tube high and the current small. We should therefore expect higher electron energies in both regions. A number of blue lines is found in the positive column, which may arise from electron collisions with single ions. The "velocity" of a number of electrons is therefore at least 19 volts and perhaps as high as 34 volts. Radiation may also play an hitherto undetermined part. Not only are there many single argon ions formed in the positive column, but also some double ions.

In the negative glow however, the blue lines present are of such an intensity that they point to electronic velocities of over 42 volts, and it seems certain that double ions are formed by single electron impacts. Thus it seems that in this region also, the average electronic energy is rather greater than in cases I and II.

The oxygen "series" spectrum is strong in the negative glow, and less so in the positive column. The notation in Table IV is Fowler's. Two striking pairs of lines; 2897–5 and 2884–2 are found in the ultraviolet. The resonance and ionisation potentials are given by Foote and Mohler,[17] as 7.9 and 15.5 volts respectively, and further, the second and third ionisation potentials of 32 and 50 volts are given by Payne.[18] According to Fowler,[19] the series spectrum is due to the neutral oxygen atom, and this is excited by collision of 15.5 volts. To dissociate the molecule and ionise an atom requires, according to Hogness and Lunn,[20] a velocity of 20 volts.

Though the oxygen atom may be ionised by a 15.5 volt collision, the dissociation of the molecule by a 7.5 volt collision has not been observed. The greater excitation in the negative glow is attributed to the greater proportion of electrons having energies of 20 volts in that region.

The elementary spectrum is due, according to Fowler,[19] to ionised oxygen, and the calculated potential for excitation is 29.5 volts, which is in close accord to the value given by Payne.[18] This spectrum is more strongly developed in the negative glow, as is to be expected, and where it occurs in the positive column may be attributed to a cumulative process.

Plate IV. Argon 50 percent—Oxygen 50 percent. In this Plate the argon spectrum is naturally stronger than in Plate III. From the distribution of the red and blue spectra, it appears that the average electronic energy in the negative glow is about 38 volts, and that in the positive column the majority of electrons have energies of about 16 volts. The oxygen spectrum occurs in the same manner as before, but the number of lines is diminished by the smaller proportion of oxygen present. It is evident that until more has been done, co-relating the exciting potentials and the spectra emitted, it will be very difficult accurately to interpret all the data available.

In the discharge in hydrogen and helium, Keys and Home[1] found the Balmer lines more strongly developed in the striation than in the

[17]Foote and Mohler, Bull. Bur. Stand. **16,** 669 (1920).
[18]Miss Payne, "Stellar Atmospheres". Harvard (1925).
[19]Fowler, Proc. Roy. Soc. **110,** 476 (1926).
[20]Hogness and Lunn, Phys. Rev. **27,** 732 (1926).

negative glow, whereas the reverse appears in hydrogen and argon. This may be due to the fact that in argon and hydrogen the ionisation potential of argon is but slightly less than that of hydrogen, whereas that of helium is one and a half times as great. An electron having a velocity of a little over 15 volts would probably make an elastic collision with a helium atom, and could still ionise a hydrogen atom; but the same electron colliding with an argon atom would ionise the latter and lose its kinetic energy. Thus in Plates I and II the red argon spectrum was very intense and the hydrogen primary spectrum weak. A further number of mixtures must be tried under different conditions to form a basis for a general theory.

Observations on Striae

1. Striae were produced in every mixture tried, and in some cases remained steady for several hours.

2. As the pressure was gradually diminished, a critical value was reached at which a group of from three to ten striae suddenly disappeared from the negative end of the positive column. This group reappeared again several times, but if the pressure still diminished, finally vanished completely. The process was reversed by increasing the pressure. Every time such a group was dropped, the current fell to about one quarter of its original value.

3. Inclined striae occurred when the tube had not been used for several days, and these could be set in rapid rotation by a uniform magnetic field. *Spontaneous rotation of striae,* due presumably to the earth's field, was noticed in helium and oxygen. The rotation of a column is a periodic phenomenon, and must be connected with a periodic cause. The current, even when a direct source was used, has been found to be periodically intermittent in the discharge, as proved by the rotating mirror, the telephone receiver and the cathode-ray oscillograph, and this must be considered in any explanation of the rotation. The inclination of striae is attributed to initial unequal charges on the walls of the tube which may deviate the streams of ions in the discharge. The inclination disappears in about half an hour, doubtless when the wall charges have become equalized by the ions.

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