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On the Spectra of Argon

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VII. *On the Spectra of Argon.*

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[PLATE 3.]

THROUGH the kindness of Lord RAYLEIGH and Professor RAMSAY I have been enabled to examine the spectrum of this gas in a very accurate spectroscope, and also to take photographs of its spectra in a spectrograph fitted with a complete quartz train. The results are both interesting and important, and entirely corroborate the conclusions arrived at by the discoverers of argon.

The results of my examination are given in a table of wave-lengths, which follows, and on a map of the lines accurately drawn to scale, accompanying this paper (Plate 3). The map is 40 feet long, and the probable error of position of any line on it is not greater than 1 millimetre.

Argon resembles nitrogen in that it gives two distinct spectra according to the strength of the induction current employed. But while the two spectra of nitrogen are different in character, one showing fluted bands and the other sharp lines, both the argon spectra consist of sharp lines. It is, however, very difficult to get argon so free from nitrogen that it will not show the nitrogen flutings superposed on its own special system of lines. I have used argon prepared by Lord RAYLEIGH, Professor RAMSAY, and myself, and, however free it was supposed to be from nitrogen, I could always at first detect the nitrogen bands in its spectrum. These, however, disappear when the induction spark is passed through the tube for some time, varying from a few minutes to a few hours. The vacuum tubes best adapted for showing the spectra are of the ordinary Plücker form having a capillary tube in the middle. For photographing the higher rays which are cut off by glass I have used a similar tube, "end on," having a quartz window at one end. I have also used a Plücker tube made entirely of quartz worked before the oxy-hydrogen blow-pipe. I have not yet succeeded in melting platinum or iridio-platinum wire terminals into the quartz, as they melt too easily, but a very good spectrum is obtained by coating the bulbs outside with tin foil, connected with the terminals of the induction coil.

The pressure of argon giving the greatest luminosity and most brilliant spectrum is 3 millims. At this point the colour of the discharge is an orange-red, and the spectrum is rich in red rays, two being especially prominent at wave-lengths 696·56 and 705·64. On passing the current the traces of nitrogen bands disappear, and the argon spectrum is seen in a state of purity. At this pressure the platinum from the poles spatters over the glass of the bulbs, owing to what I have called "electrical evaporation,"* and I think the residual nitrogen is occluded by the finely-divided metal. Similar occlusions are frequently noticed by those who work much with vacuum-tubes.

If the pressure is further reduced, and a Leyden jar intercalated in the circuit, the colour of the luminous discharge changes from red to a rich steel blue, and the spectrum shows an almost entirely different set of lines. The two spectra, called for brevity red and blue, are shown on the large map, the upper spectrum being that of "blue" argon, and the lower one that of "red" argon. It is not easy to obtain the blue colour and spectrum entirely free from the red. The red is easily got by using a large coil† actuated with a current of 3 ampères and 6 volts. There is then no tendency for it to turn blue. The blue colour may be obtained with the same coil by actuating it with a current of 3·84 ampères and 11 volts, intercalating a jar of 50 square inches surface; the make-and-break must be screwed up so as to vibrate as rapidly as possible. With the small coil a very good blue colour can be obtained by using three GROVE's cells and a Leyden jar of 120 square inches surface, and a very rapid make-and-break. It appears that an electromotive force of 27,600 volts is required to bring out the red, and a higher E.M.F. and a very hot spark for the blue. It is possible so to adjust the pressure of gas in the tube that a very slight alteration of the strength of the current will cause the colour to change from red to blue, and *vice versâ*. I have occasionally had an argon tube in so sensitive a state, that with the commutator turned one way the colour was red, and the other way blue. Induction coils actuated by a continuous current are never symmetrical as regards the polarity of the induced current, and any little irregularity in the metallic terminals of the vacuum-tube also acts as a valve. The red glow is produced by the positive spark and the blue by the negative spark.

I have taken photographs of the two spectra of argon partly superposed. In this way their dissimilarity is readily seen.‡ In the spectrum of the blue glow I have counted 119 lines, and in that of the red glow 80 lines, making 199 in all. Of these 26 appear to be common to both spectra.

I have said that the residual nitrogen is removed by sparking the tube for some time when platinum terminals are sealed in. This is not the only way of purifying the argon. By the kindness of Professor RAMSAY, I was allowed to take some vacuum tubes to his laboratory and there exhaust and fill them with some of his purest argon. On this occasion I simultaneously filled, exhausted, and sealed off two Plücker tubes, one having platinum and the other aluminium terminals. On testing the gas immediately after they were sealed off, each tube showed the argon spectrum, con-

* 'Roy. Soc. Proc.,' vol. 50, p. 88, June, 1891.

† The coil used has about 60 miles of secondary wire, and when fully charged gives a torrent of sparks 24 inches long. The smaller coil gives six-inch sparks when worked with six half-pint GROVE's cells.

‡ Photographs of the different spectra of argon, and other gaseous spectra for comparison, were projected on the screen.

taminated by a trace of nitrogen bands. The next day the tube with platinum terminals was unchanged, but that having aluminium terminals showed the pure spectrum of argon, the faint nitrogen bands having entirely disappeared during the night. After an hour's current and a few days' rest the tube with platinum terminals likewise gave a pure argon spectrum. When a mixture of argon with a very little nitrogen is submitted to the induced current in a tube made of fused and blown quartz, without inside metallic terminals, the nitrogen bands do not disappear from the argon spectrum, but the spectra of argon and nitrogen continue to be seen simultaneously.

A vacuum-tube was filled with argon and kept on the pump while observations were made on the spectrum of the gas as exhaustion proceeded. The large coil was used with a current of 8·84 ampères and 11 volts, no jar being interposed. At a pressure of 3 millims. the spectrum was that of the pure red glow. This persisted as the exhaustion rose, until, at a pressure of about half a millimetre, flashes of blue light made their appearance. At a quarter of a millimetre the colour of the ignited gas was pure blue, and the spectrum showed no trace of the red glow.

A striking instance of a change of spectrum from nitrogen to argon was shown in a tube filled with argon kindly sent me by Lord RAYLEIGH. It had been prepared from the atmosphere by sparking, and it was considered to contain about 3 per cent. of nitrogen. This argon was passed into an exhausted tube and then rarefied to a pressure of 75 millims. and kept on the pump. At this pressure the nitrogen conducted all the induction current, the spectrum showing nothing but the nitrogen bands. The pump was slowly kept going and spectrum observations were continuously taken. When the pressure fell to about 3 millims. a change came over the spectrum, the nitrogen bands disappeared, and the spectrum of argon took its place, the only contamination being a little aqueous vapour, due to my not having sufficiently dried the gas. I took photographs of the spectrum given by this tube in the two stages, one showing the pure nitrogen bands and the other the argon lines, each being compared with the spectrum of argon prepared by Professor RAMSAY. Observations have shown that the spectra given by argon, obtained by the sparking method of Lord RAYLEIGH and by the magnesium method of Professor RAMSAY from the atmosphere, are identical.

It was of interest to see how little argon could be detected in admixture with nitrogen by combined pumping and passage of the current. Some argon prepared by myself,* having 60 to 70 per cent. of nitrogen with it, was put into a small tube furnished with large platinum terminals. Exhaustion was carried to 3 millims., and

* When a current of 65 volts and 15 ampères, alternating 130 times a second, is passed through the primary of my large coil, an arching flame, consisting of burning nitrogen, issues from each of the secondary poles, meeting in the middle. When once started, the poles can be drawn asunder till the flame bridges across 212 millims. When the terminals are more than 46 millims. apart, the flame will not strike across. By enclosing this flame in a reservoir over alkaline water and feeding it with air and oxygen I can burn up a litre of air an hour.

the tube was then sealed off. The spark from the large coil, actuated with a current of 3·84 ampères and 11 volts, was then put on, and the spectrum examined continuously. At first it showed only the nitrogen bands; in about half an hour the nitrogen began to fade and the argon lines appeared, and in a few minutes later the tube was just short of non-conducting. The colour of the gas was rich steel blue, and the spectrum was that of the blue argon glow. Here the small diameter of the bulbs of the tube and the large platinum wires facilitated much spattering or "electrical evaporation" of the platinum; the pressure also was the one most suitable for that phenomenon. To this I attribute the rapid occlusion of the residual nitrogen.

An experiment was now made to see if the small quantity of argon normally present in the atmosphere could be detected without previous concentration. Nitrogen was prepared from the atmosphere by burning phosphorus, and was purified in the usual manner. This gas, well dried over phosphoric anhydride, was passed into a vacuum tube, the air washed out by two fillings and exhaustions, and the tube was finally sealed off at a pressure of 52 millims. It was used for photographing the band spectrum of nitrogen on several occasions, and altogether it was exposed to the induction current from the large coil for eight hours before any change was noticed. The last time I used it for photographing the nitrogen spectrum difficulty was experienced in getting the spark to pass, so I increased the current and intercalated a small jar. The colour immediately changed from the reddish-yellow of nitrogen to the blue of argon, and on applying the spectroscope the lines of argon shone out with scarcely any admixture of nitrogen bands. With great difficulty, and by employing a very small jar, I was able to take one photograph of this changed spectrum and compare it with the spectrum of argon from Professor RAMSAY, both being taken on the same plate, but the tube soon became non-conducting, and I could not then force a spark through except by employing a dangerously large current. Whenever a flash passed it was of a deep blue colour. Assuming that the atmosphere contains 1 per cent. of argon, the 3 millims. of nitrogen originally in the tube would contain 0·03 millim. of argon. After the nitrogen had been occluded by the spattered platinum this pressure of argon would be near the point of non-conduction.

In all cases, when argon has been obtained in this manner, the spectrum has been that of the blue-glowing gas. Very little of the red rays can be seen. The change from red to blue is chiefly dependent on the strength and heat of the spark; partly also on the degree of exhaustion. Nitrogen, when present, conducts the current easiest. As the exhaustion increases and the conductivity of the nitrogen diminishes, that of the red-glowing argon rises, until, at a pressure of about 3 millims., its conductivity is at the greatest, and the luminosity is best. Beyond that point the conductivity of the red form seems to get less, and that of the blue form to increase, till the vacuum approaches a fraction of a millimetre, when further pumping soon renders it non-conducting. It is not improbable, and I understand that independent observations have already led both the discoverers to the same conclusion, that the gas argon is not a simple body, but is a mixture of at least two elements, one of which glows red and the other blue, each having its distinctive spectrum. The theory that it is a simple body has, however, support from the analogy of other gases. Thus, nitrogen has two distinct spectra, one or the other being produced by varying the pressure and intensity of the spark. I have made vacuum tubes containing rarefied nitrogen, which show either the fluted band or the sharp line spectrum by simply turning the screw of the make-and-break, exactly as the two spectra of argon can be changed from one to the other.

The disappearance of the red glow and the appearance of the blue glow in argon as the exhaustion increases also resembles the disappearance of the red line of hydrogen when exhaustion is raised to a high point. PLÜCKER, who was the first to observe this occurrence, says:* "When RUHMKORFF's small induction coil was discharged through a spectral tube enclosing hydrogen, which was gradually rarefied to the highest tenuity to be reached by means of GEISSLER's exhauster, finally the beautiful red colour of the ignited gas became fainter, and passed gradually into an undetermined violet. When analysed by the prism, Hα (the red, C, line) disappeared, while Hβ (the green, F, line), though fainter, remained well defined. Accordingly, light of a greater length of wave was the first extinguished."

The line spectrum of nitrogen is not nearly so striking in brilliancy, number, or sharpness of lines as are those of argon, and careful scrutiny fails to show more than one or two apparent coincidences between lines in the two spectra. Between the spectra of argon and the band spectrum of nitrogen there are two or three close approximations of lines, but a projection on the screen of a magnified image of the two spectra partly superposed shows that two at least of these are not real coincidences.

I have looked for indications of lines in the argon spectra corresponding to the corona line at 531·7, the aurora line at 557·1, and the helium line at 587·5, but have failed to detect any line of argon sufficiently near these positions to fall within the limits of experimental error.

I have found no other spectrum-giving gas or vapour yield spectra at all like those of argon, and the apparent coincidences in some of the lines, which on one or two occasions are noticed, have been very few, and would probably disappear on using a higher dispersion. Having once obtained a tube of argon giving the pure spectra, I can make no alteration in it, except that which takes place on varying the spark or increasing the exhaustion, when the two spectra change from one to the other. As far, therefore, as spectrum work can decide, the verdict must be that Lord RAYLEIGH and Professor RAMSAY have added one, if not two, members to the family of elementary bodies.

* "On the Spectra of Ignited Gases and Vapours." By Drs. PLÜCKER and HITTORF, 'Phil. Trans.,' Part I., vol. 155, p. 21.

WILLIAM CROOKES. January 24, 1895.

THE Two Spectra of Argon.

Blue.		Red.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
		764·6	2	
		750·6	4	
		737·7	3	
		726·3	2	
		705·64	10	
		696·56	9	
		684·2	2	
		675·4	6	
		666·4	6	
662·8	4			
		640·7	9	
		637·7	2	
		630·2	4	
		628·1	2	
623·2	4			
		621·0	6	
617·3	6	617·3	6	Coincident.
		614·3	2	
612·0	6			
		609·9	4	
		605·6	2	
		604·5	3	
603·8	8	603·8	8	Coincident.
		593·5	1	
592·6	4	592·6	4	Coincident.
		590·9	6	
		588·7	6	
		585·8	4	
		583·4	2	
		580·3	1	
		577·1	2	
		574·6	6	
		568·3	2	
		565·1	9	
		561·0	9	
		556·7	2	
		555·7	10	
		552·0	1	
		550·1	2	
		549·65	8	
		545·6	6	
		544·4	2	
		542·1	4	
		525·8	6	
		522·2	7	
		518·58	10	
		516·5	9	

THE Two Spectra of Argon—(continued).

Blue.		Red.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
514·0	10			
506·5	10	506·5	4	Coincident.
501·2	2	501·2	4	Coincident.
500·7	9			
496·55	9	496·55	4	Coincident.
493·8	10	493·8	2	Coincident.
487·9	10	487·9	4	Coincident.
484·75	1			
480·50	7			
476·30	1			
473·45	6			
472·66	2			
		470·12	8	
465·65	5			
		462·95	5	
460·80	8			
		459·45	2	
458·69	6			
457·95	6			
454·35	7			
		451·40	2	
450·95	8	450·95	9	Coincident.
447·83	6			
442·65	10			
442·25	10			
439·95	10			
437·65	9			
436·90	9			
434·85	10			
		434·50	5	
433·35	9	433·35	9	Coincident.
		430·05	9	
429·90	9			
427·70	3			
427·20	7	427·20	8	Coincident.
426·60	6	426·60	4	Coincident.
425·95	8	425·95	9	Coincident.
425·15	2	425·15	3	Coincident.
422·85	6			
420·10	10	420·10	10	Coincident.
419·80	9	419·80	9	Coincident.
419·15	9	419·15	9	Coincident.
418·30	8	418·30	8	Coincident.
416·45	8	416·45	4	Coincident.
415·95	10	415·95	10	Coincident.
		415·65	6	
413·15	3			
410·50	8			
407·25	8			
404·40	8	404·40	9	Coincident.
403·30	1			
401·30	8			
397·85	1			
396·78	3			

THE Two Spectra of Argon—(continued).

Blue.		Red.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
394·85	9	394·85	10	Coincident.
394·35	3			
393·18	3			
392·85	9			
392·75	3			
391·50	1			
		390·45	8	
389·20	5			
387·55	2			
387·18	2			
386·85	8			
385·15	10			
384·55	1			
383·55	2	383·55	3	Coincident.
382·75	2			
380·95	4			
380·35	1			
379·95	1			
378·08	9			
		377·15	1	
377·05	2			
376·60	8			
373·85	3			
372·98	10			
371·80	4			
		363·25	2	
363·17	1			
		362·37	1	
		362·28	1	
361·75	2			
360·50	3	360·50	5	Coincident.
358·70	10			
358·03	9			
357·50	9			
356·65	2	356·65	4	Coincident.
356·40	2			
		356·28	1	
356·00	2			
355·82	7			
355·45	4	355·45	6	Coincident.
354·75	4			
354·45	7			
353·43	4			
352·05	3			
351·92	4			
351·35	6			
350·88	4			
349·00	10			
347·57	7			
345·35	1			
338·80	1			
309·27	5			
308·48	4			
306·47	2			

THE Two Spectra of Argon—(continued).

Blue.		Red.		
Wave-length.	Intensity.	Wave-length.	Intensity.	
304·27	3			
299·82	1			
297·86	1			
294·27	2			
292·96	1			
283·02	1			
279·44	2			
273·45	2			
270·72	0·5			
269·30	1			
266·12	2			
265·26	3			
262·95	1			
257·12	2			
256·07	1			
248·49	1			
243·85	2			
224·66	3			

119 lines in the "Blue" Spectrum.
80 lines in the "Red" Spectrum.

199 total lines.
26 lines common to the two spectra.

NOTE.—In the spectroscope the lines of argon appear almost equally fine, but of very different intensities. This difference of brightness is represented in the accompanying map by a variation in the thickness of the lines, faint lines being made narrow and strongly luminous lines being widened. In some cases two or three strong lines are too close together to enable their intensities to be represented in this way without overlapping. This is the case with lines 442·65 and 442·25, with lines 420·10, 419·80, and 419·15, and with lines 415·95 and 415·65. In these cases I have indicated the centres of the strong lines by short projecting lines beneath.

THE SPECTRA OF ARGON.