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THE EFFECT ON WAVELENGTH IN ARC SPECTRA OF INTRODUCING VARIOUS SUBSTANCES INTO THE ARC.

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It has been shown by Fabry and Buisson[1] and in Kodaikanal Observatory Bulletins[2] that spectrum lines which are unsymmetrical in width in the electric arc undergo abnormal displacements in the sun when compared with the displacements of symmetrical lines. It has also been shown in Kodaikanal Observatory Bulletins[3] and by others that unsymmetrical lines are displaced under varying conditions in the electric arc, a typical instance being the displacement near the poles of the arc which has commonly been called the "pole effect." Reasons were given in the Kodaikanal Observatory Bulletins referred to for ascribing these displacements of unsymmetrical lines to varying conditions of vapour density although it was stated[4] that for the phrase "density of vapour" that of "density of ions" might have to be substituted. Experiments have now been made and are described in this paper with a view to deciding whether varying density of vapour or of ions is the real cause of displacement of unsymmetrical lines.

2. The method of experiment has been to introduce various substances in turn into the arc giving the spectrum under investigation. It is to be expected that if into a copper arc, for instance, is introduced a substance which is more easily ionised than copper, the density of ions will be increased, whilst the density of copper vapour will probably be reduced (though not necessarily so if the atoms of copper are vaporised in the arc in clusters[5]). The comparative ease of ionisation is, unfortunately, known for only a few substances which are suitable for use in the electric arc. More unfortunately still for our present purpose, the electric arc is a complicated phenomenon whose features are not completely understood ; for instance, the arc voltage is known to vary with the nature of the materials forming the arc but its effect on ionisation is not known ; and again the energy necessary to volatilise different substances from electrodes will influence the energy available for ionisation. Possibly even the temperature of the arc varies with the materials of the electrode which would at once influence the ionisation. So that even if we know that substance A is more easily ionised than substance B, we cannot definitely say whether introducing A into the arc between electrodes of B will increase or decrease the ionisation in the arc. It is, however, practically certain that except by a coincidence of circumstances, the ionisation will be changed, and by trying a variety of substances some may be found to increase the ionisation although perhaps others will decrease it. The method of experiment has therefore been to take various substances which were available and to determine whether introducing them in turn into an arc giving spectrum lines which seemed favourable for study caused any displacement of these lines. The method is consequently not very systematic, and the experiments can only be regarded as

[1] Fabry and Buisson, Astrophysical Journal, 31. 97. 1910.
[2] Kodaikanal Observatory Bulletins, Nos. 38, 53.
[3] " " " Nos. 40, 53
[4] " " " No. 40, page 90.
[5] Royds, Astrophysical Journal, 45. 112. 1917 and Kodaikanal Observatory Bulletin, No. 54, page 195.

explorative, but the displacements were found to be so large as to make it desirable to publish these preliminary experiments before attempting a more systematic investigation.

3. The copper arc was first chosen for study as the lines λλ 4531, 4509, 4480 have been found to be fairly sharp lines requiring short exposures whilst the first and last are sensitive to displacement at the poles of the arc. These three lines are all widened more towards the red than towards the violet, and their displacements at the negative pole of an arc between copper electrodes are + 0·032 A, + 0·014 A, + 0·028 A, respectively. On account of its greater steadiness of burning, the arc for these experiments was between a lower positive electrode of copper and an upper negative electrode of carbon. The arc was always used with a bead of copper on the copper pole. Two electrodes of copper and two of carbon were prepared; one of each was kept uncontaminated from other substances and used to give the comparison spectrum as against the spectrum from the other pair to the copper bead of which had been added the substance whose effect was to be tested. The spectrograph has been described previously[1], the dispersion in this region being about 1·33 mm. to the angstrom.

4. As the effect was found to be greatest when the arc was very short, the results for the arc of length between 1 and 2 millimeters will be given first. The length of the arc was controlled by the length of its image, magnified 3·2 times on the slit plate, care being taken that the arc did not burn into a crater in the carbon or run down the side of the copper bead so as to avoid any false estimate of the true length of the arc. The first half of the exposure of the comparison spectrum was made before and the second half after the spectrum of the arc with substance added. The spectra to be compared were arranged in adjacent strips by means of an occulting shutter which could be moved in front of the slit between the exposures. The current through the arc was about 6 amperes in all the experiments and was kept constant in any experiment to within ¼ ampere. The effects of the following substances were tried :—

(*a*) A small quantity of metallic sodium somewhat smaller than the size of the copper bead on the electrode was added to the copper bead. On striking the arc the sodium burns up into a flame so that it is uncertain how much sodium is left when the arc is brought on to the slit a few moments later, but the arc burns very steadily with the bright yellow light of sodium. The exposure was about 3 minutes compared with 7 seconds without sodium.

(*b*) Iron and aluminium were added to new copper beads in turn. The amount of iron was estimated to be about three times that of the copper, but the exposure required was only half of that when the bead was pure copper.

(*c*) The following salts were added to new copper beads in turn : calcium chloride requiring 2 seconds exposure, sodium carbonate requiring 1 minute, and potassium carbonate requiring 2 minutes.

(*d*) As pure nickel and pure silver were not available, the effect of these metals was tested by comparing copper alloys of these metals with pure copper. These alloys were ready to hand in Indian nickel and silver coins, requiring 2 seconds and 1½ minutes exposures, respectively.

(*e*) A small quantity of soda glass was melted on to a copper bead and required 1 second exposure only.

The effects of these substances on the wavelengths of the three copper lines studied are given in the following table. The number of photographs on which each value is based is given in brackets.

TABLE I.—MEAN DISPLACEMENTS OF COPPER LINES CAUSED BY INTRODUCING DIFFERENT SUBSTANCES INTO THE ARC.

	Na.	Calcium chloride.	Glass.	Sodium carbonate.	Fe.
4531	+ 0·049A (10)	+ 0·035A (4)	+ 0·032A (3)	+ 0·025A (6)	+ 0·016A (5)
4509	+ 0·018A (3)	+ 0·012A (6)	+ 0·010A (3)	+ 0·006A (6)	+ 0·004A (3)
4480				+ 0·022A (6)	

[1] Evershed, Kodaikanal Observatory Bulletin, No. 36.

	Ag.	Al.	Ni.	Potass. carbonate.
4531	+ 0·015A (5)	+ 0·014A (3)	+ 0·009A (8)	+ 0·006A (6)
4509	+ 0·009A (5)	+ 0·004A (3)	+ 0·002A (8)	+ 0·002A (6)
4480				+ 0·005A (6)

It is not to be expected that very consistent values will be obtained in each experiment owing to the impossibility of introducing exactly the same amount of material in different experiments and owing to the fact that the arc was very short. Table II has therefore been given to show the actual displacements observed in each experiment for the line λ 4531 :

TABLE II.—DISPLACEMENTS OF THE CU LINE 4531 IN EACH INDIVIDUAL EXPERIMENT.

Experiment No.	Na.	Calcium chloride.	Glass.	Sodium carbonate.	Fe.	Ag.
1	+ 0·040A	+ 0·043A	+ 0·025A	+ 0·005A	+ 0·016A	+ 0·017A
2	+ 0·021	+ 0·031	+ 0·041	+ 0·015	+ 0·017	+ 0·011
3	+ 0·096	+ 0·025	+ 0·030	+ 0·032		+ 0·020
4	+ 0·101	+ 0·040		+ 0·026		+ 0·014
5	+ 0·043			+ 0·037		+ 0·013
6	+ 0·055			+ 0·033		
7	+ 0·062					
8	+ 0·042					
9	+ 0·005					
10	+ 0·022					
Mean	+ 0·049	+ 0·035	+ 0·032	+ 0·025	+ 0·016	+ 0·015

Experiment No.	Al.	Ni.	Potass. carbonate.
1	+0·011A	+0·014A	−0·004A
2	+0·016	+0·007	+0·008
3	+0·015	+0·011	+0·023
4		+0·006	−0·006
5		+0·024	+0·009
6		−0·001	+0·003
7		+0·010	
8		0·000	
Mean	+0·014	+0·009	+0·006

It seems surprising that the addition of certain substances should reduce the exposure required for the copper lines. If it be argued that the short exposure is a consequence of increased vapour density, vapour density cannot be the controlling factor since the addition of soda glass which shortens the exposure to 1 second has an effect of the same sign as the addition of metallic Na, which lengthens the exposure to 3 minutes.

5. The following evidence is given as proof that the displacements observed are real and correctly interpreted as due to the addition of substances into the arc :—

(*a*) By the practice of giving half the exposure of the comparison spectrum before and after the spectrum under test the presence of spurious displacements such as those caused by temperature changes during the experiment would have been detected. Moreover, it is unlikely that temperature changes during the short exposures required could be appreciable. The absence of displacements of this kind is, however, proved by the fact that the displacements vary from line to line, depending only on the unsymmetrical character of the lines, and as will be seen later, symmetrical lines have zero displacement.

(*b*) Apparent displacements of unsymmetrically widened lines can be produced by overexposing one of the two spectra under comparison the displacement being in the direction of the greater widening. These apparent displacements can only be avoided by giving a minimum exposure to each spectrum so that the exact position of greatest density in the spectrum line is not obliterated by overexposure. In these experiments the best exposure was tried out before photographs for measurement were taken, and no plates were measured in which there was a danger of error through overexposure.

(*c*) The displacements are really due to the introduction of another substance into the arc and not to any other previously known cause. It was previously known that these three copper lines λλ 4531, 4509, 4480, will be displaced towards the red (1) at the poles of the arc, (2) with increased current and (3) with decreased length of the arc. Many of the displacements observed are much greater than any possible displacement due to such causes. Firstly, the displacement of the line λ4531 at the negative pole of the very short arc (1 to 2 mm.) between Cu positive and C negative is only + 0·001A, at the positive pole +0·002A : secondly, the current can easily be kept constant to within $\frac{1}{4}$ ampere ; and thirdly although there may be some difficulty in maintaining very short arcs absolutely ~~constant in length, the~~ variations in length in any experiment was many times less than the change from $1\frac{3}{4}$ mm. to 4 mm. which caused a displacement of 4531 of + 0·012A : the displacement due to any variations in length of arc during any experiment must therefore have been considerably less than this.

(*d*) Control experiments were also made to verify the reality of the displacements and to test the effect of any probable variations in the arc conditions. The exact procedure adopted in testing the effect of any substance was followed except that no substance was introduced. The measured displacement in the control experiments never exceeded 0·003A, the mean being + 0·001A.

6. It is seen from Table I that the displacement of the more unsymmetrical lines 4531, 4480 is greater than that of the less unsymmetrical line 4509. There are no symmetrical copper lines in the same region of the spectrum to test whether they would be displaced or not. The symmetrical lines of iron in this region were therefore used for the test. A bead composed of a mixture of copper and iron on the positive pole gave the lines of both metals simultaneously and its spectrum was compared with that using a similar bead into which metallic sodium had been added. The copper lines, presumably already displaced by the presence of iron as shown in Table I, were further displaced by adding sodium by + 0·069 A, + 0·013A, +0·055A (mean of 2 photographs) for the lines 4531, 4509 and 4480, respectively, whilst the mean displacement of the 3 symmetrical iron lines 4528, 4494, 4466 was + 0·0003A.

7. The effect of introducing substances into the long arc is very much smaller, even at the poles, than the effect in the short arc. When metallic sodium is added to the copper bead on the positive pole, the length of the arc being 10 mm., the displacement was only + 0·004A (mean of 4 determinations) when comparing the region near the positive pole in each arc. The case of the displacement at the centre of the long arc due to the introduction of substances is of great practical importance because many wavelength determinations in the past have been made from the centre of the long arc without, in many cases, account being taken of the presence of other substances in the arc. The displacement at the centre of an arc 10 mm. long when glass was melted into the copper bead was + 0·001A, the mean of 5 determinations, which although too few to establish the reality of so small a displacement, suffice to show the order of magnitude for this line. It is clear that the effect is small unless a spectrum line is more sensitive than the copper line 4531.

8. We may thus summarize the results for the copper lines. Under suitable conditions the unsymmetrical lines of copper may undergo large displacements in the direction of their greater widening as a result of introducing other substances into the arc. If the view that the displacements are due to a change in ionisation in the arc as a result of introducing substances into the arc is correct, it follows that all the substances, chosen more or less at random, whose effect on copper was tried, increased the ionisation in the arc.

9. Experiments with copper lines having given positive results, similar experiments were tried with the ca cium triplet λλ 4586, 4581, 4578, which, although widened more unsymmetrically towards the red than the

copperr lines first chosen, are less easy to measure accurately. The calcium comparison spectrum was produced by an arc between a commercial flame arc carbon as positive pole, and a plain ordinary carbon as negative. It was considered that this would give more constant conditions than would be possible by introducing a calcium salt into a carbon arc. The tests for the effect of other substances were carried out with an exactly similar pair of carbons, the substances being placed into the crater of the flame carbon. When the arc is very short the edge of this crater prevents any light from reaching the spectrograph. A longer arc was therefore used than in the case of the copper arc, and these experiments were carried out with an arc 4 mm. in length, the current strength being 3 amperes. The results for calcium are not as consistent as one would like, but this is attributed mainly to inconstancy of the arc conditions owing to the wandering of the arc over the positive pole in which were situated irregularly globules of calcium material and of the substance introduced. Table III shows the mean displacements for the different lines of the triplet and Table IV shows individual values for the line 4586.

TABLE III.—MEAN DISPLACEMENTS OF CALCIUM LINES CAUSED BY INTRODUCING DIFFERENT SUBSTANCES INTO THE ARC.

—	Cu.	Glass.	Fe.	Silver coin.	Nickel coin.
4586	+0·002A (7)	−0·002A (6)	−0·005A (3)	−0·012A (5)	−0·020A (5)
4581	+0 002A (5)	0·000A 6)	−0·006A (3)	−0·012A (5)	−0·022A (5)
4578	+0 002A (1	−0·002A (5)	−0·005A (2)	−0·014A (5)	−0·020A (5)

TABLE IV.—DISPLACEMENTS OF THE CA LINE 4586 IN EACH INDIVIDUAL EXPERIMENT.

Experiment number.	Cu.	Glass.	Fe.	Silver coin	Nickel coin.
1	+0 005A	+0·017A	−0·007A	−0·008A	−0·006A
2	−0·005	−0·011	−0 003	−0·017	−0·036
3	−0 001	−0·009	−0·004	−0·014	−0 028
4	+0 001	0·000	..	−0·011	−0 012
5	−0·001	−0·005	...	−0 012	−0·019
6	+0·009	−0·007	...	...	...
Mean.	+0·002A	−0·002A	−0·005A	−0·012A	−0·020A

The following observations were also made, although not in very good agreement with those in Table III ;—taking the arc with copper added as standard, replacing the copper by iron caused displacements of — 0·016A. — 0·016A. — 0·014A for the 3 lines of the Ca triplet, and replacing the copper by nickel coin caused displacements of — 0·009A, — 0·008A, — 0·010A.

Using a flame arc carbon as negative pole and taking the arc with a positive pole of copper as standard, making the positive pole iron caused displacements of — 0·008A, — 0·008A, — 0·010A for the 3 lines of the Ca triplet.

10. The displacements of the calcium triplet being principally negative, they are not by themselves conclusive as to whether the displacements are due to a reduction of vapour density or to other causes such as a reduction of ionisation in the arc. The displacements of the copper lines being positive, can, however, be definitely said not to be due to an increase in the vapour density, and are attributed in this paper, largely on account of the rational explanation which will be developed §§ 11–13, to an increase in the ionisation in the arc.

11. Stark[1] has suggested that the widening of the spectrum lines emitted by a radiating atom is caused by the electrical field exerted by surrounding atoms. He has shown that in general a spectrum line emitted

[1] Stark, quoted by Fulcher, Astrophysical Journal, 41, 359, 1915.

by a gas in an electrical field of definite value is split up into a number of components. Since a radiating gas will be partially ionised, each radiating atom will find itself in an electric field which will not have the same value for all atoms, and the average effect will be a broadening of the spectrum lines. Stark has pointed out that spectrum lines broaden symmetrically or unsymmetrically according as whether the resolution in an electrical field is symmetrical or unsymmetrical. It is obvious that the displacements of unsymmetrical lines under different conditions of the electric arc as described in this and previous Bulletins and by others, as well as their abnormal displacements in the sun can also be interpreted by their unsymmetrical resolution in an electric field. The evidence which has been given by Takamine[1] also confirms the intimate relation between the Stark effect in electric fields and the displacements of unsymmetrical lines near the poles of the arc. There can now be no doubt that the displacements and broadening of unsymmetrical lines find a ready explanation as an effect of an electric field.

12. A further confirmation of this is furnished by the change in the character of lines of certain spectrum series. It was shown[2] that in the first subordinate series of barium the second members are unsymmetrically widened towards the red, whilst succeeding members are unsymmetrical towards the violet, but the Stark effect for this metal is not available. For copper and silver, however, Takamine[3] has shown that the direction of displacement in an electric field is not the same for the different members of the subordinate series. It is found that the unsymmetrical character and pole effect correspond closely with the behaviour in an electric field, as is seen from Table V, where v denotes towards the violet and r towards the red. The correspondence is not exact; e.g., the copper pair 3861, 3825 are not definitely unsymmetrical in the arc and their negative pole displacement seems to be slightly to the red (+ 0·003A) although they are difficult to measure; certain it is, however, that they are less unsymmetrical towards the red and less displaced than the pair 4531, 4480, whereas in the general run of series they would be more unsymmetrical and more displaced.

TABLE V.—RELATION OF THE UNSYMMETRICAL CHARACTER AND POLE EFFECT OF CERTAIN SERIES LINES TO THEIR BEHAVIOUR IN AN ELECTRIC FIELD.

Series.	Line.	Displacement in electric field.	Unsymmetrical character.	Displacement at negative pole of arc.
Cu I N.S.	5220	v	v	......
	5218	v	v	......
	5153	v	v	......
	4063	r	r	r
	4062	r	r	r
	4022	r	r	r
	3688*	r	r	r
	3654	r	r	r
Cu II N.S.	4531	r	r	r
	4480	r	r	r
	3861	v	doubtful	r?
	3825	v	doubtful	r?
Ag I N.S.	5471	......	v	......
	5465	......	v	......
	5209	......	v	......
	4212	r	r	r
	4210	v	v	v
	4055†	r (v)	r (v)	r (v)
	3810‡	v	v	v
	3682	v	v	v

1 Takamine, Astrophysical Journal, 50, 53, 1919.
2 Royds, Astrophysical Journal, 41, 154, 1915 and K.O. Bulletin No. 43.
3 Takamine, l.c.

* The Cu line 3688 has a faint companion in the arc in air, apparently corresponding to the 4063 line
† The Ag line 4055 requires investigation; it is probably a double line. See paragraph 13.
‡ The Ag line 3810 has a faint companion apparently corresponding to the 4212 line. According to Takamine the separation is 0·86A.

13. We have evidence that electric fields are operating in the electric arc from the fact that lines which are faint or absent in the discharge in vacuo and appear strong only in an electric field are present in the spectrum of the arc in air. This has not been very thoroughly tested here, but it has been found that Ni lines given by Takamine, though not appearing in the published arc spectra of Ni, such as the line 4037·7, are actually present in the arc spectrum. The best instance appears to be a silver line near 4055. Kayser and Runge give two silver lines 4211 and 4055 as reversed in the arc. Liveing and Dewar, and also Eder and Valenta[1] have shown that 4211 is not a reversed line but two separate unreversed lines, which is apparently confirmed by the arc in vacuo. The same tests on the arc in air which show 4211 to be two lines will show that 4055 is also two unreversed lines, the more refrangible of which is unsymmetrical towards the red and the less refrangible unsymmetrical towards the violet: indeed, they are very similar to the 4211 pair, but closer together.[2] The reason why the published spectra of the arc in vacuo give only a single line at 4055 becomes clear from the photographs of Takamine in which it is seen that the less refrangible line only appears in an electric field. It should be pointed out that according to the wavelength measurements made here it is the more refrangible component of the 4055 pair which belongs to the first subordinate series, the less refrangible apparently belonging to the combination series which is nearly coincident with the former.

14. Interpreting the displacements of unsymmetrical lines in the sun and arc as due to electric fields, we can proceed to find the magnitudes of the average electric fields which are causing the displacements. Different lines in the same spectrum do not, however, lead to the same value for the electric field, possibly because of the assumption that the effect in an electric field is proportionate to the field strength. There can be no doubt, for instance, that the displacements of the Cu pair 4531, 4480, under different conditions of the electric arc are practically equal, whereas Takamine gives them as displaced by an electric field of 44,000 volts/cm by + 0·035A and + 0·100A, respectively. Assuming proportionality to field strength and taking the displacements at the negative pole given in paragraph 3, viz., + 0·032 A, + 0·028 A, these two Cu lines give for the field operating at the negative pole of a copper arc the very large and inconsistent values of 40,300 volts/cm and 15,700 volts/cm, respectively, greater than the field operating at the centre of the arc. Other elements give smaller and more consistent values. Taking the negative pole displacements given in previous bulletins for all the elements for which Takamine has given the Stark effect, we find the following values for the electric field at the negative pole in excess of that at the centre of the arc:—Fe (6 lines) 5,970 volts/cm, Na (2 lines) 4,575 volts/cm, Ni (4 lines) 3,380 volts/cm. Similarly, taking the solar displacements of the unsymmetrical lines of Fe, Na, and Ni from Kodaikanal Observatory Bulletins, and making an allowance for the Doppler shift as deduced from the symmetrical lines at the same depth in the sun, we find that the electric field in the sun is less than that at the centre of the electric arc by the following amounts:—Fe (3 lines) 2,420 volts/cm, Na (2 lines) 1,870 volts/cm, Ni (11 lines) 2,300 volts/cm. We may therefore take it that the field at the negative pole is of the order of 4,000 volts/cm greater than that at the centre of the arc, whilst the field in the sun is of the order of 2,000 volts/cm less than that at the centre of the arc.

15. It can easily be shown that fields of this order of magnitude can be accounted for by the field exerted by surrounding atoms. Debye[3] has calculated the average electric field due to ionisation, assuming that it depends only on the number of ions and the ionic charge, and finds the law that the field is proportional to (ionic charge) × (number of ions per c.c.)$^{\frac{2}{3}}$. The average electric field in which an atom finds itself when a gas at N.T.P., is completely ionised he gives as being of the order of 1,350,000 volts/cm. At 4000° K, the temperature of the arc, this becomes 225,000 volts/cm, and at 6000° K, the temperature of the sun, and atmospheric pressure it is 172,000 volts/cm.

16. If our knowledge of the conditions obtaining in the arc were complete we should now be in a position to make deductions concerning conditions in the sun. Making reasonable assumptions regarding the ionisation

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[1] See Eder and Valenta, Denksch. Wien. Akad. 63, 189, 1896 and Beitrage zur Photochemie, page 161.

[2] Pure silver was not available for these tests. Silver coins were used but it was ascertained that no copper lines nor ghosts of copper lines could be interfering.

[3] Debye, Phys. Zeitschr. 20, 160, 1919.

in the arc does not, however, lead to results which are plausible. From the work of Saha an ionisation in the arc of 1 per cent is not unreasonably large, but it leads to a field of 10,000 volts/cm at which field strength many lines ought to be several angstroms wide, but are in fact fairly sharp. It appears probable that Debye's law given in the previous paragraph is incorrect. It is difficult to believe that the field due to ions which are frequently colliding with atoms can be independent of their diameters and of the frequency of collision, and unless their independence can be established Debye's law falls to the ground. If a given mass of radiating gas, for example, were heated at constant volume and constant ionisation (controlled, say, from outside), the pressure would rise and we should expect a shift due to pressure, but according to Debye there would be no change in the average field strength and therefore, in the light of paragraph 17, no pressure shift. Moreover, the most firmly established law of pressure shifts is that of direct proportionality to pressure, whereas Debye's law requires proportionality to the $\frac{2}{3}$rds power of the pressure.

17. An important point is the ultimate cause of pressure shifts, Stark having suggested that asymmetry in an electric field is the cause. Here again, different lines in the same spectrum do not give consistent values for the field strength; e.g., the copper line 4063 requires nearly 3,000 volts/cm per atmosphere increase of pressure, whilst 4531 requires 28,000 volts/cm per atmosphere. Unless the direction of displacement under pressure follows that of the asymmetry in an electric field, we can at once dismiss the Stark effect as a possible cause of pressure shifts. It is true that lines which are unsymmetrically resolved or displaced towards the red in an electric field have large pressure shifts, and that lines which are symmetrical in the arc have such small pressure shifts that the corresponding displacement or asymmetry in an electric field may not be detectable, but the situation as regards lines which are unsymmetrically widened towards the violet in the arc and are unsymmetrically resolved or displaced towards the violet in an electric field is not so satisfactory. For, whilst Gale and Adams[1] for Fe, Duffield[2] for Ni and Miller[3] for Ca have found that lines unsymmetrical towards the violet are displaced to the violet by pressure, Humphreys[4] has many examples of such lines being displaced to the red; e.g., Ca triplet and satellites at 4456,35,25, Cu doublet and satellite 5220, 5218, 5153, Mg triplet 3838, 32, 29, Ni line 5155, Sr triplet and satellites 4971, 4876, 4832. These discrepancies require careful investigation.

18. Nevertheless, an obscure feature of pressure shifts can be readily explained on the hypothesis of the Stark effect. Pressure displacements in the furnace and in the spark are greater than in the arc whilst the widening is also greater in these sources. Since the greater widening is very probably a Stark effect, so presumably would the greater pressure shift, both being due on the interpretation given in this paper to greater ionisation in the furnance and in the spark under pressure.

19. King explains[5] the asymmetry and displacements of lines in the arc, tube-arc, and spark as due to the density of high speed electrons. I consider that the suggestion made in this paper that these effects are due to the electrical field in which the radiating atom finds itself offers a more rational, though not necessarily inconsistent, explanation. King shows that under the extreme conditions of the tube-arc nearly all lines show as unsymmetrical, even certain "flame" lines of iron. It would appear, therefore, that the difference between unsymmetrical lines and those which have generally been referred to as symmetrical is mainly one of degree; this is required if the explanation of pressure shifts in paragraph 17 is correct, although again there is the inconsistency of the H and K lines of Ca which King finds to be slightly unsymmetrical towards the violet being, as he points out, displaced to the red under pressure.

20. If the view expressed in this paper is correct that asymmetry and displacements are effects of the electric field due to ionisation of the gas, then since ionisation increases with temperature so should also the asymmetry and displacement of spectrum lines. As passing from the arc to the sun shows an opposite effect

[1] Gale and Adams, Astrophysical Journal, 37, 391, 1919.

[2] Duffield, Phil. Trans. R.S. 215, 205, 1915.

[3] Miller, Astrophysical Journal, 53, 224, 1921.

[4] Humphreys, Astrophysical Journal, 6, 169, 1897. See also Humphreys on *Pressure shift of violet sided lines*, Astrophysical Journal, 31, 459, 1910.

[5] King, Astrophysical Journal, 41, 373, 1915.

it would follow that the fall in density more than counterbalances the rise in temperature and denotes that the partial pressure of ions is less in the sun than in the arc. It is to be expected, however, that there will be a displacement of unsymmetrical lines in sunspots relative to the photosphere where the temperature is higher, but the magnitude of the displacement cannot yet be predicted from theory.

21. Suitable lines unsymmetrical towards the violet were not readily available in this preliminary study of the effect of adding substances into the arc, but it is desirable to confirm the expectation that they will be displaced in the opposite sense to lines unsymmetrical towards the red.

Summary.—1. These experiments were undertaken with a view to deciding whether density of vapour or density of ions is the cause of the displacements of unsymmetrical lines under varying arc conditions.

2. In a short arc certain lines of copper which are unsymmetrically widened towards the red are displaced to the red by introducing various substances into the arc; the less unsymmetrical lines undergo smaller displacement, and symmetrical lines are not displaced at all.

3. The effect is smaller at the poles of a long arc and insignificant at the centre of a long arc for the lines studied.

4. In a calcium arc lines unsymmetrical towards the red are shifted slightly towards the red, or towards the violet according to the substance introduced.

5. It is suggested that these displacements are caused by changes in the ionisation in the arc when extraneous substances are introduced into the arc.

6. There is now considerable evidence that the asymmetry and displacement of lines under varying arc conditions and their abnormal displacement in the sun follow very closely their asymmetry and displacement in an electric field. The electric field operating in the arc and the sun is probably the intermolecular field due to surrounding ions and electrons. On this view the average electric field at the negative pole of the arc is of the order of 4000 volts/cm greater than that at the centre of the arc and in the sun 2,000 volts/cm less than at the centre of the arc. Until the ionisation in the arc is investigated and the average electric field due to ions has been satisfactorily worked out we are unable to apply these data to the determination of the partial pressure of ions in the sun.

7. The view that there are electric fields in the arc is supported by the presence in arc spectra of those lines which in the vacuum arc are only in evidence in a strong electrical field.

8. Although many features of pressure displacements can be explained as due to the increase in the intermolecular electrical fields owing to the increase in the partial pressure of ions, there are some difficulties. The point which first requires experimental elucidation is the direction of the pressure shift of lines unsymmetrical towards the violet concerning which evidence is contradictory.

9. Further examples have been found of series in which the character of the lines reverses as we pass down the series.

This work was carried out whilst Mr. Evershed was still Director, and it is a pleasure to acknowledge my indebtedness to his interest and suggestions.

THE OBSERVATORY, KODAIKANAL,
14th April 1923.

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