

as when rotation has been incomplete a mere mechanical vibration has at once restored the maximum effect.

10. That heat, magnetism, constant electric currents, mechanical strains and vibrations, have all some effect on the result.

III. "On the Identity of Spectral Lines of Different Elements."

By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry,
and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University
of Cambridge. Received May 12, 1881.

THE question of the identity of spectral lines exhibited by different elements is one of great interest, because it is very improbable that any single molecule should be capable of taking up all the immense variety of vibrations indicated by the complex spectrum of iron or that of titanium, and it might therefore be expected that such substances consist of heterogeneous molecules, and that some molecules of the same kind as occur in these metals should occur in more than one of the supposed elements. Further, the supposed identity of certain lines in the spectra of more than one element has been made by Mr. Lockyer the ground of an argument in support of a theory as to the dissociation of chemical elements into still simpler constituents, and in reference to this he wrote ("Proc. Roy. Soc." vol. 30, p. 31), "the 'basic' lines recorded by Thalén will require special study with a view to determine whether their existence in different spectra can be explained or not on the supposition that they represent the vibrations of forms, which, at an early stage of the planet's history, entered into combination with other forms, differing in proximate origin, to produce different 'elements.'"

Young, on examining with a spectroscope of high dispersion the 70 lines given in Ångström's map as common to two or more substances, has found that 56 are double or treble, 7 more doubtful, and only 7 appear definitely single ("American Journal of Science," vol. xx, 119, p. 353), and he remarks, "The complete investigation of the matter requires that the bright line spectra of the metals in question should be confronted with each other and with the solar spectrum under enormous dispersive power, in order that we may determine which of the components of each double line belongs to one and which to the other element." It is this confronting of the bright line spectra of some of the terrestrial elements which we have attempted, and of which we now give an account. For the dispersion we have used a reflecting grating similar to that used by Young, with 17,296 lines to the inch, and a ruled surface of about $3\frac{1}{2}$ square inches; telescope and

collimator, each with an aperture of $1\frac{1}{2}$ inch and focal length 18 inches, the lenses being of quartz, cut perpendicularly to the axis and unachromatised, giving a very good definition with monochromatic light. The chromatic aberration is in this case an advantage, for when the telescope is in focus for lines in the spectrum of any given order, the overlapping parts of spectra of different orders are out of focus, and their brightness consequently more or less enfeebled. We have sometimes used green or blue glasses to enhance this result. The telescope and the collimator were generally fixed at about 45° , the collimator being more nearly normal to the grating than the telescope, and the grating moved to bring in successive parts of the spectra. For the parts of the spectra less refrangible than the Fraunhofer line E the spectrum of the third order was employed, for the more refrangible rays that of the fourth order. The source of light was the electric arc taken in a crucible of magnesia or lime; and for the examination of any supposed coincidence first one metal was introduced into the crucible and the line to be observed placed on the pointer of the eyepiece, the second metal was next introduced, and then in most cases, as detailed below, *two* lines were seen where only one was visible before, and the pointer indicated which of the two belonged to the metal first introduced. In some cases where both metals were already in the crucible, we had to reinforce the spectrum of one of the metals by the introduction of more of that metal, which generally brought out the spectrum of that metal more markedly than the other, and enabled us to distinguish the lines with a high degree of probability. Thus the crucibles of magnesia, or the carbons, always contain sufficient lithium to show the orange line and the calcium line heretofore supposed coincident with it (wave-length 6101.9), but we observed these lines quite distinct and separated by a distance, estimated by the eye in comparison with the distance of neighbouring titanium lines, at about one division of Ångström's scale. On dropping a minute piece of lithium carbonate into the crucible the less refrangible line was seen to expand, and for a short time to be reversed, the other line remaining narrow and quite unaltered. When the lithium had evaporated, and both lines were again narrow, a small piece of Iceland spar was dropped into the crucible, which immediately caused the expansion, and on one occasion the reversal, of the more refrangible line, while now the less refrangible line was unaffected.

In this way we satisfied ourselves that the calcium line is the more refrangible of the two, and is probably represented by the line at wave-length 6101.9 in Ångström's normal solar spectrum, while the lithium line appears to be unrepresented.

In the case of iron, which gives such a multitude of lines, it was *à priori* probable that some lines would be coincident, or nearly so, with lines of other elements; and in fact we find that in five-sixths of

the supposed coincidences lines of iron are involved. We have, therefore, chiefly directed our attention to iron lines.

Taking iron and titanium, we find that we can resolve the lines at the wave-lengths following:—

6064·7* is a wide double, the iron line less refrangible than the titanium by something like a division on Ångström's scale. Young did not resolve this line, probably because he was looking for a much closer double line.

5714·09. A very close double, the iron the less refrangible, but not in Thalén's list.

5661·65. A double titanium line, but there appears to be a single iron line between the titanium lines.

5489·05. A titanium line, but we could not see any iron line in the arc at this place, and no such iron line is in Thalén's list.

5486·94. The iron line is more refrangible than the titanium.

5446·07. Rather a close double, the iron line the less refrangible.

5428·96. A wider double, the iron line the less refrangible.

5403·28. The iron line in this is the more refrangible.

5396·19. The iron line is the less refrangible.

5006·72. We have not resolved this line; but it is not given as an iron line in Thalén's list.

4990·48. We have not resolved this line; but it is a very strong titanium line, and the titanium may have overpowered the iron line if they are not coincident.

4690·69. The iron line is given by Thalén as slightly less refrangible than the titanium line, but we did not resolve this line (see Appendix to this paper).

4426·9. Not given as an iron line in Thalén's list.

4307·25. The iron line is given by Thalén as slightly more refrangible than the titanium line. We have not resolved this line, the titanium line being weak.

4293·96. The iron is given by Thalén as slightly less refrangible than the titanium, but we did not resolve this line, or make out that there is any titanium line at this place.

4287·47. This is not given as an iron line in Thalén's list.

4171·77. We have repeatedly looked for this titanium line but have not seen it in the arc.

In the case of calcium it was more difficult to resolve close doubles, because the introduction of a very small quantity of a calcium compound into the arc for the purpose of identification caused such an expansion of the calcium lines as to overpower in many cases their weaker neighbours.

* The numbers by which the lines are here designated are the wave-lengths of the corresponding Fraunhofer lines taken from the catalogue of oscillation frequencies in the Report of the British Association, 1878, p. 37.

6461·98. Not down as an iron line in Thalén's list. If it be an iron line, we are unable to distinguish it from the calcium line (see Appendix).

5601·84. The iron line in this double is less refrangible than the calcium line.

5597·31. A rather close double in which the iron line is the more refrangible.

5348·75. Clearly double, the iron line less refrangible than the calcium line.

5269·59. A very close double, the iron line less refrangible than the calcium.

5041·32. A close double, but distinctly separable, the iron line the less refrangible. Kirchhoff gives the iron and calcium lines as separate, but the calcium line less refrangible than the iron.

4877·57. We could not resolve this line; though Young has resolved the corresponding solar line.

4585·36 } There are no iron lines at these places in Thalén's list, nor
4578·37 } could we detect any in the arc though the positive
4580·93 } pole was of iron.

4407·8 seems to be an iron line, though not in Thalén's list, but the calcium line, if there be one at this place in the arc, is so faint that we could not certainly make it out.

4379·16 also seems to be an iron line not in Thalén's list, but we could find no calcium line in the arc corresponding to it.

4375·46 is not given as a calcium line in Thalén's list, and we could see no calcium line at this place.

4307·25 seems to be a very close double, not distinctly divisible, as both lines are somewhat diffuse, but the iron a little less refrangible if it expands symmetrically, and so given by Kirchhoff and by Thalén.

4301·95. The iron line here is faint, and it is more refrangible than the calcium line.

4298·56. Close but distinctly divisible double, the iron less refrangible than the calcium line.

4271·33 had the appearance of a very close double, as when calcium chloride was introduced into the crucible, the line expanded more on its less refrangible side, as if the iron line were rather more refrangible than the calcium line; but we could not definitely separate the two. The two lines are not given as exactly coincident by Thalén.

The lines 4249·81, 4246·89, 4233, 4143·14, 4131·52 are doubtful calcium lines; at least, we could not detect any such lines when calcium chloride was introduced into the arc, though the other calcium lines in the neighbourhood were well developed.

4097·55 does not seem to be an iron line, and we could detect no such line in the arc when the positive pole was of iron.

Of supposed common lines of nickel and iron:—

5168·48 is a close double, but the iron is less refrangible than the nickel line.

5145·87 we could not resolve, but it is not down as an iron line in Thalén's list.

5142·1 is double, and the iron line the less refrangible, but it was difficult to separate the two lines by reason of their diffuse character.

5136·9 is a very close double, the iron line more refrangible and weaker than the nickel line.

4854·85 we have not been able to find any iron line here in the arc.

Of supposed coincident lines of manganese and iron :—

5340·38 is a close double of manganese and iron, but still definitely divisible, the iron line being the more refrangible of the two.

5254·21 is rather a wide double, with the iron line the more refrangible.

4489·49, also plainly double, has the iron line more refrangible than the manganese line.

4414·77 is a close double, but distinctly separable, the iron line the less refrangible.

4054·48. There is a faint iron line here slightly more refrangible than the manganese line.

The magnesium and iron lines in b_4 are separable, the iron line being less refrangible.

Of chromium lines supposed coincident with iron lines :—

5207·78 is plainly double, the iron line being the less refrangible.

5203·88 not clearly resolved, but the iron line seems the less refrangible.

4654·07. We failed to detect any chromium line at this place, though the chromium line at 4646·6 was bright and strong, as well as a line at 4650·5.

4646·6 we could not resolve, but Thalén gives no line of iron in his list at this place.

4369·27 does not appear to be an iron line; we could detect no such line in the arc, and it is not given in Thalén's list. There is an iron line about one division of Ångström's scale less refrangible.

Of supposed coincident lines of iron and cobalt :—

5265·94 is decidedly double, and the more refrangible of the two lines due to cobalt.

5352·57 we did not resolve with certainty, but cobalt expanded the line more on the less refrangible side.

5681·52. The iron line here is decidedly more refrangible than that of sodium.

We have examined further the supposed coincident lines of cobalt and calcium, and of chromium and calcium, and find that 6121·34 is plainly resolvable, and the cobalt line is the less refrangible of the two.

4289·44 and 4274·63 are both close doubles, with the chromium lines the less refrangible. The latter line is difficult to resolve.

5856·6 is plainly resolvable, the calcium line more refrangible than the nickel line.

5480·29. This is a double line of titanium, and the strontium line is more refrangible than either titanium line. They form a not very close triplet.

5424·8. The barium line lies between the titanium line and the iron line next it (5423·7), and the iron line is a very little more refrangible than the barium line.

The indium line 4101·2 we found very difficult to separate from the hydrogen line (*h*), as the latter had to be taken from the spark in a tube, and is both faint and diffuse, but several observations all led to the conclusion that the indium line is very slightly less refrangible than that of hydrogen.

We have also directly compared the iron line at 5316·07 with the solar spectrum, and found that the iron line corresponds with the less refrangible of the two solar lines at this place, so that the coronal line is in all probability the other line of the pair.

There are still a few cases of supposed coincidences which we have not examined. The results which we have recorded strongly confirm Young's observations, and leave, we think, little doubt that the few as yet unresolved coincidences either will yield to a higher dispersion, or are merely accidental. It would indeed be strange, if amongst all the variety of chemical elements, and the still greater variety of vibrations which some of them are capable of taking up, there were no two which could take up vibrations of the same period. We certainly should have supposed that substances like iron and titanium, with such a large number of lines, must each consist of more than one kind of molecule, and that not single lines, but several lines of each, would be found repeated in the spectra of some other chemical elements. The fact that hardly single coincidences can be established is a strong argument that the materials of iron and titanium, even if they be not homogeneous, are still different from those of other chemical elements. The supposition that the different elements may be resolved into simpler constituents, or into a single one, has long been a favourite speculation with chemists; but however probable this hypothesis may appear, *à priori*, it must be acknowledged that the facts derived from the most powerful method of analytical investigation yet devised give it scant support.

Appendix. May 13, 1881.

The following supposed coincidences have been resolved, in addition to those before mentioned :—

6449·27. This is rather a wide double, the calcium line being more refrangible than that of barium.

6461·98. This is a close double, but the iron is less refrangible than the calcium line.

6438·35. A wide double, the cadmium more refrangible than the calcium line.

6407·38. The iron line is decidedly more refrangible than the strontium line.

4690·69. Not resolved before only from the faintness of the iron line, which is less refrangible than the titanium line.

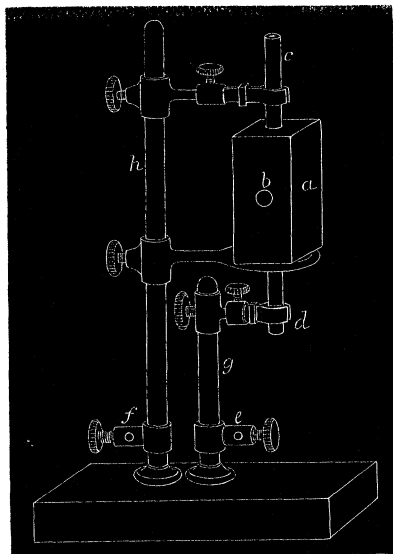


Figure representing the arrangement of crucible by which most of the observations in the foregoing paper were made. *a*, block of dense magnesia; *b*, horizontal hole for observation; *c*, upper perforated carbon through which substances were dropped into the arc; *d*, lower carbon, sometimes drilled and filled with metal; *e*, connexion for positive electrode; *f*, connexion for negative electrode; *g* and *h*, brass pillars fixed on wooden block.

