

it follows that

$$\left. \begin{aligned} {}^kU_{r,n} &= \frac{(-1)^r}{[r]} \cdot (x^k D^k)^{-1} \cdot (x^{k+r} D^{k+r}) \cdot y^{(n-r)}, \quad . \quad . \quad . \quad . \quad . \\ &= \frac{(-1)^r}{[r]} \cdot \frac{\Gamma(xD - k + 1)}{\Gamma(xD - k - r + 1)} \cdot y^{(n-r)}, \quad . \quad . \quad . \quad . \quad . \\ &= \frac{(-1)^r}{[r]} \cdot x^k \frac{[xD]}{[xD - r]} \cdot x^{-k} y^{(n-r)}, \quad . \quad . \quad . \quad . \quad . \\ &= \frac{(-1)^r}{[r]} \cdot x^{k+r} D^r \cdot x^{-k} y^{(n-r)}, \quad . \quad . \quad . \quad . \quad . \end{aligned} \right\} (10a)$$

$$\left. \begin{aligned} {}^kU_{n,n} &= \frac{(-1)^n}{[n]} \cdot \frac{\Gamma(xD - k + 1)}{\Gamma(xD - k - r + 1)} \cdot y, \quad . \quad . \quad . \quad . \quad . \\ &= \frac{(-1)^n}{[n]} \cdot x^k \frac{[xD]}{[xD - n]} \cdot x^{-k} y, \quad . \quad . \quad . \quad . \quad . \\ &= \frac{(-1)^n}{[n]} \cdot x^{k+n} D^n \cdot x^{-k} y, \quad . \quad . \quad . \quad . \quad . \end{aligned} \right\} (10b)$$

Observe that, since r, n are supposed positive integers, these symbolic ratios always consist of a finite number of factors (viz. r, n respectively), and are therefore always interpretable, whatever be the value of k .

May 18, 1876.

Dr. J. DALTON HOOKER, C.B., President, in the Chair.

The Presents received were laid on the table, and thanks ordered for them.

The following Papers were read:—

1. "Absorption-Spectra of Iodine." By Sir JOHN CONROY, Bart., M.A. Communicated by A. G. VERNON HARCOURT, Lee's Reader in Chemistry in the University of Oxford. Received April 12, 1876.

Iodine, as is well known, when in very thin layers, appears red by transmitted light; and when in solution the colour of the liquid depends not only on the amount of iodine contained in it, but also on the nature of the liquid in which it is dissolved.

Schultz-Sellaack has pointed out (Pogg. Ann. vol. cxl. p. 334) that the liquids in which iodine is soluble may be divided into two classes:—

first, those with which it gives reddish-brown solutions, like alcohol; and secondly, those with which it gives violet ones, as bisulphide of carbon; and also that the colours of these two solutions correspond respectively with the colour of solid iodine, when seen by transmitted light, and with that of iodine vapour.

Andrews (Brit. Assoc. Report, 1871) has also remarked that iodine vapour and the solution of iodine in bisulphide of carbon are dichroic, while such is not the case with its solution in alcohol.

As I am not aware of any other observations on the absorption of light by iodine in solution or in the solid state having been published, I have the honour of having an account of some experiments I have recently made on this subject communicated to the Royal Society.

For these observations I have used one of Browning's spectroscopes with a single dense-glass prism of 60° , as with a greater amount of dispersive power it became more difficult to observe the beginning and end of the absorption. The spectroscope was firmly screwed to the wall of the room, with the collimator pointing vertically downwards, the light from a paraffin-lamp being reflected along it by a mirror—the width of the slit and the position of the mirror and lamp remaining unaltered during the course of the experiments, in order that the different absorption-spectra should, as far as possible, be comparable with each other. The solution whose absorption was to be observed was contained in a small beaker, supported by the ring of a retort-stand between the mirror and the slit of the collimator.

This arrangement was adopted in order to be able to observe the absorption through various thicknesses of the same solution, without having to use a wedge-cell, as some of the liquids in which iodine is soluble act very quickly on the cement with which such cells are fastened together.

A vertical scale was attached to the beaker, so that by gradually pouring a solution into it, the absorption through different known thicknesses could be observed, the solutions of iodine in bisulphide and tetrachloride of carbon being covered with a thin layer of water to prevent their evaporating.

When the absorption-spectra of solid and liquid iodine were to be observed, the beaker was replaced by a large cork which fitted the ring of the retort-stand, and through which a hole had been bored in a line with the axis of the collimator, and the glass slips between which the iodine had been melted laid on this. In the case of the liquid iodine, the low conductive power for heat of the cork retarded the cooling of the glass, and facilitated the observation of the absorption.

The telescope of the spectroscope, the eyepiece of which was furnished with cross wires, was carried by an arm moving over a divided arc; and the position of 10 of the principal lines in the solar spectrum having been observed, from these measurements, and from the wave-

lengths of the same lines, as determined by Ångström, a curve was constructed, by means of which the readings of the spectroscope were reduced to wave-lengths.

Solid Iodine.

Layers of iodine sufficiently thin to be transparent can be readily obtained, as Schultz-Sellack has remarked, by squeezing melted iodine between two pieces of flat, well-polished glass: it is only necessary to place a small fragment of iodine between two pieces of glass which have been previously well cleaned with alcohol, and heat them over a spirit-lamp till the iodine melts, and then press them together. I have obtained the best results by heating the iodine till it just melts, placing the pieces of glass on a smooth block of wood and squeezing them together with a flat cork.

The layers of iodine thus obtained are not usually of uniform thickness; and, in addition to this, they contain so little iodine that I was unable to determine their thickness by ascertaining the weight and area of the film. When seen, however, by reflected and transmitted light, the iodine film usually appears surrounded by coloured rings; and as these alter their position and shape when the glass slips are pressed together, they must be due to a thin layer of air, and not to any substance adhering to the glass; and consequently the layers of iodine are probably less than $\cdot 00004$ inch, or $\cdot 001016$ mm., in thickness.

When seen by transmitted light, these layers of iodine vary in colour from a deep brownish red, through different shades of brown, to a more or less pure yellow, according to the thickness and nature of the film; for, as is shown in the paper "On the Polarization of Light by Crystals of Iodine" (*infra*, p. 51), the colour of the transmitted light apparently does not depend solely on the thickness of the layer of iodine through which it passes. These films correspond in colour with alcoholic solutions of iodine of different strength, and the absorption-spectra are very similar—the whole of the blue end of the spectrum being cut off, and the absorption extending further and further towards the less refrangible end of the spectrum, as the thickness of the film increases, till at length only light having a wave-length of about 650 (in "tenth-metres"), or slightly more refrangible than the C line, passes through; and a very slight increase in the thickness of the film is sufficient to stop this also.

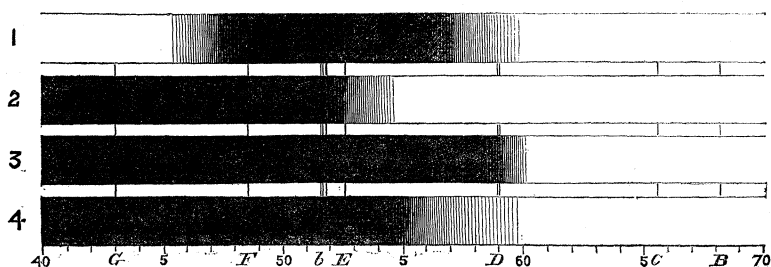
Fig. 4 shows the appearance with a film of medium thickness, the strong absorption ending at a point about one third of the distance between E and D, together with a certain amount of darkening extending to about D, and represents the mean results from measurements of the absorption-spectra of seven different films of iodine.

Liquid Iodine.

With a little careful management it is usually possible to melt one of these thin layers of iodine by heating it over the flame of a spirit-lamp,

without causing it either to be dissipated in vapour or to run together. The liquid iodine appears to be more transparent than the solid; for a layer which appears a deep red colour by transmitted light when hot, sometimes becomes perfectly opaque on cooling. When hot it is also of a deeper red than when cold; and the spectroscope shows that while the less-refrangible rays of the spectrum are freely transmitted, there is more absorption of those of mean refrangibility than is the case with solid iodine.

Fig. 3 shows the absorption-spectrum as deduced from five observations. Just as is the case with solid iodine, light of a wave-length of about 650 suffers the least amount of absorption during its passage through a layer of iodine.



Iodine in Solution.

As I have before mentioned, the liquids in which iodine is soluble may be divided into two classes: first, those with which it forms brownish-red solutions, as alcohol, ether, ethyl bromide, Dutch liquid, benzole, glycerine, potassium iodide in an aqueous solution, hydrogen chloride, &c.; second, those with which it forms violet solutions: this latter class is less numerous, and as far as I have hitherto been able to ascertain by actual experiment, only consists of the following substances—the bisulphide, tetrachloride, and monochloride of carbon, chloroform, phosphorous terchloride, tin tetrachloride, and under certain circumstances, as will be hereafter mentioned, hydrogen sulphate. In Watts's 'Dictionary of Chemistry,' vol. i. p. 881, it is stated that the solution of iodine in chloral has a purple colour.

In order to obtain solutions of iodine of a known strength, some of the liquids in which it is soluble being very volatile, a small glass weighing-tube closed with a cork was nearly filled with iodine which had been crushed small with the edge of a platinum spatula. A stoppered flask holding 25 c. c. was filled with the liquid in which the iodine was to be dissolved; and the tube having been weighed, a small quantity of iodine was shaken out of it, and the tube again weighed, and so on, till the desired amount had been added to the liquid.

In this way solutions of iodine in bisulphide and tetrachloride of carbon,

chloroform, alcohol, and in aqueous solutions of potassium iodide were prepared, and the absorption produced by different thicknesses of these solutions observed.

Solutions of iodine in alcohol, and of iodine in an aqueous solution of potassium iodide, of different strengths were then prepared, and the absorption produced by layers of these solutions, varying in thickness from 5 mm. to 25 mm., was observed.

Solutions of iodine in both liquids were, when of equal strength, of the same colour and the absorption-spectra were similar, and also similar to that of the solid iodine, except that the absorption did not appear to extend quite so far down the spectrum; but as the transition from strong absorption to none at all is a very gradual one, it is somewhat difficult to determine the exact point at which the absorption ends. Fig. 2 represents the mean results obtained from thirty observations through different thicknesses of the alcohol solutions.

Iodine dissolved in bisulphide of carbon absorbs most strongly light of mean refrangibility; and the absorption-spectrum resembles that of the vapour of iodine as represented in the map to M. Thalen's memoir, '*Le spectre d'absorption de la vapeur d'Iode*' (Upsal, 1869), except that the absorption is continuous, and does not extend quite so far towards the less-refrangible end of the spectrum.

Fig. 1 represents the mean result of eighty-one measurements of the position of the absorption produced by different thicknesses of these solutions. The rays whose wave-lengths lie between 450 and 560 (approximately) are first absorbed; and as the thickness of the layer or the concentration of the solution is increased, the absorption extends towards both ends of the spectrum, though more rapidly towards the less-refrangible one.

Just as was the case with the solution of iodine in alcohol, and with solid and liquid iodine, light of a wave-length of about 650 passes unabsorbed through a considerable thickness of the solution; but a thickness which is sufficient to stop the whole of the red rays still allows the blue and violet ones to pass; hence, whilst dilute solutions of iodine in bisulphide of carbon and other liquids of that class appear of a kind of red, when the light passes through a greater thickness, or the solution is more concentrated, they appear blue or violet.

Iodine is insoluble in cold hydrogen sulphate; but when some fragments of iodine are placed in a test-tube, partially filled with strong hydrogen sulphate, and the tube heated, the iodine first melts, and then gradually colours the liquid, till it becomes about the same tint as a very dilute solution of iodine in bisulphide of carbon.

·0100 grm. of iodine was placed in a test-tube containing 25 c.c. of strong hydrogen sulphate, and the test-tube carefully heated over a spirit-lamp until the whole of the liquid iodine had disappeared; the acid appeared of the same colour as a solution of iodine in chloroform, containing about the same amount of iodine. The colour of the acid did not

alter on cooling ; after standing 24 hours the upper layer of acid for a depth of about one centimetre from the surface had become colourless ; but at the end of five months the acid in the lower part of the tube was still pink, the upper half having become colourless, and a small quantity of a black powder having settled at the bottom.

Only a very small quantity of iodine can be held in solution by the hydrogen sulphate when cold, as any excess separates out in minute crystals.

It does not appear probable that the difference in the colour of the solutions which iodine forms with liquids of these two classes depends on any chemical fact, as both classes contain substances of very dissimilar chemical composition. I have not, however, as yet been able to ascertain any common property possessed by all the liquids of either class, beyond (as, indeed, is obvious) that all those in which iodine forms violet solutions are volatile liquids of high specific gravity.

It has been shown by various observers (H. Morton, Pogg. Ann. vol. clv. p. 573 ; Hagenbach, Pogg. Ann. vol. cxlvi. p. 533 ; Kraus, 'Chlorophyllfarbstoffe,' p. 53) that the position of the absorption-bands of substances in solution vary to a certain extent with the liquid in which they are dissolved ; but this would appear to depend on some other cause ; for, in addition to the displacement being small, it differs in amount with different liquids ; whilst in the case of iodine, as far as I have been able to observe, the position of the absorption is the same for all the liquids belonging to one of the two classes. The action on light of iodine dissolved in alcohol greatly resembles the effect it produces when in the solid state ; whilst the absorption of its solution in carbon bisulphide, and in other liquids of that class, bears, as has been pointed out to me by Professor Stokes, the same relation to the absorption-spectrum of the vapour as the spectrum of the solution of a coloured gas (nitrogen peroxide for example) does to that of the gas.

II. "On the Polarization of Light by Crystals of Iodine." By Sir JOHN CONROY, Bart., M.A. Communicated by A. G. VERNON HARCOURT, Lee's Reader in Chemistry in the University of Oxford. . Received April 12, 1876.

On examining by means of a Nicol prism the light reflected from the surface of a layer of iodine, obtained by heating a fragment of that substance and then squeezing it between two plates of glass, as described in the preceding paper, I found that the film did not appear of uniform brightness, and that when the Nicol was rotated the relative brilliancy of different parts of the film changed—a portion that had appeared dark when the principal section of the Nicol was vertical, became bright when it was horizontal, and *vice versa* ; and, also, if instead of altering the

