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The Absorption Spectra of the Vapours of Benzene and Its Homologues, at Different Temperatures and Pressures, and of Solutions of Benzene

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XIII. *The Absorption Spectra of the Vapours of Benzene and its Homologues, at Different Temperatures and Pressures, and of Solutions of Benzene.*

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[PLATES 32–33.]

INTRODUCTION.

THE absorption spectrum of benzene in a state of vapour and in solution was photographed by W. A. MILLER ('Phil. Trans.,' 1862, vol. 152, II., pp. 861–887). It was also photographed by me in 1880 ('J. Chem. Soc.,' 1881, vol. 39, p. 153; 1882, vol. 41; 1885, vol. 47, pp. 685–757), with the instrument and by the method described in the 'Scientific Proceedings of the Royal Dublin Society' in 1881 (vol. iii., p. 93, New Series) and 'J. Society of Arts,' 1885. For these investigations a molecular weight in milligrammes was employed to test the molecular absorption of the hydrocarbon, but the quantity of vapour was too large even at low temperatures, and the temperature, as since ascertained, was in other experiments too high to admit of the numerous absorption bands being observed, although a series of bands had been photographed from very dilute solutions of benzene in alcohol. The continuous rays which accompany the lines in the emission spectrum of the strongly condensed spark of cadmium were found to afford the best source of light in the region of short wave-lengths.

J. PAUER, in 1897 ('WIEDEMANN'S Annalen,' vol. 61, p. 363), also used the cadmium spectrum precisely in the same manner for a more complete investigation of benzene and its homologues, but his experiments were not quantitative, although he compared the same substances in the states of vapour, of liquid, and in solution at a temperature of 20° C. He accurately measured 29 different narrow bands characteristic of the spectrum of the vapour of benzene. More recently this work has been repeated by WILHELM FRIEDERICHS ('Zeitschrift f. Wissenschaftl. Photographie,' 1905, vol. 3, p. 154) and by LEONARD GREBE (*loc. cit.*, 1905, p. 363).

FRIEDERICHS used a quartz vacuum-tube containing hydrogen as a source ot continuous rays; while GREBE used the continuous spectrum described by KONEN, when a powerful spark is passed between poles of aluminium immersed in water. The exposure necessary in FRIEDERICHS' experiments was from 12 to 21 hours, in GREBE'S from $\frac{3}{4}$ to 1 hour. Only the maximum of absorption of the bands was measured by these investigators and not their width, but the widening of the bands is an important feature in the spectrum when changes of temperature and pressure occur. I have re-investigated the vapours of the aromatic hydrocarbons recently by means of the continuous rays emitted by condensed sparks passed between various electrodes, but for measurements in the ultra-violet the cadmium continuous spectrum which accompanies the lines of that element has alone been employed, because it has been found, on the whole, to yield the most satisfactory results.*

The vapours of benzene and some of its derivatives have been examined (1) at different temperatures and constant pressure, and (2) at different pressures, the temperature being constant. The several different spectra photographed prove the correctness of the previous measurements of PAUER, FRIEDERICHS, and GREBE, though these do not show complete agreement among themselves.

Thus the band at wave-length 2694 (FRIEDERICHS) is a real one and not, as GREBE believed, a mere marking or scratch on the photographic film; also the band at 2631 observed by FRIEDERICHS is undoubtedly a benzene band; so likewise are those at 2633 and 2638 observed by GREBE, but believed by him to be due to an impurity.

Experimental.

The benzene was a portion of 2 litres obtained from Kahlbaum which had been crystallised and was free from thiophene. A quantity of 250 c.c. was recrystallised, the crystals being pressed between folds of blotting paper, melted and redistilled. Its boiling-point was constant at 81° C. and 763 mm. barometric pressure.

The Absorption Spectra at Varying Temperatures.

An arrangement was used similar to that employed by PAUER, with the exceptions that the tube was of bronze 150 mm. long, fitted into a rectangular water-bath which was deep enough to hold the small flask of benzene as well as the immersed tube; also the metal tube was closed at each end by a quartz plate cemented on to a flange with seccotine, or fish glue, and could be exhausted, partially or completely, at any temperature.

The bath in different experiments, according to the temperature required, was filled with water or glycerine. Brazed to the bronze tube were two smaller tubes for inlet and outlet of air or a neutral gas. The inlet was connected with the side tube of the flask containing the benzene, the outlet with a reversible aspirator which holds

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* 'Roy. Soc. Proc.,' 1906, A, vol. 78, pp. 243–245. PAUER arrived at the same conclusion, see footnote on p. 365 *loc. cit.*

1 litre of water. The volume of air aspirated through the benzene in each experiment could be exactly measured; it served to vaporise the liquid and charge the tube with vapour. After using the aspirator for a few minutes the taps were closed and the temperature taken by a thermometer kept in the bath, the liquid in which was constantly stirred. In front of the end of the tube is a quartz lens, and behind the lens the electrodes which give the emission spectrum, the rays being focussed upon the slit of a quartz spectrograph.

The plates were exposed from two to five minutes, but as a rule the exposure was not more than two minutes. After one exposure the temperature of the bath was raised and another exposure made immediately below the first, and so on, going through the same manipulations as for the previous exposure. From the vapour-pressure curve and the ascertained temperatures in the bath the quantity of benzene presumably in the tube at each exposure was calculated.

The actual quantity of the hydrocarbon present in the tube was afterwards determined by the gas analysis of its contents at the different temperatures.

The capacity of the tube was 79 c.c. and its length 150 mm. It will be seen that, as the calculated and found quantities at 12°·7 C. are very nearly the same, the molecule of benzene in a state of vapour is the same at temperatures below its boiling-point as at 20° C. above it. At higher temperatures the analytical data show that the air was far from saturated with the vapour, inasmuch as at 53° C. there were only 6 mgrm. more of benzene in 79 c.c. than at 12°·7 C., whereas the calculated quantity is 72 mgrm. more.

THE Contents of the Tube.

Temperatures.	Vapour pressures of benzene.	Weight of benzene.	
		Calculated.	Found.
° C.	mm.	grm.	grm.
12·7	53	0·0184	0·0179
25·7	95	0·0316	0·0203
43	205	0·0643	0·0211
53	297	0·0904	0·0239

As the results of the gas analyses were not altogether of a character to be relied upon, another series of determinations was made by burning the vapour in a combustion tube with cupric oxide and weighing the products of combustion. In this way also it was found that the results obtained were very irregular, and after many combustions had been repeated, which yielded figures varying in an unaccountable manner, it was concluded that to ensure a determination of the amount of benzene under examination in each case a very complicated apparatus would have to be constructed, all the tube connections being of metal or of glass. It must not be overlooked that the time occupied in making the analyses was much longer than in taking the photographs, and as the vapour had to be transferred from one vessel to another, this admitted of changes occurring in the composition of the vapour, by condensation at one period and saturation at another. Moreover, at low pressures there was a difficulty experienced in extracting all the vapour from the tube and submitting it to analysis.

The Absorption Spectrum of Benzene Vapour at Constant Temperature and Reduced Pressures.

In the first experiments at reduced pressures a glass tube was used with glass taps, the same arrangement being used for vaporising the benzene, but the outlet tube, instead of being connected with an aspirator, was connected by a glass T-piece with a filter-pump and a pressure gauge. Air was drawn through the benzene and regulated by the flow from the pump until the mercury in the gauge was steady; the exhaustion still proceeding, the exposure of the plate was made, after which the exhaustion was continued until a steady and further reduction in the pressure was obtained, when another exposure was made, and so on. In this way the vapour was continually being removed at one end of the tube and renewed at the other, but always at the same pressure for each exposure. Photographs were taken at temperature 11°·5 C., and 778 mm., 483 mm., 253 mm. and 21 mm. pressure. It was observed that in the first series of experiments the photographs taken at reduced pressures were all somewhat weak, and the tube for working at low pressures would probably be improved by being lengthened to render the absorption bands more distinct. The spectra were photographed on Cadett and Neale's spectrum plates, developed with ferrous oxalate, and cleared with a solution of alum acidified with nitric acid. Some few photographs were taken on "Rainbow" Warwick plates, the period of exposure being the same in each case, namely, two minutes.

The Measurement of the Spectra.

The plates were measured with a micrometer made many years ago by the late Mr. A. Hilger, the screw of which, according to my instructions, was made of platinoid, because this metal is rustless. The pitch of the screw is 100 turns to the inch. It carries a microscope made by Zeiss, which has fine definition and a flat field. The instrument is fitted on a stand tilted at an angle of 45° C. to facilitate prolonged observation through the microscope. Measurements to the 1/10,000th of an inch are easily made; but in the case of absorption bands this cannot always be accomplished, because it is difficult to determine, under the necessary magnification, where the bands begin and end. The wave-length at the edges on each side of a band were measured whenever they were broad enough and well-defined. In some cases two very narrow bands were seen so close together that the space between them could not be measured, and this explains why they have been assigned the same wave-length. In like manner, where a rather broad band ended and another commenced, it was found impossible to measure the two points with certainty, although an extremely narrow space could be seen between them. Each spectrum was measured twice independently, and the bands for the most part were described. For constructing an interpolation curve, the spectra of lead, tin, and cadmium were photographed with a very narrow slit and short exposure with a self-induction coil in circuit, by which means the spark lines were rendered sharp and narrow. But as the locus of the foci lies exactly in the same plane, the 18 lines of cadmium between Cd 17 and Cd 26 are alone sufficient, and latterly were adopted.

The linear dispersion on the original spectra is such that between Cd 17, λ 2748·68, and Cd 26, λ 2144·44, there are 2781·1 linear divisions of the micrometer scale = 2·7011 inches, which are equivalent to a difference of 604·24 Ångström Units between the above wave-lengths. The dispersion at the less refrangible end, Cd 17, increases from 3·3 divisions to 6·3 divisions for 1 Ångström Unit at the more refrangible end, Cd 26.

When the wave-length measurements had been tabulated in the usual manner, it appeared as if the bands in the different spectra of the same substance bore no relation to each other; accordingly, they were rearranged in four columns, so that obviously related bands or groups fell upon the same horizontal lines or thereabouts, and the changes in the spectra caused by increase of temperature or diminution of pressure are thus rendered obvious. Nevertheless, if the spectrum observed at pressure 759·5 mm. and temperature 12°·7 C. be compared with that taken at 778 mm. and temperature 11°·5 C., it will be seen that there is a considerable difference between them, which may roughly be indicated by the former conditions yielding 55 measurable bands, while the latter gives only 36. This is not to be accounted for by a difference merely in the quantity of benzene in the tube, as the following statement will show:—

The calculated weight of benzene in 79 c.c., the capacity of the tube—

	° C.		mm.	grm.
At	11·5	and	778	= 0·0175
„	12·7	„	759·5	= 0·0184
„	100	„	757	= 0·2021
„	100	„	4	= 0·0011

The tube used for different pressures was not the same, although of the same length; that for different temperatures being of glass, there may have been some reflection from the inner surface by which the absorption bands would be rendered less distinct, and this most probably is partly, if not entirely, the cause of the differences in the two series of spectra.

In the examination of other aromatic hydrocarbons the bronze tube was used, and such differences do not occur.

On the tabulated statement the wave-lengths of the bands measured by PAUER, FRIEDERICHS, and GREBE, are quoted for comparison.

The accuracy of the measurements compares favourably with those made by FRIEDERICHS and by GREBE, who employed a small concave grating of 1 metre radius, because, as I have previously shown, the separation of the lines of different refrangibilities, with a quartz spectrograph having only one Cornu's prism of 60° C., is very great in the ultra-violet, when the quartz lenses are not achromatised. The standard lines of reference were the wave-lengths of the cadmium spark spectrum determined by EDER and VALENTA.

There is evidence that the differences in the measurements of the bands in the different spectra observed by them are not due to inaccuracies, but to actual differences in the positions, or in the width of the bands; this arises from the different temperatures and pressures at which the several observations were made. Much more careful attention to atmospheric pressure and temperature becomes necessary when prolonged exposures extending from 1½ to 24 hours are made than when the period is only two minutes, but even under the latter conditions it is important.

On examining the various plates of spectra it was at once observed that, as the temperature rises, the bands which lie at the less refrangible end between λλ 2650 and 2700 (see Plates 32 and 33, figs. 1 and 5) become sharper and more intense; at the same time the bands in the more refrangible rays between λλ 2300 and 2500 become feeble, but this is because they are merged in a general absorption which weakens the emission spectrum. Pairs of bands in the less refrangible rays, which are so weak as to be barely visible at 25° C., become well defined and strong at 43° C. and 53° C. For examples, take the following. The measurements are recorded on each side of the bands when they are distinctly visible; the stronger edge of a group of bands is indicated by the thickened line of the angle.

At *t*	A band visible.	Only just visible.
12°·7 C.	╱2670 │2672	— 2631

At *t*	A band, sharp and strong.	A faint band.	A band just visible.
25° C.	╱2670 │2672	╱2661 │2664	╱2625 │2631

At *t*	A strong band.	A faint band.	A faint band.	A faint band.
43° C.	╱2669 ⎸ 2672	╱2660 ⎸ 2663	╱2629 ⎸ 2631	2625 —

At *t*	Four strong and well-defined bands.			
53 °C.	╱2669 ⎸ 2672	╱2661 ⎸ 2663	2631 —	╱2625 ⎸ 2626

There are likewise four feeble bands between wave-lengths 2260 and 2300, of which only one or two are visible at temperatures below 53° C.

The spectrum at 11°·5 C. and 21 mm. pressure is comparable with that at 12°·7 C. and 759·5 mm. bar. As the pressures increase, the temperature being constantly the same, gradual changes occur, as are seen, at constant pressure and increased temperatures up to 53° C. (Figs. 3 and 4, from 591 mm. to 88 mm., and from 67·5 mm. to 28·5 mm. pressure.)

Grebe observed a regularity in the differences between the wave-length of the bands, and he arranged them in twelve groups, seven of which are complete, and similarly constituted in that they contain in each group six bands. Of the five other groups, one contains five bands, and the others four in each group. An arrangement similar to that of Grebe fails to show such a relationship between the more numerous bands which I photographed; nevertheless, the very appearance of the photographs affords evidence of great regularity in their arrangement in similarly constituted groups of bands, which are separated by similar intervals. The reason of this is quite intelligible when the changes in each band and in the constitution of the groups brought about by changes of temperature are closely examined. The first group lies, for instance, between λλ 2589 and 2650; then there is an isolated band—or possibly it is a feeble narrow group—about λ 2670. The next group lies between λλ 2528 and 2560, the third between λλ 2469 and 2500, the fourth between λλ 2416 and 2430, the fifth between λλ 2365 and 2380, or thereabouts, but the termination is difficult to see, because of the general absorption which renders the last band less distinct. These groups, which were measured at 12°·7 C., are seen to be composed principally of a very strong band and one narrow and less strong, which order is repeated generally four times in the same group, then a weak band is seen lying close to the strongest, but on the more refrangible side. (See fig. 1, about λ 2540, at temperatures about 12°·7 C. to 53° C.) The bands diminish in intensity as the refrangibility decreases. The groups of vapour bands appear to be caused by the overlapping of two or more similarly constituted spectra differing in intensity. The bands described as strong which fall within this description number fifty-four, there being twenty-seven in each of the two spectra. In addition to these there are thirty feeble bands, which also fall into two series of similar groupings, but with less regularity. To render this evident they have all been mapped according to a scale of inverse wave-lengths, or oscillation frequencies, with the result that the entire number of bands observed between the limits of 12°·7 C. and 25° C., under a pressure of 759·5 mm., is resolved into four spectra (see map, p. 484), of which two are strong and two are weak.

The Spectrum of Toluene.

The specimen of toluene was obtained from Kahlbaum. It boiled with no variation at 111° C., with the barometer at 763 mm. Rise of temperature from 10° C. to 90° C. has very little effect upon the toluene spectrum (see fig. 5), that is to say, the constitution of the groups of bands in rays less refrangible than λ 2400 is scarcely altered, and the number of bands is not increased, they only widen, but the general absorption of the more refrangible rays increases, and the change is decidedly greater at 100° C. Variations in pressure at 11° C. likewise scarcely affect the bands (see fig. 6), but the alteration is chiefly in the rays more refrangible than λ 2300. It is very remarkable that the series of bands and their particular grouping, which is characteristic of the benzene molecule, is greatly modified by the very simple substitution of CH_3 for H. It was remarked by GREBE that the spectrum is quite different from that of benzene, but on careful observation of the different temperatures and pressures at which benzene and toluene have been photographed this is seen to be not quite correct. The different temperatures at which the spectra were photographed were 10°, 30°, 40°, 50°, 60°, 70°, 80°, 90°, and 100° C. (fig. 5), with a barometric pressure of 751 mm. This series shows to perfection that the general absorption gradually increases with the temperature. There is a very feeble absorption of the continuous rays by toluene at all pressures, the last line of cadmium, λ 2144, being quite cut off, and all lines more refrangible than wave-length 2471 are weakened.

The following grouping of the toluene bands shows every band measured from that substance. The numbers in brackets represent six bands observed by GREBE which do not appear on my photographs :—

I.	II.	III.	IV.	V.	VI.
2695	—	—	—	—	—
44	2689	—	—	—	—
2651	43	2687	—	—	—
29	2646	45	2682	—	—
2622	29	2642	45	2674	—
20	2617	26	2637	41	2670
2602	18	2616	26	2633	39
31	2599	22	2611	27	2631
2571	31	2594	21	2606	27
30	2568	36	2590	18	2604
2541	38	(*2558*) ?	—	(*2588*) ?	—
35	2530	37	—	35	—
(*2506*) ?	38	(*2521*) ?	—	2553	—
83	2492	40	—	—	—
(*2423*) ?	75	(*2481*) ?	—	—	—
48	2417	70	2471	—	—
2375	58	2411	63	—	—
—	2359	58	2408	—	—
—	—	2353	59	2397	—
—	—	—	2349	—	2391

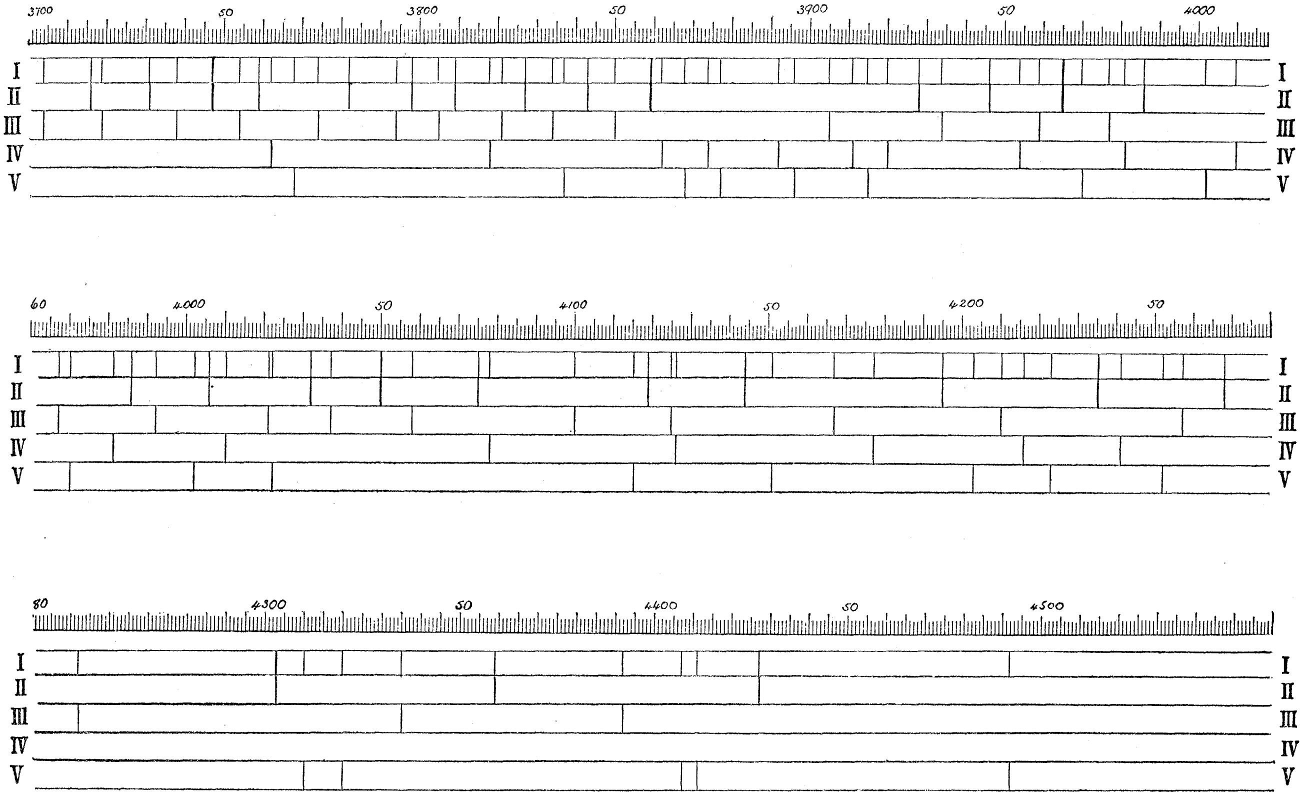
A regularity is apparent in the differences between the wave-lengths of the successive bands in the six different groups.

On the Relationship between the Bands of Benzene and Toluene.

It will be seen on comparing their measurements that, without being precisely similar, all the bands of toluene have corresponding bands in the benzene spectrum. Where the former are weak and the latter strong it might be supposed that a trace of benzene was contained in the toluene, but where both groups of bands are strong it is evident that they are common to both spectra, even when the bands show slight differences between the values of their wave-lengths. The principal difference lies in the most important groups of bands in the toluene spectrum being situated more in the direction of the red rays than the corresponding groups in benzene, but notwithstanding this shift of the bands to a less refrangible region which had long previously been observed in the spectra of solutions, a similarity in constitution is to be seen between certain groups of bands in toluene and others in benzene. Furthermore, both spectra have one very strong band in common; though this is best shown on the photographs, a tabulated statement of the measurements of the spectra also makes it apparent. The bands of toluene appear generally in pairs of similar intensity, while those of benzene are composed, as already stated, of one strong band and one slightly less strong. The pairs of the toluene bands diminish in intensity as they lie more towards the more refrangible rays, and if the individual narrow bands were brought closer together they would constitute a group scarcely distinguishable from one of the benzene groups. This suggests that the same vibratory motions are taking place

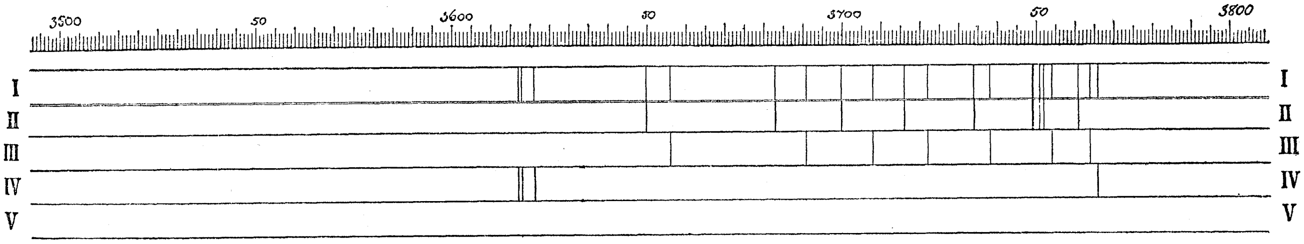
MAP OF ABSORPTION BANDS.

The Absorption Spectrum of Benzene Vapour Drawn to a Scale of Oscillation Frequencies and the Bands Divided into Four Series.



I. The whole spectrum.
II. First series, strong bands.
III. Second series, strong bands.
IV. Third series, weak bands.
V. Fourth series, weak bands.

The Absorption Bands in the Least Refrangible Rays Observed at Reduced Pressures varying from 206 mm. to 37 mm. at a temperature of 100° C.



within the benzene and the toluene molecules, but as the bands of toluene are shifted into rays of longer wave-length, or less oscillating frequency, and are more widely separated, this effect must be attributed to the weighting of the molecule by the addition of CH_2 to the benzene. To compare the spectra properly, benzene at 50° C. and toluene at 80° C. should be chosen, since both substances at these temperatures are 30° C. below their boiling-points.

Grebe has compared the ethylbenzene spectrum with that of toluene and found the bands of the one to be contained in the other.

The Homologues of Benzene and Toluene.

The principal homologues of benzene and toluene* were studied and their spectra measured and compared. The hydrocarbons were obtained on different occasions from Kahlbaum and were found to have the correct boiling-points. They were redistilled and their boiling-points taken immediately before being used. The following is a list of these substances. Their boiling-points were constant:—

		° C.		mm. bar.
Ethylbenzene	boiling-point	136·5	at	766.
Dimethylbenzenes, or *xylenes*—				
1 : 2 or *ortho*	,,	144	,,	763.
1 : 3 ,, *meta*	,,	138	,,	765.
1 : 4 ,, *para*	,,	138·5	,,	765.
Methyl-propyl benzene 1 : 4, or cymene . .	,,	177	,,	769.
Trimethylbenzene 1 : 3 : 5, or mesitylene .	,,	165	,,	758.

The leading features of the three xylenes, cymene, and mesitylene, at different temperatures and constant pressure, are spectra with comparatively few bands or groups of bands; they have not been reproduced and therefore a detailed description of the photographs is given. They are each distinguished by a most powerful absorption of all rays at elevated temperatures, extending from about λλ 2800 to 2340, but on lowering the temperature the rays between these limits are transmitted, at first only feebly, and more strongly subsequently. The highest temperatures at which the substances were examined are described first in each case.

Description of the Spectra.

Ortho-xylene vapour. (Table XII., p. 512.)

At 121° C.—Complete absorption commences abruptly at approximately λ 2800, which is so intense that the strong cadmium lines are extinguished. This absorption

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* See also Pauer, 'Wiedemann's Ann.,' 1897, 61, pp. 363–379; W. Friederichs, 'Zeitschr. f. Wissenschaftl. Photogr.,' 1905, vol. 3, p. 154; L. Grebe, *loc. cit.*, 1905, p. 363.

is continuous to about λ 2340. The three lines Cd λλ 2329, 2318·8, and 2288 are feebly transmitted.

At 100° C.—There is a sharp abrupt absorption commencing at λ 2748, which is complete until the group of lines λλ 2329 to 2265 is reached, and these are transmitted.

At 72° C.—The same absorption occurs, but is not abrupt and not so intense. The rays are feebly transmitted near λλ 2748, 2575, and as far as λ 2329.

At 45° C.—There is a complete, but feeble, transmission of all rays as far as λλ 2329, 2234·9.

At 20° C.—The same, but stronger, extending to λ 2194·7, which is feeble. A feeble band is seen near λ 2700.

Meta-xylene vapour. (Table XIII., p. 513.)

At 100° C.—There is almost a complete absorption which is not abrupt, from λλ 2700 to about 2350. Rays are transmitted from λλ 2350 to 2234.

At 70° C.—The rays are feebly transmitted from λλ 2680 to 2234, but a broad and weak band extends from λλ 2600 to 2500.

At 40° C.—The rays are well transmitted to λ 2194·7, but they are crossed by 12 groups of absorption bands.

At 11° C.—The rays are well transmitted, but with fewer bands.

Para-xylene vapour. (Table XIV., p. 514.)

At 100° C.—The spectrum is transmitted as far as λ 2802; beyond λ 2794 there is complete absorption to λ 2350. Bands are seen at λλ 2802 and 2800. Rays are transmitted at λ 2288.

At 70° C.—The same, but the bands are more distinctly visible.

At 40° C.—The spectrum is transmitted, except where the bands occur, as far as λ 2334·9.

At 10° C.—A similar spectrum, with the bands more conspicuous.

On comparing the spectra of the three xylenes (dimethylbenzenes) with that of benzene by inspection of the original photographs, the greatest similarity is seen between the *meta*-xylene and benzene in so far as the grouping of the bands is concerned, and the positions in which they are situated. There is also the fact that the bands in *meta*-xylene are well defined, like those of benzene. Some of the bands which are apparently common to the two substances are much reduced in width in *meta*-xylene, as, for instance, those at λλ 2609 and 2606, and those bands in the spectrum of *meta*-xylene which lie between λλ 2748·7 and 2575 fuse, or merge into one another rapidly as the temperature rises, and are rendered indistinct by an increasing general absorption. The correspondence of the one spectrum with the other is best seen by superposing one on the other; the groups are then easily identified.

Para-xylene has a spectrum which differs to some extent in constitution from that of *meta*-xylene. The groups of bands are situated in the same region as those in the *meta*-xylene; but bands appear in the *para*- at low temperatures which are seen only at higher temperatures in the *meta*-derivative.

The *para*-xylene shows a number of bands in the less refrangible region at higher temperatures which do not appear at all in the *meta*-xylene spectrum. In character the bands are more diffuse than in the *meta*-xylene, and not so sharply defined.

Ortho-xylene has an absorption spectrum which contains groups of bands similar to those in the *meta*- and *para*-isomers, but they are much more diffuse, and at first sight the spectrum bears but a slight resemblance to that of benzene.

Thus the similarity between the spectra of *ortho*-, *meta*-, and *para*-xylene and that of benzene is greatest with *meta*-xylene; it decreases with *para*-xylene, and is decidedly the least in the case of *ortho*-xylene. From the chemical point of view of position isomerism it is not easy to account for this difference, since it would rather be expected that either the *ortho*- or the *para*-xylene would most nearly resemble the ethylbenzene or toluene.

Ethylbenzene has a spectrum closely resembling that of benzene, and it occupies a position between toluene and *meta*-xylene, which is its natural position.

The spectra of ethylbenzene and toluene are almost identical, both as regards the number of bands and their wave-length; where a difference in wave-length occurs, the band in the ethylbenzene spectrum is generally somewhat shifted more towards the red than the corresponding toluene band, which again is to be attributed to the weighting of the molecule. Tables X. and XI., pp. 510, 511.

Ethylbenzene shows a much greater similarity to toluene than toluene does to benzene, the substitution of CH_3 for H in the side chain producing but a slight alteration in the spectrum.

A Comparison of the Absorption Spectra of the same Quantity of Benzene Vapour under Different Conditions as to Temperature and Pressure.

Photographic plate I., spectrum 1, fig. 1. (See Plate 32.)

The spectrum is produced by 0·0179 grm. of benzene at 12°·7 C. and 53 mm. of pressure.

Photographic plate III., spectrum 2. Not reproduced.

This is produced by 0·0179 grm. of benzene at 100° C. and 69 mm. pressure.

The two spectra differ widely; at 12°·7 C. the spectrum is divided into groups of well-defined absorption bands which extend through the region lying between wave-lengths 2700 and 2250. At 100° C. the positions of the different groups are still well defined, but the individual bands of the groups cannot be clearly distinguished, by reason of a general absorption overlying that portion of the photograph where the bands are seen to be the strongest at the lower temperature of 12°·7 C.

In addition to this change, a very strong and well-defined group of bands comes out clearly at the less refrangible end below wave-length 2575. These are seen in fig. 4 at 67·5 mm. and 22·5 mm. pressure and 100° C. Only the strongest band of this group appears at 12°·7 C. The principal differences observed between the benzene spectra at low and high temperatures with varying pressures may be summed up as follows:—At 100° C. the same quantity of benzene vapour produces greatly increased general absorption, extending over that part of the spectrum in which the groups of bands occur. At 100° C. the characteristic absorption is greatly increased at the less refrangible end of the spectrum, giving rise to a strong and well-defined series of bands, of which previously there had been only rudimentary indications. At 100° C. the bands have a peculiar sharpness, particularly those of the series less refrangible than wave-length 2575.

Benzene. (Fig. 1.)

The numbers of bands observed in the spectra at 759·5 mm. bar. and different temperatures, in a glass tube:—

° C.	Bands.	
At 12·7	55	
„ 25·0	84	
„ 43·0	82	The increased general absorption decreases the number of bands.
„ 53·0	56	

The numbers of bands observed at 11°·5 C. and different pressures, in a brass tube:—

(Fig. 2.)

mm.	Bands.
At 778	36
„ 483	38
„ 253	46
„ 21	44

The numbers of bands observed in the spectra at 100° C. and at different pressures:—

(*Not reproduced.*)

	mm.	Bands.	
Photographic plate I., No. 13.	At 683	9	A general absorption extinguishes many of the bands. There is a gradual increase, principally at the less refrangible end, in the number of bands on reduction of pressure.
	„ 589	13	
	„ 478	14	
	„ 381	16	
	„ 279	17	
	„ 172	18	

(Fig. 3.)

	mm.	Bands.	
Photographic plate II., No. 14.	At 767	5	A great general absorption extinguishes nearly all the bands, then a gradual increase in their number follows on reduction of pressure, the increase being at the less refrangible end of the spectrum.
	„ 591	9	
	„ 484	9	
	„ 332	12	
	„ 206	13	
	„ 142	11	
	„ 99	14	
	„ 88	15	

At 100° C. and different pressures :—

(*Not reproduced.*)

	mm.	Bands.	
Photographic plate III., No. 15.	At 92	25	At these reduced pressures there is a large increase in the number of bands; the principal groups of bands are all visible.
	„ 69	36	
	„ 43	50	

(Fig. 4.)

	mm.	Bands.	
Photographic plate IV., No. 16.	At 67·5	31	The barometer stood at 757 mm. There is a large and regular increase in the number of the bands on reduction of pressure as far as 15·5 mm. The effect of the general absorption and of the selective absorption is well seen. There is at pressures varying from 9 mm. to 4 mm. a gradual decrease in the number of bands on reduction of pressure, because, although the bands in the centre of the spectrum are visible, those at the less refrangible end, which at 767 mm. pressure are well seen, do not now appear, the quantity of substance being insufficient. In fact, there is at first a shifting of the general absorption towards the less refrangible rays, and subsequently the bands seen at this end are extinguished. The regularity in the variation of the spectra is obvious on photographic plates II. and IV. (Nos. 14 and 16).
	„ 52·5	54	
	„ 37·5	60	
	„ 28·5	72	
	„ 22·5	75	
	„ 15·5	88	
	„ 9·0	52	
	„ 5·0	38	
	„ 4·0	30	

In conclusion I have much pleasure in acknowledging the great care with which my assistant, Mr. A. G. G. LEONARD, A.R.C.Sc.I., has photographed and accurately measured all of the vapour spectra of benzene and its homologues under different conditions, and the precise account he has rendered of the numerous analyses of the vapours, which were performed in different ways.

TABLE I.—Absorption Bands in the Spectrum of Benzene Vapour at Different Temperatures and a Barometric Pressure of 759·5 mm.

Abbreviations :—s., strong ; f., feeble ; n., narrow ; v.s., very strong ; b., broad.

Well-marked groups of bands are indicated by /———— in the first column.

Similar bands, or groups, are indicated by the same Greek letters.

	12°·7 C. λ.	25° C. λ.	43° C. λ.	53° C. λ.	References.* λ.	
		2745 f.	2741 f.	2744 f.		
		40 f.	32 f.			
		36 f.	09 f.			
		2694 f.	2695 f.	2695 } f.	2694 F.	
				92 }		
		89 f.	89 f.	89 } f.	89 G.	
				88 }	88 F.	
				83 }	84 G.	
			81 f.	80 }	81 F.	FRIEDERICHS' 1st group.
	2678 }		78 }	78 }	78 G.	
	76 }	76 f.	75 }	75 }	75 F., 76 G.	
α	72 }	72 } s.	72 } s.	72 } s.	71 G.	
	70 }	69 }	69 }	69 }	70 G. F. & P.	
		66	67 } f.	67 } f.		
		64	64 }	64 }	65 G.	
		61 } f.	63 } f.	63 } s.		
		60 }	60 }	61 }	61 F.	
		58 f.		58 f.	59 G.	
		54 f.	55 v.f.		55 G.	
		50 f.	50	48	49 G.	
		45 f.	47 } f.	46	45 G.	FRIEDERICHS' 2nd group.
			44 }		43 G.	
	39 f.	39 f.	39 f.	40 } f.		
	36 f.	36 f.	37 f.	37 }	38 F.	
β			36 f.	36 } f.	37 G.	
	34 f.		33 f.n.	34 }	33 F. & G.	
	31	31	31 } f.	31 s.	31 F.	
		28	29 }	28 f.	28 G.	
			27 f.	26 } s.		FRIEDERICHS' 3rd group.
		25	25 f.	25 }	25 F. & G.	
	22 } s.	22	22 } f.	22 f.		
		21 }	21 }	20 } s.	20 G.	
		19 }	19	19 }		
	17 }	17	17 } s.b.	17 } s.b.		
	16 } s.				14 F. & G.	
		15 } s.				
γ	13 }	13 }	13 }	13 }	13 P.	
	12 } s.	12 } s.	11 } s.	11 } s.	10 P.	PAUER'S group I.
	08 }	08 }	08 }	08 }	09 G.	
	06	06	07 } s.	07 } s.	04 G.	
	05 } s.	05 } s.			03 F.	
	03 }	02 }	02 }	02 }	02 P.	

* P., PAUER ; F., FRIEDERICHS ; G., GREBE.

TABLE I. (continued).

	12°·7 C. λ.	25° C. λ.	43° C. λ.	53° C. λ.	References. λ.	
	2601 } s.					
	2599 }	2599 } s.	2600 } s.	2600 } s.		
γ	97 } s.	97 }	2597 }	2597 }	2598 F. & G.	
	93 }					
		96 } s.b.	96 } s.	97 } s.		
	90	91 }	91 }	91 }	93 P. F. & G.	
		89 f.	89 f.		88 F.	FRIEDRICHS' 4th group.
			85 f.	85 f.n.	87 G.	
				83 f.n.		
		81 f.	80 f.	81 f.		
				79 f.	78 G.	
	72	71 f.	71 } f.	72 }	73 G.	
			70 }	69 }	70 F. & P.	
	65 }	66 f.	67	67 f.	68 F., 66 G.	
	62 }	62 f.	63 } s.	62	64 F., 63 G.	
	61 }	60 f.	61 }	59	61 F.	
	59 }					
	58 } f.		60 } s.		58 G.	
		56 f.	57 }			
	54 }	54 f.	55	55	55 G.	
	53 } s.	53 } s.		54 }		
	52 }	52 }	52 } s.	51 }	53 G.	
δ			50 }		50 F. & P.	PAUER'S group II.
	51 } b.	50 } s.b.	49 } s.b.			
	46 }	47 }	46 }		47 G. & P.	
	43 n.	44 } s.b.	43 } s.b.		43 G. & F.	
	42 } s.	42 }				
	40 }		39 }			
	38 }	38 } s.b.	38 }		38 F.	
	35 }	34 }	35 }		37 G.	
	33 } s.b.	33 } s.b.	33 } s.b.		35 P., 34 G.	
	29 }	29 }	27 }	27	30 F.	
	28	28 } s.			28 P.	
	27 } f.	26 }			26 F. & G.	
		25 } f.	24 } s.b.	25 } s.		
	23 }	22 }	21 }	22 }		
		20 f.	20 } f.		20 G.	
			19 }	19		
	16 } f.	16 } s.	18 } s.	17 }	16 F.	
	13 }	13 }	12 }	12 }		FRIEDRICHS' 5th group.
	12 } f.		11 } f.		11 G.	
	09 }	08 f.	09 }	09	10 F. & P.	
			08 } f.		08 G.	
		06 f.	05 }	06		
	01 f.	01 } f.	02 } f.	01 } b.v.f.		
	2499	2499 }	2499 }		00 F. & G.	
η		98 } f.	99 } s.			
				2496 }	2497 P., 96 G.	
	96 n.	96 }	97 }			
			96 } s.		95 P.	
		94 } f.	94 }	94	94 G.	
			93 } s.			
		91 }		91		
	89 n.	91 } f.			89 G., 88 P.	PAUER'S group III.
	87	87 }	87 }			

TABLE I. (continued).

	12°·7 C. λ.	25° C. λ.	43° C. λ.	53° C. λ.	References. λ.	
		2486			2485 G.	
	2483					
		84 } b.	2484 } s.			
	82 } s.					
	81	80	79		81 F.	
	79	79 f.			79 G.	
θ	78 } s.		78 } f.		78 P.	
	77	77 f.				
			75			
	74 } s.b.	74 } b.	73 } f.		74 G., 72 P.	
	71	69	67		70 G. & F.	
	69 n.	69 n.			67 G. & P.	
	69 } f.					
	64	66	66 } s.		67 G. & P.	
		65	64		63 F. G. & P.	
	58 } f.	57 } s.	57 } s.	2457 } f.	58 F.	
	55	54	54	55	56 P.	
	53 f.		53 } f.		54 G.	
			51	52	51 F.	
			50 } f.			FRIEDERICHS' 6th group.
			47		48 G.	
	44 } f.	44 } f.b.	43 } b.		45 P.	PAUER'S group IV.
	43	39	38		38 G., 40 P.	
		37 f.	36 f.		36 G.	
	33 } f.	33 f.				
	31					
		30 f.			30 F. & G.	
ι	29 } f.					
	27	28 f.	27 f.		27 P.	
	26 } f.				26 G. & F.	
	24	24 f.	24 f.		23 G., 25 P.	
	20 } f.b.	20 f.	20 f.		20 F. & P.	
	18	18 } f.b.			19 G.	
	17 } s.		17 } b.			
	16				15 F.	
	15 f.	13	13			
	13 } f.	11 f.	11 } f.		12 G. & P.	
	09	10 f.	09	09 f.	08 F. & G.	
	02	03 } f.	03 } s.	03 f.	04 F.	
		00	00		00 G. & P.	
			2398 f.		2397 F.	
		2394 f.	94 f.	2395	94 G.	
		86 v.f.	91 f.		92 G.	
κ		85 v.f.	84 f.		88 F.	
		80 f.n.			81 F., 82 G.	
	2379 f.n.		77 f.		78 G., 77 P.	
	76	75 f.				
		73 f.			73 G.	FRIEDERICHS' 7th group.
			72 f.			
		69	68		70 G. & F.	
	65	64 } f.	65 } f.		62 P.	
		62	61		60 G.	
		58	58 f.		56 F., 57 G.	
		52				

TABLE I. (continued).

	12°·7 C. λ.	25° C. λ.	43° C. λ.	53° C. λ.	References. λ.	
			2349 v.f.		2347 G., 46 F.	
		2343	43 v.f.			
			42 f.		41 G., 37 F.	
			30	2330		FRIEDERICHS' 8th group.
		24	24 s.	25	28 F.	
				20	19 F.	
		08	07	15	08 F.	
			05	07	05 F.	
			2294	2295		
		2277		77		FRIEDERICHS' 9th group.*
				69	2270 F.	
			59	67	59 F.	
	2226			†		
	55 bands	84 bands	82 bands	56 bands		

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* In KAYSER'S 'Handbuch der Spectroscopie,' vol. III., p. 368, these bands are given as the beginnings of a probable 9th group.

† On the photographs several distinct and well-defined bands are seen here, but under the microscope they are too indistinct to be measured.

TABLE II.—Absorption Bands in the Spectrum of Benzene Vapour at 11°·5 C. and Different Pressures.

Abbreviations :—s., strong ; f., feeble ; n., narrow ; v.s., very strong ; b., broad.

	778 mm. λ.	483 mm. λ.	253 mm. λ.	21 mm. λ.		778 mm. λ (continued).	483 mm. λ (continued).	253 mm. λ (continued).	21 mm. λ (continued).
		2700 f.n.	2706 f.				2678*		2680*
		2695 } f.	2695 } f.			2676 f.	76 n.	78 }	78 }
		91 }	91 }	2691 n.			75 n.	75 }	75 }
		90 }	90	89 n.					75*
		88 }	85		α	71 } s.	71 } s.b.	71 } s.	71 } s.
		81 } f.	83 } f.	82 }		69 }	69 }	69 }	69 }
		78 }	80 }	80 }			67 }		

* A very narrow distinct band at each of these positions lies so close to the next band as not to be distinctly measureable. See pp. 478, 479.

Table II. (continued).

	778 mm. λ.	483 mm. λ.	253 mm. λ.	21 mm. λ.		778 mm. λ (continued).	483 mm. λ (continued).	253 mm. λ (continued).	21 mm. λ (continued).
		2666 } f.		2666 f.		2549 } f.b.		2547 n.	
	2663 } f.	63 } s.	61 } s.	61 }		45 }			
	60 }	59 }	60 }	59 }	δ	44 } f.b.	43 }	44 n.	
		58	53 f.n.	58			40 }		
		51 } f.	51 f.n.	51 } f.		39 }			
		47 }		47 }		38 } f.b.			
				47 } f.		34 }			
		44 f.		44 }		30 } f.b.	30		
		38 f.	40 }				29 }		
		36 f.	35 }	39 }		27 }		27	27
				37 }			26 }		
				36 }		25 } f.			
β			34 n.	34 }			24 }	24 } s.	24 }
		33 } f.		33 n.		22 }		22 }	22 }
		31 }	31 } s.	31 }			21 }		21 } b.
		30	29 }	30 }				19	19 }
		26 }	28 } s.	28 } f.		16 } f.			18 } s.
		25 }	25 }	25 }			15 }	14 } s.	16 }
				23 } f.		13 }		13 }	
		22 n.		22 }			11 }	11 } f.	
	21 }		21 } s.	21 } s.			10 } f.		09
	19 }	19 }	19 }	19 }	η	08	08 }	07 }	
	18 n.	18 }	18 } s.b.	17 }				07 } f.	07
	16 } b.	17 } s.b.		16 }		01		06 }	
				15 } s.		2496		2497	
	13 }	12 }	13 }	13 }		93 } v.f.			
γ	11 }	11 } s.b.	12 } s.b.	11 } s.		88 }			
	08 }	08 }	08 }	08 }		85 } f.			
	07 } s.b.	07 } s.b.	08 } s.	07 } s.b.		81 }			
	02 }	02 }	02 }	02 }		79 } f.			
	01 } s.b.	00 } s.b.	01 } s.	00 } s.	θ	77 }			
	2598 }	2597 }	2597 }	2597 }		75 } f.			
	97 } s.b.	97 } s.b.	97 } s.	96 } s.				72 } b.	
	91 }	91 }	91 }	91 }		70 }			
		90 } f.	89 n.	88				69 }	
		87 }				68 } f.		67 } b.	
	*87 } f.	87 } f.				64 }		64 }	
	87 }	85 }	85 n.	85		58 } f.		58 } b.	
		84 } f.			ι	55 }		55 }	
		82 }	82 n.	82		18 } f.		07 } b.	
		81		77		13 }		05 }	
	71	71 } s.b.	72 } s.	71 } s.		2377			
		69 }	71 }	70 }	κ	25			
	68	68 } f.		69 } f.					2334 n.f.
		67 }		67 }					26
	62 n.	63 } f.	63	65 } f.				2295 n.	24
	61 n.	62 }	62	62 }				79	
			60	60				68	
	59 } f.b.		56 n.	55			2277		2277
	55 }								
	53 } b.		52 n.						
	50 }		49 n.			36 bands	39 bands	46 bands	44 bands

TABLE III.—The Absorption Spectrum of Benzene Vapour, at 100° C. and Different Pressures, in a Column 150 mm. long.

Abbreviations :—f., feeble ; s., strong ; r.s., rather strong ; v.s., very strong ; n., narrow ; b., broad ; v.n., very narrow ; n.s., narrow, strong.

(Photographic Plate No. 1, 1906–7.)

683 mm. λ.		589 mm. λ.		478 mm. λ.		381 mm. λ.		279 mm. λ.		172 mm. λ.	
2743	f.	2741·5	f.	2719	r.s.	2719	f.	2717	v.f.	2703·5	f.
41		40		16		15		12	v.f.	00·5	f.
39	f.	38	f.	13	f.	12	s.	06	r.s.	2698	
36		19	r.s.	09·5		09·5		03		94	s.
26	f.	15		05·5	s.	05	s.	01	r.s.	91	
15		13	r.s.	03		03		2699		90	s.
14	f.	09		01·5	s.	00	s.	96	s.	86	
09		06	s.	2699		2697·5		92		82	v.s.
08	r.s.	03		96	s.	96	s.	90	s.	79	
03		00·5	s.	94		91		87		78	s.
02	r.s.	2697·5		91	s.	89	s.	84	v.s.	75	
2698		96	s.	88		87		80		72	s.
96	r.s.	91		85	s.	84	s.	78	s.	69	
91		90	s.	80		79		75		66	f.n.
90	r.s.	87		78	s.	78	s.	72	s.	65	f.n.
87		84·5	s.	75		75		68·5		62	v.s.
84	r.s.	79		73	s.	73	s.	66	n.s.	59·5	
79		78	s.	69		68		65	n.f.	58	f.n.
		75		66	n.s.	66	n.s.	63	v.s.	54	f.n.
		73	s.	65·5	v.n.	65	v.n.	59		52	f.n.
		68		63	s.	63·5	v.n.	58	f.n.	48	f.
		66	n.s.	59·5		62	s.	56	f.n.	44·5	f.
		64	f.	58	f.n.	59		2284·5	b.f.	2284	b.f.
		59·5		2277·5	f.	58	s.	77·5	s.	75·5	s.
				75		57		75		75	
						55	f.n.	74	f.n.	74	n.f.
						2277·5	f.				
						75					
9 bands		13 bands		14 bands		16 bands		17 bands		18 bands	

TABLE IV.—The Absorption Spectrum of Benzene Vapour, at 100° C. in a Column 150 mm. long, at Different Pressures.

Abbreviations :—f., feeble ; s., strong ; n., narrow ; n.f., narrow, feeble ; n.s., narrow, strong ; r.s., rather strong ; v.f., very feeble ; f.n., feeble, narrow.

(Photographic Plate No. 2, 1906–7.)

767 mm. λ.		591 mm. λ.		484 mm. λ.		332 mm. λ.		206 mm. λ.		142 mm. λ.		99 mm. λ.		88 mm. λ.	
2761	f.	2761	f.	2741	n.	2741	f.	2718	v.f.	2706	s.	2706	s.	2706	f.
57		57·5		40	n.	39		15		03		03		02	
56	f.	54	f.	19	f.	18	f.	13	v.f.	2699·5	s.	00	s.	00	r.s.
56		40	n.s.	15·5		14·5		09		97		2697		2697	
40·5	n.f.	39	n.s.	13	f.	13	f.	06	r.s.	94	s.	94	s.	94	s.
40	n.	38	f.	09·5		09		03		90		90		90	
37	f.	35		06	r.s.	06	r.s.	00	s.	88	s.	89	s.	88	s.
35		18	f.	03		03		2697		85		85		85	
		14		00	r.s.	00	s.	95	s.	83	s.	82·5	s.	82	s.
		13	f.	2697		2697·5		91		79		79		78	
		08		96	r.s.	96	s.	89	s.	78	s.	77	s.	77	s.
		07	f.	91		90		86		74		74		73·5	
		02		89·5	r.s.	89	s.	83·5	s.	71·5	s.	71	s.	71	s.
		01	f.	87		85·5		78		67		66		67·5	
		2697		83	f.	83·5	s.	77	s.	64	n.f.	64	n.f.	64	f.n.
				79·5		78		74		62	n.f.	62	n.f.	62	f.n.
						77	f.	72	s.	60	s.	60	s.	59	s.
						74		67		57·5		57		57	
						70	f.	64	n.f.	56	f.	56	v.f.	56	f.
						66		63·5	n.f.			53·5	v.f.	53	v.f.
						64	f.	60	s.			51	v.f.	52	v.f.
						59·5	f.	58				2275	f.	46	v.f.
								56	f.					2275	f.
5 bands		9 bands		9 bands		12 bands		13 bands		11 bands		14 bands		15 bands	

TABLE V.—The Absorption Spectrum of Benzene Vapour, at 100° C. and at Different Pressures, in a Column 150 mm. long.

Abbreviations:—f., feeble; n., narrow; n.f., narrow, feeble; s., strong; v.f., very feeble; v.s., very strong; r.s., rather strong.

(Photographic Plate No. 3, 1906–07.)

92 mm. λ.		69 mm. λ.		43 mm. λ.		92 mm. λ.	69 mm. λ (continued).		43 mm. λ (continued).	
2704	f.	2706	v.f.	2700·5	f.		2598	f.	2569·5	n.f.
03		03		2697			94		66	n.f.
00·5	f.	01	f.	96	f.		93·5	f.	64	f.
2698		2698		94			88		60	
95	r.s.	95	f.	89	f.		86	n.f.	59	f.
92		91		86·5			83	n.f.	55	
89	r.s.	89·5	f.	83·5	f.		79·5	n.f.	28·5	f.
86		87		81			76·5	f.	27	r.s.
82	s.	82·5	f.	77	f.		70	s.	25·5	
80		80·5		74			68		24	f.
77	r.s.	77	r.s.	71	s.		67	f.	21	
75		74		68			2325	s.	20	f.
71	v.s.	70	v.s.	65	n.f.		24		19	
69		68·5		63	n.f.		2298	v.f.	16	f.
66	n.f.	65	n.f.	60	f.		94		12	
61	v.s.	62	n.f.	58			77·5	s.	09	f.n.
59·5		59·5	r.s.	37	f.		76		2468	f.
58	n.f.	58		34					66·5	r.s.
55	n.f.	56	n.f.	33	f.				64	
53	n.f.	54	n.f.	32					57	r.s.
48	n.f.	52	n.f.	28	r.s.				54·5	
46	f.	48	n.f.	26					52·5	f.
42		37	r.s.	25	f.				52	
39	f.	35		24·5					13	f.
34		34	r.s.	23	f.				12	
2591	n.f.	32		21					11	f.
87·5	n.f.	30·5	f.	19	f.				09	
85	n.f.	28·5		17	s.				03	f.
83	n.f.	28	r.s.	16					2386·5	f.
78	n.f.	26		15	s.				82	
2324	v.f.	25		10					77	r.s.
00·5	v.f.	24		09	s.				75	
2295	v.f.	23		05					74	f.
85	f.	21		04	s.				72·5	
80		19	n.	2599					69	
77	f.	18·5	f.	97·5	s.				67	
		16		94					61	
		14	f.	93	s.				25	r.s.
		10		88					24	
		09	f.	85·5	n.f.				2277·5	f.
		05		83	n.f.					
		02	f.	78	n.f.					
		2599·5		77	n.f.					
25 bands							36 bands		50 bands	

TABLE VI.—Absorption Bands of Benzene Vapour, in a

Abbreviations :—s., strong ; v.s., very strong ; r.s., rather

(Photographic

67·5 mm. λ.		52·5 mm. λ.		37·5 mm. λ.		28·5 mm. λ.		22·5 mm. λ.	
2706	f.	2706	f.	2706	f.	2703	v.f.	2701	v.f.
03		02		03		2700	v.f.		
00	f.	00	f.	01	f.				
2697		2697·5		2698					
95	r.s.	95	f.	96	f.	2694·5	r.s.	2694	v.f.
91		91		92·5		91			
90	r.s.	89	r.s.	90	f.	89	r.s.	88	f.
87		87		87		86		77	f.
82·5	r.s.	83	r.s.	84	f.	84	v.f.		
81		80·5		81		81			
77	r.s.	77	r.s.	78	r.s.	77	r.s.		
74		74		74		75		71	s.
71	v.s.	71	v.s.	71	v.s.	71	v.s.	69·5	
68		68		68·5		69		66	f.
65	f.	65	f.	68	v.f.	66	v.f.	65	f.
61	s.			65		64·5	v.f.	64	r.s.
58		60	s.	64	v.f.	62	s.	60	
		58		62		59·5		59	f.
56	f.n.			61	s.	58	v.f.	45	f.
		56	f.n.	59		48	v.f.	36	
				57·5	v.f.	47	v.f.	31	r.s.
				56		39	r.s.	29	r.s.
47	f.n.	49	f.	55	v.f.	37			
45	f.n.			52		36	r.s.		
43	f.n.	41		50	v.f.	35		25	r.s.
				46		33·5	r.s.		
37	r.s.	37	r.s.	38	f.	31·5		22	n.f.
35		35		37		30	r.s.	21	r.s.
34	r.s.	34	r.s.	36	f.	29·5		19	
32		32		33		28	r.s.	17	r.s.
31	r.s.	31	f.	31	f.	26	r.s.		
30		29		29·5		24		16	v.s.
28	r.s.	28	f.	28·5	r.s.	22	s.	13	
27		27		28		18		11	n.s.
26	f.	26	r.s.	26	r.s.	16	v.s.	10	v.s.
		24·5		25		12		08	
21·5		23	r.s.	24·5	r.s.	10	v.s.	06	v.s.
		22		22		07		05	
		19·5	r.s.	19·5	f.	06	v.s.	04·5	v.s.
		17		19	r.s.	01·5		02	
		16	f.	16·5				01	v.s.
		15		15	s.	00	v.s.		
		14	f.	11					
		11		10	s.	2597		2598	
		09·5	r.s.	05·5		96	v.s.	96	v.s.
		05·5		05		91		92	

Column of 150 mm., at 100° C. and Different Pressures.

strong; f., faint; v.f., very faint; n., narrow; b., broad.

Plate No. 4.)

15·5 mm. λ.		9 mm. λ.		5 mm. λ.		4 mm. λ.	
2703	f.						
02	f.						
2698							
97	f.						
94							
91	f.	2692	v.f.				
88		88	v.f.				
77	f.	78	v.f.				
76		75				2676	v.f.
72	s.	72	f.				
71		71					
70	s.	70	f.			70·5	n.f.
69		69		2669	n.v.f.	70	f.
67	v.f.	67	f.				
65	v.f.	66		66	n.v.f.	66	f.
64	r.s.	61	v.f.				
60		59	v.f.			47	v.f.
39	v.f.	39	f.				
36		36					
31	r.s.	34	f.				
30		33					
30	r.s.	31	f.				
28		30					
28	r.s.	29					
25		26	f.				
24	f.	25					
22		23	v.f.				
22	r.s.	22					
19·5		21	r.s.				
18	n.s.	19					
16·5	n.s.	17	n.r.s.				
16	s.	16	v.s.	16	s.	16	r.s.
13		13		12		13	
11·5	n.f.						
11	s.	11	s.	10	r.s.	10	r.s.
08		08		07		08	
07	s.	07	s.	06	r.s.	06	r.s.
05·5		05		04·5		05	
04·5	v.s.	04·5	v.s.	04	s.	04	s.
03		02		02		02	
01	r.s.						
00		00	s.	00	r.s.	00	s.
2599	s.					2597·5	
98		2597·5		2597			
96	v.s.	94·5	v.s.	94	v.s.	94·5	v.s.
91		91		91		91	

TABLE VI.

67·5 mm. λ.		52·5 mm. λ.		37·5 mm. λ.		28·5 mm. λ.		22·5 mm. λ.	
					s.				
		2605	r.s.	2599·5		2588	v.f.	2589	v.f.
		00		99	s.	85	v.f.	86	v.f.
		2598	f.	95		84	v.f.	82	v.f.
		95		97	s.	71	r.s.	71	f.
		94	f.	91		69		68	f.
				90	v.f.	69	r.s.	65	f.
		88		88		66·5		63·5	
2586	f.n.	87	n.f.	87	v.f.	65	s.	63	s.
85	f.n.	84	n.f.	85		61		61	
84	f.n.	79	n.f.	83	v.f.	59·5	r.s.	59	n.r.s.
80	s.n.	77	n.f.	81·5	f.	59	s.	59	s.
77	f.n.	70	r.s.	79		55		55·5	
		68		72	s.	54	s.	54	n.r.s.
		67	f.	71		50		53·5	s.
		65·5		69	r.s.	50	s.	51	
				67		46		50	s.
				65·5	r.s.	43	s.	46	
				62		40		44	s.
				59	r.s.			40	
				56					
						38	r.s.	38	s.
						35		35	
						33	r.s.	33	s.
				30	f.	29		29	
						28	s.	27	r.s.
				27		27		24	r.s.
		24	r.s.	24	r.s.	24	s.	22	
		22		22		21		21	f.
		20	f.	21	f.	19	r.s.	19	
		18·5		19·5		17	r.s.	16	s.
		16	f.	16	r.s.	14	s.	13	
		12		13		12		11	f.
				10	f.	11	s.	08	
						08		07	f.
						06·5	r.s.	06	
								04	f.
								02	
								01	s.
						00·5	r.s.		
						2498			
						98	f.	2496	
						96		94	s.
						93·5	f.	91	
						90		91	s.
								86·5	
						88	f.		
						85			
						83	f.	83	s.
						81		78	
						80	f.		
						79			
						78	f.		
						76		78	s.
						73		77	

(continued).

15·5 mm. λ.		9 mm. λ.		5 mm. λ.		4 mm. λ.	
		2565	r.s.				
2562	n.r.s.	62					
60	n.f.						
59·5	f.	59	r.s.	2557	f.	2559	f.
56		55		55		55	
54	n.f.	54	n.f.				
54	s.	52	s.	52	f.	52	r.s.
51		51		50		51	
50	n.f.	49·5	f.				
49	s.	49	s.	49	f.	49	r.s.
46		46		46		46·5	
45	s.					44	v.f.
43		43	s.			42	
42	s.	41	v.s.	41	s.	41	s.
40		40		39		40	
39	r.s.						
38		38	s.	37	s.	37·5	n.r.s.
36	r.s.	35·5	s.	35	r.s.	35	n.r.s.
35		35		34			
33	v.s.	33	v.s.	32	v.s.	32	v.s.
29		29		28		29	
27	n.f.	27	f.	27	f.	27	v.f.
25	f.						
22							
21	f.						
19							
18	f.	14·5	v.f.				
12·5		13					
12	f.						
08							
07	f.						
06							
04	f.						
02							
01	f.	01	f.	01	f.		
2499		2498·5	f.	2499			
97	f.			98	f.		
96		96		97			
93	f.	93	f.	96·5	f.		
91		91		95			
90	r.s.			94	v.f.		
89		89	f.	92			
88	r.s.	87	r.s.	91	v.f.	2487	n.f.
87				90			
84	s.	83	s.	89	v.f.	83	f.
82		81		87·5		82	s.
81	s.			86	n.r.s.		
80				83·5	r.s.	80	
79	n.r.s.	78·5	n.s.	82			
78	s.	77	s.	81	s.	77	n.f.
76		76		79			

TABLE VI.

67·5 mm. λ.		52·5 mm. λ.		37·5 mm. λ.		28·5 mm. λ.		22·5 mm. λ.	
		2470	f.			2469	f.	2474	s.
								69	
						68	r.s.	68·5	n.s.
		67		2467	f.	67	r.s.		
		66·5	f.	65		64		65	f.
		64		63	f.	58	r.s.	58	s.
		62	f.	61		54		54	
		59		58	r.s.				
		57	f.	56					
		55							
						44	v.f.	45	s.
								39	
								39	s.
								30	
								28	s.
								26	s.
								24	
								22	s.
								19·5	
				18	f.	17	s.	18	v.s.
						13		15·5	
				13				13	s.
				10·5	f.	09·5	f.		
						06	f.		
		03	f.	04	v.f.	04		03	r.s.
		2396	f.	02		03	f.	00	
						01		2399	f.
								94	
						2390	f.	91	f.
				2385	v.f.	86		86	
						84	f.	85	f.
								83	
								81	f.
								77	
				77	v.f.			76·5	s.
						75	r.s.	75	
				73	v.f.	73	r.s.	74	r.s.
						72		72	
						70	r.s.	70	r.s.
2368·5	v.f.			67·5	r.s.	68·5		68	
62		66	f.			65	s.	66	s.
				63		64		62·5	
								62	f.

(continued).

15·5 mm. λ.		9 mm. λ.		5 mm. λ.		4 mm. λ.	
2473·5	v.s.	2475	v.s.	2477	s.	2472	s.
69		70		76		70	
68	n.r.s.			72	v.s.		
66·5	f.			69·5			
64·5							
57	f.	57	v.f.				
54		56					
54	f.						
52							
50	f.						
48							
45	f.						
40							
38	f.						
37							
36	f.						
33·5		31·5	v.f.	30	v.f.		
30	f.	29·5					
29	r.s.	29	v.f.	28·5		28	v.f.
27		26·5		28	v.f.	26·5	
26	r.s.	26	v.f.	26		26	v.f.
24·5		24		25·5	v.f.	24	
24·5	n.r.s.			24			
23							
22·5	r.s.	22	v.f.	22	v.f.	22	v.f.
21		19·5		19		19·5	
20	r.s.						
19							
18	v.s.	18	v.s.	17	v.s.	18	v.s.
15·5		15·5		15		15·5	
13·5	n.r.s.						
12	r.s.						
09							
07	v.f.						
04·5	v.f.						
01							
2396	v.f.						
90	v.f.						
89	f.						
87							
86	f.						
84							
82	f.						
81				2381	f.		
77·5	v.f.	2377	r.s.	79			
75·5	r.s.	75		78	f.		
75				77			
74	r.s.			76	r.s.		
72				75·5			
70	f.						
68·5							
66	r.s.	65	f.	64·5	f.b.	2365	v.f.
62		63					
60				59	f.		

TABLE VI.

67·5 mm. λ.		52·5 mm. λ.		37·5 mm. λ.		28·5 mm. λ.		22·5 mm. λ.	
				2361	r.s.	2360	f.	2360	f.
		2358	f.	58		58		58	
				58	r.s.	53	f.	54	f.
				56		49		49	
2354	v.f.	54	f.	54	b.r.s.	26	v.s.	25·5	s.
		49·5		49		24		24	
		46	f.	47	r.s.				
		43		44					
		40	f.	37	f.				
		37	f.	33·5				2277·5	r.s.
		34	f.	25·5	v.s.			77	
26	s.	26	s.	24		2266	r.s.		
24		24·5		03	v.f.	63			
20	r.s.	20·5	r.s.	2295·5	v.f.	59·5	s.		
18		18		86·5	v.f.	59			
		05	f.	82·5					
01	f.	01	f.	77·5	r.s.				
		2298	f.						
2295·5	f.	95·5	f.						
86	r.s.	87	r.s.						
82		82·5							
79	s.	78							
77		76							
31 bands		54 bands		60 bands		72 bands		75 bands	

(continued).

15·5 mm. λ.	9 mm. λ.	5 mm. λ.	4 mm. λ.
2356·5 } r.s. 54 49·5 } v.f. 45·5 44 } s.		2355 52 } v.f.	
2259·5 f.			
88 bands	52 bands	38 bands	30 bands

TABLE VII.—A Comparison of the Intensity of the Absorption Bands in the Vapour-Spectrum of Benzene (i.) at 100° C. and Different Pressures, and (ii.) at Temperatures below its Boiling-point, and Constant Pressure.

Strong bands and groups are indicated by one line, very strong by two lines, on the margin of the Columns I. and II.

Abbreviations:—f., feeble; s., strong; v.s., very strong; n., narrow; b., broad; v.f., very feeble; n.s., narrow strong.

I. λ.		II. λ.		I. λ.		II. λ.		I. λ.		II. λ.	
		2757	f.	2587	f.	2587·5	f.n.	2437	f.	2437	f.
		56	f.		A pair	86	f.n.	33	f.	33·5	f.
		54	f.	85	f.	85	f.n.	30	f.	30	s.
2744	f.			83	f.	83	f.n.	28	f.	28	s.
40	f.	40	f.	81	f.	80	s.	24	f.	24	s.
36	f.	36		79	f.	78	f.n.			23	s.n.
32	f.			77		76·5	f.n.	20		21	s.
		15	s.	69		68	s.	18	f.	19·5	s.
09	f.	09	s.	67	f.	66	n.f.			15·5	v.s.
06	f.	03	s.	61	s.	60	f.	13	s.	13	s.
		2698	s.	57	s.	55	f.	09	f.	09	s.
2691	f.	91	s.	54	f.	54	s.			07	v.f.
89	f.	87	s.	51	s.	50	s.	00	s.	00	s.
80		79	v.s.	46	s.	46	s.	2394	f.	2394	f.
75		75	s.	44	n.f.	43	s.	86	f.	86	f.
69	s.	68	s.			40	s.	84	f.	83	f.
66	f.	66	f.n.	39	s.	38	s.	79	f.	77	f.
64	f.	64	f.n.	34	s.	35	s.	75	f.	75	s.
		62		29	s.	29	s.	72	f.	72	s.
60	s.	59	v.s.	26	s.	27	s.	68	f.	68	s.
58	f.	58	f.n.	22	s.					62·5	s.
54	f.	55	f.n.	21	f.	21	f.	61	f.	62	f.
50	f.	52		19	f.	19	f.	58	f.	58	f.
47	f.	48	f.n.	12	s.	12	f.	52	f.	52	v.f.
44	f.	44·5	f.	09	f.	09	f.	49	v.f.	49	v.f.
36	f.			05	f.	06	s.	43	f.	44	s.
34	n.	34	s.	01	f.	02	f.	30	f.	33·5	f.
33	s.			2499	s.	2498	s.	24	f.	24	s.
31	f.	32	s.	96	s.	96	f.	20	n.s.	18	s.
28	f.	28·5	f.	94	s.	92	v.f.	15	f.		
25	s.	26	s.	91	f.	90	f.	07	f.	05	f.
		24	f.	87	s.	87	v.f.			01	f.
21	f.	21	f.	86	n.f.	85	f.	2294	f.	2295	v.f.
19	s.	19	n.s.	81	s.	81	f.			82	s.
17	s.	17	s.	79	f.	79	f.	77	f.	77	s.
13	s.	13	v.s.	77	s.	76	f.	69	f.		
		11	s.	69	s.	69	f.	67	f.	63	s.
08	s.	08	v.s.	69	n.	68	s.	59	f.	59·5	f.
06	f.	05	v.s.	64	s.	64	s.	26	n.f.		
02	s.	02	v.s.	54	s.	54	s.				
2597	s.	2598	v.s.	52	f.	52	f.				
91	s.	92	v.s.	47	f.	48	f.				
89	f.	88	s.	39	f.b.	39	s.				

Observations.—From Table VII. it is at once seen that the absorption bands at 100° C. are almost identical with those at lower temperatures. At 100° C., however, the series of bands in the region near λ 2700 develops strongly, and the bands show a peculiar sharpness and definition; this series at lower temperatures is very ill defined, and the bands themselves appear feeble. There are many bands which appear faint in Column I. which are strong in Column II., and *vice versâ*; this change is not restricted to any one particular region of the spectrum, but extends throughout. As a rule, however, the strongest bands in the one column are the strongest in the other.

It has already been noted in the record of the spectrum of benzene vapour at temperatures below its boiling-point, that bands sometimes appear so close together that a separate measurement of each is impossible; at 100° C., on the other hand, these pairs are frequently so split up that each band is easily measurable, as, for instance, λ 2587, Column I., is a close but feeble pair; in Column II. it becomes λ 2587·5 and 2586, both being feeble and narrow.

TABLE VIII.—Absorption Bands in the Spectrum of Toluene Vapour at Different Temperatures and Constant Pressure of 751 mm.

Abbreviations:—s., strong; f., feeble or faint; n., narrow; v.s., very strong; b., broad; v.b., very broad.

Corresponding groups of bands are indicated on the different toluene spectra by the same Greek letters.

	10° C. λ.	30° C. λ.	40° C. λ.	50° C. λ.	60° C. λ.	70° C. λ.	80° C. λ.	90° C. λ.	100° C. λ.
	2689 f. 82	2689 f. 82 f.	2682 75	2690 f. 87 f. 83 s.	2689 f. 82 s.	2688 f. 82 f.	2690 f. 88 f. 84 f.	2695 f. 90 f. 85 f. 82 s.	2695 f. 90 88
α	79 75 } f. 73 70 } s.	79 74 } f. 72 70 } s.	72 70 }	78 75 } s. 72 70 } s.	78 73 } s. 72 70 } s.	77 75 } s. 72 70 } v.s.	78 75 } s. 72 70 } s.	77 74 } s. 71 69 } v.s.	84 82 } s. 78 74 } s. 72 70 } s.
		51 43 } v.f.	51 42 } f.	54 42 } f.			51 f.b. 45 f.b.	51 42 } v.f.	51 42 } v.f.
β	41 38 } s. 36 34 } s.	41 38 } s. 35 33 } s.	40 37 } s.	40 37 } s.	40 37 } s.	40 37 } s.	41 40 } s. 37 33 } s.	40 36 } s. 35 33 } s.	41 36 } s. 35 33 } s.
		31 f.		11 f.			31 f.	10 f.	

TABLE VIII. (continued).

	10° C. λ.	30° C. λ.	40° C. λ.	50° C. λ.	60° C. λ.	70° C. λ.	80° C. λ.	90° C. λ.	100° C. λ.
	2610 } s.	2608 } s.	2608 } s.	2608 } s.	2608 } s.	2609 } s.	2608 } s.	2608 } s.	2607 } f.
	07 }	06 }	06 }	06 }	06 }	06 }			
γ	06 } n.	05 } s.	05 } s.	05 } s.	05 s.	05 s.	05 }	05 }	
	05 }	04 }	04 }	04 }			05 } s.	05 } s.	03 }
		02 } f.					04 }	03 }	
		2599 }			00 } s.				
	2596 } s.	96 } f.							
	94 }	94 }							
δ	91 } s.	91 } s.	91 } s.	91 } s.	2591 }				
					90 } s.				
	89 }	89 }	89 }	89 }	88 }				
	72 f.	71 f.	72 } f.	71 f.	71 f.	71 f.	71 f.	70 f.	71 f.
	69 f.	68 f.	68 }	68 f.	68 f.	69 f.	68 f.	68 f.	68 f.
	54	54 f.	54 f.	53 f.	53 f.		53·5 f.	53 f.	53 f.
	44 } s.	43 } s.		46 } s.	45 } s.	46 } s.	46 } s.	43 } f.	
	42 }	41 }	41 s.	41 }	41 }	41 }	41 }	41 }	
η	33 } s.	33 } s.	33 } s.	34 } s.	33 } s.	33 } s.	33 } s.	33 } s.	34 } f.
	32 }	30 }	30 }	30 }	30 }	30 }	30 }	29 }	30 }
					27 f.				
θ	2474 } s.	2474 } s.	2474 } s.	2474 } s.	2473 } s.	2474 } s.	2774 } s.	2474 } s.	2473·5 } s.
	71 }	71 }	71 }	71 }	71 }	71 }	71 }	71 }	71 }
		20 f.	20 f.	20 f.	23 } f.	24 } f.	24 } f.	24 } v.f.	24 } v.b.
					17 }	17 }	18 }	13 }	
					11 f.		11 } b.v.f.		
								09 f.	
					03 } v.f.				
					2397 }	01 } v.f.			
								03 } v.b.f.	
						2391 }	2391 }		
					81 } v.f.	82 } v.f.	83 } v.f.		
					75 }	75·5 }	75 }		
					59 f.	59			
					2355		2353 f.		
								2342 }	
						2349 v.f.			
									2328 }
	16 bands	20 bands	14 bands	18 bands	22 bands	17 bands	22 bands	21 bands	16 bands

TABLE IX.—The Absorption Spectrum of Toluene Vapour at Different Pressures and Constant Temperature of 11° C.

Abbreviations :—s., strong ; f., feeble or faint ; v.f., very feeble ; b., broad.

Corresponding groups of bands are indicated on the different toluene spectra by the same Greek letters.

	763 mm. λ.		563 mm. λ.		371 mm. λ.		174 mm. λ.		43 mm. λ.	
	2695	f.								
	88	f.			2688	f.				
	84	f.			84	s.				
			2682	f.	82					
							2681	f.	2681	f.
	75	f.	75	f.	76	s.			75	f.
					73		73	f.	73	
α	72	s.	72	s.	72	v.s.	72	s.	72	f.
	70		70		70		69		69	
	51	f.								
	46	f.			46	f.				
	41	s.	39	s.	43					
β	36		36		39	s.	39	s.	39	s.
	35	s.	35	s.	37		36		36	
	33		33		35	s.	34	s.	34	s.
			30	v.f.b.	30		32		31	
					29	f.				
	22	f.	22		22					
	19		21	f.	20	f.			20	f.
			18		17		19	f.	17	
					16	f.	16		08	f.
	08	f.	07	s.	07	s.	07	f.	07	f.
	06		05		05				05	
γ	05	f.	05	s.	04	s.				
	03		02		02		02		02	f.
	2594	f.	2595	f.	2595	f.	2594	f.		
δ	91		90		91				2591	f.
	90	f.	89	f.	90	f.	90			
	87		87				89	f.	89	f.
					87		87		87	
					76	f.	70	f.	70	f.
					68		67	f.	67	f.
							59	f.		
			54	f.			54			
	41	f.	52		52	f.b.	52	f.	52	f.
	38		43	f.						
η	33	s.	38							
	30		30		31		30	f.		
θ	2471	f.	2471	s.	2471	f.	2470	f.	2470	f.
	19	f.	19	f.						
	18 bands		16 bands		17 bands		15 bands		15 bands	

TABLE X.—Absorption Bands in the Spectrum of Ethylbenzene Vapour at Different Temperatures and Constant Pressure.

Abbreviations:—s., strong; b., broad; f., feeble or faint; v.s., very strong.

(Photographic Plate 5*a*, 31.5.06.)

Corresponding groups of bands are indicated in the different spectra by the same Greek letters.

	16°·5 C. λ.			40° C. λ.			70° C. λ.			100° C. λ.	
α	2673			2681	f.		2681	b.		2716	s.
	72			78		α	77			13	
	70		α	75	s.b.		73	s.		10	s.
	67			67			67			06	
	41	s.		57	f.b.		52	b.			
β	39			43			45				
	37	s.	β	40	f.	β	42	f.			
	35			39			34				
New ϵ	33	s.	ϵ	36	f.	ϵ	33	f.			
	32						29	f.			
	31	s.		30	f.						
	28			29							
	09	f.		25							
γ	07										
	06	s.	γ	06	f.						
	05										
New ζ	03	s.									
			ζ	02	f.						
	01										
	2597	v.s.									
			δ	2596	f.						
δ	94										
	93	b.		72	b.						
	86			64							
New ι	84			62	f.						
	82			59							
	71	f.b.		56	f.						
	63			51							
	45	s.	η	46	f.						
η	43			43							
	40	s.		40	f.						
	38			35	f.						
	35	s.		2480	f.						
	32		θ	76							
θ	2476	s.		73							
	73			22	f.						
	20			20			2420	f.			
	18			19							
	2379	n.		2379·5	n.		2379	n.			
	19 bands			18 bands			8 bands			2 bands	

NOTE.—In the above spectra there is an intense general absorption between λλ 2678 and 2329; the powerful line, Cd 18, λ 2573 being quite blotted out. The absorption increases in intensity with rise in temperature, until at 100° C. all but two bands have disappeared.

A distinguishing feature in this spectrum is the appearance of four new bands: λλ 2632–33 s., 2628–31 s., 2601–03 s., and 2582–84. They do not occur in the spectra of either benzene or toluene.

TABLE XI.—Absorption Bands in the Spectrum of Ethylbenzene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—s., strong ; b., broad ; f., feeble or faint ; v.s., very strong.

(Photographic Plate 5*b*, 5.9.06.)

	20° C. λ.			36° C. λ.			52° C. λ.		71° C. λ.		100° C. λ.
α	2671	s.	α	2671	b.s.	α	2689	f.	2421	f.	
	69			63			81		15·5		
	69	s.	β	40	f.		78	s.b.	12	f.	Complete absorption of all rays between λλ 2716 and 2331. Cd 18 not visible.
	67			36			63		02		
	66	n.		35	f.		58	b.v.f.	2366	v.f.	
β	40	f.	New ε	32			23				
	36			31	s.		18	v.f.			
	35	s.		25			17				
	33			20	f.		2365	v.f.	Cd 18 very faintly seen through the general absorption extending from λλ 2654 to 2475.		
New ε	31	s.b.		18							
	14		γ	16	f.b.						
γ	05	s.		02			General absorption very strong on either side of Cd 18, this line being very faintly visible.				
	03			01	f.						
	02	s.	δ	2598							
δ	2599			94	s.						
	97	n.f.		91							
	95	s.	η	53							
	91			47							
New ι	88	v.f.		45	s.						
	84			40							
	82	v.f.		38	s.						
	80			35·5							
	54	f.		31	s.						
η	49			29							
	43	s.	θ	2472							
	41			70							
	38	s.		18	s.						
	35·5			16							
	32	s.		2363	v.f.						
	30										
θ	2473	s.									
	71										
	18	f.									
	17										
	2365	v.f.									
	17 bands			15 bands			5 bands		3 bands		

The bands of the ε group are difficult to measure because they become merged into one broad band by the over-lapping general absorption at temperatures above 40° C. See Table X.

TABLE XII.—Absorption Bands in the Spectrum of Orthoxylene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—s., strong ; f., feeble or faint ; b., broad.

(Photographic Plate 6, 1.6.06.)

20° C. λ.	45° C. λ.	Observations on the spectra at higher temperatures.
2696 ⎫ s.	2710 ⎫ b.s.	At 72° C. All rays were transmitted as far as λ 2738, and absorbed from λ 2738 to 2497. From λ 2497 they were again transmitted to 2243, but very feebly to λ 2332. At 100° C. Rays transmitted to λ 2738. An intense absorption continued from λ 2738 to 2421. Rays were transmitted from λ 2421 to 2265. At 121° C. Rays were transmitted to λ 2800, and intensely absorbed from λ 2749 to 2332. They were transmitted again from λ 2332 to 2269.
94 ⎭	2695 ⎭	
91 ⎫ s.	95 ⎫ s.	
90 ⎭	94 ⎭	
89 ⎫ s.	91 ⎫ s.	
84 ⎭	89 ⎭	
60 ⎫ s.	87 ⎫ s.	
58 ⎭	83 ⎭	
57 ⎫ s.	78 ⎫ f.	
52 ⎭	77 ⎭	
50 ⎫ s.	71 ⎫ f.	
47 ⎭	66 ⎭	
42 ⎫ f.	63 ⎫	
39 ⎭	60 ⎭	
36 f.	59 ⎫	
19 f.	56 ⎭	
12 ⎫ s.	52 ⎫	
09 ⎭	50 ⎭	
08 ⎫ s.	47 ⎫	
05 ⎭	45 ⎭	
02 ⎫ s.	44 ⎫	
01 ⎭	42 ⎭	
2597 ⎫ f.	41 ⎫	
94 ⎭	39 ⎭	
91 ⎫ f.	36 ⎫	
86 ⎭	33 ⎭	
72	30	
71 ⎫ f.	19 f.	
69 ⎭	16 f.	
63 f.	01 f.	
61 f.	2594 f.	
52	84 f.	
49 ⎫	70	
46 ⎭	59 f.	
45 ⎫		
42 ⎭		
40 ⎫		
38 ⎭		
26		
23 bands	21 bands	

TABLE XIII.—Absorption Bands in the Spectrum of Metaxylene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—s., strong ; f., feeble ; b., broad ; v.b., very broad ; n., narrow.

(Photographic Plate 7, 30.3.06.)

11° C. λ.		40° C. λ.				70° C. λ.		100° C. λ.	
2713	} b.	2673	}			2689		2732	}
08		71				79	} v.b.	26	
05	} b.	70	}			65		19	f.
2698		68				60	} v.b.	16	} f.
94	} f.	67	}			28		10	
89		64							
44	}	51	}			2420	}		
42		45				18			
36		42	}						
34	}	39				2366	}	2368	}
28		36	}			64		64	
09	n.	34				26		26	
06	n.	32							
03	}	30	}						
01		28							
2597	} s.	25				Between λλ 2612 and 2504 there is a strong absorption band.		Between λλ 2652 and 2429 there is intense absorption. The rays from λ 2429 to 2241 are transmitted.	
95		22		2481					
44	} n.	19		78					
43		18	}	74	} s.				
38	f.	16		71					
34	} s.	13	}	32					
32		10		29					
06	n.	08	}	22	n.				
01	n.	04		20					
2498	} f.	02	}	19	} s.				
94		2599		17					
94	n.	97	} s.	2379					
90	n.	94		77		7 bands		6 bands	
84	n.	90	f.	67	}				
82		83	}	64					
79		78							
75	} s.	57							
73		54	}						
71		52							
22	n.	51	}						
19	}	49							
18		46	}						
		41							
		40	}						
		37							
		35	} s.						
		30							
		27							
		04							
		01	n.						
2377	}	2491	n.						
75		89	n.						
		83	}						
26 bands		82		41 bands					

It is a distinguishing feature of the bands in the metaxylene vapour spectrum that all more refrangible than λ 2600 are narrower and better defined than those in paraxylene, and again the bands in the latter are better defined and less diffuse, although broad, than those in the spectrum of orthoxylene.

TABLE XIV.—Absorption Bands in the Spectrum of Paraxylene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—s., strong ; f., feeble or faint ; b., broad ; n., narrow ; s.b., sharp, broad ; s.n., sharp, narrow ; f.n., faint, narrow ; f.b., feeble, broad.

10° C. λ.	40° C. λ.	70° C. λ.	100° C. λ.
2747 } b. 39 } 38 } b. 32 } 30 } b. 26 } 19 } f.b. 14 } 00 f. 2688 78 } s.b. 70 } 68 s.n. 65 } b. 54 } 52 } b. 47 } 45 } 44 } 42 } 41 } 34 33 } 30 } 24 f. 22 } 19 } 18 } 15 } 12 n. 06 } f. 02 } 2599 n. 97 } b. 88 } 87 n. 66 } f. 62 } 60 n. 54 } f. 52 } 41 } b. 37 } 36 } f. 34 } 33 } f. 32 } 16 } f. 07 } 00	2747 } b. 39 } 38 } b. 32 } 30 } b. 26 } 22 } f. 19 } 16 } b. 12 } 09 } 06 } 02 } b. 2698 } 94 } b. 85 } 83 n. 81 n. 78 } b. 69 } 68 n. 65 } b. 55 } 52 } b. 47 } 42 } 40 } 35 f. 31 f. 25 n. 23 } b. 19 } 19 } b. 14 } 12 } 11 } 2597 } b. 87 } 85 n. 62 f. 60 f.	2791 } b. 84 } 77 n. 73 } b. 68 } 66 n. 63 } b. 50 } There is intense absorption from λ 2762 to 2416. The rays from λ 2416 to 2265 are transmitted. Hence the above is an intense and very broad absorption band.	2802 f.n. 00 } f.b. 2795 } 94 } b. 85 } 83 } f.b. 78 } 77 } 69 } 66 n. 65 } 52 } There is an intense absorption band from λ 2790 to 2416. The rays from λ 2416 to 2288 are transmitted.
30 bands	25 bands	6 bands	8 bands

Table XV.—Absorption Bands in the Spectrum of Cymene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—f., feeble ; b., broad.

17°·5 C. λ.	40° C. λ.	70° C. λ.	100° C. λ.
Weak bands not easily measured	2719 13 f.	2720 15 b.	2726 13
	2676 72 f.	14 08 b.	12 07
	69 61 f.	2677 73 b.	2676 72
	58 42 f.	69 61 b.	68 60
	38 32 f.	60 53 b.	58 52
	28 21 f.	49 42 b.	38 34
	2592 81 f.	38 34 b.	32 24
		28 19 b.	2599 93
		2591 87 b.	91 84
	7 bands	9 bands	9 bands

All rays beyond λ 2580 are completely absorbed.

Table XVI.—Absorption Bands in the Spectrum of Mesitylene Vapour at Different Temperatures and Constant Pressure.

Abbreviations :—f., feeble ; v.b., very broad.

18°·5 C. λ.	45° C. λ.	72° C. λ.	100° C. λ.	120° C. λ.	140° C. λ.
2717 12 f.	2717 12 f.	2717 12 f.	2737 07 f.v.b.	Very feeble throughout.	All rays absorbed beyond λ 2749
09 05 f.	09 06 f.	12 06 f.			

All rays beyond λ 2705 are completely absorbed.

TABLE XVII.—Similar Groups of Absorption Bands which occur in the Vapour Spectra of Benzene, Toluene, Ethylbenzene, and the three Isomeric Xylenes.

Benzene and Toluene are compared at ordinary temperatures, and also at 30° C. below their respective boiling-points, at atmospheric pressures.

Abbreviations :—s., strong ; f., feeble ; n., narrow ; b., broad ; v.s., very strong.

	Benzene. 12°·7 C. λ.	Toluene. 10° C. λ.	Benzene. 50° C. λ.	Toluene. 80° C. λ.	Ethyl-benzene. 20° C. λ.	*o*-Xylene. 20° C. λ.	*m*-Xylene. 11° C. λ.	*p*-Xylene. 10° C. λ.
			2690 } f.	2690 f.				
			88 }	88 f.				2688
			80	84 f.				
	2678 } b.	2679 } f.	78 } f.	78 } s.				78 } s.b.
α	76 }	75 }	75 }	75 }				70 }
	72 } s.	73 } s.	72 } s.	72 } s.	2670 } s.			
	70 }	70 }	70 }	70 }	67 }			
				51 f.b.				
				45 f.b.			2644 }	
		41 } s.	40 } f.	41 } s.	41 } s.	2642 } f.	42 }	42 }
	39 f.	38 }	37 }	40 }	39 }	39 }		41 }
β	36 f.	36 } s.	36 } f.	37 } s.	37 } s.	36 f.		
	34 f.	34 }	34 }	33 }	35 }			33 }
	31 f.		31 s.	31 f.				30 }
	12 } s.	10 } s.	11 } s.	08 } s.	09 } s.	12 } s.	09 n.	
	08 }	07 }	08 }	05 }	07 }	09 }		
	06	06 } s.	07 } s.	05 } s.	06 } s.	08 } s.		
γ	05 } s.	05 }	02 }	04 }	05 }	05 }	06 n.	06 } f.
	03 }							02 }
			00 } s.	2595 } s.	2597 } v.s.	2597 } f.	2597 } s.	2597 } b.
	2597 } s.	2596 } s.	2597 }	93 }	94 }	94 }	95 }	
δ	95 }	94 }						
	90 s.	91 } s.	97 } s.	90 } s.	93 } b.	91 } f.		
		89 }	91 }	88 }	86 }	86 }		88 }
	72 f.	72 f.	69 f.	71 f.		71 } f.		
			67 f.	68 f.		69 }		
			51 f.	53·5 f.				
	43 n.							
	42 } s.	44 } s.		46 } s.	45 } s.	45 }	44 } n.	
	40 }	42 }		41 }	43 }	42 }	43 }	
η					40 } s.			
					38 }			
	33 } s.b.	33 } s.		33 } s.	35 } s.		34 } s.	33 } f
	29 }	32 }	27 s.	30 }	32 }		32 }	32 }
θ	2474 } s.b.	2474 } s.		2474 } s.	2476 } s.			
	71 }	72 }		71 }	73 }			
				24 } f.				
				18 }				
			09 f.	11 } b.f.				
			95 f.					
				2391 }				
				83 } f.				
				75 }				
			49 f.	53 f.				

TABLE XVIII.—Table of Wave-length Measurements of the Heads of Strong Bands which appear to be Common to Benzene and its Homologues.

Abbreviations :—f., feeble ; n., narrow.

Benzene.	Toluene.	Ethylbenzene.	*o*-Xylene.	*m*-Xylene.	*p*-Xylene.	Cymene.	Mesitylene.
*2670	2670	2667	—	2668	2670	2672	—
2639	2638	2639	2639	2642	2641	2642	—
2634 f.	2634	2635	2636 f.	2634	2630	2634	—
*2608	2607	2607	2609	2609 n.	2611	—	—
*2603	2605	2605	2605	2606 n.	2602 f.	—	—
*2595	2594	2594	2594	2595	2597	2593	—
*2590	2589	2586	2586	2590 f.	2588	2587	—
*2540	2542	2543	2542	2543	—	—	—
*2529	2532	2532	—	2532	—	—	—
*2471	2472	2473	—	2473	—	—	—

* The bands marked thus are those which appear strongly throughout this group of hydrocarbons.

On the Relation of the Absorption Bands in the Spectrum of Benzene Vapour at Atmospheric Pressures and Temperatures to the Bands Observed in Solutions of Benzene in Alcohol.

PAUER compared the groups of bands in the absorption spectrum of benzene with the bands observed in the liquid itself and in solution in alcohol. The total number of bands observed in the vapour was 29, in a column 10 cm. long, containing atmospheric air charged with benzene vapour at a temperature of 20° C. These he divided into four groups, with three additional bands commencing as it were a fifth group. He assigns five bands to the liquid and to the solution respectively. He describes the spectrum of the vapour as being composed of fine lines. That they have this appearance is probably due partly to the low temperature and small quantity of the benzene examined, and partly to the small dispersion of his instrument, which was fitted with one Cornu's quartz prism of 60° and quartz lenses of short focus, achromatised with fluor spar. The angle of inclination of the photographic plate to the normal of the lens would thus be not much less than 90°, whereas with uncorrected lenses it would be approximately 22°.

The greater the length of focus of the lenses, if of plain quartz, the greater is the separation of the lines; thus, if the focus for the line D, λ 5893, be about 900 mm., that for Cd 26, λ 2144, will be 776 mm., making a difference of about 5 inches, and on photographs taken with a dispersion of only one quartz prism and such lenses the linear distance measured between Cd 17, λ 2748, and Cd 26, λ 2144, is 87 mm., the last line showing a fine reversal. This affords evidence of accurate focussing and perfect definition.

With a quartz train consisting of two half prisms of 30° of opposite rotation to a single prism of 60°, the lenses being of 325 mm. focus, the linear distance between the same lines measured on a photograph is about 55 mm. (See 'Chem. Soc. Trans.,' 1898, vol. 73, p. 695.)

The absorption spectra of a series of solutions of benzene were photographed by HARTLEY and DOBBIE with the quartz train of three prisms, and it was observed that the bands were sharpest where the rays are of shorter wave-length, and are gradually weakened in the opposite direction as if they were composed of groups of lines or very narrow bands, closer together and stronger on the side of the least refrangible rays. Both FRIEDERICHS and GREBE have compared the positions of the heads of the bands in these spectra with respect to the heads of the groups in the vapour spectra of the same substance as measured by them. Shortly described, the differences between the spectra of the solution and the vapour are such that the former are very broad and few in number, the latter multitudinous, very narrow, and arranged in groups. The corresponding bands and groups in the spectra of the two different states differ in the bands of the solution being shifted by a definite number of wave-length differences towards the less refrangible rays, both the bands and groups of bands being degraded in the same direction. This is shown on reference to fig. 7, where the spectra of exactly the same quantity of benzene, in the state of vapour and of solution, are photographed on the same plate, at the same time, and with the same exposure. Here it may be remarked that the displacement is not at all evident from PAUER'S measurements, which are here quoted.

Heads of bands . .	I.	II.	III.	IV.	V.
	λ.	λ.	λ.	λ.	λ.
Solution	2590	2535	2480	2420	2360
Vapour.	2592	2528	2467	2412	2362

Of the more recent series of numbers taken for comparison, the measurements made by GREBE exhibit a greater regularity in their differences than those quoted by FRIEDERICHS. It will be convenient to name the spectra of the vapour *vapour spectra*, and those of solutions *solution spectra*. As neither the quantity of substance in the state of vapour, nor the barometric pressure at the time, were taken into account by PAUER, FRIEDERICHS, and GREBE, and as the two latter experimenters do not mention the temperature at which the benzene was vaporised, it is difficult to make a strict comparison with their measurements; but it will be seen that the regularity in the differences is more striking if the benzene *vapour spectrum* at 12°·7 C. and barometer 759·5 mm. is compared with the alcoholic solution containing very nearly the same quantity of benzene, since the conditions under which the former were photographed correspond more closely with those under which the solutions were examined. The following tabulated statement will render this evident :—

Heads of bands	I.	II.	III.	IV.	V.	VI.
	λ.	λ.	λ.	λ.	λ.	λ.
Solution spectrum	2681	2599	2541	2483	2429	2376
Vapour spectra :—						
(1) Grebe	2665	2587	2526	2463	2412	2360
Differences	16	12	15	20	17	16
(2) At 12°·7 C. and 759·5 mm. bar.	2670	2589	2528	2469	2416	2365
Differences	11	10	13	14	13	11
(3) At 11°·5 C. and 778 mm. bar.	2669	2591	2527	2470	2413	—
Differences	12	8	14	13	16	—

The measurements taken from *vapour spectrum* (3), at 11°·5 C. and 778 mm. bar., show the absorption to have so greatly increased that Band VI. has entirely disappeared.

The difference between the *solution spectrum* and the *vapour spectrum* at 12°·7 C. and 759·5 mm. bar. is that the former is shifted from 10 to 14 Ångström Units in the direction of the less refrangible rays.

On the photograph fig. 4, it will be seen that both the *solution bands* and the groups of *vapour bands* fade away in the direction of the visible rays. Owing to the weakness of the continuous rays beyond λ 2329, which is partly caused by the general absorption exerted by the benzene thereabouts, it is desirable that those bands which clearly appear on the original photograph fig. 4 should be recorded because the printing process does not reproduce them. There are also bands which become too indistinct under the magnifying power used to admit of their being accurately measured with the micrometer, although quite visible under ordinary inspection.

Vapour Bands.—One band is seen at λ 2200, and several near λλ 2194 and 2234. One band at least is visible between λλ 2265 and 2238. Two bands about λ 2300, one of these is at 2279. One band is seen at λ 2326, and another between λλ 2321 and 2318. There are several very definite bands about λ 2700. These are all in addition to those of which measurements have been already recorded.

Solution Bands.—The general absorption caused by the benzene solution is so intense as to completely obliterate the strong cadmium lines λλ 2194, 2144, and 2114, and also the continuous rays which otherwise are seen to occupy the spaces between them. Three bands occur with heads at λλ 2600, 2616·5, and 2642, and another, commencing at λ 2682, extends towards the less refrangible rays.

Between the vapour spectra (2) and (3) there is an important difference due to the lowering of the temperature by 1°·2 C., and increasing the pressure by 23·5 mm. The quantity of benzene was practically the same in both cases: in (2) the weight found was 0·0179 grm., and in (3) that calculated from the vapour pressure was 0·0175 grm. The difference is seen in (3), where the increased general absorption cuts off Band VI. entirely. It also widens the absorption bands, so that the heads are measurable at a point from 1 to 3 Ångström Units extended towards the rays of shorter wave-lengths.

A *solution band* is thus seen to be the aggregate effect of the absorption of rays caused by a group of *vapour bands*, which is modified by the greater density, and consequently greater dispersion, of the liquid medium in which the substance is dissolved, and it is shifted towards the red in accordance with KUNDT's rule (A. KUNDT, 'Pogg. Ann.,' Jubelband, 1874, p. 620). The slightly different positions of the *four vapour spectra* (see map, p. 484), their similarity in constitution, and the manner in which they overlap, afford an explanation of the reason for the spectrum of benzene being composed of six principal groups of *vapour bands* and six corresponding *solution bands*. The constitution and properties of the *vapour spectra* account also for four of the *solution bands* being similarly constituted, and of greater width and intensity than the others, with approximately the same persistency or coefficient of extinction; they also account for the isolated narrow bands at each end of the spectrum. It is evident, on examining the map (on p. 484) and comparing it with the photographs (figs. 1 and 4), that where the four vapour spectra overlap to the greatest extent, the four most regularly constituted and intense groups of bands are to be found, and the four most intense *solution bands* naturally occur. At either end, where the overlapping is less complete or does not occur, the first and sixth *solution bands* are situated, and likewise the narrow and unimportant groups and isolated bands. Under certain conditions, such as diminished pressure or increased temperature, other feeble bands of the vapour appear distinctly at either end of the spectrum, and with reduction of pressure they become strong bands at the less refrangible end. A further noticeable feature in each of the four *vapour spectra* is that the bands are generally grouped together in threes and fours, also occasionally in fives, and as this affects the constitution of the *solution bands*, and particularly their width, it possibly may account for their number being six.

The Homologues of Benzene.

It has been shown that a displacement of the general absorption towards the less refrangible rays in *solution spectra* is caused when the molecule is loaded by the replacement of one or more H atoms in benzene by elements of greater atomic weight, or by radicals or complex groupings such as Cl, Br, CH_3, C_2H_5, or $CH{\cdot}CH_3{\cdot}CH_3$, the displacement being the greater the heavier the load. As regards the selective absorption, there is a complete divergence from the spectrum of benzene, inasmuch as one broad band and two or more narrow ones, or a single broad band, takes the place of the several bands characteristic of this hydrocarbon. Isomeric hydrocarbons differ from one another, each having its own peculiar spectrum, even when the isomerism is due to the positions of the substituted hydrogens in the benzene ring. That which has been observed with respect to *solution spectra* has been ascertained by the foregoing experiments to apply to *vapour spectra*. This was recognised also by PAUER. It is more particularly evident in the *vapour spectra* of the three xylenes, in cymene, and in mesitylene, that several groups of narrow bands are merged into one broad band, the measurements of which, as regards breadth, intensity, and position in the spectrum, are different for each substance; at the same time the general absorption is shifted towards the less refrangible rays and is sometimes greatly increased. This suggests not only a lowering of the kinetic energy of the molecules, but some irregularity in their motion which gives rise to an increased number of shocks or encounters (see Tables XII., XIII., XIV., and XVI.).

After a careful examination of the tables of wave-length of *vapour bands* and comparing them with the photographs, it does not appear to be evident that the greater molecular weight of a benzene homologue shifts all the bands towards the red, though it is apparent that certain of the bands are so shifted; it is also clear that certain groups of bands are common to benzene, toluene, ethylbenzene and *o*-xylene, and that these are the bands affected. But the weighting of the molecule, besides diminishing the number of the *vapour bands*, causes the general absorption to extend further towards the rays of longer wave-length. At constant pressure the effect of rise of temperature might be expected to cause an increased number of molecules to cross the path of the rays, which is the same in effect as increasing the quantity of substance, or lengthening the column of vapour; reduction of pressure would therefore be expected to have an opposite effect, by reducing their number and increasing the mean path of the molecules—the absorption bands, if caused by vibrations within the molecule, would as a consequence become more distinct. This is, in fact, what is actually seen in the least refrangible groups, between λλ 2750 and 2500, particularly when benzene vapour is maintained at 100° C. and the pressure is gradually reduced to 4 mm. (See fig. 2; for the wave-lengths also Table VI.) The quantity of benzene in the 79 c.c. is only 0·0011 grm. in weight, at 4 mm. pressure.

It has been experimentally shown that increase of mass, of density, and of temperature operate in the same manner upon the rays entering a column of benzene vapour: in the first place, the general absorption is increased by an extension towards the visible rays and it is also intensified; in the second place, the bands of absorption broaden, become diffuse, and coalesce. As the bands attributed to the internal vibrations of the parts of the molecule in different isomeric hydrocarbons become diffuse and coalesce, partaking of the character of the general absorption, and as this is not confined to one part of the spectrum, namely to the less refrangible or transmitted rays, but is a selective absorption, it cannot be due to simply a loading of the molecule; if it were, then it would be impossible to distinguish between the three isomeric xylenes, or to identify them by a simple inspection of their absorption spectra, or even to distinguish them from ethylbenzene.

It may be conceived to be due in part to an irregularity in the motions of the molecules, such as would arise from encounters between unsymmetrically shaped bodies; or if of symmetrical form, such as vortex rings or spheres, the rings or spheres being not throughout of uniform density; in other words, the distribution of mass within the molecule being different for each isomer.

The same effect upon the spectrum as that due to a want of uniformity in the distribution of the mass of the parts within the molecule could be brought about by periodic contractions and expansions occurring within it.

It is conceivable that it might be caused by a transference of a part of the intra-molecular energy to the kinetic energy of the molecule, the intra-molecular vibrations being actuated by the radiant energy of the spark.

A striking feature in all the benzene homologues examined is the existence in their spectra of certain bands which remain unaffected by temperature and pressure, and these bands are common to all the substances, whether they be isomeric substances or not. They are the bands which are subject to displacement when the molecules are weighted, and their displacement is uniform and measurable in Ångström Units.

It is necessary to refer to the constitution of the *solution spectrum* of benzene as photographed by Messrs. BALY and COLLIE, because they have ascribed to benzene exactly seven, and no more than seven, *solution bands* ('Chem. Soc. Trans.,' 1905, vol. 87, p. 1332).

The head of a band appears at wave-length 2656, and this they consider to be the second of the *solution bands.* Every *solution band* must have its origin in a group of *vapour bands*, or it may be derived from a single *vapour band.* A study of the vapour spectrum under varying conditions of temperature and pressure shows that the second *solution band*, which is narrow and of very feeble intensity at ordinary temperatures, is not represented by any corresponding band or group in the vapour spectrum at the same temperature and with the same quantity of substance which gives rise to six groups of bands.

At a temperature of 45° C. and barometer 759·5 mm. the vapour spectrum has two feeble narrow bands at wave-lengths 2636 and 2633. FRIEDERICHS and also GREBE measured a vapour band at λ 2633, which apparently corresponds to the solution band measured by BALY and COLLIE at 2656, but it is narrow and feeble, and there is no strong band or group near with which it might be confounded. The same *solution band* has been photographed (HARTLEY and DOBBIE, 'Chem. Soc. Trans.,' 1898, vol. 73, p. 695), but it was found to be too feeble to be measured, and also it was different in character from the six principal bands. Moreover, its position was so close to the first band at the least refrangible end that it might easily have been mistaken for an extension of it caused by dilution or by decreasing the quantity of substance.

A narrow and feeble *solution band* was measured at λ 2330, which FRIEDERICHS considered as corresponding to a *vapour band* measured by him at λ 2305. It has a considerable intensity, inasmuch as it withstands dilution to a far greater extent than the band under discussion; it is the eighth band.

Furthermore, a ninth band has been photographed, which apparently corresponds to the ninth group of *vapour bands* measured by FRIEDERICHS (see p. 493).

That six, and not seven, bands have generally been referred to as the characteristic feature of the benzene *solution spectrum* arises from the fact that six bands appeared to be similarly constituted, that is to say, each of them was sharpest and strongest at the more refrangible side, and became gradually weaker and less well defined on the side towards the red, but in the seventh feeble band this constitution was not evident. The greatest importance has always been attached to the four strongest bands, because, as already intimated, they are of similar intensity and constitution, and occur at approximately regular intervals. Moreover, there are similar groups of four bands in the spectra of naphthalene and anthracene ('Trans. Chem. Soc.,' 1898, vol. 73, p. 695).

The following tabulated statement of the numerical values in wave-lengths of the intervals (or transmitted rays) between each two successive absorption bands—that is to say, the space between the tail of the first and the head of the second band, and so on, with the differences between the more refrangible edges of successive bands—is of a particular interest in this connection:—

SOLUTION BANDS of Benzene.

(HARTLEY and DOBBIE) Band.	Intervals, or transmitted rays, separating successive bands measured in Ångström Units, with the wave-length measurements of the width of the bands.	Differences in wave-lengths between the more refrangible edges of successive bands.
I.	2709 to 2681	82
	Interval 63	
II.	2618 to 2599	58
	" ————45	
III.	2554 to 2541	56
	" ————44	
IV.	2497 to 2485	56
	" ————48	
V.	2437 to 2429	53
	" ————50	
VI.	2379 to 2376	46
	" ————32	
VII.	2344 to 2330	

The four principal solution bands are indicated by the bracket in the last column, showing regular differences in wave-lengths varying between 58 and 53 Ångström Units between the more refrangible edges of successive bands.

Comparison of the Wave-lengths of the Heads of Bands in Solution and Vapour Spectra yielded by the same Quantity of Benzene (see fig. 7, Plate 32).

Heads of bands.		Differences. Ångström Units.	Number of band.	Differences in wave-lengths between the heads of successive bands. Ångström Units.	
Solution. λ.	Vapour. λ.			Solution.	Vapour.
2682	2670	12	I.		
				40	40
(1) 2657					
2642	2630	12	II.		
				25·5	
(2) 2630					
2616·5			III.		40
				16·5	
2614					
2600	2590	10	IV.		
				61	67
2539	2523	16	V.		
				59	57
2480	2466	14	VI.		
				50·5	51
2426·5	2411	15·5	VII.		
2376	2360	16	VIII.		
					34
	2326		IX.		
					47
	2279		X.		

Note.—(1) A feeble band, the width of which is measured; it appears to correspond with a feeble band in the vapour, λ 2630. (2) These two bands appear to be the result of the splitting of a broad band, the head of which is at λ 2600. It corresponds to the vapour band at λ 2590.

It will be remarked that in the first series of bands taken from solution spectra there are only seven, in the second there are eight, and in the vapour spectrum there are nine bands. Here again it will be seen, also, that the differences between corresponding bands in *solution* and *vapour* spectra respectively, as was shown on p. 519, amount to from 10 to 16 Ångström Units, which represent the shift towards the visible spectrum of different bands measured in solutions.

Summary and Conclusions.

The variations in the *vapour spectra* at different temperatures and pressures may be explained by the fact that there are two kinds of absorption which are sharply defined and may be differentiated; these are distinguished by the terms general and selective absorption. First, by rise of temperature, the general absorption is broadened and extended towards the less refrangible rays, the effect of which is to cause not only the narrow absorption bands but also the emission spectrum of metallic lines and diffused rays to become obscured, while the feeble narrow bands become strong and increase in number in that part of the spectrum which is unaffected by the general absorption. By reduction of pressure, temperature being constant, the general absorption is decreased, so that, consequent upon a diminution in the quantity of substance under observation in the tube, the narrow absorption bands become more numerous, but neither by rise of temperature nor reduction of pressure is the position of these bands altered. Secondly, the selective absorption is manifest in all the narrow individual bands and groups of bands, such as those that have just been referred to as unaltered in position by variations in temperature and pressure. The former, or general, absorption appears to be due to the translatory kinetic energy of the molecules. The selective absorption is to be explained by the vibrations of the atoms or atom-complexes within the molecules, so that they are not affected in the same manner as the translatory molecular movements by rise of temperature; they are not subject to displacement. When a larger number of molecules passes the slit, a greater number of the intra-molecular vibrations is brought into the field, and therefore feeble bands become intensified. Also bands not discernible at ordinary temperatures become apparent, and more intense as the temperature of the vapour rises. Moreover, by reduction of pressure and consequent greater duration of undisturbed motion of the molecules, the bands attributed to the intra-molecular vibrations become sharp and distinct.

The selective absorption is best studied by raising the general absorption to a maximum (at 100° C.) and studying the spectra as modified subsequently by reduction of pressure. By proceeding in this manner the changes in the spectra due to the general absorption may be eliminated (see figs. 3 and 4, Plate 33).

The Homologues of Benzene and Isomeric Substances.

In toluene and ethylbenzene spectra it is shown (1) that there are bands and groups of bands apparently having the same origin as those in benzene, and they are similarly constituted, but by the weighting of the molecule they are shifted into rays of less refrangibility, that is to say, with reduced oscillation frequencies; (2) there are bands which do not suffer displacement, but appear to be common to benzene and its homologues; (3) by increase of temperature and reduction of pressure the homologues of benzene suffer less change in the constitution of their spectra than benzene itself. Thus the bands and groups of bands are not affected to the same extent, neither is their number so largely increased or their intensity so augmented.

The principal changes in the spectra of *ortho*- and *para*-xylene, occasioned by rise of temperature, are an increase in the general absorption over a wide range of the spectrum, which decreases the number of bands in parts of the spectra which are unaffected in the *meta*-xylene. The merging of the narrow bands in the different parts of the spectra of the three isomers is evidently connected with the positions in the benzene ring where substitution of CH_3 for hydrogen has been effected.

It is proved that benzene vapour at 100° C. has the same molecular mass as at 25° C. or 12°·7 C., so that at lower temperatures the molecules are not associated when in a state of vapour.

The absorption bands at 100° C. are seen on comparison to be almost identical with those at lower temperatures, but at 100° C. there is this difference, that the bands in the region about λ 2700 are of augmented intensity, with a peculiar sharpness and definition which is wholly wanting at lower temperatures, as they then appear feeble and ill defined, or do not appear at all.

The similar groups of bands occurring in benzene and toluene, and the close similarity between the spectra of toluene and ethylbenzene, with the further resemblance between meta-xylene, toluene, and ethylbenzene, is evidence that the peculiar mode of vibration of the benzene nucleus, or ring-structure, is in a great measure unaffected by the side chain substitution in these compounds.

The important influence of the position of the substituted hydrogen in benzene upon the number and position of bands in the spectra of the homologues is clearly demonstrated.

The general absorption observed in *solution spectra*, like that in *vapour spectra*, is also apparently caused by the translatory motion of the molecules. The selective absorption, consisting of the coalescence of several narrow bands, is regarded as due to the intra-molecular motions; motions of the atoms, or atom-complexes, within the molecules, upon which, if the solution be concentrated, a general absorption is superposed. These observations are in accord with the conclusions arrived at in 1882 and 1885 upon evidence derived from the examination of solution spectra.

DESCRIPTION OF PLATES.

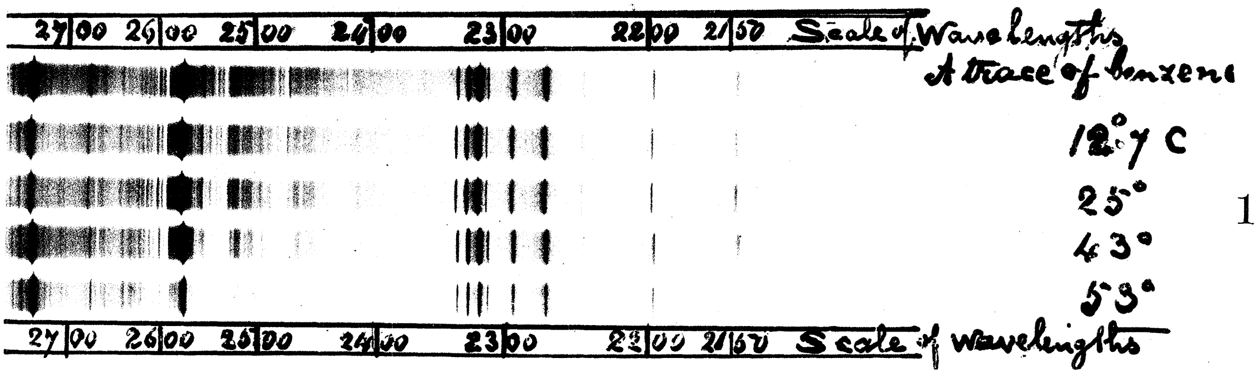
PLATES 32 AND 33.

The original photographs were taken on plates measuring 5 × 4 inches, on which the continuous rays and the cadmium lines appear dark. Good examples are figs. 6 and 7, where the cadmium spectrum is shown at the head of each series. The reproductions are from negatives slightly enlarged to about one and a half times the size of the originals.

Particulars of figures will be found facing the plates.

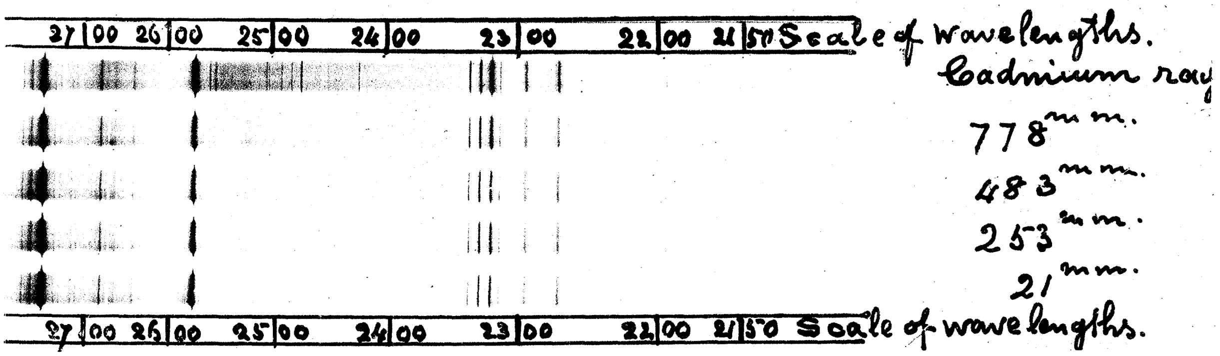
The emission spectrum being dark the absorption bands appear white, or approaching to whiteness, according to whether they are strong or weak bands. On figs. 1 and 4 it will be seen that instead of the pure emission spectrum appearing at the head of the series a trace of benzene vapour gained access to the tube interposed between the spark and the slit of the spectrograph, when air was passed into it, and the absorption bands due to this trace of benzene are very distinctly shown. The reproductions do not compare in delicacy with silver prints taken from the original negatives, owing to a granulation resembling that of a lithograph, which somewhat impairs their definition.

1


2700 2600 2500 2400 2300 2200 2150 Scale of Wavelengths
A trace of benzene
12°.7 C
25°
43°
53°
2700 2600 2500 2400 2300 2200 2150 Scale of wavelengths

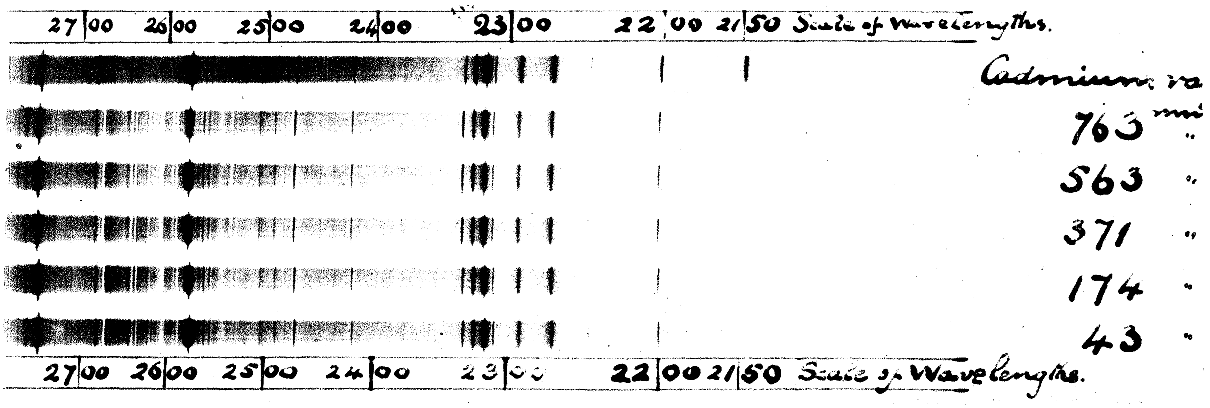
1

2


2700 2600 2500 2400 2300 2200 2150 Scale of wavelengths.
Cadmium ray
778 mm.
483 mm.
253 mm.
21 mm.
2700 2600 2500 2400 2300 2200 2150 Scale of wavelengths.

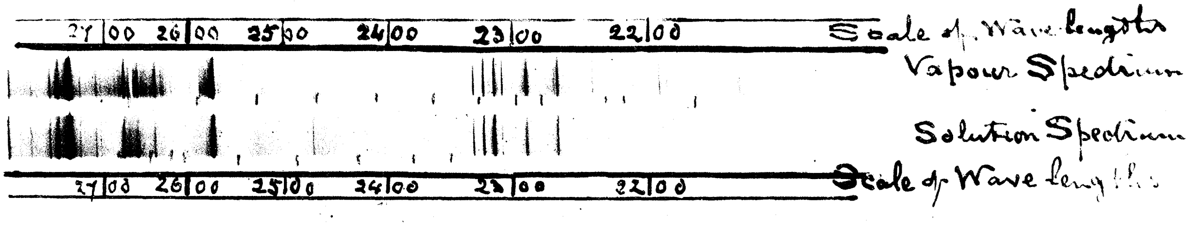
2

6


2700 2600 2500 2400 2300 2200 2150 Scale of wavelengths.
Cadmium ra
763 mm
563 ..
371 ..
174 ..
43 ..
2700 2600 2500 2400 2300 2200 2150 Scale of Wavelengths.

6

7


2700 2600 2500 2400 2300 2200 Scale of Wavelengths
Vapour Spectrum
Solution Spectrum
2700 2600 2500 2400 2300 2200 Scale of Wave lengths

7

PLATE 32.

Fig. 1. Four spectra of benzene at a pressure of 759·5 mm., and at different temperatures, varying from 12°·7 C. to 53° C. This series of photographs shows the head of a group of bands, being a narrow and somewhat feeble band, which is succeeded by a very strong band, about λ 2540 at 12°·7; it increases in strength down to 53° C. On the original plate bands are also seen about λ 2280, λ 2300, λ 2330, λ 2350, at 25° C., 43° C., and 53° C. For details see Table I., pp. 490–493.

Fig. 2. Four spectra of benzene at pressures varying from 778 mm. to 21 mm., and at a constant temperature of 11°·5 C., see Table II., pp. 493, 494. The original plate is an exceedingly delicate one, very difficult to reproduce and impossible to render satisfactorily. The head of the group at λ 2540, a narrow band, is very distinctly seen on the silver print of each of these spectra, but is very imperfectly shown on the reproduction.

Fig. 6. Five spectra of toluene at different pressures and a constant temperature of 11° C. Table IX., p. 509.

Fig. 7. The vapour-spectrum and solution-spectrum taken from the same quantity of benzene, and at the same time, for comparison. See pp. 519, 520. Bands and the heads of groups of bands are indicated by marks below the two spectra. They are well seen on the original plates, although not all visible on the reproductions.

PLATE 33.

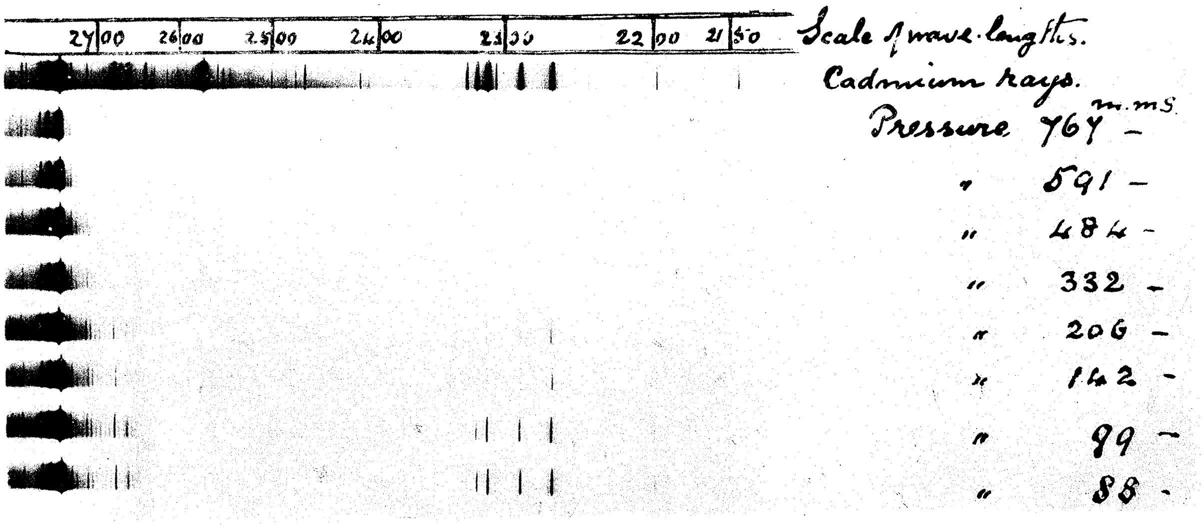
Figs. 3 and 4. Seventeen spectra of benzene vapour at different pressures, varying from 767 mm. down to 4 mm., at a constant temperature of 100° C., in a column 150 mm. long. These two series of spectra, the one in continuation of the other, show completely what was only indicated on fig. 2. See Table IV., p. 496, and Table VI., pp. 498–505.

On fig. 3, the least refrangible group of bands is well shown about λ 2700, at 484 mm. pressure, and continues to 88 mm.

On fig. 4, the bands about λ 2700 are strong at pressures from 67·5 mm. to 28·5 mm. At the latter pressure the bands at λ 2600 become well defined. From 67·5 mm. to 22·5 mm. the bands at λ 2280, and near to λ 2300 are visible.

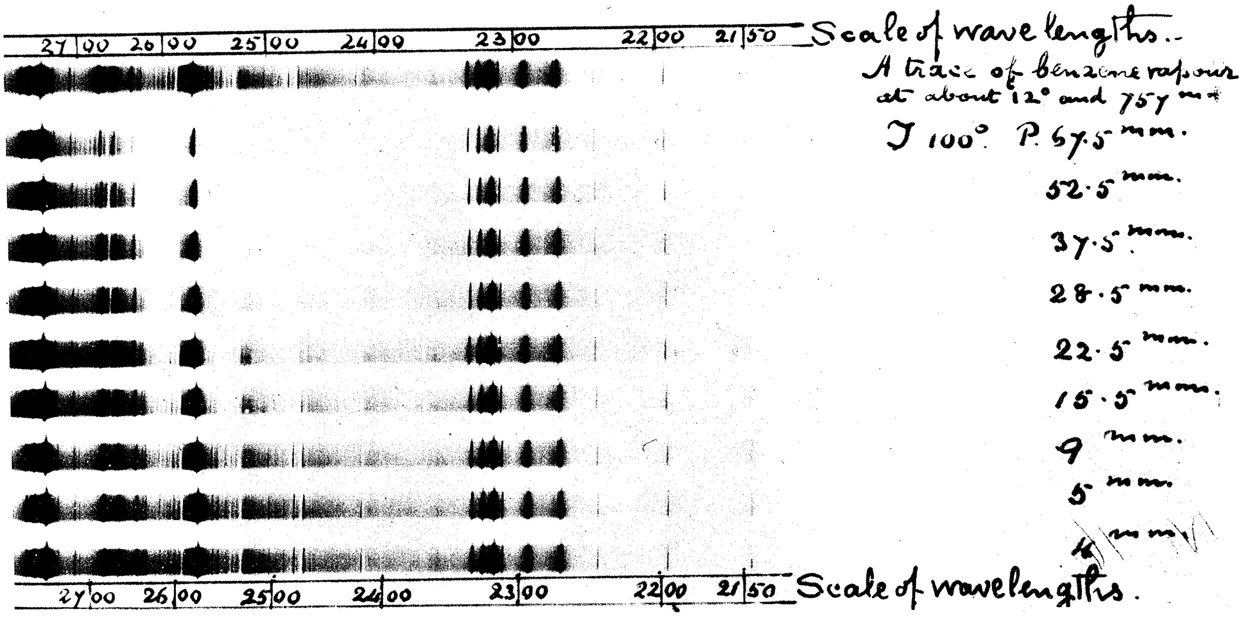
Fig. 5. This is a very fine series of spectra of toluene vapour at nine different temperatures from 10° C. to 100° C., and at a constant pressure of 751 mm., in a column 150 mm. long. See Table VIII., pp. 507, 508.

3


27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of wave-lengths.
Cadmium rays.
Pressure 767 m.ms –
" 591 –
" 484 –
" 332 –
" 206 –
" 142 –
" 99 –
" 88 –

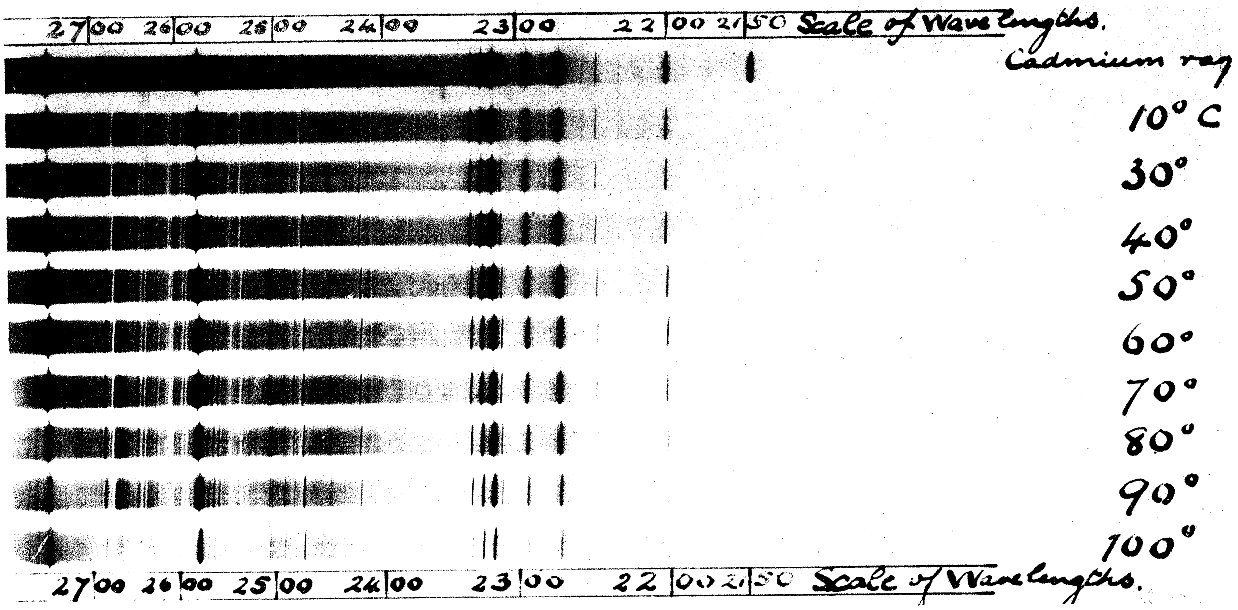
3

4


27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of wave lengths.
A trace of benzene vapour at about 12° and 757 mm
T 100° P. 67.5 mm.
52.5 mm.
37.5 mm.
28.5 mm.
22.5 mm.
15.5 mm.
9 mm.
5 mm.
4 mm.
27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of wavelengths.

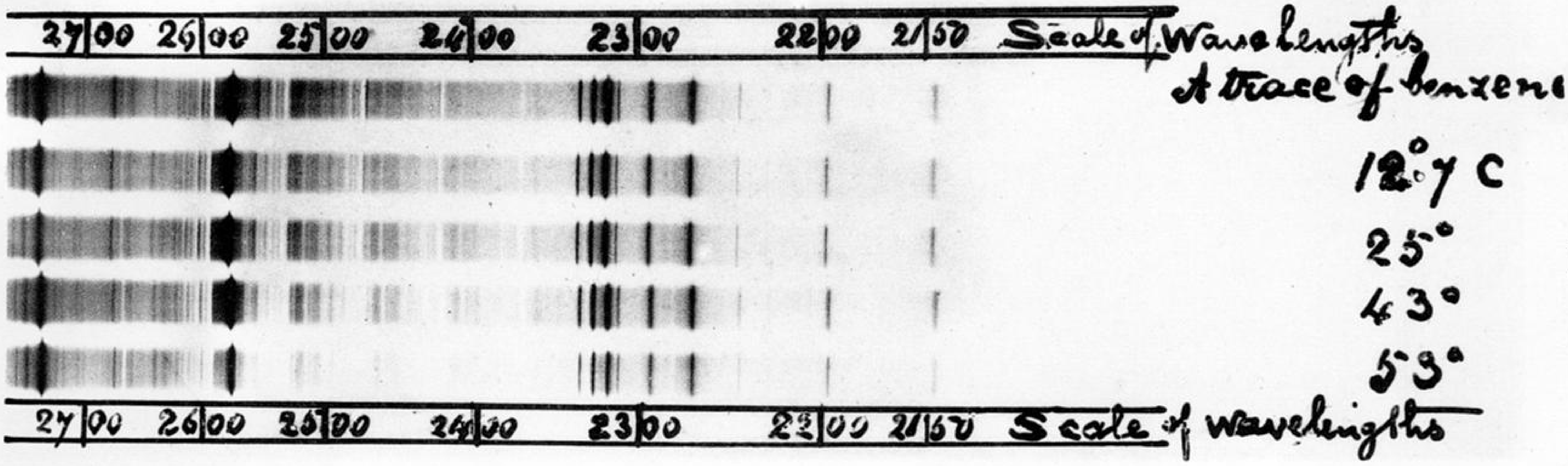
4

5

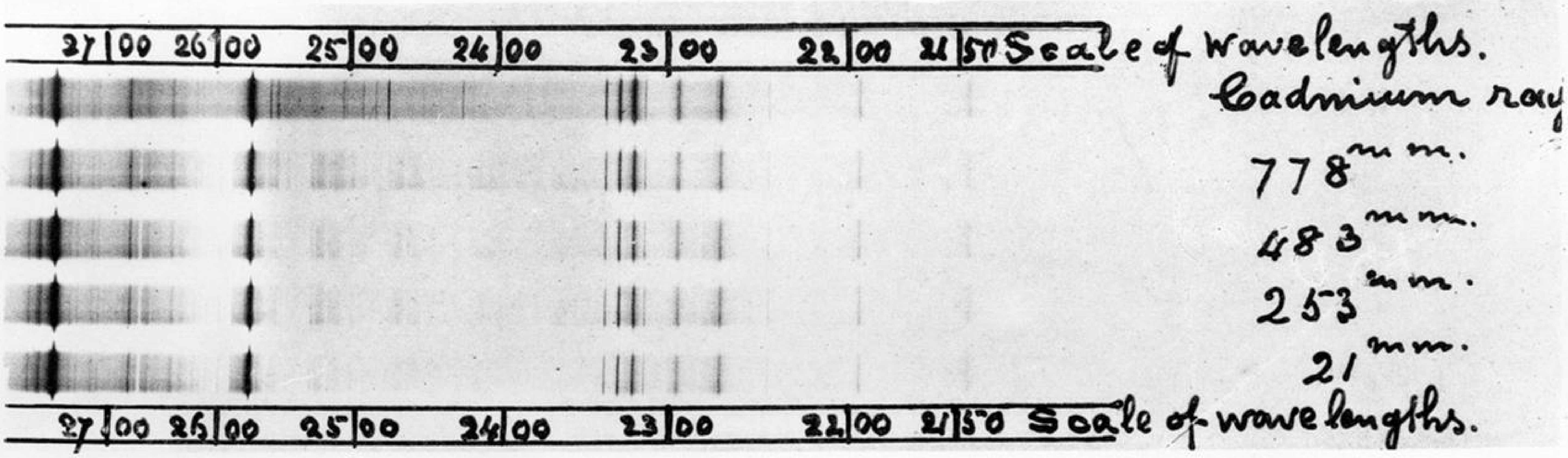

27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of Wave lengths.
Cadmium ray
10° C
30°
40°
50°
60°
70°
80°
90°
100°
27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of Wavelengths.

5

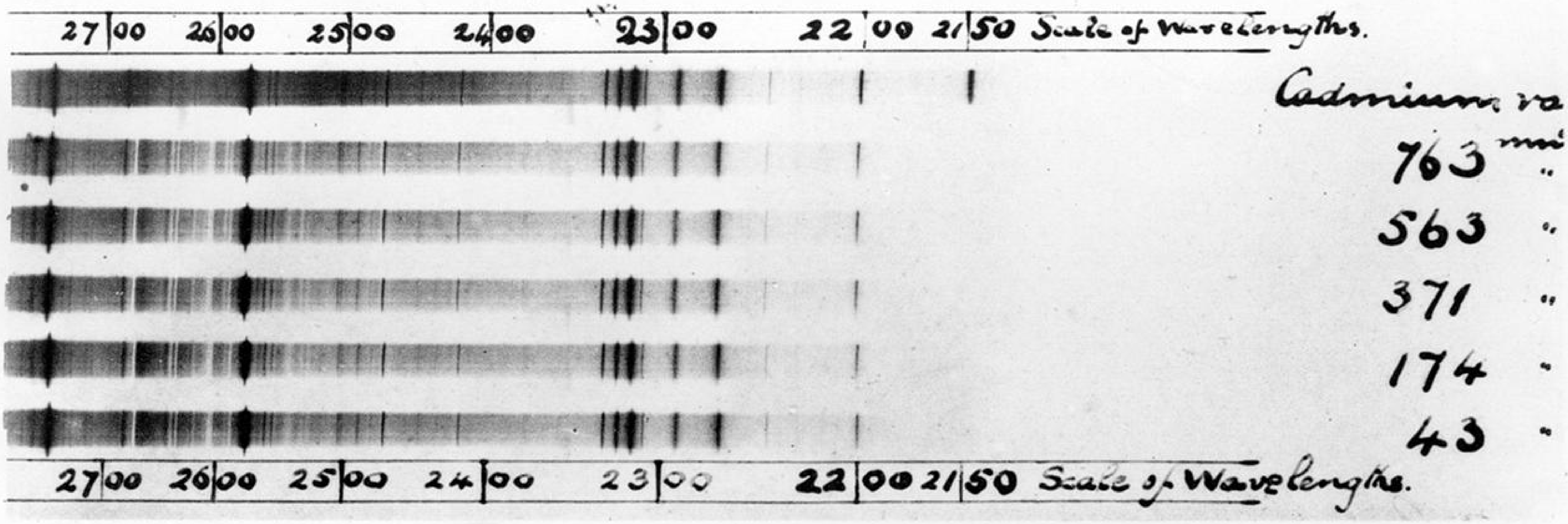
1


27|00 26|00 25|00 24|00 23|00 22|00 21|50 Scale of Wavelengths
A trace of benzene
12°·7 C
25°
43°
53°
27|00 26|00 25|00 24|00 23|00 22|00 21|50 Scale of wavelengths

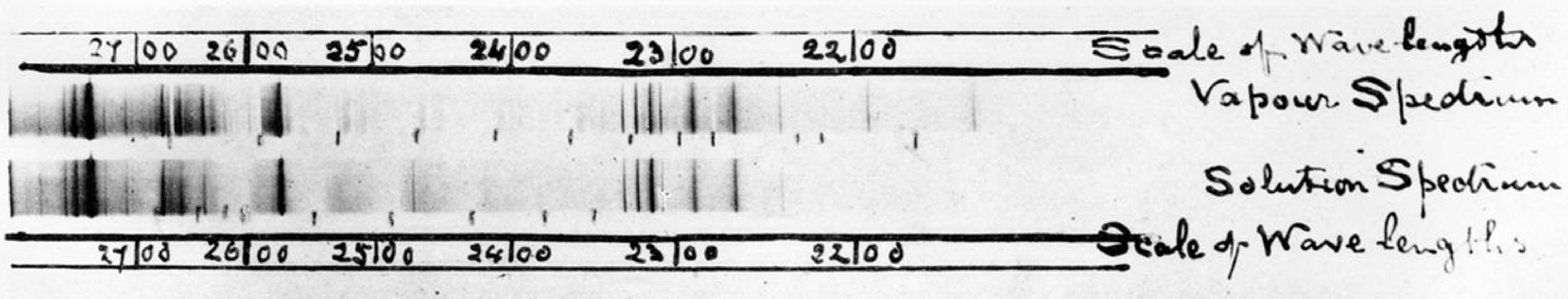
2


27|00 26|00 25|00 24|00 23|00 22|00 21|50 Scale of wavelengths.
Cadmium ray
778 mm.
483 mm.
253 mm.
21 mm.
27|00 26|00 25|00 24|00 23|00 22|00 21|50 Scale of wavelengths.

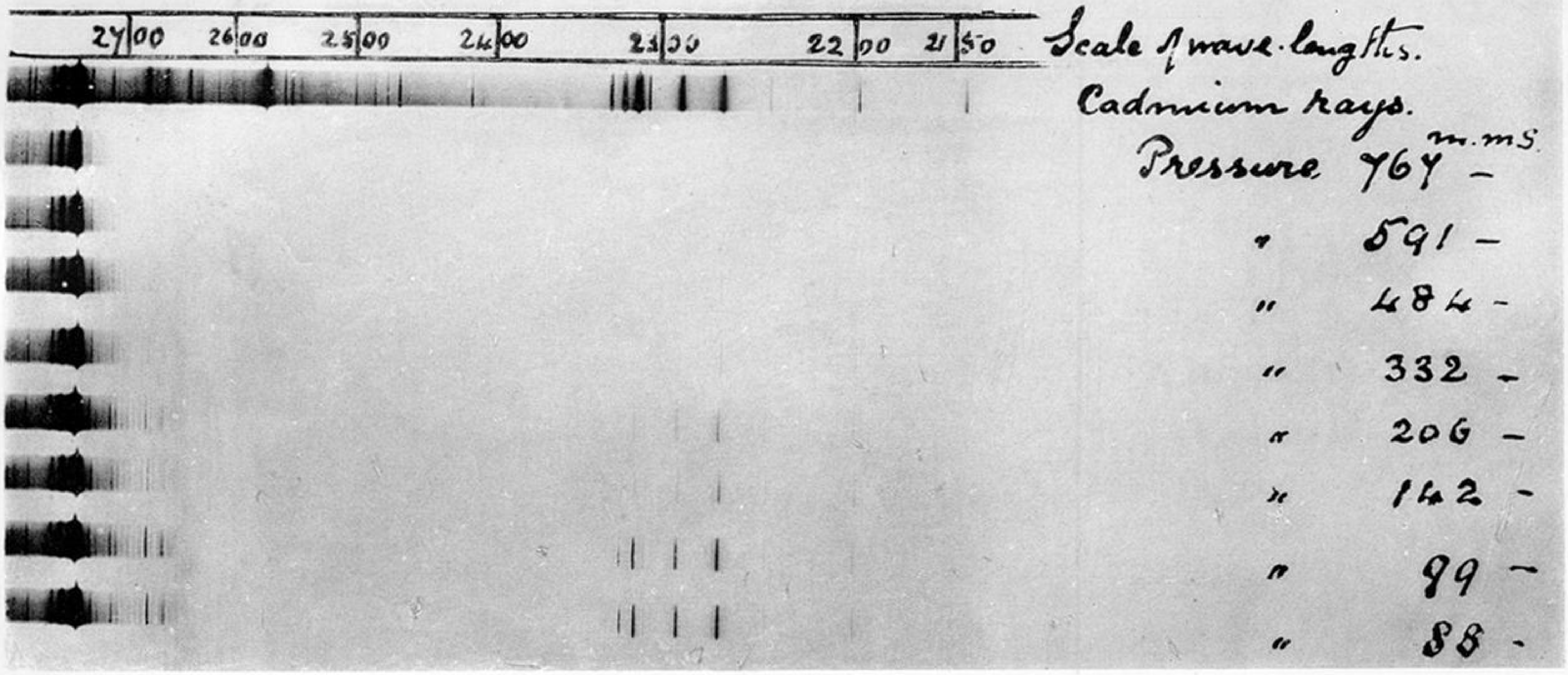
6


27|00 26|00 25|00 24|00 23|00 22|00 21|50 Scale of wavelengths.
Cadmium ra
763 mm
563 "
371 "
174 "
43 "
27|00 26|00 25|00 24|00 23|00 22|00 21|50 Scale of Wavelengths.

7

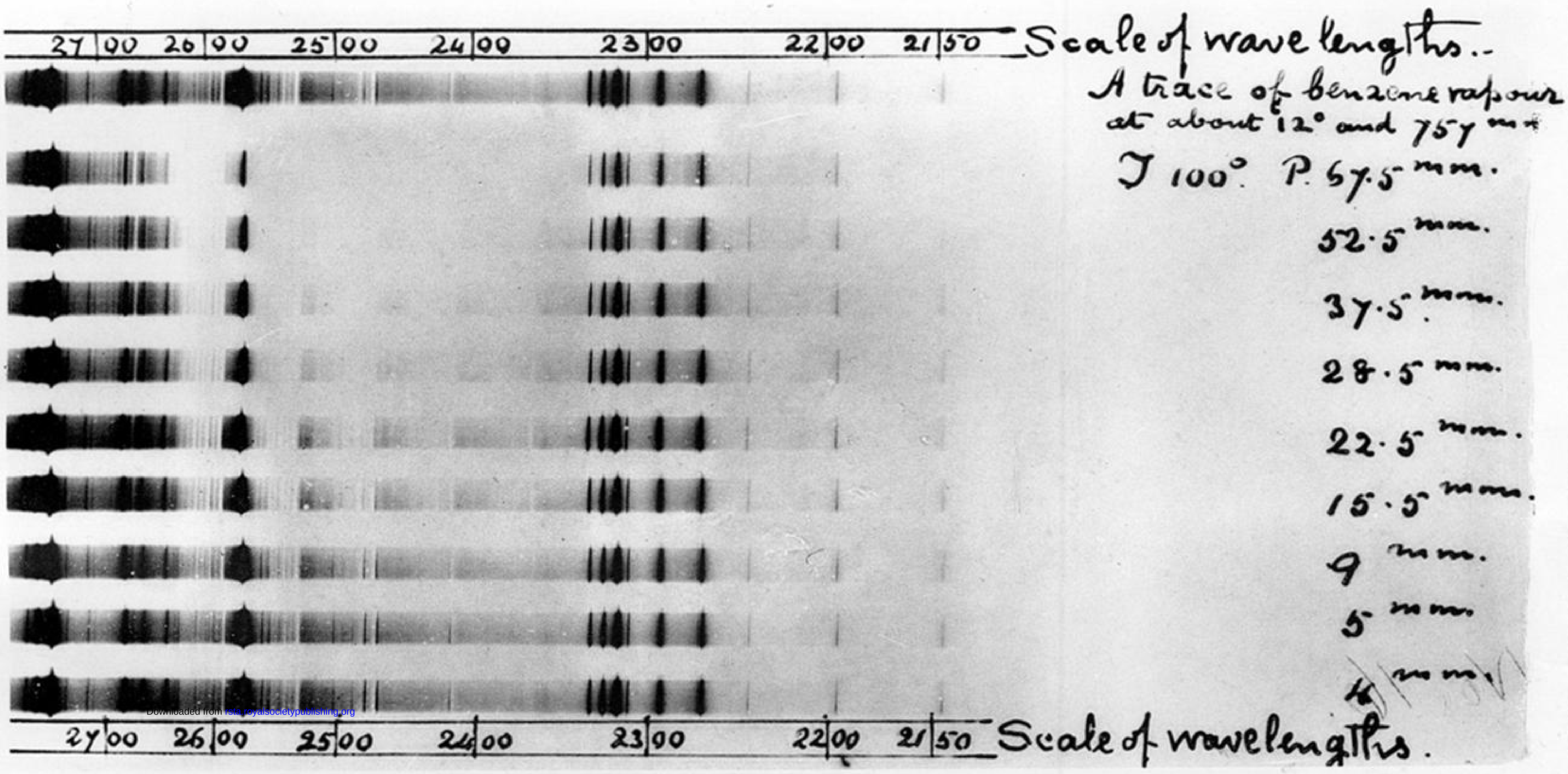

27|00 26|00 25|00 24|00 23|00 22|00 Scale of Wave-lengths
Vapour Spectrum
Solution Spectrum
27|00 26|00 25|00 24|00 23|00 22|00 Scale of Wave lengths

3


27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of wave-lengths.
Cadmium rays.
Pressure 764 m.ms. -
" 591 -
" 484 -
" 332 -
" 206 -
" 142 -
" 99 -
" 88 -

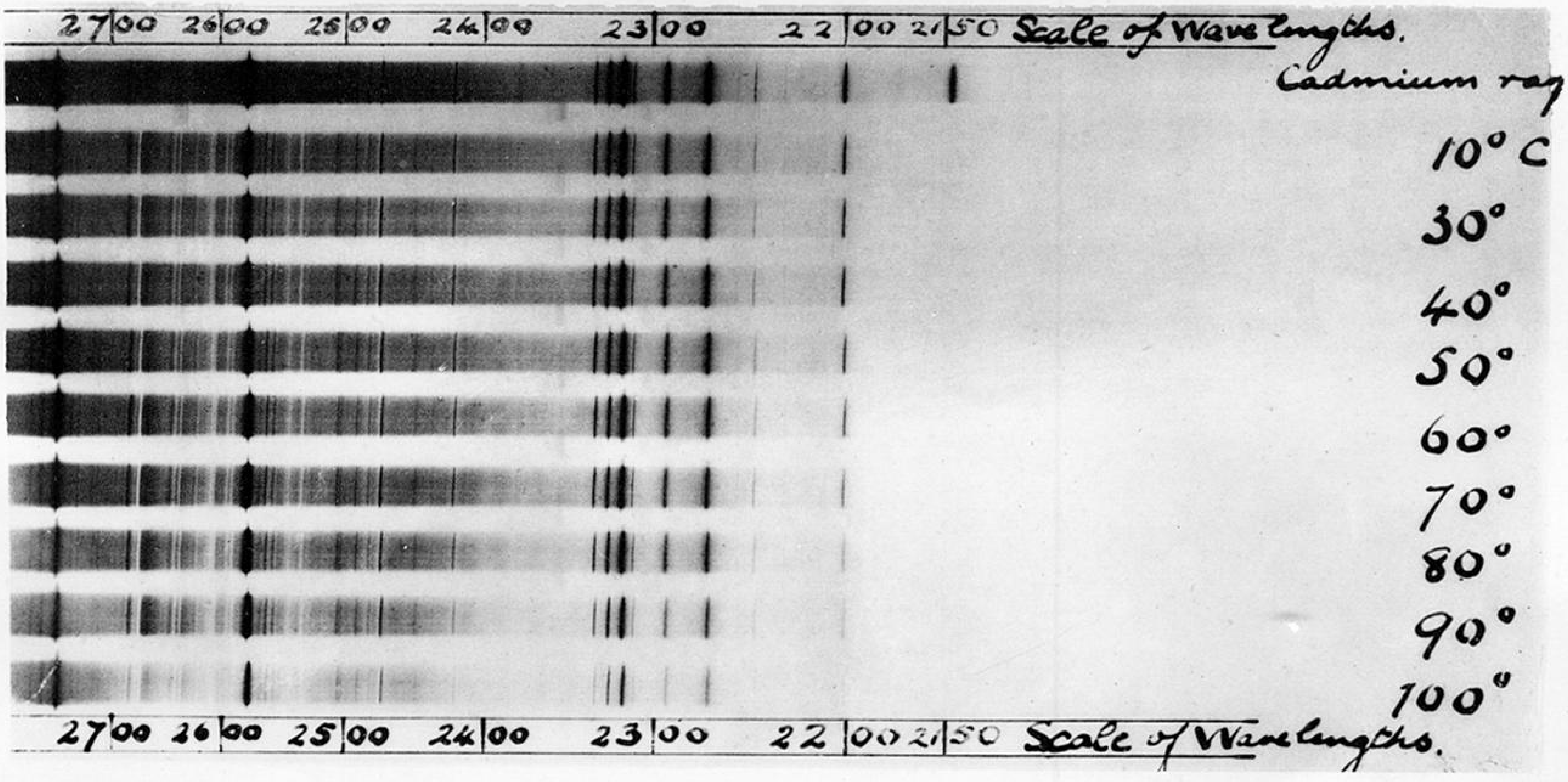
3

4


27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of wave lengths..
A trace of benzene vapour at about 12° and 757 mm
T 100°. P. 67.5 mm.
52.5 mm.
37.5 mm.
28.5 mm.
22.5 mm.
15.5 mm.
9 mm.
5 mm.
4 mm.
27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of wavelengths.

4

5


27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of Wave lengths.
Cadmium ray
10° C
30°
40°
50°
60°
70°
80°
90°
100°
27|00 26|00 25|00 24|00 23|00 22|00 21|50
Scale of Wavelengths.

5