

XVII. *On the Relation between the Sun's Altitude and the Chemical Intensity of Total Daylight in a Cloudless Sky.* By HENRY E. ROSCOE, F.R.S., Professor of Chemistry in Owens College, Manchester, and T. E. THORPE, Ph.D., Professor of Chemistry in Anderson's University, Glasgow.

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THE difficulty of securing in England a sufficient number of consecutive cloudless days to render it possible to determine with any degree of accuracy the relation existing between the sun's altitude and the chemical intensity of total daylight, induced us to undertake a series of measurements on the west coast of Portugal, where during the months of July and August the sky is generally cloudless. The method of measurement employed was that described by one of us in previous communications to the Royal Society, founded upon an exact estimation of the tint which standard sensitive paper assumes when exposed for a given time to the action of daylight*.

The observations, the results of which are given in the following communication, were made in the autumn of 1867, through the kindness of THOMAS CRESWELL, Esq., at the Quinta do Estero Furado, situated on the flat table-land on the southern side of the Tagus, about $8\frac{1}{2}$ miles to the south-east of Lisbon, lat. $38^{\circ} 40'$ N. and long. 9° W. The sensitive paper was exposed in the plane of the horizon, the instrument being placed upon a carefully levelled stand at the height of 4 feet 5 inches above the level of the ground in a sandy field having a clear horizon, the most considerable object in the neighbourhood being a house distant 130 paces to the west, the roof of which subtended an angle of 7° with the plane of the paper.

All the experiments were made in the following order:—

1. The chemical action of total daylight was observed in the ordinary manner.
2. The chemical action of the diffused daylight was then observed by throwing on to the exposed portion of the sensitive paper the shadow of a small blackened brass ball placed at such a distance that its apparent diameter seen from the position of the paper was slightly larger than that of the sun's disk.
3. The chemical action of total daylight was again determined.
4. That of the diffused daylight was a second time ascertained.

The means of Observations 1 and 3 and of 2 and 4 were then taken. The sun's altitude was determined immediately before and immediately after the foregoing observations of chemical intensity, the altitude at the time of observation being ascertained by interpolation. A box-sextant made by WORTHINGTON, of London, was employed with an

* Bakerian Lecture, Philosophical Transactions, 1865, Part II. p. 605.

artificial horizon of black glass, which was carefully levelled before each observation. The watch used could be read to quarter seconds, and the Lisbon mean time was obtained by regulating the watch by means of the time-ball of the Lisbon Naval Arsenal, which falls at 1 P.M., and afterwards ascertaining the amount of the watch's daily variation. In cases in which the altitude could not be determined by experiment, it has been calculated from the following formula,

$$\cos \phi = \cos \delta \cdot \cos t \cdot \cos p + \sin \delta \sin p,$$

in which

δ represents the sun's declination,

p represents the latitude of the place = $38^{\circ} 40'$,

and t represents the sun's hour-angle.

It was necessary, in the first place, to ascertain what error was introduced into the determination of diffused daylight by any accidental variation in the distance of the brass ball from the sensitive paper. A series of experiments were made with this object on August 8th, 1867, at 9 A.M., the blackened ball being placed at distances varying from 140 millims. to 230 millims. above the silvered paper. These experiments showed that the ball placed at

140 millims.	gave mean reading	143.3	or Chemical Intensity	0.116
160	„ „ „	143.6	„ „	0.116
190	„ „ „	141.9	„ „	0.116
230	„ „ „	136.8	„ „	0.118

consequently the height of the blackened ball may safely vary between 140 and 190 millims. without producing any appreciable error.

The following gives the elements of an observation, and may serve as a sample of the others, 134 in number, which were all carried out in a manner exactly similar, and form the data from which are derived the conclusions drawn in this paper.

August 5th, 1867.

Determination of Altitude.—

	Observed time. h m	Calculated time. h m	Observed double altitude.	Sun's altitude.
1st Observation.	3 37 P.M.	3 57 P.M.	71° 42'	35° 51'
2nd „	3 41 P.M.	4 1 P.M.	70 00	35 00

Determination of Chemical Intensity.—

Observed time 3^h 39^m to 3^h 40^m. Calculated time 3^h 59^m to 4^h.

	Readings on calibrated strip.	Mean.
I. Total daylight	100, 97, 97, 105, 103, 106, 102	=101
II. Diffused . .	110, 108, 112, 116, 116, 117, 108, 110	=112
III. Total . . .	104, 100, 100, 97, 100, 102, 107, 105, 103	=102
IV. Diffused . .	108, 112, 113, 108, 115, 114, 107	=111

By reference to the calibration Table of the strip the following numbers were found to correspond to the above readings.

Time 3^h 59^m P.M. Sun's altitude 35° 25'.

Observed Chemical Intensity.—

Direct sunlight.	Diffused light.	Total daylight.
0·069	0·138	0·207

The meteorological conditions of the time of observation were also carefully observed.

Clouds 0·0. Fine breeze, S.S.W.	{	Dry-bulb thermometer 81°·0 F. Wet-bulb thermometer 69°·0 F.
Barometer at sea-level 763·9 millims.	{	Aqueous vapour in 1 cub. ft. 5·7 grains. Relative humidity=50.

One of the 134 sets of observations was made as nearly as possible every hour, and they thus naturally fall into seven groups, viz.—

- (1) Six hours from noon, (2) five hours from noon, (3) four hours from noon, (4) three hours from noon, (5) two hours from noon, (6) one hour from noon, and (7) noon.

Each of the first six of these groups contains two separate sets of observations, viz. those made before noon marked A.M., and those made after noon and marked P.M.

One of us has already pointed out*, from measurements made at Kew, that the mean chemical intensity of total daylight for hours equidistant from noon is the same. That this result is a general one is fully borne out by the inspection of the following Tables, giving the results of 134 series of observations; the single experiments made at the same hour being grouped together, and those of the hours equidistant from noon being placed side by side.

TABLE I. (1.)

A.M.							P.M.						
Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.	Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.
11.	6	h m 6 4	10° 33'	000	·049	·049	19.	6	h m 6 0	11° 31'	·000	·056	·056
29.	9	6 6	10 15	·001	·033	·034	28.	8	6 2	10 43	·000	·041	·041
48.	12	6 9	10 20	·001	·040	·041	40.	9	6 0	10 58	·000	·034	·034
							47.	10	6 0	10 50	·002	·050	·052
			31 08	·002	·122	·124	57.	12	5 59	10 22	·000	·034	·034
		Means	10 23	·000	·041	·041	67.	21	5 51	10 02	·000	·031	·031
							76.	22	6 0	7 58	·000	·031	·031
							86.	23	6 0	7 20	·000	·026	·026
							97.	24	5 47	9 50	·002	·038	·040
							107.	26	5 49	8 37	·000	·031	·031
							118.	27	5 51	8 04	·000	·029	·029
							128.	28	5 53	7 17	·000	·022	·022
										113 32	·000	·423	·427
									Means	9 28	·000	·035	·035

* Philosophical Transactions, 1867, p. 558.

TABLE I. (2.)

A.M.							P.M.						
Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.	Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.
12.	6	h m 7 1	20° 59'	·024	·095	·119	18.	6	h m 5 0	23° 15'	·035	·069	·104
30.	9	7 2	21 10	·023	·062	·085	27.	8	5 2	22 10	·027	·072	·099
49.	12	7 1	20 20	·032	·063	·095	39.	9	5 6	21 26	·026	·060	·086
87.	24	6 54	17 29	·017	·058	·075	46.	10	5 0	22 15	·045	·069	·114
108.	27	7 6	19 17	·017	·057	·074	66.	21	5 4	19 07	·013	·051	·064
119.	28	7 1	18 18	·016	·059	·075	75.	22	5 1	19 15	·023	·060	·083
129.	29	7 1	18 24	·016	·047	·063	85.	23	4 58	19 24	·024	·068	·092
132.	30	6 59	17 56	·017	·050	·067	96.	24	5 0	18 50	·022	·060	·082
			153 53	·162	·491	·653	106.	26	5 4	17 22	·017	·058	·075
		Means	19 14	·020	·061	·082	117.	27	4 58	18 23	·015	·059	·074
										201 27	·247	·626	·873
									Means	20 09	·025	·062	·087

(3.)

A.M.							P.M.						
Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.	Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.
13.	6	h m 8 0	32° 25'	·081	·111	·192	10.	5	h m 4 0	35° 21'	·069	·138	·207
31.	9	7 59	31 58	·053	·101	·154	17.	6	4 0	34 49	·049	·116	·165
50.	12	8 0	31 49	·079	·103	·182	26.	8	4 1	34 11	·060	·112	·172
58.	21	8 2	30 43	·050	·097	·147	38.	9	4 12	31 50	·049	·096	·145
77.	23	8 0	30 23	·044	·097	·151	45.	10	4 0	34 04	·081	·109	·190
88.	24	7 59	29 58	·051	·087	·138	65.	21	4 10	29 29	·041	·087	·128
98.	26	8 0	29 58	·051	·098	·149	74.	22	3 58	31 21	·036	·118	·154
109.	27	8 1	29 57	·045	·096	·141	84.	23	3 59	30 53	·043	·077	·120
120.	28	8 0	29 41	·047	·093	·140	95.	24	4 0	30 36	·051	·100	·151
130.	29	7 59	29 38	·032	·080	·112	105.	26	4 2	29 38	·053	·092	·145
133.	30	8 0	29 38	·036	·084	·120	116.	27	4 5	28 40	·053	·097	·150
			336 08	·569	1·047	1·606				350 52	·585	1·143	1·727
		Means	30 33	·052	·097	·146			Means	31 54	·053	·104	·157

(4.)

A.M.							P.M.						
Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.	Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.
14.	6	h m 9 0	44° 13'	·102	·124	·226	9.	5	h m 3 2	46° 25'	·105	·158	·263
51.	12	9 2	43 33	·154	·129	·283	25.	8	3 1	45 46	·142	·136	·278
59.	21	8 59	41 16	·144	·129	·273	44.	10	3 3	44 59	·139	·128	·267
68.	22	9 0	41 38	·089	·124	·213	56.	12	2 59	45 02	·069	·083	·152
78.	23	8 59	41 20	·091	·109	·200	64.	21	3 1	42 35	·086	·114	·200
89.	24	8 58	40 58	·079	·104	·183	73.	22	3 0	42 34	·114	·116	·230
99.	26	9 1	41 21	·083	·114	·197	83.	23	2 58	42 20	·103	·104	·207
110.	27	9 7	41 09	·108	·120	·228	104.	26	3 2	40 42	·094	·116	·210
121.	28	9 5	41 00	·090	·112	·202	115.	27	3 0	40 45	·091	·112	·203
131.	29	9 0	40 48	·098	·098	·196	127.	28	3 0	40 23	·075	·110	·185
134.	30	9 5	41 35	·082	·096	·178	137.	30	3 6	38 25	·070	·089	·159
			458 51	1·120	1·259	2·379				469 56	1·088	1·266	2·354
		Means	41 43	·102	·114	·216			Means	42 43	·099	·115	·214

TABLE I. (5.)

A.M.							P.M.							
Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.	Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.	
		h m	° ′						h m	° ′				
4.	5	10 0	54 50	·109	·180	·289	8.	5	2 5	56 26	·143	·150	·293	
15.	6	10 0	54 58	·182	·128	·310	37.	9	2 0	56 01	·095	·118	·213	
21.	8	10 2	54 59	·157	·130	·287	55.	12	1 59	55 36	·091	·106	·197	
33.	9	9 57	53 55	·122	·121	·243	94.	24	1 57	52 25	·149	·114	·263	
41.	10	10 5	54 54	·215	·168	·383	126.	28	2 2	50 12	·091	·112	·203	
52.	12	10 0	53 42	·152	·104	·256	136.	30	2 2	49 09	·080	·118	·198	
60.	21	10 1	52 12	·142	·158	·300				319 49	·649	·718	1·367	
69.	22	9 58	51 40	·157	·116	·273				Means	53 18	·108	·120	·228
79.	23	9 58	51 27	·155	·112	·267								
90.	24	10 5	52 25	·107	·112	·219								
100.	26	10 2	51 27	·161	·120	·281								
111.	27	10 3	51 26	·155	·118	·273								
122.	28	10 3	51 21	·133	·120	·253								
			689 16	1·947	1·687	3·634								
		Means	53 01	·149	·130	·279								

(6.)

A.M.							P.M.							
Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.	Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.	
		h m	° ′						h m	° ′				
5.	5	11 00	64 01	·173	·182	·355	7.	5	1 0	65 22	·130	·180	·310	
16.	6	11 07	64 29	·215	·128	·343	24.	8	1 1	64 35	·167	·148	·315	
22.	8	11 00	63 25	·149	·124	·273	36.	9	12 59	64 22	·110	·124	·234	
34.	9	10 58	62 56	·153	·127	·280	54.	12	1 0	63 28	·162	·114	·276	
42.	10	11 00	62 55	·237	·156	·393	63.	21	12 58	60 51	·258	·126	·384	
53.	12	11 01	62 24	·212	·114	·326	72.	22	12 59	60 27	·288	·144	·432	
61.	21	11 00	60 04	·201	·140	·341	82.	23	12 59	60 08	·178	·106	·284	
70.	22	11 05	60 15	·263	·125	·388	93.	24	1 0	59 39	·223	·121	·344	
80.	23	11 02	59 45	·263	·115	·378	114.	27	12 59	58 39	·250	·166	·416	
91.	24	11 00	59 15	·186	·128	·314	125.	28	1 11	57 06	·158	·114	·272	
101.	26	10 59	58 35	·236	·126	·362	135.	30	1 0	57 36	·099	·124	·223	
112.	27	11 00	58 18	·178	·118	·296				672 13	2·023	1·467	3·490	
123.	28	11 05	58 32	·187	·118	·305				Means	61 07	·184	·133	·317
			794 54	2·653	1·701	4·354								
		Means	61 09	·204	·131	·335								

NOON. (7.)

Expt.	Date.	Hour.	Altitude.	Sun.	Sky.	Total.
		h m	° ′			
6.	5	12 0	68 21	·186	·188	·374
23.	8	12 0	67 31	·213	·177	·390
35.	9	12 0	67 14	·218	·126	·344
43.	10	11 59	66 58	·248	·172	·420
62.	21	12 0	63 32	·278	·132	·410
71.	22	12 0	63 12	·225	·120	·345
81.	23	11 59	62 51	·254	·114	·368
92.	24	11 58	62 31	·199	·118	·317
102.	26	12 2	61 50	·210	·128	·338
113.	27	12 2	61 29	·213	·122	·335
124.	28	12 7	61 06	·191	·116	·307
			707 35	2·435	1·513	3·948
		Means	64 14	·221	·138	·359

The results are more clearly seen in the following Table.

TABLE II.

Time.	Mean altitude.	Mean chemical intensity.			Number of observations.	Diff.
		Sun.	Diffused.	Total.		
h m						
6 0 A.M.	10° 23'	0·000	0·041	0·041	3	+ ·003
6 0 P.M.	9 28	0·000	0·035	0·035	12	
7 0 A.M.	19 14	0·020	0·061	0·082	8	-0·025
5 0 P.M.	20 09	0·025	0·062	0·087	10	
8 0 A.M.	30 33	0·052	0·097	0·146	11	-0·005
4 0 P.M.	31 54	0·053	0·104	0·157	11	
9 0 A.M.	41 43	0·102	0·114	0·216	11	+0·001
3 0 P.M.	42 43	0·099	0·115	0·214	11	
10 0 A.M.	53 01	0·149	0·130	0·279	13	+0·025
2 0 P.M.	53 18	0·108	0·120	0·228	6	
11 0 A.M.	61 09	0·204	0·131	0·335	13	+0·009
1 0 P.M.	61 07	0·184	0·133	0·317	11	
12 0 Noon.	64 14	0·221	0·138	0·359	11	

The numbers contained in columns 3 and 4 of Table II. give the relation between direct sunlight and diffuse daylight. These sets of numbers, expressed graphically in terms of the altitude, are seen on Plate XXX. fig. 3; the dotted curve indicating the intensity of the diffused light, the black curve that of the direct sunlight. These two curves intersect at an altitude of 50°, at which elevation, therefore, the place of equal chemical illumination occurs for a surface placed in the plane of the horizon.

The fact that the curve of direct sunlight cuts the base line at 10° bears out the conclusion which one of us has already announced, namely, that at altitudes below 10° direct sunlight is robbed of almost all its chemically active rays.

The curves (fig. 1) show the daily march of chemical intensity at Lisbon, as a mean of all the observations, compared with that at Kew for the preceding August, and at Pará for the preceding April. The number representing the mean chemical intensity at Kew is 94·5, at Lisbon 110, and at Pará 313·3; light of the intensity 1·0 acting for twenty-four hours being taken as 1000.

If we now arrange the observations according to the sun's altitude, we have:—

TABLE III.

Number of observations.	Mean altitude.	Chemical intensity.		
		Sun.	Sky.	Total.
15.	9° 51'	0·000	0·038	0·038
18.	19 41	0·023	0·062	0·085
22.	31 14	0·052	0·100	0·152
22.	42 13	0·100	0·115	0·215
19.	53 09	0·136	0·126	0·262
24.	61 08	0·195	0·132	0·327
11.	64 14	0·221	0·138	0·359

Fig. 2 gives the graphical representation of the relation of the total chemical intensity as ordinate to the sun's altitude as abscissa. The relation between the altitude and chemical intensity for altitude above 10° is here seen to be accurately represented by a straight line. The position of the experimentally determined points are noted, and serve to show how closely they lie to the straight line.

In former communications* it has been shown that a similar relation between altitude and chemical intensity of total daylight has been found to hold good at Heidelberg, Kew, and Pará; and that although the chemical intensity for the same altitude at different places and at different times of the year may greatly vary according to the varying transparency of the atmosphere, yet that the relation at the same place between altitude and intensity is always represented by a straight line. Thus the mean intensities at Lisbon and Pará for 30° are 0.15 and 0.44 respectively, whilst for 60° they are 0.32 and 0.80. That this variation in the direction of the straight line expressed by the constant in the formula, given in the paper last referred to, is due to the opalescence of the atmosphere, we have evidence of in the fact that, for equal altitudes, the higher intensity is always found where the mean temperature of the air is greater, as in summer, when we compare the same place at different seasons, or as we approach the equator, when we compare different places. The first of these conditions of variation is clearly seen if we compare the Kew observations for the same altitudes, but for different times of the year. The following Table clearly shows that the altitude in the warmer half of the year is invariably accompanied by a higher chemical action than that in the colder, and this is attributable to the varying opalescence, which is certainly a function of the atmospheric temperature, and is less marked as we approach the summer solstice or pass towards the equator.

Comparison of Chemical Intensities at Kew, 1866.

Month.	Time of observation.	Corresponding altitude.	Chemical intensity of total daylight.
I. {	October	23 10	0.059
	August	23 58	0.115
II. {	November ...	14 52	0.035
	September ...	14 14	0.058
III. {	March	28 36	0.075
	June.....	29 52	0.106
IV. {	April	38 06	0.116
	July	30 05	0.141

It is interesting to observe the close agreement which exists between the measurements made at Lisbon with sensitive paper, and the luminous intensities calculated from observations made at Heidelberg by a totally different method. In 1859 Professor BUNSEN, and one of us in Part IV. of 'Photochemical Researches,' gave curves of the

* Roscoe, Philosophical Transactions, 1867, p. 555.

chemical action effected, (1) by sunlight, (2) by diffused daylight on the horizontal unit of surface situated at various localities on the earth's surface.

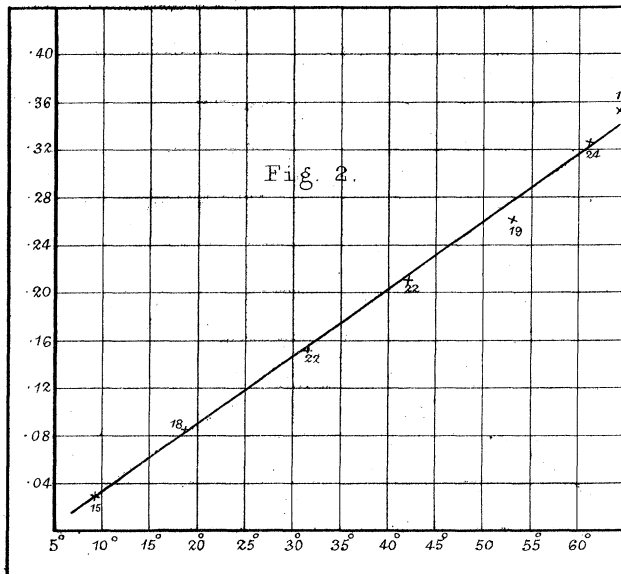
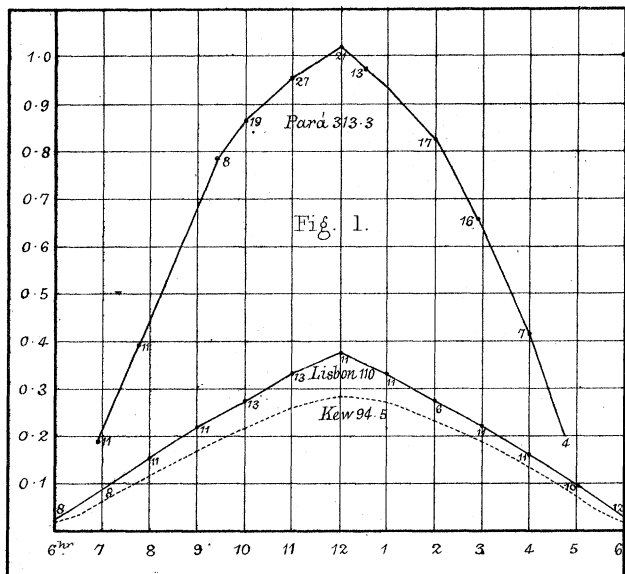
A comparison of the unit of measure there taken can unfortunately not be made with that used in the Lisbon experiments; but if we reduce the observational results for Lisbon (lat. $38^{\circ} 40'$ N.) and the calculated one for Naples (lat. $40^{\circ} 52'$ N.) to a common measure by assuming that the action of the direct sunlight at noon is equal in both cases, and reduce the other points in the Naples curve in the same ratio, we obtain the two curves B, B', fig. 4, whilst the corresponding curves for Lisbon are given on fig. 4, A, A'.

The correspondence between the results of the measurements above described and those made by a totally different method is further shown by the close coincidence of the "phases of equal chemical illumination" for sun- and diffuse-light as determined by both methods. In a former communication* it has been shown that in all places where the sun rises to a height of more than $20^{\circ} 56'$ above the horizon the chemical action effected by the diffuse daylight exceeds that of the direct sunlight at first; and that as the sun gradually rises a point is reached at which both sunlight and diffuse daylight produce exactly the same amount of chemical action, whilst beyond this point the effect of the sunshine is more powerful. This phase of equal illumination was calculated from theoretical considerations, and the result was confirmed by experiment, the difference between the calculated and the experimental points of equality amounting in mean to about thirty-five minutes. By reducing the chemical intensity of the direct sunlight in Table III. to that which the sunlight would produce on a plane perpendicular to the incident rays, we find that the phase of equal chemical intensity in reality is one which lasts for some time, that it begins near the calculated altitude of $18^{\circ} 48'$, but that it continues for about an hour. When, however, the sun reaches an elevation of 35° , the intensity of the sun's perpendicular rays becomes greater than that of the total diffuse light acting on a horizontal surface.

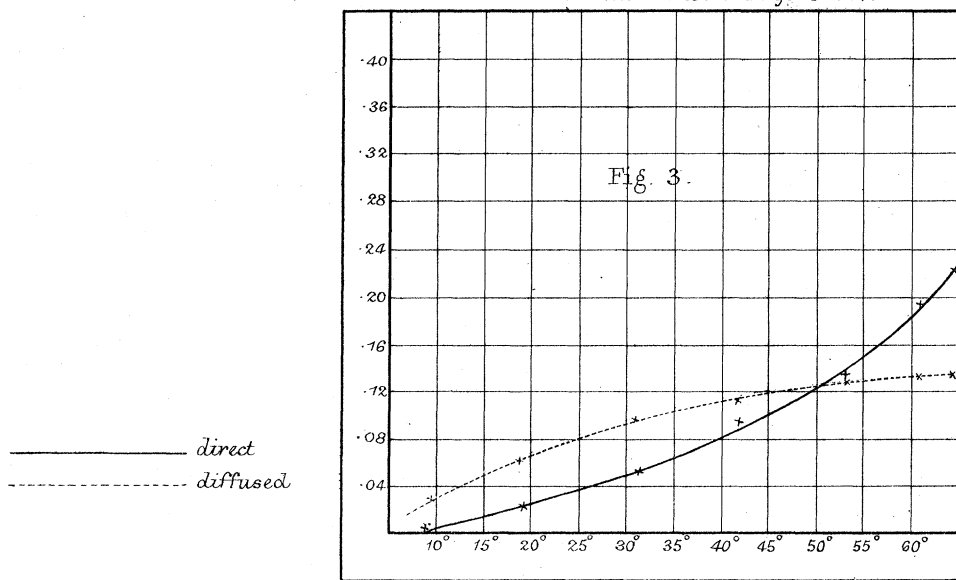
* BUNSEN and ROSCOE, "Photochemical Researches.—Part IV.," Phil. Trans. 1859, p. 915.

Curves shewing March of Total Chemical Intensity for Sunshine.
 Para April 1866. Kew and Lisbon. August 1866 & 1867.

Curve shewing Relation of Total Chemical Intensity
 to Sun's Altitude. Lisbon August 1867.



Curves shewing Relation of direct & diffused Chemical Intensity
 to Sun's Altitude.—Lisbon August 1867.



Lisbon (Lat. 38° 40')

Naples (Lat. 40° 52')

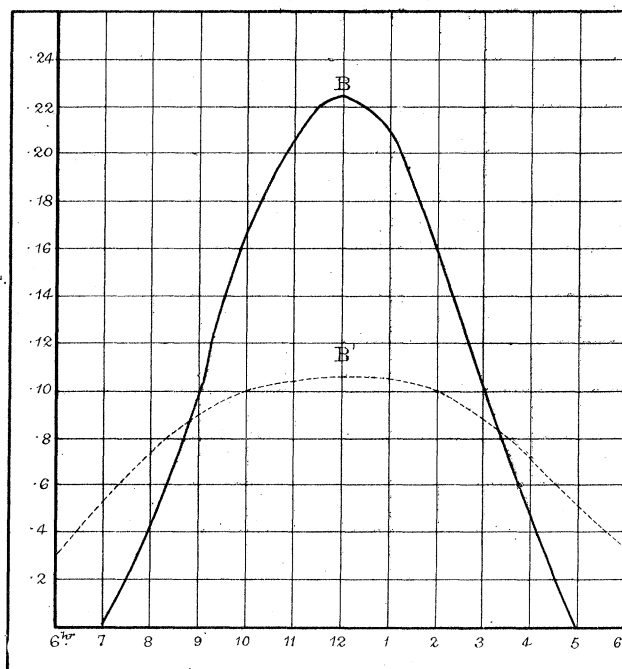
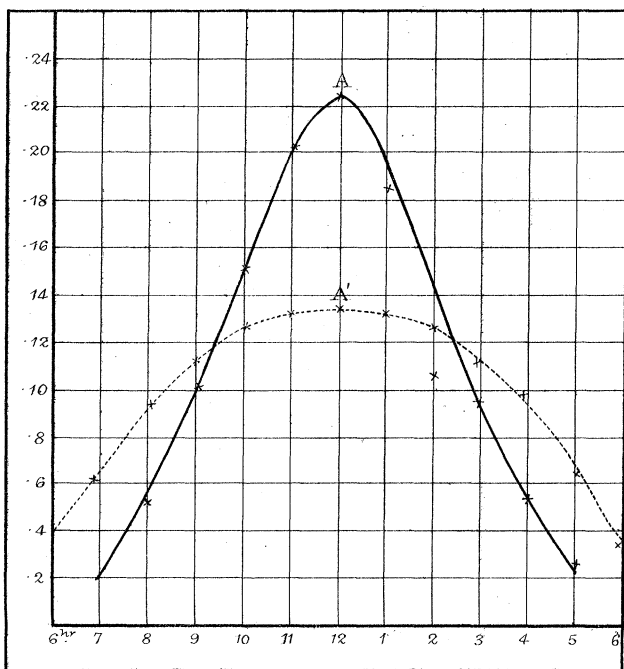


Fig. 4.