XXXVI. *On the Influence of Temperature on the Refraction of Light.*

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FRAUNHOFER, in his original measurements of the fixed lines of the spectrum, noted the thermometer, and those who since his time have occupied themselves with the determination of refractive indices, must have frequently noticed that changes of temperature affect the amount of refraction; yet of the many observations now on record, few have affixed to them the temperature at which they were made. BADEN POWELL has drawn out some refractive indices of the same substance taken at different temperatures, but remarks that the whole subject, both as to the facts of the case and as to their bearing on the theoretical formulæ, remains to be investigated *. Among his beautiful researches on light, M. JAMIN has recently published one or two experiments on refraction, heat, and density †; but, with this exception, he has left untouched the great question of the influence of temperature.

Some years ago BADEN POWELL kindly lent his instrument to one of us for the purpose of investigating this question. It is described and figured in the Report of the British Association for 1839. It consists essentially of a small telescope moving on a circle graduated so finely, that by means of a vernier and magnifying glass it may be read to 10″; to ensure accuracy, there is a vernier at each end of the moveable arm: in front of the telescope are appliances for fixing any solid prism, or a hollow prism capable of containing liquids, in such a position that there may be seen through it a ray of light proceeding from a distant slit. The telescope may be moved till a fine wire fastened in the field of view is brought to coincide with any of FRAUNHOFER's lines in the prismatic spectrum thus obtained, and the angle indicated by the position of the telescope on the graduated circle may be read off. In our recent joint research, as we desired to measure the positions of the extreme lines A and H, it was necessary to work with the full light of the sun; its mirrored image, therefore, was kept behind the narrow slit by means of a heliostat, and the eye was protected from the glare of the yellow rays by means of a cobalt-blue glass. Liquids were experimented on, and their temperature was changed by means either of a spirit-lamp or of a freezing mixture round the hollow prism, on a day when there was little or no moisture in the atmosphere to condense on the cold glass. A thermometer, which had been corrected by a standard instrument, was placed in the liquid contained in the hollow prism. In the experiments two practical difficulties had

* See his work on 'The Undulatory Theory as applied to the Dispersion of Light,' p. 125.

† Comptes Rendus, 29 Dec. 1856, and 23 Nov. 1857.

always to be contended with: the one was the proper fixing of the prism, so that its edge should be parallel with the slit, and that at the same time it should be kept in such a position as to indicate the minimum deviation. It was found necessary to fix this position at the commencement of the experiment, and to retain the same through all variations of temperature, though the angle of minimum deviation must vary slightly with the change of refraction; not, however, in the vast majority of cases, to an appreciable extent. A more serious difficulty was that of determining the precise temperature at which an observation was made, especially when the temperature of the liquid was much lower or higher than that of the surrounding air or brass-work; but it was to a great extent overcome by stirring the liquid in the prism with the immersed thermometer-bulb just before taking a measurement; and this had the additional advantage of bringing out the lines more distinctly; for where a liquid is very sensitive to heat and but little dispersive, as is the case with ether, the spectrum becomes too misty to see the lines unless the liquid be uniform in its temperature. A plan adopted in order to obtain observations on two or more lines at precisely the same temperature, was to bring the wire of the telescope exactly over one line, read the angle, and while it still coincided, or when next it did so, move it suddenly till it came over the other line.

The substances more or less fully examined have been bisulphide of carbon; water; ether; methylic, vinic, amylic and caprylic alcohols; hydrate of phenyl, and hydrate of cresyl, the two principal constituents of creasote; phosphorus; oil of cassia; and camphor dissolved in alcohol.

Bisulphide of Carbon.—The following Table gives the mean results of many observations made on pure colourless bisulphide of carbon, boiling at 43° C.

Temperature.	Refractive index of A.	Refractive index of D.	Refractive index of H.	Difference per 5° (D).	Length of spectrum.	Dispersive power.
0° C.	1·6217	1·6442	1·7175	0·0045	0·0958	0·1487
5	1·6180	1·6397	1·7119	0·0051	0·0939	0·1469
10	1·6144	1·6346	1·7081	0·0043	0·0937	0·1477
15	1·6114	1·6303	1·7035	0·0042	0·0921	0·1462
20	1·6076	1·6261	1·6993	0·0041	0·0917	0·1463
25	1·6036	1·6220	1·6942	0·0038	0·0906	0·1460
30	1·5995	1·6182	1·6896	0·0042	0·0901	0·1457
35	1·5956	1·6140	1·6850	0·0037	0·0894	0·1456
40	1·5919	1·6103	1·6810	0·0042	0·0891	0·1459
42·5	1·5900	1·6082	1·6778		0·0878	0·1443

The three columns that give the refractive indices of the fixed lines of the spectrum A, D, and H respectively, speak for themselves.

The next column represents the amount of change of refractive index which the substance exhibits, for each 5° of temperature. For this change the term *sensitiveness* is proposed. The difference is evidently uniform, or nearly so, the irregularities being within the limits of errors of observation. It is reckoned from the indices of the line D, as that line very nearly represents the point of mean refraction in the spectrum, and a glance will suffice to show that were it reckoned for either A or H, the average would be somewhat different, the whole amount of difference of refraction between 0° C. and 42°·5 C. being for A, 0·0317, for D, 0·0360, and for H, 0·0397. This fact is exhibited, though under another form, in the succeeding column, where the refractive index for A is subtracted from that for H; and as these lines are at the two extremities of the prismatic image, $\mu_H - \mu_A$ represents the measureable length of the spectrum. It evidently decreases as the temperature rises.

The last column gives the dispersive power at the different temperatures, that is, the ratio between the length of the spectrum and the mean refraction, or $\frac{\mu_H - \mu_A}{\mu_D - 1}$.

The refractive indices of all the larger lines at 15° C. have been thus determined:—

A.	B.	C.	D.	E.	F.	G.	H.
1·6114	1·6177	1·6209	1·6303	1·6434	1·6554	1·6799	1·7035

Water.—Distilled water, which had been boiled to expel the air, was examined, as also Wenham Lake ice-water. The following Table gives the average of several determinations:—

Temperature.	Refractive index of A.	Refractive index of D.	Refractive index of H.	Sensitiveness per 5° (D).	Length of spectrum.	Dispersive power.
0° C.	1·3291	1·3330	1·3438		0·0147	0·0429
5	1·3290	1·3329	1·3436	0·0001	0·0146	
10	1·3288	1·3327	1·3434	0·0002	0·0146	0·0439
15	1·3284	1·3324	1·3431	0·0003	0·0147	
20	1·3279	1·3320	1·3427	0·0004	0·0148	0·0445
25	1·3275	1·3317	1·3420	0·0003	0·0145	
30	1·3270	1·3309	1·3415	0·0006	0·0145	0·0438
35	1·3264	1·3303	1·3410	0·0006	0·0146	
40	1·3257	1·3297	1·3405	0·0006	0·0148	0·0449
45	1·3250	1·3288	1·3396	0·0009	0·0146	
50	1·3241	1·3280	1·3388	0·0008	0·0147	0·0448
55	1·3235	1·3271	1·3380	0·0009	0·0145	
60	1·3223	1·3259	1·3367	0·0012	0·0144	0·0441
65	1·3218	1·3249	……	0·0010		
70	1·3203	1·3237	1·3344	0·0012	0·0141	0·0435
80	1·3178	……	1·3321	0·0012(A)	0·0143	

The experiments of Jamin were also made with water. He was desirous of determining whether the index of refraction varied *pari passu* with the density, which it should do if the theory of emission be the correct one; accordingly he gradually cooled down water to the freezing-point, and found that the index steadily increased, passed 4° C., the point of maximum density, and still increased till 0°. Hence he deduced the independence of the two phenomena, change of density, and change of refraction by heat. His instrument, being constructed so as to take advantage of the phenomena of interference, is more delicate than that employed by us, but it is more difficult to obtain numerical data by it. Our determinations were performed repeatedly and most carefully on water near the freezing-point: they confirm the observations of the French physicist, but show at the same time that the remarkable reversion of the change of density at 4° C. is not without its influence on the amount of sensitiveness; the change of refractive index between 10° and 5° being 0·0002, while that between 5° and 0° is only 0·0001. This fact, however, will come out more plainly on a reference to the following Table, which represents the refractive indices of one of the series of observations made with especial view to this point. The indices are calculated to five places of decimals.

Temperature.	Refractive index of A.	Refractive index of D.	Refractive index of H.
0° C.	......	1·33374	......
1	1·32913	......	1·34377
2	1·32913	......	1·34377
3	1·32913	......	......
4	1·32902	1·33367	1·34366
6·5	......	1·33356	1·34366
9	1·32882	1·33342	1·34337
11	1·32879	......	1·34331

Nor is this the only indication of the influence of change in density exhibited by the Table of indices of water. It is there evident that the sensitiveness of water is greater at high than at low temperatures; so is its change of density; but the two do not proceed *pari passu*. It is well known also that water becomes much lighter specifically as it freezes; it has also been observed that the refractive index of ice is much less than that of water. The following determinations will show that the two changes are almost identical in amount, or rather that the ratio between the density and the mean refraction, $\mu_D - 1$, is almost constant. The refractive index of ice was determined for D at 1·3089 and

Substance.	Mean refraction.	Specific gravity.	Refractive power.
Ice at ... 0°	0·3089	0·9184*	2973
Water at 0°	0·3330	1·0000	3003

The similarity is here so close as to suggest the idea that the slight discrepancy is due to errors of experiment. If it be so, water has not changed its refractive power by passing from the liquid to the solid state, and another deduction of M. JAMIN may be made more general. He found that the refraction of water under different pressures varied in precise accordance with the amount of condensation, and concluded that "it may be admitted that this law of constancy of the refractive power is worthy of acceptance when the water does not change its physical condition, and remaining at the same temperature, is submitted to variable pressure." The law may prove to be worthy of acceptance even when water does change its physical condition from the liquid to the solid.

The refractive indices of the principal fixed lines were determined as follows at a temperature of 15° C.:—

* According to PLAYFAIR and JOULE, Mem. Chem. Soc. vol. ii.

A.	B.	C.	D.	E.	F.	G.	H.
1·3284	1·3300	1·3307	1·3324	1·3347	1·3366	1·3402	1·3431

These measurements agree very closely with those previously published by FRAUNHOFER and by POWELL.

Ether.—Anhydrous ether boiling at 35° C. gave the following results*:—

Temperature.	Refractive index of A.	Refractive index of D.	Refractive index of H.	Sensitiveness per 5° (D).	Length of spectrum.	Dispersive power.
5° C.	1·3585	1·3622	1·3740	0·0030	0·0155	0·0428
10	1·3555	1·3592	1·3707	0·0026	0·0152	0·0423
15	1·3529	1·3566	1·3683	0·0021	0·0154	0·0431
20	1·3508	1·3545	1·3658	0·0026	0·0150	0·0423
25	1·3485	1·3519	1·3635	0·0023	0·0150	0·0426
30	1·3460	1·3496	1·3611	0·0024	0·0151	0·0432
34	1·3442	1·3477	1·3595		0·0153	0·0440

The following measurements of the principal fixed lines were obtained at 15° C. :—

A.	B.	C.	D.	E.	F.	G.	H.
1·3529	1·3545	1·3554	1·3566	1·3590	1·3606	1·3646	1·3683

Alcohol.—The following Table represents the mean results of many experiments performed with absolute alcohol. In order to prevent the alcohol absorbing water from the surrounding atmosphere during the course of the experiments, they were performed on frosty days when the air contained no moisture.

Temperature.	Refractive index of A.	Refractive index of D.	Refractive index of H.	Sensitiveness per 5° (A).	Length of spectrum.	Dispersive power.
0° C.	1·3658	....	1·3811	0·0019	0·0153	
5	1·3639	....	1·3793	0·0022	0·0154	
10	1·3617	1·3658	1·3769	0·0017	0·0152	0·0415
15	1·3600	1·3638	1·3751	0·0022	0·0151	0·0415
20	1·3578	1·3615	1·3730	0·0024	0·0152	0·0419
25	1·3554	1·3598	1·3706	0·0017	0·0152	0·0419
30	1·3537	1·3578	1·3687	0·0024	0·0150	0·0418
35	1·3513	1·3556	1·3661	0·0018	0·0148	0·0416
40	1·3495	1·3536	1·3643	0·0020	0·0148	0·0417
45	1·3475	1·3514	1·3624	0·0024	0·0149	0·0424
50	1·3451	1·3491	1·3599	0·0022	0·0148	0·0423
60	1·3407	1·3437	1·3558		0·0151	0·0439

The refractive indices were thus determined for all the principal fixed lines at 15° C.

A.	B.	C.	D.	E.	F.	G.	H.
1·3600	1·3612	1·3621	1·3638	1·3661	1·3683	1·3720	1·3751

Wood Spirit.—The purest specimen of methylic alcohol which we could obtain, but which, when rendered anhydrous, had too low a boiling-point, was examined on a day when the dew-point was as low as 0°·6 C.

* This Table was substituted during the printing for a less accurate one.

Temperature.	Refractive index of A.	Refractive index of D.	Refractive index of H.	Sensitiveness per 5° (A).	Length of spectrum.	Dispersive power.
0° C.	1·3378	....	1·3519	0·0017	0·0141	
5	1·3361	....	1·3500	0·0018	0·0139	
10	1·3343	1·3379	1·3483	0·0013	0·0140	0·0414
30	1·3292	....	1·3432	0·0022	0·0140	
40	1·3247	1·3297	1·3387	0·0030	0·0140	0·0424
50	1·3187	....	1·3331		0·0144	

This Table, though imperfect, suffices to show the close analogy in every respect between methylic and ethylic alcohol.

Amylic Alcohol and *Caprylic Alcohol*.—These two alcohols, the specimen of the first boiling at 130° to 132° C., that of the second at about 181° C., yielded results very comparable with those of the alcohols previously examined, though they are more refractive than their congeners lower in the series. Indeed, it seems probable that an advance in refractive power occurs with each increment of $C_2 H_2$. A similar advance in the length of the spectrum is also perceptible, but not in the sensitiveness. The following Table will sufficiently exhibit this:—

Alcohol.	Temperature.	Refractive index of A.	Refractive index of H.	Sensitiveness per 10°.	Length of spectrum.
Methylic:—	0° C.	1·3378	1·3519	0·0035	0·0141
$C_2 H_4 O_2$	10	1·3343	1·3483		0·0140
Ethylic:—	0	1·3658	1·3811	0·0041	0·0153
$C_4 H_6 O_2$	10	1·3617	1·3769		0·0152
Amylic:—	0	1·4084	1·4263	0·0024	0·0179
$C_{10} H_{12} O_2$	10	1·4060	1·4238		0·0178
Caprylic:—	0	1·4291	1·4504	0·0039	0·0213
$C_{16} H_{18} O_2$	10	1·4252	1·4454		0·0202

Hydrate of Phenyl.—A specimen of this substance, the principal constituent of creasote, boiling at 187° C., was examined. It was solid at the ordinary temperature, but on cooling gradually in the prism, it remained liquid even at 12°·5 C. The addition of a little solid hydrate caused the whole then to fly into crystals with the evolution of sensible heat. As this body has also a great attraction for water, the experiment was performed on a very cold dry day.

Temperature.	Refractive index of A.	Refractive index of D.	Refractive index of H.	Sensitiveness per 5° (D).	Length of spectrum.	Dispersive power.
13° C.	1·5377	1·5488	1·5886	0·0025	0·0509	0·0927
25	1·5321	1·5429	1·5823	0·0016	0·0502	
30	1·5301	1·5413	1·5802	0·0027	0·0501	0·0925
35	1·5276	1·5386	1·5773	0·0024	0·0498	
40	1·5254	1·5362	1·5748	0·0025	0·0494	0·0921
45	1·5230	1·5337	1·5717	0·0026	0·0487	
50	1·5205	1·5311	1·5692	0·0024	0·0487	0·0916
60	1·5156	1·5262	1·5637	0·0024	0·0481	0·0914
65	1·5132	1·5238	1·5616	0·0029	0·0484	
70	1·5109	1·5209	1·5587		0·0476	0·0913

The principal fixed lines were found to have the following refractive indices at 13° C.:—

A.	B.	C.	D.	E.	F.	G.	H.
1·5377	1·5416	1·5433	1·5488	1·5564	1·5639	1·5763	1·5886

Hydrate of Cresyl.—A portion of creasote, which after repeated distillations boiled at 201° to 205° C., was submitted to examination. It consisted mainly, no doubt, of the higher homologue of hydrate of phenyl, which has been designated hydrate of cresyl, differing from it by one increment of $C_2 H_2$; yet the liquid could scarcely be considered a pure specimen of that substance. It gave results almost identical with those obtained with hydrate of phenyl, in the amount of refraction, dispersion, and sensitiveness.

Phosphorus.—As phosphorus is one of the most refractive substances known, and an element, it was thought desirable to determine the change produced in its relation to light by change of temperature. The fixed lines of the spectrum, however, could not be recognized through melted or solid phosphorus; and when of the ordinary pale yellow colour, it absorbed the extreme red about A. By employing a red glass as an absorbent medium, the following determinations of the position of the orange-red ray about C were obtained:—

Temperature.	Refractive index of C (about)	Sensitiveness per 5° C.
30° C.	2·0741	
		0·0032
35	2·0709	
		0·0032
40	2·0677	
		0·0037
45	2·0640	
		0·0037
50	2·0603	
		0·0046
55	2·0557	
		0·0042
60	2·0515	
		0·0042
65	2·0473	
		0·0051
70	2·0422	

The extreme violet ray at 40° had, as nearly as could be determined, a refractive index of 2·2356, giving the enormous length of the spectrum 0·1679, from C to H.

Solid phosphorus, at 35° C., was found to give the index 2·1168 for the orange-red ray. On solidifying, this substance also experiences a great increase of density.

Oil of Cassia.—As this oil is reputed to be one of the most dispersive substances known, and highly refractive too, it presents points of great interest; but unfortunately it is no definite chemical compound; and the specimen examined by us, and which was said to be very pure, was far less dispersive than that employed by the Rev. Baden Powell. It had also a slight yellow tint, arising from the partial absorption of the most refrangible rays. The following determinations were made, the line G being necessarily measured instead of H:—

Temperature.	Refractive index of A.	Refractive index of D.	Refractive index of G.	Sensitiveness for 5° (A).	Length of spectrum, $\mu_G - \mu_A$.	Dispersive power.
25° C.	1·5700	1·5880	1·6414	0·0022	0·0714	0·1214
30	1·5678	....	1·6389	0·0025	0·0711	
35	1·5653	1·5832	1·6361	0·0024	0·0708	0·1214
40	1·5629	1·5796	1·6328	0·0029	0·0699	0·1206
45	1·5600	....	1·6296	0·0026	0·0696	
50	1·5574	....	1·6266	0·0027	0·0692	
60	1·5520	1·5690	1·6200		0·0680	0·1195

Camphor in Alcohol.—Alcohol, saturated with camphor at about 25° C., was rendered considerably more refractive and dispersive, but its sensitiveness remained almost exactly the same.

A comparison of the observations here noted seems to warrant the following conclusions:—

I. In every substance the refractive index diminishes as the temperature increases. The comparative amount of sensitiveness varies greatly, from 0·0042 per 5° C. in phosphorus to as little as 0·0002 in water.

II. The length of the spectrum varies as the temperature increases. In the case of highly dispersive bodies, as bisulphide of carbon and hydrate of phenyl, it decreases considerably; in the case of less dispersive bodies, as the alcohols, it decreases to a less extent; while with water the decrease is scarcely appreciable.

III. In some substances the dispersive power is diminished, in others it is augmented by a rise of temperature; that is, in such substances as bisulphide of carbon, it is the numerator of the function $\frac{\mu_H - \mu_A}{\mu_D - 1}$ that decreases fastest, while in such substances as water it is the denominator.

IV. The sensitiveness of a substance is independent of its specific refractive or dispersive power. Thus water and ether are very similar as to the actual amount of the refraction and dispersion exhibited by them at the ordinary temperature, but ether is many times more sensitive to heat than water is.

V. The amount of sensitiveness is not directly proportional to the change of density produced by alteration of temperature, yet there is some relationship between the two phenomena. This has been already pointed out in reference to water; and in general those substances that are most affected in density by heat are the most sensitive.

VI. No sudden change of sensitiveness occurs near the boiling-point; at least, this is true in respect to bisulphide of carbon, ether, and methylic alcohol.

The Rev. T. P. DALE originated this inquiry. He too is responsible for the calculations, and Dr. GLADSTONE for all the angular measurements on which they are based, and the purity of the substances employed.