

XXXII.—*Molecular Refraction and Dispersion of various Substances.*

By J. H. GLADSTONE, Ph.D., F.R.S.

SINCE the paper on the refraction equivalents of the elements, published in the *Phil. Trans.* of 1879, a considerable number of observations of refractive indices have accumulated in my note books, besides those which have been published from time to time. It seems desirable to make a permanent record of such as may be valuable in determining the optical constants.

Effect of Change of Temperature.

Amongst the earliest of these unpublished observations are some that were made to determine how far the law holds good that the

specific refractive energy of a body is unaffected by temperature. The method employed was that of determining the refraction for different lines of the spectrum on a hot summer's day, preserving the specimen carefully until the following winter, and then redetermining it. I give only those made upon bisulphide of carbon and benzene, as they are substances referred to in the paper by Dale and myself, in the *Phil. Trans.* of 1863, and the present observations may be regarded as more exact than those given therein.

Bisulphide of Carbon.

Temp. C.	Density.	μ_A .	μ_B .	μ_C .	μ_D .	μ_E .	μ_F .	μ_G .	μ_H .
10·0°	1·2793	1·6153	1·6217	1·6250	1·6344	1·6471	1·6592	1·6837	1·7078
24·5	1·2593	1·6045	1·6109	1·6143	1·6235	1·6362	1·6483	1·6722	1·6954
1·5	1·2909	1·6227	1·6288	—	1·6417	—	1·6672	—	1·7159
23·0	1·2594	1·6070	1·6134	—	1·6260	—	1·6504	—	1·6972
30·0	1·2494	1·6026	1·6087	—	1·6213	—	1·6458	—	1·6922

Benzene.

Temp. C.	Density.	μ_A .	μ_B .	μ_C .	μ_D .	μ_E .	μ_F .	μ_G .	μ_H .
10·0°	0·8868	1·4935	1·4965	1·4983	1·5029	1·5091	1·5148	1·5258	1·5355
21·5	0·8773	1·4887	1·4917	1·4934	1·4979	1·5040	1·5095	1·5205	1·5304
2·0	0·8979	1·5021	1·5053	—	1·5122	—	1·5242	—	1·5460
23·7	0·8760	1·4893	1·4928	—	1·4993	—	1·5109	—	1·5320
28·6	0·8709	1·4860	1·4897	—	1·4960	—	1·5094	—	1·5279

The first two lines in each case represent one specimen, and the three following another specimen.

The following tables give the refractive index divided by the density, or, in other words, the specific refractive energy:—

Bisulphide of Carbon.

Temp. C.	$\frac{\mu_A - 1}{d}$.	$\frac{\mu_B - 1}{d}$.	$\frac{\mu_C - 1}{d}$.	$\frac{\mu_D - 1}{d}$.	$\frac{\mu_E - 1}{d}$.	$\frac{\mu_F - 1}{d}$.	$\frac{\mu_G - 1}{d}$.	$\frac{\mu_H - 1}{d}$.
10·0°	0·4809	0·4859	0·4885	0·4959	0·5058	0·5153	0·5344	0·5532
24·5	0·4803	0·4851	0·4878	0·4951	0·5053	0·5148	0·5338	0·5522
1·5	0·4824	0·4871	—	0·4971	—	0·5168	—	0·5546
23·0	0·4820	0·4871	—	0·4971	—	0·5164	—	0·5536
30·0	0·4823	0·4872	—	0·4973	—	0·5169	—	0·5540

Benzene.

Temp. C.	$\frac{\mu_A - 1}{d}$	$\frac{\mu_B - 1}{d}$	$\frac{\mu_C - 1}{d}$	$\frac{\mu_D - 1}{d}$	$\frac{\mu_E - 1}{d}$	$\frac{\mu_F - 1}{d}$	$\frac{\mu_G - 1}{d}$	$\frac{\mu_H - 1}{d}$
10·0°	0·5564	0·5598	0·5619	0·5670	0·5740	0·5804	0·5929	0·6038
21·5	0·5570	0·5604	0·5624	0·5675	0·5745	0·5807	0·5933	0·6046
2·0	0·5592	0·5628	—	0·5704	—	0·5838	—	0·6081
23·7	0·5585	0·5626	—	0·5700	—	0·5832	—	0·6073
28·6	0·5580	0·5623	—	0·5695	—	0·5849	—	0·6062

These tables serve to confirm the conclusion arrived at by Dale and myself, in 1863, and now generally received, that "the specific refractive energy of a liquid is a constant not affected by temperature." We considered at that time that "there is some influence * * * which gives rise to the slight progression of most of the calculated products;" this is generally believed to be the case, but the differences in the above tables may be attributable simply to experimental error.

Carbon Compounds.

The following table gives observations on various carbon compounds. Those marked with an asterisk are from specimens kindly furnished me by Dr. Perkin:—

Substance.	Formula.	Temp. C.	Den- sity.	μ_A .	μ_D .	μ_F .	μ_H .
Pentane.....	C_5H_{12}	6·5°	0·6365	1·3607	1·3649	—	1·3769
Heptane	C_7H_{16}	12·0	0·6895	1·3875	1·3917	1·3966	1·4046
"	"	23·0	0·6809	1·3826	1·3867	1·3917	1·3991
"	"	7·6	0·6935	1·3904	—	1·3995	1·4073
Amylene*	C_5H_{10}	20·2	0·6568	1·3776	—	1·3887	1·3991
Benzene*	C_6H_6	18·5	0·8815	1·4927	1·5027	1·5144	1·5357
Toluene.....	C_7H_8	24·1	0·8566	1·4800	1·4893	1·5002	1·5195
Metaxylene*.....	C_8H_{10}	22·5	0·8641	1·4876	—	1·5079	1·5277
Paraxylene*	"	23·7	0·8602	1·4854	—	1·5058	1·5253
Orthoxylene*	"	24·1	0·8758	1·4928	—	1·5129	1·5328
Cinnamene.....	C_8H_8	21·0	0·9111	1·5318	1·5446	1·5615	1·5936
" 2nd spec.*	"	21·4	0·9179	1·5336	—	1·5645	1·5973
" after standing	"	25·0	0·9223	1·5333	—	1·5635	1·5957
"	"	26·4	0·9214	1·5330	—	1·5629	1·5957
"	"	30·0	0·9192	1·5303	—	1·5608	1·5928
"	"	33·0	0·9161	1·5293	—	1·5593	1·5917
β -Butenylbenzene,*	$C_{10}H_{12}$	21·0	0·9008	1·5269	1·5390	1·5545	1·5834
Diamylene*	$C_{10}H_{20}$	17·6	0·7710	1·4327	—	1·4445	1·4554
Cedrene	$C_{15}H_{24}$	13·0	0·942	1·5011	—	1·5133	1·5258
Carbon tetrachloride	CCl_4	10·5	1·6058	1·4604	1·4661	1·4729	1·4843
"	"	12·0	1·598	1·4616	1·4674	—	1·4868

Substance.	Formula.	Temp. C.	Den- sity.	μ_A .	μ_D .	μ_F .	μ_H .
Carbon tetrachloride	„	19.5°	1.586	1.4599	—	1.4733	1.4851
„ „ „ „ *	„	12.3	1.6095	1.4599	1.4656	1.4726	1.4835
„ „ dichloride...	C_2Cl_4	12.5	1.6232	1.5006	1.5087	—	1.5859
Chloroform.....	$CHCl_3$	12.5	1.50245	1.4453	1.4506	1.4570	1.4677
Bromoform*.....	$CHBr_3$	19.0	2.891	1.5875	1.5980	1.6107	1.6334
Methyl iodide*.....	CH_3I	21.0	2.274	1.5185	1.5293	1.5423	1.5652
Methylene diiodide*	CH_2I_2	10.5	3.344	1.7275	1.7559	1.7750	1.8229?
Acetylene bromide	$C_2H_2Br_2$	20.0	2.256	1.5332	1.5428	—	1.5751
Ethylene bromide*...	$C_2H_4Br_2$	10.5	2.2008	1.5361	1.5446	—	1.5722
Ethyl bromide*.....	C_2H_5Br	8.0	1.487	1.4263	1.4320	—	1.4503
Ethyl iodide*.....	C_2H_5I	7.0	1.9671	1.5124	1.5222	1.5343	1.5551
Allyl tribromide*...	$C_3H_5Br_3$	7.0	2.4277	1.5824	1.5912	—	1.6205
Trimethylene iodide*	$C_3H_6I_2$	7.5	2.589	1.6347	1.6479	1.6643	1.6940
Isobutyl iodide*.....	C_4H_9I	7.0	1.6296	1.4958	1.5036	1.5140	1.5312
Glycerin.....	$C_3H_8O_3$	15.7	1.2594	1.4673	—	1.4778	1.4866
Chlorofumaric chlor- ide*.....	$C_4HCl_3O_2$	25.7	1.5692	1.5088	1.5185	—	1.5556
Allylacetic acid*....	$C_5H_8O_2$	7.5	0.9903	1.4283	1.4341	—	1.4522
Amyl formate.....	$C_6H_{12}O_2$	11.5	0.8832	1.3910	1.3951	1.4000	1.4084
Diallylacetic acid*...	$C_8H_{12}O_2$	7.0	0.9618	1.4513	1.4574	—	1.4776
Ethyl acetyltri- thylenecarboxylate	$C_8H_{12}O_3$	25.2	1.0425	1.4383	1.4441	—	1.4629
Ethyl maleate*.....	$C_8H_{12}O_4$	7.5	1.0806	1.4405	1.4465	—	1.4659
Ethyl fumarate*.....	$C_8H_{12}O_4$	7.5	1.0693	1.4404	1.4471	—	1.4694
Ethyl chlorofumar- ate*.....	$C_8H_{11}ClO_4$	24.0	1.19517	1.4531	1.4598	—	1.4831
Ethyl acetyltetra- methylenecarboxyl- ate*.....	$C_9H_{14}O_3$	24.5	1.0605	1.7469	1.4772	—	1.5033
Safrole.....	$C_{10}H_{10}O_2$	11.3	1.0963	1.5286	1.5390	1.5524	1.5769
„ „ „ „	$C_{10}H_{10}O_2$	23.3	1.0813	1.5212	1.5314	—	1.5679
Orthoallylanisole*...	$C_{10}H_{12}O$	20.0	0.9932	1.5467	1.5604	—	1.6154
Isomyl oxide*.....	$C_{10}H_{20}O$	11.8	0.7826	1.4076	—	1.4169	1.4258
α -Parabutenylanisole*	$C_{11}H_{14}O$	19.0	0.9797	1.5426	1.5559	1.5733	1.6093
β -Parabutenylanisole*	„	23.0	0.9796	1.5360	1.5487	—	1.5976
Trimethylene cyan- ide*.....	$(CH_2)_3(CN)_2$	23.2	0.9888	1.4318	1.4365	1.4420	1.4514
Diethylamine*.....	$(C_2H_5)_2NH$	22.0	0.7050	1.3805	—	1.3906	1.3993
Triethylamine*.....	$(C_2H_5)_3N$	21.2	0.7280	1.3961	—	1.4067	1.4165
Propylamine*.....	$C_3H_7NH_2$	23.5	0.7140	1.3827	1.3873	1.3927	1.4011
„ „ „ „	„	6.5	0.7329	1.3922	—	1.4022	1.4111
Dipropylamine*.....	$(C_3H_7)_2NH$	23.2	0.7356	1.3983	—	1.4083	1.4172
„ „ „ „	„	4.4	0.753	1.4086	—	1.4191	1.4281
Tripropylamine*.....	$(C_3H_7)_3N$	22.8	0.7535	1.4121	1.4171	1.4229	1.4326
„ „ „ „	„	4.4	0.7703	1.4197	—	1.4306	1.4408
Propionitrile*.....	C_3H_5N	24.0	0.7816	1.3619	1.3659	1.3701	1.3778
Methyldiphenyl- amine*.....	$(C_6H_5)_2CNH_3$	24.6	1.0466	1.5998	1.6166	1.6391	1.6774
Benzylaniline*.....	$C_{13}H_{13}N$	24.8	1.0619	1.5974	1.6118	1.6301	1.6663?
„ „ „ „	„	26.3	1.0609	1.5967	1.6111	1.6297	1.6660?
Methyl sulphate*...	$(CH_3)_2SO_4$	20.0	1.3269	1.3843	—	1.3921	1.3984
Ethyl thiocyanate*...	C_2H_5SCN	20.0	1.0099	1.4593	—	1.4732	1.4864
Ethylthiocarbimide*	„	16.5	1.0030	1.5055	—	1.5279	1.5493
Stannic ethide.....	$(C_2H_5)_4Sn$	—	1.4089	1.5065	1.5143	—	1.5403
Zincic ethide.....	$(C_2H_5)_2Zn$	8.0	1.245	1.4936	—	1.5141	1.5336

From the foregoing data the molecular refraction can be calculated by dividing the index, minus unity, by the density, and multiplying by the molecular weight, $\frac{\mu - 1}{d}P$. The molecular dispersion is the difference between the molecular refraction of the lines A and H, or more shortly, $\frac{\mu_H - \mu_A}{d}P$. The theoretical values for the molecular refraction of any compound may be arrived at by adding together the recognised atomic refractions of the constituent elements; and the molecular dispersion can be reckoned on the same principle.

The following table contains the atomic refraction and dispersion of the elements with which we are concerned in this paper:—*

Substance.	At. wt.	R _A .	R _H - R _A .
Carbon	12	5.0	0.26
" double linked	"	6.1	0.51 or 0.66
Hydrogen	1	1.3	0.04
Chlorine, with compound radicles	35.5	9.9	0.45
" in olefines, &c.	"	10.0	0.50
Bromine, with compound radicles	80	15.3	1.03
" in olefines, &c.	"	15.2	1.22
Iodine, with compound radicles	127	24.5	2.60
" in olefines, &c.	"	25.35	3.65
Oxygen, double bond	16	3.4	0.18
" single bonds	"	2.8	0.10
Sulphur, double bond	32	16.0	2.6
" single bonds	"	14.1	1.2
Nitrogen, in nitriles	14	4.1	0.10
" in bases	"	5.1	0.38
Tin	118	18.6 ²	—
Zinc	65	9.8	—

In the following table (next page) are given the experimental and the theoretical values for the molecular refraction and dispersion of the carbon compounds.

A glance at this table will show that in the case of pentane and most of the other substances the experimental and the theoretical numbers are in fairly close accordance in respect of both the optical properties. In some cases, however, there is an evident discrepancy; and it may be noticed that where a marked discrepancy occurs between

* The actual figures are taken from my paper on "Refraction Equivalents" (*American Journal of Science*, 29, 55), and on "Dispersion Equivalents" (*Proc. Roy. Soc.*, 1887, 42, 401), and from Messrs. J. H. and G. Gladstone's paper on "Fluorobenzene, and other Allied Compounds" (*Phil. Mag.*, 1891, 31, 1). At present these must be taken as only approximative, pending a full revision of the subject, which I hope shortly to be in a position to undertake.

Substance.	Formula.	Experimental.		Theoretical.	
		Molr. refrn.	Molr. dispn.	Molr. refrn.	Molr. dispn.
Pentane	C_5H_{12}	40·80	1·83	40·6	1·78
Heptane	C_7H_{16}	56·20	2·48	55·8	2·46
Do.	"	56·19	2·42	"	"
Do.	"	56·29	2·44	"	"
Amylene	C_6H_{10}	40·24	2·24	40·2	2·20
Benzene	C_6H_6	43·59	3·81	44·4	4·20
Toluene	C_7H_8	51·55	4·25	52·0	4·54
Metaxylene	C_8H_{10}	59·81	4·92	59·6	4·88
Paraxylene	"	59·80	4·93	"	"
Orthoxylene	"	59·64	4·85	"	"
Cinnamene	C_8H_8	60·70	7·06	59·2	5·6
Do. 2nd specimen	"	60·46	7·22	"	"
Do. after standing	"	60·10	7·06	"	"
β -Butenylbenzene	$C_{10}H_{12}$	77·20	8·23	74·4	6·28
Diamylene	$C_{10}H_{20}$	78·57	4·12	78·2	3·90
Cedrene	$C_{15}H_{24}$	108·52	5·35	108·4	5·36
Carbon tetrachloride	CCl_4	44·15	2·30	45·0	2·26
Do.	"	44·48	2·43	"	"
Do.	"	44·66	2·44	"	"
Do.	"	44·00	2·26	"	"
Carbon dichloride	C_2Cl_4	51·20	3·60	52·2	3·32
Chloroform	$CHCl_3$	35·42	1·78	36·3	1·80
Bromoform	$CHBr_3$	51·41	4·02	51·9	3·96
Methyl iodide	CH_3I	32·37	2·92	33·4	2·98
Methylene diiodide	CH_2I_2	58·30	7·65?	58·8	7·64
Acetylene bromide	$C_2H_2Br_2$	43·95	3·46	45·2	3·54
Ethylene bromide	$C_2H_4Br_2$	45·80	3·08	45·6	3·12
Ethyl bromide	C_2H_5Br	31·25	1·76	31·8	1·75
Ethyl iodide	C_2H_5I	40·64	3·38	41·0	3·32
Allyl tribromide	$C_3H_5Br_3$	67·41	4·41	67·1	4·64
Trimethylene iodide	$C_3H_6I_2$	72·57	6·77	71·8	6·22
Isobutyl iodide	C_4H_9I	55·98	4·00	56·2	4·00
Glycerin	$C_3H_8O_3$	34·14	1·41	33·8	1·40
Chlorofumaric chloride	$C_4HCl_3O_2$	60·80	5·59	61·6	4·31
Allylacetic acid	$C_5H_8O_2$	43·25	2·41	43·8	2·40
Amyl formate	$C_6H_{12}O_2$	51·35	2·29	51·8	2·32
Diallylacetic acid	$C_8H_{12}O_2$	65·69	3·83	66·2	3·84
Ethyl acetyltrimethylene- carboxylate	$C_8H_{12}O_3$	65·59	3·68	65·2	3·02
Ethyl maleate	$C_8H_{12}O_4$	70·11	4·04	70·2	3·92
Ethyl fumarate	"	70·85	4·66	72·4	4·72
Ethyl chlorofumarate	$C_8H_{11}ClO_4$	78·29	5·18	81·0	5·13
Ethyl acetyltetramethylene- carboxylate	$C_9H_{14}O_3$	75·29	5·39	—	—
Safrole	$C_{10}H_{10}O_2$	78·11	7·14	78·0	6·48
Do.	$C_{10}H_{10}O_2$	78·09	6·99	78·0	6·48
Orthoallylanisoil	$C_{10}H_{12}O$	81·46	10·24	—	—
Isoamyl oxide	$C_{10}H_{22}O$	82·29	3·68	81·4	3·58
α -Parabutenylanisoil	$C_{11}H_{14}O$	89·71	11·09	—	—
β -Parabutenylanisoil	"	88·65	10·17	—	—
Trimethylene cyanide	$(CH_2)_3(CN)_2$	41·05	1·85	41·0	1·74
Diethylamine	$(C_2H_5)_2NH$	39·40	1·95	39·4	1·86
Triethylamine	$(C_2H_5)_3N$	54·95	2·83	54·6	2·54

Substance.	Formula.	Experimental.		Theoretical.	
		Molr. refrn.	Molr. dispn.	Molr. refrn.	Molr. dispn.
Propylamine	$C_3H_7NH_2$	31·62	1·52	31·8	1·52
Do.		31·57	1·52		
Dipropylamine	$(C_3H_7)_2NH$	54·69	2·59	54·6	2·54
Do.		54·80	2·62		
Tripropylamine	$(C_3H_7)_3N$	78·21	3·89	77·4	3·56
Do.		77·91	3·92		
Propionitrile	C_3H_5N	25·47	1·12	25·6	1·08
Methyldiphenylamine	$(C_6H_5)_2CNH_2$	104·88	13·56	100·2	9·08
Benzylaniline	$C_{13}H_{13}N$	102·94	11·92	"	"
Methyl sulphate	$(CH_3)_2SO_4$	36·49	1·34	—	—
Ethyl thiocyanate	C_2H_5SCN	39·57	2·33	39·7	2·28
Ethylthiocarbimide	"	43·85	3·80	43·8	4·18
Stannic ethide	$(C_2H_5)_4Sn$	84·12	5·54	84·6	—
Zincic ethide	$(C_2H_5)_2Zn$	48·88	3·97	42·8	—

theory and experiment in the refraction, a still greater proportionate discrepancy frequently occurs in the dispersion.

The following points in regard to some of the substances may be worthy of notice:—

Heptane.—The substance examined was Professor Thorpe's specimen derived from *Pinus sabiniana*, which has good claims to be considered as specially pure. It will be observed that the molecular refraction is about 0·4 higher than that calculated from theory. This suggests the idea that CH_2 is not exactly 7·6, as usually assumed, but about midway between that number and 7·7. From a general comparison of the data existing in 1884, I was led to assign to it the value of 7·63 (Trans., 1884, 45, 251). The theoretical molecular dispersion coincides well with the experimental.

Amylene.—The addition made for the one pair of double-linked carbons in the dispersion is the lower figure 0·5*, as in the allyl compounds.

Benzene.—This specimen was made from benzoic acid. Its molecular refraction and dispersion agree with those determined from specimens prepared in the ordinary way. They are both decidedly less than the figures calculated from the general run of aromatic compounds.

Toluene.—The same remarks apply, but the discrepancy is only about half as great. These peculiarities of benzene and toluene are commented upon, so far as refraction is concerned, in my paper on

* That is, the difference between 0·26 (the atomic dispersion for ordinary carbon) and 0·51 (the lower value for a double-linked carbon atom) twice over.

"Refraction Equivalents" (Trans., 1884, **45**, 253). I am not yet able to find any explanation.

Xylenes.—The three xylenes agree very closely in molecular refraction and dispersion, the considerable difference in their indices being compensated by corresponding differences in their densities. The orthoxylene is practically identical with the theoretical values; and the others, unlike the previous members of the series, are not lower, but even a trifle higher than theory.

Cinnamene and Butenylbenzene.—In these two cases, in which there are four pairs of double-linked carbons, the experimental values are decidedly higher than the theoretical. They may be added to the substances referred to in my paper (*Proc. Roy. Soc.*, **31**, 329), in which I ventured to assign a still higher value than 6.1 to a carbon atom, which "has all four of its units of atomicity satisfied by other carbon atoms, each of which has the higher value of 6.0 or 6.1."

Cedrene.—The specimen examined was prepared with great care. It indicates only one pair of double-linked carbon atoms, which is more probable than the constitution formerly ascribed to the essential oils of the $C_{15}H_{24}$ group. I hope to revert to this subject on some future occasion.

HALOGEN COMPOUNDS.—With these there will be found a general agreement between experiment and theory; but it ought to be stated that several of the observations recorded in this table were used among other data for determining the values of chlorine, bromine, and iodine in different states of combination. Nevertheless, I doubt if these values have been exactly estimated as yet; at any rate, there seem to be discrepancies. Thus the experimental values for tetrachloride of carbon and for chloroform given in the table are in good accordance with previous determinations of the same substances, and they indicate a dispersion equivalent for chlorine of at least 0.50, but a refraction equivalent of from 9.7 to 9.9 instead of 10.0.

Carbon Dichloride and Acetylene Bromide.—In both of these substances we should expect a double linking, and though the numbers do not agree very well, both optical properties point in that direction.

OXYGEN COMPOUNDS.—The compounds containing oxygen present some peculiarities worthy of notice. There are three cases of isomerides differing in their optical properties; and some bodies of extremely high refraction.

Ethyl Maleate and Fumarate.—The optical properties of ethyl maleate answer very well to what may be expected of a substance having the composition of $C_8H_{12}O_4$ with one double linking, which gives in the dispersion the higher value of 0.8. Ethyl fumarate, on the contrary, indicates rather two double linkings, both giving the

additional value of 0·8 in the dispersion. The molecular magnetic rotation, according to Perkin, is also higher in the fumarate than the maleate. There are, however, a chlorine substitution product of ethyl fumarate, and another of fumaric acid, which do not altogether bear out this view.

Safrole.—This oil was prepared in my laboratory. The optical properties are fairly accordant with the formula $\text{CH}_2\langle\text{O}\rangle\text{C}_6\text{H}_5\cdot\text{C}_3\text{H}_5$, the substance containing a phenyl nucleus with its three double linkings, and another pair of double-linked carbons in the side-chain. It differs from anethol in not requiring us to suppose the existence of any carbon of a still higher refraction than 6·1.

Allylacetic Acid and Diallylacetic Acid.—These two are interesting, as they agree perfectly with one another, and with the theory that has been for some time established for allyl compounds, viz., that 2·2 is to be added to the molecular refraction, and 0·5 to the molecular dispersion, for each unsaturated C_3H_5 .

The Anise Oils.—These are all so high that they indicate the extreme value for one of the carbons which has been already referred to under the head of cinnamene. The orthoallylanisoil of Perkin is the same as what is generally called anethol, and agrees with former determinations. The two isomeric parabutenylanisoils appear to differ in optical properties.

NITROGEN COMPOUNDS.—The compounds of nitrogen in the list, whether they are nitriles or cyanides, all give refraction and dispersion equivalents so nearly coincident with theory as to leave no doubt that the optical properties confirm the chemical views of their composition. The following points also are worthy of notice :—

Propylamines.—Beneath the determinations of the three specimens at a low temperature are placed those of the same specimens made on a very hot day, though the latter have been already published. They show that the difference of 17° or 18° makes so little difference in the molecular refraction or dispersion that it is not to be distinguished from the ordinary error of experiment.

Methyldiphenylamine and Benzylaniline.—This pair of isomeric bodies differ in their optical properties, and both appear to be above what would be theoretically required ; but aniline itself, according to several observers, has a higher refraction and dispersion than might be expected, and one which would almost exactly account for the experimental figures for benzylaniline. The methyldiphenylamine has still higher optical properties.

Ethyl Thiocyanate and Ethylthiocarbimide.—The first of these isomerides gives results quite in accordance with the chemical view of its constitution. The figures are similar to those obtained by

Nasini. The second gives much higher values, which, however, agree closely with the isothiocyanate of Nasini, and a previous determination of my own. They indicate that the sulphur is united by two bonds, which necessitates also a double linking of the carbons.

Stannic Ethide.—This confirms fairly the value formerly assigned for the refraction of tin from the determinations of its tetrachloride. The dispersion of tin has not yet been given; but if it is calculated from the tetrachloride (*Phil. Trans.*, 1869, 28) it will be 2.42, whilst stannic ethide will give 2.66. The *zinc ethide*, on the contrary, differs widely from what might be expected from the refraction of zinc salts in solution. The specimen was prepared in my laboratory, and the refraction agrees substantially with that deduced from Bleekrode's observation. The values of the two metals as determined from these ethides would be—

$$\begin{array}{llll} \text{Tin} & \dots\dots & R_A = 18.1 & \dots\dots R_H - R_A = 2.66 \\ \text{Zinc} & \dots\dots & R_A = 15.9 & \dots\dots R_H - R_A = 2.53 \end{array}$$

Halogen Compounds.

In addition to the halogen compounds contained in the preceding list, there occur in my note books the following, which do not contain carbon:—

Substance.	Formula.	Temp. C.	Density.	μ_A .	μ_D .	μ_F .	μ_H .
Silicon tetrachloride....	SiCl ₄ ...	10.5°	1.504	1.4156	1.4207	—	1.4360
" "	"	14.0	1.4987	1.4139	—	1.4248	1.4334
Silicon tetrabromide....	SiBr ₄ ...	15.5	2.7906	1.5586	—	1.5794	1.5988
Titanium tetrachloride..	TiCl ₄ ...	10.5	1.744	1.5928	1.6112	—	—
" " ..	" ..	—	1.7228	1.5851	1.6039	1.6296	1.6814

The figures give the following molecular values:—

Substance.	Formula.	R_A .	$R_H - R_A$.
Silicon tetrachloride.....	SiCl ₄	47.11	2.33
" "	"	47.09	2.22
Silicon tetrabromide.....	SiBr ₄	69.76	5.02
Titanium tetrachloride.....	TiCl ₄	65.26	—
" "	"	65.20	10.74

Silicon Tetrachloride.—These two observations, made from different specimens, not only agree remarkably well with one another, but also with the value published by Haagen as far back as 1867, from whose

Substance.	Formula.	Temp. C.	Density.	μ_A .	μ_B .	μ_C .	μ_D .	μ_E .	μ_G .	μ_H .
Benzene	C_6H_6	7.5°	0.8881	1.4972	—	1.5024	1.5070	1.5189	—	1.5402
Toluene.....	C_7H_8	7.5	0.8704	1.4895	—	1.4941	1.4982	1.5097	—	1.5297
Caoutchouc.....	$C_{10}H_{16}$	17.2	0.8396	1.4665	—	1.4700	1.4733	1.4818	—	1.4963
Naphthalene monobromide.....	$C_{10}H_7Br$	17.5	1.5403	1.6463	—	1.6553	1.6638	1.6879	—	1.7360
Cinnamic alcohol	$C_9H_{10}O$	13.0	1.0318	1.5465	—	1.5525	1.5579	1.5734	—	1.6022
α -Methyl orthoxyphenylate of methyl	$C_{11}H_{12}O_3$	10.5	1.1442	1.5570	1.5617	—	1.5717	1.5929	1.6213	1.6419
β -Methyl orthoxyphenylate of methyl	"	10.0	1.1527	1.5720	1.5781	—	1.5904	1.6175	1.6553	1.6818
Aniline.....	C_6H_7N	7.5	1.0322	1.5780	—	1.5847	1.5921	1.6102	—	1.6449
Methyl diphenylamine.....	$CH_3N(C_6H_5)_2$	24.6	1.0466	1.5998	—	1.6083	1.6166	1.6391	1.6634	1.6774
Carbon bisulphide.....	CS_2	16.0	1.2706	1.6116	—	1.6213	1.6308	1.6556	—	1.7032

numbers R_a would be calculated at 47.06, and $R_y - R_a$ at 1.428, which is about equivalent to 2.27 for $R_H - R_A$. From this the refraction equivalent of silicon, 7.4 was deduced. Assuming that chlorine in the tetrachlorides has the same value as in the organic olefine compounds, Mr. George Gladstone and I, in our paper on Fluorides (*loc. cit.*), estimated the refraction equivalent of silicon at 7.07, and the dispersion equivalent at 0.32. These figures are not well supported by the specimen of tetrabromide of silicon, for which I am indebted to Professor Thorpe. The refraction equivalent calculated from it on similar principles would be as much as 9.6, and the dispersion equivalent only 0.14.

Titanium Tetrachloride.—The two specimens agree well. An early experiment of mine, published in 1869, gave R_A as 65.08, and indicated a similar length of spectrum. The refraction does not differ widely from an observation made by H. Becquerel. Reckoning as in the case of the carbon and silicon compounds, titanium would appear to have a refraction equivalent of 25.2, and the enormous dispersion equivalent of about 8.7.

Additional Lines of the Spectrum.

My notes frequently contain observations of lines in the spectrum, other than A, D, F, and H, more particularly in those substances that have a high dispersive power. As these may be interesting in some inquiries, the more important ones are subjoined, whether the substances have been given already in this or in previous papers.

I hope, with the permission of the Society, shortly to give a further communication dealing with various observations upon the refraction and dispersion of substances in solution.
