rotation of freshly dissolved crystalline fructose. It is thus proved to have the same cause as the mutarotation reaction, namely, the slow establishment in solution of the equilibrium between the α and β forms of the sugar.

From the stereochemical theory a formula is deduced which allows the calculation of the rotatory power of the unknown forms of many of the natural and synthetic glucosides. From these calculated values the theory permits a calculation of the influence of the end groups of the glucosides on the rotatory power of the asymmetric carbon atom to which they are attached. The results, which are shown in the figure, indicate that the influence of the group is chiefly due to its weight, and that the rotation of the affected carbon atom changes greatly with the weight for introduced groups of small weight but is constant for those of large weight.

The specific rotations of the unknown α-*d*-fructose and the unknown forms of mannose, maltose, melibiose, xylose, and lyxose are calculated.

[PHOENIX PHYSICAL LABORATORY CONTRIBUTIONS, NO. 17.]

THE CHANGE IN REFRACTIVE INDEX WITH TEMPERATURE. I.

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A considerable amount of work has been done on the determination of the refractive indices of a number of organic liquids at different temperatures.[1] Brühl and W. H. Perkin used this change in refractive index with change in temperature as a means of following the equilibrium between the two forms of certain tautomeric substances. Their results in some instances do not agree.[2]

It was decided, therefore, to attempt to follow these changes more carefully by determining the refractive indices for the sodium and the three hydrogen lines at intervals of 2° or 3° over a range of 50° or 60°, using the purest chemicals obtainable and samples from different sources when possible. In order to be able to judge whether the changes observed with tautomeric substances were normal or not, it was necessary to follow the changes in the refractive indices of other substances with

[1] Landolt-Bornstein-Meyerhoffer's Tabellen give a very complete summary.

[2] Perkin, in his paper on "Influence of Temperature on the Refractive Power and on the Refraction Equivalents of Acetylacetone and of Ortho- and Para-toluidine," *J. Chem. Soc.*, **69**, 1, concludes with: "It would seem, therefore, that there must be some unnoticed source of error in the refractometer used by Brühl, when it is employed for temperatures somewhat above those of the atmosphere." Brühl in "Studien über Tautomerie," *J. pr. Chem.*, **50**, 192, referring to the fact that the molecular refraction of acetylacetone as determined by Perkin decreased with rise in temperature, whereas his own experimental observations showed it to increase, remarked: "Worauf diese Widersprüche beruhen, vermag ich nicht zu erklären."

change in temperature just as carefully, in order to find the general course of the phenomena in question.

In this paper, the method of working is briefly described first, then the experimental results obtained so far are given, then some theoretical conclusions following directly from these results will be discussed, and finally some observations on ethyl acetacetate will be spoken of.

Apparatus and Method.—Thanks to the kindness of Professor J. L. R. Morgan, it was possible to use in this investigation a Pulfrich refractometer with the arrangement for heating the liquid to be studied, belonging to the Department of Physical Chemistry. The heating spirals, etc., supplied with the apparatus were used, and since refractometers of this type have been described a number of times, especially recently in great detail by C. Chéneveau,[1] who used among other refractometers one exactly similar to the one used here, only a few points in connection with its use will be mentioned. The refractive indices were obtained for the sodium (D_1) and the three hydrogen (C, F, and G′) lines compared to air at about 20°. The thermometers used read to tenths of a degree, one between 0° and 50°, the other between 50° and 100°. Since the measurements were made over a fairly large range of temperature, it may be possible that the substance was not always at the temperature indicated by the thermometer, or that there may be a lag in the refractive index on account of which the true reading could only be obtained after some time. These sources of possible error were overcome by taking the readings at different intervals of time after the thermometer had become stationary, sometimes making a measurement after a few minutes, in other cases waiting an hour or more, and also by making the measurements around 40° (for instance) in one case by heating from the room temperature upward, and in the other by heating to a higher temperature for some time and then allowing to cool to the lower temperature. No attempt was made to take the readings at any one fixed temperature determined upon beforehand, but the readings were taken at the points for which the heating conditions for the time being gave a constant temperature. The time of taking the four readings occupied generally less than two minutes, and the temperature was read both before and after. The temperature did not remain constant to a tenth of a degree for considerable lengths of time, but did within a degree for an hour or more, while for the time required for the readings it remained practically constant. In this way, it is hoped, constant errors were avoided and by taking a sufficient number of readings between about 20° and 75° and plotting the results, the true course of the change within these limits of temperature could be determined. The record of the temperature and the time was of course carefully kept, but will not be given here as no general effect was notice-

[1] *Ann. chim. phys.* [8], **12**, 145.

able except in one case (ethyl acetacetate). Corrections for the zero point were introduced. The corrections for the prism at different temperatures were taken from the tables furnished by Zeiss.

The substances for which the measurements were made were diisoamyl, dimethylaniline, *n*-heptyl alcohol, benzyl alcohol, *n*-butyric acid, and the tautomeric substances acetylacetone and ethyl acetacetate. The choice of substances may seem peculiar, but in order to find the general course of the change under investigation it was desirable to use as many different classes of substances as possible and in picking out the individual member of each class to study, those substances with high boiling points lying close together were chosen, since this investigation will be extended to mixtures (in varying proportions) and their refractive indices at different temperatures, as more light, probably, will be thrown on the state of the tautomeric substances under these conditions than in the study of the pure liquids. The substances obtained from Kahlbaum were measured as received and after distillation, practically the same results being obtained in the two cases. The other substances were distilled before they were used in some cases, in others not. The boiling points given are not intended to represent accurately the true temperatures, as the thermometer used was not calibrated carefully and the pressures were not determined, but are only given to show the constancy of the temperatures at which the substances distilled.

The densities were determined with an Ostwald pycnometer which had been used by Dr. Eric Higgins.[1] Some time was saved by using the calibration curve for different temperatures as carefully determined by him. The densities are compared to the density of water at 4° and the results of others recalculated to this basis when necessary, when used for comparison.

Experimental Results.

In this section the results for diisoamyl, dimethylaniline, *n*-heptyl alcohol, benzyl alcohol, *n*-butyric acid, and acetylacetone will be given. On plotting the refractive indices against the temperatures and drawing curves, it was found that for all four lines, as well as for the densities for these substances, the smoothed curves are straight lines in every case. All points naturally do not lie on the curves, but the difference is not greater in any case than the difference between two experimental results. The curves are not reproduced in this paper since the scale on which they would have to be drawn would not show the details satisfactorily. It may suffice to give all the experimental determinations here and the equations which represent the curves for all the cases. The results will be tabulated as follows:

[1] Morgan and Higgins, This Journal, 30, 1055.

The refractive indices determined for the C, D, F and G′ lines.

The densities determined.

The five equations representing the curves.

The experimental results of others compared with those calculated for the required temperatures from the equations.

The changes in the refractive indices and in the density for 1° as calculated from the equations.

The dispersions for 10° and 80° calculated from the equations.

Strictly speaking, the curves hold only as far as experiments have been made as regards the temperature, but it seems fair to extend them a short distance above and below. The dispersions (and later in the theoretical part, the refractive powers) have therefore been calculated for 10° and for 80°, in all probability without introducing any sensible errors. The dispersions have been taken from the curves and not from the experiments directly, since the latter may contain the errors due to two series of experiments, while the former eliminate to a great extent these accidental errors.

DIISOAMYL.

Kahlbaum's, undistilled.

t.	*C.*	*D.*	*F.*	*G′.*
21.2	1.40589	1.40793	1.41303	1.41742
22.3	530	739	243	666
23.3	512	717	226	653
25.1	413	611	125	547
25.8	378	587	096	532
30.0	199	399	1.40907	345
32.6	085	291	797	227
36.2	1.39937	137	635	059
36.8	912	112	617	041
40.5	754	1.39948	442	1.40859
43.0	661	851	347	765
45.8	515	716	204	641
47.9	418	623	111	509
49.9	331	533	026	429
51.6	249	442	1.39930	357
52.0	235	423	907	339
53.7	143	354	835	269
57.9	1.38963	160	646	085
61.0	829	017	509	1.39948
67.0	529	1.38729	211	.....
72.9	265	463	1.38936	370

Kahlbaum's redistilled, b. 156.5°–7.0° (uncorr.).

t.	*C.*	*D.*	*F.*	*G′.*
22.5	1.40536	1.40738	1.41254	1.41687
23.2	502	702	215	651
26.0	388	588	102	527
30.7	190	384	1.40895	325
37.6	1.39896	093	593	016
43.7	634	1.39815	326	1.40743

t.	*C*.	*D*.	*F*.	*G'*.
46.1	508	687	190	618
51.2	281	471	1.39965	390
54.7	111	313	800	235
58.2	1.38950	160	627	048
62.9	742	1.38932	420	1.39844
67.3	541	718	223	...
70.3	410	598	089	518

DENSITY.

	Vol. in cc.	Wt. in grams.	d_4^t
23.3	10.0170	7.225	0.7213
23.5	10.0171	7.224	0.7212
34.4	10.0191	7.142	0.7128
43.5	10.0209	7.071	0.7056
49.9	10.0220	7.024	0.7008
56.8	10.0233	6.973	0.6956
62.9	10.0245	6.926	0.6909
70.1	10.0258	6.870	0.6852

(1*a*) $n_C/1.41537 + t/3187.175 = 1$

(1*b*) $n_D/1.41750 + t/3173.24 = 1$

(1*c*) $n_F/1.42280 + t/3127.03 = 1$

(1*d*) $n_{G'}/1.42710 + t/3143.39 = 1$

(1*e*) $d/0.7392 + t/960 = 1$

DENSITY.

	t.	Found.	Calc.
Schiff[1]	9.8°	0.7358	0.7317
Lachowicz[2]	22.°	0.72156	0.7223
Just[3]	22.°	0.7463	0.7223

	C.	*D*.	*F*.	*G'*.	*d*.
Change per degree	0.000444	0.0004467	0.000455	0.000454	0.00077

	D — *C*.	*F* — *D*.	*G'* — *F*.
Dispersion, 10°	0.00210	0.00522	0.00430
Dispersion, 80°	0.00191	0.00464	0.00437

DIMETHYLANILINE.

Merck's (mono-free), undistilled.

t.	*C*.	*D*.	*F*.	*G'*.
17.6	1.55296	1.55968	1.57765	1.59489
20.0	171	840	631	320
25.4	1.54917	574	368	1.58975
30.1	685	345	124	802
34.0	491	160	1.56930	639
43.7	023	1.54681	417	067
52.9	1.53557	201	1.55935	1.57589
63.1	038	1.53695	390	013 (?)
64.1	008	655	356	044 (?)
71.3	1.52620	259	1.54965	1.56582 (?).

[1] *Ann.*, **220**, 88 (1883).

[2] *Ibid.*, **220**, 172 (1883).

[3] *Ibid.*, **220**, 156 (1883).

Kahlbaum's, undistilled.

t.	*C.*	*D.*	*F.*	*G'.*
17.9	1.55279	1.55953	1.57752	1.59433
18.0	282	952	744	430
18.6	255	925	720	395
20.0	172	835	629	339
21.0	143	817	596	268
27.0	1.54830	480	323	1.58943
30.7	668	326	134	775
30.8	656	304	096	755
37.9	297	1.54948	1.56716	365
42.0	098	749	508	142
45.7	1.53906	542	303	1.57935
55.8	429	078	1.55820	454
56.2	412	052	766	403
62.1	125	1.53760	489	092

Kahlbaum's redistilled, b. 189.5° (uncorr.).

t.	*C.*	*D.*	*F.*	*G'.*
18.4	1.55250	1.55914	1.57710	1.59422
24.6	1.54959	620	396	059
27.1	847	502	267	1.58954
32.5	570	230	1.56989	651
34.8	448	091	871	526
37.9	284	1.54945	700	368
41.5	103	758	517	172
44.4	1.53962	607	367	006
47.3	806	443	207	1.57783 (?)
49.4	721	365	101	753
52.3	603	259	1.55991	612
52.6	586	238	960	578
58.9	265	1.53915	626	331 (?)
59.3	256	898	614	239 (?)
64.3	1.52988	627	334	009 (?)
65.3	931	581	281	1.56900 (?)
65.8	911	555	263	882 (?)
67.3	827	467	180	825 (?)
67.7	806	456	154	842 (?)
69.6	724	351	050	696 (?)
73.4	511	156	1.54842	447 (?)

The determination of the G' line, especially at the higher temperatures, was rendered difficult by the yellow color of the dimethylaniline.

DENSITY.

t.	Vol. in cc.	Wt. in gms.	d_4^t.
21.3	10.0167	9.567	0.9551
36.2	10.0195	9.448	0.9429
43.3	10.0208	9.390	0.9371
53.4	10.0227	9.310	0.9289

(2a)	$n_C/1.56175$	+	$t/3155.05$	=	1
(2b)	$n_D/1.56845$	+	$t/3143.19$	=	1
(2c)	$n_F/1.58675$	+	$t/3057.32$	=	1
(2d)	$n_{G'}/1.60417$	+	$t/2976.20$	=	1
(2e)	$d/0.95305$	+	$t/1179.45$	=	1

		C.		D.	
	t.	Found.	Calc.	Found.	Calc.
Perkin[1]	8.	1.55828	1.55779	1.56489	1.56446
"	89.7	1.51704	1.51738	1.52315	1.52337
Brühl[2]	20.	1.55203	1.55185	1.55873	1.55846

		F.		G'.	
	t.	Found.	Calc.	Found.	Calc.
Perkin	8.	1.58369	1.58260	.....	.....
"	89.7	1.53979	1.54019	.....	.....
Brühl	20.	1.57658	1.57637	1.59332	1.59339

		d.	
	t.	Found.	Calc.
Brühl[2]	20	0.9575	0.9566
Perkin[1]	10	0.9654	0.9648
	20	0.9570	0.9566
	30	0.9493	0.9484
	40	0.9410	0.9401
	50	0.9328	0.9318
	60	0.9246	0.9236
	70	0.9162	0.9153
	80	0.9077	0.9070
	90	0.8991	0.8988
Menschutkin[3]	18	0.9580	0.9583

		d.	
	t.	Found.	Calc.
Renard and Guye.[4]	10.9	0.964	0.9641
	41.0	0.939	0.9392
	55.0	0.927	0.9277
	78.9	0.907	0.9080
	96.0	0.892	0.8938

	C.	D.	F.	G'.	d.
Change per degree	0.000495	0.000499	0.000519	0.000539	0.000825

	D—C.	F—D.	G'—F.
Dispersion, 10°	0.00666	0.01810	0.01722
Dispersion, 80°	0.00638	0.01670	0.01582

n-Heptyl Alcohol.

Kahlbaum's, undistilled.

t.	C.	D.	F.	G'.
22.1	1.42118	1.42326	1.42851	1.43288
22.3	110	322	839	293
22.8	090	299	813	255
27.1	1.41918	122	645	090
29.5	816	029	542	1.42982
33.5	667	1.41874	388	821
37.4	514	725	237	661
40.1	407	623	135	579
43.3	330	533	045	486

[1] *J. Chem. Soc.*, **61**, 287 (1892).
[2] *Ann.*, **235**, 14 (1886).
[3] *Centralb.*, **1898**, II, 478.
[4] *J. chim. phys.*, **5**, 81 (1907).

t.	*C.*	*D.*	*F.*	*G'.*
46.8	216	410	1.41927	373
48.5	138	321	853	311
51.2	042	230	741	171
54.3	1.40904	104	614	095
56.5	836	034	546	1.41968
59.5	708	1.40912	410	844
62.3	613	816	310	737
65.9	466	668	162	613
69.1	350	552	035	497
72.8	192	390	1.40894	343

Kahlbaum's redistilled, b. 172.5–3.0° (uncorr.).

22.4	1.42116	1.42326	1.42843	1.43281
22.7	088	297	823	263
24.4	043	242	770	196
27.7	1.41905	105	627	084
34.5	622	1.41821	340	1.42772
41.3	370	575	090	535
48.4	075	295	1.41797	239
55.5	1.40869	060	573	042
61.7	615	1.40828	331	1.41775
71.5	235	422	1.40937	397

DENSITY.

t.	Vol. in cc.	Wt. in gms.	d_4^t.
25.5	10.0175	8.196	0.8182
35.1	10.0193	8.131	0.8115
43.7	10.0209	8.070	0.8053
51.7	10.0224	8.014	0.7996
61.3	10.0242	7.946	0.7927
68.4	10.0255	7.895	0.7875

(3*a*) $n_C/1.42952 + t/3788.42 = 1$

(3*b*) $n_D/1.43141 + t/3867.43 = 1$

(3*c*) $n_F/1.43693 + t/3722.62 = 1$

(3*d*) $n_{G'}/1.44144 + t/3729.48 = 1$

(3*e*) $d/0.8364 + t/1173.87 = 1$

	t.	*C.* Found.	*C.* Calc.	*F.* Found.	*F.* Calc.
Eijkmann[1]	16.5	1.42343	1.42329	1.43079	1.43056

	t.	*d.* Found.	*d.* Calc.
Eijkmann[1]	16.5	0.8235	0.8246
Perkin[2]	15.	0.8300	0.8257
"	25.	0.8228	0.8182
Gartenmeister[3]	0	0.8355	0.8364
Cross[4]	0	0.838	0.8364
"	16.	0.829	1.8250
"	27.	0.821	0.8172

[1] *Rec. trav. chim.*, **12,** 157 (1893).
[2] *J. pr. Chem.*, **31,** 511 (1884).
[3] *Ann.*, **233,** 255 (1886).
[4] *Ibid.*, **189,** 2.

	C.	*D.*	*F.*	*G'.*	*d.*
Change per degree....	0.000377	0.000370	0.000386	0.0003865	0.0007125

	D — C.	*F — D.*	*G' — F.*
Dispersion, 10°.................	0.00196	0.00536	0.00451
Dispersion, 80°.................	0.00246	0.00426	0.00447

Benzyl Alcohol.

Kahlbaum's, undistilled.

t.	*C.*	*D.*	*F.*	*G'.*
21.4	1.53529	1.54011	1.55251	1.56325
21.6	523	009	241	327
22.0	505	1.53979	208	290
22.1	498	972	201	282
24.6	398	885	113	194
27.8	268	748	1.54978	061
30.9	090	562	773	1.55840
33.2	1.52910	374	602	675
37.7	700	177	382	450
40.7	566	057	261	333
43.7	453	1.52929	125	202
46.3	355	830	033	114
48.5	259	738	1.53937	015
50.6	181	659	869	1.54948
60.7	1.51809	291	474	550
63.9	708	196	354	442
65.8	652	128	322	389
69.4	493	1.51951	126	203

Kahlbaum's redistilled, b. 199.3–9.8° (uncorr.).

t.	*C.*	*D.*	*F.*	*G'.*
24.5	1.53347	1.53833	1.55058	1.56138
25.6	325	801	035	114
28.2	220	702	1.54927	009
30.0	148	625	859	1.55940
33.4	1.52999	467	708	777
36.8	874	339	573	657
38.8	774	248	472	549
42.5	619	087	302	381
46.3	395	1.52870	075	145
49.5	274	734	1.53938	1.54999
52.8	159	637	797	862
55.8	059	523	707	770
58.9	1.51905	360	558	619
63.3	718	214	409	469
64.5	664	129	323	384
66.4	607	069	252	314
73.2	353	1.51799	1.52982	038

Merck's redistilled, b. 200.5–1.0° (uncorr.).

21.5	1.53500	1.53987	1.55228	1.56298
22.0	463	943	175	259
22.1	458	938	175	253
32.4	1.52951	418	1.54652	1.55723
37.6	712	179	398	476

t.	*C.*	*D.*	*F.*	*G'.*
42.0	527	000	202	288
47.7	424	1.52897	114	180
54.1	132	604	1.53795	1.54872
56.2	040	503	704	778
60.0	1.51890	355	541	608
63.5	759	228	425	493
67.6	594	064	266	328

DENSITY.

t.	Vol. in cc.	Wt. in gms.	d^t_4.
22.4	10.0169	10.477	1.0459
32.9	10.0189	10.399	1.0379
40.2	10.0202	10.341	1.0320
53.0	10.0226	10.245	1.0222
57.8	10.0235	10.208	1.0184
63.6	10.0246	10.163	1.0138
71.4	10.0261	10.104	1.0078
23.1	10.0170	10.466	1.0448
40.3	10.0202	10.335	1.0314
51.5	10.0223	10.249	1.0226

The benzyl alcohol showed a tendency to dissolve the cement binding together the glass cup and the prism, causing considerable annoyance at times.

(4a) $n_C/1.54407 + t/3611.99 = 1$

(4b) $n_D/1.54875 + t/3644.12 = 1$

(4c) $n_F/1.56160 + t/3549.09 = 1$

(4d) $n_{G'}/1.57259 + t/3494.67 = 1$

(4e) $d/1.0616 + t/1415.47 = 1$

	t.	*C.* Found.	*C.* Calc.	*D.* Found.	*D.* Calc.
Brühl[1]	20.	1.53474	1.53552	1.53955	1.54025
Eijkmann[2]	19.8	1.53541	1.53560	.....	.....

	t.	*F.* Found.	*F.* Calc.	*G'.* Found.	*G'.* Calc.
Brühl	20.	1.55178	1.55277	1.56232	1.56353
Eijkmann	19.8	1.55251	1.55288	.....	.....

	t.	*d* Found.	*d* Calc.
Brühl[1]	20.	1.0427	1.0467
Eijkmann[2]	19.8	1.0429	1.0466
Perkin[3]	4.	1.0579	1.0585
	10.	1.0531	1.0541
	20.	1.0450	1.0466
	30.	1.0371	1.0391
	40.	1.0293	1.0316
	50.	1.0215	1.0241
	60.	1.0133	1.0166
	70.	1.0050	1.0091
	80.	0.9966	1.0016

[1] *Ann.*, **203**, 1 (1880). [2] *Rec. trav. chim.*, **12**, 186 (1893). [3] *J. Chem. Soc.*, **69**, 1198 (1896).

	C.	*D.*	*F.*	*G'.*	*d.*
Change per degree.......	0.0004275	0.000425	0.000440	0.000450	0.000750

	D—C.	*F—D.*	*G'—F.*
Dispersion, 10°.................	0.00471	0.01270	0.01089
Dispersion, 80°.................	0.00488	0.01165	0.01019

n-BUTYRIC ACID.

Kahlbaum's, undistilled.

t.	*C.*	*D.*	*F.*	*G'.*
21.3	1.39537	1.39733	1.40230	1.40632
23.5	456	652	150	551
24.2	436	634	123	536
24.4	415	612	105	520
28.6	266	462	1.39955	368
30.3	194	392	884	313
34.5	025	223	712	121
37.8	1.38904	112	590	1.39994
41.5	751	1.38938	425	844
44.6	626	818	298	707
46.7	540	716	208	606
50.1	402	602	075	481
52.9	277	477	1.38951	359
56.8	144	339	815	224
60.8	1.37953	128	611	013
66.2	740	1.37927	395	1.38788
68.1	633	818	295	710
72.1	478	658	131	533

Kahlbaum's redistilled, b. 160° (uncorr.).

t.	*C.*	*D.*	*F.*	*G'.*
20.3	1.39582	1.39777	1.40271	1.40685
23.0	459	662	157	567
31.1	161	364	1.39850	255
32.7	093	291	779	...
37.5	1.38902	104	587	1.39994
41.4	743	1.38944	433	826
45.4	567	767	243	662
48.8	426	622	101	512
52.7	288	485	1.38960	363
57.3	124	319	794	193
59.3	055	244	714	112
63.8	1.37846	055	506	1.38920
66.2	735	1.37935	404	785
72.1	497	670	142	555

DENSITY.

t	Vol. in cc.	Wt. in gms.	d^t_4.
24.7	10.0173	9.550	0.9534
32.4	10.0188	9.475	0.9457
40.8	10.0203	9.392	0.9373
48.0	10.0217	9.322	0.9302
58.8	10.0237	9.220	0.9198
67.4	10.0254	9.136	0.9113

The same difficulty was experienced in the determination of the refractive indices as with benzyl alcohol, the binding material being attacked.

$$(5a)\quad n_C/1.40392 + t/3523.02 = 1$$
$$(5b)\quad n_D/1.40580 + t/3558.99 = 1$$
$$(5c)\quad n_F/1.41077 + t/3540.21 = 1$$
$$(5d)\quad n_{G'}/1.41508 + t/3502.60 = 1$$
$$(5e)\quad d/0.9777 + t/992.640 = 1$$

	t.	*C*. Found.	*C*. Calc.	*D*. Found.	*D*. Calc.
Brühl[1]	20.	1.39578	1.39595	1.39789	1.39790
Landolt[2]	20.	1.39554	1.39595	.....	.....
Eijkmann[3]	19.1	1.39811	1.39631	.....	.....
"	80.9	1.37205	1.37168	.....	.....
Scheij[4]	20.	.....	.....	1.39906	1.39790

	t.	*F*. Found.	*F*. Calc.	*G'*. Found.	*G'*. Calc.
Brühl	20.	1.40280	1.40280	1.40691	1.40700
Landolt	20.	1.40246	1.40280	1.40649	1.40700
Eijkmann	19.1	1.40512	1.40316	.....	.....
"	80.9	1.37852	1.37853	.....	.....

	t.	*d*. Found.	*d*. Calc.
Brühl[1]	20.	0.9587	0.9580
Landolt[2]	20.	0.9594	0.9580
Eijkmann[3]	19.1	0.9599	0.9589
"	80.9	0.8983	0.8980
Scheij[4]	20.	0.9590	0.9580
Winkelmann[5]	20.	0.9603	0.9580
Traube[6]	20.	0.9624	0.9580
Perkin[7]	15.	0.9662	0.9629
"	25.	0.9560	0.9531
Lüdeking[8]	25.	0.9521	0.9531

	C	*D*.	*F*.	*G'*.	*d*.
Change per degree	0.0003985	0.000395	0.0003985	0.000404	0.000985

	D—C.	*F—D*.	*G'—F*.
Dispersion, 10°	0.00191	0.00493	0.00426
Dispersion, 80°	0.00216	0.00466	0.00390

[1] *Ann.*, **203,** 19 (1880).
[2] *Pogg. Ann.*, **122,** 545 (1864).
[3] *Rec. trav. chim.*, **12,** 157 (1893).
[4] *Ibid.*, **18,** 169 (1899).
[5] *Ann. Physik* [2], **26,** 113 (1885).
[6] *Ber.*, **19,** 885 (1886).
[7] *J. pr. Chem.*, **32,** 530 (1885).
[8] *Ann. Physik* [2], **27,** 76 (1886).

ACETYLACETONE.

Kahlbaum's undistilled.

t.	*C.*	*D.*	*F.*	*G'.*
26.3	1.44114	1.44566	1.45801	1.46951
29.2	1.43931	378	604	746
31.7	780	223	438	586
33.7	653	097	299	437
36.6	501	1.43936	135	275
39.5	426	866	060	194
43.1	231	663	1.44855	1.45990
46.8	035	463	640	762
48.4	1.42943	378	545	655
50.6	841	277	440	532
54.3	711	142	271	372
58.8	462	1.42890	010	104
61.0	333	763	1.43880	1.44963
64.5	145	573	668	749
67.7	1.41967	386	489	557
71.6	756	161	253	333
74.6	577	1.41969	071	144

Kahlbaum's redistilled, b. 136.5–7.0° (uncorr.).

t.	*C.*	*D.*	*F.*	*G'.*
25.6	1.44191	1.44649	1.45880	1.47028
27.4	056	511	737	1.46881
27.8	068	517	751	893
28.1	017	467	699	846
29.7	1.43948	391	622	770
31.1	872	324	540	681
34.5	626	092	277	421
36.2	569	002	212	349
38.2	503	1.43937	149	286
42.2	226	679	1.44845	1.45987
46.2	025	457	630	754
48.1	1.42928	371	512	624
51.9	685	102	255	369
55.8	505	1.42918	069	181
57.9	434	877	1.43984	085
62.4	134	562	670	1.44782
65.5	070	506	569	653
69.1	1.41814	218	322	417
73.6	622	047	092	168

Sample from Chemical Museum, distilled; b. 137–8°.

25.5	1.44193	1.44649	1.45892	1.47030
26.3	134	587	822	1.46962
30.7	1.43857	301	527	673
34.9	660	093	272	412
45.7	058	1.43492	1.44668	1.45787

DENSITY.

t.	Vol. in cc.	Wt. in gms.	d^t_4.
23.7	10.0171	9.746	0.9729
32.0	10.0187	9.668	0.9650
42.1	10.0206	9.570	0.9550
50.9	10.0222	9.486	0.9465
64.4	10.0248	9.358	0.9335
72.0	10.0262	9.285	0.9261
28.6	10.0180	9.598	0.9681
38.7	10.0199	9.600	0.9581
52.0	10.0224	9.473	0.9452
65.8	10.0250	9.343	0.9320

(6*a*) $n_C/1.45520 + t/2745.47 = 1$

(6*b*) $n_D/1.45987 + t/2703.32 = 1$

(6*c*) $n_F/1.47305 + t/2561.83 = 1$

(6*d*) $n_{G'}/1.48489 + t/2538.21 = 1$

(6*e*) $d/0.9948 + t/1041.83 = 1$

	t.	*C.* Found.	*C.* Calc.	*D.* Found.	*D.* Calc.
Brühl[1]	16.7	1.44927	1.44678	1.45409	0.45077
	18.1	1.44837	1.44597	1.45314	1.45002
	42.7	1.44102	1.43220	1.44557	1.43674
	72.4	1.43046	1.41683	1.43497	1.42070
Perkin[2]	6.5	1.45459	1.45175	.....	.....
	8.0	1.45390	1.45096	.....	.....
	9.5	1.45270	1.45016	.....	.....
	11.	1.450067	1.44937	1.454957	1.45385
	15.5	1.44930	1.44735	.....	.....
	99.0	1.40240	1.40273	.....	.....
	99.2	1.40210	1.40262	.....	.....
	99.3	1.400321	1.40257	1.404135	1.40617

	t.	*F.* Found.	*F.* Calc.	*G'.* Found.	*G'.* Calc.
Gladstone[3]	18.4	1.4678	1.46247	.....	.....
Perkin	6.5	1.47259	1.46931	1.48524	1.48109
	8.0	1.47200	1.46845	1.48451	1.48041
	9.5	1.47053	1.46759	1.48315	1.47973
	11.	1.467571	1.46672	1.479223	1.47905
	15.5	1.46718	1.46414	1.47939	1.47701
	99.0	1.41656	1.41612	1.42605	1.42698
	99.2	1.41604	1.41601	1.42555	1.42686
	99.3	1.414139	1.41595	1.423518	1.42680

[1] *J. pr. Chem.* [2], **50,** 119 (1894).
[2] *J. Chem. Soc.*, **62,** 844; **69,** 3.
[3] *Ibid.*, **59,** 290 (1891).

	t.	d. Found.	d. Calc.
Brühl[1]	16.7	0.9778	0.9789
	18.1	0.9769	0.9775
	42.7	0.9519	0.9540
	72.4	0.9226	0.9257
Perkin[2]	4.	0.9897	0.9910
	10.	0.9834	0.9853
	20.	0.9731	0.9757
	30.	0.9632	0.9662
	40.	0.9531	0.9566
	50.	0.9431	0.9471
	60.	0.9333	0.9375
	70.	0.9235	0.9280
	80.	0.9139	0.9184
	90.	0.9041	0.9089
Schenck and Ellenberger[3]	0.0	0.999	0.9948
	17.0	0.981	0.9786
	34.0	0.965	0.9624
	60.2	0.939	0.9373
	77.7	0.922	0.9206
	79.3	0.921	0.9191
	109.5	0.891	0.8903
	139.5	0.862	0.8616

	C.	D.	F.	G'.	d.
Change per degree	0.000530	0.000540	0.000575	0.000585	0.000955

	D — C.	F — D.	G' — F.
Dispersion, 10°	0.00450	0.01290	0.01174
Dispersion, 80°	0.00379	0.01046	0.01104

Theoretical.

In discussing the refractive powers of different substances, the three expressions

$$\text{I}\ \ (n^2-1)/d \qquad \text{II}\ \ (n-1)/d \qquad \text{III}\ \ (n^2-1)/(n^2+2)d$$

have been chiefly made use of at different periods, although the first two have been discarded to a great extent in favor of the last in recent times. The question of the constancy of these expressions with change in temperature or pressure is an important one and has been treated of often. Without entering in any way into the theoretical bases underlying these expressions and without introducing any new conceptions except those based on the experiments just described, or later speaking of possible explanations, it may be of interest to see to what the introduction of these results into the expressions may lead. As shown in the experimental part, the relation between the refractive index and the temperature (as

[1] *Z. pr. Chem.* [2], **50**, 119 (1894).
[2] *J. Chem. Soc.*, **62**, 844; **69**, 3.
[3] *Ber.*, **37**, 3451 (1904).

well as between the density and the temperature) can best be expressed by straight lines or their equations within certain limits of temperature for the substances used. Denoting the relation between the refractive index and the temperature by the equation $n/a + t/b = 1$ and that between the density and the temperature by the equation $d/a' + t/b' = 1$ in which n denotes the refractive index for a given line; t, the temperature; a, b, constants for any one substance for one line within certain limits of temperature; and a', b', constants for the substance depending upon the density; and substituting the values for n and for d from these equations in the expressions for the refractive powers and simplifying, the following are obtained:

$$\text{I.}\quad \frac{n^2 - 1}{d} = \frac{(a - at/b)^2 - 1}{a' - a't/b'} = \frac{b'a^2}{a'b^2}\left[-t + 2b - b' + \frac{(b - b')^2 - b^2/a^2}{b' - t}\right]$$

The term outside the brackets is constant. As t increases, of the expression inside the brackets, $-t + 2b - b'$ decreases, while the fraction increases, since b' is always greater than t (b' in words denoting the temperature at which the substance would have zero density if the linear relation held). With increasing t, the first part of the expression within the brackets will have the preponderating influence, and therefore the expression I will decrease as the temperature is increased.

$$\text{II.}\quad \frac{n - 1}{d} = \frac{a - at/b - 1}{a' - a't/b'} = \frac{ab'}{ba'} + \frac{b'}{a'b}\cdot\frac{ab - ab' - b}{b' - t}.$$

The first term is constant; as t increases, the second term will increase, and if the numerator is positive (or $ab - ab' - b > 0$) $(n-1)/d$ will increase, if negative (or $ab - ab' - b < 0$), $(n-1)/d$ will decrease, while if $ab - ab' - b = 0$, $(n-1)/d$ will be constant and equal to ab'/ba'.

$$\text{III.}\quad \frac{n^2 - 1}{(n^2 + 2)d} = \frac{(a - at/b)^2 - 1}{(a - at/b)^2 + 2}\cdot\frac{1}{(a' - a't/b')} = \frac{b'}{a'(b' - t)}\left[1 - \frac{3/a^2}{(1 - t/b)^2 + 2/a^2}\right].$$

As t increases, the fraction without the brackets increases. Since $t/b < 1$ as t increases $(1 - t/b)$ decreases, $(1 - t/b)^2$ decreases, the denominator of the fraction within the brackets decreases, the fraction increases, and the expression within the brackets decreases. The value of III therefore as t increases may increase or decrease or remain constant, depending upon the relative values of the term within and the term without the brackets.

The constancy of the three expressions (I, II and III) with increasing temperature depends therefore upon the values of the four constants, a, b, a', and b', or on the slopes of the curves, or in other words, upon the relative values of the temperature coefficients of the refractive index and the density.

The refractive powers of the six compounds studied for the C and G' lines as calculated from the three expressions are given below at intervals of ten degrees from 10° to 80°.

DIISOAMYL.

	n_C.	d.	$(n_C^2-1)/d$.	$(n_C-1)/d$.	$(n_C^2-1)/(n_C^2+2)d$.
10°	1.41093	0.7315	1.3544	0.5618	0.3393
20°	1.40649	0.7238	1.3515	0.5616	0.3397
30°	1.40205	0.7161	1.3486	0.5614	0.3401
40°	1.39761	0.7084	1.3457	0.5612	0.3404
50°	1.39317	0.7007	1.3428	0.5611	0.3407
60°	1.38873	0.6930	1.3398	0.5609	0.3410
70°	1.38429	0.6853	1.3370	0.5608	0.3414
80°	1.37985	0.6776	1.3341	0.5606	0.3417

$(ab - ab' - b = -34.90)$

	$n_{G'}$.	$(n_{G'}^2-1)/d$.	$(n_{G'}-1)/d$.	$(n_{G'}^2-1)/(n_{G'}^2+2)d$.
10°	1.42255	1.3994	0.5777	0.3478
20°	1.41801	1.3964	0.5775	0.3482
30°	1.41347	1.3935	0.5774	0.3486
40°	1.40893	1.3906	0.5773	0.3489
50°	1.40439	1.3876	0.5771	0.3493
60°	1.39985	1.3847	0.5770	0.3497
70°	1.39531	1.3817	0.5768	0.3501
80°	1.39077	1.3788	0.5767	0.3504

$(ab - ab' - b = -27.50)$

DIMETHYLANILINE.

	n_C.	d.	$(n_C^2-1)/d$.	$(n_C-1)/d$.	$(n_C^2-1)/(n_C^2+2)d$.
10°	1.55680	0.9648	1.4756	0.5771	0.3335
20°	1.55185	0.9566	1.4721	0.5769	0.3339
30°	1.54690	0.9484	1.4687	0.5767	0.3343
40°	1.54195	0.9401	1.4654	0.5765	0.3347
50°	1.53700	0.9318	1.4621	0.5763	0.3351
60°	1.53205	0.9236	1.4586	0.5761	0.3355
70°	1.52710	0.9153	1.4553	0.5759	0.3359
80°	1.52215	0.9070	1.4520	0.5757	0.3363

$(ab - ab' - b = -69.66)$

	$n_{G'}$.	$(n_{G'}^2-1)/d$.	$(n_{G'}-1)/d$.	$(n_{G'}^2-1)/(n_{G'}^2+2)d$.
10°	1.59878	1.6129	0.6206	0.3540
20°	1.59339	1.6087	0.6203	0.3544
30°	1.58800	1.6046	0.6200	0.3548
40°	1.58261	1.6005	0.6197	0.3553
50°	1.57722	1.5964	0.6194	0.3558
60°	1.57183	1.5923	0.6191	0.3563
70°	1.56644	1.5882	0.6188	0.3569
80°	1.56105	1.5841	0.6185	0.3575

$(ab - ab' - b = -93.90)$

n-Heptyl Alcohol.

	n_C.	d.	$(n_C^2-1)/d$.	$(n_C-1)/d$.	$(n_C^2-1)/(n_C^2+2)d$.
10°	1.42575	0.8293	1.2453	0.5134	0.3088
20°	1.42198	0.8221	1.2432	0.5133	0.3091
30°	1.41820	0.8150	1.2408	0.5131	0.3093
40°	1.41443	0.8079	1.2385	0.5130	0.3096
50°	1.41065	0.8008	1.2362	0.5128	0.3099
60°	1.40688	0.7936	1.2340	0.5127	0.3101
70°	1.40311	0.7865	1.2317	0.5125	0.3104
80°	1.39934	0.7794	1.2294	0.5124	0.3106

$(ab - ab' - b = - 50.86)$

	$n_{G'}$.	$(n_{G'}^2-1)/d$.	$(n_{G'}-1)/d$.	$(n_{G'}^2-1)/(n_{G'}^2+2)d$.
10°	1.43758	1.2862	0.5276	0.3163
20°	1.43371	1.2839	0.5275	0.3166
30°	1.42985	1.2815	0.5274	0.3169
40°	1.42598	1.2791	0.5273	0.3171
50°	1.42211	1.2767	0.5271	0.3174
60°	1.41825	1.2744	0.5270	0.3177
70°	1.41439	1.2721	0.5269	0.3180
80°	1.41052	1.2697	0.5268	0.3182

$(ab - ab' - b = - 45.70)$

Benzyl Alcohol.

	n_C.	d.	$(n_C^2-1)/d$.	$(n_C-1)/d$.	$(n_C^2-1)/(n_C^2+2)d$.
10°	1.53979	1.0541	1.3006	0.5121	0.2975
20°	1.53552	1.0466	1.2974	0.5117	0.2977
30°	1.53125	1.0391	1.2941	0.5113	0.2979
40°	1.52697	1.0316	1.2909	0.5108	0.2981
50°	1.52269	1.0241	1.2875	0.5104	0.2982
60°	1.51842	1.0166	1.2843	0.5100	0.2983
70°	1.51415	1.0091	1.2810	0.5095	0.2984
80°	1.50987	1.0016	1.2777	0.5091	0.2986

$(ab - ab' - b = - 220.4)$

	$n_{G'}$.	$(n_{G'}^2-1)/d$.	$(n_{G'}-1)/d$.	$(n_{G'}^2-1)/(n_{G'}^2+2)d$.
10°	1.56809	1.3840	0.5389	0.3104
20°	1.56359	1.3805	0.5385	0.3106
30°	1.55909	1.3769	0.5381	0.3108
40°	1.55459	1.3734	0.5376	0.3109
50°	1.55009	1.3698	0.5371	0.3111
60°	1.54559	1.3662	0.5367	0.3113
70°	1.54109	1.3626	0.5362	0.3115
80°	1.53659	1.3589	0.5357	0.3117

$(ab - ab' - b = - 224.9)$

n-Butyric Acid.

	n_C.	d.	$(n_C^2-1)/d$.	$(n_C-1)/d$.	$(n_C^2-1)/(n_C^2+2)d$.
10°	1.39994	0.9678	0.9918	0.4132	0.2504
20°	1.39595	0.9580	0.9903	0.4133	0.2508
30°	1.39197	0.9482	0.9888	0.4134	0.2511
40°	1.38798	0.9383	0.9874	0.4135	0.2514
50°	1.38399	0.9285	0.9859	0.4136	0.2518
60°	1.38001	0.9186	0.9845	0.4137	0.2522
70°	1.37602	0.9088	0.9831	0.4138	0.2525
80°	1.37204	0.8989	0.9817	0.4139	0.2529

$(ab - ab' - b = +29.45)$

	$n_{G'}$.	$(n_{G'}^2-1)/d$.	$(n_{G'}-1)/d$.	$(n_{G'}^2-1)/(n_{G'}^2+2)d$.
10°	1.41104	1.0240	0.4247	0.2566
20°	1.40700	1.0226	0.4248	0.2570
30°	1.40296	1.0212	0.4250	0.2573
40°	1.39892	1.0199	0.4252	0.2577
50°	1.39488	1.0185	0.4253	0.2581
60°	1.39084	1.0172	0.4255	0.2585
70°	1.38680	1.0159	0.4256	0.2589
80°	1.38276	1.0146	0.4258	0.2594

$(ab - ab' - b = +49.20)$

Acetylacetone.

	n_C.	d.	$(n_C^2-1)/d$.	$(n_C-1)/d$.	$(n_C^2-1)/(n_C^2+2)d$.
10°	1.44990	0.9853	1.1187	0.4566	0.2727
20°	1.44460	0.9757	1.1139	0.4557	0.2726
30°	1.43930	0.9662	1.1091	1.4547	0.2724
40°	1.43400	0.9566	1.1043	0.4537	0.2722
50°	1.42870	0.9471	1.0994	0.4526	0.2720
60°	1.42340	0.9375	1.0945	0.4516	0.2718
70°	1.41810	0.9280	1.0895	0.4505	0.2716
80°	1.41280	0.9184	1.0845	0.4495	0.2714

$(ab - ab' - b = -256.5)$

	$n_{G'}$.	$(n_{G'}^2-1)/d$.	$(n_{G'}-1)/d$.	$(n_{G'}^2-1)/(n_{G'}^2+2)d$.
10°	1.47904	1.2053	0.4862	0.2878
20°	1.47319	1.1994	0.4850	0.2876
30°	1.46734	1.1934	0.4837	0.2874
40°	1.46149	1.1874	0.4824	0.2871
50°	1.45564	1.1814	0.4811	0.2868
60°	1.44979	1.1753	0.4798	0.2865
70°	1.44394	1.1692	0.4784	0.2862
80°	1.43809	1.1630	0.4770	0.2859

$(ab - ab' - b = -316.2)$

In all these cases, the refractive power, no matter which formula is used, increases or decreases continuously with rising temperature. A discussion of other regularities will be deferred until data for more substances are at hand.

In conclusion, the molecular refractions for the C line as calculated according to Brühl[1] using the expression $(n_c^2-1)/(n_c^2+2)\cdot M/d$ (M = molecular weight), are given together with the values found at 10° and 80°.

		Found.	Calc.
Diisoamyl	10°	48.1806	47.916
	80°	48.5214	
Dimethylaniline	10°	40.3535	39.581
	80°	40.6923	
n-Heptyl alcohol	10°	36.4384	35.709
	80°	36.6508	
Benzyl alcohol	10°	32.1300	32.393
	80°	32.2488	
n-Butyric acid	10°	22.0352	22.118
	80°	22.2552	
Acetylacetone	10°	27.2700	Diketo — 25.315
	80°	27.1400	Mono-enol — 26.329
			Dienol — 27.343

Ethyl Acetacetate.

In determining the refractive indices of ethyl acetacetate, it was found that the freshly distilled (under diminished pressure) substance gave different values from those obtained after the substance had been standing for some time. The difference is not large, but this observation was made repeatedly. The following series of determinations will show the general trend:

SUBSTANCE DISTILLED FEB. 3, 11:00 A.M.

	t.	*C*.	*D*.	*F*.	*G'*.
Feb. 3, 2:30 P.M.	18.0	1.41733	1.41957	1.42539	1.43043
Feb. 3, 2:45 P.M.	18.7	715	946	515	013
Feb. 3, 3:50 P.M.	20.2	655	889	460	1.42943
Feb. 7, 1:20 P.M.	20.0	703	935	512	1.43019
Feb. 7, 1:55 P.M.	19.6	720	953	521	018
Feb. 8, 10:30 A.M.	20.7	663	922	473	1.42954
Feb. 10, 10:45 A.M.	18.4	777	1.42016	578	1.43075
Feb. 11, 10:00 A.M.	20.6	693	1.41927	495	1.42999
Feb. 12, 11:00 A.M.	21.0	672	906	481	971
Mar. 3, 10:20 A.M.	19.9	705	940	508	1.43012

The ester was kept in the cup of the refractometer until February 12th, and after that in a beaker covered with another beaker and exposed to the sun when possible, permitting free access to the air at all times, with only such variations in temperature occurring as took place in the laboratory. A study of these results show that there is a marked increase in the refractive index with the time, apparently reaching a maximum value. Attempting to reduce these results to the common basis of 20°,

[1] The following values are used in calculating: Single-bonded C —2.365; H —1.103; Hydroxyl O —1.506; Carbonyl O —2.328; N —3.02; Double bond — 1.836. The benzene nucleus is assumed to have three double bonds.

which can only be done in an approximate manner using the temperature coefficients for C —0.00038, D —0.00036, F —0.00032, and G′ —0.00042, assuming the temperature coefficients to be the same at all times, which cannot be far wrong owing to the limited range of temperature, the following are obtained:

Time after distillation.	*C.*	*D.*	*F.*	*G′.*
$3^1/_2$ hours.......	1.41657	1.41885	1.42475	1.42959
$3^3/_4$ "	665	899	473	958
$4^5/_6$ "	663	896	466	951
98 "	703	935	512	1.43019
99 "	705	939	508	001
120 "	690	947	495	1.42983
168 "	716	958	527	1.43008
191 "	717	949	514	025
216 "	710	942	513	013
29 days..........	701	936	505	008

This table shows the change more clearly. For comparison the results obtained by Brühl[1] at 20° are given:

C —1.41720; D —1.41976; F —1.42532; G′ —1.43000.

Schaum[2] found 1.41937 for the D line at 20°.

A large number of determinations of the refractive index were made at higher temperatures, but they are of no use since the state of the substance at the time of making the measurements at any one temperature evidently depended upon the length of time the substance had been maintained at that temperature, as well as the temperature at which it had been maintained for some time previously. These conditions, or rather the effect produced by them, are entirely unknown quantities in these measurements, which must therefore be discarded.

An attempt can, however, be made to follow the change at 20°. There can be no decomposition of the substance taking place, since the change appears to stop after a certain point has been reached. The values of the refractive index right after the distillation (A) (the temperature of which did not rise above 85°), and after constant values have been attained (B) may be put equal to

	C.	*D.*	*F.*	*G′.*
A..................	1.4165	1.4188	1.4246	1.4295
B..................	1.4171	1.4194	1.4251	1.4301

The most obvious explanation of the change is that the equilibrium between the two tautomeric forms is different at high temperatures from what it is at lower, and that in cooling suddenly, as in condensation, the equilibrium at the lower temperature, is not attained at once but only

[1] *Ann.*, **203**, 26 (1880).
[2] *Ber.*, **31**, 1964 (1898).

after some time. Traube[1] found that the density of ethyl acetacetate 15 minutes after distillation was 1.02443, and 20 hours later, 1.02467, evidently a change exactly similar to the one described here. These densities as found by Traube are somewhat lower than those given by others, but since the change is the important factor, the comparative values will serve. For the density right after distillation, the value 1.0244 will be taken, and after equilibrium is reached 1.0247. The refractive powers then for the C line calculated from formulas II and III will be:

	$(n_C-1)/d.$	$(n_C^2-1)/(n_C^2+2)d.$
Immediately after distillation	0.4066	0.2452
At equilibrium	0.4070	0.2455

There is evidently a change in structure taking place, manifesting itself by the change in refractive power. The molecular refraction calculated according to Brühl would be 31.382 for the keto form and 32.545 for the enol form. From the above (last column) the molecular refraction is found to be 31.876 immediately after distillation and 31.915 at equilibrium, indicating that, at ordinary temperatures, very nearly equal amounts of the two isomers are present, while at higher temperatures, more of the keto form is present than at lower, the difference, however, being small. The matter cannot of course be considered settled satisfactorily as yet, owing to the more or less approximate nature of some of the data used, but the results given point to interesting possibilities.

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[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.]

ISO-OCTANE.

BY LATHAM CLARKE.

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In this paper are described the preparation and properties of iso-octane or 2-methyl heptane, $(CH_3)_2CHCH_2CH_2CH_2CH_2CH_3$, the study of which has been taken up in the continuation of a research on the octanes begun some time ago in this laboratory.

Iso-octane is the ninth hydrocarbon to be prepared in the series C_8H_{18}, of which there are eighteen possible members. A list of the nine octanes so far prepared is given herewith.

Normal octane,[2] $CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$.

Iso-octane, or 2-methyl heptane, $(CH_3)_2CH_2CH_2CH_2CH_2CH_2CH_3$.

[1] *Ber.*, **29**, 1719 (1898).

[2] Riche, *Ann. Chem.* (Liebig), **117**, 265. Schorlemmer, *Ibid.*, **161**, 280; **147**, 227; **152**, 152. Zincke, *Ibid.*, **152**, 15. Paterno and Peratoner, *Ber. d. Chem. Ges.*, **22**, 467.