solid, white calcium hydroxide; this broke the circuit and the electrolysis was discontinued.

The amalgam was at once washed, dried, and analyzed; it gave 0.091 and 0.092 per cent. Ca. The current efficiency was, therefore, 29 per cent.

The remainder of the amalgam was filtered through chamois skin by suction, but no solid was obtained.

Upon comparing our yields of these amalgams with those of Kerp and Böttger, it will be seen that, by means of a simpler and much less laborious process, we have succeeded in obtaining far better results. The chlorine evolved during the electrolysis had no appreciable action on the platinum foil, so it was not considered necessary to use a carbon anode.

In the analysis of the solid amalgams left behind on filtration, our results are in several instances higher than those obtained by Kerp and Böttger. This is especially true in the case of solid lithium amalgam, in which we obtained 0.875 per cent. of lithium, while Kerp and Böttger found only 0.70 per cent. It is possible that, owing to the greater quantity of the solid amalgam at our disposal, the separation was more complete; we also increased the efficiency of the filtration, however, by alternately pressing the palm of the hand over the top of the Gooch crucible until the pressure became very low in the suction flask, and then lifting it off and allowing the air to rush through and sweep the mother liquor along with it. This was repeated 4 or 5 times. The significance of our analytical difference can be seen from the fact that the formula $LiHg_5$ theoretically requires 0.70 per cent. of lithium, while the formula $LiHg_4$ corresponds to 0.87 per cent. We have reason to believe that Kerp and Böttger did not succeed by filtration in entirely removing the mother liquor from the crystalline amalgams, and we are repeating their work, with the addition that we separate the last traces of the mother liquor left behind on filtration, by means of a high-speed electric centrifugal machine. The results will be published in the near future.

URBANA, ILL.

[PHOENIX PHYSICAL LABORATORY CONTRIBUTIONS, NO. 19.]

THE CHANGE IN REFRACTIVE INDEX WITH TEMPERATURE. II.

BY K. GEORGE FALK.

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In the first paper[1] the results obtained in determining the refractive indices for the three hydrogen and the sodium lines for diisoamyl, dimethylaniline, *n*-heptyl alcohol, benzyl alcohol, *n*-butyric acid, and acetylacetone at a number (thirty to fifty) of temperatures between 15° and 75° were given. The equations showing the relation between the refractive indices and the temperatures as well as the densities (which

[1] THIS JOURNAL, 31, 86 (1909.)

were also determined) and the temperatures were deduced from these results. These equations represented straight lines in every case. The refractive powers, using the expressions $(n^2 - 1)/d$, $(n - 1)/d$, and $(n^2 - 1)/(n^2 + 2)d$ were calculated for temperatures between 10° and 80° for the C and G′ lines for these substances. Some observations with ethyl acetacetate were also described.

In this paper the results obtained with isobutyl acetate, ethyl *n*-butyrate, isoamyl acetate, methylhexyl ketone, nitrobenzene, monomethylaniline, benzyl cyanide, and benzaldehyde will be given. The apparatus and method of determining the refractive indices and the densities were exactly the same as that described in the first paper and will therefore not be repeated. At the suggestion of the Editor of this Journal, all of the experimental results will not be enumerated in detail as was done before, but for each substance only a few results will be given, the equations for the curves which were obtained again by plotting the experimental results being the more useful and indicating sufficiently well perhaps the relations sought. A number of refractive indices calculated from these equations are given in the tables showing the refractive powers. In every case again, the curves were found to be straight lines and the agreement between the experimental results and the equations is just as satisfactory as with the results which were given in the first paper; the accuracy of the equations in reproducing the experimental work can therefore be judged from these. The results found in the density determinations are however given again for the various temperatures. The substances used were obtained from Kahlbaum in every case.

Isobutyl Acetate.—16 determinations with undistilled substance, 18 with redistilled, b. 115.5–6.0° (uncorr.), between 16.8° and 71.3°. The following were obtained with redistilled ester:

t.	*C.*	*D.*	*F.*	*G′.*
17.6	1.38984	1.39174	1.39656	1.40076
36.7	1.38084	1.38267	1.38741	1.39142
53.2	1.37302	1.37523	1.37947	1.38346
71.3	1.36408	1.36597	1.37045	1.37451

t..........	21.1	30.8	41.1	52.1	61.0	70.5
d..........	0.8684	0.8583	0.8475	0.8359	0.8264	0.8163

$$(7a)\quad n_C/1.39830 + t/2943.79 = 1$$
$$(7b)\quad n_D/1.40013 + t/2963.17 = 1$$
$$(7c)\quad n_F/1.40520 + t/2907.31 = 1$$
$$(7d)\quad n_{G'}/1.40950 + t/2876.53 = 1$$
$$(7e)\quad d/0.8907 + t/845.05 = 1$$

	C.	*D.*	*F.*	*G′.*	*d.*
Change per degree........	0.000475	0.000473	0.000483	0.000490	0.001054

	D—C.	F—D.	G'—F.
Dispersion, 10°	0.00175	0.00497	0.00423
Dispersion, 80°	0.00199	0.00427	0.00374

Ethyl n-Butyrate.—22 determinations with undistilled substance, 20 with redistilled, b. 118.5–9.0° (uncorr.), between 18.0° and 73.7°. The following results were obtained with redistilled ester:

t.	C.	D.	F.	G'.
18.0	1.39123	1.39313	1.39787	1.40179
36.8	1.38219	1.38409	1.38886	1.39284
54.4	1.37397	1.37582	1.38043	1.38446
71.7	1.36513	1.36704	1.37155	1.37583

t	18.5	27.3	34.6	45.8	57.0	68.7
d	0.8803	0.8711	0.8633	0.8515	0.8394	0.8264

(8a) $n_C/1.40004 + t/2921.83 = 1$

(8b) $n_D/1.40196 + t/2911.77 = 1$

(8c) $n_F/1.40669 + t/2913.86 = 1$

(8d) $n_{G'}/1.41105 + t/2873.42 = 1$

(8e) $d/0.9002 + t/841.725 = 1$

	t.	d. F'd.	d. Calc.	C. F'd.	C. Calc.	F. F'd.	F. Calc.	G'. F'd.	G'. Calc.
Landolt[1]	20.0	0.8892	0.8788	1.39404	1.39046	1.40073	1.39703	1.40460	1.40225
Eijkmann[2]	15.4	0.8829	0.8837	1.39271	1.39266	1.39927	1.39925	.....	.....

	C.	D.	F.	G'.	d.
Change per degree	0.000479	0.0004815	0.000483	0.000491	0.00107

	D — C.	F — D.	G' — F.
Dispersion, 10°	0.00189	0.00472	0.00428
Dispersion, 80°	0.00172	0.00461	0.00372

Isoamyl Acetate.—19 determinations with undistilled substance, 17 with redistilled, b. 137.0–7.5° (uncorr.), between 19.0° and 75.8°. The following were obtained with redistilled ester:

t.	C.	D.	F.	G'.
21.5	1.39796	1.39991	1.40481	1.40925
41.1	1.38906	1.39101	1.39579	1.40035
57.0	1.38191	1.38385	1.38855	1.39265
70.3	1.37563	1.37749	1.38226	1.38613

t	15.5	25.6	35.0	43.5	52.7	62.5	69.8
d	0.8746	0.8648	0.8559	0.8475	0.8384	0.8287	0.8214

(9a) $n_C/1.40785 + t/3073.30 = 1$

(9b) $n_D/1.40973 + t/3101.40 = 1$

(9c) $n_F/1.41479 + t/3059.00 = 1$

(9d) $n_{G'}/1.41907 + t/3056.46 = 1$

(9e) $d/0.8898 + t/910.95 = 1$

[1] *Pogg. Ann.*, **122**, 545 (1864).

[2] *Rec. trav. chim.*, **12**, 277 (1893).

	C.	D.	F.	G'.	d.
Change per degree......	0.000458	0.0004545	0.0004625	0.000464	0.000977

	D − C.	F − D.	G' − F.
Dispersion, 10°.................	0.00191	0.00498	0.00427
Dispersion, 80°.................	0.00216	0.00442	0.00416

Methylhexyl Ketone.—23 determinations with undistilled substance, 16 with redistilled, b. 169–70° (uncorr.), between 15.8° and 73.3°. The following were obtained with redistilled ketone:

t.	C.	D.	F.	G'.
15.8	1.41530	1.41747	1.42277	1.42706
36.9	1.40636	1.40851	1.41363	1.41801
54.9	1.39870	1.40084	1.40587	1.41072
73.3	1.39062	1.39261	1.39762	1.40201

t..........	17.5	27.0	36.9	46.3	53.5	61.5	69.7
d..........	0.8211	0.8133	0.8051	0.7973	0.7912	0.7844	0.7773

(10a) $n_C/1.42228 + t/3318.67 = 1$

(10b) $n_D/1.42437 + t/3308.23 = 1$

(10c) $n_F/1.42965 + t/3310.74 = 1$

(10d) $n_{G'}/1.43453 + t/3251.60 = 1$

(10e) $d/0.8363 + t/976.323 = 1$

	t.	d. F'd.	d. Calc.	C. F'd.	C. Calc.	D. F'd.	D. Calc.
Brühl[1]..............	20	0.8185	0.8196	0.41390	1.41370	1.41613	0.41576
Eijkmann[2]..........	16.3	0.8201	0.8227	0.41506	1.41529	.....	.....
Eijkmann...........	81.2	0.7665	0.7687	1.38625	0.38745	.....	...

		F. F'd.	F. Calc.	G'. F'd.	G'. Calc.
Brühl...............	20	1.42133	1.42101	1.42569	0.42571
Eijkmann...........	16.3	1.42252	1.42261	.....	.....
Eijkmann...........	81.2	1.39305	1.39457	.....	.....

	C.	D.	F.	G'.	d.
Change per degree.......	0.000429	0.0004305	0.000432	0.000441	0.000857

	D − C.	F − D.	G' − F.
Dispersion, 10°.................	0.00207	0.00527	0.00479
Dispersion, 80°.................	0.00197	0.00514	0.00418

Nitrobenzene.—Kahlbaum's prepared from crystallized benzene; 27 determinations between 21.2° and 73.1° from which the following are chosen:

t.	C.	D.	F.
21.2	1.54487	1.55157	1.57006
38.9	1.53670	1.54332	1.56137
55.6	1.52901	1.53548	1.55323
73.1	1.52086	1.52739	1.54455

[1] *Ann.*, **203**, 29 (1880).

[2] *Rec. trav. chim.*, **12**, 171 (1893).

Owing to the yellow color of the nitrobenzene, it was impossible to determine the refractive index of the G′ line.

t	18.1	28.7	37.9	46.1	57.0	64.7	71.8
d	1.2047	1.1942	1.1851	1.1772	1.1664	1.1588	1.1517

$$(11a)\quad n_C/1.55453 + t/3393.55 = 1$$
$$(11b)\quad n_D/1.56146 + t/3339.79 = 1$$
$$(11c)\quad n_F/1.58027 + t/3249.52 = 1$$
$$(11e)\quad d/1.2225 + t/1240.00 = 1$$

	t.	C. Fd.	C. Calc.	D. Fd.	D. Calc.	F. Fd.	F. Calc.
Brühl[1]	20.0	1.54593	1.54537	1.55291	1.55212	1.57124	1.57055
Christiansen[2]	18.0	1.5437	1.54629	1.5503	1.55305	1.5687	1.57152

	t.	d. Fd.	d. Calc.		t.	d. Fd.	d. Calc.
Walden[3]	0.	1.2220	1.2225	Friswell[6]	3.8	1.2220	1.2188
Walden[3]	25.	1.1972	1.1978	Friswell[6]	13.	1.2116	1.2097
Walden[3]	50.	1.1732	1.1732	Friswell[6]	28.	1.1931	1.1948
Walden[4]	0.	1.2222	1.2225	Kahlbaum[7]	20.	1.20328	1.2028
Brühl[1]	20.	1.2039	1.2028	Perkin[8]	4.	1.2193	1.2186
Guye and Baud[5].	11.	1.2075	1.2117	Perkin[8]	15.	1.2082	1.2077
Guye and Baud[5].	20.	1.1998	1.2028	Perkin[8]	30.	1.1937	1.1929
Guye and Baud[5].	25.	1.1955	1.1978	Perkin[8]	45.	1.1788	1.1781
Guye and Baud[5].	50.	1.1728	1.1732	Perkin[8]	60.	1.1638	1.1633

	C.	D.	F.	d.
Change per degree	0.000458	0.000467	0.000486	0.000986

	D — C.	F — D.
Dispersion, 10°	0.00684	0.01862
Dispersion, 80°	0.00621	0.01729

Monomethylaniline.—9 determinations with undistilled substance, 21 with redistilled, b. 191.5–2.0° (uncorr.), between 16.6° and 71.9°. The following were obtained with redistilled amine:

t.	C.	D.	F.
16.6	1.56618	1.57292	1.59123
33.9	1.55764	1.56428	1.58211
53.7	1.54823	1.55486	1.57248
70.4	1.54002	1.54647	1.56377

[1] *Ann.*, 200, 188 (1880).
[2] *Pogg. Ann.* (Neue Folge), **19**, 259 (1883).
[3] *Z. physik. Chem.*, **65**, 141 (1908).
[4] *Ibid.*, **55**, 229 (1906).
[5] *Arch. Sci. Phys. Geneve*, 11, 466.
[6] *J. Chem. Soc.*, **71**, 1013 (1897).
[7] *J. ph. Ch.*, **26**, 646.
[8] *J. Chem. Soc.*, **69**, 1180 (1896). Only a few of the values found by Perkin are given. These have been recalculated to the d_4^t basis.

The G′ line was very indistinct so that no attempt was made to measure it.

t..........	18.0	31.0	41.8	52.3	60.2	69.2
d..........	0.9879	0.9775	0.9687	0.9602	0.9537	0.9463

(12*a*) $n_C/1.57404 + t/3279.25 = 1$
(12*b*) $n_D/1.58104 + t/3236.85 = 1$
(12*c*) $n_F/1.59928 + t/3177.24 = 1$
(12*e*) $d/1.0025 + t/1237.84 = 1$

	t.	*d*. F'd.	*d*. Calc.	*C*. F'd.	*C*. Calc.	*D*. F'd.	*D*. Calc.
Brühl[1]..............	21.2	0.9851	0.9853	1.56348	1.56386	1.57021	1.57068

F. F'd.	*F*. Calc.	*G′*. F'd.	*G′*. Calc.
1.58823	1.58862	1.60322	.....

	C.	*D*.	*F*.	*d*.
Change per degree.......	0.000480	0.0004885	0.000503	0.000810

	D—C.	*F—D*.
Dispersion, 10°..........................	0.00691	0.01810
Dispersion, 80°..........................	0.00632	0.01708

Benzyl Cyanide.—Kahlbaum's redistilled, b. 227–9° (uncorr.). 31 determinations between 16.9° and 70.4°.

t.	*C*.	*D*.	*F*.	*G′*.
16.9	1.52133	1.52570	1.53705	1.54753
34.0	1.51418	1.51849	1.52975	1.54008
51.1	1.50702	1.51114	1.52229	1.53218
70.4	1.49868	1.50253	1.51367	1.52379

t......	22.1	30.3	40.6	50.7	60.4	70.0
d......	1.0166	1.0099	1.0015	0.9933	0.9853	0.9775

(13*a*) $n_C/1.52835 + t/3657.11 = 1$
(13*b*) $n_D/1.53281 + t/3623.00 = 1$
(13*c*) $n_F/1.54436 + t/3563.92 = 1$
(13*d*) $n_{G'}/1.55484 + t/3520.40 = 1$
(13*e*) $d/1.0347 + t/1268.32 = 1$

	t.	*d*. F'd.	*d*. Calc.	*C*. F'd.	*C*. Calc.	*D*. F'd.	*D*. Calc.	*F*. F'd.	*F*. Calc.
Brühl[2]....	20.2	1.0176	1.0182	1.51977	1.51991	1.52422	1.52427	.....	.....
Eijkmann[3]	17.5	1.0171	1.0204	1.52033	1.52103	.....	.....	1.53585	1.53668

	t.	*d*. F'd.	*d*. Calc.
Walden[4]..........	0	1.0325	1.0347
Walden[4]..........	25	1.0125	1.0143
Walden[4]..........	50	0.9919	0.9939
Perkin[5]...........	4	1.0296	1.0314
Perkin[5]...........	15	1.0205	1.0225
Perkin[5]...........	25	1.0124	1.0143

[1] *Z. physik. Chem.*, 16, 216 (1895).
[2] *Ibid.*, 16, 218 (1895).
[3] *Rec. trav. chim.*, 12, 185 (1893).
[4] *Z. physik. Chem.*, **65**, 138 (1908).
[5] *J. Chem. Soc.*, **69**, 1206 (1896).

	C.	*D.*	*F.*	*G'.*	*d.*
Change per degree.......	0.000418	0.000423	0.000433	0.0004415	0.000816

	D — C.	*F — D.*	*G' — F.*
Dispersion, 10°..................	0.00441	0.01145	0.01039
Dispersion, 80°..................	0.00406	0.01075	0.00980

Benzaldehyde.—Special Kahlbaum. 28 determinations between 17.3° and 71.6°:

t.	*C.*	*D.*	*F.*	*G'.*
19.5	1.53943	1.54563	1.56233	1.57738
37.1	1.53152	1.53767	1.55392	1.56862
53.9	1.52367	1.52961	1.54579	1.56046
71.6	1.51567	1.52180	1.53727	1.55135

t.......	15.7	25.5	36.6	48.7	57.9	67.0
d.......	1.0567	1.0480	1.0382	1.0274	1.0195	1.0110

(14*a*) $n_C/1.54828 + t/3392.40 = 1$

(14*b*) $n_D/1.55439 + t/3404.86 = 1$

(14*c*) $n_F/1.57137 + t/3317.33 = 1$

(14*d*) $n_G/1.58700 + t/3204.21 = 1$

(14*e*) $d/1.0705 + t/1207.80 = 1$

		d.		*C.*		*F.*		*G'.*	
	t.	*F'd.*	*Calc.*	*F'd.*	*Calc.*	*F'd.*	*Calc.*	*F'd.*	*Calc.*
Landolt[1]..	20.	1.0455	1.0528	1.53914	1.53915	1.56235	1.56189	1.57749	1.57710

t.	*4.*	*20.*	*40.*	*60.*	*80.*	*100.*
Perkin[2] F'd *d*..................	1.0591	1.0447	1.0274	1.0094	0.9908	0.9725
Calc. *d*.................	1.0670	1.0528	1.0350	1.0173	0.9995	0.9818

The densities are higher throughout than those given by other observers.

	C.	*D.*	*F.*	*G'.*	*d.*
Change per degree......	0.0004565	0.0004565	0.000474	0.000495	0.000887

	D — C.	*F — D.*	*G' — F.*
Dispersion, 10°.................	0.00611	0.01681	0.01542
Dispersion, 80°.................	0.00611	0.01558	0.01395

In calculating the refractive powers of these substances for a number of temperatures, the three expressions $(n^2 - 1)/d$, $(n - 1)/d$, and $(n^2 - 1)/(n^2 + 2)d$ were again made use of. Since the first $(n^2 - 1)/d$ is perhaps now only of historical interest, the values obtained from it will only be given for the extreme temperatures.[3] It will be necessary

[1] *Pogg. Ann.*, **122**, 545 (1864).

[2] *J. Chem. Soc.*, **69**, 1242 (1896).

[3] On page 101 of the former paper, the statement is made that this expression will decrease in value as the temperature is increased. This is not necessarily true in every case, but depends upon the relative values of the two parts of the expression within the brackets. In general its value will decrease, and this has been found to be the case with the substances used in this investigation.

to give the results for the four lines measured in this paper in full, and to facilitate comparison, the results calculated for the substances described in the first paper for the D and F lines, which were not given at the time, will also be shown.

Diisoamyl.—The value of $(n_D^2 - 1)/d$ at 10° is 1.3625, and at 80° 1.3419; of $(n_F^2 - 1)/d$ at 10° 1.3827, and at 80° 1.3609.

t.	n_D.	$(n_D - 1)/d$.	$(n^2_D - 1)/(n^2_D + 2)d$.	n_F.	$(n_F - 1)/d$.	$(n^2_F - 1)/(n^2_F + 2)d$.
10	1.41303	0.5646	0.3409	1.41825	0.5718	0.3447
20	1.40857	0.5645	0.3412	1.41370	0.5716	0.3450
40	1.39963	0.5641	0.3419	1.40460	0.5711	0.3456
60	1.39070	0.5638	0.3426	1.39550	0.5707	0.3463
80	1.38176	0.5634	0.3433	1.38640	0.5702	0.3470

Dimethylaniline.—$(n_D^2 - 1)/d$ at 10° is equal to 1.4971, at 80° 1.4734; $(n_F^2 - 1)/d$ at 10° 1.5561, at 80° 1.5300.

t.	n_D.	$(n_D - 1)/d$.	$(n^2_D - 1)/(n^2_D + 2)d$.	n_F.	$(n_F - 1)/d$.	$(n^2_F - 1)/(n^2_F + 2)d$.
10	1.56346	0.5840	0.3369	1.58156	0.6028	0.3457
20	1.55847	0.5838	0.3373	1.57637	0.6025	0.3461
40	1.54849	0.5834	0.3381	1.56599	0.6020	0.3470
60	1.53851	0.5830	0.3389	1.55561	0.6016	0.3478
80	1.52853	0.5827	0.3398	1.54523	0.6011	0.3487

n-Heptyl Alcohol.—$(n_D^2 - 1)/d$ at 10° is equal to 1.2521, at 80° 1.2382; $(n_F^2 - 1)/d$ at 10° 1.2706, at 80° 1.2535.

t.	n_D.	$(n_D - 1)/d$.	$(n^2_D - 1)/(n^2_D + 2)d$.	n_F.	$(n_F - 1)/d$.	$(n^2_F - 1)/(n^2_F + 2)d$.
10	1.42771	0.5158	0.3101	1.43307	0.5222	0.3134
20	1.42401	0.5158	0.3104	1.42921	0.5220	0.3137
40	1.41661	0.5157	0.3110	1.42149	0.5217	0.3142
60	1.40921	0.5156	0.3117	1.41377	0.5214	0.3147
80	1.40181	0.5155	0.3123	1.40605	0.5210	0.3152

Benzyl Alcohol.—$(n_D^2 - 1)/d$ at 10° is equal to 1.3144, at 80° 1.2924; $(n_F^2 - 1)/d$ at 10° 1.3518, at 80° 1.3278.

t.	n_D.	$(n_D - 1)/d$.	$(n^2_D - 1)/(n^2_D + 2)d$.	n_F.	$(n_F - 1)/d$.	$(n^2_F - 1)/(n^2_F + 2)d$.
10	1.54450	0.5166	0.2997	1.55720	0.5286	0.3055
20	1.54025	0.5162	0.2999	1.55280	0.5282	0.3057
40	1.53175	0.5155	0.3003	1.54400	0.5273	0.3060
60	1.52325	0.5147	0.3006	1.53520	0.5265	0.3063
80	1.51475	0.5139	0.3009	1.52640	0.5256	0.3067

n-Butyric Acid.—$(n_D^2 - 1)/d$ at 10° is equal to 0.9973, at 80° 0.9884; $(n_F^2 - 1)/d$ at 10° 1.0116, at 80° 1.0027.

t.	n_D.	$(n_D - 1)/d$.	$(n^2_D - 1)/(n^2_D + 2)d$.	n_F.	$(n_F - 1)/d$.	$(n^2_F - 1)/(n^2_F + 2)d$.
10	1.40185	0.4152	0.2515	1.40678	0.4203	0.2542
20	1.39790	0.4153	0.2519	1.40280	0.4205	0.2546
40	1.39000	0.4156	0.2527	1.39483	0.4208	0.2554
60	1.38210	0.4160	0.2534	1.38686	0.4211	0.2562
80	1.37420	0.4163	0.2542	1.37889	0.4215	0.2570

Acetylacetone.—$(n^2_D - 1)/d$ at 10° is equal to 1.1321, at 80° 1.0964; $(n^2_F - 1)/d$ at 10° 1.1702, at 80° 1.1286.

t.	n_D.	$(n_D-1)/d$.	$(n^2_D-1)/(n^2_D+2)d$.	n_F.	$(n_F-1)/d$.	$(n^2_F-1)/(n^2_F+2)d$.
10	1.45447	0.4613	0.2751	1.46730	0.4743	0.2818
20	1.44907	0.4603	0.2749	1.46155	0.4730	0.2815
40	1.43827	0.4582	0.2745	1.45005	0.4705	0.2810
60	1.42747	0.4560	0.2741	1.43855	0.4678	0.2803
80	1.41667	0.4537	0.2736	1.42705	0.4650	0.2796

Isobutyl Acetate.

	$(n^2_C-1)/d$.	$(n^2_D-1)/d$.	$(n^2_F-1)/d$.	$(n^2_{G'}-1)/d$.
10°	1.0701	1.0760	1.0918	1.1053
80°	1.0546	1.0613	1.0758	1.0885

t.	d.	n_C.	$(n_C-1)/d$.	$(n^2_C-1)/(n^2_C+2)d$.	n_D.	$(n_D-1)/d$.	$(n^2_D-1)/(n^2_D+2)d$.
10	0.8802	1.39355	0.4471	0.2714	1.39540	0.4492	0.2726
20	0.8697	1.38880	0.4471	0.2718	1.39067	0.4492	0.2730
40	0.8486	1.37930	0.4470	0.2725	1.38121	0.4492	0.2737
60	0.8275	1.36980	0.4469	0.2732	1.37175	0.4492	0.2745
80	0.8064	0.36030	0.4468	0.2739	1.36229	0.4493	0.2752

t.	n_F.	$(n_F-1)/d$.	$(n^2_F-1)/(n^2_F+2)d$.	$n_{G'}$.	$(n_{G'}-1)/d$.	$(n^2_{G'}-1)/(n^2_{G'}+2)d$.
10	1.40037	0.4548	0.2756	1.40460	0.4596	0.2782
20	1.39554	0.4548	0.2759	1.39970	0.4596	0.2786
40	1.38588	0.4547	0.2767	1.38990	0.4595	0.2793
60	1.37622	0.4546	0.2774	1.38010	0.4593	0.2800
80	1.36656	0.4546	0.2782	1.37030	0.4592	0.2807

Ethyl n-Butyrate.

	$(n^2_C-1)/d$.	$(n^2_D-1)/d$.	$(n^2_F-1)/d$.	$(n^2_{G'}-1)/d$.
10°	1.0644	1.0703	1.0851	1.0986
80°	1.0487	1.0545	1.0700	1.0824

t.	d.	n_C.	$(n_C-1)/d$.	$(n^2_C-1)/(n^2_C+2)d$.	n_D.	$(n_D-1)/d$.	$(n^2_D-1)/(n^2_D+2)d$.
10	0.8895	1.39525	0.4444	0.2697	1.39714	0.4465	0.2708
20	0.8788	1.39046	0.4443	0.2700	1.39233	0.4464	0.2712
40	0.8574	1.38088	0.4442	0.2707	1.38270	0.4464	0.2719
60	0.8360	1.37130	0.4441	0.2714	1.37307	0.4463	0.2726
80	0.8146	1.36172	0.4440	0.2721	1.36344	0.4462	0.2733

t.	n_F.	$(n_F-1)/d$.	$(n^2_F-1)/(n^2_F+2)d$.	$n_{G'}$.	$(n_{G'}-1)/d$.	$(n^2_{G'}-1)/(n^2_{G'}+2)d$.
10	1.40186	0.4518	0.2736	1.40614	0.4566	0.2762
20	1.39703	0.4518	0.2740	1.40123	0.4566	0.2766
40	1.38737	0.4518	0.2748	1.39141	0.4565	0.2774
60	1.37771	0.4518	0.2756	1.38159	0.4565	0.2781
80	1.36805	0.4518	0.2764	1.37177	0.4564	0.2789

Isoamyl Acetate.

	$(n^2_C-1)/d$.	$(n^2_D-1)/d$.	$(n^2_F-1)/d$.	$(n^2_{G'}-1)/d$.
10°	1.1013	1.1074	1.1234	1.1371
80°	1.0845	1.0918	1.1068	1.1210

t.	d.	n_C.	$(n_C-1)/d$.	$(n^2_C-1)/(n^2_C+2)d$.	n_D.	$(n_D-1)/d$.	$(n^2_D-1)/(n^2_D+2)d$.
10	0.8800	1.40327	0.4583	0.2775	1.40518	0.4604	0.2786
20	0.8703	1.39869	0.4581	0.2778	1.40064	0.4603	0.2789
40	0.8507	1.38953	0.4579	0.2784	1.39155	0.4602	0.2796
60	0.8312	1.38037	0.4576	0.2789	1.38246	1.4601	0.2803
80	0.8116	1.37121	0.4574	0.2795	1.37337	0.4600	0.2810

t.	n_F.	$(n_F-1)/d$.	$(n^2_F-1)/(n^2_F+2)d$.	$n_{G'}$.	$(n_{G'}-1)/d$.	$(n^2_{G'}-1)/(n^2_{G'}+2)d$.
10	1.41016	0.4661	0.2816	1.41443	0.4709	0.2842
20	1.40554	0.4660	0.2820	1.40979	0.4709	0.2846
40	1.39629	0.4658	0.2826	1.40051	0.4708	0.2853
60	1.38704	0.4656	0.2833	1.39123	0.4707	0.2860
80	1.37779	0.4655	0.2839	1.38195	0.4706	0.2867

Methylhexyl Ketone.

	$(n^2_C-1)/d$.	$(n^2_D-1)/d$.	$(n^2_F-1)/d$.	$(n^2_{G'}-1)/d$.
10°	1.2211	1.2281	1.2462	1.2628
80°	1.2068	1.2139	1.2323	1.2477

t.	d.	n_C.	$(n_C-1)/d$.	$(n^2_C-1)/(n^2_C+2)d$.	n_D.	$(n_D-1)/d$.	$(n^2_D-1)/(n^2_D+2)d$.
10	0.8277	1.41799	0.5049	0.3045	1.42006	0.5075	0.3058
20	0.8192	1.41370	0.5050	0.3049	1.41576	0.5076	0.3062
40	0.8020	1.40512	0.5051	0.3057	1.40715	0.5077	0.3070
60	0.7849	1.39654	0.5052	0.3065	1.39854	0.5078	0.3079
80	0.7677	1.38796	0.5054	0.3073	1.38993	0.5079	0.3087

t.	n_F.	$(n_F-1)/d$.	$(n^2_F-1)/(n^2_F+2)d$.	$n_{G'}$.	$(n_{G'}-1)/d$.	$(n^2_{G'}-1)/(n^2_{G'}+2)d$.
10	1.42533	0.5139	0.3091	1.43012	0.5196	0.3122
20	1.42101	0.5140	0.3096	1.42571	0.5197	0.3126
40	1.41237	0.5142	0.3105	1.41689	0.5198	0.3135
60	1.40373	0.5144	0.3114	1.40807	0.5199	0.3144
80	1.39507	0.5146	0.3123	1.39925	0.5201	0.3153

Nitrobenzene.

	$(n^2_C-1)/d$.	$(n^2_D-1)/d$.	$(n^2_F-1)/d$.
10°	1.1564	1.1740	1.2220
80°	1.1403	1.1568	1.2031

t.	d.	n_C.	$(n_C-1)/d$.	$(n^2_C-1)/(n^2_C+2)d$.
10	1.2126	1.54995	0.4535	0.2627
20	1.2028	1.54537	0.4534	0.2630
40	1.1831	1.53621	0.4533	0.2636
60	1.1633	1.52705	0.4531	0.2643
80	1.1436	1.51789	0.4529	0.2649

t.	n_D.	$(n_D-1)/d$.	$(n^2_D-1)/(n^2_D+2)d$.	n_F.	$(n_F-1)/d$.	$(n^2_F-1)/(n^2_F+2)d$.
10	1.55679	0.4592	0.2654	1.57541	0.4745	0.2727
20	1.55212	0.4590	0.2657	1.57055	0.4743	0.2730
40	1.54278	0.4588	0.2663	1.56083	0.4740	0.2736
60	1.53344	0.4586	0.2670	1.55111	0.4737	0.2743
80	1.52410	0.4583	0.2676	1.54139	0.4734	0.2749

Monomethylaniline.

	$(n^2_C-1)/d$.	$(n^2_D-1)/d$.	$(n^2_F-1)/d$.
10°	1.4708	1.4926	1.5503
80°	1.4484	1.4692	1.5207

t.	d.	n_C.	$(n_C-1)/d$.	$(n^2_C-1)/(n^2_C+2)d$.
10	0.9944	1.56924	0.5725	0.3296
20	0.9863	1.56444	0.5723	0.3300
40	0.9701	1.55484	0.5719	0.3308
60	0.9539	1.54524	0.5716	0.3315
80	0.9377	1.53564	0.5712	0.3323

t.	n_D.	$(n_D-1)/d$.	$(n^2_D-1)/(n^2_D+2)d$.	n_F.	$(n_F-1)/d$.	$(n^2_F-1)/(n^2_F+2)d$.
10	1.57615	0.5794	0.3329	1.59425	0.5976	0.3414
20	1.57127	0.5792	0.3333	1.58922	0.5976	0.3418
40	1.56150	0.5788	0.3341	1.57916	0.5970	0.3427
60	1.55173	0.5784	0.3348	1.56910	0.5966	0.3435
80	1.54196	0.5780	0.3356	1.55904	0.5962	0.3443

Benzyl Cyanide.

	$(n^2_C-1)/d$.	$(n^2_D-1)/d$.	$(n^2_F-1)/d$.	$(n^2_{G'}-1)/d$.
10°	1.2889	1.3020	1.3362	1.3675
80°	1.2737	1.2863	1.3196	1.3503

t.	d.	n_C.	$(n_C-1)/d$.	$(n^2_C-1)/(n^2_C+2)d$.	n_D.	$(n_D-1)/d$.	$(n^2_D-1)/(n^2_D+2)d$.
10	1.0265	1.52417	0.5106	0.2981	1.52858	0.5149	0.3002
20	1.0184	1.51999	0.5106	0.2985	1.52435	0.5149	0.3006
40	1.0021	1.51163	0.5106	0.2993	1.51589	0.5148	0.3014
60	0.9857	1.50327	0.5105	0.3000	1.50743	0.5148	0.3021
80	0.9694	1.49491	0.5105	0.3008	1.49897	0.5147	0.3029

t.	n_F.	$(n_F-1)/d$.	$(n^2_F-1)/(n^2_F+2)d$.	$n_{G'}$.	$(n_{G'}-1)d$.	$(n^2_{G'}-1)/(n^2_{G'}+2)d$.
10	1.54003	0.5261	0.3057	1.55042	0.5362	0.3105
20	1.53570	0.5260	0.3060	1.54601	0.5361	0.3109
40	1.52704	0.5259	0.3068	1.53718	0.5361	0.3117
60	1.51838	0.5259	0.3076	1.52835	0.5360	0.3126
80	1.50972	0.5258	0.3084	1.51952	0.5359	0.3134

Benzaldehyde.

	$(n^2_C-1)/d$.	$(n^2_D-1)/d$.	$(n^2_F-1)/d$.	$(n^2_{G'}-1)/d$.
10°	1.3027	1.3205	1.3698	1.4156
80°	1.2861	1.3046	1.3522	1.3951

t.	d.	n_C.	$(n_C-1)/d$.	$(n^2_C-1)/(n^2_C+2)d$.	n_D.	$(n_D-1)/d$.	$(n^2_D-1)/(n^2_D+2)d$.
10	1.0617	1.54371	0.5121	0.2972	1.54982	0.5178	0.3000
20	1.0528	1.53915	0.5121	0.2976	1.54526	0.5179	0.3004
40	1.0350	1.53002	0.5121	0.2985	1.53613	0.5180	0.3013
60	1.0173	1.52089	0.5120	0.2993	1.52700	0.5180	0.3022
80	0.9995	1.51176	0.5120	0.3001	1.51787	0.5181	0.3031

t.	n_F.	$(n_F-1)/d$.	$(n^2_F-1)/(n^2_F+2)d$.	$n_{G'}$.	$(n_{G'}-1)/d$.	$(n^2_{G'}-1)/(n^2_{G'}+2)d$.
10	1.56663	0.5337	0.3075	1.58205	0.5483	0.3144
20	1.56189	0.5337	0.3080	1.57710	0.5482	0.3148
40	1.55241	0.5337	0.3089	1.56720	0.5480	0.3157
60	1.54293	0.5337	0.3098	1.55730	0.5478	0.3166
80	1.53345	0.5337	0.3107	1.54740	0.5477	0.3175

In comparing the change in the refractive powers with the change in temperature for the substances for which results have been given, it will be noticed that the values of the expression $(n - 1)/d$ increase, decrease, or remain practically constant for the different substances. The change for any one line for a given substance is always continuous, either increase or decrease. When the value apparently remained constant, this change was also taking place but was too slight to be appreciable when the calculations were limited to four significant figures but may be seen with five significant figures. For the present the tautomeric substances acetylacetone and ethyl acetacetate will be left out of the discussion. The expression $(n^2 - 1)/(n^2 + 2)d$, when used for calculating the refractive powers, always gave an increasing value with rise in temperature, this increase being small in some cases, larger in others. It will be necessary to return to this point later. The following table shows the results obtained in calculating the molecular refractions with the latter expression for the C line for 10° and 80° and comparing these values with those obtained by using Brühl's values for the atomic refractions. In the first paper, the value calculated for dimethylaniline by this method[1] was given incorrectly and should have been 40.666 instead of 39.581.

		$(n^2_C - 1)M/(n^2_C + 2)d$. Found.	Calc. according to Brühl.
Dimethylaniline	10°	40.354	40.666
	80°	40.692	
Isobutyl acetate	10°	31.482	31.409
	80°	31.772	
Ethyl *n*-butyrate	10°	31.285	31.409
	80°	31.703	
Isoamyl acetate	10°	36.075	35.980
	80°	36.335	
Methylhexyl ketone	10°	35.322	36.531
	80°	35.647	
Nitrobenzene	10°	32.312	32.373
	80°	32.385	
Monomethylaniline	10°	35.267	35.398
	80°	35.556	
Benzyl cyanide	10°	34.878	35.325
	80°	35.194	
Benzaldehyde	10°	31.503	31.009
	80°	31.811	

[1] In place of taking N as 3.02 in all cases as before, the following values are used here: N in secondary aryl amines — 3.408; N in tertiary aryl amines — 4.105; N in aliphatic nitriles — 3.176; NO_2 in nitroaryls — 7.16. The value calculated for the keto form of ethyl acetacetate in the former paper also requires correction and should be 31.531 instead of 31.382. This error was caused by taking the value of hydroxyl O instead of ether O for the ester.

This table shows that the calculated values for the molecular refractions agree equally well with the experimental results obtained at 80° as at 10°, and extends the use of this method of determining the structures of organic compounds to temperatures other than 20°, permitting its application to substances solid under ordinary conditions but melting at somewhat elevated temperatures, if the density and the refractive index both be determined for the higher temperature. The statement must be emphasized that these molecular refractions are not constant with increase in temperature, but increase regularly. This increase is, however, small enough within the range of temperature used not to interfere with the usefulness of the method. This increase with temperature has been observed before,[1] but whether the atomic refractions deduced by Brühl are an inherent property of the atoms themselves and as such their physical constants, or empirical constants obtained by a study and comparison of a large number of compounds, their importance and usefulness remains the same.[2]

In attempting to apply this method for determining structure to tautomeric substances, trouble is met with. Assuming a mixture of the two forms, enol and keto, of a given substance present, there would be the effect of each upon the other as possibly modifying or influencing the refractive index and its change with temperature to be accounted for. This may be considerable in closely related compounds such as these. Furthermore, the change in value of the molecular refraction which each form would undergo if present alone is unknown. These changes it is true are small, but the total change which can take place in passing from one form entirely over to the other is also small. It seems therefore almost hopeless to attempt to obtain quantitative results as to the amounts of the two forms present in a tautomeric mixture and the changes brought about by increase in temperature by this method. At present all that appears possible is to obtain qualitative relations as to whether one form is present in great excess and the direction in which change of temperature changes the equilibrium, using the method more to confirm purely chemical quantitative measurements than as an independent method. For acetylacetone the molecular refraction indicates that at 10° the substance is present to a great extent in the dienol form, tending to go over into the keto form (mono- or di-) on raising the temperature. The values found were 27.270 at 10° and 27.140 at 80° (calculated 27.243—dienol, 26.329—monoenol, 25.315—diketo). Since the normal change is for an increase in molecular refraction with rise in temperature, this decrease in acetylacetone denotes a greater change than would appear at first sight from the lack of constancy, although the effect of each form

[1] Perkin, *J. Chem. Soc.*, 69, 1070 (1895) and others.

[2] Cf. Perkin, *Ibid.*, p. 1167.

upon the other is an unknown quantity. With regard to ethyl acetacetate, as stated in the first paper, there was a lag in the refractive index when the substance was cooled from a higher temperature. For the ordinary temperature (20°) Brühl[1] gave the results shown in the first two columns:

	Found.		Calc.		Found.
C line............	31.89	Keto	31.53	After distillation.....	31.876
		Enol	32.55	On standing...........	31.915
D line............	31.99	Keto	31.78	After distillation.....	32.032
		Enol	32.72	On standing.........	32.058

In the last column the results of the first paper are given. Brühl concluded from his results that the substance was present entirely in the keto form. His value for the D line is slightly lower than that found here and also than that given by Schaum,[2] and using this new value together with the C line, it appears, assuming the true values of the keto form to be those calculated, as though some, at any rate, of the substance were present in the enol form, the amount decreasing with rise in temperature.

Since it has been shown that the refractive powers increase with rise in temperature for these substances, and from the choice of substances this increase cannot be an accidental property of a certain class, it may be of some interest to look for a cause or reason for this regularity. That the expression $(n^2 - 1)/(n^2 + 2)d$ did not give strictly constant values was indicated by Lorentz at the time of deducing it.[3] In discussing the effect of temperature and change of state on the refractive powers calculated from his formula, he stated: "Was nun die Ursachen der immer in gleicher Richtung wiederkehrenden Abweichungen betrifft, so kann man darüber nur Muthmassungen anstellen. Sie könnten z. B. ihren Grund haben in einer Aenderung der Molecüle, in einem Einflusse derselben auf die Eigenschaften des Aethers, in einer Abweichung von den gewöhnlichen Wirkungsgesetzen der Electricität für moleculare Entfernungen oder endlich in den Complicationen, welche eintreten könnten, wenn die Molecüle einen grossen Theil des Körperarmes einnehmen. Es wäre indess voreilig, eine dieser Hypothesen, deren Zahl sich noch wohl vermehren liesse, schon jetzt weiter anszuarbeiten."

A number of attempts[4] have been made to modify the Lorentz expression, or to deduce other expressions which would give constant results when the refractive indices and densities under varying conditions were substituted. Most of these attempts were not founded upon any satisfactory theoretical basis, and while interesting in so far as constant results were obtained, possessed no deeper significance.

[1] *Ber.*, **25**, 369 (1892).
[2] *Ber.*, **31**, 1964 (1898).
[3] *Pogg. Ann.*, *Neue Folge*, **9**, 663 (1880).
[4] Chéneveau, *Ann. chim. phys.* [8], **12**, 145; gives a very complete list.

Recently, R. C. Maclaurin,[1] basing his work upon certain fundamental assumptions regarding the ether, deduced a dispersion formula for transparent media which reproduced the experimental results for the refractive indices of several substances over a very large range with great accuracy. This formula, analogous to the other expressions for refractive power, for this purpose may under certain assumptions be brought into the form $(n^2 - 1)/(n^2 + a)d$ = const., in which a is a constant depending for its value "on the influence of the electrons in the immediate vicinity of the point where the disturbance is considered." The data at hand permits of the calculation of a assuming it not to be affected by the change in temperature or by any possible absorption. The following table gives the average values for the four lines (in some cases three) for the different substances, the percentage error column showing the greatest percentage deviation of the values for the separate lines from this mean. This error is partly due to experiment and probably partly to the assumption of constancy for varying temperature, and perhaps to other causes.

	a.	Percentage error.
Diisoamyl	3.83	5.5%
Dimethylaniline	4.28	3.4
n-Heptyl alcohol	3.97	15.1
Benzyl alcohol	3.07	13.3
n-Butyric acid	6.45	11.3
Isobutyl acetate	4.45	5.8
Ethyl *n*-butyrate	4.48	5.3
Isoamyl acetate	3.97	10.8
Methylhexyl ketone	5.45	5.1
Nitrobenzene	4.46	3.1
Monomethylaniline	4.38	1.8
Benzyl cyanide	5.10	1.2
Benzaldehyde	5.31	3.6
Acetylacetone	1.26	11.1

The refractive powers of the substances when Lorentz's expression (or in terms of the expression given above, when $a = 2$) was used, increased with the temperature but only to a small extent, so that it is surprising to find that in order to obtain constant results with the expression based on Maclaurin's dispersion formula as shown above, a must have a value so much larger than two. In every case except acetylacetone, a is greater than 2, indicating again the exceptional position of this substance, due to its being a tautomeric mixture of the two forms, the relative amounts changing with the temperature. It is interesting to note that the isomeric substances, isobutyl acetate and ethyl *n*-butyrate, have practically the same value, 4.45 and 4.48, respectively, for the constant. A study of a may aid in throwing light upon the nature of the forces within the molecule.

[1] "On Optical Dispersion Formulae," *Proc. Roy. Soc.* A, **81**, 367 (1908).

Conclusions.

The refractive indices and the densities of a number of organic liquids belonging to different classes were determined for a large number of temperatures between 15° and 75°, and the curves plotted showed the refractive index to be a linear function of the temperature within the experimental error in every case.

The refractive powers were calculated for temperatures from 10–80°; the expression $(n^2 - 1)/d$ gave decreasing values as the temperature increased, $(n^2 - 1)/(n^2 + 2)d$ gave increasing values for normal (not tautomeric) substances, $(n - 1)/d$ in some cases gave increasing, in others decreasing values.

It is shown that the molecular refractions calculated by using Brühl's values for atomic refractions gave results agreeing with the experimental values as well at high as at low temperatures.

The state of the equilibrium between the two forms of tautomeric substances can only be arrived at qualitatively by means of refractive powers.

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THE SOLUBILITY OF SALTS IN CONCENTRATED ACIDS.[1]

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Introduction.

That the solubility of chemical compounds in aqueous solutions is affected by the presence of other dissolved substances has long been known. Quantitative investigations of these solubility relations have been more numerous than almost any other physical-chemical studies, and since the introduction of the theory of electrolytic dissociation into chemical thought the field has been of increased interest to chemists, who have found in this theory an explanation, whether or not complete, of facts previously inexplicable. Of these almost countless investigations, those of Nernst,[2] A. A. Noyes,[3] and Arrhenius[4] may be noted as the most widely known and probably the most influential in shaping the opinions of chemists on this important matter.

The researches mentioned above, together with the many others not

[1] Presented before the New York Section of the American Chemical Society, on May 14, 1909.

[2] *Z. physik. Chem.*, **4**, 372 (1889).

[3] *Ibid.*, **6**, 241 and 385 (1890); **9**, 603 (1892); **12**, 162 (1893); **16**, 125 (1895); **27**, 267 and 279 (1898); **28**, 518 (1899).

[4] *Ibid.*, **31**, 197 (1899).