7. The following data are submitted.

Heat of inversion of sucrose by hydrochloric acid at 20° = 10.4 ± 0.06 gram calories per gram.

Heat of solution of sucrose in water at 20° to ca. 4% sucrose concentration = 3.43 ± 0.02 gram calories per gram.

Heat of solution of sucrose in 1.64 molar hydrochloric acid, at 20° to ca. 4% sucrose = 4.23 ± 0.05 gram calories per gram.

Heat of solution, anhydrous α-glucose in water and in 1.64 molar hydrochloric acid, at 20° to ca. 4% glucose = 13.9 ± 0.1 gram calories per gram.

NEW YORK CITY.

[CONTRIBUTION FROM THE POLYTECHNIC INSTITUTE OF WARSAW.]

ATOMIC REFRACTION.

BY W. SWIENTOSLAWSKI.

Received March 17, 1920.

In 1911, F. Eisenlohr[1] published new calculations of the refractivities of carbon, hydrogen, and other atoms in organic compounds. These calculations do not differ from those used by J. W. Brühl, because both authors assumed that the molecular refractions of the organic compounds are equal to the sums of the refractions of the separate atoms.

$$M_D = \Sigma A_D.$$

According to this supposition, the computation of atomic refraction depends on the average value of the refraction of the CH_2 group and those of certain atoms. If, however, the individual atomic refractions show even small deviations, this method cannot be used.

In order to determine the limits of variations in the refractions caused by carbon and hydrogen atoms in the compounds which contain only the linkings C–C and C–H, I have used the following method of calculation.

1. If we denote by r_C, r_H, and r_{CH_2} the refractions for the D lines of carbon, hydrogen, and the CH_2 group, the molecular refraction, M_D, of the hydrocarbon C_nH_m can be expressed by the following equation,

$$M_D = nr_{CH_2} + (m - 2n)r_H + \Sigma\Delta r_C + \Sigma\Delta r_H, \qquad (1)$$

or

$$M_D = nr_{CH_2} + (m - 2n)r_H + \Sigma\Delta r,$$

where

$$\Sigma\Delta r = \Sigma\Delta r_C + \Sigma\Delta r_H.$$

Equation 1 cannot be solved when the increments $\Sigma\Delta r$ are not known; therefore, we can compute the quantities r_C and r_H only by reference to several chosen compounds, thus obtaining the average values of r_C and r_H on the supposition that $\Sigma\Delta r = 0$.

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[1] *Z. physik. Chem.*, **75**, 605 (1911).

2. In some cases it is more advantageous to use the quantities r_{C-C} and r_{C-H}, corresponding to refractions of the atomic linkings C–C and C–H, especially when it is desirable to compare these quantities with the thermochemical data. It is clear that the quantities r_{C-C} and r_{C-H} can be computed when r_C and r_H are known, for we have

$$r_{C-C} = 0.5 r_C$$
$$r_{C-H} = r_H + 0.25 r_C.$$

I have selected as the basis of calculation the following compounds, *n*-pentane, 2-methyl-butane, *n*-hexane, *n*-octane, di-isobutyl, di-isoamyl, cyclopentane, and cyclohexane.

Table I contains the values of the molecular refractions M_D and the equations connecting r_{CH_2}, r_H, and $\Sigma \Delta r$. These equations were solved by the method of least squares.

TABLE I.

	Name.	Formula.	M_D.	Equation.
1	*n*-Pentane	C_5H_{12}	25.23	$5r_{CH_2} + 2r_H + \Sigma \Delta r = 25.23$
2	*iso*-Pentane	C_5H_{12}	25.25	$5r_{CH_2} + 2r_H + \Sigma \Delta r = 25.25$
3	*n*-Hexane	C_6H_{14}	29.84	$6r_{CH_2} + 2r_H + \Sigma \Delta r = 29.84$
4	*n*-Octane	C_8H_{18}	39.16	$8r_{CH_2} + 2r_H + \Sigma \Delta r = 39.16$
5	Di-*iso*butyl	C_8H_{18}	39.11	$8r_{CH_2} + 2r_H + \Sigma \Delta r = 39.11$
6	Di-*iso*amyl	$C_{10}H_{22}$	48.33	$10r_{CH_2} + 2r_H + \Sigma \Delta r = 48.33$
7	Cyclopentane	C_5H_{10}	23.12	$5r_{CH_2} + \Sigma \Delta r = 23.12$
8	Cyclohexane	C_6H_{12}	27.72	$6r_{CH_2} + \Sigma \Delta r = 27.72$

Upon the assumption that $\Sigma \Delta r = 0$, we obtain the average values of $r_C = 2.490$, $r_H = 1.066$, and $r_{CH_2} = 4.622$, for our 8 selected hydrocarbons.

Table II contains a comparison of the observed and calculated values of M_D.

TABLE II.

Name.	Formula.	M_D (obs.).	(calc.).	Δr.	$\Delta\%$.
n-Pentane	C_5H_{12}	25.23	25.24	—0.01	—0.04
iso-Pentane	C_5H_{12}	25.25	25.24	+0.01	+0.04
n-Hexane	C_6H_{14}	29.84	29.86	—0.02	—0.07
n-Octane	C_8H_{18}	39.16	39.11	+0.05	+0.13
Di-*iso*butyl	C_8H_{18}	39.11	39.11	0.00	0.00
Di-*iso*amyl	$C_{10}H_{22}$	48.33	48.35	—0.02	—0.04
Cyclopentane	C_5H_{10}	23.12	23.11	+0.01	+0.04
Cyclohexane	C_6H_{12}	27.72	27.73	—0.01	—0.04
				$\Delta\% =$	±0.07

The small differences between the observed and calculated values show that Δr is very small, and that, therefore, it is very probable that the atomic refractions remain constant in the 8 compounds, at any rate within ±0.07%.

Comparing the values of r_C, r_H, and r_{CH_2} thus obtained with those of F. Eisenlohr

	r_C.	r_H.	r_{CH_2}.
F. Eisenlohr....................	2.418	1.100	4.618
W. Swientoslawski...............	2.490	1.066	4.622
	Deviation % = +3.0%	Deviation % = —3.1%	Deviation % = +0.09%

we see that his value for r_{CH_2} is in sufficient agreement with mine; those for r_C and r_H differ widely ($\pm 3.0\%$).

In order to explain why Eisenlohr's calculations of molecular refractions show a sufficient agreement with the direct measurements, it should be observed that the value of M_D for numerous organic substances arises from two terms

$$M_D = nr_{CH_2} + \Sigma r_X.$$

The first term nr_{CH_2}, is very large, while the second one, corresponding to the refraction of other atoms or groups in the molecule is always small. Therefore, small errors in the determination of the values of r_C and r_H, etc., do not exert any marked influence on the calculated values of M_D. Yet the determination of the real values of r_C and r_H is of great importance for our science.

As regards our computation, we can only maintain that the values found for r_C and r_H correspond to the average values of atomic refractions in the cases of the 8 compounds cited. By using a larger number of equations, for example,

$$\left.\begin{array}{l} M_D = nr_{CH_2} + 2r_H + \Sigma\,\Delta r \text{ for hydrocarbons } C_nH_{2n+2}. \\ M'_D = nr_{CH_2} + \Sigma\,\Delta r \text{ for hydrocarbons } C_nH_{2n}. \\ M''_D = nr_{CH_2} - 2r_H + \Sigma\,\Delta r \text{ for hydrocarbons } C_nH_{2n-2}. \\ M'''_D = nr_{CH_2} - 4r_H + \Sigma\,\Delta r \text{ for hydrocarbons } C_nH_{2n-4}. \end{array}\right\} \begin{array}{l} \text{containing} \\ \text{only the link-} \\ \text{ings C–C and} \\ \text{C–H;} \end{array}$$

and by introducing new hydrocarbons C_nH_{2n-2}, C_nH_{2n-4}, etc., it is probable that we might obtain slightly different values for r_C, r_H, and r_{CH_2}. Therefore, this problem cannot be considered definitely solved.

In order to show that the refraction of carbon and hydrogen depends on the constitution of the hydrocarbons, in Table III are given the observed values of M_D for several compounds and those calculated from the formula, $M_D = \Sigma r_C + \Sigma r_H$, where r_C and r_H are the average values of atomic refraction obtained from the 8 hydrocarbons cited. For this purpose the methyl derivatives of polymethylene hydrocarbons have been chosen.

It is interesting to observe that all the deviations vary between 0.00 and +0.94%, excluding one case (1;1-dimethyl-cyclohexane, where $\Delta = -0.05\%$ according to Lange's value). In some cases the deviations are very remarkable; for example, in the case of methyl-cyclohexane, which has been investigated so carefully by Kishner and Eisenlohr, the considerable deviation of between +0.34% and +0.37% is observed.

TABLE III.

Name.	Formula.	M_D.	Author.	nr_{CH_2}.	Δr.	$\Delta\%$.
Methyl-cyclohexane	C_7H_{14}	32.47	Kishner	32.35	+0.12	+0.37
Methyl-cyclohexane	C_7H_{14}	32.46	Eisenlohr	32.35	+0.11	+0.34
1,1-Dimethyl-cyclohexane	C_8H_{16}	37.12	Perkin	36.98	+0.14	+0.38
1,1-Dimethyl-cyclohexane	C_8H_{16}	36.96	Lange	36.98	—0.02	—0.05
1,2-Dimethyl-cyclohexane	C_8H_{16}	37.02	Eykmann	36.98	+0.04	+0.11
1,3-Dimethyl-cyclohexane	C_8H_{16}	37.26	Eykmann	36.98	+0.28	+0.76
1,4-Dimethyl-cyclohexane	C_8H_{16}	37.28	Eykmann	36.98	+0.30	+0.81
Dihydro-laurolene	C_8H_{16}	37.12	Perkin	36.98	+0.14	+0.38
Dihydro-*iso*-laurolene	C_8H_{16}	36.99	Perkin	36.98	+0.01	+0.03
1,2,4-Trimethyl-cyclohexane	C_9H_{18}	41.66	Eykmann	41.60	+0.06	+0.14
1,2,4-Trimethyl-cyclohexane	C_9H_{18}	41.75	Eykmann	41.60	+0.15	+0.36
1,3,5-Trimethyl-cyclohexane	C_9H_{18}	41.99	Eykmann	41.60	+0.39	+0.94
Pulegane	C_9H_{18}	41.74	Eykmann	41.60	+0.14	+0.34
Dihydro-campholene	C_9H_{18}	41.66	Eykmann	41.60	+0.06	+0.14

The only possible conclusion to be drawn from the data of Table III is, that *the refraction of carbon and hydrogen in the 8 selected compounds is not identical with that in the methylenic polymethylene hydrocarbons: the introduction of the* CH_2 *group* produces a small, but appreciable increase, Δr, in the molecular refraction.

In another paper it will be shown that the *methyl group exerts a similar effect upon the heat of formation of the atomic linkings C–C and C–H.*

In the case of compounds which contain other atoms in the molecule (for example, oxygen) the results obtained from F. Eisenlohr's values differ from those obtained by me, and the differences are found to be greater, the larger the value of Σr_X in the equation

$$M_D = nr_{CH_2} + \Sigma r_X,$$

where nr_{CH_2} corresponds to the refraction of the CH_2 group and Σr_X to that of the rest of the molecule.

For example, in the case of ketones and aldehydes, we have

$$\Sigma r_X = r_o + \Sigma \Delta r,$$

where r_o corresponds to the refraction of oxygen in the carbonyl group. In this case my calculations and those of Eisenlohr are in sufficient agreement because Σr_X is very small.

The calculations for ketones and aldehydes are given in Table IV.

Eisenlohr assumes $r_o = 2.211$, which value differs from mine ($r_o = 2.196$) by about +0.67%.

On comparing the various values of r_o in Table IV, considerable deviations from the average value, $r_o = 2.20$, are evident. These can be accounted for by supposing that the refraction of the carbonyl group, or of the oxygen, is variable and depends on the constitution of the molecule.

TABLE IV.

Name.	Formula.	M_D.	nr_{CH_2}.	$r_0 + \Sigma \Delta r$.
Acetone	CH_3COCH_3	16.15	13.87	2.28
Methylethyl-ketone	$CH_3COC_2H_5$	20.67	18.49	2.18
Diethyl-ketone	$C_2H_5COC_2H_5$	25.18	23.11	2.07
Methylpropyl-ketone	$CH_3COC_3H_7$	25.20	23.11	2.09
Methyl-*iso*-propylketone	$CH_3COC_3H_7$	25.24	23.11	2.13
Ethylpropyl-ketone	$C_2H_5COC_3H_7$	29.71	27.73	1.98
Methyl-*iso*-butylketone	$CH_3COC_4H_9$	30.01	27.73	2.28
Oenanthol	$C_7H_{14}O$	34.79	32.35	2.44
Methylhexyl-ketone	$CH_3COC_6H_{13}$	39.28	36.98	2.30
Methylnonyl-ketone	$CH_3COC_9H_{19}$	53.00	50.84	2.16
n-Butyl-aldehyde	C_4H_9COH	20.64	18.49	2.15
iso-Butyl-aldehyde	C_4H_9COH	20.68	18.49	2.19
			Average, $r_0 + \Sigma \Delta r$ =	2.196

This can be proved, for if we assume that $\Delta r = 0$, we may calculate the values of r_{CH_2} and r_0 by the method of least squares from the series of equations

$$M_D = nr_{CH_2} + r_0 + \Sigma \Delta r.$$

Thus, we obtain $r_{CH_2} = 4.631$ and $r_0 = 2.137$.

The differences between M_D and the calculated values $(nr_{CH_2} + r_0)$ are given in Table V.

TABLE V.

Name.	M_D.	$nr_{CH_2} + r_0$.	Δr.	$\Delta\%$..
Acetone	16.15	16.03	+0.12	+0.74
Methylethyl-ketone	20.65	20.66	—0.01	—0.05
Diethyl-ketone	25.18	25.29	—0.11	—0.44
Methylpropyl-ketone	25.20	25.29	—0.09	—0.35
Methyl-*iso*-propylketone	25.24	25.29	—0.05	—0.20
Methyl-*iso*-butylketone	30.01	29.92	+0.09	+0.30
Ethylpropyl-ketone	29.71	29.92	—0.21	—0.70
Oenanthol	34.79	34.55	+0.24	+0.70
Methylhexyl-ketone	39.28	39.19	+0.09	+0.23
Methylnonyl-ketone	53.00	53.08	—0.08	—0.15
n-Butyl-aldehyde	20.64	20.66	—0.02	—0.10
iso-Butyl-aldehyde	20.68	20.66	+0.02	+0.10
			Average, $\Delta\%$ =	+0.34

A comparison of the percentage deviations in Tables II and V shows that the refraction of the carbonyl group or of carbonyl oxygen varies within wide limits, and that the *deviations cannot be explained as being due to experimental errors.*

If we examine the following data

$$\begin{array}{llllll}
CH_3CO.CH_3 & 2.28 & C_2H_5CO.CH_3 & 2.18 & i\text{-}C_4H_9CO.H & 2.19 \\
& \}-0.09 & & \}-0.11 & & \}+0.09 \\
CH_3CO.C_2H_5 & 2.18 & C_2H_5CO.C_2H_5 & 2.07 & i\text{-}C_4H_9CO.CH_3 & 2.28 \\
& \}-0.09 & & \}-0.09 & & \\
CH_3CO.C_3H_7 & 2.09 & C_2H_5CO.C_3H_7 & 1.98 & &
\end{array}$$

we observe that the replacement of a methyl group by an ethyl or by a *n*-propyl group is accompanied by a considerable diminution in the value of r_o. These diminutions are almost identical in all cases and vary within narrow limits (—0.09 and —0.11). Likewise, we must note that the methyl group, when it is substituted for hydrogen in aldehydes, effects a very noticeable change equal to +0.09, when the rest of the molecule is *iso*-C_4H_9CO, for example.

The data of F. Eisenlohr which concern the atomic refractions of ether compounds, are not in agreement with those computed above. These variations pertain to the alcohols, ethers, and esters. This paper is not intended to give complete discussion of the question, but only to demonstrate by some example that the exact determination of the refractions r_C and r_H is indispensable in all calculations which deal with this problem.

If we calculate values for M_D for the alcohols and ethers by the formula

$$M_D = nr_{CH_2} + 2r_H + r_o + \Sigma\,\Delta r$$

it is clear that an error in the value assumed for r_H causes an error in the value of r_o. Table VI contains the calculated values of r_o assuming, as above, that $r_{CH_2} = 4.622$, $r_H = 1.066$, and that $\Sigma\,\Delta r = 0$.

TABLE VI.

Name, alcohol.	Formula.	M_D.	$nr_{CH_2} + 2r_H$.	$r_o + \Delta r$.
Methyl	CH_3OH	8.22	6.75	1.47
Ethyl	C_2H_5OH	12.74	11.38	1.36
n-Propyl	C_3H_7OH	17.52	16.00	1.52
iso-Propyl	C_3H_7OH	17.54	16.00	1.54
n-Butyl	C_4H_9OH	22.13	20.62	1.51
iso-Butyl	C_4H_9OH	22.16	20.62	1.54
Trimethyl-carbinol	C_4H_9OH	22.22	20.62	1.60
iso-Amyl	$C_5H_{11}OH$	26.74	25.24	1.50
iso-Amyl (ferm.)	$C_5H_{11}OH$	26.77	25.24	1.53
n-Heptyl	$C_7H_{15}OH$	36.05	34.49	1.56
Methylhexyl-carbinol	$C_8H_{17}OH$	40.56	39.11	1.35
			Average, =	1.494

The average value, $r_o = 1.494$, differs from that of Eisenlohr ($r_o = 1.525$) by about +2.03%.

In Table VII, the data for the refractions of oxygen in the ethers are given.

TABLE VII.

Name.	Formula.	M_D.	$nr_{CH_2} + 2r_H$.	$r_o + \Sigma\,\Delta r$.
Methylal	$CH_3.O.CH_2.O.CH_3$	19.19	16.00	1.60
Acetal	$(CH_3.CH_2O)_2.CH.CH_3$	33.13	29.86	1.64
Ethylpropyl ether	$C_2H_5.O.C_3H_7$	26.95	25.24	1.71
Ethyl ether	$C_2H_5.O.C_2H_5$	22.43	20.62	1.81
			Average, =	1.663

The value obtained by F. Eisenlohr is 1.643, which differs from 1.663 by about —1.2%.

It is to be noted that quite aside from this disagreement, the values of r_C, r_H, r_O, etc., are not constant. The calculation of average values of atomic refraction cannot be accepted as a satisfactory solution of the question before us.

In another paper I shall compare these results with the thermochemical data. In comparison I shall attempt to justify the selection of the 8 hydrocarbons as a basis for the calculation of the average values r_{CH_2}, r_C and r_H.

WARSAW, POLAND.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF PRINCETON UNIVERSITY.]

THE EXPLANATION OF AN APPARENT ANOMALY OUTSTANDING IN THE RESULTS OF MEASUREMENT OF DISSOCIATION PRESSURES.

BY ALAN W. C. MENZIES.

Received March 29, 1920.

After brief reference to the nature of the anomaly in question and to the various explanations offered to account for it, it is proposed to adduce experimental results, supported by results of a parallel nature drawn from the work of others, to show that this apparent anomaly is disposed of by a knowledge of the real facts of the case.

The Nature of the Anomaly.—In 1888, Tammann,[1] applying a form of the gas-current saturation method to the measurement of the dissociation pressures of salt hydrates near 35°, obtained results which, while somewhat erratic,[2] were uniformly higher by from 2 to 5% than the results obtained by Frowein[3] with the tensimeter. This anomaly was confirmed by Schottky,[4] working under Nernst's guidance, who found that the initial dissociation pressures developed in tensimetric measurements were higher than the equilibrium values. In 1911, Partington[5] added further confirmation, again using the gas-current saturation method, although not in a form identical with Tammann's.

Explanation of the Anomaly.—Thoughtful elucidations and critical discussions have been offered by Tammann,[6] Nernst,[7] Partington,[6] Brereton Baker,[8] and Campbell,[9] those of Nernst and of Campbell being especially instructive. Lack of space forbids their outlining or consideration here.

[1] Tammann, *Ann. Physik.*, 33, 322 (1888).

[2] Cf. Menzies, THIS JOURNAL, 42, 978 (1920).

[3] Frowein, *Z. physik. Chem.*, 1, 5 (1887).

[4] Schottky, *ibid.*, 64, 415 (1908).

[5] Partington, *J. Chem. Soc.*, 99, 466 (1911).

[6] *Loc. cit.*

[7] Nernst, *Z. physik. Chem.*, 64, 425 (1908).

[8] Baker, *Ann. Rep. Progress Chem.*, 8, 34 (1912).

[9] Campbell, *Trans. Faraday Soc.*, 10, 195 (1914).