[Contribution from the Polytechnic Institute of Warsaw.]

THE THERMOCHEMISTRY OF HYDROCARBONS ACCORDING TO P. W. ZUBOW'S DATA.

By W. Swiętoslawski.

Received March 6, 1920.

In a previous paper[1] I undertook the systematic analysis of the thermochemical data on organic compounds, using the determinations of J. Thomsen, M. Berthelot, Stohmann, W. Louginine, and others. However, the investigations of Emil Fischer and Wrede[2] and of the author[3] have made it clear that all of the data of thermochemistry must be recalculated and corrected before an analysis and a summary of them can be made.

With this in view, I have recently recalculated[4] the very exact experimental material, accumulated between 1892 and 1911 by P. W. Zubow in Louginine's thermochemical laboratory, and in the present communication I wish to examine the results of this recalculation, believing that such an examination will prove useful, even before all the other previous thermochemical investigations have been recalculated.

The Equations of Combustion.

If we denote the heat of formation of the molecules O_2, CO_2, and H_2O from their separate atoms by $2w$, $4z$ and $2u$, and the heats of formation of the atomic linkings, C–H and C–C by x and y, we obtain for a given hydrocarbon C_nH_m, containing only such linkings, the following equation of combustion

$$\left(\frac{4n - m}{2}\right)y + mx + \left(2n + \frac{m}{2}\right)w + A = 4nz + mu,$$

where A signifies the molar heat of combustion of C_nH_m. When the equation is transformed to

$$\left(2n - \frac{m}{2}\right)(y + w - 2z) + m\,(x + w - z - u) + A = 0 \quad (1)$$

we see that the terms $y + w - 2z$ and $x + w - z - u$ are repeated in the equation as many times as the linkings C–C and C–H occur in the hydrocarbon C_nH_m.

We shall call the terms $y + w - 2z$ and $x + w - z - u$ the thermochemical characteristics of the atomic linkings C–C and C–H. They contain the constants w, z and u, and the variables x and y, which depend upon the constitution of the hydrocarbon. It is clear that x and y correspond in Equation 1 to the average values of the heats of formation of the above mentioned linkings.

---

[1] *Z. physik. Chem.*, **65**, 513; **67**, 78 (1909); **72**, 49 (1910); *Bull. Acad. Cracovie*, **1909**, 941.

[2] *Sitz. Akad. Wiss. Math.-Nat. Klasse*, **1908**, p. 129.

[3] *J. Russ. Phys.-Chem. Soc.*, **46**, 935, 1284, 1293, 1302 (1914).

[4] This Journal, **42**, 1092 (1920).

If we choose definite values of x and y, so that x = const. and y = const., by comparing several hydrocarbons, Equation 1 must be completed by the addition of $(\Sigma\Delta x + \Sigma\Delta y) = \Sigma\Delta(x, y)\ (2n - m/2)\ (y + w - 2z) + m(x + w - z - u) + \Sigma\Delta(x, y) + A = 0$, where $\Sigma\Delta(x, y)$ represents the increase of the heats of formation of the separate atomic linkings C–C and C–H in the hydrocarbons examined.

Thermochemical Characteristics of the C-C and C-H Linkings.

One purpose of this paper is to explain within what limits the values of the thermochemical characteristics $x + w - z - u$ and $y + w - 2z$ can vary in hydrocarbons not containing unsaturated bonds. The analysis of this problem can be performed in two ways, (1) by solving the equations of combustion

$$4(x + w - z - u) + A_1 = 0$$
$$6(x + w - z - u) + (y + w - 2z) + A_2 = 0$$

for methane and ethane; or (2) by computing the average values of x and y for another assumed hydrocarbon, supposing $\Sigma\Delta(x, y) = 0$. Having established values of the thermochemical characteristics of the linkings C–C and C–H, we can then compute the increments $\Sigma\Delta(x,y)$ for other hydrocarbons.

In the previous papers I have chosen the first method, adopting for A_1 and A_2 M. Berthelot's and J. Thomsen's determinations of the heats of combustion of methane and ethane. However, at present it seems to me that the values of A_1 and A_2 are not entirely trustworthy, because at that time the measurements could not be made with the precision now required.

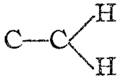
With the intention of using the second method, I have chosen the newly corrected data of P. W. Zubow for the 4 saturated and polymethylene hydrocarbons and the heat of combustion of naphthalene, as redetermined by Dickinson in the Bureau of Standards in 1915, and by the author in 1917 in Louginine's thermochemical laboratory, and have computed, by the method of least squares, the average magnitudes of $(x + w - z - u$ and $(y + w - 2z)$ for the following 5 substances, n-hexane, n-octane, n-decane, cylcohexane and naphthalene.

The heats of combustion of these substances were corrected to the gaseous state at the boiling point, and the computation was performed by supposing $\Sigma\Delta(x, y) = 0$.

Abbreviating: $(x + w - z - u) = X$ and $(y + w - 2z) = Y$ we obtain the following 5 equations:

Cyclohexane	$6Y + 12X + \Sigma\Delta(x,y) + 946.2 = 0$
n-Hexane	$5Y + 14X + \Sigma\Delta(x,y) + 998.5 = 0$
n-Octane	$7Y + 18X + \Sigma\Delta(x,y) + 1317.7 = 0$
n-Decane	$9Y + 22X + \Sigma\Delta(x,y) + 1630.4 = 0$
Naphthalene	$16Y + 8X + \Sigma\Delta(x,y) + 1258.0 = 0$

From which we obtain $X = -52.76$ cal., $Y = -52.25$ cal., $Z = Y + 2X = -157.77$ cal.

The same result can be obtained if the equations are modified by introducing the magnitudes $Z = Y + 2X$, corresponding to the thermochemical characteristic of the  $C-C\begin{smallmatrix}H\\H\end{smallmatrix}$ group. Then, for

Cyclohexane $6Z = -946.2$;
n-Hexane $5Z + 4X = -998.5$;
n-Octane $7Z + 4X = -1317.7$;
n-Decane $9Z - 4X = -1630.4$;
Naphthalene $16Z - 24X = -1258.0$.

Whence: $X_1 = -52.78$ cal., $Y_1 = -52.22$ cal., $Z_1 = -157.78$ cal.

It is interesting that if the last equation (for naphthalene) is excluded, the solution of the first 4 equations gives

$$X_2 = -52.82 \text{ cal.}, \; Y_2 = -52.11 \text{ cal.}, \; Z_2 = -157.75 \text{ cal.}$$

These numbers differ very little from the above-mentioned ones. The deviations are less than 0.02% for the thermochemical characteristic of the C_2H_2 group, 0.11% for the C–H linking, and about 0.25% for the C–C linking.

If we adopt the values $X = -52.76$ cal., $Y = -52.25$ cal., $Z = -157.77$ cal., and introduce them into our equations of combustion, we obtain the following deviation ($\Delta\%$) between the calculated and measured values.

TABLE I.

Name.	$A_{gas.}$	$\Sigma X + \Sigma Y$.	Δ.	$\Delta\%$.
n-Hexane	998.5	999.9	+1.4	+0.14
n-Octane	1317.7	1315.4	−2.3	−0.17
n-Decane	1630.4	1631.0	+0.6	+0.04
Cyclohexane	946.2	946.6	+0.4	+0.04
Naphthalene	1258.0	1258.1	+0.1	+0.01
				$\Delta\% = \pm 0.08\%$

The deviations ($\Delta\%$) vary within the narrow limits ± 0.08%, depending evidently on the errors of experiment and on the impurities of the samples burned. Therefore, it is very probable that the thermochemical characteristics of the C–C and C–H linkages really remain constant in these 5 hydrocarbons.

The comparison of the values obtained above with those computed by the first-mentioned method is very interesting, but we must observe that only Thomsen's data are to be considered for this comparison, because the correction of Berthelot's measurements, performed in 1887 and 1901, is attended by many difficulties. Thomsen's data can be in some degree corrected because his apparatus was designed for the combustion of gaseous substances and all the details of his experiments are sufficiently known. When, therefore, we introduce the corrections (1) for changing his thermometer readings to the hydrogen scale (a diminution of about —0.3%), and (2) for the newer determinations of the heat capacity of water (also a diminution of about —0.1%), we are justified in believing that the remaining corrections are small and are due chiefly to impurities in the burned samples.

The corrected and uncorrected values of Thomsen for A_1 and A_2 for methane and ethane, and the thermochemical characteristics X and Y are as follows.

	Uncorr.	Corr.		
Methane	211.9	$A_1 = 211.1$	$X = -52.78$ cal.	$Z = -157.8$ cal.
Ethane	370.4	$A_2 = 368.9$	$Y = -52.22$ cal.	

There is complete agreement between the values for X, Y and Z, calculated in these different ways. As a consequence it is most probable that the thermochemical characteristics of the C–C and C–H linkings in the 7 different hydrocarbons mentioned are really constant.

Furthermore, the values obtained for X, Y and Z can be adopted as a basis for the thermochemical analysis of other hydrocarbons in order to

TABLE II.

No.[1]	Name.	Formula.	$A_{gas.}$	$\Sigma X \underset{(-)}{+} \Sigma Y.$	$\Sigma\Delta(x,y).$
	1. Derivatives of Cyclobutane.				
2.	Methyl-cyclobutane..........	C_5H_{10}	792.1	788.9	—3.2
	2. Derivatives of Cyclopentane.				
3.	Cyclopentane...............	C_6H_{10}	791.5	788.9	—2.6
7.	Methyl-cyclopentane.........	C_6H_{12}	947.4	946.6	—0.8
16.	1,3-Dimethyl-cyclopentane...	C_7H_{14}	1102.1	1104.4	+2.3
23.	1,2,4-Trimethyl-cyclopentane	C_8H_{16}	1259.2	1262.2	+3.0
29.	1-Methyl-*n*-propyl-cyclopentane	C_9H_{18}	1418.9	1419.9	+1.0
	3. Derivatives of Cyclohexane.				
8.	Cyclohexane................	C_6H_{12}	946.2	946.6	+0.4
17.	Methyl-cyclohexane..........	C_7H_{14}	1104.2	1104.4	+0.2
24.	1,1-Dimethyl-cyclohexane.....	C_8H_{16}	1256.4	1262.2	+5.8
25.	1,3-Dimethyl-cyclohexane.....	C_8H_{16}	1252.4	1262.2	+9.8[2](?)
26.	1,4-Dimethyl-cyclohexane.....	C_8H_{16}	1243.2	1262.2	+19.0(?)
30.	1,2,3-Trimethyl-cyclohexane....	C_9H_{18}	1413.3	1419.9	+6.6
31.	1,3,3-Trimethyl-cyclohexane...	C_9H_{18}	1411.5	1419.9	+8.4
37.	1-Methyl-*n*-propyl-cyclohexane	$C_{10}H_{20}$	1572.8	1577.7	+4.9
	4. Derivatives of Cycloheptane.				
18.	Cycloheptane...............	C_7H_{14}	1100.6	1104.4	+3.8
27.	Methyl-cycloheptane.........	C_8H_{16}	1260.2	1262.2	+2.0
32.	Ethyl-cycloheptane..........	C_9H_{18}	1426.1	1419.9	—6.2[2](?)

[1] The numbers correspond to those in the tables of Zubow's data published in THIS JOURNAL, 42, 1092 (1920).

[2] It seems to me that the values for the 2 dimethyl-cyclohexanes (1,3) and (1,4) are too small, and that for ethyl-cycloheptane too great. The heats of combustion for these compounds should be redetermined.

find out whether the heats of combustion of the C–C and C–H linkages remain constant or change with the constitution.

The Polymethylene Hydrocarbons.

The equation of combustion for a polymethylene hydrocarbon C_nH_{2n} is $nY + 2nX + \Sigma\Delta(x, y) + A = 0$; or, $nZ + \Sigma\Delta(x, y) + A = 0$. Whence we can compute the increment, $\Sigma\Delta(x,y) = -A - nZ$.

In Table II are given the corresponding data for the 17 polymethylene hydrocarbons, burned by P. W. Zubow.

Examining the above mentioned values of $\Sigma\Delta(x, y)$ we note that the heats of formation of the atomic linkings C–C and C–H are not constant, but depend upon the structure of the hydrocarbons. Indeed, if we should simplify the analysis by supposing x = const., or $\Sigma\Delta x = 0$, then by dividing the increments $\Sigma\Delta y$ by the number of the C–C linkings in the ring, we obtain the following comparison.

Table III.

	Formula.	$\Sigma\Delta y/n$.
Polymethylene Hydrocarbons.		
Cyclopentane	C_5H_{10}	−0.5
Cyclohexane	C_6H_{12}	+0.1
Cycloheptane	C_7H_{14}	+0.5
Methyl Derivatives.		
Methyl-cyclobutane	C_5H_{10}	−0.8
Methyl-cyclopentane	C_6H_{12}	−0.2
Methyl-cyclohexane	C_7H_{14}	+0.0
Methyl-cycloheptane	C_8H_{16}	+0.3
Dimethyl Derivatives.		
1,3-Dimethyl-cyclopentane	C_7H_{14}	+0.5
1,1-Dimethyl-cyclohexane	C_8H_{16}	+1.0
1,3-Dimethyl-cyclohexane	C_8H_{16}	+1.7 (?)
1,4-Dimethyl-cyclohexane	C_8H_{16}	+3.1 (?)
Trimethyl Derivatives.		
1,2,4-Trimethyl-cyclopentane	C_8H_{16}	+0.6
1,2,3-Trimethyl-cyclohexane	C_9H_{18}	+1.1
1,3,3-Trimethyl-cyclohexane	C_9H_{18}	+1.4
Methyl-*n*-propyl Derivatives.		
1-Methyl-3-*n*-propyl-cyclopentane	C_9H_{18}	+0.2
1-Methyl-3-*n*-propyl-cyclohexane	$C_{10}H_{20}$	+0.8

Table III is self-explanatory. We see that increasing the number of carbon atoms in the ring causes a remarkable increase in the heat of formation of the C–C linkings, and that the introduction of the methyl or the methyl and *n*-propyl groups does not affect this property.

On the other hand, the heat of formation of C–C linkings increases on the introduction of methyl groups in the polymethylene hydrocarbons.

TABLE IV.

Derivatives of Cyclopentane. Name.	$\Sigma\Delta y/n$.	Derivatives of Cyclohexane. Name.	$\Sigma\Delta y/n$.
Cyclopentane	—0.5	Cyclohexane	+0.1
Methyl-cyclopentane	—0.2	Methyl-cyclohexane	+0.0
1,3-Dimethyl-cyclopentane	+0.5	1,1-Dimethyl-cyclohexane	+1.0
1,2,4-Trimethyl-cyclopentane	+0.6	1,2,3-Trimethyl-cyclohexane	+1.1

These facts show that the constancy of the heat of formation of the C–C and C–H linkings found in the 7 hydrocarbons first chosen cannot be accepted as a general property, but on the contrary the variability in the heat of formation of these linkings must be accepted as definitely confirmed. This variation is, however, not considerable and can be discovered only by means of very exact measurements, and by burning very pure substances.

The Unsaturated Hydrocarbons.

Our equations of combustion for hydrocarbons containing unsaturated C=C linkings, do not differ from the above mentioned ones for saturated hydrocarbons and for naphthalene, but the introduction of the symbol $2y_2$ for the heat of formation of the C=C linking is more convenient for computation. The equation of combustion for an unsaturated hydrocarbon $C_nH_{2n} + m$ is then as follows

$$(n - 2)(y + w - 2z) + 2n(x + w - z - u) + 2(y_2 + w - 2z) + \Sigma\Delta(x,y) + A = 0.$$

Rearranging, we obtain,

$$n(y + w - 2z) + 2n(x + w - z - u) + \Sigma\Delta(x,y) - 2(y - y_2) + A = 0$$

or

$$nY + 2nX + \Sigma\Delta(x,y) - 2(y - y_2) = 0$$

and finally

$$2(y - y_2) - \Sigma\Delta(x,y) = A + \Sigma X + \Sigma Y.$$

The term $2(y - y_2)$ shows the difference between the heats of formation of 2 single bonds C–C and of a double one C=C.

P. W. Zubow burned a considerable number of unsaturated polymethlene hydrocarbons, and 2 aliphatic hydrocarbons. In Table V are collected the corresponding data and the computed values.

Table V shows a marked variability in the magnitude of $2(y - y_2) - \Sigma\Delta(x,y)$. The small number of aliphatic hydrocarbons investigated do not permit of any generalization. It is clear only that the heat of formation of the C=C linking is smaller than that of 2 single C–C linkings. If we accept this variability of the two terms $2(y - y_2)$ and $\Sigma\Delta(x,y)$, it is also very probable that the sum $2(y - y_2) - \Sigma\Delta(x,y)$ can increase, diminish, or remain constant, depending upon how the separate terms change.

TABLE V.

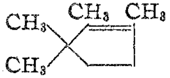
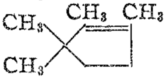
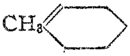
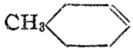
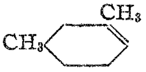
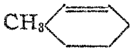
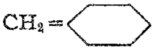
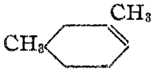
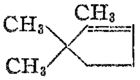
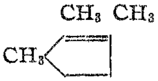
No.	Name.	Formula and Structure.	A_{gas}.	$\Sigma X + \Sigma Y$. (—)	$2(y-y_2)$ — $\Sigma\Delta(x,y)$.
		Aliphatic Hydrocarbons.			
9.	Hexylene	C_6H_{12} $C_3H_7.CH = CH.CH_3$	961.9	946.6	15.3
1.	Trimethyl-ethylene	C_5H_{10} $(CH_3)_2C = CH(CH_3)$	803.2	788.9	14.3
		Derivatives of Cyclopentene.			
20.	Trimethyl-cyclopentene	C_8H_{14} 	1206.9	1208.9	—2.0
21.	Laurolene	C_8H_{14} 	1207.0	1208.9	—1.9
		Derivatives of Cyclohexene.			
6.	Cyclohexene	C_6H_{10} 	900.9	893.4	7.5
11.	Methyl-(1)-cyclohexene-(1)	C_7H_{12} 	1053.6	1051.1	2.5
12.	Methyl-(1)-cyclohexene-(3)	C_7H_{12} 	1055.9	1051.1	4.8
13.	Methylene-cyclohexene	C_7H_{12} 	1056.6	1051.1	5.5
22.	1,3-Dimethyl-cyclohexene	C_8H_{14} 	1209.5	1208.9	0.6
		Derivative of Cycloheptene.			
15.	Cycloheptene	C_7H_{12} 	1063.0	1051.1	11.9

TABLE VI.

No.	Name.	Formula.	Structure.	$2(y-y_2)-\Sigma\Delta(x,y)$.	$\Sigma\Delta(x,y)$.	$2(y-y_2)$.
6.	Cyclohexene	C_6H_{10}		7.5	0.0	7.5
11.	Methyl-cyclohexene-1,1	C_7H_{12}		2.5	0.2	2.7
12.	Methyl-cyclohexene-1,3	C_7H_{12}		4.8	0.2	5.0
13.	Methylene-cyclohexane	C_7H_{12}		5.5	0.2	5.7
22.	1,3-Dimethyl-cyclohexene-3	C_8H_{14}		6.6	5.8	6.4
20.	Trimethyl-cyclopentene	C_8H_{14}		—2.0	3.0	1.0
21.	Laurolene	C_8H_{14}		—1.9	3.0	1.1

With regard to polymethylene hydrocarbons containing the C=C linking, the diminution of $2(y-y_2)-\Sigma\Delta(x,y)$ is very remarkable. It can depend upon 2 causes: upon the diminution of the heat of formation of the

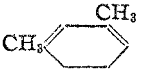
C = C linking, $2y_2$; or upon the increase of $\Sigma\Delta(x,y)$. But above we observed in the case of methyl derivatives of polymethylene hydrocarbons the increase of these numbers, then simplifying the analysis we can suppose that the increases $\Sigma\Delta(x,y)$ remain the same in the case of saturated and unsaturated hydrocarbons, C_nH_{2n} and C_nH_{2n-2}.

Accepting this supposition, Table VI gives the corresponding data.

In spite of the approximate nature of these calculations, it is clear that the heat of formation of the unsaturated C = C linking varies within very wide limits. It is also probable that $2(y - y_2)$ can in separate cases be equal to zero, when $2y = 2y_2$ (for example in naphthalene), or may differ but little from zero as in the case of laurolene and isolaurolene.

The data for hydrocarbons containing 2 unsaturated bonds could also be used for the confirmation of the above statements, if the number of hydrocarbons which have been investigated were not so few.

TABLE VII.

No.	Name.	Formula.	Structure.	$A_{gas.}$	$\frac{\Sigma X + \Sigma Y}{(-)}$	$\frac{4(y-y_2)-}{-\Sigma\Delta(xy)}$.
4.	Dihydrobenzene	C_6H_8		843.1	840.1	3.0
13.	1,3-Dimethyl-dihydrobenzene,	C_8H_{14}		1162.7	1155.6	7.1

If we accept the constancy of $\Sigma\Delta(x,y)$ in the saturated and unsaturated hydrocarbons, we obtain the following numbers for $2(y - y_2)$,

	$4(y - y_2) - \Sigma\Delta(x,y)$.	$\Sigma\Delta(x,y)$.	$2(y - y_2)$.
Dihydrobenzene[a]	3.0	0.0	1.5
1,3-Dimethyl-dihydrobenzene	7.0	5.8	6.4

[a] It must also be noted that Zubow's value 843.1 for dihydrobenzene does not agree with Stohmann's. The latter made a correction for the gaseous state of +9.9 cal., for the hydrogen scale of —0.3%, and for the true heat capacity of water of —0.1%, giving 856.4. If we accept this number, we obtain $4(y - y_2) - \Sigma\Delta(x,y) = 16.3$ or $2(y - y_2) = 8.1$.

The same results can be obtained in another way, namely, by using data corresponding not to the substances in the gaseous state, but to the liquid at 18°. If we subtract, for example, the equation of combustion of cyclohexene from the one for cyclohexane,

Cyclohexane: $6Y + 12X + \Sigma\Delta(x,y) + A_1 = 0.$

Cyclohexene: $2(y - y_2) + 7Y + 10X + \Sigma\Delta'(x,y) + A_2 = 0$

we obtain,

$$-2(y - y_2) + 2X - Y + \Sigma\Delta(x,y) - \Sigma\Delta'(x,y) + A_1 - A_2 = 0.$$

Assuming $\Sigma\Delta(x,y) = \Sigma\Delta'(x,y)$, we can compute $2(y - y_2) = A_2 - A_1 - 2X + Y$, where $X = -52.76$ cal., $Y = -52.25$ cal., $A_1 = 936.3$ cal., and $A_2 = 891.2$ cal. Finally $2(y - y_2) = 8.2$ cal. Similarly, by the first method of computation, we obtained $2(y - y_2) = 7.5$ cal.

Table VIII gives several examples of this computation.

TABLE VIII.

Compared hydrocarbons.	A_2.	A_1.	$2(y - y_2)$.	Computated by the first method.
Methyl-1-cyclohexene-1. Methyl-cyclohexane....	1040.9	1091.8	2.4	2.7
Methyl-1-cyclohexene-3.......................	1043.6	1091.8	5.1	5.0
1,1,2-Trimethyl-cyclopentene-2. 1,2,4-Trimethyl-cyclopentane.......................	1193.3	1245.4	1.2	1.0

The complete agreement of the results obtained shows that both methods can be used to evaluate $2(y - y_2)$.

Summary.

1. By analysis of the equations for the combustion of hydrocarbons we obtain the terms $(y + w - 2z) = Y$ and $(x + w - z - u) = X$, corresponding to the heats of combustion of the linkings C–C and C–H. These terms have been named the thermochemical characteristics of the C–C and C–H linkings.

2. The analysis showed the constancy of the thermochemical characteristics of the C–C and C–H linkings in the following 5 hydrocarbons, *n*-hexane, *n*-octane, *n*-decane, cyclohexane, and naphthalene. Therefore, if the molecule of naphthalene contains the double bond C=C, the heat of formation of this double bond is exactly the same as that of 2 single C–C linkings.

3. Likewise the thermochemical characteristics of C–H and C–C bonds are the same in methane and ethane as in the above mentioned 5 hydrocarbons, the computation being based on the corrected data of Thomsen.

4. The following values for the thermochemical characteristics of C–C and C–H linkages and of the homologous difference were computed and adopted, $x = -53.72$ cal., $Y = -52.25$ cal., $Z = 2X + Y = -157.77$ cal.

5. In spite of the proved constancy of the thermochemical characteristics of the C–C and C–H linkages in 5 saturated, one polymethylene and one aromatic hydrocarbons, further analysis has shown its variability in other hydrocarbons which have been examined.

6. It is definitely established, that the heat of formation of the C–C linking increases with the increase in the number of carbon atoms in the ring of polymethylene hydrocarbons, and that the heat of formation of the same linking is increased by the replacement of a hydrogen atom by a methyl or *n*-propyl group.

7. The increase in y is not considerable. In the case of polymethylene hydrocarbons it varies within the limits -0.5 to $+0.5$ in the series of cyclopentane, cyclohexane, and cycloheptane. It varies within the limits -0.8 to $+1.7$ when 1, 2, or 3 methyl groups are introduced in the molecule of the polymethylene hydrocarbons which have been studied.

8. The analysis of the data on unsaturated hydrocarbons shows a very

important difference $2\ (y - y_2)$ between the heat of formation of 2 single linkages, C–C, and of the double one, C=C. This difference, due to the change of constitution of the hydrocarbons examined, varies within the very large limits +8.0 cal. to +1.0 cal. In special cases it is possible that $2(y - y_2)$ can be equal to zero (for example, in naphthalene).

All of these computations are based on the newly corrected, very exact measurements, accumulated by only one investigator, P. W. Zubow.

The values of thermochemical characteristics can at present be considered as rough material for further mathematical elaboration of theories of valence.

WARSAW, POLAND.

[THIRTIETH CONTRIBUTION FROM THE COLOR LABORATORY, BUREAU OF CHEMISTRY, DEPARTMENT OF AGRICULTURE.]

"THE ABSORPTION SPECTRA OF THE NITRIC ESTERS OF GLYCEROL."

BY ELLIOT QUINCY ADAMS.

Received March 18, 1920.

Hepworth,[1] from a study of the absorption spectra of the nitric esters of glycerol, concludes that it is evident that:

"(1) The labile and stable forms of nitroglycerin are physical isomerides, and both forms are identical in aqueous solution.

"(2) Commercial nitroglycerin is more absorptive than pure nitroglycerin.

"(3) The order of increasing absorption in aqueous solution is β-mononitrate, α-mononitrate, α,γ-dinitrate, α,β-dinitrate, and tri-nitrate.

"(4) α-Methylin[2] dinitrate is rather more absorptive than glycerol α,β-dinitrate.

"(5) The displacement of a hydrogen atom of one of the hydroxyl groups of glycerol by a nitro group produces a much more profound change in the absorption spectrum than the displacement of one or both hydrogen atoms of the remaining hydroxyl groups.

"(6) There does not appear to be any numerical proportionality between the number of hydrogen atoms of the hydroxyl groups displaced by nitro groups and the degree of absorption for any particular dilution."

The absorption spectra are given in 3 plots of the logarithm of the relative thickness in mm. of 0.00005 N aqueous solution against the oscillation frequency.[3]

To determine whether there is any proportionality between the number of nitrate radicals and the absorption, it is necessary first to consider

---

[1] Harry Hepworth, *J. Chem. Soc.*, 115, 840–7 (1919).

[2] α-Methylin is glycerol α-methyl ether. The parts of the summary in fine print are not referred to again in this paper.

[3] In the scales of logarithms a decimal point has been omitted. It is fairly evident that the standard concentration is 1/20,000 *gram molecular*. The oscillation frequency is the reciprocal of the wave length in mm.