

THE ELECTRONIC CONCEPTION OF VALENCE AND HEATS OF COMBUSTION OF ORGANIC COMPOUNDS*

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(Preliminary Communication)¹

Introduction

The relation between the amount of heat given off by a substance upon combustion and its chemical constitution appears from its very conception to be of fundamental importance. An enormous amount of experimental work has been carried out in thermochemistry. There has also been no lack of attempts to correlate the heats of combustion of the compounds with their chemical constitution. It is, of course, beyond the scope of this preliminary paper to review, even briefly, the various works upon the subject. Sufficient to say, however, that these attempts have not led to any definite concept as to the correlation of valence notions and the heats of combustion of organic compounds. Even the most recent paper on the subject² falls short in that direction. The latter attributes different values for the carbon to carbon and carbon to hydrogen linkages. The equations he sets up are rather complicated³ and thus obscure the main issues involved.

Furthermore, the constants are applicable only to hydrocarbons and cannot be extended very readily to include other types of organic compounds, such as the alcohols, aldehydes, ketones, nitrogen and sulfur derivatives, etc.

It seemed, therefore, highly desirable to consider this problem not from the mathematical standpoint, evaluation of constants from simultaneous equations, as it has been handled before, but from the standpoint of our modern conception of valence. A statement of some of the concepts involved is given below in the form of postulates.

Statement of Postulates

Postulate 1. Heat of combustion is due to the liberation of energy in the interdisplacement⁴ or shift of electrons between atoms or molecules.

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² Swietoslawski; J. Am. Chem. Soc. **42**, 1312 (1920).

³ Swietoslawski gives the following equation of combustion of any hydrocarbon, C_nH_m :

$$(2n - \frac{m}{2})(y - w - 2z) - m(x - w - z - u) - A = 0$$

Where $(y - w - 2z)$ and $(x - w - z - u)$ represent the thermochemical characteristics of the atomic linkages C-C and C-H respectively, A denotes the molar heat of combustion of C_nH_m . In these equations w, z, u are constants while x and y are variables, depending on the structure of the hydrocarbons.

⁴ We are using this rather inaccurate expression of the "number of electrons interdisplaced" in the sense that the electrons are displaced in the direction of the oxygen atom, or atoms. Furthermore, a direct consequence of this notion is that any system in which the relative position of the electrons, with respect to carbon and oxygen, is the same as in carbon dioxide, will not furnish any heat upon combustion. Throughout the paper the word "interdisplaced" is to be assigned the above meaning.

The heat of combustion of a substance is usually defined as the heat evolved in the oxidation of unit mass of the substance. In terms of our modern conception of valence, oxidation means the removal or the displacement of electrons. It should thus be possible to correlate, at least empirically, the heat of combustion with the total number of electrons that have been displaced.

Postulate 2. The heat of combustion of a compound is a function of the total number of electrons interdisplaced, and must be an integral multiple of the heat value given by one electron.

Thus, if we ascribe the heat liberated in the combustion of methane to the displacement of the electrons between the carbon and oxygen atoms, then the molar heat of combustion of methane would be X times 8, if X is the amount of heat¹ liberated by the interdisplacement of an electron between the carbon and oxygen atoms.

Postulate 3. The net amount of energy in the form of heat liberated by the interdisplacement of an electron from an arrangement such as exists in a methane type of molecule to that of the carbon dioxide type is approximately 26.05 Kcal. per mole per electron².

On the above basis, we have only to consider two types of systems, viz., the methane and carbon dioxide systems, provided other concomitant changes are included in the constant. The constant, considered above, is characteristic only when the electrons migrate from an arrangement such as exists in the methane type of molecule to that existing in the carbon dioxide type. Therefore, if a pair of electrons in methane are displaced from the carbon, the constant will be applicable only to the six electrons that have retained their position near the carbon, for the two displaced electrons will give off a different amount of heat than the others.

It is understood, of course, that the value of X is made up of different factors. Presumably, the methane carbon in giving up an electron would absorb a certain amount of heat, Y , while the oxygen molecule in taking up an electron would liberate an amount of heat, Z . The important point, however, is the difference $Z - Y = X$, which quantity is constant if the electrons always traverse the same distance between the carbon and oxygen atoms. This value of X can, therefore, be easily obtained by dividing the experimentally determined value of the heat of combustion of methane by eight, the number of electrons displaced. Or, if we make the simple assumption that all saturated hydrocarbons contain an arrangement of electrons with respect to the carbon

¹ For those not versed in the electronic concepts the following may serve as a very simple guide in estimating the total number of electrons present. Write the ordinary structural formula, then designate all the hydrogen atoms as positive, oxygen negative; the carbon atom will then have the reverse sign of the element attached to it. The sign between two carbon atoms is of no consequence. Make any one of them positive, the other will then have the opposite sign. Count, then, the number of negative signs, multiply that number by two, for each bond corresponds to a pair of electrons, and the value thus obtained gives the total number of electrons that have to be multiplied by X in order to give the heat of combustion. (See also, for additional information, Postulate 3 and the discussion under each heading).

² The sum total of the energy in the form of heat evolved by the interdisplacement of one electron in ergs is readily obtained from the above value, i. e. $(26050 \times 4.185 \times 10^7) \div 6.06 \times 10^{23} = 1.79 \times 10^{-12}$ ergs.

atoms similar to that of methane (see Postulate 5), an assumption which is well justified by the excellent agreement of the calculated and the experimentally determined values, then the value of X could be obtained by dividing the heat of combustion of the hydrocarbon by the total number of electrons interdisplaced. In evaluating X we have used the mean of the values of the heat of combustion of normal octane, determined by T. W. Richards and Jesse and by Zubow, namely 1302.9 and divided that by 50, the number of electrons interdisplaced when octane burns to carbon dioxide and water. The value, thus obtained, of the heat supplied by the interdisplacement of one electron, namely 26.05 Kg. Cal. per mole per electron, should then be immediately applicable to the calculation of heats of combustion of all types of saturated hydrocarbons.

Postulate 4. The displacement of the electrons from the methane arrangement to that of the carbon dioxide type occurs in stages.

This postulate is merely a corollary to the Bohr conception that around each atomic center there exists a "particular" set of orbits. The postulate concerns itself only with those orbits that lie outside the "normal" valence orbit and the displacement of the electrons from the valence orbit into outside orbits. From this standpoint, therefore, when we speak of the eight electrons of methane we refer to the eight valence electrons located in the "normal" valence shell.

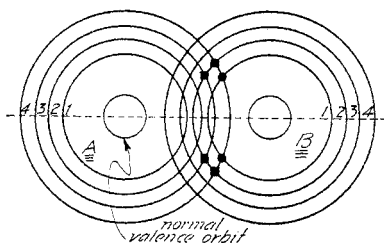


FIG. 1

The above postulate also implies that two atoms can share a pair of electrons in any of their respective orbits and that the kinetic and potential energy of the system will depend, therefore, upon the electronic structure of the molecule. To make clearer the meaning implied by this last statement let us consider the following case. Let Figures A and B represent only the orbits of two atoms, A and B, of a molecule.

The orbits intersect and the two atoms can hold a pair of electrons in common at the points of intersection of any two orbits. The position of these shared electrons with respect to their individual valence orbit will depend upon the affinity of the two atoms for electrons and the nature of the other atoms attached to A and B. Thus, if the atom B has a greater affinity for electrons than atom A, we may assume that the two electrons will be in the first orbit of B and the fourth orbit of A, as indicated by circles in the figure. Other positions are also possible, for instance, the second orbit of B and the fourth or third orbit of A, as indicated by squares on the figure. The two atoms may thus share a pair of electrons in such a way as to give rise to various degrees of polarity.

Presumably, the displacement of electrons from the valence orbit into outside orbits requires energy, while the reverse of this process liberates energy. The difference " X " (see Postulate 3) or the energy evolved in the interdis-

placement of an electron from a valence orbit that it occupies in a methane carbon to that of a valence orbit that it occupies in carbon dioxide is thus really a summation of the energy differences evolved in the interdisplacement of the electrons through the various orbits. In the case of oxygen compounds, therefore, it is very easy to note that the farther the electrons are displaced from the carbon atom, the nearer they are to the oxygen atom, i. e., the nearer to an arrangement of a carbon dioxide type, and the smaller will be the energy liberated by the combustion of the compound. It is of great interest and importance that the different stages of polarity between atoms in organic compounds, as interpreted from the data on heats of combustion, can be readily correlated with the chemical properties of the compounds.

Postulate 5. The pair of electrons held together by two carbon atoms in saturated hydrocarbons may be considered midway between their respective normal valence shells and the orbit which the electrons occupy in carbon dioxide.

The total energy which they supply upon combustion is thus the same as if we had a pair of electrons held in the valence shell of one carbon atom of the methane type. (see Postulate 4.) This is a rather plausible assumption and one that is well justified by the agreement between calculated and observed values.

In all of our calculations, we shall treat, therefore, the pair of electrons held together by two carbon atoms as supplying the same amount of heat as a pair of electrons held in the valence shell of a methane carbon atom, and will refer to it in that sense.

Choice of data. It would be profitable now to examine the application of these simple postulates and see, first how they help to predict the heats of combustion of organic compounds, and secondly, how they supply an experimental basis for the determination of the factors that influence the chemical properties of the various types of organic molecules; for instance, the theoretical basis for the difference in the chemical properties of primary, secondary, and tertiary alcohols. The present paper will be devoted entirely to the first aspect of the problem, while a second paper by the one of us (Kh.) will be devoted to a correlation of heats of combustion and chemical properties of organic compounds. In choosing the experimental data for comparison with the calculated values of the heats of combustion, we were compelled to use only the data of a few observers; since the data of different observers do not agree well at all times. Whether the difference is due to faulty manipulation, such as incomplete combustion, impurities in the sample burned, etc., is not for us to decide. We have, therefore, been led to use only the data of the following observers: T. W. Richards and collaborators, Zubow (the corrected values given by Swietoslawski¹), Stohmann and his collaborators, Roth, Fisher and Wrede, and a few others. Our calculations also refer to the amount of heat given off in Kg. Cal. per mole at constant pressure. All the data, except the results of Richards'

¹ Swietoslawski: J. Am. Chem. Soc. **42**, 1092 (1920).

investigations, and the data of Zubow, mentioned above, were taken from Landolt-Börnstein "Tabellen", 1912. The data are discussed under various heads such as saturated hydrocarbons, unsaturated hydrocarbons, primary alcohols, secondary alcohols, tertiary alcohols, acids, etc.

Saturated Hydrocarbons

The molecular heat of combustion of any saturated hydrocarbon is given by the formula: $H = 26.05 \times N$; where H is the heat of combustion in Kg. Cal. per mole of the substance; 26.05 Kg. Cal. represents the amount of heat liberated by the interdisplacement per electron per mole from an orbit of a methane type to that of a carbon dioxide type (see Postulates 2 and 3) and where N is the number of electrons in the molecule that have the same position around the carbon atoms as in methane. This exceedingly simple calculation is based upon the assumption that all saturated hydrocarbons have an arrangement of electrons with respect to the carbon atom similar to that of methane. (see Postulate 5.) This assumption is well justified by the excellent agreement between the calculated and experimentally determined values¹.

The molecular heats of combustion of eighteen saturated hydrocarbons are given in Table I. In no case, except the three compounds (15, 16, 17) does the difference between the calculated and observed values exceed 0.3 to 0.4 percent. We believe that the heats of combustion of these hydrocarbons would bear re-investigation. Swietoslawski also recommends that in the article we have referred to previously.

Comparison of our formula for saturated hydrocarbons with the formulae of Clarke² and Swietoslawski³. It is not claimed by us that better agreement between the calculated and experimentally determined values for saturated hydrocarbons is obtained by the use of our formula over that of Swietoslawski, for the agreement in both cases is well within the limits of experimental error. We find also that the compounds 15, 16, 17 (Table I), which according to our

¹ It is understood that this constant is applicable to combustions of carbon compounds in which the electrons are interdisplaced in the direction of the valence shells of oxygen atoms, but would not necessarily hold whenever other atoms are used as oxidizing agents. While the principle involved in the combustion of compounds with other oxidizing agents, say chlorine, is the same as with oxygen, a different amount of heat would presumably be evolved. It would be of great theoretical interest and significance to ascertain whether there is such a difference. The latter of course, would not invalidate any of the concepts developed, but, instead of 26.05 Kg. Cal. per electron per mole, some other constant would have to be used to designate the amount of heat evolved in the interdisplacement of one electron between the two atoms or molecules. Instead of actually determining the heats of combustion of compounds, in chlorine, one might attain the same results by the combustion of compounds containing what we ordinarily call "positive chlorine", namely chloramides, chloramines, etc., in oxygen. From the values thus obtained it would be a very simple matter to calculate the heat effect due to the interdisplacement of electrons between the carbon or nitrogen atoms and the chlorine atom acting as the oxidizing agent. This point will be discussed more thoroughly in a later paper by the one of us (Kh.).

² F. W. Clarke: Proc. Wash. Acad. Science, Vol. 5 (1903).

³ $(2n - \frac{m}{2})(y - w - 2z) - m(x - w - z - u) - A = 0$

TABLE I
Saturated Hydrocarbons

Name	Number of Electrons	Calculated	Observed	% Difference
1 N. Hexane	38	989.9	992.4 St. Kl. 989.8 Zub.	-0.3 0.0
2 N. Octane	50	1302.5	1302.7 Zub. 1303.1 Rich., Je.	0.0 0.0
3 2-Methyl heptane	50	1302.5	1304.5 Rich., Je.	-0.2
4 2,5-Dimethyl hexane	50	1302.5	1301.7 Rich., Je.	+0.1
5 3,4-Dimethyl hexane	50	1302.5	1302.3 Rich., Je.	0.0
6 3-Ethyl hexane	50	1302.5	1300.9 Rich., Je.	+0.1
7 Hexadecane	98	2552.1	2562.7 St.	-0.4
8 N. Decane	62	1615.1	1610.2 Zub.	+0.3
9 Methyl cyclobutane	30	781.5	784.2 Zub.	-0.3
10 Methyl cyclopentane	36	937.8	937.9 Zub.	0.0
11 Cycloheptane	42	1094.1	1087.3 Zub.	+0.6
12 Cyclohexane	36	937.8	936.3 Zub. 937.5 Rich., Je.	+0.2 0.0
13 Methyl cyclohexane	42	1094.1	938.8 Rich., Je.	-0.1
14 1,1-Dimethyl cyclohexane	48	1250.4	1091.8 Zub.	+0.2
15 1,3-Dimethyl cyclohexane	48	1250.4	1242.5 Zub.	+0.7
16 1,4-Dimethyl cyclohexane	48	1250.4	1238.0 Zub.	+1.0
17 1,3,3-Trimethyl cyclohexane	54	1466.7	1228.8 Zub.	+2.5
18 1,3-Dimethyl cyclopentane	42	1094.1	1394.7 Zub. 1090.7 Zub.	+0.9 +0.3

calculation show a deviation of over one percent, show the same deviation according to Swietoslawski's formula, and Swietoslawski even states that the experimental values of these compounds must be in error. What we do wish to emphasize is that the formula employed by Swietoslawski is quite complicated, containing three constants and two variables, and also that there is no definite physical meaning to the terms in the equation. Furthermore, Swietoslawski's formula can be used only in the calculation of saturated hydrocarbons but cannot be extended to include other types of molecules, ethylene and acetylene compounds, etc.

The equation of Clarke is not only subject to the same objections as the equation of Swietoslawski, but to a number of others. Thus, Clarke gives the following equation for the heat of combustion of any hydrocarbon; saturated, ethylene, and acetylene:

$$\frac{4K}{12a + 6B - c - 8n} = \text{Constant}$$

where "K" represents the heat of combustion of any hydrocarbon; "a" the number of CO₂ molecules produced; "B" the number of molecules of gaseous H₂O; "C" the number of oxygen molecules dissociated during combustion, and "n" the number of atomic unions or likings in the single molecule of the compound burned. The rigid application of this equation to ethylene or acetylene compounds leads to an absurdity—for it is necessary to assume that only one bond evolves heat, the extra bonds "being in abeyance and thermally inoperative." It is impossible to reconcile our views of unsaturated derivatives with such an assumption. Furthermore, Clarke states that the important "fundamental fact throughout is the union of an atom with an atom, the mode of combination, the structure, being an entirely subordinate affair." In accordance with our postulates it is primarily this mode of combination, or structure, which determines the heat of combustion. Clarke's formula also is entirely too laborious and on the whole it gives a poorer agreement between calculated and experimentally determined values than our formula. Furthermore, as will be shown in a later paper, all of the factors used in our formulae, in contradistinction from that of the other investigators mentioned, have a physical interpretation and can be correlated with the chemical properties of the various classes of organic molecules. The premises upon which our formula rests are thus entirely different from either that of Clarke or Swietoslawski, and the superiority of it is readily seen from application of it in the calculation of combustion of other types of organic molecules.

Unsaturated hydrocarbons. From the standpoint of the data of the heats of combustion of unsaturated derivatives the latter may be divided into two classes. First, the class of unsaturated compounds which contain an arrangement of electrons around the carbon atoms similar to the saturated hydrocarbons, i. e., share the electrons in such a manner as to produce the same heat effect (Type I). Secondly, the class of unsaturated derivatives which contain a pair of displaced electrons. To the first class belong all of the benzene hydrocarbons and conjugated systems; to the second class, the ethylene derivatives.

TABLE II
 Unsaturated hydrocarbons (Type I)

Name	Number of Electrons	Calculated	Observed	% Difference
1 Benzol	30	781.5	782.3 Roth., Au. 781.8 Rich., Ba.	-0.1 0.0
2 1,3-Dimethyl-dihydrobenzene	44	1146.2	1148.2 Zub. —	-0.2
3 Cycloheptene	40	1042.0	1040.9 Zub.	-0.7
4 Methyl-1-cyclohexene-1	40	1042.0	1040.9 Zub.	+0.1
5 Methyl-1-cyclohexene-3	40	1042.0	1042.6 Zub.	-0.1
6 Toluene	36	937.8	936.9 Rich., Ba.	+0.2
7 Ethyl benzene	42	1094.1	1089.8 Rich., Ba.	+0.4
8 Xylene (ortho)	42	1094.1	1090.2 Rich., Ba.	+0.4
9 Xylene (meta)	42	1094.1	1090.2 Rich., Ba.	+0.4
10 Xylene (para)	42	1094.1	1086.4 Rich., Ba.	+0.8
11 Mesitylene	48	1250.4	1251.9 St., Ro. 1241.7 Rich., Ba.	0.0 +0.7
12 Propyl benzene	48	1250.4	1250.0 Gen.	0.0
13 Isopropyl benzene	48	1250.4	1244.6 Rich., Ba. 1251.6 Gen.	+0.5 -0.1
14 Pseudocumene	48	1250.4	1245.5 Rich., Ba.	+0.4
15 Butyl benzene (tert.)	54	1406.7	1238.8 Rich., Ba.	+1.0
16 Naphthalene	48	1250.4	1398.4 Rich., Ba. 1236.0 Rich., Je. 1236.7 Fi., Wr.	+0.6 +1.2 +1.2
17 Pentamethyl benzol	60	1563.0	1234.2 St., Kl., La.	+1.3
18 Diphenyl	58	1510.9	1555.5 St., Kl., La.	+0.5
19 Diphenyl methane	64	1666.8	1495.0 St., La. 1656.6 St., Kl. 1660.9 Schmdl.	+1.0 +0.7 +0.4
20 1,6-Diphenyl hexadien-1,5	90	2344.5	2344.9 Roth.	0.0

TABLE II (continued)

Name	Number of Electrons	Calculated	Observed	% Difference
21 Triphenyl methane	92	2396.4	2388.7 Sehmdl.	+0.3
			2381.7 St. Kl.	+0.6
22 Triphenyl methyl	91	2370.4	2381.0 Sehmdl.	-0.5
23 Tetrahydrobenzol	34	885.7	894.0 Roth.	-0.9
			892.8 St. Kl.	-0.8
			891.2 Zub.	-0.6
24 Dihydrobenzol	32	833.6	848.6 St. La.	-2.0
			833.2 Zub.	0.0
25 2,4-Hexadien	34	885.7	886.1 Roth., Moo.	0.0
26 Laurolene	46	1198.3	1194.5 Roth.	+0.4
27 1-Methyl-3-methane cyclohexene-1	44	1146.2	1150.8 Roth.	-0.4
28 1,5-Dimethyl-3-methene cyclohexene-1	50	1302.5	1299.1 Roth., Peters	+0.3
29 1, Ethyl-5-dimethyl cyclohexene-1	50	1510.9	1506.7 Roth.	+0.3
30 Isobutenyl cyclohexene-1	56	1458.8	1463.5 Roth., Ell.	-0.3
31 1,5-Dimethyl-3-ethene cyclohexene-1	56	1458.8	1457.4 A., R., E.	+0.1
32 1,5-Dimethyl-3-isopropene-cyclohexene-1	62	1615.1	1610.9 Roth., Peters	+0.3

TABLE IIa

Unsaturated hydrocarbons (Type II)

1 Trimethyl ethylene	30	794.5	796.0 Zub.	-0.2
2 Hexylene	36	950.8	952.6 Zub.	-0.2
3 Camphene	56	1471.8	1469.4 A., R., E.	+0.2
4 Methylene cyclohexene	40	1055.0	1052.0 Roth.	+0.3
5 Ethylene cyclohexene	46	1211.2	1209.2 Roth.	+0.2
6 Sylvestren	56	1471.8	1466.5 A., R., E.	+0.4

The formula used in the calculation of the heats of combustion of unsaturated derivatives of the first type is therefore, the same as in the saturated hydrocarbons, namely $H = 26.05 \times N$. Table II gives the values for thirty-two unsaturated hydrocarbons of this type. On the whole the agreement is very striking and satisfactory¹.

The heats of combustion of unsaturated derivatives of the second type indicate that they contain a pair of electrons displaced from the carbon atom or atoms. Reference to the diagram of Postulate 4 will help to make this clear. For, in these molecules, two carbon atoms share one pair of electrons in the same manner as two carbon atoms of saturated hydrocarbons, but the second pair of electrons is removed from both of the nuclei. Thus, it can be located in shell 3 of atom A and shell 4 of atom B. The molecule will thus have an electric moment in that part of the molecule. Furthermore, since energy is required to move electrons from the normal valence shell of the carbon atom to shells outside the valence shell, that amount of energy should be considered in the calculation of the ethylene derivatives. The formula for the calculation of ethylene derivatives is therefore $H = 26.05 \times N + A$, where A is the amount of energy necessary to move a pair of electrons from the normal valence shell to the position they occupy in ethylene derivatives. This value of A we find to be a fraction of the constant employed: namely, 13 Kg. Cal. per mole. The equation for ethylene derivatives therefore, becomes: $H = 26.05 \times N + 13$. The values, for seven unsaturated hydrocarbons of Type II, are given in Table II (a). The agreement between the calculated and experimentally determined values is most gratifying.

Primary Alcohols, Ethers, Esters

We find, from the close agreement of the predicted and calculated values for the saturated and unsaturated hydrocarbons, that the application of the notion of the non-polar conception of valence to the calculation of heats of combustion is a very useful one. However, unless it can be extended to include all types of compounds, it would hardly be very advantageous over other formulae. In the case of alcohols, we run into considerable difficulty if the completely non-polar structure is used. However, if we make use of the concepts developed in postulate 4, namely, that when two atoms share a pair of electrons in common, the position of the electrons in the respective orbits of the atoms depends upon the affinity of the two atoms for electrons, the calculation is simplified once more².

It is quite evident that, owing to the great affinity of oxygen atoms for electrons, the pair of electrons binding the carbon and oxygen atoms in primary

¹ It is most significant that for most benzene hydrocarbons the calculated value is somewhat higher than the experimentally determined value. This is due to a diminution of the energy of the system due to the benzene nucleus. Once this is taken into account in the calculation of the heat of combustion the agreement is then even more striking. It is omitted here in order to avoid confusion and will be discussed in detail in a later publication.

² It is necessary to assume on this basis that intramolecular oxidation-reduction reactions are accompanied by the evolution of heat.

alcohols will be in the inner shell of the oxygen atom (close to the normal valence shell) and in the outer shell of the carbon atom. The energy liberated by the combustion of a molecule of this type should, therefore, be smaller than that for the hydrocarbons, which is in accord with the experimental facts. However, the two displaced electrons in the alcohols do not occupy the same position with respect to the carbon and oxygen atoms as they occupy in carbon dioxide—in order to obtain that condition they have to be displaced still further from the carbon atom and thereby put nearer to the oxygen atom. This process liberates heat and the amount of heat liberated should be the same for all primary alcohols, unless the other groups present in the molecule affect the position of these electrons. Take, for instance, the case of methyl alcohol. The difference between it and methane is that two of the electrons have been displaced in the direction of the oxygen atom. If these two displaced electrons occupy, with respect to carbon and oxygen atoms, the same position as in carbon dioxide the heat of combustion of methyl alcohol should be

$$6 \times 26.05 = 156.3 \text{ Kg. Cal. per mole}$$

The value obtained experimentally is 170 Kg. Cal. per mole. This shows that the two electrons binding the oxygen and carbon atoms do not occupy the same position as in carbon dioxide and that the amount of energy, in the form of heat, which they liberate in attaining that position is equal to about 13 Kg. Cal. per mole. This should, therefore, be the correction factor for all primary alcohols and the heat of combustion of any primary alcohol is given by the expression $H = 26.05 \times N + 13$. We find the same formula to hold for aliphatic ethers and esters, of course, in the case of the ethers the constant enters twice, for in these molecules there are two such pairs of displaced electrons.

In the case of the aromatic ethers the effect of the benzene ring on the position of the electron must be considered. The concepts involved, however, are too complicated to be taken up in this preliminary communication. A very good agreement with the experimentally determined values is obtained though by the use of the formula given for primary alcohols. The justification for the use of this formula can be readily inferred from the heats of combustion of phenols. The results indicate (at any rate for the purpose of calculation of heats of combustion) that the position of the shared electrons between the carbon and oxygen atoms in phenols is very nearly the same as in carbon dioxide¹.

Tables III, IV and V give the values of ten primary alcohols, fifteen others, and twenty-five esters calculated on this basis. It will be noted that the agreement is very close with the values actually obtained, except in the case of unsaturated derivatives of the ethylene series. They are given again in Table IVa, with the correction allowed for in the case of unsaturated derivatives (see Table IIa); namely, thirteen is added to the value calculated on the non-polar basis.

¹ See discussion under tertiary alcohols.

TABLE III
Primary Alcohols

Name	Number of Electrons	Calculated	Observed	% Difference
1 Methyl alcohol	6	169.3	170.61 Rich., Da.	-0.8
2 Ethyl alcohol	12	325.6	327.04 Rich., Da.	-0.4
3 Propyl alcohol	18	481.7	485.8 Rich., Da.	-0.1
4 Butyl alcohol	24	638.0	638.3 Rich., Da.	-0.1
5 Isobutyl alcohol	24	638.0	637.1 Rich., Da.	+0.2
6 Heptyl alcohol	42	1107.1	1104.0 Zub.	+0.3
7 Benzyl alcohol	34	898.7	895.8 St., Ro.	+0.4
			895.2 St., Kl., La.	+0.4
			892.3 Schmdl.	+0.8
8 Cyclobutyl carbinol	28	742.4	747.8 Zub.	-0.8
9 Cyclohexyl carbinol	40	1055.2	1047.2 Zub.	+0.8
10 Saligenin	32	846.6	846.4 B. Ric.	0.0

TABLE IV
Aromatic Ethers

1 Anisol	34	898.7	906.0 St., La.	-0.9
2 Phenetole	40	1055.0	901.8 St., Ro.	-0.4
3 M-Cresol methyl ether	40	1055.0	1057.9 St. Ro., H.	-0.2
4 Hydroquinone dimethyl ether	38	1016.0	1058.0 St., Ro., H.	-0.3
5 Resorcin dimethyl ether	38	1016.0	1015.7 " " "	0.0
6 Phenyl propyl ether	46	1212.3	1023.6 " " "	-0.7
			1214.3 " " "	-0.2

TABLE IV (continued)

Name	Aromatic Ethers		% Difference
	Number of Electrons	Calculated	
7 p-Cresol ethyl ether	46	1212.3	Observed 1214.0 St., Ro., H.
8 m-Xylenyl methyl ether	46	1212.3	" " " "
9 p-Xylenyl ethyl ether	52	1367.6	" " " "
10 Thymol methyl ether	58	1523.9	" " " "
11 Methyl chavicol*	50	1315.5	1335.9 St., La.
12 Anethole*	50	1315.5	1325.1 St., La.
13 α -Ethoxy styrol	50	1315.5	1316.2 Roth
14 Eugenol*	48	1263.4	1287.8 St., La.
15 Isoeugenol*	48	1263.4	1278.8 St., La.

TABLE IVa

Aromatic Ethers		% Difference
1 Methyl chavicol	50	1328.5
2 Anethole	50	1328.5
3 Eugenol	48	1276.4
4 Iso-eugenol	48	1276.4
		1335.9 St., La.
		1325.1 St., La.
		1287.8 St., La.
		1278.8 St., La.

TABLE V

Esters		% Difference
1 Methyl iso-butyrate	26	690.3
2 Dimethyl acrylic methyl ester*	30	794.5
3 Methyl benzoate	36	950.8
4 Methyl p-oxybenzoate	34	898.7
		693.4 Rich., Jc.
		805.2 Roth
		944.4 St., Ro., H.
		896.3 St., Kl., La.

TABLE V (continued)

Name	Number of Electrons	Esters		% Difference
		Calculated	Observed	
5 Methyl salicylate	34	898.7	899.2 St., Ro., H.	-0.2
6 Methyl anisate	40	1068	1069.8 St., Kl., I.a.	-0.2
7 Methyl ester cyclo-hexenyl-acetic acid	46	1211.3	1211.3 Roth., Ell.	0.0
8 Cyclohexylidene acetic methyl ester*	46	1224.3	1217.7 Roth., Ell.	+0.5
9 Methyl cinnamate	46	1211.3	1214.2 St., Kl., La.	-0.3
10 Methyl pinonate	56	1481.8	1478.8 Roth., O.	+0.2
11 Dimethyl carbonate	12	338.6	340.8 Zub.	-0.7
12 Diethyl carbonate	24	651.2	647.9 Zub.	+0.5
13 Ethyl sorbate*	38	1002.9	1013.0 Roth.	-1.0
14 Ethyl benzoate	42	1107.0	1099.8 St., Ro., H.	+0.6
15 Ethyl salicylate	40	1055.0	1052.3 St., Ro., H.	+0.3
16 Ethyl p-oxybenzoate	40	1055.0	1043.0 St., R., H.	+1.2
17 Cyclo hexenyl acetic ethyl ester	52	1367.6	1361.7 Roth.	+0.4
18 Propyl benzoate	48	1263.4	1255.8 St., Ro., H.	+0.6
19 Propyl p-oxybenzoate	46	1211.3	1201.8 St., Ro., H.	+0.8
20 Propyl salicylate	46	1211.3	1206.9 St., Ro., H.	+0.4
21 Iso butyl benzoate	54	1419.7	1412.8 St., Ro., H.	+0.5
22 Iso butyl salicylate	52	1367.6	1366.9 St., Ro., H.	+0.1
23 Amyl benzoate	60	1576.0	1571.1 St., Ro., H.	+0.3

Secondary and Tertiary Alcohols, Phenols, and Polyhydroxy Alcohols

On the basis of the same concept as that developed for primary alcohols, we estimate that the two electrons binding the carbon and oxygen atoms, in secondary alcohols, are not completely displaced in the direction of the oxygen atom, i. e., they do not occupy the same positive relation to the carbon and oxygen atoms as in carbon dioxide. In the combustion of the compound and the displacement of this pair of electrons in the direction of the oxygen atom a certain amount of heat is evolved. We find that amount to be equal to 6.5 Kg. Cal. per mole. The heat of combustion of secondary alcohols is, therefore, given by the expression $H = 26.05 \times N + 6.5$.

It is self-evident that for polyhydroxy alcohols a combination of the formula for primary and secondary alcohols should be used, namely

$$H = 26.05 \times N + 13a + 6.5b$$

where a and b are respectively the number of primary and secondary alcohol groups in the molecule.

In the case of tertiary alcohols and phenols the pair of electrons holding the carbon and oxygen atoms may be assumed, for the purpose of calculation of heats of combustion, to occupy the same relative position with respect to carbon and oxygen atoms as in carbon dioxide. This pair of electrons, therefore, does not supply any heat upon combustion. The authors appreciate the fact that this statement is not rigidly correct, since the data warrant such an assertion only to the extent that the displacement of the electrons toward the oxygen atom in tertiary alcohols is much more complete than in the case of primary or secondary alcohols. The results obtained, however, on the basis of a complete transfer of the electrons are quite satisfactory, although they do not preclude the possibility of a slight non-polarity (say three Kg. Cal. per mole). We have not made that correction, however, for the data in most cases are not sufficiently accurate, although we believe it should be applied. The heat of combustion of any tertiary alcohol or phenol¹ is, therefore, given by the expression (1) $H = 26.05 \times N$, or (2) $H = 26.05 \times N + 3.5$. In our calculations we made use of formula 1.

The values for a number of compounds are given in Tables VI, VII and VIII. The agreement between the calculated and observed values, in the case of the 35 compounds calculated, is good. In only a few cases does the error exceed five-tenths of one percent².

Ketones

In the case of ketones we find that the four electrons holding the carbon and oxygen atoms do not occupy relatively the same position as in carbon diox-

¹ See footnote, p. 629. We might mention also that the numerical values obtained by the introduction of the new concept into the formula are better than those given in Table VII. As stated before, these points will be elaborated upon in a latter paper by Kharasch.

² Where the difference is rather large, one percent or so, it is evident from the structure of the compound that considerable difficulty would be experienced in obtaining it in pure condition.

TABLE Va

Name	Number of Electrons	Esters Calculated	Observed	% Difference
1 Dimethyl acrylic methyl ester	30	807.5	805.2 Roth	+0.3
2 Cyclohexylidene acetic methyl ester	46	1224.3	1217.7 Roth	+0.6

TABLE VI

Secondary Alcohols				
1 Pinacoline alcohol	36	943.8	938.6 Zub.	+0.6
2 Diallyl carbinol*	38	995.9	1028.0 Zub.	-3.3
3 Cycloheptanol	40	1048.5	1050.2 Zub.	-0.2
4 β -methyl cyclopentanol	34	891.7	887.6 Zub.	+0.5
5 Cyclohexanol	34	891.7	889.8 Zub.	+0.2
6 1,3-Dimethyl cyclohexanol-2	46	1204.3	1196.0 Zub.	+0.7

TABLE VII

Tertiary Alcohols and Phenols				
1 Trimethyl carbinol	24	625	629.3 Zub.	-0.7
2 Dimethyl ethyl carbinol	30	781.5	784.6 Zub.	-0.4
3 Allyl methyl ethyl carbinol*	40	1042.0	1050.1 Zub.	-0.5
4 Triethyl carbinol	40	1094.1	1080.0 Zub.	+1.4
5 1,3-Dimethyl cyclohexanol (3)	46	1198.3	1192.5 Zub.	+0.5
6 Ethyl dipropyl carbinol	54	1406.7	1386.0 Zub.	+1.4
7 Phenol	28	729.4	732.9 St., La.	-0.5

TABLE VII (continued)
Tertiary Alcohols and Phenols

Name	Number of Electrons	Calculated	Observed	% Difference
8 Catechol	26	677.3	685.5 St., La.	-1.3
9 Resorcinol	26	677.3	683.7 St., La.	-1.0
10 Hydroquinone	26	677.3	683.6 St., La.	-1.0
11 Phloroglucinol	24	625.2	617.9 St., La.	+1.2
12 o-Cresol	34	885.7	883.5 St., Ro., H.	+0.3
13 m-Cresol	34	885.7	881.4 St., Ro., H.	+0.5
14 p-Cresol	34	885.7	883.4 St., Ro., H.	+0.3
15 o-Xylenol	40	1042.0	1036.1 St., Ro., H.	+0.6
16 m-Xylenol	40	1042.0	1038.4 St., Ro., H.	+0.4
17 p-Xylenol	40	1042.0	1036.3 St., Ro., H.	+0.6
18 Pseudocumenol	46	1198.3	1192.4 St., Ro., H.	+0.5
19 Thymol	52	1354.6	1354.1 St., Ro., H.	0.0
20 Carvacrol	52	1354.6	1355.8 St., Ro., H.	-0.1
21 Diphenyl carbinol	62	1615.1	1616.9 St., La., Kl.	-0.1
			1614.8 Schmdl.	+0.1
22 Triphenyl carbinol	90	2344.5	2343.0 St., Kl., La.	0.0
TABLE VIa				
1 Diallyl carbinol	38	1021.9	1028.0 Zub.	-0.6
TABLE VIIa				
1 Allyl methyl ethyl carbinol	40	1055.0	1050.1 Zub.	+0.5

TABLE VIII
Poly Hydroxy Alcohols

Name	Number of Electrons	Calculated	Observed	% Difference
1 Glycerine	14	396.7	397.3 St., La.	-0.2
2 Erythrit	18	508.9	504.8 St., La.	+0.4
3 Pentaerythrit	24	656.2	661.9 St., La.	-0.9
4 Arabit	22	617.1	612.4 St., La.	+0.8
5 Mannit-d	26	727.3	728.3 St., La.	-0.2
6 Duleit	26	727.3	729.9 B., Vi.	-0.3
			724.4 St., La.	-0.5
7 Perseit	30	837.5	836.6 St., La.	+0.1

TABLE IX

	Ketones	
1 Methyl ethyl ketone	22	579.1
2 Diethyl ketone	28	735.4
3 Methyl propyl ketone	28	735.4
4 Methyl isopropyl ketone	28	735.4
5 Pinacolone	34	891.7
6 Methyl butyl ketone	34	891.7
		582.3 Zub.
		735.6 Zub.
		734.6 Zub.
		733.9 Zub.
		891.8 Zub.
		895.2 Zub.
		-0.6
		0.0
		+0.1
		+0.2
		0.0
		-0.4

TABLE IX (continued)

Name	Number of Electrons	Ketones		% Difference
		Calculated	Observed	
7 Ethyl allyl ketone*	32	839.6	858.1 Roth.	
8 Allyl acetone*	32	839.6	857.7 Roth.	
9 Dipropyl ketone	40	1048.0	1050.5 Zub.	-0.2
10 Methyl hexyl ketone	46	1204.3	1205.1 Zub.	-0.1
11 Diallyl acetone*	48	1256.4	1282.3 Roth., Moo.	
12 Acetyl trimethylene*	26	683.3	691.0 Zub.	
13 β -methyl cyclo pentanone	32	839.6	833.4 Roth., Moo.	+0.8
14 Acetyl cyclo butane	32	839.6	856.8 Roth., Moo.	+1.9
15 β -methyl cyclo hexanone	38	995.9	994.8 Zub.	+0.1
16 Cyclo heptenone	38	995.9	996.7 Zub.	+0.1
17 Ethyl cyclo pentenone	38	995.9	990.4 Zub.	+0.5
18 1,3-Dimethyl cyclo pentenone	38	995.9	989.8 Zub.	+0.6
19 1,3-Dimethyl cyclo hexenone	42	1100.2	1102.2 Zub.	-0.2
20 1,3-Dimethyl cyclo hexanone	44	1152.7	1129.8 Zub.	+2.0
21 1,1,5-Trimethyl-cyclo hexanone	48	1256.4	1248.4 Zub.	+0.7

TABLE IXa

1 Ethyl allyl ketone	32	852.6	858.1 Roth.	-0.7
2 Allyl acetone	32	852.6	857.7 Roth.	-0.6
3 Diallyl acetone	48	1282.4	1282.3 Roth.	0.0
4 Acetyl trimethylene	26	696.3	691.0 Zub.	+0.8

ide. The amount of heat liberated before that condition is attained is equal to 6.5 Kg. Cal. per mole. Whether this heat value is due to one or to two pairs of displaced electrons cannot be ascertained from the heat of combustion. The behaviour of ketones from a chemical standpoint, i. e., absorption reactions of different ketones, etc., throws considerable light upon this subject (See particularly postulates 4 and 5) and will be dealt with in a later paper.

The heat of combustion of ketones is, therefore, given by the formula

$$H = 26.05 \times N + 6.5$$

the same expression as used in the case of secondary alcohols.

The agreement is excellent in eighteen of the twenty-one ketones given. Those marked with an asterisk, namely, ethylene derivatives, are also given in Table IXa, with the usual correction for ethylene derivatives. A number of ketones given in the "Tabellen" have been omitted here, not because they do not agree with the calculated values, but merely on account of their complexity. It seemed to us that the chances of obtaining compounds in pure condition are greater for the simpler compounds than the very complex ones, and for the purpose of checking up on the hypothesis advanced, we have selected compounds with that end in view.

Acids

The heat of combustion of acids is given by the expression $H = 26.05 \times N$. This formula implies that the electrons binding the carbon and oxygen atoms in the carboxyl group have an arrangement of electrons similar to that existing in carbon dioxide and, therefore, do not supply any heat upon combustion. (See however, the discussion under tertiary alcohols.) It will also be noticed that in the case of the acids that are liquids the percent difference is negative, i. e., the calculated values are slightly lower than the experimentally determined values, while in the case of the acids that are solids the calculated values are higher than the experimentally determined values. The reason for this is fairly obvious: the constant used in the formula refers to the heat of combustion in the liquid state, and to obtain the heat of combustion of a solid the heat of fusion of the compound should be subtracted from the value calculated according to the formula. Unfortunately, the heats of fusion of most of the compounds given in the tables are unknown and thus, it is impossible to apply the correction. However, it has been noticed in the case of the acids whose heats of fusion have been determined experimentally, that the values of the heats of fusion of these compounds are approximately one half percent of their total heat of combustion. Once this fact is taken into account the already striking agreement between the calculated and experimentally determined values is brought out more conspicuously.

Some important relationships between cis and trans isomers from the standpoint of their energy values are also apparent. Thus, we find that the cis isomer has a heat of combustion larger than the trans isomer by 6.5 Kg. Cal. per mole. This important phase of cis-trans isomerism from the stand-

TABLE X
Acids

Name	Number of Electrons	Calculated	Observed	% Difference
1 Propionic	14	364.7	367.6 St., Kl., Ia., Off.	-1.0
2 Butyric	20	521.0	525.8 St., Kl., Ia., Off.	-0.8
3 N-valeric	26	677.3	682.3 St., Kl., Ia., Off.	-0.8
4 Caproic	32	837.6	839.2 Fi., Wr.	-0.3
5 Isobutyl acetic	32	833.6	838.2 St., Kl., Ia., Off.	-0.2
6 Diethyl acetic	32	833.6	838.2 St., Kl., Ia.	-0.5
7 Ethyl propyl acetic	38	989.9	838.2 St., Kl., Ia.	-0.5
8 Dipropyl acetic	44	1146.2	995.5 St., Kl., Ia.	-0.7
9 Lauric	68	1771.4	1152.8 St., Kl., Ia.	-0.6
10 Palmitic	92	2397.1	1773.5 St., La.	-0.1
11 Glycollic	6	169.3	2400.8 St., Kl.	-0.2
12 Crotonic*	18	468.9	166.8 St., Kl.	+1.5
13 Tiglic*	24	625.2	479.2 St., Kl.	
14 Angelic*	24	625.2	478.2 St., Kl.	
15 Allyl acetic*	24	625.2	627.0 St., Kl.	
16 Laevulinic	22	573.1	635.2 St., Kl.	
17 Hydrosorbic acid*	30	782.5	642.3 Roth., Ell.	
18 Sorbic*	28	729.4	577.4 B., Theh.	
19 Geranic*	52	1365.6	796.2 Fi., Wr.	-0.7
20 Oxalic	2	52.1	743.7 St., La.	
			744.8 Fi., Wr.	
			1380.5 Roth., Moo.	
			60.2 St., Kl., Ia.	

TABLE X (continued)

Name	Number of Electrons	Acids		% Difference
		Calculated	Observed	
21 Malonic	8	208.4	207.4 St., Kl., La.	+0.5
22 Succinic	14	364.7	357.0 St., Kl., La.	+2.0
23 Methyl malonic	14	364.7	362.6 St., Kl., La.	+0.7
24 Glutaric	20	521.0	515.2 St., Kl.	+1.1
25 Ethyl malonic	20	521.0	518.2 St., Kl., La.	+0.6
26 Diethyl malonic	32	833.6	833.4 St., Kl., La., Off.	0.0
27 Pimelic	32	833.6	823.1 St., Kl., La.	+1.2
			828.3 St., Kl.	+0.6
28 Citric	18	474.9	475.0 St., Kl., La.	0.0
29 Ethyl propyl malonic	38	989.9	989.5 St., Kl., La.	0.0
30 Azelaic	44	1146.2	1142.0 St., Kl., La.	+0.4
31 Dipropyl malonic	44	1146.2	1146.9 St., Kl., La., Off.	0.0
32 Heptyl malonic	50	1302.5	1303.7 St., Kl., La., Off.	-0.1
33 Fumaric*	12	312.6	320.3 St., Kl., La.	
			319.7 Roth.	
34 Maleic*	12	312.6	326.4 St., Kl., La.	
35 Itaconic*	18	463.9	476.1 St., Kl.	
36 Citraconic*	18	468.9	487.9 St., Kl.	
37 Mesaconic*	18	468.9	477.4 St., Kl.	
38 α,β -hydromuconic	24	625.2	629.4 St., Kl.	-0.7
39 β,γ -Hydromuconic	24	625.2	629.7 St., Kl.	-0.7
40 Allyl malonic*	24	625.2	638.4 St., Kl.	
41 Aconitic	18	468.9	475.6 St., Kl., La., Off.	-1.8
42 Capric (act)	32	833.6	831.0 Zub.	+0.3

TABLE X (continued)

Acids				% Difference	
Name	Number of Electrons	Calculated	Observed		
43 Cyclohexane-carbon acid	36	937.8	934.0 Zub.	+0.3	
44 Hexahydro-m-tolyl acid	42	1094.1	1086.2 Zub.	+0.8	
45 Cyclooctane acid (act)	42	1094.1	1089.2 Zub.	+0.5	
46 Cycloheptane acid	42	1094.1	1087.9 Zub.	+0.6	
47 Trimethylene-carbon acid*	18	468.9	483.7 Zub.		
48 Cyclobutane carbon acid*	24	625.2	639.2 Zub.		
TABLE Xa					
1 Crotonic	18	481.9	479.2 St., Kl.	+0.6	
2 Angelic	24	638.2	478.2 St., Kl.	+0.7	
3 Allyl acetic	24	638.2	635.4 " "	+0.5	
4 Hydrosorbic	30	795.5	642.3 Roth., Ell.	-0.7	
5 Fumaric	12	325.6	796.2 Fi., Wr.	-0.1	
6 Maleic	12	325.6	319.7 Roth.	+1.8	
7 Itaconic	18	481.9	320.3 St., Kl., Ia.	+1.6	
8 Citraconic	18	481.9	326.4 St., Kl., Ia.	-0.3	
9 Mesaconic	18	481.9	476.1 St., Kl.	+1.2	
10 Allyl malonic	24	638.2	487.9 St., Kl.	-1.0	
11 Trimethylene carbon acid	18	481.9	477.4 St., Kl.	+1.0	
12 Cyclobutane acid	24	638.2	638.4 St., Kl., Ia.	0.0	
			483.7 Zub.	-0.4	
			639.2 Zub.	-0.2	

point of the concept developed in postulate 4 will be dealt with in a later paper by Kharasch. In this preliminary communication no stress has been put upon that point in order not to complicate unduly the fundamental concepts developed.

Nitro Compounds

The close relationship between nitro compounds and amines, and the fact that the latter can be made from the former, prompts us to take up first the discussion of the nitro compounds. We have tacitly assumed, in all of our previous calculations, that the electrons holding atoms together can occupy any intermediate position between a "methane" arrangement of the electrons around the carbon to that of a "carbon dioxide" type. It is self-evident, that when two carbon atoms are concerned, the position of the two binding or valence electrons is immaterial from the standpoint of the total energy of the system. The heat of combustion of the system is the same irrespective of the position of the two electrons¹. However, if an oxygen atom is introduced into the molecule then the position of the two electrons is of vital importance. If they are in the same position relative to the carbon atom as they were in the hydrocarbon, then we would expect that the heat of combustion of this system would be the same as that of the hydrocarbon. On the other hand, if they are displaced from that mean position in the direction of the oxygen atom—then the energy of the system should be lower. Thus, the heats of combustion of tertiary alcohols were found to be less than those of the corresponding hydrocarbons by an amount of heat corresponding to almost the complete displacement of two electrons from the carbon to the oxygen atom. In a sense, therefore, these compounds may be considered polar in that part of the molecule. In the case of primary alcohols, however, the electrons are not completely displaced in the direction of the oxygen atom. They can still give off 13 Kg. Cal. per mole before the displacement may be considered complete.

The considerations developed above are particularly instructive when one considers the case of nitro compounds. The nitrogen atom in these compounds does not evolve any heat upon combustion and we could omit it entirely from our calculations, if it were not for two factors involved: first, that the nitro group is attached to a carbon atom, and secondly, the fact that the nitro group acts as an oxidizing agent. The question then arises whether, when we treat, say, hexane with nitric acid to form nitro hexane, the two electrons, that held the hydrogen atom to the carbon atom have been displaced in the direction of the nitrogen atom. If they have been displaced in the nitration reaction a certain amount of heat must have been evolved and the heat of combustion of nitro hexane should be smaller than that of hexane. The experimental data point quite conclusively to the fact that such is the case, if we make the assumption that the sum total of heat evolved is the same when an electron is displaced from a carbon atom into the direction of the inner shells of an oxygen atom or a nitric acid nitrogen atom. This assumption is probably quantita-

¹ See, however, footnote, p. 629.

tively incorrect, but perhaps within the limit of the error of the determination of heats of combustion of organic compounds. Once we accept this notion, however, our calculations indicate that the pair of electrons holding the carbon and nitrogen atoms together are not displaced completely in the direction of the nitrogen atom. Before they assume, with respect to the carbon atom, a position similar to the one they occupy in carbon dioxide, 13 additional Kg. Cal. per mole are evolved¹. The heat of combustion of nitro compounds is, therefore, given by the formula: $H = 26.05 \times N + 13$.

The agreement of the calculated and experimentally determined values, although varying considerably is still sufficiently close to bear out the fundamental relationship involved. It should also be borne in mind that the constant, 26.05 is applicable to the combustion of liquid compounds, and that the heat of combustion of a solid would be smaller than that of the liquid by an amount corresponding to the heat of fusion. The only values of the heats of fusion of nitro compounds given in the literature are for m-dinitrobenzene and o-nitrophenol and in the case of m-dinitrobenzene once this is taken into account the difference instead of being 0.8% is only 0.1% while the o-nitrophenol is still within 0.3% of the calculated value. The correction should be applied and it is gratifying to note that our calculated values are larger than the experimentally determined ones. Once the heats of fusion of these compounds become available a still better check of the calculated values will then be possible. We also had to use the data of other observers than the ones mentioned in the introduction. A closer scrutiny of the data will be given in a subsequent paper with the correction that should be applied to the results of some investigators².

Primary Amines

The calculation of the heats of combustion of amines presents a very difficult problem from the quantitative standpoint of the heat contributed by the different groups in the molecule. The problem has two distinct features. In the first place, it is important to know the position of the pair of electrons binding the carbon and "NH₂" group nitrogen; secondly, since the "NH₂" group nitrogen is converted into nitrogen gas, it must have been oxidized by the oxygen, and thus it contributes a certain amount of heat. Of course, it is understood that a number of other factors enter into the mechanism, but it was thought well worth while not to burden this first publication with them.

¹ From this standpoint, the formulae employed by various organic chemists for nitro compounds, viz: $\begin{array}{c} \text{H} \\ | \\ \text{H}-\text{C}- \\ | \\ \text{H} \end{array} + \text{N} \begin{array}{c} \text{O} \\ \uparrow \\ \text{O} \end{array}$ is in error. The pair of binding electrons are nearer to the

nitrogen atom than to the carbon atom, making the nitrogen almost negative and the carbon almost positive. (It all depends upon whether CO₂ is considered a polar or non-polar compound). This seems to be quite a plausible structure, since we would expect that such a powerful oxidizing agent as a nitric acid nitrogen would be capable of oxidizing the carbon atom. The reduction of the nitro compounds to the corresponding amines, does not then involve any additional postulate such as would be required, if the nitrogen were assumed to contain five positive charges in the nitro compounds.

² The data for the ketoximes will be discussed in the next paper. We might mention however, that the data throw considerable light on the electronic structure of these compounds.

TABLE XI
Nitro Compounds

Name	Number of Electrons	Calculated	Observed	% Difference
1 Nitro methane	6	169.3	169.6 Swi.	+0.2
2 Nitro ethane	12	325.6	170.0 B., Ma.	-0.5
3 Nitro propane	18	481.9	322.5 B., Ma.	+1.0
4 o-Dinitrobenzene	26	703.4	478.3 Swi.	+0.7
5 m-Dinitrobenzene	26	703.4	703.7 B., Ma.	0.0
6 p-Dinitrobenzene	26	703.4	697.2 B., Ma.	+0.8
7 Sym. trinitrobenzene	24	664.2	695.6 B., Ma.	+1.1
8 Unsym. trinitrobenzene	24	664.2	664.0 B., Ma.	0.0
9 o-Nitrophenol	26	690.3	678.6 B., Ma.	-2.0
10 m-Nitrophenol	26	690.3	688.4 Mat. Del.	+0.3
11 p-Nitrophenol	26	690.3	688.4 Swartz	+0.3
12 Nitrobenzene	28	742.4	689.3 Mat., Del.	+0.2
13 m-Nitro toluene	34	898.7	734.7 Swartz	+1.0
14 o-Nitro ethoxy benzene	38	1016.0	889.5 Swartz	+1.0
15 p-Nitro ethoxy benzene	38	1016.0	1017.5 Swartz	+0.1
16 m-Nitro ethoxy benzene	38	1016.0	1006.0 Swartz	+1.0
			1009.0 Swartz	+0.7

It has been our aim throughout to introduce as few assumptions as possible, and it seemed logical, therefore, to assume that the same amount of heat is evolved when an electron migrates from an "NH₂" nitrogen atom as from a methane carbon atom. This may be an erroneous assumption from a quantitative standpoint, and it probably is so, but perhaps within the limits of experimental error of the determination of heats of combustion. The second assumption is that the pair of electrons binding the carbon and "NH₂" group nitrogen has retained the same position it held in nitro compounds. This assumption is a rather plausible one and one that is in complete agreement with the mechanism of reduction of nitro compounds, and would mean that the position of the pair of electrons binding the carbon atom to other groups is not changed, when we go from a nitro compound to a primary amine and to the corresponding primary alcohol.

Once we make these assumptions the heat of combustion of primary amines is given by the expression $H = 26.05 \times N + 13$.

Upon this basis the aromatic and aliphatic amines exhibit a very interesting variation in the relative position of the electrons between the nitrogen and carbon atoms, if the heat of combustion is taken as a criterion. That such a difference is brought out by the calculation of heats of combustion is most gratifying for the difference in the properties of the two classes of amines is well known. Thus, we find that in the case of the aliphatic amines, the above formula gives a good agreement with the experimentally determined values, while in the case of the aromatic amines the following formula gives a better agreement, $H = 26.05 \times N$. It merely means that the pair of electrons binding the nitrogen and carbon atoms are more displaced from the carbon atom in the direction of the nitrogen atom in aromatic amines than in the aliphatic amines and therefore, no correction is necessary in the formula of the former compound. The case is analogous to the difference in the positions of the pair of electrons between the carbon and the oxygen atoms in primary and tertiary alcohols. (See discussion under tertiary alcohols and also footnote p. 629.)

The validity of the postulates advanced and other points of interest, namely the reason underlying the difference in chemical properties, particularly basicity of aliphatic and aromatic amines will be discussed later. We wish to emphasize once more that this is merely a preliminary paper, and that a number of other relationships will be pointed out in two papers in preparation at the present time by one of us (Kh.)

The data for primary aliphatic amines, with the correction allowed for, are given in Table XII, and that for the aromatic amines in Table XIII. The agreement on the whole is very satisfactory, the difference not exceeding one half percent, except in the case of methyl and ethyl amines. These compounds will be discussed more thoroughly in the next paper and the cause for the discrepancy pointed out.

Amides, Anilides and Amino Acids

On the basis of the method developed in the case of primary amines, the heats of combustion of a number of nitrogen derivatives have been calculated.

TABLE XII
Primary Amines (Aliphatic)

Name	Number of Electrons	Calculated	Observed	% Difference
1 Methyl amine	9	247.5	257.4 Lem.	-5.0
2 Ethyl amine	15	403.7	410.6 Lem.	-1.8
3 Propyl amine	21	560.0	561.2 "	-0.2
4 n-Butyl amine	27	716.3	717.3 "	+0.3
5 t-Butyl amine	27	716.3	717.3 "	-0.1
6 Isoamyl amine	33	872.6	871.3 "	+0.1
7 Hexyl amine	39	1029.0	1027.5 "	+0.1
8 Heptyl amine	45	1185.2	1185.0 "	0.0
9 Benzyl amine	37	976.8	970.8 "	+0.7

TABLE XIII
Primary Amines (Aromatic)

1 Aniline	31	807.5	811.4 St., Hau.	-0.5
2 o-Toluidine	37	963.8	815.9 Lem.	-1.0
3 p-Toluidine	37	963.8	965.5 Pet.	-0.2
4 m-Toluidine	37	963.8	959.4 Pet.	+0.4
5 Pseudo cumidine	49	1276.4	966.5 Pet.	-0.3
6 p-Anisidine	35	924.7	1272.4 Lem.	+0.4
			928.7 Lem.	-0.4

We find, also, that the pair of electrons binding the carbon and nitrogen atoms in amides, anilides and amino acids, occupy a different position than in the case of primary amines of the aliphatic series, if the heat of combustion is to be taken as the criterion. The pair of binding electrons may be considered completely displaced from the carbon atom, i. e., occupying the same relative position as in CO_2 , in the direction of the nitrogen atom. (See, however, the discussion under tertiary alcohols—the same principle holds true in this case.) No correction is, therefore, necessary for this pair of electrons, and the formula for these types of compounds becomes: $H = 26.05 \times N$. In the table we are noting the total number of electrons interdisplaced, irrespective of whether the interdisplacement of electrons occurs between a carbon and an oxygen atom, or an oxygen and a nitrogen atom. The limitations of such a method of treatment are duly realized, and the point has been discussed already in the case of primary amines.

The agreement between the calculated and experimentally determined values is most gratifying, particularly in view of the fact that the constant employed, 26.05 Kg. Cal. per mole per electron, holds only for the heat of combustion of liquid compounds. The calculated values should, therefore, be larger than the experimentally determined values of the heat of combustion of those compounds which are solid. We find that to be the case. However, since the heats of fusion of these solids are presumably not very high, we should not expect the difference to be very large, but there should be that trend in the case of all of these compounds.

Of the forty-two compounds given in Table XIV, half of the compounds agree within four-tenths of one percent, while only eight compounds differ by more than one percent. That the data are of great significance is self-evident since it accounts for the combustion of the nitrogen derivatives on the same basis as that of the carbon compounds without any additional postulates. In some measure, it is thus a direct substantiation of the method and hypothesis employed in the calculation of the heats of combustion.

General Discussion

An attempt has been made in this paper to develop, on the basis of the non-polar conception of valence, the relation between the chemical constitution of a substance and the amount of heat liberated by it upon combustion. The notion of partial polarity had to be resorted to in order to explain the heats of combustion of unsaturated derivatives, alcohols, ketones, aldehydes, nitro compounds, amines, and other types of organic molecules not mentioned in this communication. The assumptions were made, however, not altogether unlikely; as a matter of fact they are included in the non-polar conception of valence¹.

There are two concepts that we consider most important from the standpoint of the calculation of heats of combustion and the elucidation of the chemical behavior of organic compounds. The first notion, which is rather

¹ G. N. Lewis: J. Am. Chem. Soc. 35, 1448 (1913)

TABLE XIV

Name	Number of Electrons	Amides		Observed	% Difference
		Calculated			
1 Acetamide	11	286.5		289.2 St., Schm.	+1.5
				288.4 Be., Fo.	-1.0
2 Propionamide	17	442.8		440.3 St., Schm.	+0.5
				436.5 Ba., Fo.	+1.5
3 Malonamide	14	364.7		361.1 St., H.	+1.0
4 Butyramide	23	599.1		596.7 St., Schm.	+0.6
5 Isobutyramide	23	599.1		596.5 St., Schm.	+0.6
6 Succinamide	20	521.0		509.7 St., H.	+2.4
7 Succinamide	17	442.7		439.4 Be., Fo.	+0.7
				438.3 St., H.	+1.0
8 Isovaleramide	29	755.4		752.3 St., Schm.	+0.4
9 Dimethyl malonamide	26	677.3		686.5 St., Schm.	-1.5
10 Oxaminic acid	5	130.1		132.7 St., H.	-1.8
				128.8 Mat.	+1.0
11 Oxamide	8	208.1		203.4 St., H.	+2.5
12 Diethyl malonamide	38	989.9		995.8 St., H.	-0.7
13 Benzamide	33	859.5		853.0 Be., Fo.	+0.8
14 Phthalimide	33	859.5		850.4 St., Schm.	+1.1

TABLE XIV (continued)

Anilides—Amino Acids

Name	Number of Electrons	Calculated	Observed	% Difference
15 Urea	6	156.3	152.3 St., La.	-3.0
16 Glycocoll	9	234.3	233.4 Fi., Wr.	+0.4
			234.7 St., La.	-0.2
17 Alanin	15	390.6	388.1 St., La.	+0.7
			389.7 Fi., Wr.	+0.3
18 Ioserin	13	344.5	343.7 Fi., Wr.	+0.3
19 Aspartic acid	15	390.6	385.3 St., La.	+1.5
			385.9 Fi., Wr.	+1.5
20 Asparagine	18	468.8	463.8 St., La.	+1.2
21 Glycyl glycine	18	468.9	471.1 St., La.	-0.5
22 Barbituric acid	14	364.7	359.0 Fi., Wr.	+1.5
23 Uric acid	18	468.6	461.4 Mat.	+1.8
			460.7 St., La.	+2.0
24 Methyl hydrouracil	24	625.2	618.2 Fi., Wr.	+1.2
25 4-Methyl uracil	22	573.1	566.1 Fi., Wr.	+1.4
26 Leucine	33	859.5	858.0 R., A.	+0.2
			856.5 St., La.	+0.4
			857.8 Wr.	+0.2
27 Veronal	38	989.4	984.0 Fi., Wr.	+0.5
28 Acetanilide	39	1015.8	1017.5 B., Fo.	-0.2
			1011.4 St., Schm.	+0.4

TABLE XIV (continued)
Anilides—Amino Acids

Name	Number of Electrons	Calculated	Observed	% Difference
29 Propionanilide	45	1172.1	1168.8 St., Schm.	+0.4
30 Hippuric acid	39	1015.8	1013.6 B., A.	+0.2
			1013.4 St., Schm.	+0.2
31 Skatol	45	1172.1	1171.4 B., A.	+0.1
32 α -Methyl indol	45	1179.1	1169.6 B., A.	+0.2
33 Benzoyl alanine	45	1172.1	1169.3 St., Schm.	+0.3
34 Benzoyl sarcosine	45	1172.1	1181.0 St., Schm.	+0.8
35 Hemipinamide	42	1093.9	1100.1 St., Lie.	-0.6
			1099.3 Roth.	-0.5
36 Benzanilide	61	1588.9	1577.1 St., Schm.	+0.8
37 Phenacyl amino acetic acid	45	1172.2	1166.1 St., Schm.	+0.6
38 o-Methyl hippuric	45	1172.2	1168.9 St., Schm.	+0.4
39 m-Methyl hippuric	45	1172.2	1168.2 St., Schm.	+0.4
40 p-Methyl hippuric	45	1172.2	1168.7 St., Schm.	+0.3
41 p-Methoxy hippuric	43	1133.1	1136.3 St., Schm.	-0.3
42 Leucyl glycol glycine	51	1328.5	1339.9 Fi., Wr.	-0.9
43 4-Phenyl uracil	43	1133.1	1132.2 Fi., Wr.	-0.1
44 o-Tolyl alanine	51	1328.5	1323.0 St., Schm.	-0.4
45 p-Tolyl-alanine	51	1328.5	1320.8 St., Schm.	-0.6

fundamental, is, that in oxidation reactions of carbon compounds, electrons are displaced from the carbon atom only in pairs, and furthermore the displacement occurs in definite stages from the normal valence shell until an arrangement of a carbon dioxide type is attained. The second notion, that when two carbon atoms share two pairs of electrons in common one pair occupies the same position as in the saturated hydrocarbon molecule, while the other pair is displaced from this normal valence shell into outer shells. The molecule may be considered, then, to have an electric moment in that part of it owing to this pair of displaced electrons. Furthermore, the extent of this displacement depends upon the other groups attached to the two carbon atoms. Reference to the postulates 3, 4 and 5 will help to clarify considerably these fundamental concepts¹.

The agreement between the calculated and experimentally determined values is very striking. Preliminary calculation of the heats of combustion of other types of compounds besides those mentioned in this paper, viz., oximes, chlorine, bromine, fluorine, and all sulfur derivatives, have also been made. The agreement is sufficiently close to bear out the fact that the fundamental concept of combustion, in the sense developed, is correct.

The possibilities of applying the heats of combustion to the elucidation of the electronic structures of organic compounds is self-evident. Thus, a number of important theoretical deductions such as the electronic structure of acetylenes, ethylenes, conjugated systems, cyclic structures, benzene, substitution in the benzene ring, etc., agree very well with the known experimental facts. We hope to discuss this prediction of chemical properties from the standpoint of the electronic structure of organic compounds in a future paper. We might add that, on the whole, this hypothesis gives us an excellent insight into the chemistry of organic reactions, and, that the knowledge gained of the electronic structures of the molecules helps us to interpret a number of now considered abnormal, interesting and bewildering reactions which are so abundant in our literature.

Summary

1. The hypothesis has been advanced that heat of combustion is due to an interdisplacement of electrons between atoms and molecules.
2. It has been assumed that, in the combustion of carbon compounds with oxygen, when an electron is displaced from the "methane arrangement" to that of the "carbon dioxide type" heat is evolved to the extent of 26.05.Kg. Cal. per mole.
3. It has been assumed that intramolecular oxidation-reduction reactions are accompanied by the evolution of heat.

¹ It is extremely instructive to examine our present day concepts of heats of formation of organic compounds from the standpoint of the views developed in this paper. We see at once the ambiguity involved in the concept, as applied to all classes of organic molecules. This point will be discussed in a later paper by one of us.

4. It has been necessary to assume that, in nitro compounds, the two valence electrons which hold the nitrogen and carbon atoms are displaced in the direction of the nitrogen atom.

5. The two valence electrons which hold the nitrogen and carbon atoms retain their relative positions in going from the nitro compounds to amines and alcohols in the aliphatic but not in the aromatic series.

6. The heats of combustion of 278 compounds have been calculated on the basis of the concepts developed in this paper. The agreement, on the whole, is very striking.

7. The prediction of the chemical properties and reactions of organic compounds from the standpoint of the electronic structure of these molecules will be given in subsequent papers.

8. The postulates underlying the calculation of heats of combustion are very readily extended to the calculation of other physical constants and will be discussed in later papers by us.

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