A THERMOCHEMICAL CONSTANT.

PRELIMINARY NOTICE.

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It is well understood by all who have closely considered the subject, that the so-called "heats of formation" of chemical compounds are not true physical constants, but complexes of various factors. Take for example the "heat of formation" of hydriodic acid, which, according to Thomsen, has the value of —610 small calories, when calculated from gaseous iodine. This quantity, however, is only the algebraic sum of at least three quantities, one plus and two minus, as the following equation shows:

$$H_2 + I_2 = 2HI - 610 \times 2 \text{ cal.}$$

That is, heat is expended in decomposing the molecules of hydrogen and iodine, and liberated by the subsequent union of the separated atoms, the sum of the three factors being negative. The entire series of changes is endothermic; but the final step, the combination of hydrogen and iodine, must be an exothermic operation.

In most cases, thermochemical data are even more complex than in this instance, for they involve factors representing changes of physical state. The "heat of formation" of carbon dioxide, for instance, implies the gasification of carbon, the dissociation of carbon and oxygen molecules, and the actual energy of union; it is, therefore, as ordinarily determined, no true measure of chemical force. These distinct factors are not, as yet, separately measurable: their sum is difficult to interpret; and to many chemists, therefore, the complexity of thermochemistry has seemed to be hopeless. No general conclusions of unimpeachable validity have been developed from thermochemical research, and so the entire subject has fallen somewhat into disfavor. One constant alone has attracted wide-spread attention—the neutralization constant of acids by bases—and this, having a value of 13,700 calories, represents the union of hydroxyl and hydrogen ions to form water. This constant has strengthened the theory of electrolytic dissociation, and I hope now to show that it has still wider significance.

In the fourth volume of his classical "Thermochemische Untersuchungen," Thomsen gives data relative to the heat of combustion of 120 organic substances. These data have peculiar value, for the reason that they are strictly comparable throughout. Every substance burned was taken in the state of gas, at constant pressure, reduced to a uniform temperature of 18°, the products of combustion being gaseous carbon dioxide and *liquid* water. Upon careful scrutiny the results exhibit systematic regularities of homologous character, and this fact, which is elaborately considered by Thomsen, tends to establish confidence in the accuracy of his data. Other observers, doubtless, have done their work equally well, but no other body of measurements known to me is so homogeneous and so self-consistent as these.

In discussing his observations, Thomsen uses the so-called "heat of formation" of carbon dioxide from solid, amorphous carbon, and that of water with the latter reckoned as liquid. With these values he computes the "heat of formation" of the different substances studied, but always upon the supposition that the reactions start from the several elements in their normal molecular condition. These heats are evidently not absolute, for they involve the uncertain factors due to changes of physical state, and are therefore, as I have already shown, complexes rather than constants. Furthermore, much of Thomsen's reasoning depends upon hypotheses which have been more or less questioned, so that although his conclusions are most interesting, they have not found universal acceptance. Many important and striking relations are shown, but their significance is not fully established.

In one respect, Thomsen's data are imperfectly suited to discussion. Although he starts with gas and ends partly with gas, his water is reckoned as liquid. For the best consideration, the process of combustion should deal with gases throughout, both for substance and for products; then only can extraneous physical disturbances be practically eliminated, and the chemical part of the phenomenon be studied with the fewest complications. Fortunately, the obvious correction can be easily applied, at least approximately, and when that is done a new order of regularities appears.

According to Thomsen[1] the molecular heat of formation of liquid water from its elements at 18°, is 68,357 calories. For gaseous water the value varies with temperature, and may be represented at 100° by the quantity 58,069. At 18°—the standard

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[1] Vol. II. pp. 52 to 56.

temperature of the combustion experiments—this figure reduces to 57,934. The difference between gaseous and liquid water, then, is 10,423 calories, and this quantity should be subtracted from the heat of combustion of any organic substance as many times as there are molecules of water produced. Thus, for the heat of combustion of methane, CH_4. Thomsen gives 211,930 calories. Two molecules of water are formed; we subtract, therefore, twice 10,423, and the value for gaseous substances throughout becomes 191,084. One gram-molecule of methane burning as gas, and with all the products of combustion reckoned as gaseous, gives 191,084 calories. In this way I have adjusted Thomsen's data, and in their new form they become the basis of my own calculations.

With values thus reduced we can now write equations which shall represent in thermochemical terms the process of combustion of any organic substance which, upon burning, undergoes complete dissociation. Any hydrocarbon, for example, when burning to form carbon dioxide and water, must have its atoms completely torn apart before they can combine with similarly dissociated atoms of oxygen. Let x represent the *absolute* molecular heat of formation of CO_2: y the absolute heat of formation of water: z the heat lost by the dissociation of the oxygen molecule; and r the heat lost by the decomposition of the substance burned; then, for CH_4. the equation becomes

$$x + 2y - 2z - r = 191,084.$$

This is a simple case; in other instances the equations must be doubled, or, in the study of organic halides and nitrogen compounds, quadrupled in order to avoid fractional molecules of oxygen, of nitrogen, or of the halogen element. For the sake of uniformity I prefer to write quadrupled equations throughout, and then the formula for the combustion of methane is

$$4x + 8y - 8z - 4r = 764,336.$$

Unfortunately, equations of this kind are indeterminate, for every new formula introduces a new quantity, and so the unknowns are always in excess. A direct algebraic solution is therefore impossible, and at first sight it would seem as though the entire system of equations was valueless. That this impression is incorrect I shall endeavor to show. Upon careful examination the equations exhibit regularities which suggest hypotheses: upon the latter, trials can be based, and in that way values are discoverable which satisfy the equations in a fairly conclusive manner.

By long study of this kind I have arrived at a general formula of curious significance, at least as regards the aliphatic hydrocarbons and their non-oxygenated derivatives. Let K represent the heat of combustion for any one of these hydrocarbons; then in the quadrupled formula $4K$ must be taken. Now let a be the number of molecules of CO_2 produced; b the number of molecules of H_2O; c the number of oxygen molecules dissociated; and n the number of atomic unions or linkings in the compound burned. Then, taking these data directly from the quadrupled equation, we have the following expression:

$$\frac{4K}{12a + 6b - c - 8n} = \text{a constant.}$$

The two plus quantities in the divisor represent combinations; the two minus quantities stand for decompositions; all the terms of the fundamental equation are thus utilized. For methane, as shown in the quadrupled equation, $4K = 764{,}336$, $a = 4$, $b = 8$, $c = 8$, and $n = 4$, the last figure representing the four unions of hydrogen atoms with carbon. In ethane $n = 7$, in propane 10, etc., all linkings, whether of hydrogen with carbon, or carbon with carbon, being equal in value. Now $(12 \times 4) + (6 \times 8) - (8 \times 1) - (8 \times 4) = 56$—the divisor in the case of methane. The quotient obtained is 13,649, and this I have indicated as a constant. In the following table for fourteen aliphatic hydrocar-

		4K.			
Compound.	Formula.	H_2O as liquid.	H_2O as gas.	Divisor.	Quotient.
Methane	CH_4	847720	764336	56	13649
Ethane	C_2H_6	1481760	1356684	98	13844
Propane	C_3H_8	2116848	1950080	140	13929
Trimethyl methane	C_4H_{10}	2748760	2540300	182	13957
Tetramethyl methane	C_5H_{12}	3388440	3138288	224	14010
Diisopropyl	C_6H_{14}	3996800	3704956	266	13928
Ethylene	C_2H_4	1333400	1250016	92	13587
Propylene	C_3H_6	1970960	1845884	134	13776
Isobutylene	C_4H_8	2602480	2435712	176	13839
Isoamylene	C_5H_{10}	3230520	3022060	218	13862
Acetylene	C_2H_2	1240200	1198508	86	13936
Allylene	C_3H_4	1870200	1786816	128	13959
Diallyl	C_6H_{10}	3731280	3522820	254	13869
Dipropargyl	C_6H_6	3531520	3406444	242	14076
				Average.	13873

bons its constant character appears. All the computations rest upon Thomsen's determinations, adjusted in the manner which I have described. In fixing the value of n, actual unions only are counted; double or triple carbon bonds reckon as one alone, the extra bonds being in abeyance, and thermally inoperative. In C_2H_2 for instance, $n = 3$; in ethylene, $n = 5$; in dipropargyl $n = 11$. n, therefore, for all chain molecules, equals the number of atoms in the compound minus one.

To trimethylene, if it be regarded as a ring-compound with nine unions in the molecule, the formula does not apply. The aromatic hydrocarbons also demand separate examination, and the formula for them must be modified by the introduction of a constant factor which represents the strength of the carbon ring. Since these special cases will be considered in my complete memoir later, their discussion may be omitted here.

The organic halides, sulphides and nitrogen compounds are well covered by the general formula, provided that in each case an appropriate factor be added to the divisor to indicate the halogen, sulphur dioxide or nitrogen produced upon combustion. Thus, for complete combustion of the halides, when halogen molecules are formed, the modification of the formula is as follows. Let h represent the number of chlorine molecules produced. h_1 the bromine molecules, and h_2 the iodine; then

$$\underset{\text{Chlorides.}}{\frac{4K}{12a + 6b + h - c - 8n}} = \underset{\text{Bromides.}}{\frac{4K}{12a + 6b + 2h_1 - c - 8n}} =$$

$$\underset{\text{Iodides.}}{\frac{4K}{12a + 6b + 4h_2 - c - 8n}} = \text{const.}$$

Thomsen gives data for twenty-two of these compounds, and only three of them are exceptional. Chlorobenzene, carbonyl chloride, and carbon tetrachloride fail to yield the usual constant, and their consideration is therefore deferred. The remaining nineteen compounds are given in the first of the following tables.

In dealing with the organic compounds of nitrogen, the same fundamental formula seems to hold, only it becomes necessary to divide the available data into two groups in which the factor for nitrogen has two distinct values. In the nitriles and cyanides when m represents the number of molecules of nitrogen set free,

Compound.	Formula.	4K.		Divisor.	Quotient.
		H_2O as liquid.	H_2O as gas.		
Methyl chloride	CH_3Cl	707800	645262	47	13729
Ethyl chloride	C_2H_5Cl	1336440	1232210	89	13845
Propyl chloride	C_3H_7Cl	1969520	1823598	131	13921
Isobutyl chloride	C_4H_9Cl	2600360	2412746	173	13947
Chlorethylene	C_2H_3Cl	1193360	1130722	83	13617
Chloropropylene	C_3H_5Cl	1813480	1709250	125	13674
Allyl chloride	C_3H_5Cl	1818720	1714490	125	13716
Ethylene chloride	$C_2H_4Cl_2$	1185440	1102056	80	13776
Ethylidene chloride	$C_2H_4Cl_2$	1185640	1102256	80	13778
Chloracetol	$C_3H_6Cl_2$	1815520	1690444	122	13840
Chloroform	$CHCl_3$	428120	407274	29	14044
Chlorethylene chloride	$C_2H_3Cl_3$	1049920	987382	71	13907
Tetrachlorethylene	C_2Cl_4	760280	760280	56	13576
Methyl bromide	CH_3Br	738840	676302	49	13802
Ethyl bromide	C_2H_5Br	1367280	1263050	91	13880
Propyl bromide	C_3H_7Br	1997160	1851238	133	13919
Allyl bromide	C_3H_5Br	1848480	1744250	127	13734
Methyl iodide	CH_3I	784320	721782	53	13619
Ethyl iodide	C_2H_5I	1414920	1310690	95	13797
				Average,	13796

CYANOGEN COMPOUNDS.

Compound.	Formula.	4K.		Divisor.	Quotient.
		H_2O as liquid.	H_2O as gas.		
Hydrocyanic acid	HCN	634480	613634	45	13636
Cyanogen	C_2N_2	1038480	1038480	76	13664
Acetonitrile	C_2H_3N	1248560	1186022	87	13632
Propionitrile	C_3H_7N	1885800	1781570	129	13819
				Average,	13688

AMINES.

Compound.	Formula.	4K.		Divisor.	Quotient.
		H_2O as liquid.	H_2O as gas.		
Methylamine	CH_5N	1033280	929050	69	13465
Ethylamine	C_2H_7N	1662680	1516758	111	13664
Propylamine	C_3H_9N	2302960	2115346	153	13826
Isobutylamine	$C_4H_{11}N$	2901440	2672134	195	13703
Amylamine	$C_5H_{13}N$	3562320	3291322	237	13423
Dimethylamine	C_2H_7N	1681840	1535918	111	13837
Diethylamine	$C_4H_{11}N$	2938000	2708694	195	13891
Trimethylamine	C_3H_9N	2330520	2142906	153	14006
Triethylamine	$C_6H_{15}N$	4209520	3896830	279	13967
Allylamine	C_3H_7N	2125120	1979198	147	13463
				Average,	13725

the factor is $3m$. In the amines it is $9m$. The divisors therefore become for cyanogen compounds, $12a + 6b + 3m - c - 8n$, and for amines, $12a + 6b + 9m - c - 8n$, the dividend in each case being $4K$ and the quotient a constant as heretofore. Leaving the oxygen compounds such as nitrates, etc., temporarily out of account, we have data for eighteen substances. Of these, ammonia, aniline, pyridine and piperidine are exceptional, and must be reserved for future consideration; the remaining fourteen are regular, as shown in the last tables.

In the combustion of organic sulphur compounds, at least in the cases given by Thomsen, SO_2 is produced, and this implies a distinct factor to be added to the divisor of the general formula. If s represents the number of molecules of SO_2 formed, the factor to be taken is $9s$, and the divisor becomes $12a + 6b + 9s - c - 8n$. Some of the compounds studied were cyanogen derivatives, and with these the factor $3m$ must also be taken into account, as in the nitriles, etc., which have already been considered. For thiophene, carbon disulphide, and carbonyl sulphide exceptional conditions hold, and their consideration will therefore be deferred. The remaining substances are as follows:

		$4K$.			
Compound.	Formula.	H_2O as liquid.	H_2O as gas.	Divisor.	Quotient.
Hydrogen sulphide ..	H_2S	546840	505148	38	13293
Methyl mercaptan....	CH_4S	1195240	1111856	80	13898
Ethyl mercaptan.....	C_2H_6S	1822600	1697524	122	13914
Methyl sulphide	C_2H_6S	1829400	1704324	122	13970
Ethyl sulphide.......	$C_4H_{10}S$	3068680	2964450	206	14390
Methyl sulphocyanide	C_2H_3NS	1595800	1533262	111	13813
Methyl mustard oil...	C_2H_3NS	1568240	1505702	111	13565
Allyl mustard oil.....	C_4H_5NS	2701440	2597210	189	13742
				Average,	13823

Two of the quotients in this group, it will be observed, are unsatisfactory, but as they diverge in opposite directions it is not necessary to reject them from the mean.

We have now examined the heats of combustion of seventy of the compounds studied by Thomsen. Fifty-five of these give close approximations to a constant when tested by the formula, and fifteen are either exceptional or erroneous. Many of the fifteen are explicable, but not without more detail than would be admissible in a preliminary notice. My final memoir will deal with them all.

There still remain, unconsidered, about fifty other substances which contain, in addition to hydrogen and carbon, more or less oxygen within their molecules. They are therefore, upon burning, incompletely dissociated, for the oxygen atoms must remain combined with one or another of the elements associated with it. Furthermore, fewer external oxygen molecules are broken up during the process of combustion, and therefore the factor c of the general formula must undergo modification. The quantity n, also, no longer represents absolute dissociation of the molecule burned, and its significance, therefore, changes. The formula, however, with proper modifications, still applies, and the same constant appears as its quotient. For present purposes one series of compounds, the alcohols, will serve to illustrate the principle; the others must wait until some future time. In this series, still using quadrupled formulas for the sake of uniformity, the symbol c of the divisor represents the external oxygen consumed; and c_1 indicates the number of oxygen molecules contained in the alcohol. The formula then becomes

$$\frac{4K}{12a + 6b - c - c_1 - 8n} = \text{const.},$$

and the results of its application are as follows:

		4*K*.			
Compound.	Formula.	H_2O as liquid.	H_2O as gas.	Divisor.	Quotient.
Methyl alcohol......	CH_4O	728920	645536	48	13448
Ethyl alcohol........	C_2H_6O	1362120	1237044	90	13745
Propyl alcohol.......	C_3H_8O	1994520	1827752	132	13846
Isopropyl alcohol	C_3H_8O	1973280	1806512	132	13686
Isobutyl alcohol	$C_4H_{10}O$	2633960	2425550	174	13939
Trimethyl carbinol...	$C_4H_{10}O$	2565360	2356900	174	13546
Isoamyl alcohol......	$C_5H_{12}O$	3280280	3030128	216	14028
Dimethylethyl carbinol............	$C_5H_{12}O$	3241800	2891648	216	13387
Allyl alcohol	C_3H_6O	1859040	1733964	126	13762
Propargyl alcohol....	C_3H_4O	1724400	1641016	120	13675
Ethylene glycol......	$C_2H_6O_2$	1192440	1067364	82	13017

Average. 13646
Omitting ethylene glycol, 13706

Taken altogether, the data so far presented summarize thus, the figure given being, for each set of substances, the mean value of the quotient.

Hydrocarbons, 14 compounds	13873
Halogen compounds, 19 compounds	13796
Cyanides, 4 compounds	13688
Amines, 10 compounds	13725
Sulphur compounds, 8 compounds	13823
Alcohols, 11 compounds	13646
Average, 66 compounds	13773

What now, is the meaning of the formula used, and of the constant which is derived from it?

Before attempting to answer this question I may properly point out that the formula itself can be condensed and simplified. Taking the hydrocarbons, as the least complex of the series studied, the formula may be given in three forms, as follows:

$$\frac{4K}{12a + 6b - c - 8n} = \frac{4K}{11(a + \frac{b}{2}) - 8n} = \frac{4K}{11c - 8n} = \text{const.}$$

The difference between these expressions arises from the fact that the oxygen used is always proportional to the carbon and hydrogen burned, but all three give the same quotient. The first and most elaborate form, however, is the one to be preferred, for the reason that it gives in detail all the factors of the original equations. In it the constant appears as a function of all the changes which have taken place, the substances produced being indicated with the plus sign, while the substances destroyed are represented by minus quantities. The other formulas may be easier to apply, but they are much less simple to interpret.

Looking now to the constant itself, 13,773, we see that it is sensibly identical in value, within the limits of experimental uncertainty, with the neutralization constant of 13,700 calories. The latter is purely chemical in its character, uncomplicated by extraneous physical considerations, and it represents a union of the simplest kind, one bond joining two ions. In short, it seems to be a definite unit of thermochemical change, of which the quantities discussed in this paper are multiples, and by whose aid the original equations, hitherto indeterminate, may be satisfied. Let us examine the general formula in more detail.

If we take the constant 13,773 calories as our unit, the fundamental formula may be written

$$\frac{4K}{12a + 6b - c - 8n} = 1, \text{ or one unit,}$$

and hence, $12a + 6b - c - 8n = 4K$; that is, each molecule of a or CO_2 produced by the combustion has a value of 12 units, each molecule of water is represented by 6 units, each molecule of oxygen by 1, and each atomic linking in one molecule of the substance under investigation by 8/4, or 2. These quantities represent the actual heat of formation of the several molecules from gaseous, dissociated atoms, and when they are introduced into the original equations the latter are satisfied.

Let us recur to the equation for methane:

$$x + 2y - 2z - r = 191{,}084.$$

$$\begin{aligned} x &= 12 \times 13773 = 165276 \\ 2y &= 12 \times 13773 = 165276 \\ -2z &= 2 \times (-13773) = -27566 \\ -r &= 8 \times (-13773) = -110184 \\ \text{Sum} &= 192822 \end{aligned}$$

a quantity which exceeds Thomsen's mean value by 0.91 per cent. As Thomsen's separate determinations vary among themselves by 0.99 per cent., the agreement is satisfactory. The calculated value is about 0.2 per cent. higher than his highest.

This one example is enough to show, for present purposes, the method of computation, but to illustrate its effectiveness a few more instances may be given in condensed form. Each equation represents the combustion of four molecules of the substance named, the water produced being reckoned as gaseous.

Compound.	Equation	Calculated.	Variation. Per cent.
Ethane........	$8x + 12y - 14z - 4r = 1356684$	1349754	0.51
Propylene.....	$12x + 12y - 18z - 4r = 1845884$	1845582	0.04
Methyl chloride	$4x + 6y + 2h - 7z - 4r = 645262$	647331	0.32
Allyl bromide..	$12x + 10y + 2h_1 - 17z - 4r = 1744250$	1749171	0.28
Ethyl iodide...	$8x + 10y + 2h_2 - 13z - 4r = 1310690$	1308435	0.17
Propionitrile ..	$12x + 14y + 2m - 19z - 4r = 1781570$	1776717	0.28
Ethylamine ...	$8x + 14y + 2m - 15z - 4r = 1516758$	1528803	0.79

The agreements, as shown in the percentage column, are reasonably close; the absolute variations, to be compared with Thomsen's data, should be divided by four. It must be remembered that Thomsen's determinations vary among themselves; that they represent measurements at constant pressure and not at constant volume; that there is a small uncertainty in the adjustment from liquid to gaseous water; and that other unnoted corrections should possibly be applied. Take it for all in all, the validity of the constant may be looked upon as established, and a fair estimate of absolute thermochemical values has been attained. The neutralization constant, as determined with different acids and bases, shows fully as great variations, and yet there can be little doubt as to its authenticity and meaning.

It would be most unwise to assume, from the evidence here presented, that the constant under discussion governs all chemical combinations. It applies to the classes of compounds considered in this paper, but there are others to which, in all reasonable probability, it does not apply. Its significance, however, is very great, and it suggests a general law. *In any class of compounds, the heat of formation is proportional to the number of atomic linkings within the molecule, and seems to bear no relation to the masses of the atoms which are combined.* Among organic substances, this relation is very clear, and is implied in the factor $8n$ which occurs in all forms of the general formula. For these compounds the fundamental unit appears to be double the constant, or 27,600 in round numbers. Multiply this by four, the number of unions in the molecule, and we have the *absolute* heats of formation, from gaseous, dissociated atoms, of methane, of methyl chloride, bromide, or iodide, and of chloroform, all these quantities being equal. Multiply by seven, and the value for ethane is obtained, and so on throughout the aliphatic hydrocarbons and their immediate derivatives. For other compounds, as in the aromatic group, the coefficent of n seems to be other than 8, but here the actual number of atomic unions is uncertain. For inorganic substances, considered in the gaseous state, the data are too few, and constants of different magnitude may control their formation. On this subject, speculation would be premature, and I must reserve my conclusions regarding it until later. Probably, however, the general principle will hold, and the absolute heat of formation of any substance will prove to be a function of the number of atomic unions within the molecule; that is, of the number of chemical acts involved in its production.