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The Significance of Chemical Bond Energies

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In view of recently reported departures from bond additivity of chemical energies of formation, a purely empirical study has been made of the significance of chemical bond energies. If one assumes that the energy of formation is made up of bond energies and interaction energies between the bonds as well, it is shown that both of these two types of energy are *indeterminate* so far as thermochemical data are concerned. Under certain simple conditions on the interaction energies *apparent* bond additivity would obtain and one could then define apparent bond energies. In case these additivity conditions are not valid, it is further shown how the energy of formation can be expressed in terms of the apparent bond energies with a correction term involving the numerical departures from the additivity conditions. It is also shown that under a transformation of reference state to excited states of the atoms: (1) the additivity characteristics are invariant, and (2) the bond resonance energies as defined by Pauling are invariant, and therefore the reference of bond energies to excited states has no significance so far as these resonance energies are concerned. A discussion of atomic and bond additivity is given for physical quantities in general. It is

pointed out that the energy connected with the nuclear motions, that is the heat content plus the zero-point energies of the vibrations, may be of the order of one-tenth the total energy of formation. Since this latter energy would not be expected on the whole to exhibit bond regularities, it is therefore proposed that "electronic" energies be introduced for the study of structural regularities in the energies of formation. A study is then made of available data in terms of the proposed scheme. Because of the lack of accurate data it is at present not possible to make a very thorough test. But a certain amount of information is obtained from the excellent data of Rossini on some of the CHO compounds, and so far as reliable data are available reasonable results are obtained, which indicate that in some cases the departures from additivity may be considerably greater than ordinarily supposed. It is further pointed out that Pauling's bond resonance energies could not accurately be considered as pure bond quantities if the interactions were appreciable, and that this may be the reason in part, that his electronegativity map cannot on the whole be used successfully to predict the electric moments of chemical bonds.

SINCE considerable importance is attached to bond energies in theoretical chemistry, and since there seems to be some arbitrariness in their definition, it was thought worth while to consider in a somewhat general manner what empirical inferences one is justified in making on the basis of experimentally determined heats of formation. It is a well-known fact that the energies of formation of molecules from their atomic constituents can approximately be accounted for on the assumption that each chemical bond type has associated with it a characteristic energy in the sense that the bond energies are additive. Some of the arguments of theoretical chemistry are based on the general validity of this principle. For example, it has sometimes been rather naturally inferred from the empirical facts, that each chemical bond has associated with it a definite electronic configuration, independent of the other bonds to the same atom.

Actually departures from additivity are observed and usually attributed to experimental error or to "dipole effects." For example, it is well known that the C—C bond energy calculated

from the paraffins is about 0.2 v.e. less than that obtained from the diamond crystal. Also Rossini¹ has recently reported a discrepancy of about 0.3 v.e. for the paraffins and alcohols, and Pauling² has mentioned a discrepancy of 0.3–0.5 v.e. for the primary and branched alcohols. For the purpose of studying such deviations empirically it is proposed to consider the consequences of assuming a more general type of energy model, which admits the possibility of "bond interactions." To be more precise, it will be assumed as a second approximation, that the energy of formation of a molecule may be considered to consist of a set of energies associated with the "bonds" and an additional set associated with "pairs of bonds" to the same atom.

For the sake of generality it will be convenient to consider not necessarily a single molecular type, but a more generalized system of atoms connected in any of the various ways allowed by the valence conditions. The discussion will for the present be further restricted to saturated

¹ F. D. Rossini, *J. Chem. Phys.* **2**, 145 (1934).

² L. Pauling, *J. Am. Chem. Soc.* **54**, 3570 (1932).

systems, containing only single bonds. (Such a model would be expected to apply only when the valence angles of the individual atoms are all equal, or nearly equal, as for valencies up to four; and only when the interactions between atoms not bound to a common atom are negligible.)

There will be associated with the bond between the atoms X_i and X_j an energy R_{ij} ; and with the pair of bonds X_i-X_j and $X_i-X_{j'}$ to the atom X_i , an energy $R_{ijj'}$. The energy of the system of molecules can then be written:

$$E = \sum_{ij}^{\text{bonds}} R_{ij} + \sum_i^{\text{atoms}} \sum_{j, j'}^{\text{pairs}} R_{ijj'}.$$

One may then ask the following question. Are there any possible conditions on the $R_{ijj'}$ such that the second, or double summation term of E could be expressed in the form of a single summation term like the first term, independent of the number of like bonds in the system? That is, are there any simple conditions on the interaction constants, such that the interaction energy would be experimentally indistinguishable from the bond energy, so far as E is concerned?

It can be shown as follows that the conditions:

$$R_{ijj'} - (R_{iji}/2 + R_{i'jj}/2) = 0 \quad (1)$$

are *sufficient* conditions for apparent bond additivity: If the atom X_i has the valence v_i , there will be $v_i(v_i-1)/2$ terms of the type $R_{ijj'}$ associated with the atom X_i , and each quantity $R_{iji}/2$ will occur (v_i-1) times in the summation over the atoms X_i , when the substitution (1) is made. Hence one can write:

$$\sum_{i, j'}^{\text{pairs}} R_{ijj'} = \sum_{ij}^{\text{bonds}} \frac{1}{2}(v_i-1)R_{iji}.$$

This shows that the atoms X_i and X_j may be considered to contribute additional energies

$$\frac{1}{2}(v_i-1)R_{iji} \quad \text{and} \quad \frac{1}{2}(v_j-1)R_{jji}, \quad \text{respectively,}$$

to the bond energy R_{ij} , independent of the numbers of bonds of the various types present. One can then write:

$$E = \sum_{ij}^{\text{bond types}} N_{ij}E_{ij},$$

where

$$E_{ij} = R_{ij} + \frac{1}{2}(v_i-1)R_{iji} + \frac{1}{2}(v_j-1)R_{jji}$$

and N_{ij} is the number of bonds ij in the system. The quantities E_{ij} may be called the apparent bond energies. Thus one sees that a sufficient condition for apparent bond additivity is the simple condition that the interaction energy between two unlike bonds to the same atom be equal to the average of those for the two corresponding pairs of like bonds,—with no restriction on the order of magnitude of the interaction energies! For example, a special case of this condition would obtain if all the interactions were equal to one another.

It can further be shown that the conditions (1) are also necessary conditions for bond additivity of the type previously discussed. Since the proof is somewhat lengthy and of only mathematical interest, it is not included here. It is a simple matter to prove it for any special types of compound.

One can also enquire under what conditions a given system of bond energies designated by S_{ij} may equally well be interpreted formally as interaction energies $S_{ijj'}$. In terms of the energies S_{ij} one can *always* define a system of energies $S_{ijj'}$, in fact by the following equations:

$$\begin{cases} S_{ij} = \frac{1}{2}(v_i-1)S_{iji} + \frac{1}{2}(v_j-1)S_{jji}, & (i \neq j) \\ S_{ii} = (v_i-1)S_{i ii}, \\ S_{jj} = (v_j-1)S_{j jj}, \\ S_{iji} = S_{i ii}/2 + S_{ijj}/2, \\ S_{jji} = S_{j ii}/2 + S_{ijj}/2. \end{cases}$$

For an aggregate of only two types of atoms, X_i and X_j , these equations will represent a system of only five equations in the six quantities $S_{ijj'}$ to be defined. The two quantities $S_{i ii}$ and $S_{j ii}$ are uniquely defined. Therefore any one of the other four of these interaction constants is completely arbitrary, and it will be possible always to represent a system S_{ij} formally in terms of an equivalent system $S_{ijj'}$ in a single infinity of different ways. For a system of n atomic types there will be $n(n-1)/2$ degrees of arbitrariness in the choice of interaction constants.

This arbitrariness can be expressed in another way; namely, by considering the set of bond energies defined by $T_{ij}=0$, and calculating the equivalent $T_{ijj'}$, as the $S_{ijj'}$ previously. Hence it

is always possible to add to a system of bond energies R_{ij} a system of interaction energies of the type $T_{ij'}$ without changing the total energy E . This system of energies will, of course, have the same degree of arbitrariness as the system $S_{ij'}$.

DEPARTURES FROM APPARENT BOND ADDITIVITY

In the above discussion it has been stated that the necessary and sufficient conditions for apparent bond additivity are given by the Eqs. (1). If these latter conditions are not valid, one may write:

$$R_{ij'} - (R_{ij}/2 + R_{i'j'}/2) = \delta_{ij'}, \quad (2)$$

where it may be noted that the $\delta_{ij'}$ differ from zero only when $j \neq j'$. With the use of Eqs. (2) the total energy may be rewritten:

$$E = \sum_{ij}^{\text{bond types}} N_{ij} R_{ij} + \sum_i^{\text{atoms pairs}} \sum_{i, j'} \times \{ \frac{1}{2} (R_{ij} + R_{i'j'}) + \delta_{ij'} \}.$$

And if it be noted that the quantities

$$\frac{1}{2} (R_{ij} + R_{i'j'})$$

represent a system of energies obeying the transformation conditions (1), then one can write:

$$E = \sum_{ij}^{\text{bond types}} N_{ij} E_{ij} + \sum_i^{\text{atoms pairs}} \sum_{i, j'} \delta_{ij'}, \quad (3)$$

where the E_{ij} have the same form as in the previous case of perfect additivity. In addition there is here a correction term to be summed over all pairs (i, j') for which $j \neq j'$. The correction term will depend not only on the numbers of bonds N_{ij} and the numbers of atoms N_i , but also on the manner in which the atoms are connected. For example different isomers may have different correction terms. In order to specify the connections of the generalized system under consideration, one can imagine various subtypes of the atoms X_i according to the particular set of atoms $X_{i_1} \cdots X_{i_{v_i}}$ to which the atom X_i is bound. These subtypes may be symbolized by: $X_i^{i_1 \cdots i_{v_i}}$ and their frequency of occurrence in the system

by: $N_i^{i_1 \cdots i_{v_i}}$. For the purposes of the present discussion, the system is then completely specified by these latter numbers. The correction term can be expressed as:

$$\sum_{i, j'}^{\text{pair types}} p_{ij'}^{i_1 \cdots i_{v_i}} \delta_{ij'},$$

where the $p_{ij'}^{i_1 \cdots i_{v_i}}$ represent the total number of interactions of the type $R_{ij'}$ in the system, and are expressed by linear forms, with integral coefficients, in the $N_i^{i_1 \cdots i_{v_i}}$. They may be regarded as characteristic indices for the system or molecule as regards bond additivity. They do not include the particular $N_i^{i_1 \cdots i_{v_i}}$ for which the j 's are all identical.

When departures from additivity are admitted, it is, of course, arbitrary how one defines bond energies, because one can always apply appropriate correction terms. But since the above analysis suggests a simple and natural definition, it will be used as an empirical basis for the discussion of thermochemical data. If one restricts oneself to particular types of compound, it may be possible in some special cases to obtain apparent additivity, but if one *assumes* additivity for a particular set of compounds and calculates appropriate bond energies, one does this in general at the expense of having to ignore discrepancies in other compounds. This is illustrated by the previously mentioned discrepancies, and by still other fairly large discrepancies, which seem to appear consistently for the first members of homologous series and are usually ignored by taking an average for the series.

In addition to offering a possible explanation for the observed discrepancies, the above analysis leads to the significant conclusion, that thermochemical data alone can offer no possibility of distinguishing between interaction energy and bond energy in the usual sense. In the case of perfect apparent additivity it is impossible to obtain any information whatsoever concerning the relative amounts of the two types of energy. Even in the case of departures from additivity, with the model considered here, it would at most be possible to obtain from the observed $\delta_{ij'}$ a lower limit for the absolute values of the largest $R_{ij'}$.

REFERENCE OF BOND ENERGIES TO EXCITED STATES

Bond energies have sometimes been referred to excited states of the constituent atoms. For example, Pauling has calculated bond energies referred to the 5S state of the carbon atom, because the tetravalent carbon atom has been supposed to be closely related to this latter state of the atom. With reference to the present treatment one can consider what significance such a reference to excited states could have on the basis of thermochemical data alone. It will be supposed that the energy E referred to normal atoms is given by Eq. (3). If one wishes to refer the energy of formation to excited states, it is obvious that this energy will be increased by an amount

$$\sum_i^{\text{atoms}} N_i \epsilon_i,$$

where N_i is as before the number of atoms X_i in the system, and ϵ_i is the excitation energy of the atom X_i relative to the normal state. Now one can imagine the energy ϵ_i to be divided equally between the v_i bonds to the atom X_i , and then write:

$$E = \sum_{ij}^{\text{bond types}} N_{ij} (E_{ij} + \epsilon_i/v_i + \epsilon_j/v_j) + \sum_{ij, ij'}^{\text{pairs}} p_{ij, ij'}^i \delta_{ij'}^i.$$

Hence it is seen that the characteristic apparent bond energies are increased, but that the additivity correction remains invariant under such a transformation. From this it can be inferred not only that perfect additivity would not be altered by such a transformation, a well-known fact, but also that the quantities $\delta_{ij'}^i$ obtained from heats of formation would be invariant to the particular choice of reference states.

PAULING'S BOND RESONANCE ENERGIES

With regard to this transformation one can make a further inference concerning the resonance energy of a bond as calculated by Pauling. These resonance energies were defined by:

$$\Delta_{ij} = E_{ij} - \frac{1}{2}(E_{ii} + E_{jj})$$

and calculated on the assumption of perfect additivity. They are supposed to represent the

resonance energy between a "normal covalent bond" and the ionic bond. If the E_{ij} are referred to normal states, then the E_{ij}^* referred to excited states will be given by: $E_{ij}^* = E_{ij} + \epsilon_i/v_i + \epsilon_j/v_j$, whence it is immediately obvious that $\Delta_{ij}^* = \Delta_{ij}$. In other words, the resonance energies calculated on the assumption of perfect additivity for a particular set of compounds will be invariant to the transformation from normal to excited states. It will vary somewhat with the choice of compounds, corresponding to the departures from additivity.

When one admits departures from additivity, or even when one admits interactions obeying the additivity requirement (1), it is a difficult question as to what one should consider a "normal covalent bond" in the sense of Pauling's calculations. So far as the empirical calculations for an electronegativity map are concerned, it might seem just as well to calculate resonance energies in terms of the apparent bond energies E_{ij} as defined in the present analysis. But a simple calculation of the resonance energies shows that they are not independent of the interactions except under very special conditions.

CALCULATION OF THE INTERACTION INCREMENTS

Considering again the "interaction increments," $\delta_{ij'}^i$, it is evident that one should be able to calculate them directly from the thermochemical data without calculating energies of formation at all, since they are invariant under a transformation to excited states. Energies of formation are most frequently calculated from experimental heats of combustion. The energy of formation is then given by a linear equation in the numbers N_i :

$$E = \sum_i^{\text{atom types}} N_i \mu_i - (K + \lambda).$$

The quantities μ_i are constants derived from the auxiliary thermochemical reactions involved, and depend on the particular atomic states of reference. K is the heat of combustion measured in any physical state; and λ , the heat of vaporization from the same state. It will be supposed that the calculations are referred to normal atoms. Then the energy of formation can be expressed also in the form (3). Combining the two ex-

pressions for the energy of formation one can eliminate E and write:

$$-(K+\lambda) = \sum_{\text{bond types } ij} N_{ij}(E_{ij} - \epsilon_i/v_i - \epsilon_j/v_j) + \sum_{i, jj'} p_{ij'}^i \delta_{jj'}^i.$$

This shows that the negative quantities $-(K+\lambda)$ have the same bond additivity characteristics as the energies of formation E . Hence one could calculate the $\delta_{jj'}^i$ directly from the experimental quantities. In fact one does not even need to specify the μ_i since the quantities in parentheses will be determined from the data without a knowledge of their constitution, and are themselves invariant to the choice of reference. But since it is useful to determine energies of formation and bond energies, this latter method will not be used in the subsequent applications. The actual energies will be calculated with reference to normal states, since the foregoing discussion has shown that the introduction of excited states has no special significance for the present considerations.

ATOMIC ADDITIVITY

From the previous discussion of excited states, it is obvious that an additive system of any "atomic" physical quantities R_i can always be replaced by an additive system of bond quantities R_{ij} defined by:

$$R_{ij} = R_i/v_i + R_j/v_j.$$

These equations define the R_{ij} uniquely. The reverse transformation will be possible when

$$\Delta_{ij} = R_{ij} - (R_{ii}/2 + R_{jj}/2) = 0.$$

If this latter condition does not hold the corresponding quantity E can be written:

$$E = \sum_i^{\text{atoms}} \frac{1}{2} v_i R_{ii} + \sum_{ij}^{\text{bonds}} \Delta_{ij}.$$

From the foregoing one sees that the condition that bond quantities R_{ij} be representable as atomic quantities R_i is simply that the quantities Δ_{ij} , similar in form to the resonance energies defined by Pauling, should vanish; whereas the condition that interaction quantities $R_{jj'}$ be

representable as bond quantities R_{ij} was seen to be simply that the quantities $\delta_{jj'}^i$ should vanish. As regards additivity then the Δ_{ij} might be regarded as characterizing an abnormality in the interactions associated with conventional bonds; and the $\delta_{jj'}^i$, an abnormality in the interactions between atoms not bound to each other but to the same atom, X_i .

One can summarize the above results by stating the following general additivity rules:

(I) An additive system of atomic quantities can always be replaced by an additive system of bond quantities R_{ij} , uniquely defined as above. The reverse transformation will be possible when the Δ_{ij} vanish.

(II) An additive system of bond quantities R_{ij} can always be replaced by an additive system of interaction quantities $R_{jj'}$, in an infinite variety of ways as previously defined. The reverse transformation will be possible when the $\delta_{jj'}^i$ vanish.

These principles have a number of obvious consequences, the most significant of which is the following. If for the sake of argument one admits purely formally the possibility of atomic bond and interaction energies, it is impossible from the experimental energies E to assign unique quantities R_i , R_{ij} and $R_{jj'}$ to the different types of atoms, bonds and interactions, respectively. So far as energies are concerned, it is therefore impossible to justify unambiguously the use of such terms as atomic, bond, and interaction energies. In fact, the only quantities uniquely determinable from the energies of formation are the invariant quantities Δ_{ij} and $\delta_{jj'}^i$. While the consideration of atomic energies has no special significance here, except in the formal transformation to excited states, the latter discussion was included for the sake of generality and because of its possible interest for empirical studies of refractivity and other physical quantities.

It is perhaps worth repeating here that the present discussion represents an attempt to determine only the purely empirical significance of chemical bond energies. This discussion has shown that apparent bond additivity does not, as frequently inferred, necessarily permit the assignment of characteristic energies to chemical bonds

disregarding the possibility of interactions. No attempt is made here to discuss bond and interaction energies from the point of view of an extended quantum analysis. Such an analysis is promised from the studies of Van Vleck and his students.

APPLICATIONS

In order to determine the quantities δ_{ij}' from experimental data it is first necessary to determine the indices p_{ij}' for the various compounds to be considered. These can be determined by directly counting the number of interactions of the type R_{ij}' in the molecule; but it is sometimes more convenient to express them in terms of the characteristic subtype numbers previously introduced. In Table I are shown the

TABLE I. Subtypes in CHO compounds.

CCCC n_0	CCCH n_1	CCHH n_2	CHHH n_3	CHHHH n_4
	CCCCO n_1'	CCCHO n_2'	CCHHO n_3'	CHHHO n_4'
		CCCOO n_2''	CCHOO n_3''	CHHOO n_4''
			CCOOO n_3'''	CHOOO n_4'''
				COOOO n_4''''
OOO m_0	OOC m_1	OCC m_2	HH r_0	HC r_1
	OOH m_1'	OCH m_2'		HO r_1'
		OHH m_2''		
$\begin{cases} p_{\text{CH}}^{\text{C}} = 3n_1 + 4n_2 + 3n_3 + 2n_3' + 2n_3'' + n_3''' \\ p_{\text{CO}}^{\text{C}} = 3n_1' + 2n_2' + n_3' + 4n_2'' + 2n_3'' + 3n_3''' \\ p_{\text{OH}}^{\text{C}} = n_2' + 2n_3' + 3n_4' + 2n_3'' + 4n_4'' + 3n_4''' \\ p_{\text{CH}}^{\text{O}} = m_2' \\ p_{\text{CO}}^{\text{O}} = m_1 \\ p_{\text{OH}}^{\text{O}} = m_1' \end{cases}$				

various possible subtypes for CHO compounds (compounds of carbon, hydrogen and oxygen containing only single bonds), together with new and simpler symbols to designate their frequency of occurrence in the molecule. Expressions for the six different p_{ij}' are also given.

It is a characteristic of the p_{ij}' that the group numbers n , m or r corresponding to groups for

which all the surrounding atoms are alike (e.g., CCCC or CHHHH) never occur. Therefore the correction term vanishes for compounds made up of such groups alone, and one can obtain the apparent bond energies from compounds of the latter type, if they exist. In these cases then the bond energies can be calculated as in the case of perfect additivity. For the particular case of CHO compounds the molecules H_2 , H_2O , CH_4 , and the diamond crystal (neglecting surface effects) are compounds of the latter type. The energies of formation of these compounds serve to determine the bond energies E_{HH} , E_{OH} , E_{CH} , and E_{CC} , respectively. Compounds containing only COOOO or OCC groups are not known, and the energy E_{CO} must be determined indirectly. The possibility that O_4 is made up of O_{OO} groups with normal bonds will be discussed later in connection with the determination of the bond energy E_{OO} .

CH COMPOUNDS

As a special case of CHO compounds one can consider CH compounds, including all the paraffins, diamond and hydrogen, H_2 . There will be just four constants to be determined from the experimental data; namely, E_{CC} , E_{CH} , E_{HH} , and $\delta_{\text{CH}}^{\text{C}}$. In principle it would seem a fairly simple matter to test the present point of view by means of a study of the energies of formation of the paraffins. The bond energy E_{CC} would be obtained from the diamond crystal; and E_{CH} , from methane. Then the values of $\delta_{\text{CH}}^{\text{C}}$ as calculated from the different paraffins should all be the same.

But if one attempts to make an accurate study of thermochemical data, several difficulties are encountered:

(1) Thermochemical data, such as heats of combustion, seem in very few cases to have been determined with an accuracy better than 0.1 v.e. Of the older data Thomsen's values seem to be fairly reliable, as judged from the agreement with more recent data. For a few organic compounds Rossini³ has recently made some excellent measurements of the heat of combustion.

³ F. D. Rossini, Bur. Standards J. Research **6**, 1, 37 (1931); **7**, 329 (1932); and **8**, 119 (1933).

(2) It is customary to calculate energies of formation of the molecule from the isolated elements at a temperature of 20°C. The heat of combustion is usually determined at this latter temperature approximately, and if the substance is not burned from the gaseous state, it is necessary to know the heat of vaporization at 20°C. Since one usually finds in the literature the heat of vaporization at the boiling point, for example, a knowledge may be required of the specific heat of the liquid, or solid, and of the vapor for temperatures from 20°C to the boiling point, or to the point at which the sublimation energy has been determined. Sometimes these data are available, but more frequently they are not, and one must make an estimate subject to appreciable error in some cases.

(3) Added to these there is a more fundamental difficulty: The conventional energies of formation give the total energy of the molecule at 20°C. This energy may be regarded as made up of an electronic and a nuclear energy of opposite sign associated with the nuclear motions and their corresponding potential energy. One part of this nuclear energy will consist of the heat content of the gas per molecule, and another part will be the sum of the zero-point energies of the fundamental modes of nuclear vibration. The zero-point energy is in general much larger than the heat content at 20°C. For example, the zero-point energy corresponding to a frequency of 3000 cm^{-1} is about 0.2 v.e., while the heat content per degree of freedom on the equipartition theory, $\frac{1}{2}kT$, is only about 0.01 v.e., and unless the frequency is very low only a small fraction of the classical energy is excited. So far as the order of magnitude of the frequencies is concerned there seems to be in general one mode of vibration which may be imagined to be associated roughly with each chemical bond. Besides these "valence" frequencies there are usually many other frequencies associated with deformation or free rotation. Therefore one does not expect the nuclear energy to exhibit bond additivity. In fact, it seems surprising that approximate bond additivity has been observed at all. In view of these considerations one would expect at most that the electronic energy might show structural regularities. It is therefore proposed in the following

to introduce electronic energies of formation. These energies will be greater (arithmetically) than the ordinary energies by an amount equal to the nuclear energy. They will, of course, not correspond to an actual state of the molecule, but will be analogous to the energy of a diatomic molecule corresponding to the theoretical minimum of potential energy.

One might suggest that the observed departures from additivity could possibly be accounted for entirely in terms of the nuclear energies, but as will be seen in the following, it seems to be necessary to introduce some additional feature into the energy model in order to correlate empirically the observed energies of formation. In the following an attempt will therefore be made to correlate existing data in terms of the interaction increments δ_{ij}' .

Because of the lack of accurate experimental data it is at present not possible to make a very thorough test of the present point of view; but some information can be obtained from data on CHO compounds, particularly from the excellent data of Rossini. In Table II are given the

TABLE II.

$2\text{O} = \text{O}_2 + 5.09\text{ v.e.}$
$2\text{H} = \text{H}_2 + 4.44\text{ v.e.}$
$\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}(\text{g}) + 2.508\text{ v.e.}$
$\text{H}_2 + \frac{1}{2}\text{O}_2 = \text{H}_2\text{O}(\text{l}) + 2.966\text{ v.e.}$
$\text{C}(\text{g}) = \text{C}_{\text{graphite}} + 6.67\text{ v.e.}$
$\text{C}_{\text{graphite}} + \text{O}_2 = \text{CO}_2 + 4.075\text{ v.e.}$
$\text{C}_{\text{graphite}} = \text{C}_{\text{diamond}} - 0.008\text{ v.e.}$

constants of the auxiliary reactions used in the calculations. These lead to the following equation for the heat of formation in v.e. of CHO compounds of the type discussed here:

$$E = 10.745N_{\text{C}} + 3.703N_{\text{H}} + 2.545N_{\text{O}} - (K + \lambda) + E_{\text{N}}.$$

An error in the constants of this equation may affect the calculated bond energies E_{ij} , but will not affect the δ_{ij}' , as is obvious from the previous discussion of additivity. (It may also be noted here that the introduction of the nuclear energies E_{N} alters what has been said of the additivity characteristics of $-(K + \lambda)$. Instead of these latter quantities the quantities $-(K + \lambda) + E_{\text{N}}$ will now have the same additivity characteristics as the energies E .)

PARAFFINS

In Table III are given the theoretical expressions for the electronic energies E of the

TABLE III.

Substance	E
CH ₄	$4E_{CH}$
C ₂ H ₆	$E_{CC} + 6E_{CH} + 6\delta^C_{CH}$
C ₃ H ₈	$2E_{CC} + 8E_{CH} + 10\delta^C_{CH}$
C ₄ H ₁₀	$3E_{CC} + 10E_{CH} + 14\delta^C_{CH}$
CH ₃ OH	$E_{OH} + E_{CO} + 3E_{CH} + 3\delta^C_{OH} + \delta^O_{CH}$
C ₂ H ₅ OH	$E_{OH} + E_{CO} + E_{CC} + 5E_{CH} + 2\delta^C_{OH} + \delta^O_{CH} + 5\delta^C_{CH}$
(CH ₃) ₂ O	$2E_{CO} + 6E_{CH} + 6\delta^C_{OH}$
(C ₂ H ₅) ₂ O	$2E_{CO} + 10E_{CH} + 4\delta^C_{OH} + 10\delta^C_{CH}$
H ₂ O	$2E_{OH}$
H ₂ O ₂	$2E_{OH} + E_{OO} + 2\delta^O_{OH}$
O ₄	$4E_{OO}$ (?)

various compounds to be studied. The first energy difference in the normal paraffin series is $E_{CC} + 2E_{CH} + 6\delta^C_{CH}$, whereas all the other differences are of the same value $E_{CC} + 2E_{CH} + 4\delta^C_{CH}$. Rossini³ has given accurate data for methane and ethane, but unfortunately there does not seem to be available any very accurate data on the higher members of the series. For the calculation of the nuclear energy of these two molecules assignments have been made for the fundamental modes of vibration by Vedder and Mecke⁴ and by Eucken and Parts,⁵ respectively. These data together with the heat of combustion of diamond should serve to determine fairly accurately the constants E_{CC} , E_{CH} and δ^C_{CH} .

The nuclear energy is obtained as the sum of (1) the translational and rotational energy $(6/2)kT$, or $(5/2)kT$ for diatomic molecules, (2) the vibrational heat content as calculated from the Einstein equation, $\Sigma h\nu_0/(e^{h\nu_0/KT} - 1)$, and (3) the zero-point energy $\Sigma h\nu_0/2$. In the case of diamond the zero-point energy was obtained by the application of Debye's equation for the specific heat of solids. The average frequency was calculated from the maximum frequency given by specific heat data. (This average frequency is very nearly the average of the observed Raman frequencies for diamond.) The heat content of

diamond at 20°C, $\int_0^{293^\circ K} C_p dT$, amounts to only about 0.01 v.e. per bond.

As will be seen in Table IV the nuclear energies

TABLE IV.

Substance	$E - E_N$	E_N	E (v.e.)
Diamond $C_n/2n$	3.330	0.130	3.460
CH ₄	16.337	1.251	17.588
C ₂ H ₆	27.565	1.971	28.536
CH ₃ OH	20.192	1.428	21.620
C ₂ H ₅ OH	31.673	2.212	33.885
(CH ₃) ₂ O	31.172	2.120	33.292
(C ₂ H ₅) ₂ O	53.914	3.393	57.307
H ₂	4.440	0.320	4.760
H ₂ O	9.493	0.629	10.122
H ₂ O ₂	10.99	0.706	11.696
O ₃	6.15	0.258	6.408
O ₄	10.19	0.316	10.51

are by no means very small quantities, but may amount to about one-tenth of the total energy in some cases. The calculated value of δ^C_{CH} is -0.05 v.e. (Table V). Hence the contribution per

TABLE V.

$E_{CC} = 3.460$	$\delta^C_{CH} = -0.051$	$\Delta_{CH} = +0.287$
$E_{HH} = 4.760$	$\delta^O_{CH} = -0.087$	$\Delta_{OH} = ?$
$E_{OO} = ?$	$\delta^C_{OH} = -0.266$	$\Delta_{CO} = ?$
$E_{CH} = 4.397$	$\delta^C_{CO} = -0.262$	
$E_{CO} = 4.253$	$\delta^O_{OH} = ?$	
$E_{OH} = 5.061$	$\delta^O_{CO} = ?$	

CH₂ group is about 0.2 v.e. As previously stated, Thomsen's values of the heat of combustion of the higher paraffins are probably not sufficiently accurate to make a fair test, since his value for ethane, for example, differs by about 0.2 v.e. from the more recent value of Rossini. Besides, it is at present not possible to make an accurate assignment of the fundamental modes of vibration in these molecules. If one does not take into consideration the correction for nuclear energy, Thomsen's data lead to successive energy differences which differ from one another by as much as 0.3 v.e. But the average of these differences, together with the constants obtained from methane and ethane, indicates that the nuclear energy per CH₂ group should be about 0.7 v.e. on the average. This is just about the value one would estimate from a consideration of the fundamental modes of vibration similar to that of Kohlrausch⁶ in terms of group frequencies and

⁴ H. Vedder and R. Mecke, *Zeits. f. physik. Chemie* **A86**, 137 (1933).

⁵ Eucken and Parts, *Zeits. f. physik. Chemie* **B20**, 184 (1933).

⁶ K. W. F. Kohlrausch, *Der Smekal-Raman Effect*.

valence frequencies. In fact, such a consideration shows that it would require an assignment of unreasonably high frequencies to account for the total discrepancies, i.e., on the assumption that $\delta_{\text{CH}}^{\text{C}} = 0$.

Alcohols and ethers: Rossini has given accurate data on the heats of combustion of CH_3OH and $\text{C}_2\text{H}_5\text{OH}$, but for the nuclear energy it is necessary to make an estimate similar to that discussed above. Such an estimate will probably not be greatly in error, since the general range of the various frequency types is fairly well known from the Raman spectra. From these compounds and water one obtains E_{OH} , $(E_{\text{CO}} + \delta_{\text{CH}}^{\text{C}})$, and $\delta_{\text{OH}}^{\text{O}}$.

For methyl and ethyl ether it was necessary to use Thomsen's data and to estimate the nuclear frequencies as before. Such a procedure may at least give an idea of the order of magnitude of the δ_{ij}^i in question. From data on these and the previous compounds the values of E_{CO} , $\delta_{\text{CH}}^{\text{C}}$, $\delta_{\text{CO}}^{\text{C}}$ were calculated.

The value -0.266 obtained for the constant $\delta_{\text{OH}}^{\text{C}}$ seems to indicate rather definitely that some of the δ_{ij}^i may be considerably larger than $\delta_{\text{CH}}^{\text{C}} = -0.05$ v.e. It should be pointed out that the value for $\delta_{\text{OH}}^{\text{C}}$ was obtained from the accurate data of Rossini and an estimated value for the nuclear energy; and it seems very improbable that this estimated nuclear energy could be in error by an amount sufficient to account for the large value of $\delta_{\text{OH}}^{\text{C}}$. On the other hand, the values for E_{CO} , $\delta_{\text{CH}}^{\text{C}}$ and $\delta_{\text{CO}}^{\text{C}}$ are much less certain than the previous values, since they are based partially on Thomsen's data for the ethers.

A list of the constants obtained for CHO compounds is given tentatively in Table V. It is of interest to note that the δ_{ij}^i are all negative, whereas the Δ_{ij} are all positive.

Since values as great as 0.2 v.e. are rather definitely indicated by the accurate data on the alcohols, it therefore seems natural to ask the question whether in some cases the δ_{ij}^i may not be even larger, and whether the peculiarities of some compounds, or the nonexistence of others, may not to some extent be connected with the existence of large interactions. For example, on the basis of thermochemical data alone, one might speculate concerning the nature of the bonds in O_3 and O_4 as follows.

In order to obtain the bond energy E_{OO} it would be convenient to have data on a compound containing only oxygen atoms and normal bonds, similar to the case of diamond for the bond energy E_{CC} . O_2 is, of course, excluded because of its magnetic properties, etc. O_3 and O_4 are ordinarily supposed not to contain normal bonds because of the large value of E_{OO} required as compared to that obtained from H_2O_2 on the assumption of perfect additivity. Nevertheless it may be of interest to see how large a value of $\delta_{\text{OH}}^{\text{O}}$ would be required to make these compounds fit into the present scheme. O_3 would not be suitable for the calculation of the normal bond energy E_{OO} because of the considerable strain implied by the triangular structure with normal bonds. On the other hand, O_4 would probably be only very slightly strained.

From O_4 the bond energy E_{OO} is thus calculated to be 2.63 v.e. (The nuclear energy is again estimated by comparison with that of ozone.) From H_2O_2 and H_2O one then obtains a value of -0.53 v.e. for $\delta_{\text{HO}}^{\text{O}}$, which is only about twice that obtained for $\delta_{\text{OH}}^{\text{C}}$, and of the same sign. Further, if one calculates the strain energy of O_3 relative to the bond energy in O_4 , one obtains the value 1.48 v.e., which is of the same order of magnitude as that calculated by Pauling for trimethylene, 1.06 v.e. In Table VI are given the additional constants obtained from these questionable speculations:

TABLE VI.

$E_{\text{OO}} = 2.63$	$\delta_{\text{OH}}^{\text{O}} = -0.53$	$\Delta_{\text{OH}} = +1.366$
		$\Delta_{\text{CO}} = +1.198$

The latter speculations are actually probably not valid, since the spectroscopic data of Ellis and others seem to indicate that O_4 consists of two loosely bound O_2 molecules. The latter calculations were made, however, simply to ascertain how large a value of the interaction increment $\delta_{\text{HO}}^{\text{O}}$ would be required for a normal O_4 structure. Since the value obtained was only twice that obtained in other cases, the argument sometimes given for abnormal bonds, on the basis of bond energies, seems questionable.

In view of the considerable limiting importance of the interactions R_{ij}^i , as indicated by the δ_{ij}^i , it seems that Pauling's⁷ resonance

⁷ For a discussion of resonance energies see L. Pauling, reference 2, and L. Pauling and J. Sherman, J. Chem. Phys.

energies Δ_{ij} cannot be regarded as pure bond resonance energies. In fact, as was seen, the present considerations put only a sort of lower limit on the $R^i_{jj'}$, which may actually be considerably larger than is indicated by the $\delta^i_{jj'}$. Further, Pauling's bond energies were calculated without correcting for the nuclear energy, and therefore differ considerably from those obtained from the electronic energies. (The fact that Pauling's bond energies were calculated with reference to the excited state 5S of the carbon atom has no effect on the resonance energies. It may be of interest to point out that Pauling estimated the excitation energy 5S as 1.00 v.e.; whereas the extrapolation of recent spectral data of Edlén indicates a value of about 4.1 v.e. for this energy.) It also seems possible that the importance of the interaction energies, as well as of the nuclear energies, may be partially responsible for the fact that Pauling's electronegativity map cannot in all cases be correlated successfully with electric moment data.

Because of the scarcity of accurate data it does not at present seem worth while to extend the calculations to other types of compound. But mention should be made of the data of Kharasch⁸ on several isomeric heptanes. The heats of combustion of all these isomers were found to be very nearly equal to one another; whereas the energies of formation would be expected to differ from one another in general. An accurate comparison should, however, take into consideration differences in heats of vaporization and in nuclear energies. It seems possible that the

introduction of branched chains could alter these latter quantities considerably. Actually, data of Thomsen and others on the butanes and pentanes do indicate differences in the heats of combustion for the different isomers. The constancy in the observed heats of combustion for the isomeric heptanes might be due to a fortuitous compensation of the various factors involved.

In calculating the interaction constants $\delta^i_{jj'}$, it appears that these quantities may be quite considerable, but the corresponding deviations may often be compensated by nuclear energies, etc., and the departures from additivity thus masked in the ordinary previous types of analysis. It is therefore necessary that the data used should be very accurate in order to obtain reliable results. In order to make a further test of the present analysis it would be especially desirable to have combustion data on the higher alcohols, secondary and tertiary alcohols, glycols, cyclic paraffins, the esters of orthocarbonic acid, and the chlorine derivatives of methane and ethane. It is hoped that the present discussion will stimulate further research of this kind.

DOUBLE BONDS

The previous discussion was confined to molecules containing only single bonds; but in compounds where there is no appreciable resonance associated with the shift of a double bond, it is easily seen that the analysis can be extended to molecules containing double bonds, by considering a carbon atom with one or two double bonds as trivalent or bivalent, respectively, and using appropriate constants. For the case of two double bonds to a single carbon atom it would be of especial interest to have data on the compound allene.

1, 606 (1933). I am very much indebted to Dr. Sherman for helpful discussions and for kindly putting at my disposal a large amount of collected data on heats of combustion.

⁸M. S. Kharasch, Bur. Standards J. Research 2, 359 (1929).