An Empirical Bond-additivity Method for the Calculation of Diamagnetic Susceptibilities of Simple Organic Molecules.

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The Pascal system of calculating susceptibilities of diamagnetic organic molecules is composed of (*a*) atomic and bond constants and (*b*) structural correction terms. The constants of (*a*) are equivalent to a set involving bond terms only.

A modified bond-additivity system is described, in which the structural correction terms take the form of " bond interactions," the results obtained being compared with some recent experimental values. Where the Pascal system gives poor results, the new system often appears more reliable. For the relatively simple compounds studied, few serious differences have been found between experimental and calculated values. The possible extension of the system to more complex structures is briefly indicated, and attention drawn to the frequently rather large variations between different authors' experimental values.

CALCULATION of the diamagnetic susceptibilities of the simplest organic molecules, by purely theoretical methods, has as yet failed to yield values in even approximate agreement with experiment. For instance, all values for methane are much too high. In the absence of a satisfactory theoretical treatment a system of a type devised by Pascal, and recently reviewed and modified by Pacault (*Rev. sci.*, 1948, **86**, 38), can be of great value for the correlation of experimental data and for the investigation of structural problems. Recent results (Trew, *Trans. Faraday Soc.*, 1953, **49**, 604; Angus, *Bull. Soc. chim. France*, 1949, **16**, *D*, 483; Broersma, *J. Chem. Phys.*, 1949, **17**, 873) demonstrate that the method is not entirely satisfactory for all simple organic compounds. The constants suggested by Broersma (*loc. cit.*) give better results for some compounds but his method contains certain undesirable features. Contrary to the views expressed by Pascal, Pacault, and Hoarau (*Compt. rend.*, 1951, **233**, 1078) differences between calculated and experimental values cannot always be removed by modification of numerical constants, particularly for branched-chain hydrocarbons and alkyl halides.

A new empirical system of calculation of magnetic susceptibility is now presented which appears to avoid some of the difficulties encountered with the Pascal system. Only a limited number of structural types has so far been dealt with, but it is hoped to extend these later. The present system has been developed along lines suggested partly by analogy with recent theoretical treatments of other additive properties in such compounds. A considerable simplification is made possible by the use of the following characteristic property of additivity systems.

Ideal Additivity Systems.—Consider the structures which can be built up from r different elements, using only single or multiple covalent bonds, and where each particular element displays only a single numerical valency throughout. Suppose that for every one of these structures, the numerical value of some property P can be represented by the equation:

$$P = \sum_{\mathrm{J}} n_{\mathrm{J}} \cdot p_{\mathrm{J}} + \sum_{\mathrm{JK}} n_{\mathrm{JK}} \cdot p_{\mathrm{JK}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where n_{J} is the number of J atoms in the structure, p_{J} a constant characteristic of the atom J, n_{JK} the number of J–K bonds (single and multiple bonds being considered separately), and p_{JK} a constant for the bond J–K.

Under these conditions, the property P can be described as satisfying an " ideal additivity system," consisting of the constants $p_{\mathrm{J}}, p_{\mathrm{JK}}$, etc. Although an unlimited number of equations such as (1) can be written for different structures, the maximum number of these which can be independent is s, the total number of different bond types. There are however $(r + s)$ unknowns, so that the constants of the additivity system are not uniquely defined by the observed P values, and in fact there is an infinite number of different sets of constants which will satisfy the equations. A particular additivity system is defined by giving arbitrary values to ***any r*** of the constants: the remaining s constants can then be determined by solution of the equations for s experimentally measured structures (the "reference standards"). Since for every structure there exists a linear relation between the numbers of atoms and of bonds, it can be proved that all the additivity systems derived from the same set of reference standards will give the same calculated value for P of any compound outside the reference set.

The same result will hold if an "average" member of an homologous series is taken as reference standard, instead of a single substance. A formal proof of this property of ideal additivity systems is given in the Appendix, for the case of compounds containing the elements carbon, hydrogen, and oxygen only.

The Pascal System.—The set of constants given by Pascal can be divided into two distinct types of term, represented by A and B such that:

$$\chi = \sum A + \sum B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where χ is the *molar* diamagnetic susceptibility (usually denoted by χ_m). $\sum A$ consists of the constants of an ideal additivity system, as defined above, whilst $\sum B$ contains only structural correction terms. This division, although not always clear in the original form of the system, can be achieved by simple manipulation. Now since $\sum A$ and $\sum B$ are completely independent, the result of the previous section can be applied to $\sum A$. In forming $\sum A$, Pascal assigned values to bonds and atoms in very arbitrary fashion, *e.g.*, all single bonds were given zero bond term, and some atoms, such as carbonyl-oxygen, had bond and atomic terms combined. An entirely equivalent system can be constructed, in which all atomic terms are zero, and a bond term is assigned to every bond in the molecule, $\sum B$ being retained in its original form. This system will give results identical with those of the Pascal system in all cases, provided suitable values are assigned to the bond constants. Pascal, Pacault, and Hoarau (*loc. cit.*) gave a set of bond constants equivalent to the atomic and bond constants of their revised Pascal system. They attributed the equivalence of the two systems to the fact that in compounds of the lighter elements, the main contribution to the diamagnetism arises from the electrons of the bonds. This assertion, even if justified, is not needed to explain the equivalence of the two systems, which arises from the properties of ideal additivity systems. In the new system proposed here, all atomic constants will be taken as zero, and the structural correction terms for simple molecules will be expressed in a somewhat different, and more systematic, form.

The Modified Bond-additivity System.—The observation that the diamagnetic susceptibility of an unconjugated molecule could be expressed as the sum of terms characteristic of the various bonds might be most simply interpreted as indicating that the bonding electrons are accommodated in completely localised molecular orbitals, each pair of bonding electrons contributing a characteristic amount to the observed susceptibility. Contributions from inner-shell electrons would, by arguments previously adduced, be capable of inclusion in the bond terms. This is an over-simplification, and Dewar and Pettit (*J.*, 1954, **1625**) found that, in order to obtain a satisfactory interpretation of the heats of formation of some series of aliphatic compounds, it was necessary to use a perturbation method in which the localised bond structure was taken as the unperturbed system, and the bond interactions as small perturbations. In a similar way it would seem reasonable to take the deviations of the diamagnetic suceptibilities of simple aliphatic molecules from bond additivity as second-order perturbation terms arising from bond interactions. Although the analogy must not be pressed too far, agreement between calculated and experimental susceptibilities obtained so far indicates that it is not unreasonable.

In order to keep the number of bond interaction terms within reasonable limits, two assumptions are made: (*a*) that in unconjugated systems only "nearest-neighbour" interactions are important, and (*b*) that interactions involving bonds in which one atom is hydrogen can be neglected. The second assumption is the more serious, but is supported by Altmann's work (*Proc. Roy. Soc.*, 1951, *A*, **210**, 327; see also Dewar and Pettit, *loc. cit.*).

The values of the constants of the system presented here have been deduced from experimental results published within the last 12 years which, though not comprehensive, are thought to be fairly representative. The sources used are listed at the foot of Table 3. Application of the method to various classes of compound reveals the following particular features.

(a) *Saturated aliphatic hydrocarbons.* Recent work by Trew (*loc. cit.*) has shown the existence of an " end-effect " in the lower members of this series. Since definite evidence has yet to be published of a similar effect in other homologous series, no attempt will be made to include, in the present treatment, terms allowing for an end-effect. Instead, compounds containing less than seven carbon atoms will not be considered.

By analogy with Dewar and Pettit's result (*loc. cit.*), it might be expected that for a straight-chain hydrocarbon C_nH_{2n+2} :

$$\chi_n = (2n + 2)\chi_{\mathrm{C-H}} + (n - 1)\chi_{\mathrm{C-C}} + (n - 2)\lambda_{\mathrm{C-C-C}} \quad . \quad . \quad . \quad . \quad (3)$$

where $\chi_{\mathrm{C-H}}$, etc., are bond terms, and $\lambda_{\mathrm{C-C-C}}$ is an interaction term. (All susceptibility values in this and following sections are recorded in 10^{-6} c.g.s. units and the negative signs are omitted.) Since the bond terms have no theoretical significance, an arbitrary value of $\chi_{\mathrm{C-C}}$ which includes $\lambda_{\mathrm{C-C-C}}$ may be employed, and this procedure will be adopted in the following discussion.

Equation (3) then becomes :

$$\chi_n = (2n + 2)\chi_{\mathrm{C-H}} + (n - 1)\chi_{\mathrm{C-C}} - \lambda_{\mathrm{C-C-C}} \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The one term $-\lambda_{\mathrm{C-C-C}}$ must be retained since there is one less interaction term than C–C bond terms.

Similarly for the hydrocarbon $C_{n+1}H_{2n+4}$

$$\chi_{n+1} = (2n + 4)\chi_{\mathrm{C-H}} + n\chi_{\mathrm{C-C}} - \lambda_{\mathrm{C-C-C}} \quad . \quad . \quad . \quad . \quad . \quad (5)$$

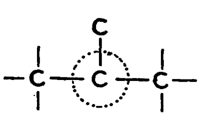
In a branched-chain saturated hydrocarbon with one tertiary carbon atom, three C–C–C bond interactions may be considered in the unit (I) as represented by broken lines. In a linear hydrocarbon with the same number of carbon atoms, there would be only two such interactions C—C—C—C. If the values of the $\lambda_{\mathrm{C-C-C}}$ were numerically the same for both cases, as present experimental data indicate, then, for the branched-chain hydrocarbon :

$$\chi_n' = (2n + 2)\chi_{\mathrm{C-H}} + (n - 1)\chi_{\mathrm{C-C}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

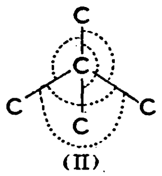
This assumption may, however, be an over-simplification (which might be shown by subsequent more precise experimental measurements) and in that case an extra term λ_3 must be introduced to denote the value for the extra C–C–C interaction due to the tertiary carbon atom; so if there are m_3 such tertiary atoms, then :

$$\chi_n' = (2n + 2)\chi_{\mathrm{C-H}} + (n - 1)\chi_{\mathrm{C-C}} - \lambda_{\mathrm{C-C-C}} + m_3\lambda_3 \quad . \quad . \quad . \quad (7)$$

Application of these equations to Trew's results (*loc. cit.*) enables the various constants to be evaluated. The numerical values giving best agreement over the whole series of compounds measured are given in Table 1.



(I)



(II)

(III)

Equation (7) implies that each additional tertiary carbon atom produces the same increase (1·4 units) in diamagnetism. There is some indication that when tertiary carbon atoms are close together their total effect is somewhat reduced, but Trew's results for isomeric decanes are consistent with equation (6) within the limits of experimental error.

Similarly, if there is a quaternary carbon atom, it might be supposed that there are six C–C–C interactions [cf. (II)] instead of three for the corresponding linear hydrocarbon [cf. (III)]. Hence, if it could be assumed that all these interactions were equal, then for a C_n hydrocarbon containing m_4 quaternary carbon atoms :

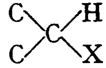
$$\chi_n'' = (2n + 2)\chi_{C-H} + (n - 1)\chi_{C-C} - (1 - 3m_4)\lambda_{C-C-C} \quad . \quad . \quad . \quad (8)$$

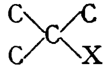
This equation is, however, not satisfied by the available data. However, an equation in reasonable agreement with experiment can be obtained by replacing the term $3m_4\lambda_{C-C-C}$ by $m_4\lambda_4$, where λ_4 is a constant for the three extra terms and is considerably less than $3m_4\lambda_{C-C-C}$. Thus for a hydrocarbon $C_nH_{2n+2}(n > 7)$ with m_3 tertiary and m_4 quaternary carbon atoms :

$$\chi = (2n + 2)\chi_{C-H} + (n - 1)\chi_{C-C} - \lambda_{C-C-C} + m_3\lambda_3 + m_4\lambda_4 \quad . \quad . \quad . \quad (9)$$

There is a close analogy between this result and that obtained by the use of group susceptibilities as suggested by Trew (*loc. cit.*).

(b) *Alkylbenzenes.* Broersma's and Trew's results (*locc. cit.*) on monoalkylbenzenes indicate that there is an abnormally low CH_2 increment in passing from benzene to toluene, but that subsequent lengthening of the carbon chain produces an increment of almost constant magnitude, with the normal value of 11·7 units. This is in harmony with spectroscopic and chemical evidence that the difference in conjugative effect of different alkyl groups is relatively small, as pointed out for instance by Dewar and Pettit (*loc. cit.*). In consequence, the susceptibilities of the monoalkylbenzenes can be reasonably accounted for by introduction of a single interaction term λ_{Ph-C}, representing the interaction of the benzene ring with the first C–C bond attached to it. Two additional points concerning the calculation of the susceptibilities of alkylbenzenes must be noted, (*a*) that $-\lambda_{C-C-C}$ must be included in all cases (except for benzene itself), and (*b*) that the nuclear carbon atom to which the side chain is attached is not regarded for the present purpose as a tertiary carbon atom. Further it is convenient to define a quantity $\chi_{C-C(ar)} = 5{\cdot}14$, such that the molar susceptibility of benzene $= 6\chi_{C-C(ar)} + 6\chi_{C-H}$. The small amount of recent work on dialkylbenzenes is insufficient to extend the system to such structures at present. It does appear that terms depending on the relative orientation of the substituents may be necessary.

(c) *Oxygen-containing compounds.* The available data on these compounds are consistent with the assumption that the three interaction terms λ_{C-C-O}, λ_{C-O-O}, and λ_{C-O-C} are roughly equal and have a value of 1·4 units. The calculation of the susceptibilities of certain of these compounds can be simplified by defining a " tertiary " carbon atom as one in a structure 

, in which X is either C or O. A " quaternary " carbon is similarly defined for the structure 

. These definitions include as special cases the conventional use of the terms in connection with the hydrocarbons. In case of doubt with regard to the application to complex structures, the alternative, but longer, method of writing down the interaction terms in full can be used, but this requires more care in dealing with compounds such as tertiary alcohols. As an example of the simpler method of calculation the susceptibility of propan-2-ol can be expressed as :

$$\chi = 7\chi_{C-H} + 2\chi_{C-C} + \chi_{C-O} + \chi_{O-H} - \lambda_{C-C-C} + \lambda_3 + \lambda_{C-C-O}$$

The particular choice of χ_{C-O} made here, necessitates the inclusion of λ_{C-C-O} in the calculated susceptibility of any alkoxy-group (primary, secondary, or tertiary) in addition to λ_3 or λ_4 where necessary. This convention avoids difficulties which would otherwise arise in compounds containing a " quaternary " carbon atom. The values of χ_{C-O} and χ_{O-H} given in Table 1 were derived principally from Angus and Hill's results (*Trans. Faraday Soc.*, **1943**, **39**, 185). Very recently Sacconi and Cini (*Atti Accad. naz. Lincei*, 1954, **14**, 237) published results for a number of alcohols, which they claim to have great accuracy. Their values are on the whole 1—2% higher than those of Angus and Hill, but the increments between different members of the series are roughly the same. If these higher values are substantiated, slightly higher values of χ_{C-O}, χ_{O-H}, or perhaps λ_{C-C-O} will be needed. This adjustment, which would necessarily involve many other terms too, would seem to be as yet somewhat premature.

No extensive measurements on simple aldehydes and ketones have yet been undertaken. According to Angus (*Nature*, 1946, **158**, 705), the aliphatic aldehydes have slightly greater susceptibilities than the isomeric ketones, the difference being of the order of 0·6 unit. From this evidence a tentative value of $\lambda_{C-C=O} = -0{\cdot}6$ will be assumed. This value does not apply in carboxylic acid derivatives, where the corresponding term is practically zero. This difference is hardly surprising in view of the very different nature of a carbonyl group in the two classes of compound.

In dealing with aromatic acids, esters, ketones, etc., only two new terms are required. One of these is λ_{Ph-O}, analogous to λ_{Ph-C} already discussed, and is a term used when an oxygen atom is directly attached to the benzene ring. The second arises in structures such as benzoic acid, where, for the first time in this work, we have to deal with a conjugated system (with the exception, of course, of the aromatic nucleus itself). The effect of simple conjugation on diamagnetic susceptibilities can be included in the system, by introduction of interaction terms between pairs of conjugated double bonds, or a double bond and an aromatic nucleus, one C–C bond apart. The term required here will be denoted $\lambda_{Ph-C=O}$. As in the case of $\lambda_{C-C=O}$, it is not surprising to find that a somewhat different value of $\lambda_{Ph-C=O}$ is required in carboxylic acid derivatives from that in aldehydes and ketones.

In the above discussion, no account has been taken of the possibility that the interaction term between two bonds may depend on the angle between them. Where the compounds considered contain oxygen atoms and double bonds, there will almost certainly be considerable variations in inter-bond angles, but the results obtained so far indicate that to a first approximation this effect can be neglected.

(d) *Alkyl halides.* Here again, the experimental data are satisfied by use of an interaction term $\lambda_{C-C-Cl} = \lambda_{C-C-Br} = 1{\cdot}4$. Thus the definition of "tertiary" and "quaternary" carbon atoms given previously can be extended to include X = Cl and Br. Calculation of the susceptibility of a particular alkyl halide then follows exactly the method used for an alcohol, *e.g.*, for *iso*propyl chloride, $(CH_3)_2CHCl$:

$$\chi = 7\chi_{C-H} + 2\chi_{C-C} + \chi_{C-Cl} - \lambda_{C-C-C} + \lambda_3 + \lambda_{C-C-Cl}$$

Values for terms such as λ_{Ph-Cl} have not yet been deduced, since they can be obtained only from the experimental value for a single compound (*e.g.*, chlorobenzene), no independent check being possible. It is also possible that in compounds of the type of benzyl chloride a small interaction term may be needed for bonds which are not "nearest neighbours," but the small amount of evidence on this point is indecisive.

Table 1 gives the numerical values of the constants so far derived.

TABLE 1. *Provisional values of bond and interaction terms.*

(a) *Bond terms* (χ_{X-Y}).

X–Y	C–C	C–H	C–C(ar)	C–O	C=O	O–H	C–Cl	C–Br
χ_{X-Y}	3·70	4·00	5·14	3·15	5·10	5·85	20·10	30·8

(b) *Interaction terms.*

$\lambda_{C-C-C} = \lambda_{C-C-O} = \lambda_{C-O-C} = \lambda_{C-C-Cl} = \lambda_{C-C-Br} = \lambda_3 = 1{\cdot}4$

$\lambda_4 = 2{\cdot}1$

$\lambda_{O-C=O} = 1{\cdot}8$ $\lambda_{Ph-C} = 0{\cdot}3$ $\lambda_{Pb-O} = 0{\cdot}9$

$\lambda_{C-C=O} = -0{\cdot}6$ (aldehydes and ketones) ; 0 (carboxylic acid derivatives)

$\lambda_{Ph-C=O} = -0{\cdot}3$ (aldehydes and ketones) ; 0 (carboxylic acid derivatives)

Comparison of Results given by the Pascal System, with those of the Modified Bond-additivity System.—From the sources listed at the foot of Table 3, experimental values are available for 95 compounds, to which the constants of Table 1 should be applicable (the lower hydrocarbons, and some compounds in which tautomeric possibilities arise, are not included). For each of these compounds, the experimental susceptibility has been compared with the values calculated by (*a*) Pascal's method, numerical values given by Pacault (*loc. cit.*) being employed, and (*b*) the modified bond-additivity method. Unfortunately, it is not uncommon to find considerable differences in the values for a particular substance reported by different workers. For instance, the values recorded for methyl acetate include 42·37 (Angus and Hill, *loc. cit.*), 42·6 (Broersma, *loc. cit.*), and 43·51 (French, *Trans. Faraday Soc.*, 1947, **43**, 356). In such cases, in order to make a fair comparison, the mean of those values which are in reasonable agreement has been used, a widely divergent value being omitted. Where there is no reasonable agreement between reported values, *e.g.*, for ethyl propionate, 65·75 (Angus and Hill, *loc. cit.*), 66·51 (Broersma, *loc. cit.*), the substance has been omitted from consideration since it is evident that a redetermination is necessary.

This procedure left a total of 85 compounds, for which the bond-additivity method gave a value within 1% of the experimental mean in all but 11 cases; of these exceptions, 9 were compounds for which only a single experimental value is available. On account of the divergences in experimental values, all figures were taken only to the nearest 0·1 unit. Table 2 gives some examples of compounds in which good agreement was obtained. It can be clearly seen that in some cases both methods give results in reasonable agreement with experiment, but in others where the Pascal system is apparently unsatisfactory, the new method gives a more reliable value. Table 3 illustrates a few of the cases in which the results of the bond-additivity method are not satisfactory.

TABLE 2.

		Calculated χ				Calculated χ	
Substance	Mean exp. χ	Bond system	Pascal	Substance	Mean exp. χ	Bond system	Pascal
n-Octane	96·5 [1, 2]	96·5	100·7	*iso*Pentyl formate ...	78·4 [6]	78·8	79·6
4-Methyloctane	109·6 [1]	109·6	112·6	Ethyl *iso*butyrate ...	78·3 [4]	78·8	80·4
4 : 5-Dimethylnonane	134·5 [1]	134·7	136·3	*n*-Propyl benzoate ...	105·0 [6]	$104{\cdot}8_5$	106·1
2 : 2 : 3-Trimethylpentane	99·9 [2]	100·0	100·7	Phenyl acetate	82·0 [6]	$82{\cdot}0_5$	$82{\cdot}0_5$
				Benzyl formate	81·4 [6]	$81{\cdot}1_5$	$82{\cdot}0_5$
Toluene	65·8 [1, 2, 3]	$65{\cdot}4_5$	66·8	Ethyl phenylacetate	104·7 [6]	$104{\cdot}7_5$	105·0
n-Butylbenzene	100·8 [1]	$100{\cdot}5_5$	102·4	Acetone	$33{\cdot}9_5$ [2, 6, 7]	33·9	33·9
4 : 6 : 6-Trimethyl-1-phenylheptane ...	173·9 [1]	$174{\cdot}2_5$	173·6	Propiophenone	84·5 [8]	84·4	84·5
				*iso*Butyl chloride ...	68·6 [6]	68·6	70·3
n-Butyl alcohol	56·0 [2, 4]	56·0	57·9	Diethyl succinate ...	104·8 [5, 9]	105·1	104·9
sec.-Butyl alcohol ...	57·3 [4]	57·4	57·9	Ethylene glycol	38·8 [2]	39·1	38·8
n-Butyric acid	55·1 [2, 4, 5]	55·0	55·4	Diethyl ether	55·1 [2]	55·1	57·9

TABLE 3.

		Calculated χ				Calculated χ	
Substance	Mean exp. χ	Bond system	Pascal	Substance	Mean exp. χ	Bond system	Pascal
2 : 2 : 4-Trimethylpentane	98·3 [2]	100·0	100·7	Ethyl formate	43·2 [2, 5]	42·3	43·5
				*iso*Propyl oxalate ...	106·0 [9]	107·9	104·9

Refs.: [1] Trew, *loc. cit.* [2] Broersma, *loc. cit.* [3] Baddar and Sugden, *J.*, 1951, 308. [4] Angus and Hill, *loc. cit.* [5] French, *loc. cit.* [6] Angus, *loc. cit.* [7] French and Trew, *Trans. Faraday Soc.*, 1945, **41**, 439. [8] Cherrier, *Compt. rend.*, 1948, **226**, 1016. [9] Angus and Stott, *Trans. Faraday Soc.*, 1953, **49**, 680.

It is concluded that the system of additive bond susceptibilities and bond interaction terms presented here is more reliable for the prediction of the diamagnetic susceptibility of these simple structures than the Pascal system, even as modified by Pacault. Further, because of the relation between the ideal additivity portion of the Pascal system to that of the system presented here, it is possible to transfer any part of the Pascal–Pacault system, which is in itself satisfactory, *e.g.*, the treatment of polycyclic and heterocyclic systems, into the new system, without interfering with the existing bond terms.

APPENDIX

Consider the structures which can be built up from the elements carbon, hydrogen, and oxygen, using the following seven bond types:

(1) C–C; (2) C=C; (3) C≡C; (4) C–H; (5) C–O; (6) C=O; (7) O–H

If for these structures the property P satisfies an ideal additivity system, then for the structure α, equation (1) takes the form:

$$P = n^{\alpha}{}_{\mathrm{C}} \cdot P_{\mathrm{C}} + n^{\alpha}{}_{\mathrm{H}} \cdot p_{\mathrm{H}} + n^{\alpha}{}_{\mathrm{O}} \cdot P_{\mathrm{O}} + n^{\alpha}{}_{1} \cdot p_{1} + \dots . n^{\alpha}{}_{7} \cdot p_{7} \quad . \quad . \quad . \quad (10)$$

where $n^{\alpha}{}_{\mathrm{C}}$, $n^{\alpha}{}_{\mathrm{H}}$, and $n^{\alpha}{}_{\mathrm{O}}$ are the number of carbon, hydrogen, and oxygen atoms and $n^{\alpha}{}_{1}$, $n^{\alpha}{}_{2}$ . . . . the number of bonds of types 1, 2 . . . . By examination of a few simple formulæ it can easily be deduced that:

$$4n^{\alpha}{}_{\mathrm{C}} = 2n^{\alpha}{}_{1} + 4n^{\alpha}{}_{2} + 6n^{\alpha}{}_{3} + n^{\alpha}{}_{4} + n^{\alpha}{}_{5} + n^{\alpha}{}_{6} \quad . \quad . \quad . \quad . \quad . \qquad (11)$$

$$n^{\alpha}{}_{\mathrm{H}} = n^{\alpha}{}_{4} + n^{\alpha}{}_{7} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (12)$$

$$2n^{\alpha}{}_{\mathrm{O}} = n^{\alpha}{}_{5} + 2n^{\alpha}{}_{6} + n^{\alpha}{}_{7} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (13)$$

By use of these three equations, $n^{\alpha}{}_{\mathrm{C}}$. $n^{\alpha}{}_{\mathrm{H}}$, and $n^{\alpha}{}_{\mathrm{O}}$ can be eliminated from equation (10). Rearranging the resulting equation, we have

$$\begin{aligned} P = {} & n^{\alpha}{}_{1}(p_1 + p_{\mathrm{C}}/2) + n^{\alpha}{}_{2}(p_2 + p_{\mathrm{C}}) + n^{\alpha}{}_{3}(p_3 + 3p_{\mathrm{C}}/2) + n^{\alpha}{}_{4}(p_4 + p_{\mathrm{C}}/4 + p_{\mathrm{H}}) \\ & + n^{\alpha}{}_{5}(p_5 + p_{\mathrm{C}}/4 + p_{\mathrm{O}}/2) + n^{\alpha}{}_{6}(p_6 + p_{\mathrm{C}}/4 + p_{\mathrm{O}}) + n^{\alpha}{}_{7}(p_7 + p_{\mathrm{H}} + p_{\mathrm{O}}/2) \\ = {} & n^{\alpha}{}_{1} \, . \, R_1 + n^{\alpha}{}_{2} \, . \, R_2 + \, . \, . \, . \, . \, n^{\alpha}{}_{7} \, . \, R_7 \quad . \quad . \quad . \quad . \qquad (14) \end{aligned}$$

where $R_1 = p_1 + p_{\mathrm{C}}/2$; $R_2 = p_2 + p_{\mathrm{C}}$; etc.

Since an equation similar to (10) can be written for every structure considered, it follows that the value of P in every case can be expressed as a linear function of seven R terms. Thus only a maximum of 7 independent equations can be written, these being assigned to the reference standards. The numerical values of P specify only the R's, not the individual bond and atomic constants, which can be assigned in any way consistent with the conditions $R_1 = p_1 + p_{\mathrm{C}}/2$, etc. The infinite number of systems defined in this way will give the same calculated value for any compound outside the reference standards, since the susceptibility in all cases will depend only on R_1, R_2, etc., which are the same in all systems. It is important to note that in defining a particular additivity system, in the cases where R is the sum of two terms only, *e.g.*, R_1, R_2, and R_3 in the above example, both terms in a particular R must not be assigned arbitrary values, otherwise the equation may prove to be inconsistent. A co-ordinate linkage, *e.g.*, C→O, could be included in the list of bonds considered, since a relation would still exist between the various n's, if not quite such a simple one as when only covalent bonds were considered.

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