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Estimation of Heats of Formation of Organic Compounds by Additivity Methods

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I. Introduction

Almost two centuries ago, Dalton published his famous atomic vision of matter. Since that time chemists have slowly and methodically converted their way of talking and thinking about chemical compounds from a macroscopic point of view (formula, physical state) to a structural one (chemical bonds). With *Chemical Abstracts* having recently described the ten millionth chemical compound, chemical structures have become almost the universal and only language in discussing this enormous number of chemical species. And so it is that in the present manuscript describing traditional, macroscopic thermochemical properties, our language will be that of molecular structure.

In the best of all possible worlds, a pharmaceutical chemist, cytologist, or paleobotanist interested in exploring the structure and reactivity of a hypothetical compound would simply turn on her 99th generation desktop supercomputer, input some minimum number of descriptive parameters, and apply Schrödinger's equation to calculate detailed (and accurate) potential energy surfaces, structural parameters, and energy relationships in the time it takes to rinse out a coffee cup. Alas, the inexorable progress of hardware, software, and brainware notwithstanding, we who would welcome that state of affairs face a vanishingly small probability of experiencing it in our professional lifetimes.

The obstacles, at this stage of development in physical chemistry, do not appear to be conceptual, but simply practical: how to structure a numerical program to solve a problem involving perhaps dozens of atoms and hundreds of electrons in a tractable interval of time, when we cannot solve analytically a problem in classical mechanics involving only three bodies. Every *a priori* computation of molecular structures and/or energetics for species of more than three or four atoms must make some compromises if the practitioner wishes to see results in a matter of hours or even days. The approximations employed depend on the results that are sought after; consequently a program/model/calculation that will give satisfactory results for, say, the bond lengths of a molecule may do poorly at vibrational frequencies, and one that calculates vibrational frequencies may fail at enthalpies.

Enthalpies (or heats of formation) are the subject of this article, and since the most important practical application of enthalpies is to explore reactivities and/or equilibria, we take a kineticist's perspective in answering the question, what is a "sufficiently accurate" prediction of an enthalpy of formation. In a general reaction,

$$A + B \rightarrow C + D$$

a shift in $\Delta_r H$ (enthalpy of reaction) of 1 kcal/mol will generally result in a change in the equilibrium constant, K_{eq}, of $\exp(-500/T)$ where T is the temperature in Kelvins. At room temperature, this means a factor of over 5 in K_{eq}; the difference between, say, 90% and 64% reaction yield. Or, in terms of the time required for reaction completion, it could also mean an increase of a factor of 5. This factor of 5 is the same whether the total enthalpy of reaction is 5 kcal/mol (a relative error of 20%) or 500 kcal/mol (an error of only 0.2%). Thus, while theoreticians have struggled to attain the stage where they can with pride calculate enthalpy quantities with 2–4 kcal/mol uncertainty, they are not solving the practical problems at hand. Is 2–4 kcal/mol uncertainty easily within the theoretician's grasp? Not invariably, as an examination of the recent literature suggests.

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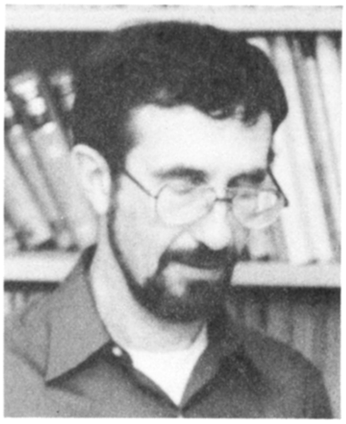
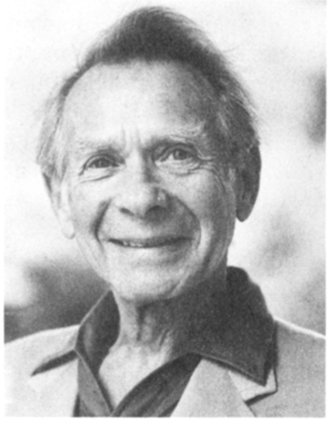


Norm Cohen received his B.A. degree in Chemistry from Reed College, Portland, OR, in 1958; his M.A. degree in Mathematics from the University of California at Berkeley in 1960; and his Ph.D. in Chemistry from the latter institution in 1963. He has been on the staff of The Aerospace Corporation since 1963 and currently is Senior Scientist in the Environmental Monitoring and Technology Department of the Space and Environment Technology Center. His research has centered on various areas of chemical kinetics, photochemistry, and thermochemistry. Areas of specialization have included the mechanisms of smog formation, theoretical prediction of reactivities of potential atmospheric pollutants, stratospheric effects of space launch activity, estimation of thermochemical properties of organic compounds, hydrocarbon combustion kinetics and thermochemistry, the kinetics of chemical laser systems, kinetics and energy transfer of hydrogen halides, and the use of trnasition-state theory for the estimation and extrapolation of reaction rate coefficients.



Sidney W. Benson received his A.B. with honors in chemistry, physics, and mathematics, in 1938 from Columbia College, and his A.M. and Ph.D. in chemical physics, in 1941 from Harvard University. He was a Professor of Chemistry at the University of Southern California from 1943 to 1964, resumed this position 1976, and is there presently. Other professional experience includes Editor-in-Chief, *International Journal of Chemical Kinetics* (1968–1983) and a position on the International Editorial Board, Elsevier Publishing Company, Holland. He has been a visiting professor at Stanford University Summers program (1968–1974), St. Andrews University, Scotland, and the University of Paris. He was the Chairman of the Department of Kinetics and Thermochemistry at Stanford Research Institute from 1963 to 1976. He has been published in more that 435 articles, books, and patents in physical chemistry, gas-phase chemistry, and thermochemistry. Recent research includes kinetics of combustion and free-radical kinetics and thermodynamics.

If the theoretician cannot solve our problems, why not turn directly to the experimentalist? The question, of course, is merely rhetorical—and not because of any Platonic bias in favor of the analytic at the expense of the synthetic. If we wish to explore the relative merits of, say, a dozen related compounds for biological activity, or atmospheric lifetimes (or any other dynamic property), we require a dozen reliably verified independent laboratory measurements. And since the number of compounds of possible interest can far exceed the number of experimentalists capable of performing the measurements, the waiting line can be exasperatingly long. Furthermore, one must not ignore the question of the probable limits of accuracy of an experimental enthalpy measurement.

What recourse has the practitioner, then? Like any good pitchmen, we discourage our readers only for the purpose of subsequently uplifting them. In the enormous gulf between the rapidly vanishing experimental measurement on the one hand, and the impossibly expensive *ab initio* calculation on the other, lies—not an abyss, but a host of semiempirical techniques that share a common—and by no means novel—philosophy: molecular properties can be systematically organized on the basis of structural similarities. What is more, some molecular parameters will have a great effect on a particular thermochemical or dynamic property, while others will be almost irrelevant. The reactivity of an aldehyde will depend only weakly (if at all) on the structure of molecule more than two carbons removed from the aldehydic site. On the other hand, the boiling point can change markedly. Thus, semiempirical procedures try to strip away the inessential and unnecessarily encumbering aspects of molecular structure in order to relate properties of interest to a tractably small number of parameters—small enough enough so that computations become routinely simple.

Semiempirical methods differ widely in the degree to which they make explicit the physical basis for their procedures: some are relatively rigorous in their justifications, while others offer no more than the pragmatic excuse that "it works". Needless to say, most chemists are much more comfortable with a procedure that can offer some explanation of why it works. A method that seems successful without explanation should not necessarily be shunned, but investigated to insure that its success is not merely fortuitous. (Sometimes making that assessment will not be trivial task, as the history of attempts to prove or disprove the astronomical relationship of planetary orbits known as Bode's Law demonstrates.)

Molecular mechanics (MM), the primary subject of this issue of *Chemical Reviews*, is basically a semiempirical method that has attained considerable sophistication. The program of MM has exquisitely been described elsewhere. Briefly, it is "... a computational method designed to give accurate structures and energies of molecules".[1] It depends on defining a small set of molecular parameters that are transferable from one molecule to another and whose values are determined by forcing fits to properties of a set of basis molecules, generally the simplest members of their respective families. Its advocates argue that "the molecular mechanics method, in principle, must be considered to be competitive with experimental determination of the structures and enthalpies of molecules".[2] MM calculations are carried out with the aid of complex computer programs that are hardly trivial, but in any case are publicly available.

If MM is considered a semiempirical approach, the subject of this article will be procedures that must be regarded as hemisemiempirical. But all are considerably simpler to apply. We review briefly several such approaches to estimating enthalpies of formation before turning more scrutinizing attention to an approach that we favor, namely Group Additivities (GA). GA shares some basic premises with MM and, we would argue, can boast a similar record of successes, without being nearly so computer-intensive. Having validated GA as a simple and reliable method, our principal GA problem today is how to make use of various kinds of experimental data for estimating numerical properties of as-yet unevaluated groups. Then, GA can be used not only to predict unmeasured properties, but also to provide a double-check on the reasonableness of published experimental data. Each of these aspects will be reviewed in succession.

What remains beyond the scope of this article is an impartial comparison of the strengths and weakness of the two approaches. Because of its simplicity of application, we would advocate GA not only as a check on experimental measurements, but also as a complement to the results of MM itself. Some practitioners might prefer to think in terms of the reverse comparison—using MM to check GA. Although both methods, as noted, depend on empirical data, they organize those data in quite different ways; consequently, what turns out to be an obstacle in one method may be handled with facility in the other. For example, GA cannot readily predict corrections for a ringed or bridged species without data for some other compound containing the same structural feature. MM, organizing empirical data in terms of force constants and geometric properties, may not suffer this limitation.

II. Methods of Estimating Enthalpies

Although our stated interest is in enthalpies of formation (at 298 K), it would serve just as well to be able to estimate enthalpies of reaction because of the definition of the latter quantity. For a chemical reaction,

$$R_1 + R_2 + \ldots R_i \leftrightarrow P_1 + P_2 + \ldots P_j$$

the enthalpy of reaction, $\Delta_r H$, is defined as the sum of enthalpies of formation of all products minus the sum of enthalpies of formation of all reagents:

$$\Delta_r H = \sum \Delta_f H_{\text{products}} - \sum \Delta_f H_{\text{reagents}} \quad (1)$$

Thus, each measured (or calculated) enthalpy of reaction gives us one new species enthalpy of formation if we know the enthalpies of formation of all the other species involved in the reaction. In the special case where the reaction is a dissociation,

$$AB \rightarrow A + B$$

the enthalpy of reaction is now the bond dissociation enthalpy (BDE). An estimation of the BDE of AB, together with the enthalpies of formation of the two resultant moieties, A and B, gives the enthalpy of the molecule AB. Another approach, which has its share of advocates, prefers the language of enthalpies of atomization rather than enthalpies of formation. The enthalpy of atomization of a molecule, A_aB_b..., is defined as

$$\Delta_a H(A_aB_b\ldots) = a\Delta_f H(A) + b\Delta_f H(B) + \ldots - \Delta_f H(A_aB_b\ldots) \quad (2)$$

where all but the last term on the right-hand side of the above equation are enthalpies of formation of the atomic constituents of molecule A_aB_b.... In the following discussion we will touch on a few older methods for estimating either BDEs, enthalpies of reaction, or enthalpies of formation, recognizing that an evaluation of each one leads to the others.

We can identify three kinds of approaches to estimating enthalpies, depending whether they relate the enthalpies to (a) global molecular properties; (b) structural molecular subunits, with regard for the location within the molecule of the subunits; and (c) structural molecular subunits regardless of location within the molecule. There are not many useful procedures of type a, other than some purely thermodynamic relationships, such as Trouton's rule, relating $\Delta_{vap}H$ to T_{bp}. Depending on one's point of view, a possible example is the Evans–Polanyi rule, which relates the activation energy for a reaction to the bond dissociation enthalpy of the bond being broken. In principle, this could give us an enthalpy if we know an activation energy; in practice, we usually employ the relationship in the other direction: to estimate an activation energy from a known BDE.

Two early methods for estimating BDEs, developed at the Soviet Institute for Chemical Physics, reviewed by Semenov,[3] fall into category b. The earlier, developed by Voevodskii, was applicable only to C–H bonds in hydrocarbons.

Voevodskii's assumptions were as follows:

(1) In an infinitely long chain of a hydrocarbon, all primary, secondary, and tertiary C–H bonds are equivalent to one another, and furthermore the groups are simply related to each other by

$$D_{\text{o,tertiary}} = D_{\text{o,secondary}} + B = D_{\text{o,primary}} + 2B \quad (3)$$

where D_o is the bond energy and B, an empirical constant.

(2) When a methyl group is introduced into the hydrocarbon, it increases the dissociation energy of a given C–H bond by an amount proportional to its distance (measured in number of C atoms) from that C–H bond

$$D_{\text{secondary}} = D_{\text{o,secondary}} + B\sum a^{ni} \quad (4)$$

where i designates the ith methyl group, and n_i is its distance from the secondary C–H bond of interest. The parameters a, B, and D_o were determined from experimental data to be 0.4, 8, and 85.6 kcal/mol, respectively. According to this formulation, the successive secondary C–H bonds in a long unbranched hydrocarbon, $CH_3CH_2CH_2CH_2CH_2$... are 93.6, 88.8, 86.9,...85.6 kcal/mol, respectively; and the secondary C–H bonds in propane and butane are 92 and 87.6 kcal/mol, respectively. This model could be updated with more recent experimental data, but it does not seem worthwhile inasmuch as we lack reliable BDE data for individual C–H bonds in large hydrocarbons. Furthermore, to the best of our knowledge, the secondary C–H bonds in propane and butane are of comparable strength, which is contrary to the assumptions of the theory. Vedeneev elaborated upon the above theory to extend it to compounds other than hydrocarbons; however, because of the problems already alluded to in the simpler theory, it seems best to pass over the modified one in silence.

An early scheme of type c was proposed by Pauling.[4] He proposed a set of constants—atomic enthalpies and BDEs—from which one could calculate any enthalpy of formation. For example, for ethane, the enthalpy of formation would be given by

$$\begin{aligned}\Delta_f H^\circ(C_2H_6) &= 6\mathrm{BDE}(\mathrm{C{-}H}) + \mathrm{BDE}(\mathrm{C{-}C}) - 2\Delta_f H(\mathrm{C}) - 6\Delta_f H(\mathrm{H})\\ &= 6(98.8) + 83.1 - 2(171.7) - 6(59.09)\\ &= -22.04\ \mathrm{kcal/mol}\end{aligned}$$

The correct value is −20.03 kcal/mol—not a large discrepancy. But for butane, C_4H_{10}, we would find

$$\begin{aligned}\Delta_f H^\circ(C_4H_{10}) &= 10\mathrm{BDE}(\mathrm{C{-}H}) + 3\mathrm{BDE}(\mathrm{C{-}C}) - 4\Delta_f H(\mathrm{C}) - 10\Delta_f \mathrm{H}(\mathrm{H})\\ &= 10(98.8) + 3(83.1) - 4(171.7) - 10(59.09)\\ &= -40.4\ \mathrm{kcal/mol}\end{aligned}$$

The correct value is −30.02 kcal/mol. We have already suggested what the difficulties with the bond additivity approach are in the brief discussion of the theory of Voevodskii: not all C–H bonds have the same BDE. Current experimental data suggest that a secondary C–H bond is 3.5 kcal/mol weaker than a primary C–H bond, thus giving rise to an error of 4 × 3.5 = 14 kcal/mol in the preceding calculation for butane.

Henceforth, we shall confine our attention to approaches of type c above: these are called *additivity* models, and c is the only one of the three categories that has proved significantly fruitful. The basic question we are concerned with is can one, conceptually, subdivide an arbitrary chemical compound into a set of smaller structural units in such a way that the thermochemical properties of that compound can be calculated from constants associated with the smaller units? That is, if we are concerned with one of these thermochemical properties, P, can we calculate this property by a relation such as

$$P(\text{Compound}) = \sum_i p(u_i) \qquad (5)$$

where u_i are the fundamental units—regardless of their position in the molecule, each of which contributes an invariant amount, p_i, to P? Such relationships are called *additivity* laws, and are fundamental in many areas of physical chemistry. An additive property is one whose value is determined by adding up the contributions from smaller units. An almost trivial example is the relationship between molecular weight of a compound and the atomic weights of its constituent atoms. Molecular weights and molecular volumes are additive; melting points or refractive indexes are not.

The earliest attempts at an enthalpy additivity scheme were prompted by the recognition that if one listed the enthalpies of straight-chain saturated hydrocarbons—methane, ethane, propane, butane, etc.—the difference between two successive enthalpies was very nearly a constant value of approximately 5.0 kcal/mol. Such the difference between successive straight chain hydrocarbons is the incremental $-CH_2-$ group, this 5.0 kcal/mol is to be associated somehow with the CH_2 structural unit. It is not possible to generalize this observation to other structural units without some ancillary assumptions, inasmuch as one cannot form a succession of compounds that differ only, say, in the number of CH_3 groups and nothing else. Nevertheless, Pitzer[5] developed a set of additivity parameters for calculating enthalpy functions $[(H^\circ - H^\circ_0)/T]$ as a function of number of C atoms and various constants. Franklin[6] extended his method to a wider range of organic compounds.

In 1958, Benson and Buss[7] (BB) discussed a hierarchy of additivity schemes and established a conceptual framework that provided a physical justification for the approach.[8] In this hierarchy, atomic additivity is the first level of approximation; the second and third are bond additivity and group additivity, respectively. (In this language, both Pauling's and Franklin's models are hybrids of two levels within the hierarchy.) Atom additivity, as observed above, is valid for such simple properties as molecular weights, but certainly not for thermochemical properties. (This should be immediately obvious, since in any balanced reaction the number of atoms is conserved; hence any atom-additive property would exhibit no net change during the course of reaction.) Bond additivities thus constitute the first nontrivial level in the BB hierarchical scheme. Although not much effort has gone into bond additivity schemes, the method offers some advantages and is discussed further in section IV.

The hierarchic level that has received the greatest attention is that of group additivities, and several schemes have been put forth. Three important schemes—since shown by Cox and Pilcher[9] to be mathematically equivalent—were developed by Laidler,[10] Allen,[11] and BB.[7] Specialized schemes for hydrocarbon enthalpies, also described and compared by Cox and Pilcher,[12] have been developed by Platt,[13] Greenshields and Rossini,[14] and Somayajulu and Zwolinski.[15] Joshi[16] proposed another additivity scheme (based on Laidler's) for alkanes and compared his calculated results for reproducing the enthalpies of 66 alkanes with those of seven earlier schemes.[13,15,17–21] Earlier schemes, not strictly group additive, were discussed and summarized by Janz in his monograph on the estimation of thermodynamic properties of organic compounds.[22] The more important approaches have been reviewed in some detail by Cox and Pilcher, and we do not repeat the details of their useful discussion; a few general remarks are sufficient for our purposes. In any case, Cox and Pilcher have demonstrated the equivalence of most group additivity schemes given appropriate algebraic transformations. Three other additivity approaches (by Yoneda,[23] Thinh *et al.*,[24] and Joback[25]) are outlined and compared by Reid *et al*[26] Yoneda's differs somewhat in practice because one starts with a base molecule (methane, cyclopentane, cyclohexane, benzene, or naphthalene) and builds up the desired molecule from it. It thus is limited to molecules that can be synthesized from one of those five starting structures. The method of Thinh *et al.* is limited to hydrocarbons. Since these methods offer no advantage over the BB method and its extension

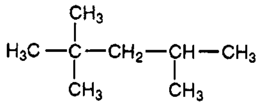


Figure 1.

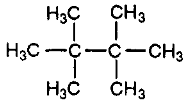


Figure 2.

and no conceptual innovations, we do not discuss them further.

III. Group Additivity: Description

A group is defined by Benson[27] as "a polyvalent atom (ligancy ≥ 2) in a molecule together with all of its ligands". A group is written as $X\text{–}(A)_i(B)_j(C)_k(D)_l$, where X is the central atom attached to *i* A atoms, *j* B atoms, etc. For example, isooctane (see Figure 1) consists of five $C\text{–}(C)(H)_3$ groups, one $C\text{–}(C)_2(H)_2$ group, one $C\text{–}(C)_3(H)$ group, and one $C\text{–}(C)_4$ group. In contrast, another octane isomer, 2,2,3,3-tetramethylbutane (Figure 2), consists of six $C\text{–}(C)(H)_3$ groups and two $C\text{–}(C)_4$ groups.

A group additivity scheme would thus provide the basis for differentiating between these two isomers. Note, however, that the groups of some octane isomers, e.g., 2-methylheptane, 3-methylheptane, and 4-methylheptane, are the same: three $C\text{–}(C)(H)_3$ groups, four $C\text{–}(C)_2(H)_2$ groups, and one $C\text{–}(C)_3(H)$ group. We could not, then, expect to differentiate between these isomers on the basis of groups alone, as defined above.

The four groups just enumerated—$C\text{–}(C)(H)_3$, $C\text{–}(C)_2(H)_2$, $C\text{–}(C)_3(H)$, and $C\text{–}(C)_4$—suffice to characterize all alkanes. We abbreviate them P, S, T, and Q, respectively, for "primary", "secondary", "tertiary", and "quaternary". (In the following paragraphs, we will use these letters alternately to designate the groups themselves or their numerical GAVs; the ambiguity should cause the reader no confusion.) However, the number of groups proliferates rapidly as one expands the parameters to encompass the entire range of organic compounds. Benson tabulates thermochemical values for 37 hydrocarbon groups, 61 oxygen-containing groups, 59 nitrogen-containing groups, 46 halogen-containing groups, 53 sulfur-containing groups, 57 organometallic groups, and 65 organophosphorous and organoboron groups.[29] In addition, there are corrections for nonbonded interactions that require some explanation.

As a prelude to discussing nonbonded interactions, it may be useful to consider the next hierarchy beyond groups, namely, components. *Components* take into account the *ligands of the ligands* of an atom. For example, one of the hydrocarbon groups is $C\text{–}(C)(H)_3$: a carbon atom bonded to three hydrogens and another carbon atom. This is the CH_3 or P, group—whether in ethane, propane, isobutane, or neopentane. *Component* additivity schemes would recognize four different kinds of P groups in hydrocarbons: P_0, P_1, P_2, and P_3, where the subscript tallies the number of hydrogen atoms attached to the *adjacent* carbon atom. Ethane thus contains two P_3 groups; propane contains two P_2 groups, isobutane contains three P_1 groups, and neopentane contains four P_0 groups. One could argue that this is still *group* additivity, if one accepts that a secondary C atoms (a C atom in a $\text{–}CH_2\text{–}$ group) is not "the same" ligand as a tertiary C atom (one in a –CH–) group, and so on; but this begs the question of atom identity.

Nevertheless, the BB group additivity approach does indeed make some allowances for different kinds of C atoms in just this way. Thus, one finds the following among the tabulated groups:

group	$\Delta_f H°(298)$, kcal/mol
$C\text{–}(C)_2(H)_2$	–4.93
$C\text{–}(C_d)(C)(H)_2$	–4.76
$C\text{–}(C_B)(C)(H)_2$	–4.86
$C\text{–}(C_t)(C)(H)_2$	–4.73

where C_d specifies a doubly bonded C atom (*i.e.*, an sp^2 C atom), C_t specifies a triply bonded C atom, and C_B specifies a C atom in a benzene ring.

Without arguing the epistemological question of whether or not these are indeed the same groups, we note that in the development of the BB group additivity method, Benson and co-workers started with the assumption that all such groups could indeed be represented as identical unless the empirical evidence demanded otherwise. Note that, in fact, the differences in enthalpies for the four groups are small—probably just barely outside the range of experimental uncertainties.

In the only full-fledged component additivity scheme that has been published to date, Pedley, Naylor, and Kirby[28] (PNK) began, in effect, with the assumption that all such components as P_0, P_1, P_2, and P_3, or the 10 analogously defined secondary components S_{ij}, and so on, are different, and require different values for their thermochemical properties. It is our opinion that, while component additivity as a method certainly has no conceptual flaws, nevertheless the database in general is neither refined nor extensive enough to provide the enormous number of components that are necessary to calculate thermochemical properties for all organic compounds.

There is another kind of correction that any additivity scheme will require: these corrections cannot be included in either group or component additivity or, for that matter, any higher hierarchical formulation. These are the corrections required because of spatial interactions that are not defined in terms of a series of chemical bonds: the most common are the 1,4, or *gauche*, interaction of two methyl groups, and the 1,5 interaction. The presence or absence of these interactions depends on relatively long-range interactions of parts of a molecule whose proximity is not implicit in bonding alone. These are the considerations that pose problems for any algorithmic approach to either group or component additivity schemes, without which the codification of computer-executable procedures for calculating thermochemical properties would be almost trivial.

Determination of Group Values. There are at least two different approaches to the determination of the numerical values of group contributions to different thermochemical properties. The first depends heavily on the experimental values for the smaller molecules, which are known to higher accuracy than those for larger analogs. Consider, for example, the enthalpy contributions for hydrocarbons. The four groups, P, S, T, and Q, have already been defined. Four relationships, involving experimental values for four small alkanes, suffice to define the numerical values of the enthalpy contributions of the four groups:

$$\Delta_f H(C_2H_6) = -20.03 = 2P$$

$$\Delta_f H(C_3H_8) = -25.02 = 2P + S$$

$$\Delta_f H(i\text{-}C_4H_{10}) = -32.07 = 3P + T$$

$$\Delta_f H(\text{neo-}C_5H_{12}) = -40.18 = 4P + Q$$

From these equations, one obtains

$$P = 0.5\Delta_f H(C_2H_6) = -10.015 \text{ kcal/mol}$$

$$S = \Delta_f H(C_3H_8) - \Delta_f H(C_2H_6) = -4.99 \text{ kcal/mol}$$

$$T = \Delta_f H(i\text{-}C_4H_{10}) - 1.5\Delta_f H(C_2H_6) = -2.03 \text{ kcal/mol}$$

$$Q = \Delta_f H(\text{neo-}C_5H_{12}) - 2\Delta_f H(C_2H_6) = -0.12 \text{ kcal/mol}$$

However, the advantage of greater precision and accuracy in the experimental data for these small alkanes is offset by the likelihood that these small molecules might be slightly irregular. In other words, the P groups in, say, hexadecane are more likely to look like the P groups in decane that in ethane. One takes this likelihood into account by redetermining the values of P, S, T, and Q on the basis of a larger database than just the four alkanes just considered. There is more than one way this can be done. For example, one could first determine the S group by looking at the list of all straight-chain alkanes and taking the average of the incremental enthalpies, since $\Delta_f H(C_nH_{2n+2}) = 2P + (n - 2)S$. Experimental values are available only for straight-chain alkanes from ethane through dodecane and three higher alkanes. If we minimize the average error for all 19 alkanes, the best value for S is −4.94; if we use only ethane through decane, the best value is −4.96. On the other hand, if we include *all* alkanes for which experimental values of $\Delta_f H(298)$ are available according to ref 28, the best value is −5.00. If we expand the database to include experimental data for alkenes, the optimum value for S drops to −4.95 again. A difference of 0.05 kcal/mol seems negligible; yet for a large hydrocarbon we can easily accumulate a discrepancy on the order of 1 kcal/mol. On the other hand, we have elsewhere presented arguments that experimental enthalpy measurements are probably no better than ±0.1 kcal/mol per carbon atom.[8] Thus, it may not be possible to choose between −4.95 and −5.00 as the best value. The uncertainties grow as one enlarges the database with other classes of compounds. Finally, one must ask—as suggested earlier—whether discrepancies are real, or could be reduced by, say, dividing the S groups into the various types of *components* and allowing the enthalpy term to be different for different components. Untimately, this is a judgement call that should not be made without careful regard for the reliability—both precision and accuracy—of the experimental database and the weighty historical stature of Occam's razor.

IV. Bond Additivity

Although the method of group additivities has proved gratifyingly successful, it cannot be denied that the large number of groups required can be a deterrent to routine application of the technique. For this reason, we should not fail to acknowledge that the much simpler method of bond additivities, while not nearly so accurate, can still be useful in the estimation of properties of molecules possessing unusual groups whose values have not yet been determined. We illustrate the method by deriving the bond additivity values (BAVs) for enthalpy of formation for the C–H, C–C, C–O, and O–H bonds. It should be stressed that these values are not the same as the bond dissociation enthalpies of the respective bonds.

BAVs can be derived from GAVs; in the following discussion we use the GAVs evaluated in section XII below. We note first that the method requires that all C–H bonds be treated as equivalent, and similarly for other bonds. Consider first the bonds of normal straight chain alkanes, namely C–H and C–C. Any straight chain alkane, C_nH_{2n+2}, can be decomposed into a sum of groups or a sum of bonds:

$$2P + (n-2)S = (n-1)[C\text{–}C] + (2n-2)[C\text{–}H]$$

where [C–C] and [C–H] designate the BAVs for the C–C and C–H bonds, respectively, and P and S designate the GAVs for the primary and secondary groups, as discussed in section II above. By taking any two values of $n > 1$, we can write two linear equations in the two unknowns, [C–C] and [C–H], which can then be solved to yield

$$[C\text{–}C] + 2[C\text{–}H] = S = -5.00$$

$$[C\text{–}C] + 6[C\text{–}H] = 2P = -20.00$$

whence

$$[C\text{–}C] = 2.5$$

$$[C\text{–}H] = -3.75$$

The value for [C–O] can be evaluated by considering an arbitrary ether, ROR. The difference in enthalpies between the ether and the alkane of the same number of carbons is, in terms of groups:

$$\Delta_f H(\text{ROR}) - \Delta_f H(\text{RR})$$
$$= 2C\text{–}(H)_2(O)(C) + O\text{–}(C)_2 - 2S$$
$$= 2(-8.1) + (-23.5) - 2(-5.0) = -29.7$$

and in terms of bonds,

$$\Delta_f H(\text{ROR}) - \Delta_f H(\text{RR}) = 2[C\text{–}O] - [C\text{–}C]$$
$$= 2[C\text{–}O] - 2.5$$

whence

$$[C\text{–}O] = {}^1/_2(-29.7 + 2.5) = -13.6$$

The [O–H] value can be derived by consideration of an arbitrary alcohol, ROH, in the same manner:

$$\Delta_f H(\text{ROH}) - \Delta_f H(\text{RH})$$
$$= C\text{–}(H)_2(O)(C) + O\text{–}(H)(C) - P$$
$$= (-8.1) + (-37.7) - (-10.0) = -35.8$$

$$\Delta_f H(\mathrm{ROH}) - \Delta_f H(\mathrm{RH}) = [\mathrm{C{-}O}] + [\mathrm{O{-}H}] - [\mathrm{C{-}H}]$$

$$= (-13.6) + [\mathrm{O{-}H}] - (-3.75)$$

whence

$$[\mathrm{O{-}H}] = -35.8 + 9.85 = -25.95$$

Benson[29] has tabulated BAVs for 32 different bonds common in organic compounds. There are, though, some special cases that do not exactly meet the requirements of strict bond additivity. For example, the benzene ring is treated as a single species with a valency of 6, and the aldehydic CO–H bond is treated as different from the simple [C–H] bond. He also has given some illustrations of how the method is applied, noting that bond additivity can predict enthalpies to within ±2 kcal/mol for some carbon compounds, but is less reliable in the case of heavy branching.

V. The Difference Method

An alternative procedure that is completely consistent with group additivity yet sometimes offers a more accurate estimating scheme is the difference method (DM). This is most useful when one knows the enthalpy of a compound—called the model compound—structurally very similar to that in which one is interested. For example, if one wishes to estimate $\Delta_f H_{298}$(2-fluorohexane), one can start with the corresponding value for 2-hexanol and make a correction for the difference between an OH and an F substituent. In the language of group additivity, one replaces the C–(O)-(H)$_2$(C) and O–(H)(C) groups by the C–(F)(H)$_2$(C) group. The rest of the molecule is assumed to be unaffected by the change, with is true given the assumptions of the group additivity method. (Possibility one needs also to make next-nearest-neighbor corrections in exercising this approach.) DM is advantageous if one is concerned with a relatively large molecule with structural properties for which accurate group values have not been identified. All the unknown parameters are then replaced by the experimental value of the structurally similar model compounds.

DM suggests itself as particularly useful if one is interested in a number of structurally similar but complex molecules for none of which has the enthalpy been measured. One then carries out measurements for one of them and uses DM to estimate the corresponding properties of the others. The method has also been used to advantage in estimating thermochemical properties of free radicals.[30,31] In general, the method will be applicable if the unknown molecule and the model differ only by a series of substitutions of groups whose numerical values are well established.

As an example, consider the following derivatives of cinnamic acid, $C_6H_5CH{=}CHCOOH$ (CA): *cis*-CA, *trans*-CA, 2-methyl-*trans*-CA, and 2-methoxy-*trans*-CA. If we take the experimental value for $\Delta_f H_{298}$ of −54 kcal/mol for *trans*-CA tabulated by PNK, we can estimate the value for the others by the difference method (where the groups are defined further in section V and the numerical values—rounded to the nearest 0.1 kcal/mol—are taken from the tables in section XII):

$$\Delta_f H_{298}(cis\text{-CA}) = -54 + cis \text{ correction} = -54 + 1.1 = -52.9$$

$$\Delta_f H_{298}(\text{2-methyl-}trans\text{-CA}) = -\,\mathrm{C_B{-}(H)} + \mathrm{C_B{-}(C)} + \mathrm{C{-}(C_B)(H)_3}$$

$$= -54 - 3.3 + 5.5 - 10.1 = -61.9$$

$$\Delta_f H_{298}(\text{2-methoxy-}trans\text{-CA}) = -54 - \mathrm{C_B{-}(H)} + \mathrm{C_B{-}(O)} + \mathrm{O{-}(C)(C_B)} + \mathrm{(C)(O)(H)_3}$$

$$= -54 - 3.3 - 0.9 - 23.0 - 10.1 = -91.3$$

The values estimated by Lias *et al.*[32] are −54, −65, and −94 kcal/mol, respectively.

VI. The Database: Experimental Methods Used To Measure Enthalpies and Their Reliability

The following discussion for alkanes is abbreviated from that of ref 8. There are four principal methods used for measuring the enthalpy of formation of a hydrocarbon: (1) determination of heat of combustion of the liquid or solid in a bomb calorimeter, (2) determination of heat of combustion of the gas or volatile liquid in a flame calorimeter, (3) determination of heat of reaction from other species whose heats of formation are well-known, and (4) determination of equilibrium constant for some reaction involving other species all of whose heats of formation are well-known.

1. Bomb Calorimetry

If a sample of solid hydrocarbon (usually in a compressed pellet; in an ampule if hygroscopic, volatile, or reactive) or liquid (in a glass or plastic ampule) is placed in an atmosphere of oxygen in a bath of fluid inside a thermally insulated container and ignited (usually by electric spark), the measured temperature rise of the heat bath can be used to determine the heat of reaction for the process

$$C_nH_m + [n + (m/4)]O_2 \rightarrow nCO_2 + (m/2)H_2O$$

from

$$\Delta_r H = \langle C_p \rangle \times \Delta T$$

The value of $\Delta_f H^\circ(C_nH_m)$ can be determined from $\Delta_r H$ (the heat of reaction), the heats of formation of the other species, and the enthalpies of the phase transitions (enantiomorphic transitions, melting, sublimation, vaporization) that take place. The experimental problems include insuring purity of reagent, complete combustion, perfect insulation (so no heat is lost), calibration for heat capacities of the temperature-measuring device (the ampule, the bath fluid, the walls of the calorimeter, and anything else involved), and accounting for the energy input from the spark. The heat capacities of the products must be known throughout the entire temperature range of combustion.

According to Stull, Westrum, and Sinke (SWS),[33] heat evolution in combustion calorimetry can be measured with a precision of 0.01%. Consider the combustion of liquid *n*-octane, for which $\Delta_r H$ at 298 K is approximately 1220 kcal/mol. The aforementioned precision means an uncertainty in heat evolution of 0.12 kcal/mol. The heats of formation of CO_2 and $H_2O_{(g)}$ are[34] −94.054 ± 0.011 and −57.10 ± 0.010 kcal/mol, respectively, at 298 K. Since 8 mol of CO_2 and 9 mol of H_2O are produced per mole of octane burned, the total uncertainty in enthalpy of formation can be as large as 0.3 kcal/mol, not taking into account uncertainties in the enthalpies of phase transitions. (In general, the uncertainty will be 0.03 kcal/mol per C atom in the alkane.) Cox and Pilcher (ref 9, Chapter 4) have compared the accuracy of various schemes for estimating $\Delta_v H$, the heat of vaporization; their comparison suggests that careful estimations are good to a few tenths of a kilocalorie per mole for two representative C_7 alkanes. Thus, on the basis of these considerations alone, we can expect experimental measurements by bomb calorimetry to have uncertainties of at least ±0.05 kcal/mol per C atom. (Most tabulated data rely on older measurements with somewhat large uncertainties.)

It is essential (although not always done) that the products of combustion be analyzed; the assumption of complete combustion is not always an accurate one. Alkane combustion proceeds in a series of steps, in which CO is always predecessor to the final product CO_2. if only 0.1% of the carbon content of an alkane is oxidized only as far as CO, the resulting error in $\Delta_f H$ will be 0.07 kcal/C atom. If an equivalent amount of carbon is reduced to graphite (solid soot/graphite is often observed after bomb combustion) the error is 0.1 kcal/C atom. In the best techniques, the amounts of CO_2 and H_2O are themselves measured to ±0.01% and the heat of combustion, $\Delta_{comb}H$, calculated on the basis of the quantities of these that have been formed.

2. Flame Calorimetry

This procedure, although useful only for the smaller hydrocarbons, avoids at least some of the complications of phase transitions that occur in bomb calorimetry. However, the technique is inherently less precise, so that the overall accuracy of enthalpy measurements is comparable for the two techniques. In a definitive flame calorimetric study of the heats of combustion of CH_4, C_2H_6, C_3H_8, C_4H_{10}, and i-C_4H_{10}, Pittam and Pilcher[35] estimated their uncertainties in the five cases to be between ±0.06 and ±0.015 kcal/mol—a good indication of the current state of the art in this field. All the alkanes were in the gaseous state, so this represents the most favorable experimental situation.

Gas-phase flame calorimetry has been used for alkanes up through C_5; liquid combustion has been used for determining enthalpies of formation of the alkanes from C_4 through C_{16}, and solid combustion, for C_{18} and higher.

3. Heats of Reaction

In principle, any reaction, not just combustion, can be used to determine $\Delta_f H$; the principal requirement is that the enthalpies of all other species involved be well-known. A frequently used reaction is the hydrogenation of the corresponding alkene; also used is isomerization, *e.g.*, the conversion of n-butane to isobutane. Other reactions include formation from H_2 and the corresponding monohalide (F, Br, Cl, or I) or, in the case of methane and ethane, dihalide. The latter techniques are generally less precise than the direct combustion. Since all three of the above techniques depend only on the First Law of Thermodynamics (any change in the internal energy of a system is equal to the sum of the heat input less the work done by the system), they are referred to as First Law Methods.

4. Equilibrium Constant Measurements

The Gibbs free-energy change for a reaction, $\Delta_r G°$, is related to the equilibrium constant by

$$\Delta_r G°_T = -RT \ln K_p$$

Differentiation with respect to T and substitution with the relationship, $G = H - TS$, gives van't Hoff's relation

$$(d \ln K_p/d\, T)_P = \Delta_r H°/RT^2 \tag{6}$$

From this, we see that the slope of a plot of $R(\ln K_p)$ vs $1/T$ gives $\Delta_r H°$. (Since $\Delta_r H°$ is not constant, the plot will exhibit some curvature.) As already discussed, from the heat of reaction, the enthalpy of formation of one species can be determined if those for the other species are known. This procedure, involving changes with temperature of enthalpy and entropy, is referred to as a Second Law method. This method has not been used for the alkanes because other, more accurate, techniques are available.

If the equilibrium constant is available only at a single temperature, one can calculate $\Delta_r S°(T)$ and evaluate $\Delta_r H°(T)$ from

$$\Delta_r H° - T\Delta_r S° = -RT \ln K_p$$

If the entropy of one of the species is not known, it can be calculated by integrating the heat capacity (either measured or calculated) from 0 K up to the temperature of interest. Since the method depends on the fact that the residual entropy at absolute zero is 0, this is called a Third Law procedure. Since there are GA methods for estimating entropies of both molecules and radicals to about 1 gibbs/mol accuracy,[29,30] this often becomes a superior method for obtaining $\Delta_r H°(T)$ when K_{eq} has been measured below about 1000 K.

VII. Use of Reaction Calorimetry To Obtain Enthalpies

While combustion calorimetry is a very direct method for obtaining heats of formation of given compounds, it is a demanding technique and beset with difficulties, some of which have been discussed above. These difficulties limit the technique to smaller organic molecules because of the inherent limitation of ±0.1 kcal/mol per atom of carbon in the compound. Thus, for a C_{10} compound we cannot expect better than ±1 kcal/mol uncertainty in $\Delta_f H°$. The problems multiply when we consider functionalized compounds such as halides, nitrogen-containing compounds, and even some classes of oxygen-containing compounds. It is difficult, for example, to obtain alcohols that are completely free of water. If they are "dry", there may be traces of borates or silicates arising from the equilibrium reaction of the alcohol with the walls of the containing vessels.

An alternative procedure is to use reaction calorimetry in solutions at room temperature or even lower to measure heats of reaction. This heat of reaction will connect heats of formation of products molecules with those of the reagents via eq 1. If all but one enthalpy of formation is known, then the unknown $\Delta_f H$ may be determined from the reaction in the solution phase. To relate it to the enthalpy of the pure compound in the liquid state, one can measure the heat of solution directly and make the appropriate correction.

Using Raney nickel catalyst, Turner[36] was able to measure heats of hydrogenation of unsaturated compounds directly. These are generally from 20 to 30 kcal/mol, so that 1 mmol of compound will liberate 20–30 cal. If this is done in, let us say, 50 cm^3 of cyclohexane solvent, the temperature rise will be approximately 0.7 °C, which can be measured with sensitive themistors to ±0.001 °C (1 part in 700). This is turn means that $\Delta_f H°$ can be measured to ±0.05 kcal/mol precision. Since catalyst can be very selective in the bonds they react with, it is possible to hydrogenate acetylenes without affecting benzenes.

Such techniques have yielded valuable data on some compounds which would be difficult to obtain in large enough quantity to perform normal combustion measurements. Because the heats are smaller, the method is much less demanding than combustion calorimetry. The method has not been exploited as much as it deserves to be. For example, our current data on the smaller alkyl fluorides may be in error by as much as 2–5 kcal/mol. It would be relatively simple to hydrofluorinate simple olefins, such as ethylene, propylene, isobutene, etc., in liquid HF at room temperature, or in HF/SbF_5 mixtures, both of which are rapid hydrofluorinaters. The heats of hydrofluorination are small—about 12 kcal/mol. Similar techniques using appropriate catalysts could be used to convert olefins to alcohols, nitroalkanes, alkyl halides, amines, and even more complex substituents. A further advantage of such techniques is that liquid chromatography can be used to analyze directly for the products and the amount of conversion that has taken place.

VIII. Use of Liquid-Phase Data To Obtain Gas-Phase Enthalpies

In the absence of direct gas-phase enthalpy data, one can use data from the liquid phase and make appropriate corrections, as exemplified in a recent study by Benson and Garland.[37] The two quantities are related by the equation

$$\Delta_f H°_{298}(g) = \Delta_f H°_{298}(l) + \Delta_v H°_{298} \qquad (7)$$

The required correction is the last term—the heat of vaporization at 298 K. However, what is usually measured and tabulated is the heat of vaporization at the boiling point, $\Delta_v H°_{T_b}$. The latter can be corrected to the former by making an approximate temperature correction:

$$\Delta_v H°_{298} = \Delta_v H°_{T_b} + (298 - T_b)\,\langle \Delta_v Cp_T \rangle \qquad (8)$$

here the last term is the average difference between heat capacities of the liquid and of the saturated vapor. An approximate expression for the temperature dependence of this term can be derived from four relationships:

(1) By definition, at the critical point

$$\Delta_v Cp_{T_c} = 0 \qquad (9)$$

(2) According to the Guye–Guldberg rule, for most regular liquids the critical point is related to the boiling point by

$$T_b/T_c = 0.625 \qquad (10)$$

(3) For many hydrocarbons,

$$\Delta_v Cp_{T_b} = -10.5 \qquad (11)$$

(4) $\Delta_v Cp$ varies approximately linearly with temperature:

$$\Delta_v Cp_{T_c} = a + bT \qquad (12)$$

From these four expressions, one can drive

$$-\Delta_v Cp_T = 28.0 - 17.5(T/T_b) \qquad (13)$$

and one can obtain $\Delta_v H°_{298}$ knowing only the values of $\Delta_v H°_{T_b}$ and T_b. Benson and Garland were thus able to assemble a database of 25 acetylenes and polyacetylenes from which to derive group values for alkynes.

A piece of data that is needed in applying eqs 7–13 is T_b, the boiling point of the compound of interest. If the structure is known, there are several empirical methods of estimating boiling points. These are described in some detail in ref 26 and are usually accurate to about 5–10 K. An error of this magnitude, in conjunction with Trouton's constant, 20 cal/mol K, will introduce an uncertainty of ±(0.1 − 0.2) kcal/mol in $\Delta_v H_{T_b}$. An error of 5% in Trouton's constant (±1 cal/mol K) will introduce an additional corresponding uncertainty of ±1 T_b cal/mol in the estimate of $\Delta_v H_{T_b}$. For example, if T_b = 500 K, the uncertainty in $\Delta_v H_{T_b}$ will be ±0.5 kcal/mol.

Alternatively, there are a number of empirical methods which have been proposed for estimating $\Delta_v H_{T_b}$ and $\Delta_v H_{298}$. Some of these are described in ref 26 and have errors on the order of about ±5%.

In a series of papers which appear to have been long neglected, Ducros *et al.*[38–41] have shown that group additivity can be applied to a series of compounds to estimate $\Delta_v H°_{298}$, whence it is possible to estimate $\Delta_f H°(g)$. For hydrocarbons, average deviations are the order of 0.1 kcal/mol.[37,39] For alcohols, which would be expected to provide a severe test because of their structural hydrogen bonding, average deviations are about 0.2 kcal/mol.[38] For the halides, nitriles, and other monofunctionalized organics, the authors chose an algebraic formula to represent the effect of chain length on primary-, secondary-, and tertiary-substituted carbons. In their next paper, Ducros *et al.* extended the method to metalorganic compounds.[40] Here, deviations are much larger.

IX. Thermochemical Analogies Used To Predict Enthalpies: Electronegativity

Bond additivity is less accurate than group additivity in estimating $\Delta_f H°$. However, it is surprisingly good at estimating $S°$ and Cp. The database requirement for a bond additivity scheme is orders of magnitude less than that required for the more accurate group additivity scheme, and so it is tempting to ask if there is not

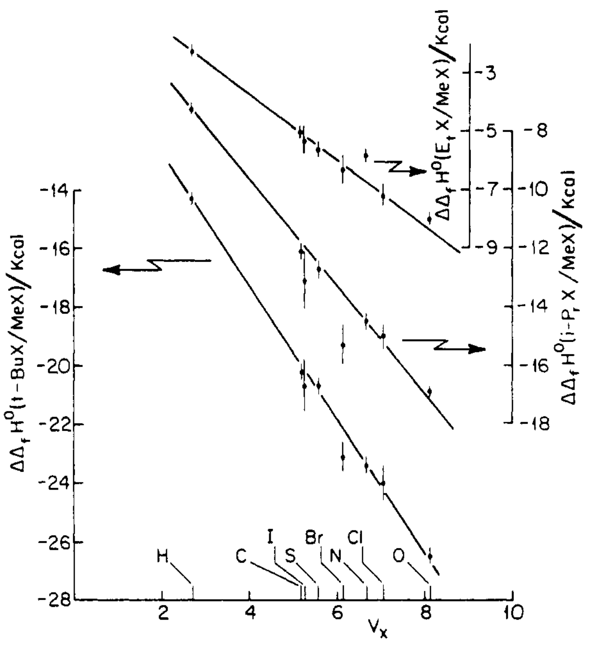


Figure 3. Linear relationships between $\Delta\Delta_f H°$ and V_X.

some way of estimating groups from bonds. What is involved in going from bond additivity to group additivity is the effect of next-nearest neighbors on the property in question. In the case of $\Delta_f H°$, we are concerned with the total energy of the compound, and this involves basically the interactions between valence electrons and the nuclei. The replacement of an H atom in a hydrocarbon by a group X involves most significantly the loss of a C–H bond and the gain of a C–X bond. At the bond additivity level this would be a constant for each such replacement. However, this is not an accurate description, and the deviations from constancy have to do with the differences in interactions of H and X with other ligands (H or C) attached to the carbon atom being substituted. Such interactions are small—on the order of 1–6 kcal/mol—and a simple scheme that can estimate them would be very attractive.

Many schemes have been suggested to estimate such interactions, some empirical and some with some theoretical foundation. Among the latter, the concept of electronegativity has played an important role. A very promising approach has been provided recently based on a new definition of electronegativity. Luo and Benson[42] have shown that linear relations exist between $\Delta_f H°(\text{MeX}) - \Delta_f H°(\text{RX})$ and V_X, where V_X is the newly defined electronegativity. Figure 3, taken from ref 42, shows three such relations for R = ethyl, isopropyl, and *tert*-butyl, while X ranges over the main group elements. V_X is defined as n_X/r_X, where n_X is the number of valence electrons of X (1 to 7), and r_X is the covalent radius of X. Deviations from the linear relation are generally within the precision of the value of $\Delta_f H°$, and better than 0.5 kcal/mol. With the availability of $\Delta_f H°$ for, let us say, CH_3X and for two different RX molecules, say, for example, RH and ROH, it is possible to evaluate the slope and intercept of the line and then to estimate values of $\Delta_f H°(\text{RX})$ for all other compounds RX where $\Delta_f H°(CH_3X)$ is known.

Such a scheme has been shown to work very well for substituted organosilicon compounds.[43,44] In the case of alkyl fluorides, this scheme has revealed inconsistencies in reported values of $\Delta_f H°$ for ethyl, isopropyl, and *tert*-butyl fluorides.[42] It has been extended to many other series where it would be expected to be useful. For example, one would expect that although carbon atoms in saturated compounds differ from those in unsaturates, there should be similar linear relations in their $\Delta_f H°$s upon substitution. Thus, it seems possible that $\Delta_f H°(C_2H_5X) - \Delta_f H°(C_2H_3X)$ would show a linear relation when plotted against V_X. Luo and Holmes[45] have shown that there is in fact a nearly linear relation in $[\Delta_f H°(CH_3X) - \Delta_f H°(C_2H_3X)]$ plotted against V_X. However, only for X = halogens or hydrogen do the values fall on the line within the uncertainty of the data, while X = F, OH, and NH_2 compounds seem to lie on a separate line, suggesting that in the sequence C_2H_3X, with X ranging over the isoelectronic sequence NH_2, OH, and F, the stability of C_2H_3X decreases with increasing electronegativity.

A more accurate relation explored by Luo and Holmes[46] is that $\Delta_f H°(\text{phenylX}) - \Delta_f H°(\text{vinylX}) = 7.1 \pm 1.5$ kcal/mol for a broad spectrum of compounds. This uncertainty is probably within the accuracy of the data. They do note a small number of exceptions (four) to this rule for which the deviations are large. However, in every case one of the $\Delta_f H°$ values is in error. One expects better agreement in this case than in the preceding example inasmuch as both benzene and ethylene have similar carbon atoms in sp^2 valence states. Luo and Holmes have demonstrated that the following relations are obeyed to within the accuracy of available experimental data:

$$\Delta_f H°(\text{allylX}) - \Delta_f H°(\text{ethylX}) = 25.2 \pm 0.5 \text{ kcal/mol}$$

$$\Delta_f H°(\text{benzylX}) - \Delta_f H°(\text{ethylX}) = 32.0 \pm 1.0 \text{ kcal/mol}$$

Since there are many more $\Delta_f H°$ known for ethylX than for allylX or benzylX, this permits the estimation of many unknown allyl or benzyl compounds from $\Delta_f H°(\text{ethylX})$. This has also led to changes in values for allylI and benzylI that had been based on questionable experimental reports. It is likely that a relation similar to the above holds for $\Delta_f H°(\text{propargylX})$ and $\Delta_f H°(\text{ethylX})$.

Many similar relations remain to be explored. For example: from the standpoint of *bond* additivity, the CH_2 groups in the following unsaturated compounds are the same:

$$CH_2{=}CH_2 \quad CH_2{=}NH \quad CH_2{=}O$$

This isoelectronic sequence, however, shows large changes in dipole moment and increasing positive character of the CH_2 group going from ethylene to formaldehyde. One would expect this to be reflected in an increasing stability on substituting a methyl group in place of an H atom in the CH_2. In fact, one finds that $\Delta_f H°(CH_3CH{=}CH_2) - \Delta_f H°(C_2H_4) = -7.6$ kcal/mol and $\Delta_f H(CH_3CHO) - \Delta_f H°(CH_2O) = -13.6$ kcal/mol. Hence, one might guess that $\Delta_f H°(CH_3CHNH) - \Delta_f H°(CH_2NH)$ would be close to the average, or −10.6 kcal/mol. $\Delta_f H°(CH_2NH)$ is 22 ± 1 kcal/mol, but $\Delta_f H°(CH_3CHNH)$ has not been measured. It would be surprising if its value differs from 11.4 kcal/mol, estimated from the average, by more than 1 kcal/mol.

In similar fashion, substituting CH_3 for H in acetylene (C_2H_2) leads to 10.5 kcal/mol greater stability, compared to 7.6 kcal/mol for similar substitution in ethylene

(C_2H_4). We anticipate that the CH group in acetylene is more electropositive than the CH_2 group in ethylene, in agreement with the above. In the case of HCN, one expects the CH group to be more electropositive than in C_2H_2, and thus it is not surprising that CH_3CN is more stable than HCN by 13 kcal/mol.

Some Applications. The most common application of estimation methods is the prediction of equilibrium constants, K_{eq}, for specified stoichiometric reactions. This in turn requires an estimation of the values of $\Delta_f H°$, $S°$, and $C_p°(T)$ for each species—products and reagents—occurring in the reaction. One reason thermochemistry has received relatively limited attention from chemists has been that in facing problems such as predicting a given K_{eq}, one or more of the needed thermochemical values, generally a value of $\Delta_f H°$, has been missing. Group additivity has provided only limited relief for such problems since GAV tables are incomplete. In the absence of pertinent groups, we can turn to the much more general database available for bond additivity, tempered by "judicious" considerations of electronegativity. Let us explore some examples.

$\Delta_f H°(CH_3NO)$, the heat of formation of nitrosomethane, is available from kinetic studies as 16.6 kcal/mol. Can we deduce from this a value for $\Delta_f H°(C_2H_5NO)$? To deduce $\Delta_f H°(C_2H_5NO)$ we need to have a value for the group [C(H)$_2$(C)(NO)]. Alternatively, and less abstractly, this is equivalent to asking the question, "What is the difference in $\Delta_f H°$ of MeX and EtX?" On the assumption that the best guide is the electronegativity of the NO group, we can look at the following differences in $\Delta_f H°$, which are known:

$$\Delta\Delta_f H°[(CH_3CH{=}CH_2) - (C_2H_5CH{=}CH_2)] = 5.0 \text{ kcal/mol}$$

$$\Delta\Delta_f H°[(CH_3CH{=}O) - (C_2H_5CH{=}O)] = 5.3 \text{ kcal/mol}$$

Both the vinyl group ($CH{=}CH_2$) and the aldehyde group ($CH{=}O$) are isoelectronic with the (NO) group. We would expect NO to be intermediate between them in electronegativity, and thus a value

$$\Delta\Delta_f H°[(CH_3NO) - (C_2H_5NO)] = 5.2 \pm 0.2 \text{ kcal/mol}$$

seems entirely appropriate. This immediately leads to a value of $\Delta_f H°(C_2H_5NO)$ = 11.4 kcal/mol, and since

$$\Delta_f H°(C_2H_5NO) = \Delta_f H°[C\text{–}(H)_3(C)] + \Delta_f H°[C\text{–}(H)_2(C)(NO)]$$

we find, for the unknown group

$$\Delta_f H°[C\text{–}(H)_2(C)(NO)] = 21.6 \text{ kcal/mol}$$

Another example is provided by the modeling of combustion chemistry where NO is a minor product and the compound, $CH_2{=}CHNO$ is of potential importance. We can start with the "known" compound, nitrosoethane (C_2H_5NO), and ask the question, "What is the enthalpy of dehydrogenation, $\Delta_{dehyd}H$, to $CH_2{=}CHNO$?" Again, isoelectronic sequences are of interest:

$$\Delta_{hyd}H°[(CH_2{=}CHCH{=}CH_2) \rightarrow (C_2H_5CH{=}CH_2)] = -26 \text{ kcal/mol}$$

$$\Delta_{hyd}H°[(CH_2{=}CHCH{=}O) \rightarrow (C_2H_5CH{=}O)] = -27.2 \text{ kcal/mol}$$

Again, it seems reasonable to assign an intermediate value of −26.6 ± 0.6 kcal/mol to the enthalpy of hydrogenation of $CH_2{=}CHNO$, and so from our derived value of $\Delta_f H°(C_2H_5NO)$ = 11.4 kcal/mol, we estimate $\Delta_f H°(CH_2CHNO)$ = 38.0 kcal/mol. From this, in turn, we can further estimate the group value

$$\Delta_f H[C_d\text{–}(H)(NO)] = 31.7 \text{ kcal/mol}$$

It is tempting to see how far such analogies can be extended. For example, it is known that $\Delta_f H°(CH_2{=}CHC{\equiv}CH)$(vinylacetylene) is 68.7 kcal/mol. Can we make an estimate of $\Delta_f H°(HC{\equiv}CNO)$ using the above estimated value for $\Delta_f H°$(vinylNO)?

Again, using hydrogenation as a starting point, we have

$$\Delta_{hyd}H°[CH_2{=}CHC{\equiv}CH \rightarrow CH_2{=}CHCH{=}CH_2] = -42.7 \text{ kcal/mol}$$

Note that the second π bond in acetylene is at right angles to the first and cannot conjugate with the vinyl group in vinylacetylene. On this basis, we might conclude that the same will be true of the vinylNO and vinylCHO compounds, and so the −42.7 kcal/mol might be directly transferable. This would then give a value of 80.7 kcal/mol for $\Delta_f H°(CH{\equiv}CNO)$ and 24.9 kcal/mol for $\Delta_f H°(HC{\equiv}CCHO)$. The uncertainty here is greater than in the previous estimates since we have only one value from which to extrapolate.

X. Temperature Dependence of Enthalpies

The discussion so far has been confined to the single temperature of 298 K. Needless to say, one often requires data at other temperatures; conversely, one may have data for different species at different temperatures, and needs to make temperature correlations to bring all data to the same temperature. Since

$$\Delta H_{T_1} - \Delta H_{T_2} = \int_{T_1}^{T_2} Cp \, dT$$

enthalpy values at one temperature can be corrected to a different temperature if the temperature dependence of the heat capacity between the two temperatures is known; and if ΔHs associated with any phase changes are known. Fortunately, group additivity has proved very successful at estimating heat capacities; most of the references that have been cited in connection with GAVs for ΔH_{298} also evaluate and discuss GAVs for Cp either for a discrete range of temperatures from 298 K up to 1500 K or at least 1000 K, or present polynomial expressions for a Cp as a function of T, such as

$$Cp = a + bT + cT^2 + dT^3 + eT^4$$

The evaluation and manipulation of these coefficients is discussed in ref 8. Phase-change enthalpies were discussed in section VIII.

XI. Free Radicals and Bond Dissociation Enthalpies

Free radicals can be partitioned into groups in the same manner as can stable molecules. Thus, the *sec-*

butyl radical, $CH_3{}^{\bullet}CHCH_2CH_3$, consists of the groups $C{-}(C^{\bullet})(H)_3$, $C^{\bullet}{-}(C)_2(H)$, S, and P. There are two classes of radical groups: radical-centered groups, such as $C^{\bullet}{-}(C)_2(H)$, and radical–adjacent groups, such as $C{-}(C^{\bullet})(H)_3$. Every radical with more than one group contains one of the former and at least one of the latter groups. The method of group additivities is assumed to apply equally well to free radicals, although the data base is hardly sufficient for establishing the precision of this approach. The procedure for evaluating GAVs is best illustrated by considering the radical groups encountered in alkyl radicals. The following discussion is abridged from ref 8, except that some of the experimental enthalpies have been reevaluated.[31] In order to apply group additivity rules to alkyl radicals, seven new groups (identified below as *a*–*g*) have to be defined and assigned enthalpy values. As O'Neal and Benson[47] have pointed out, only six of the group values are linearly independent; one of the seven can be assigned arbitrarily. As they did, we choose to set $d = P$. The other six terms can be calculated from experimentally determined enthalpies of formation of the radicals ethyl, *n*-propyl, isopropyl, *tert*-butyl, isobutyl, and neopentyl. The enthalpy of *sec*-butyl can be substituted for that of either *n*-propyl or isopropyl. The relationships are as follows:

$$a = \Delta fH°[C^{\bullet}{-}(C)(H)_2] = \Delta_f H°(\text{Et}) - P \qquad (14)$$

$$b = \Delta_f H°[C^{\bullet}{-}(C)_2(H)] = \Delta_f H°(i\text{-Pr}) - 2P \qquad (15)$$

$$c = \Delta_f H°[C^{\bullet}{-}(C)_3] = \Delta_f H°(t\text{-Bu}) - 3P \qquad (16)$$

$$d = \Delta_f H°[C{-}(C^{\bullet})(H)_3] \qquad (17)$$

$$e = \Delta_f H°[C{-}(C)(C^{\bullet})(H)_2] = \Delta_f H°(n\text{-Pr}) - \Delta_f H°(\text{Et}) \qquad (18)$$

$$= \Delta_f H°(s\text{-Bu}) - 2P - b \qquad (19)$$

$$f = \Delta_f H°[C{-}(C)_2(C^{\bullet})(H)] = \Delta_f H°(i\text{-Bu}) - \Delta_f H°(\text{Et}) - P \qquad (20)$$

$$g = \Delta_f H°[C{-}(C)_3(C^{\bullet})] = \Delta_f H°(\text{neo-Pn}) - \Delta_f H°(\text{Et}) - 2P \qquad (21)$$

In order to be consistent, the two relationships involving *e* (eqs 17 and 18) require that

$$\Delta_f H°(s\text{-Bu}) = \Delta_f H°(n\text{-Pr}) + \Delta_f H°(i\text{-Pr}) - \Delta_f H°(\text{Et}) \qquad (22)$$

It is beyond the scope of this article to reassess the best current values for radical enthalpies, which were reviewed briefly in ref 31 but are still subject to some lingering uncertainty. The values assumed here for the radical enthalpies of formation are as follows: methyl, 35.1 ± 0.15; ethyl, 28.4 ± 0.5; *n*-propyl, 23.4 ± 1.0; isopropyl, 21.0 ± 1.0; *sec*-butyl, 16.0 ± 1.0; *tert*-butyl, 11.0 ± 1.5; isobutyl, 16.0 ± 1.0; and neopentyl, 9.2 ± 1.0.

With these values, we can calculate the GAVs for radical groups *a* through *g*:

$$a = 38.4$$

$$b = 41.0$$

$$c = 41.0$$

$$d = -10.0 \text{ (assumed)}$$

$$e = -5.0$$

$$f = -2.4$$

$$g = 0.8$$

It should be noticed that the values for e and f are the same as those for the corresponding nonradical groups, *i.e.*,

$$\Delta_f H°[C{-}(C)(C^{\bullet})(H)_2] = \Delta_f H°[C{-}(C)_2(H)_2]$$

$$\Delta_f H°[C{-}(C)_2(C^{\bullet})(H)] = \Delta_f H°[C{-}(C)_3(H)_2]$$

and, by assumption,

$$\Delta_f H°[C{-}(C^{\bullet})(H)_3] = \Delta_f H°[C{-}(C)(H)_3]$$

There are not necessarily precisely equal, but their equivalence is certainly consistent with the experimental data. Hence, for simplicity, we set the respective pairs equal. This outcome points the way to simple estimation of other radical–adjacent group values in the absence of any reliable experimental data suggesting otherwise. Direct radical group evaluation will require the experimental enthalpy of formation of a free radical containing the group of interest. This is equivalent to determining a bond dissociation enthalpy, since the definition of the latter is

$$\text{BDE(A–B)} = \Delta_f H(\text{A}^{\bullet}) + \Delta_f H(\text{B}^{\bullet}) - \Delta_f H(\text{AB})$$

Dilling[48] has proposed a useful relationship between GAVs involving radical-centered groups:

$$[C^{\bullet}{-}(X)(Y)(Z)] - [C^{\bullet}{-}(H)(Y)(Z)] = (0.86 \pm 0.03)\{[C{-}(H)(X)(Y)(Z)] - [C{-}(H)_2(Y)(Z)]\} - (4.64 \pm 0.62)$$

That is, replacing an H atom ligand in a radical with some other ligand, X, is almost energetically equivalent to replacing one of 2 H ligands in a molecule with the same X ligand. The relationship was derived by examining 89 sets of data each involving four related groups. He then applies the relationship to derive new GAVs for some three dozen groups not previously evaluated.

XII. Group Additivity Values: Current Status

Almost 25 years ago, in a lengthy review in this Journal, Benson and co-workers[49] summarized what were then the best available thermochemical data and used those data to evaluate group properties for a large number of classes of organic compounds. Since then, some of their group additivity values (GAVs) have been revised in the light of better experimental data. In this section we review the progress made in developing better GAVs, comment on their reliabilities, and note what are at present the obstacles, if any, to more reliable values. Unless specifically noted otherwise, all values

Table I. Group Additivity Values for Alkane Enthalpies, $\Delta_f H°_{298}$

group	1949[a]	1969	1976	1992	no. in database[b]
$C-(C)(H)_3$ = P	-10.12	-10.08	-10.2	-10.00	248
$C-(C)_2(H)_2$ = S	-4.926	-4.95	-4.93	-5.00	296
$C-(C)_3(H)$ = T	-1.09	-1.90	-1.90	-2.40	44
$C-(C)_4$ = Q	1.74	0.50	0.50	-0.10[c]	36
gauche (1-4) correction = G		0.80	0.80	0.80	199
1-5 correction = F			1.5	1.60	16

[a] From Franklin, ref 6. [b] Total number of groups in experimental database as tabulated in Table 9 of ref 8; these include all compounds tabulated by Pedley, Naylor, and Kirby (ref 28). [c] This value is with the revised *gauche* counting scheme described in the text of ref 8; with conventional *gauche* counting, a value of +0.10 is preferred.

refer to the gas phase at 298 K. The usual approach is to tabulate only $\Delta_f H(298)$ directly, and use temperature-dependent values of Cp to calculate enthalpies at temperatures above 298 K. Furthermore, the extraction of enthalpies from experimental data occasionally requires knowledge of the entropy. Many of the references we cite also comment on recent evaluations of Cp and *S* data subsequent to ref 49.

1. Alkanes

Alkanes, providing the largest reliable database and being the starting point for any systematic analysis, have been subject to the most intensive scrutiny. The enthalpy value of ref 49 were modified slightly by Benson in *Thermochemical Kinetics*.[50] Recently, Cohen and Benson[8] reexamined the available data and recommended a new set of GAVs. The three sets of enthalpy GAVs for the four basic alkane groups are shown in Table I. Franklin's[6] earlier evaluations are also shown for historical interest. However, Frankin's method does not constitute simply an alternate set of GAVs, since some of his structural units, *e.g.* —CH═CH— (*trans*) and —CH═CH— (*cis*), are not groups as defined in section III.

The values tabulated in 1969 (ref 49) were the same as originally proposed by Benson and Buss in 1958 (ref 7). The variation with the data base used in the recommended value for the S group has already been discussed; as pointed out, the value of -5.00 in ref 8 was derived from the full alkane database up through C_{18}. But if the database is enlarged to include alkenes as well, it appears that the value of -4.95 is better. The values for T, Q, and F are subject to greater uncertainty than the others because there are comparatively few of these groups in the database. The value for G is subject to uncertainty for another reason, discussed at length in ref 8. The basic problem stems from the fact that the data for highly branched alkanes suggest that successive *gauche* groups do not contribute a constant amount of destabilizing the molecule. In ref 8 an alternative *gauche* counting scheme was proposed in order to improve the predictions for highly branched alkanes without sacrificing the basic rules of group additivity *per se*. By using the revised counting scheme the average error in calculated $\Delta_f H(298)$ is 0.58 kcal/mol for the 64 alkanes tabulated by PHK (for standard *gauche* counting, the average error is 0.77 kcal/mol).

Table II. Group Additivity Values for Alkene Enthalpies, $\Delta_f H°_{298}$

group	previous value[a]	this work	no. in database[b]
$C_d-(H)_2$	6.26	6.27	41
$C_d-(C)(H)$	8.59	8.55	58
$C_d-(C)_2$	10.34	10.19	21
$C_d-(C_d)(H)$	6.78	6.78	7
$C_d-(C_d)(C)$	8.88	8.76	3
$C_d-(C_d)_2$	4.6[c]		
$C-(C_d)(H)_3$	-10.08	-10.00	51
$C-(C_d)(C)(H)_2$	-4.76	-4.80	35
$C-(C_d)(C)_2(H)$	-1.48	-1.67	8
$C-(C_d)(C)_3$	1.68	1.77	7
$C-(C_d)_2(H)_2$	-4.29	-4.30	1
C_a (allyl: —C═C═C—)	34.2	34.00	5
cis-correction	1.00	1.10	28
alkene *gauche* correction	0.50	0.80	5

[a] From ref 29 unless noted otherwise. [b] Total number of groups in alkene and alkadiene database, based on compounds listed in ref 28. [c] From Stein (ref 51), citing DIPPR (ref 52).

There is no question, though, that this may very well be a detail that is not adequately accounted for at the level of approximation of group additivities. The question will remain open until the experimental database can be improved—both in terms of number of compounds studied and in the precision (not to mention the accuracy as well) of the measurements.

2. Alkenes

Table II lists the GAVs of ref 29 and compares them with revision derived in this study. The database consists of 39 compounds listed by PNK. The revisions reduce the average error from 0.42 to 0.36 kcal/mol—perhaps a negligible improvement in view of the uncertainties in the individual measurements. However, while either set of values is therefore acceptable, it is important to maintain consistency, and not mix values from the two different sets.

3. Alkynes

With the alkynes we run into serious problems regarding the size of the database. Some previous evaluations use the alkyne data tabulated by Stull, Westrum, and Sinke[53] who list 24 alkynes (including biacetylene and vinylacetylene). All of these save biacetylene and vinylacetylene are taken from the tabulations of Rossini *et al.*[54] Most of them are estimated values. PNK list only four compounds for which reliable measurements have been reported: ethyne, propyne, but-1-yne, and but-2-yne. From these data we could derive at best group values for only four of the groups listed: $C_t-(H)$, $C_t-(C)$, $C-(C_t)(H)_3$, and $C-(C_t)(C)(H)_2$, but there is little redundancy in the database. Alternatively, one could fit all the data in SWS, but the resultant group values would represent only fittings to estimations and would be of little more than academic interest. Recently, Benson and Garland[37] circumvented the shortage of experimental data for $\Delta_f H°_{298}(g)$ by using the larger body of data available for $\Delta_f H°_{298}(l)$ for 16 alkynes and enthalpies of hydrogenation for five phenylalkynes. The necessary calculations were discussed above in section VIII. The column in Table III labeled "this work" corrects some

Table III. Group Additivity Values for Alkyne Enthalpies, $\Delta_f H^\circ_{298}$

group	1976 value[a]	other work[b]	this work[c]	no. in database[d]
C_t–(H)	26.93	27.2	27.1	20
C_t–(C)	27.55	27.4	27.3	27
C_t–(C_t)	27.55	25.8[e]	25.3	4
C_t–(C_d)	29.2	28.5[f]	27.9	5
C–(C_t)$(H)_3$	−10.08	−10.0	−10.0	5
C–(C_t)(C)$(H)_2$	−4.73	−4.7	−4.74	18
C–(C_t)$(C)_2$(H)	−1.72	−1.7	−1.54	1
C–(C_t)$(C)_3$		0.6	1.32	4
C_d–(C_t)(H)	6.78	6.78	6.74	5
C_t–(C_B)	29.2	24.3[g]	24.6	8
C_B–(C_t)	5.68	5.68	5.68	8
C_B–(H)	3.3	3.3	3.31	40
ene–yne *cis* correction		−0.6	−0.1	2

[a] From ref 29. [b] Evaluated by Benson and Garland (ref 37), unless noted otherwise. [c] Based on groups in database (see last column). [d] Total number of groups in database consisting of compounds cited in ref 37. [e] Reevaluated by Stein and Fahr (ref 55) in 1985 to be 25.6. [f] Reevaluated by Stein and Fahr (ref 55) in 1985 to be 28.2. [g] Reevaluated by Stein and Fahr (ref 55) in 1985 to be 24.7.

Table IV. Group Additivity Values for Aromatic Enthalpies, $\Delta_f H^\circ_{298}$

group	previous value[a]	this work[b]	no. in database[c]
C_B–(H)	3.30	3.29	105 (472)
C_B–(C)	5.51	5.49	37 (95)
C–(C_B)$(H)_3$	−10.08	−10.00	20 (55)
C–(C_B)(C)$(H)_2$	−4.86	−4.91	9 (19)
C–(C_B)$(C)_2$(H)[d]	−0.98	−0.98	2 (2)
C–(C_B)$(C)_3$	2.81	2.92	6 (6)
C–$(C_B)_2(H)_2$[e]		−10.66	0 (3)
C–$(C_B)_3$(H)[f]		−1.00	0 (1)
C–$(C_B)_4$[g]		7.32	0 (1)
C–(C_B)(C_d)$(H)_2$	−4.29	−4.29	0 (0)
C_B–(C_B)[h]	4.96	5.23	2 (24)
C_B–(C_d)	5.68	5.80	0 (5)
C_d–(C_B)(C)	8.64	8.64	0 (0)
C_d–(C_B)(H)	6.78	6.80	0 (5)
C_d–$(C_B)_2$	8.0	8.0	0 (0)
C_t–(C_B)	29.2	29.2	0 (0)
ortho correction[i]	0.57	0.68	5 (33)

[a] From ref 29. [b] Based on database of last column. [c] Total number of groups in database consisting of compounds cited by PNK (ref 28) and Lias (ref 32). For groups where this number is 0, the larger database including unsaturated aromatics, naphthalene, anthracene, and other PCAHs (numbers in parentheses), was used. [d] Value based on cumene only. [e] Value based on diphenylmethane only. [f] Value based on triphenylmethane only. [g] Value based on tetraphenylmethane only. [h] Value based on biphenyl only. [i] Correction for interaction of two groups ortho to one another on a benzene ring, as in 1,2-dimethylbenzene (= *o*-xylene); essentially a 1,4-interaction.

minor numerical errors in the work of ref 37. A new nonbonded interaction (not considered explicitly in the 1969 or 1976 evaluations) is introduced: the "ene–yne *cis* correction, which occurs in molecules of the form *cis*-(n + 2)-alken-n-yne. Three groups listed in the table involve C_B, the C atom of the benzene ring; because of the large number of these groups in this database reasonably accurate values could be derived for these groups. The value for the C_B–(H) group compares very well to that derived in the following section for a completely independent database.

4. Aromatics

The benzene molecule and alkylbenzenes present two new groups: C_B–(H) and C_B–(C), representing the benzene ring C-atom bonded, respectively, to an H atom or to an alkyl C atom. (The other two ligands of a C_B atom are always two more C_B atoms.) We also need to allow for the possibility that an alkyl C atom attached to a phenyl ring [C–(C_B)(X)(Y)(Z)] is not equivalent to a similarly placed C atom attached to an alkyl C atom [C–(C)(X)(Y)(Z)]. The evaluations usually start from the assumption that they are equivalent, and the values are modified only if there seems sufficient evidence in the database to do so. This procedure led to three new groups in this evaluation not defined separately previously: C–$(C_B)_2(H)_2$, C–$(C_B)_3$(H), and C–$(C_B)_4$. The last two occur in our database only in triphenylmethane and tetraphenylmethane, respectively; there is thus considerable uncertainty in their values. The C_B–(C_B) group represents the C atom in a benzene ring bonded to a phenyl group, as in biphenyl. The "ortho" correction is for the nonbonded interaction between two adjacent ligands on a phenyl ring, for example, between the two methyls in *o*-xylene. PNK list 19 saturated benzene derivatives for which gas-phase enthalpies are available, and Lias *et al.*[32] list four more; from these values, which differ slightly from those tabulated by SWS, we have rederived group values, as shown in the third column of Table IV. Two of the groups are not represented by the compounds in the database considered; the values listed in the table are lifted from the 1976 evaluation. Contrariwise, three groups are evaluated here which were not considered separately previously.

5. Cycloalkanes and Cycloalkenes

For reasons that were discussed in ref 7 and recapitulated in ref 8, cyclic molecules cannot be evaluated by group additivity rules without some *ad hoc* assumptions. For example, one could proceed from the assumption that the $-CH_2-$ groups in cyclohexane are not the same as the common S group and proceed accordingly. Unfortunately, one soon discovers that the $-CH_2-$ groups in cyclopentane are not equivalent to those in cyclohexane, and similarly for other cycloalkanes or cycloalkenes. Benson and co-workers (ref 49, Table 33; ref 29, p 273) adopted the expedient of simply applying an additive correction to the group additivity-calculated thermochemical properties of ring compounds—retaining the assumption that all $-CH_2-$ groups in rings were equivalent to the S group. One then calculates the enthalpy of a cycloalkane, C_nH_{2n}, by the relationship

$$\Delta_f H^\circ(C_nH_{2n}) = n[\Delta_f H^\circ(S)] + F_n \qquad (23)$$

where F_n is the correction factor for the n-membered cycloalkane. The corrections for n-membered cycloalkanes and cycloalkenes are listed in Table V.

Reference 29 tabulates values for many more ring compounds; however, those listed are sufficient to suggest that there is no obvious correlation among the various correction factors. In other words, one cannot deduce a correction factor for an arbitrary ring from those for other rings. The use of group additivity, therefore, requires an *ad hoc* empirical correction factor for each ring structure of interest. However, the

Table V. Corrections To Be Applied to Ring–Compound Enthalpy Estimates

n	cyclo-alkane[a]	cyclo-alkene[b]	cyclo-alkadiene[b]	cyclo-alkatriene[b]
3	27.7	53.7		
4	26.8	29.8		
5	7.1	5.9	6.0	
6	0.7	1.4	4.8 (1,3) 0.5 (1,3)	
7	6.8	5.4	6.6 (1,3)	4.7 (1,3,5)
8	10.3	6.0 (*cis*) 15.3 (*trans*)		8.9 (1,3,5)
9	13.3	9.9 (*cis*) 12.8 (*trans*)		
10	13.1			
11	12.1			
12	5.0			
13	6.1			
14	12.8 (5.8[c])			
15	3.0			
16	3.1[d]			
17	−2.1[d]			

[a] Values from ref 8. [b] Values from ref 29. [c] See text. [d] This evaluation.

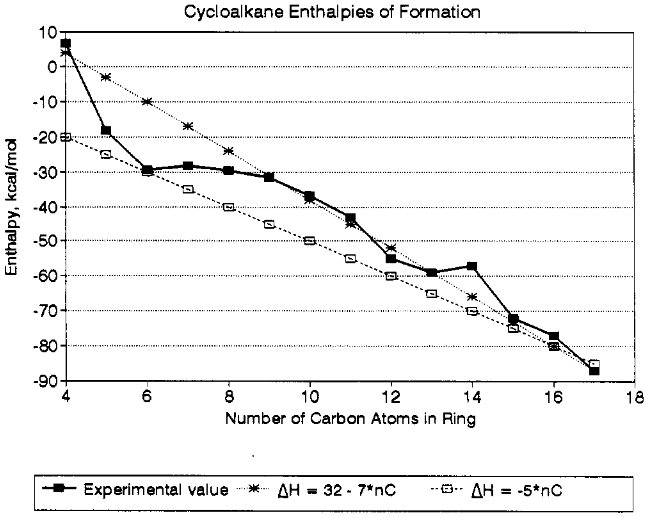


Figure 4. Experimental enthalpies of formation (298 K) of cycloalkanes as function of numbe rof carbon atoms in ring.

correction factors are independent of side chains attached to the ring, so they are by no means applicable to only a single molecule. It is possible that the disarray is not so dismal as appears from these data. If we plot the enthalpies for cycloalkanes *vs* number of carbons, we get the rather jagged graph of Figure 4. Consider, though, the possibility that the measurement for cyclotetradecane is in error by about 7 kcal/mol; if we replot the data, we can now fit the enthalpies (for $n > 8$) within about ±3 kcal/mol by

$$\Delta_f H^\circ(C_nH_{2n}) = -7n + 32 \qquad (24)$$

Of course, one cannot argue that the enthalpy contribution per $-CH_2-$ group is really −7 kcal/mol, since clearly, as n becomes large enough, a ring should not look any different from the corresponding straight chain alkane, for which the contribution is −5 kcal/mol per $-CH_2-$ group. And indeed, the graph shows that the relation, $\Delta_f H^\circ(C_nH_{2n}) = -5n$ should converge with eq 24 just beyond the range of the data. (The deviation of the experimental enthalpy from $-5n$ can be taken as a measure of the ring strain.) The point worth noting, though, is that any simple intercomparison made with the expectation of some systematic regularity suggests that the value for cyclotetradecane is unexpected. In fact, that values was not measured by the same group that reported the accepted results for all the other cycloalkanes from C_{10} through C_{17}.[56] At very least, another, independent, measurement seems desirable.

Table VI. Group Additivity Values for Fused Ring Enthalpies, $\Delta_f H^\circ_{298}$

group	1976[a]	1989[b]	this work[c]	no. in database[d]
$C_{BF}-(C_{BF})(C_B)_2$	4.8	6.90	5.53	67
$C_{BF}-(C_{BF})_2(C_B)$	3.7	4.09	4.34	37
$C_{BF}-(C_{BF})_3$	1.5	−0.65	−0.54	2
naphthalene 1,8 correction[e]			5.3	0 (5)
phenanthrene 4,5 correction[f]			9.3	0 (5)

[a] Values from ref 29. [b] From Moiseeva, Dorofeeva, and Jorish who also reevaluated $C_B-(H)$ to be 2.77. [c] Based on compounds included in database. [d] Based on compounds cited in refs 28 and 32. [e] Correction for interaction of two methyl groups on 2 C_{BS} straddling a C_{BF}, as in 1,8-dimethylnaphthalene (essentially a 1,5-type of interaction). [f] Correction for interaction of two methyl groups on 2 C_{BS} adjacent to 2 C_{BF} groups, as in 4,5-dimethylphenanthrene (essentially a 1,6-type of interaction).

The introduction of a single ring—or even more than one non-neighboring ring—into a hydrocarbon can be accommodated within the framework of group additivity satisfactorily. However, for each ring element one needs to apply a new correction factor to estimate the enthalpy of formation (or any other thermochemical property, for that matter). The calculations are subject to much larger uncertainties than in the case of the alkanes and alkenes because the experimental database is much smaller and the experimental values are subject to larger imprecisions. At present the tabulations of ref 29 represent the latest evaluations of group contributions and ring corrections, although we are in the process of updating many of these.

6. Polycyclic Aromatic Hydrocarbons (PCAHs)

Fused ring compounds (naphthalene, anthracene, phenanthrene, etc.) introduce a new type of aromatic C atom: the atom at the junction of two rings, designated C_{BF}. Three new groups immediately result, depending whether the C_{BF} atom is bonded to one, two, or three other C_{BF} atoms: $C_{BF}-(C_{BF})(C_B)_2$, $C_{BF}-(C_{BF})_2(C_B)$, and $C_{BF}-(C_{BF})_3$. [$C_{BF}-(C_B)_2$ occurs in naphthalene and anthracene; $C_{BF}-(C_{BF})_2(C_B)$, in phenanthracene; and $C_{BF}-(C_{BF})_3$, in 3,4-benzopyrene, coronene, and larger graphite-like structures or their derivatives.] These groups serve to characterize the smaller, more common fused-ring compounds such as derivatives of naphthalene, anthracene, and phenanthrene. However, larger fused rings pose further complications because each successive benzenoid ring is not structurally identical to its predecessors.

Moiseeva *et al.*[57] recently reported a reevaluation of the principal PCAH group values for heat capacities and entropies, as well as enthalpies. They determined new values for the groups $C_{BF}-(C_{BF})(C_B)_2$, $C_{BF}-(C_{BF})_2(C_B)$, and $C_{Bf}-(C_{BF})_3$, basing their evaluation on experimental data from PNK for nine PCAHs. Their results are shown in Table VI; however, we are unable to obtain satisfactory agreement with their values without drastically altering other, well-established

GAVs, and hence do not recommend their use. Instead, we list our own revised values.

While the new groups, $\mathrm{C_{BF}}$, $\mathrm{C_{BF}{-}(C_{BF})(C_B)_2}$, $\mathrm{C_{BF}{-}(C_{BF})_2(C_B)}$, and $\mathrm{C_{BF}{-}(C_{BF})_3}$, can take into account the properties of the rings themselves, one still needs to look at the effect on ring substituents. Thus for example, the nonring C atoms in 1,2-dimethylnaphthalene will not be the same distance apart as those in 2,3-dimethylnaphthalene, and so on. Furthermore, while benzene is perfectly planar, naphthalene possibly is not, and anthracene almost certainly is not. Higher analogs show more variations in bond lengths, angles, and nonplanarity. Thus, one cannot assume that all fused rings are precisely characterized by the groups so far identified: $\mathrm{C_B{-}(H)}$, $\mathrm{C_B{-}(C)}$, $\mathrm{C_{BF}}$, $\mathrm{C_{BF}{-}(C_{BF})_2}$, $\mathrm{C_{BF}{-}(C_{BF})_2(C_B)}$, and $\mathrm{C_{BF}{-}(C_{BF})_3}$, together with the earlier groups. As a consequence, when we try to predict enthalpies for 40 substituted naphthalenes, anthracenes, benzanthracenes, chrysenes, naphthacenes, and benzophenthrenes, we find an average error of almost 1.8 kcal/mol (with respect to experimental values tabulated by PNK or Lias *et al.*), with errors as large as 6–10 kcal/mol in several cases. It is highly probable that there are substantial errors in some of the experimental values, since all the dubious values are from unreplicated studies. This is clearly an area in which group additivity needs to be developed further, but the effort hardly will pay until the database is substantially larger, and the uncertainties considerably reduced.

7. Oxygenated Compounds

The group values for oxygen-containing groups in aliphatic organic compounds have been reevaluated using as a database experimental measurements compiled for 85 compounds ($\mathrm{C_1}$'s through $\mathrm{C_8}$'s) with 1 to 4 O atoms. As implied in the procedure of ref 49, certain groups always occur together, for example: $\mathrm{O{-}(H)(C_d)}$ with either $\mathrm{C_d{-}(O)(H)}$ or $\mathrm{C_d{-}(O)(C)}$, $\mathrm{O{-}(H)(C_B)}$ with $\mathrm{C_B{-}(O)}$, $\mathrm{O{-}(H)(C_t)}$ with $\mathrm{C_t{-}(O)}$, $\mathrm{CO{-}(H)(C_B)}$ with $\mathrm{C_B{-}(CO)}$, and $\mathrm{CO{-}(H)(C_t)}$ with $\mathrm{C_t{-}(CO)}$. Thus, one can evaluate only the sum of the two groups and not each one independently. Consequently, Benson *et al.* chose to assign $\mathrm{O{-}(H)(C_d)} = \mathrm{O{-}(H)(C_B)} = \mathrm{O{-}(H)(C_t)} = \mathrm{O{-}(H)(C)}$; and $\mathrm{CO{-}(H)(C_B)} = \mathrm{CO{-}(H)(C_t)} = \mathrm{CO{-}(H)(C)}$. The remaining group value is then selected to optimize agreement with experimental data. A similar procedure is applied in the case of some of the sulfur-containing groups in section XII.10.

Four groups not previously characterized have been added to the list: $\mathrm{C{-}(H)(O)_3}$, $\mathrm{O{-}(H)(C_d)}$, $\mathrm{C{-}(O)_3(C)}$, and $\mathrm{CO{-}(O)_2}$. The selected values (listed in Table VII) match the experimental values for the compounds in the database with an average error of ±1.09 kcal/mol; for 43 compounds with only one oxygen atom, the average error is only ±0.36 kcal/mol. For a few compounds ($\mathrm{CH_3COOH}$, methyl acrylate, 2,3-butanediol, and dioxybismethanol) the error is inexplicably large—more than 5 kcal/mol. Aromatic oxygen-containing groups and other oxygen-containing ring groups have not been reevaluated yet.

Table VII. Group Additivity Values for Oxygenated Compounds, $\Delta_fH^\circ_{298}$

group	1976[a]	other work	this work[b]	no. in database[c]
O–(H)(C)	-37.9		-37.85	30
O–(H)(O)	-16.3		-16.27	2
O–(H)(CO)	-58.1		-58.0	14
O–(C)(O)	-4.5		-4.5	8
O–(C)(CO)	-43.1		-43.1	6
$\mathrm{O{-}(C)_2}$	-23.2		-23.5	16
O–(O)(CO)	-19.0		-19.0	0
$\mathrm{O{-}(O)_2}$	[19.0][d]	14.7[e]	19.0	0
$\mathrm{O{-}(CO)_2}$	-46.5		-46.2	2
$\mathrm{C{-}(H)_3(O)}$	-10.08		-10.0	22
$\mathrm{C{-}(H)(O)_3}$		-28.7[e]	-26.1	1
$\mathrm{C{-}(H)_2(O)(C)}$	-8.1		-8.1	29
$\mathrm{C{-}(H)(O)(C)_2}$	-7.2		-7.2	11
$\mathrm{C{-}(H)_2(O)_2}$	-16.1		-16.7	3
$\mathrm{C{-}(H)(O)_2(C)}$	-16.3		-15.8	1
$\mathrm{C{-}(O)(C)_3}$	-6.6		-6.6	6
$\mathrm{C{-}(O)_2(C)_2}$	-18.6		-18.6	0
$\mathrm{C{-}(O)_3(C)}$		-29.6[e]	-26.0	1
$\mathrm{C{-}(H)_2(C)(CO)}$	-5.2		-5.2	12
$\mathrm{C{-}(H)(C)_2(CO)}$	[-1.7]		-1.7	3
$\mathrm{C{-}(C)_3(CO)}$	1.4		1.4	0
$\mathrm{C{-}(H)_2(CO)_2}$	-7.6		-7.6	1
CO–(H)(C)	-29.1		-29.4	5
CO–(H)(O)	-32.1		-32.1	2
CO–(H)(CO)	-25.3		-25.3	3
$\mathrm{CO{-}(C)_2}$	-31.4		-31.7	8
CO–(C)(O)	-35.1		-35.2	12
CO–(C)(CO)	-29.2		-29.1	3
$\mathrm{CO{-}(O)_2}$	-29.9	-29.7[e]	-29.9	1
CO–(O)(CO)	29.3		-29.3	4
$\mathrm{O{-}(C)(C_d)}$	-30.5		-30.5	4
$\mathrm{O{-}(C_d)_2}$	-33.0		-33.0	1
$\mathrm{O{-}(C_d)(H)}$			-44.6	1
$\mathrm{O{-}(C_d)(CO)}$	-45.2		-44.8	1
$\mathrm{C{-}(H)_2(O)(C_d)}$	-6.5		-6.9	1
$\mathrm{C{-}(H)(O)(C)(C_d)}$		-6.5[e]		0
$\mathrm{C{-}(H)_2(CO)(C_d)}$	-3.8		-3.8	0
$\mathrm{C{-}(H)(O)(C)(C_t)}$		-6.5[e]		0
$\mathrm{C{-}(H)_2(O)(C_t)}$	-6.5			0
$\mathrm{C{-}(H)_2(CO)(C_t)}$	-5.4			0
$\mathrm{C_d{-}(H)(O)}$	8.6		8.6	7
$\mathrm{C_d{-}(O)(C)}$	10.3			0
$\mathrm{C_d{-}(H)(CO)}$	5.0		5.0	6
$\mathrm{C_d{-}(O)(CO)}$	11.6			0
$\mathrm{C_d{-}(O)(C_d)}$	8.9			0
$\mathrm{C_d{-}(C)(CO)}$	7.5			0
$\mathrm{C_d{-}(C_d)(CO)}$		4.9[e]		0
$\mathrm{CO{-}(H)(C_d)}$	-29.1		-27.6	1
$\mathrm{CO{-}(O)(C_d)}$	-32.0		-28.7	5
$\mathrm{CO{-}(H)(C_t)}$	-29.1			0
$\mathrm{O{-}(H)(C_B)}$	-37.9			0
$\mathrm{O{-}(C)(C_B)}$	-23.0		-21.7	1
$\mathrm{O{-}(C_B)_2}$	-21.1		-18.9	1
$\mathrm{O{-}(C_B)(C_d)}$		-25.0[e]		0
$\mathrm{O{-}(C_B)(CO)}$	-36.7			0
$\mathrm{C{-}(H)(O)(C)(C_B)}$		-8.1[e]		0
$\mathrm{C{-}(H)_2(O)(C_B)}$	-8.1			0
$\mathrm{C{-}(H)_2(CO)(C_B)}$	-5.4			0
$\mathrm{C_B{-}(O)}$	-0.9			0
$\mathrm{C_B{-}(CO)}$	3.7			0
$\mathrm{CO{-}(H)(C_B)}$	-29.1			0
$\mathrm{CO{-}(C)(C_B)}$	-30.9			0
$\mathrm{CO{-}(O)(C_B)}$		-36.6[e]		0
$\mathrm{CO{-}(CO)(C_B)}$	-26.8			0
$\mathrm{CO{-}(C_B)_2}$	-25.8			0
Oxygen gauche	0.0		0.0	2
Ether gauche	0.5		0.5	3
Di-tertiary ether	7.8		7.8	1

[a] Values from ref 29, unless noted otherwise. [b] Based on compounds included in database. [c] Based on compounds cited in ref 28. [d] Bracketed values are best estimates. [e] Stein (ref 51), based on his reevaluation.

8. Nitrogenous Compounds

Subsequent to the 1976 compilation of Benson (ref 29), Shaw,[58-61] Batt and Robinson,[62] and Stein[51] re-

Table VIII. Group Additivity Values for Halogenated Compound Enthalpies, $\Delta_f H^\circ_{298}$

group	1976[a]	other sources	this work[b]	no. in database[c]	group	1976[a]	other sources	this work[b]	no. in database[c]
$\mathrm{C{-}(F)_3(C)}$	-158.4		-158.4	9	$\mathrm{C_d{-}(F)(Cl)}$		-43.2[f]		0
$\mathrm{C{-}(F)_2(H)(C)}$	-102.3		-116.8	2	$\mathrm{C_d{-}(F)(Br)}$		-31.3[f]		0
$\mathrm{C{-}(F)(H)_2(C)}$	-51.5		-53.2	2	$\mathrm{C_d{-}(Cl)(Br)}$		6.5[f]		0
$\mathrm{C{-}(F)_2(C)_2}$	-97.0		-105.0	1	$\mathrm{C_t{-}(F)}$			-1.3	1
$\mathrm{C{-}(F)(H)(C)_2}$	-49.0		-50.0	1	$\mathrm{C_t{-}(Cl)}$		17.8[f]	33.7	1
$\mathrm{C{-}(F)(C)_3}$	-48.5		-48.5	0	$\mathrm{C_t{-}(Br)}$		23.6[f]	31.9	1
$\mathrm{C{-}(Cl)_3(C)}$	-20.7	-24.9[f]	-18.0	5	$\mathrm{C_t{-}(I)}$	-0.3	33.8[f]		0
$\mathrm{C{-}(Cl)_2(H)(C)}$	-18.9		-17.9	5	$\mathrm{C{-}(F)(H)_2(C_d)}$			-51.9	1
$\mathrm{C{-}(Cl)(H)_2(C)}$	-16.5	-16.8;[d] -15.6[f]	-16.7	12	$\mathrm{C{-}(Cl)(H)_2(C_d)}$			-15.0	1
$\mathrm{C{-}(Cl)_2(C)_2}$	-22.0	-14.82[d]	-21.4	1	$\mathrm{C{-}(Br)(H)_2(C_d)}$			-3.0	1
$\mathrm{C{-}(Cl)(H)(C)_2}$	-14.8		-14.6	3	$\mathrm{C{-}(I)(H)_2(C_d)}$			8.1	1
$\mathrm{C{-}(Cl)(C)_3}$	-12.8	-13.06[d]	-13.5	1	$\mathrm{C{-}(C_d)(Br)(H)_2}$		-3.4[f]		
$\mathrm{C{-}(Br)_3(C)}$		12.8[f]		0	$\mathrm{C_B{-}(F)}$	-42.8			
$\mathrm{C{-}(Br)_2(H)(C)}$			1.0	0	$\mathrm{C_B{-}(Cl)}$	-3.8			
$\mathrm{C{-}(Br)(H)_2(C)}$	-5.4		-4.5	14	$\mathrm{C_B{-}(Br)}$	10.7	8.7[f]		
$\mathrm{C{-}(Br)_2(C)_2}$				0	$\mathrm{C_B{-}(I)}$	24.0	22.5[f]		
$\mathrm{C{-}(Br)(H)(C)_2}$	-3.4		-3.4	5	$\mathrm{C{-}(C_B)(F)_3}$	-162.7			
$\mathrm{C{-}(Br)(C)_3}$	-0.4		-2.0	2	$\mathrm{C{-}(C_B)(Br)(H)_2}$	-5.1	-6.9[f]		
$\mathrm{C{-}(I)_3(C)}$				0	$\mathrm{C{-}(C_B)(I)(H)_2}$	8.4			
$\mathrm{C{-}(I)_2(H)(C)}$				0	$\mathrm{CO{-}(C)(F)}$		-95.5[f]		
$\mathrm{C{-}(I)(H)_2(C)}$	8.0		8.0	6	$\mathrm{CO{-}(C)(I)}$		-20.0[f]		
$\mathrm{C{-}(I)_2(C)_2}$				0	$\mathrm{CO{-}(O)(Cl)}$		-49.2[f]		
$\mathrm{C{-}(I)(H)(C)_2}$	10.5		10.5	3	$\mathrm{CO{-}(C_B)(Br)}$		-31.7[f]		
$\mathrm{C{-}(I)(C)_3}$	13.0		12.8	1	$\mathrm{CO{-}(C_B)(I)}$		-17.6[f]		
$\mathrm{C{-}(F)_2(Cl)(C)}$	-106.3		-110.3	6	$\mathrm{C{-}(CO)(Cl)(C)(H)}$		-22.0[f]		
$\mathrm{C{-}(F)(Cl)_2(C)}$			-62.0	3	$\mathrm{C{-}(CO)(Cl)(H)_2}$		-10.2[f]		
$\mathrm{C{-}(F)_2(Br)(C)}$			-94.3	6	$\mathrm{C{-}(CO)(Cl)_2(H)}$		-12.0[f]		
$\mathrm{C{-}(F)_2(I)(C)}$			-82.6	1	$\mathrm{C{-}(CO)(Cl)_3}$		-10.5, -11.8[f]		
$\mathrm{C{-}(F)(Cl)(H)(C)}$			-64.9	3	$\mathrm{C{-}(C)(F)(NO_2)_2}$		-46.8[e]		
$\mathrm{C{-}(Cl)(Br)(H)(C)}$		-10.1[f]	-6.4	3	$\mathrm{C{-}(C_B)(F)(NO_2)_2}$		-66.2[e]		
$\mathrm{C{-}(F)(Cl)(Br)(C)}$			-62.6	1	$\mathrm{C{-}(C_d)(CN)(H)_2}$		22.9[f]		
$\mathrm{C_d{-}(F)(H)}$	-37.6		-35.1	5	$\mathrm{C{-}(N)(F)_3}$		-161.2[e]		
$\mathrm{C_d{-}(F)_2}$	-77.5		-78.2	7	$\mathrm{C{-}(C)(Cl)(O)(H)}$	-21.6			
$\mathrm{C_d{-}(F)(C)}$			-32.5	1	$\mathrm{C{-}(I)(O)(H)_2}$		3.8[f]		
$\mathrm{C_d{-}(Cl)(H)}$	-1.2		0.6	7	$\mathrm{N{-}(C)(F)_2}$	-7.8			
$\mathrm{C_d{-}(Cl)_2}$	-1.8		-1.7	4	$\mathrm{N{-}(C)(F)(NO_2)}$		-0.1[f]		
$\mathrm{C_d{-}(Cl)(C)}$	-2.1		-1.3	1	*o*-F–F	5.0			
$\mathrm{C_d{-}(Br)(H)}$	11.0	12.7[f]	11.5	3	*o*-Cl–Cl	2.2			
$\mathrm{C_d{-}(Br)_2}$		7.5[f]		0	*o*-alkyl–halogen	0.6[g]			
$\mathrm{C_d{-}(Br)(C)}$				0	*cis*-halogen–halogen	-0.3		-0.1	9
$\mathrm{C_d{-}(I)(H)}$	24.5		24.8	6	*cis*-halogen–alkyl	-0.8		-0.4	3
$\mathrm{C_d{-}(I)_2}$				0	*gauche*	1.0[h]			
$\mathrm{C_d{-}(I)(C)}$				0					

[a] Values from ref 29. [b] Based on compounds included in database. [c] Based on compounds cited in ref 28. [d] From ref 64. [e] From Batt and Robinson (ref 62). [f] From Stein (ref 51). [g] Correction applies for halogen = Cl, Br, or I only. [h] Correction applies for halogen = Cl, Br, I; none for halogen–methyl or F–halogen.

evaluated some of the nitrogen-containing groups and added some new ones. If these evaluations are used in calculations, it should be in conjunction with the original 1976 GAVs and not the new values tabulated here, inasmuch as they would not be quite consistent.

9. Halogenated Compounds

Reference 29 listed updated GAVs for many of the halogenated organic compounds originally evaluated in Benson *et al.*[49] Not included there were a series of values deduced by Alfassi *et al.*[63] for halopropene (allyl halide) groups. Kretkowski and Bozzelli[64] have recently reevaluated GAVs for all thermodynamic properties of monochloroalkanes, using literature data of PNK, SWS, and the Texas A&M Thermodynamics Research Center and, alternatively, the hydrocarbon group values of ref 29 or of ref 8. Their results for the former case are listed in Table VIII. In either case, the values differ only slightly from the 1976 evaluation. Also listed in Table VIII are revised evaluations for most halogen GAVs based on a database of 62 haloalkanes and 31 haloalkenes/ynes taken from PNK and Lias *et al.* GAVs for this class of compounds are still not entirely satisfactory, inasmuch as the average deviation for this group of 93 halogenated alkanes is approximately ±1.5 kcal/mol. It is entirely possible that some of the difficulty lies in faulty experimental measurements, many of which have not been replicated.

However, some discrepancies cannot be blamed on experimental errors. Consideration of the halogenated compounds—fluorinated ones in particular—raises a complication hiterto not discussed and, in fact, not amenable to group additivity treatment: we refer to the effects of highly polarizing substituents. The problem is illustrated by consideration of three compounds: C_2H_6, CH_3CF_3, and C_2F_6. Their enthalpies are reasonably well established as −20, −179, and −321 kcal/mol, respectively. Only two groups comprise these three compounds: $\mathrm{C{-}(H)_3}$ and $\mathrm{C{-}(F)_3}$. If group additivity were valid, we would expect $\Delta_f H^\circ(CH_3CF_3) = {}^1/_2[\Delta_f H^\circ(C_2H_6) + \Delta_f H^\circ(C_2H_6)] = -170.5$ kcal/mol. In fact, CH_3CF_3 is 8.5 kcal/mol more stable than that,

Table IX. Group Additivity Values for Organosulfur Compound Enthalpies, $\Delta_f H°_{298}$

group	1976/ 1978[a]	other work	this work[b]	no. in database[c]
$C-(H)_3(S)$[d]	−10.08		−10.00	12
$C-(C)(H)_2(S)$	−5.65		−5.64	60
$C-(C)_2(H)(S)$	−2.64		−2.95	16
$C-(C)_3(S)$	−0.55		−0.29	11
$C-(H)_2(S)_2$	−6.0		−6.00	0
$C-(C_d)(H)_2(S)$	−6.45		−6.33	2
$C-(C_B)(H)_2(S)$	−4.73		−4.73	3
$C_B-(S)$[e]	−1.80		−0.90	6
$C_d-(H)(S)$[f]	8.56		8.60	6
$C_d-(C)(S)$	10.93		10.92	1
$S-(C)(H)$	4.62		4.68	30
$S-(C)_2$	11.51		11.34	30
$S-(C_d)(C)$	13.0		11.99	1
$S-(C_d)_2$	13.5	9.85[g]	13.47	3
$S-(C_d)(H)$	6.1		6.10	0
$S-(C_B)(C)$	19.16			0
$S-(C_B)_2$	25.90		23.91	1
$S-(C_B)(H)$	11.96		11.01	1
$S-(C)(S)$	7.05		6.72	12
$S-(H)(S)$		1.9[g]		0
$S-(C_B)(S)$	14.5		13.52	2
$S-(S)_2$	3.2		3.20	0
thiirane ring correction	17.7		17.30	5
thietane ring correction	19.4		19.40	1
thiophene ring correction	−16.3		−16.50	3
thiacyclopentene ring correction	2.0		5.00	2
thiolane ring correction	1.7		1.70	3

[a] From refs 29 and 65. [b] If number of compounds in database is 0, this GAV is taken to be the same as in the second column. [c] Database consists of 73 compounds listed in PNK. [d] $C-(H)_3(S)$, $C-(SO)(H)_3$, and $C-(SO_2)(H)_3$ assigned = $C-(H)_3(C)$. [e] $C_B-(S)$ assigned = $C_B-(O)$. [f] $C_d-(H)(S)$ assigned = $C_d-(H)(O)$. [g] From Stein (ref 51).

owing to the additional C–C bond strengthening resulting from the fluorine atoms inducing a positive charge on one carbon atom while the H atoms induce a slight negative charge on the other. The values tabulated in Table VIII were derived by minimizing the average error for all the calculated enthalpies. In particular cases, one can minimize probable error by taking into account such polarization effects.

10. Organosulfur Compounds

Subsequent to the original work of Benson *et al.* in 1969,[49] Benson[65] reexamined the thermochemistry and kinetics of sulfur-containing molecules and radicals and recommended some changes in the original GAVs, as well as some new groups. We have reevaluated the GAVs for C/H/S compounds and list the current best estimates for GAVs in Table IX. The values are chosen to optimize agreement with experimental results for 73 organosulfur compounds tabulated by Pedley, Kirby, and Naylor (ref 28), and yield an average error of 0.47 kcal/mol. Groups containing both S and O, both S and N, or all three, have not been reevaluated; for these GAVs see ref 29, Stein,[51] and Shaw.[61]

11. Organophosphorus Compounds, Organoboron Compounds, and Organometallic Compounds

Groups for these compounds have not been systematically evaluated since the original work of Benson *et al.* in 1969;[49] values tabulated in *Thermochemical Kinetics* (1976) simply quote the earlier results.

12. Free Radicals

O'Neal and Benson[66] presented a general discussion on free-radical thermochemistry, experimental methods, and estimation schemes for predicting enthalpies, entropies, and heat capacities. Their Table 20 presented GAVs for 45 free radical groups. Some of the enthalpy values were revised in Table 2.14 of *Thermochemical Kinetics* (1976). We have already discussed the two extreme options in evaluating GAVs: (1) from a minimum set of well-established experimental results; or (2) by a best fit to a larger, statistically significant set of measurements. In the case of free radicals, the second option is not open: there are measurements for only a very small number of alkyl free radicals. The further refinement of free radical GAVs depends on corresponding improvements in the precision and accuracy of enthalpies of the radicals themselves. Unhappily, in some cases—most notably *tert*-butyl, *sec*-butyl and isopropyl, successive laboratory studies have not signaled a convergence of deduced values. It seems likely that experimentalists will continue to address the existing discrepancies in these small radicals enthalpies before tackling larger radicals. When better experimental values are arrived at, it will be a simple matter to recompute the radical GAVs in accordance with eqs 13–20. We have not reevaluated any GAVs for radicals at this time. Instead, we refer the reader to *Thermochemical Kinetics* (1976), revisions calculated by Ni *et al.*[67] in 1989 for seven radical groups, including two for which values were not previously assigned (these based on experimental data of Rossi *et al.*[68]), revisions calculated by Cohen (ref 31), and values estimated by Dilling (ref 48) or by Shaw.

XIII. Closing Remarks

We do not wish the reader to be left with the impression that GA—or any other computational scheme, for that matter—has solved all future thermochemical needs once and for all. There are many vacancies in the GAV tables; furthermore, we have not dealt specifically at this time with nitrogen, phosphorus, and organometallic compounds. There would be even more holes in those tables. These cannot be filled without experimental data that are, as yet, unavailable. Sections VIII and IX discuss strategies for estimating gas-phase enthalpies when direct experimental data are not at hand. The methods discussed deserve wider use and can considerably expand the roster of available GAVs. However, all aspects considered, GA will become increasingly unreliable as molecular complexity, such as number of neighboring functional groups, rings, or nonbonded interactions, increase—unless a close structural analog is available.

Two important issues merit discussion in our closing remarks. The first is the question whether *components* rather than *groups* or *bonds* will ever become the basis of choice in estimating enthalpies by an additivity procedure; the second is whether nonneighboring effects (such as *gauche*, *cis*, rings, *etc.* negate the comparative simplicity of the group additivity procedure.

Thermochemical Kinetics lists some 280 different groups for stable molecules containing C, H, O, N, S, and halogens alone; this does not include nonneighboring interactions, ring corrections, *etc.* It seems highly unlikely in the near future that the experimental database will grow sufficiently in size to justify moving up to a higher level of specificity, such as component additivity would require. (The only conceivable exception would be in the particular case of alkanes, for which there are relatively few groups and many data.) For example, PNK require 427 components to replace 29 groups. Furthermore, in many cases it is doubtful that the inherent experimental inaccuracies will ever justify the enormous effort that component additivity would require.

Nonbonded interactions are probably the ultimate factor limiting the accuracy of group additivity methods in predicting thermochemical properties of large molecules. However, the handful of cases (most have been noted in the text) in which the disagreement between calculation and experiment exceeds a few kilocalories per mole could be accounted for either by nonbonded interactions or, just as plausibly, by experimental error, since in most of those cases the assumed values depend on a single laboratory measurement. The extent to which nonbonded interactions can be systematically treated will not be known until we have a better database to rely upon. Parenthetically, we might note that for those groups for which values are already derived, it is unlikely that future measurements will change them significantly. There are very few cases for which the values of 1976 have changed by more than 0.5–1 kcal/mol.

Thus, in both issues we come back to the problem of the limitations imposed by the accuracy and extent of the experimental database. Group additivity was developed to afford a simple means of estimating unmeasured thermochemical properties. It will be superannuated if and when the database includes all molecules of interest or when *a priori* methods become so reliable and convenient as to become the procedure of choice. Until then (and for most of our professional lifetimes) it will be a useful tool for making rapid property estimates or for checking the likely reliability of existing measurements.

XIV. Some Useful Computer Programs

The following programs are all written for IBM-PC and compatible computers.

PREDICT includes a procedure for estimating heats of formation at 298 K. The program (in its version 3.2, 1989) offers the user two methods: a bond additivity method, based on ref 29, and a group additivity method that uses the procedure of Franklin discussed earlier (ref 6). The program is not very versatile, requiring the user to define the bonds or groups in the molecule of interest; the algorithm then calculates the enthalpy from a stored table of values. The software was written by R. J. Wooley and is available from Dragon Technology of Lakeland, FL.

CHETAH (Chemical Thermodynamic Data and Energy Release Computer Program, Version 4.4, 2nd ed.) estimates gas-phase thermodynamic properties of species on the basis of their molecular structures, and outputs heats of reaction, entropies, free energies of reaction, and heat capacities. The program is available from ASTM (American Society for Testing and Material), Philadelphia. Versions of the program are also available on magnetic tape for VAX machines.

NIST Structures & Properties Database and Estimation Program (NIST Standard Reference Database 25, Version 1.1, 1991), prepared by S. E. Stein, J. M. Rukkers, and R. L. Brown, is a much more sophisticated software package for estimating or retrieving thermochemical properties of gas-phase species, including molecules, positive ions, and free radicals. The program includes an internal database for 4869 species, but more significantly, it is designed to calculated enthalpies, entropies, and heat capacities using Benson's group additivity method. The user employs a graphics routine to draw a structure, from which an algorithm computes the derivable thermochemical data from stored group values. The software deduces the relevant groups from the user's drawn structure. Stein has built up a database of 440 groups, updating those in ref 29 by some from DIPPR[52] and some of his own new and revised values (discussed earlier in this review). That the user in general does not need to be able to identify the various groups that comprise the molecule of interest gives this program a considerable advantage over the other ones discussed. However, even this program cannot calculate nonneighboring effects or properties such as symmetry contributions to entropy.

XV. Acknowledgments

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XVI. References

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