BOND-ENERGY TERM VALUES IN HYDROCARBONS AND RELATED COMPOUNDS

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1. Introduction: Bond Properties.—The combination of atoms with one another to form molecules is explained in chemistry by the concept of valence, and represented by structural formulae in which the chemical bonds are shown as lines connecting the bonded atoms. The conventional line representation of the chemical bond satisfied some general needs of the chemist remarkably well, despite the fact that it is merely a symbol. More realism is acquired by defining certain bond properties and by making determined attempts to evaluate them. Typical of these properties are: equilibrium bond length, bond energy, bond force-constant, and bond dipole-moment. The bond length is unique in that it can be precisely determined within the molecule; *e.g.*, in chloromethane (CH_3Cl), both the C–Cl and the C–H bond lengths can be measured. It is also possible to measure the total energy of formation of chloromethane, its dipole moment, and the frequencies of the normal modes of vibration, but these are properties of the molecule as a whole, and whether or not it is valid to split them up into individual contributions from the bonds within the molecule remains an open question. In any event, the quantitative evaluation of bond properties depends on the manner of subdivision of the experimental data from which they are derived.

In discussing the bond-energy property, it is important at the outset to distinguish between bond-energy term values and bond-dissociation energies. The distinction may be brought out by reference once again to chloromethane; here the C–Cl bond-dissociation energy is the energy of the process:

$$CH_3Cl(g.) \rightarrow CH_3(g.) + Cl(g.)$$

and can be measured directly by electron impact or by kinetic methods. The C–Cl bond-energy term, however, is not measured directly, but is derived from the energy of atomisation of chloromethane, *i.e.*, the energy required to disrupt all the bonds in the molecule:

$$CH_3Cl\,(g.) \rightarrow C(g.) + 3H(g.) + Cl(g.)$$

This energy can be measured by thermochemical methods. The apportioning of the energy of atomisation between the C–H and C–Cl bonds defines the bond-energy term values, but there is no unique way, or even an acknowledged "best" way, of doing this.

2. Energies of Atomisation.—Heats of formation of chemical compounds are usually measured by calorimetric studies carried out at, or near to, room temperature. Most heat of formation data are therefore referred to 25°C, which has been adopted as the "standard" temperature for thermochemical purposes. Accordingly, the standard heat of formation of a compound $A_aB_bC_c$ is defined as the change in heat content for the synthesis of the compound from its elements:

$$\frac{a}{x}A_x + \frac{b}{y}B_y + \frac{c}{z}C_z \rightarrow A_aB_bC_c$$

carried out isothermally at 25°C (298·15°K), the elements, A_x, B_y, and C_z, and the product, $A_aB_bC_c$, being in their standard thermodynamic states. Should the product $A_aB_bC_c$ be solid or liquid at 25°C, the standard heat of formation, ΔH_f° (which refers to 298·15°K), includes the intermolecular binding energy of the condensed state: the latter is irrelevant to bond-energy considerations. The heat of formation required for bond-energy estimations is that of the product in the (hypothetical) ideal-gas state, and is obtained from the measured ΔH_f° value by making allowance for the heat of vaporisation (or sublimation) to the ideal-gas state at 25°C.

Provided $\Delta H_f^\circ(A_aB_bC_c, g.)$ has been determined, the heat of the atomisation process,

$$A_aB_bC_c(g.) \rightarrow aA(g.) + bB(g.) + cC(g.)$$

is derived from equation (1):

$$\Delta H^\circ(\text{atomisation})(298{\cdot}15^\circ\text{K}) \equiv \Delta H_a^\circ(298{\cdot}15^\circ\text{K})$$

$$= a\Delta H_f^\circ(A,g.) + b\Delta H_f^\circ(B,g.) + c\Delta H_f^\circ(C,g.) - \Delta H_f^\circ(A_aB_bC_c, g.) \quad (1)$$

Reliable values are available for the heats of atomisation of most of the common elements [*i.e.*, $\Delta H_f^\circ(A,g.)$, etc., in eqn. (1)] although doubt still attaches to the values currently accepted for boron, phosphorus, arsenic, antimony, and sulphur. Table 1, based mainly on a recent compilation by Brewer,[1] and on data included in the JANAF Thermochemical Tables,[2] summarises the present situation.

Values of $\Delta H_a^\circ(298{\cdot}15^\circ\text{K})$ are the basic experimental data from which bond-energy terms are normally evaluated, although, as was pointed out by Zahn[3] some thirty years ago, there are faults in this procedure. One of these arises because $\Delta H_a^\circ(298{\cdot}15^\circ\text{K})$ includes not only the internal binding energy of the molecule, but also its thermal energy of translation, rotation, and vibration; the other (and major) objection is that ΔH_a° includes the zero-point vibrational energy of the molecule. Thus the logical starting-

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[1] L. Brewer, "Electronic Structure and Alloy Chemistry of Transition Elements," A.I.M.E. Monograph Series, Interscience, New York, 1962.

[2] JANAF Thermochemical Data, ed. D. R. Stull, Dow Chemical Co., Midland, Mich., 1961—1963.

[3] C. T. Zahn, *J. Chem. Phys.*, 1934, **2**, 671.

TABLE 1. *Heats of formation of atoms at* 25°C.
(ΔH_f° values in kcal./g.-atom)

H	52·10 ± 0·06	Ca	42·81 ± 0·02 [4]	Rb	19·5 ± 1	Cs	18·7
Li	38·4 ± 0·4	Sc	88 ± 4	Sr	39·1	Ba	42·5
Be	78·25 ± 0·5	Ti	112·5	Y	98 ± 2	Hf	160 ± 5
B	132·6 ± 4	V	123	Zr	145·4 ± 0·4	Ta	186·8 ± 1
C	170·9 ± 0·45	Cr	95 ± 1	Nb	173 ± 2	W	201·8 ± 2
N	113·0 ± 1	Mn	66·7	Mo	157·5	Re	187 ± 2
O	59·56 ± 0·03	Fe	99·5	Ru	153 ± 2	Os	187 ± 2
F	18·86 ± 0·2	Co	101·6	Rh	133 ± 1	Ir	159 ± 2
Na	25·8 ± 0·1	Ni	102·8	Pd	91 ± 1	Pt	135·2
Mg	35·1 ± 0·1 [4]	Cu	81·1	Ag	68·4	Au	88·3 ± 0·9 [6]
Al	78·0 ± 0·4	Zn	31·2 ± 0·5	Cd	26·75 ± 0·2	Hg	14·65 ± 0·02
Si	108·4 ± 3 [5]	Ga	69·0	In	58 ± 2	Tl	43·0 ± 1
P	75·5	Ge	90 ± 2	Sn	72·0 ± 2	Pb	46·75 ± 0·13
S	65·65 ± 0·6	As	69 ± 3	Sb	63 ± 2	Bi	49·5 ± 1
Cl	28·92 ± 0·03	Se	49·4 ± 1	Te	46 ± 2	U	115 ± 3 [7]
K	21·3 ± 0·2	Br	26·74 ± 0·07	I	25·54 ± 0·01	Th	136·6

point for the evaluation of binding energies is the energy of the idealised process:

$$A_aB_bC_c(g., 0^\circ\text{K, without zero-point energy}) \rightarrow aA(g., 0^\circ\text{K}) + bB(g., 0^\circ\text{K}) + cC(g., 0^\circ\text{K}) \quad . \; . \; . \; . \quad (2)$$

but this, as Cottrell[8] has remarked, is hardly the most useful, since the calculation of the zero-point and thermal energy of a polyatomic molecule cannot usually be made with sufficient accuracy.

To distinguish between bond-energy terms obtained from $\Delta H_a^\circ(298{\cdot}15^\circ\text{K})$, and term values based on the ΔE of eqn. (2), Cottrell[8] refers to the latter as "binding energy terms". Fortunately, for most practical applications, it appears to make little difference whether bond-energy terms or binding energy terms are used.[9]

3. The Valence State and Intrinsic Bond Energies.—Although not stated explicitly in eqn. (1), the terms $\Delta H_f^\circ(A, g.)$, $\Delta H_f^\circ(B, g.)$, and $\Delta H_f^\circ(C, g.)$ refer to the ground-states of the atoms. Bond-energy terms based on ΔH_a° as defined by eqn. (1) have been criticised as "unrealistic" in that atoms in molecules often do not exhibit the same valence characteristics as in their ground-states. The ground-state of carbon, for instance, is the bivalent state $^3P,s^2p^2$, whereas in the majority of its compounds the

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[4] J. F. Smith, "Thermodynamics of Nuclear Materials," I.A.E.A., Vienna, 1962.

[5] S. G. Davis, D. F. Anthrop, and A. W. Searcy, *J. Chem. Phys.*, 1961, **34**, 659.

[6] D. L. Hildenbrand and W. F. Hall, *J. Phys. Chem.*, 1962, **66**, 754.

[7] M. H. Rand, "Thermodynamics of Nuclear Materials," I.A.E.A., Vienna, 1962.

[8] T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Edn., Butterworth, London, 1958, p. 104.

[9] T. L. Cottrell, *J.*, 1948, 1448.

carbon atom forms four bonds and is clearly quadrivalent. On this basis it has been argued[10] that the *promotion energy* from the ground to the quadrivalent state should enter directly into computations of carbon bond-energy terms.

The lowest lying quadrivalent state of carbon is $^5S,sp^3$ (situated 96·4 kcal./g.-atom above the ground-state, ^3P), and is consistent with the formation of four equivalent tetrahedral bonds (by mixing the *s*- and *p*-orbitals to form four sp^3 hybrids). Nevertheless, there are sound reasons for rejecting this as the valence-state[11] for quadrivalent carbon. To gain a mental picture of the latter, imagine the four hydrogen atoms in methane (CH_4) to be removed instantaneously to infinity, leaving the carbon atom with its four valence electrons in the orbitals they occupied at the instant of bond-fission. This so-called "valence state" differs from ^5S in that the four electrons are distributed in tetrahedral orbitals, $t_1t_2t_3t_4$, but with spins random relative to one another. The process of "randomising" the spins is energy-consuming and results in a non-stationary atomic state which cannot be observed experimentally. It is therefore impossible to measure the promotion energy to the valence-state, but it can be calculated by use of the Slater–Condon theory of atomic spectra.[12]

Recent calculations[13,14] place the promotion energy to the tetrahedral valence-state of carbon at *ca.* 152 kcal./g.-atom, that to the trigonal valence-state (as in olefins) at *ca.* 157 kcal./g.-atom, and that to the digonal valence-state (as in acetylenes) at *ca.* 166 kcal./g.-atom. Bond-energy terms in hydrocarbons, measured with respect to a particular valence-state, can therefore be quoted, if required, within reasonably small uncertainty limits.

More refined theoretical analysis makes it plain that the evaluation of "realistic" or "intrinsic" bond-energies involves rather more than reference to a particular valence-state. An examination by Voge[15] of methane in terms of the Heitler–London–Pauling–Slater electron-pairing theory indicated that the actual valence-state involves not only the quadrivalent configuration, $t_1t_2t_3t_4$, already described, but also includes contributions from the bivalent configuration, $t_1^2t_2t_3$, and the zerovalent configuration, $t_1^2t_2^2$. The admixture of these lower valencies with the quadrivalent configuration reduces the promotion energy to the effective valence-state and increases the stability of the methane molecule as a result of configurational interaction of the conventional sp^3-bonded methane structure with unconventional "excited" structures derived from lower-valent configurations.

Because of the difficulties of formulation of the valence-states adopted

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[10] R. Mecke, *Nature*, 1930, **125**, 526.

[11] J. H. van Vleck, *J. Chem. Phys.*, 1934, **2**, 20, 297.

[12] E. U. Condon and G. H. Shortley, "Theory of Atomic Spectra," Cambridge Univ. Press, 1935.

[13] J. Hinze and H. H. Jaffé, *J. Amer. Chem. Soc.*, 1962, **84**, 540.

[14] G. Pilcher and H. A. Skinner, *J. Inorg. Nuclear Chem.*, 1962, **24**, 937.

[15] H. H. Voge, *J. Chem. Phys.*, 1936, **4**, 581.

by atoms in molecules, it is questionable if intrinsic bond energies of real significance can be made available to the chemist at present. For certain purposes (*e.g.*, extrapolation from known thermochemical data, empirical evaluation of "resonance" or "strain" energies) the "reality" or otherwise of the bond-energy terms used is unimportant, and the lack of a set of meaningful intrinsic bond-energy terms has not mattered. On the other hand, to test the feasibility of a suggested reaction mechanism or kinetic scheme, it is frequently necessary to estimate the dissociation energy of a particular bond in a molecule or radical, and for this purpose conventional bond-energy terms are not good enough, because the rôle of the valence-state in chemical bonding can no longer be ignored. The inadequacy of bond-energy terms in this connection is brought out in Table 2, where bond-dissociation energies for several MX_n molecules are compared with the corresponding term values, E(M–X), calculated from $(1/n)\Delta H_a^\circ(298{\cdot}15^\circ\text{K})(MX_n)$. The stepwise bond-dissociation energies in MX_n are represented by $D_1 = D(X\text{–}MX_{n-1})$, $D_2 = D(X\text{–}MX_{n-2})$, etc.

TABLE 2. *Bond-dissociation energies, and bond-energy terms in* MX_n.

Molecule	D_1	D_2	D_3	D_4	$\bar{E}$(M–X)	Ref.
		(kcal./mole)				
$HgCl_2$	81	25	—	—	53	16, 2
$HgBr_2$	72	16	—	—	44	17, 2
HgI_2	61	8	—	—	35	17, 2
CH_4	102	88	124	80	99	18
CF_4	121	91	140	115	116	2, 19
CCl_4	70	63	?	?	78	20, 21
$TiCl_4$	80	101	106	124	103	2, 22
SiF_4	?	?	169	125	142	23, 24, 25
NF_3	58	?	?	—	66	26, 27
BF_3	165	?	?	—	153	24, 28
OH_2	118	102	—	—	110	29
$AlCl_3$	91	95	119	—	102	2

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[16] K. Wieland, *Helv. Chim. Acta*, 1941, **24**, 1285.

[17] K. Wieland, *Z. Elektrochem.*, 1960, **64**, 761.

[18] T. L. Cottrell, ref. 8, p. 270.

[19] E. B. Andrews and R. F. Barrow, *Proc. Phys. Soc.*, 1951, *A*, **64**, 481.

[20] A. A. Miller and J. E. Willard, *J. Chem. Phys.*, 1949, **17**, 168; J. B. Farmer, I. H. S. Henderson, F. P. Lossing, and D. G. H. Marsden, *ibid.*, 1956, **24**, 348.

[21] L. P. Blanchard and P. Le Goff, *Canad. J. Chem.*, 1957, **35**, 89.

[22] L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Rev.*, 1963, **63**, 111.

[23] J. L. Margrave, A. S. Kanaan, and D. C. Pease, *J. Phys. Chem.*, 1962, **66**, 1200.

[24] S. Wise, J. L. Margrave, H. M. Feder, and W. N. Hubbard, *J. Phys. Chem.*, 1961, **65**, 2157.

[25] J. W. C. Johns and R. F. Barrow, *Proc. Phys. Soc.*, 1958, **71**, 476.

[26] G. T. Armstrong, S. Marantz, and C. F. Coyle, *J. Amer. Chem. Soc.*, 1959, **81**, 3798.

[27] A. Kennedy and C. B. Colburn, *J. Chem. Phys.*, 1961, **35**, 1892; J. T. Herron and V. H. Dibeler, *ibid.*, 1961, **35**, 747; J. J. Kaufman, *ibid.*, 1962, **37**, 759.

[28] J. L. Margrave, *J. Phys. Chem.*, 1962, **66**, 1209.

[29] T. L. Cottrell, ref. 8, p. 187.

[*e.g.*, in CH_4, $D_1 = D(H–CH_3)$; in CH_3, $D_2 = D(H–CH_2)$; in CH_2, $D_3 = D(H–CH)$, and in CH, $D_4 = D(C–H)$]. It should be noted that in no case is there identity between D_1 and E(M–X), and that in some cases the differences are substantial; also, the E(M–X) values do not correspond to dissociation energies in the radicals derived from MX_n.

The effect of changes in the valence-state of an atom M in passing from MX_n to MX on the binding energies of the M–X bonds has been discussed in a simple way by Skinner[30] for the case of the mercury halides, and in more detail by Pilcher and Skinner[31] for the chlorides of titanium. The pattern of the stepwise dissociation energies was broadly accounted for in terms of intrinsic bond-energies, measured with respect to assumed valence-states. A semi-empirical treatment by Pedley[32] of hydrocarbons and hydrocarbon radicals based on the "magic formula" of Mulliken[33] is also noteworthy in this respect.

4. Constancy of Bond-energy Terms.—Bond-energy terms, as introduced by Fajans in 1920, and used to good effect later by Sidgwick and Pauling, were derived in a simple way from thermochemical data. It was assumed that each bond of a given type has a constant characteristic energy, transferable from one molecule to another, and that bond-energy terms are additive. In specific cases, where the experimental heat of atomisation was found to differ markedly from the sum of the bond-energy terms involved, the deviation was attributed either to steric strain (weakening the bonding) or to "resonance energy" (strengthening the bonding).

The assumption of constant transferable bond-energy terms may be examined by reference to the straight-chain paraffins, for which sufficient thermochemical and spectroscopic data are available[34,35] to provide reasonably accurate values for each of the quantities $\Delta H_a°(298{\cdot}15°\text{K})$, $\Delta H_a°(0°\text{K})$, and $\Delta B_a°(0°\text{K})$ [the latter symbolising ΔE of eqn. (2)]. These (in kcal./mole) are listed below:

	CH_4	C_2H_6	C_3H_8	C_4H_{10}	C_5H_{12}
$\Delta H_a°(298{\cdot}15°\text{K})$	397·16	674·58	954·24	1234·65	1514·56
$\Delta H_a°(0°\text{K})$	392·07	665·43	941·22	1218·24	1494·63
$\Delta B_a°(0°\text{K})$	418·92	710·69	1004·14	1298·86	1592·95

If the simplest method of evaluating bond-energy terms is adopted, it follows that, for a paraffin hydrocarbon, C_nH_{2n+2},

$$\Delta H(\text{atomisation}) = (n-1)E(\text{C–C}) + (2n+2)E(\text{C–H}) \quad . \quad . \quad (3)$$

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[30] H. A. Skinner, *Trans. Faraday Soc.*, 1949, **45**, 20; C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, Oxford, 1962, pp. 156—160.

[31] G. Pilcher and H. A. Skinner, *J. Inorg. Nuclear Chem.*, 1958, **7**, 8.

[32] J. B. Pedley, *Trans. Faraday Soc.*, 1961, **57**, 1492; 1962, **58**, 23.

[33] R. S. Mulliken, *J. Phys. Chem.*, 1952, **56**, 295.

[34] "Selected Values of the Thermodynamic Properties of Hydrocarbons," American Petroleum Institute, Project 44, Carnegie Institute of Technology, Pittsburgh, 1952 onwards.

[35] K. S. Pitzer and E. Catalano, *J. Amer. Chem. Soc.*, 1956, **78**, 4844.

where E(C–C) and E(C–H) are the bond-energy term values, presumed constant. Substitution of the heats of atomisation for C_4H_{10} and C_5H_{12} in eqn. (3) gives values for E(C–H) and E(C–C) which may then be used to calculate heats of atomisation for CH_4, C_2H_6, and C_3H_8; the differences between calculated and observed values so obtained are as follows:

	$\Delta H_a°$(298·15°K)	$\Delta H_a°$(0°K)	$\Delta B_a°$(0°K)
E(C–H)	98·73	97·27	104·15
E(C–C)	82·45	81·85	85·79
Error, CH_4	−2·24	−2·99	−2·32
C_2H_6	+0·25	+0·04	0·00
C_3H_8	+0·50	+0·64	+0·64

It is apparent that there is little to choose between the schemes based on $\Delta H_a°$(298·15°K), $\Delta H_a°$(0°K), or $\Delta B_a°$(0°K), since each leads to similar errors of prediction, which are substantial for straight-chain paraffins only in the case of methane. However, eqn. (3) fails completely to account for the differences in energy between a straight-chain paraffin and its branched-chain isomers, and these differences are sometimes large, *e.g.*, neopentane is more stable than n-pentane by *ca.* 4·7 kcal./mole (at 25°C).

The assumption of constant transferable bond-energy terms would require all gaseous redistribution reactions to be thermoneutral. (A "redistribution reaction" has been defined[35] as one in which bonds change in relative position, but not in total number or formal character, *e.g.*, $\frac{1}{2}MX_2 + \frac{1}{2}MY_2 \rightarrow XMY$.) But, as the following simple examples show, this is by no means always the case:

Reaction	ΔH (kcal./mole)	Ref.
(i) $\frac{3}{4}CF_4 + \frac{1}{4}CH_4 \rightarrow CHF_3$	+5·4	2
(ii) $\frac{3}{4}CCl_4 + \frac{1}{4}CF_4 \rightarrow CCl_3F$	+8·9	2
(iii) $\frac{1}{2}Hg(CH_3)_2 + \frac{1}{2}HgCl_2 \rightarrow CH_3HgCl$	−6·6	35
(iv) $\frac{3}{4}C(CH_3)_4 + \frac{1}{4}CCl_4 \rightarrow (CH_3)_3CCl$	−6·9	35

Many other examples could be quoted.[36]

Evidence is accumulating to show that although the equilibrium bond-lengths of the C–C and C–H bonds in paraffin hydrocarbons are approximately constant,[37] small differences do occur, even within the same molecule. The recent determinations by Lide[38] of the structure of propane and of 2-methylpropane indicate that C–H bonds vary slightly in length according to their primary, secondary, or tertiary nature, *viz.*, CH (primary) = 1·091 Å, CH (secondary) = 1·096 Å, and CH (tertiary) = 1·108 Å. The variations in length of C–H and C–C bonds with changes in

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[36] H. A. Skinner, *Rec. Trav. chim.*, 1954, **73**, 993.
[37] D. R. Lide, *Tetrahedron*, 1962, **17**, 125.
[38] D. R. Lide, *J. Chem. Phys.*, 1960, **33**, 1514, 1519.

the state of hybridisation of the carbon atoms involved are much larger[37,39] and have been recognised for some time.[40] Thus it now seems likely that the simple assumption of constant bond-energy terms is too crude, and that more subtlety is needed.

5. The Additivity of Bond-energy Terms.—The assumption that the heat of atomisation of a molecule is an additive function of bond-energy terms was questioned as long ago as 1934 by Zahn,[7] who suggested a "more general type of energy model" in which the total energy of formation of the molecule was written as a sum of terms associated with the bonds, plus a further sum associated with pairs of bonds attached to the same atom.

Zahn's model leads to the following expressions for the heats of atomisation of CH_4, C_2H_6, etc.:

$$\text{CH}_4;\quad 4E(\text{C–H}) + 6P_1 \tag{4a}$$

$$\text{C}_2\text{H}_6;\quad 6E(\text{C–H}) + E(\text{C–C}) + 6P_1 + 6P_2 \tag{4b}$$

$$\text{C}_3\text{H}_8;\quad 8E(\text{C–H}) + 2E(\text{C–C}) + 7P_1 + 10P_2 + P_3 \tag{4c}$$

$$\text{C}_4\text{H}_{10};\quad 10E(\text{C–H}) + 3E(\text{C–C}) + 8P_1 + 14P_2 + P_3 \tag{4d}$$

where P_1, P_2, and P_3 are the interaction energies associated with the bond-pairs $^{\text{H}}_{\text{H}}{>}\text{C}$, $^{\text{H}}_{\text{C}}{>}\text{C}$, and $^{\text{C}}_{\text{C}}{>}\text{C}$. If we now introduce effective bond-energy terms B(C–H) and B(C–C), defined by:

$$B(\text{C–H}) = E(\text{C–H}) + \frac{3}{2}P_1 \tag{5a}$$

$$B(\text{C–C}) = E(\text{C–C}) - 3P_1 + 6P_2 \tag{5b}$$

and a net interaction parameter, Γ, defined by

$$\Gamma = (P_1 - 2P_2 + P_3) \tag{5c}$$

the expressions (4a, etc.) may be recast as:

$$\text{CH}_4;\quad 4B(\text{C–H}) \tag{6a}$$

$$\text{C}_2\text{H}_6;\quad 6B(\text{C–H}) + B(\text{C–C}) \tag{6b}$$

$$\text{C}_3\text{H}_8;\quad 8B(\text{C–H}) + 2B(\text{C–C}) + \Gamma \tag{6c}$$

$$\text{C}_4\text{H}_{10};\quad 10B(\text{C–H}) + 3B(\text{C–C}) + 2\Gamma \tag{6d}$$

When the treatment is extended to the general case of a paraffin hydrocarbon, C_nH_{2n+2}, the Zahn energy-model gives:

$$\Delta H_{\text{a}}{}^{\circ}(\text{C}_n\text{H}_{2n+2}) = (n-1)B(\text{C–C}) + (2n+2)B(\text{C–H}) + [N_{\text{P}} - 6 + \tfrac{1}{2}N_{\text{S}}]\Gamma \tag{7}$$

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[39] B. P. Stoicheff, *Tetrahedron*, 1962, **17**, 135.

[40] C. A. Coulson, Victor Henri Memorial Volume, Desoer, Liege, 1948, p. 15.

where N_p = number of primary C–H bonds, and N_s = number of secondary C–H bonds in the molecule.

Eqn. (7) marks a decided advance on eqn. (3) in that it would account for differences in the heats of formation of isomers, provided that $\Gamma \neq 0$. The degree of improvement is shown in the comparison below of the errors in prediction of $\Delta H_a{}^\circ(298{\cdot}15^\circ\mathrm{K})$ given by eqns. (7) and (3) for the C_1—C_5 paraffins

	Eqn. (7)	Eqn. (3)		Eqn. (7)	Eqn. (3)
CH_4	—	$-2{\cdot}24$	iso-C_4H_{10}	$+0{\cdot}54$	$-2{\cdot}00$
C_2H_6	—	$+0{\cdot}25$	C_5H_{12}	$+0{\cdot}05$	—
C_3H_8	$+0{\cdot}35$	$+0{\cdot}50$	iso-C_5H_{12}	$+0{\cdot}70$	$-1{\cdot}94$
C_4H_{10}	$-0{\cdot}05$	—	neo-C_5H_{12}	$+3{\cdot}13$	$-4{\cdot}69$

Av. error: eqn. (7), 0·60; eqn. (3), 1·45.

[The values B(C–H) = 99·29 kcal./mole, B(C–C) = 78·84 kcal./mole, and Γ = 2·59 kcal./mole were adopted.]

Support for Zahn's view that the interaction between bonds must be included in the total energy expression comes from several different theoretical approaches. In one of these, Pitzer and Catalano[35] have made use of the Slater–Kirkwood formula[41] to calculate the intramolecular dispersion forces between non-bonded atoms in paraffin hydrocarbons. The calculated electron correlation energies provide a basis for the differences in stability of paraffin isomers and also account for the small energy differences between the *trans-* and *gauche-*forms of n-butane and of higher straight-chain paraffins.

Dewar and Pettit[42] have examined the interactions between localised bonds by means of quantum-mechanical perturbation theory. In the unperturbed system the electrons were assumed to occupy a set of localised, non-interacting, two-centre orbitals; this set included the anti-bonding as well as the bonding orbitals. The perturbation treatment showed that in first-order approximation the bond interactions are zero, but in second-order approximation the interactions between neighbouring bonds attached to the same atom become significant. When applied to hydrocarbons, the Dewar–Pettit treatment produces exactly the same equations as the Zahn model.

A theoretical treatment of saturated molecules by Brown,[43] based on a model different from that of Dewar and Pettit, leads nevertheless to similar general conclusions. Brown made use of the LCBO (linear combination of bond orbitals) approximation, the σ-bond orbitals being taken to be united-atom orbitals. The treatment leads to an expression for the total electronic energy of a paraffin hydrocarbon as a power series in S, the overlap

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[41] J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, 1931, **37**, 682.

[42] M. J. S. Dewar and R. Pettit, *J.*, 1954, 1625.

[43] R. D. Brown, *J.*, 1953, 2615.

integral between adjacent C–H bond orbitals. In first approximation (neglect of all terms in S), the total energy reduces to the sum of bond-energy terms; in second approximation (inclusion of terms in S, but neglect of terms in higher powers) the energy equations of Zahn are again obtained; in third approximation (inclusion of terms in S and S^2), the energy equations put forward by Allen[44] (see below) are obtained.[45]

In view of these developments, the case for rejecting the simple assumption of additivity of bond-energy terms must be considered strong, so that it now seems probable that both the basic assumptions of the elementary bond-energy scheme introduced by Fajans are unsound. Because of this, several authors have suggested schemes which differ from that of Fajans in at least one of the initial postulates. Some of the more successful of these are described in the next section.

6. Bond energy Schemes Applied to Paraffins.—(i) *Laidler's scheme.* As already stated, the C–H bonds in paraffins appear to differ slightly in length according to their primary, secondary, or tertiary nature: this adds some weight to Laidler's view[46] that the energy terms of primary, secondary, and tertiary C–H bonds are not identical. Thus, according to Laidler's scheme:

$$\Delta H_a{}^\circ(C_nH_{2n+2}) = (n-1)E_{CC}(\text{paraffins}) + N_pE_{CH}(p) + N_sE_{CH}(s) + N_tE_{CH}(t) \quad . \; . \; . \; . \; . \; . \quad (8)$$

where E_{CC} (paraffins) is presumed constant, $E_{CH}(p)$, $E_{CH}(s)$, and $E_{CH}(t)$ are the primary, secondary, and tertiary C–H bond-energy terms, and N_p, N_s, and N_t the numbers of such bonds in the molecule.

Although Laidler's scheme is additive in the bond-energy terms, it is noteworthy that it can be made equivalent to Zahn's model, provided that the term values are chosen as follows:

$$\left.\begin{array}{l}
\text{(i) } E_{CH}(\text{methane}) = E(\text{C–H}) + \frac{3}{2}P_1 \\
\text{(ii) } E_{CH}(p) = E(\text{C–H}) + P_1 + P_2 + \frac{1}{2}P_3 \\
\text{(iii) } E_{CH}(s) = E(\text{C–H}) + \frac{1}{2}P_1 + 2P_2 - P_3 \\
\text{(iv) } E_{CH}(t) = E(\text{C–H}) + 3P_2 - \frac{3}{2}P_3 \\
\text{(v) } E_{CC}\ (\text{paraffins}) = E(\text{C–C}) + 3P_3
\end{array}\right\} \quad . \; . \; . \; . \; . \; . \quad (9)$$

which would require:

$$E_{CH}(\text{methane}) - E_{CH}(p) = E_{CH}(p) - E_{CH}(s) = E_{CH}(s) - E_{CH}(t) = \tfrac{1}{2}\Gamma.$$

In applying his scheme, Laidler chose term values which do not comply with eqns. (9), so that the scheme in practice deviates from that of Zahn.

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[44] T. L. Allen, *J. Chem. Phys.* 1959, **31**, 1039.

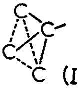
[45] H. A. Skinner, *J.*, 1962, 4396.

[46] K. J. Laidler, *Canad. J. Chem.*, 1956, **34**, 626; E. G. Lovering and K. J. Laidler, *Canad. J. Chem.*, 1960, **38**, 2367.

(ii) *Allen's scheme.* The scheme put forward by Allen[44] adds two terms to Zahn's eqn. (7), and consequently fits the empirical data for paraffins much better. The scheme leads to the equation:

$$\Delta H_a^\circ(C_nH_{2n+2}) = (n-1)B_{CC} + (2n+2)B_{CH} + (N_p - 6 + \tfrac{1}{2}N_s)\Gamma$$
$$+ (N_t + 4N_q)\Delta - mS \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (10)$$

where B_{CC} and B_{CH} are "effective" bond-energy terms, N_p, N_s, N_t, and N_q are the numbers of primary, secondary, tertiary, and quaternary carbon atoms, m is the number of 1,4 *gauche* C–H pairs, and Γ, Δ, and S are constants. $(N_t + 4N_q)$ is a measure of the total number of non-bonded C_3 trios in the molecule, *e.g.*, (I).



(I)

The term mS in eqn. (10) is included to correct for the steric repulsion of 1,4 C–H bonds *gauche* to one another: it has been known for some time[47] that the net repulsion, S, is of the order 0·5—0·8 kcal./mole per steric pair. Allen accepted $S = 0{\cdot}5$ kcal., and assumed this to be constant in all cases.

Allen's scheme correlates well with the heats of formation of C_1—C_7 paraffins, but less satisfactorily for highly branched C_8 and higher paraffins. Skinner[45] suggested that Allen's estimation of steric corrections is inadequate, and that the value of S varies according to the "rigidity" of the molecule. In favourable cases, interfering C–H bonds might twist out of positions of maximum repulsion, or gain relief by angle-widening: in other cases these release mechanisms are unprofitable, relief of one steric pair merely aggravating that of another. Skinner classified steric pairs according to their ability to take advantage of release mechanisms, and graded the values of S correspondingly.

(iii) *Tatevskii's scheme.* Tatevskii[48] has taken Laidler's scheme to its limit by assuming that not only should the C–H bonds in paraffins be classified according to their immediate environment, but that the C–C bonds should be similarly classified. According to this model, the total energy of a paraffin hydrocarbon, C_nH_{2n+2} $(n>2)$ is written:

$$\Delta H_a^\circ = \sum_{i=1}^{3} n_i E_i^{CH} + \sum_{i \leqslant j, j=1}^{4} n_{ij} E_{ij}^{CC} \quad . \; . \; . \; . \quad (11)$$

where n_i = number of CH bonds of type C_i–H, E_i^{CH} = bond-energy term of C_i–H, n_{ij} = number of CC bonds of type C_i–C_j, and E_{ij}^{CC} =

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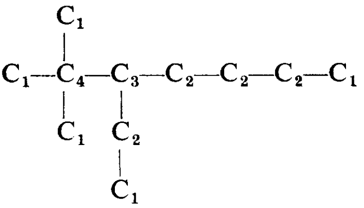
[47] S. Mizushima, "Structure of Molecules and Internal Rotation," Ch. 5., Academic Press, Inc., New York, 1954.

[48] V. M. Tatevskii, V. A. Benderskii, and S. S. Yarovoi, "Rules and Methods for Calculating the Physico-Chemical Properties of Paraffinic Hydrocarbons," translation ed. B. P. Mullins, Pergamon Press, Oxford, 1961.

bond-energy term of C_i–C_j. Evidently, n_i and n_{ij} are immediately calculable from the structural formula of the paraffin:



$C_1{-}C_4(C_1)_2{-}C_3(C_2{-}C_1){-}C_2{-}C_2{-}C_2{-}C_1$

$n_1 = 15; n_2 = 8; n_3 = 1$

$n_{12} = 2; n_{22} = 2; n_{34} = 1$
$n_{14} = 3; n_{23} = 2$

Equation (11) involves twelve energy parameters, E_i^{CH} and E_{ij}^{CC}; these are linearly dependent, since, necessarily:

$$\begin{aligned} n_1 &= 3n_{12} + 3n_{13} + 3n_{14} \\ n_2 &= 2n_{22} + n_{12} + n_{23} + n_{24} \\ n_3 &= \tfrac{2}{3}n_{33} + \tfrac{1}{3}n_{13} + \tfrac{1}{3}n_{23} + \tfrac{1}{3}n_{34} \end{aligned} \quad . \quad . \quad (12)$$

On substituting these into eqn. (11), and introducing new composite energy-terms, B_{ij}, defined by

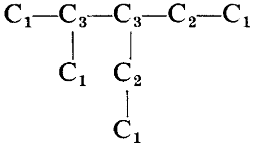
$$B_{ij} = E_{ij}^{CC} + \left(\frac{4-i}{i}\right)E_i^{CH} + \left(\frac{4-j}{j}\right)E_j^{CH} \quad . \quad . \quad . \quad . \quad (13)$$

the total energy may be re-written as

$$\Delta H_a{}^\circ = \sum_{i \leqslant j, j=1}^{4} n_{ij}B_{ij} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

involving nine parameters in all, *i.e.*, B_{12}, B_{13}, B_{14}, B_{22}, B_{23}, B_{24}, B_{33}, B_{34}, and B_{44}.

Tatevskii gives the following values for the parameters B_{ij}, applicable to calculations of $\Delta H_a{}^\circ(298{\cdot}15^\circ\text{K})$ (values in kcal./mole): $B_{12} = 477{\cdot}27$; $B_{22} = 280{\cdot}06$; $B_{33} = 147{\cdot}69$; $B_{13} = 412{\cdot}31$; $B_{23} = 214{\cdot}46$; $B_{34} = 113{\cdot}92$; $B_{14} = 379{\cdot}94$; $B_{24} = 181{\cdot}63$; $B_{44} = 79{\cdot}27$. To illustrate the method, consider the case of 3-ethyl-2-methylpentane:



$C_1{-}C_3(C_1){-}C_3(C_2{-}C_1){-}C_2{-}C_1$

$\Delta H_a{}^\circ = 2B_{13} + 2B_{12} + 2B_{23} + B_{33} = 2355{\cdot}77$ kcal./mole.
The experimental value is $2355{\cdot}30 \pm 0{\cdot}31$ kcal./mole.

(iv) *Platt's scheme*. Platt[49] has examined an energy model which is more general than that of Zahn. In Platt's treatment, the contribution of each C–C and C–H bond is supposed to be influenced not only by its nearest neighbour bonds, but also by neighbours once, twice, and further removed.

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[49] J. R. Platt, *J. Chem. Phys.*, 1947, **15**, 419; *J. Phys. Chem.*, 1952, **56**, 328.

For the αth C–C bond, the contribution E_α to the total energy of the molecule is written:

$$E_\alpha = E_{CC}^\circ + p_1 f_{\alpha 1} + p_2 f_{\alpha 2} + \ldots q_1 g_{\alpha 1} + q_2 g_{\alpha 2} + \quad . \quad . \quad . \qquad (15)$$

where p_j = effect of the jth neighbour C–C bond on E_α, q_j = effect of the jth neighbour C–H bond on E_α, $f_{\alpha j}$ = number of C–C bonds, j bonds removed along the skelton from the αth C–C, and $g_{\alpha j}$ = number of C–H bonds, j bonds distant from the αth C–C. A similar equation gives the contribution E_β from the βth C–H bond. Summation of the contributions for the whole molecule gives an expression which can be cast into the form:

$$\Delta H_a^\circ = A + a_0(N-1) + a_1 \underset{\alpha}{\Sigma} f_{\alpha 1} + a_2 \underset{\alpha}{\Sigma} f_{\alpha 2} + \ldots \quad . \quad . \qquad (16)$$

where a_1, a_2, etc., are linear combinations of p_j, q_j, etc., and N = number of carbon atoms.

Platt found that eqn. (16) is empirically much improved by adding quadratic terms, the modified formula,

$$\Delta H_a^\circ = A + a_0(N-1) + a_1 \Sigma f_{\alpha 2} + a_2 \Sigma f_{\alpha 2} + a_3 \Sigma f_{\alpha 3} + a_{11} \Sigma f_{\alpha 1}^2 + a_{12} \Sigma f_{\alpha 1} f_{\alpha 2} + a_{13} \Sigma f_{\alpha 2}^2 \quad . \; . \; . \; . \; . \; . \; . \qquad (17)$$

giving a better fit with available experimental data.

(v) *Greenshields and Rossini's scheme.* An empirical formula relating the standard heats of formation of straight-chain paraffins and their isomers has been suggested by Greenshields and Rossini:[50]

$$\Delta H_f^\circ(\text{isomer}, g.) - \Delta H_f^\circ(\text{n-alkane}, g.) = -0{\cdot}469\mathrm{C}_3 - 1{\cdot}364\mathrm{C}_4 + 1{\cdot}139\Delta P_3 + \frac{12{\cdot}508\Delta W}{n(n-1)} + 1{\cdot}978\, P_4'' + 5{\cdot}19 P_4' \quad . \qquad (18)$$

where C_3 = number of tertiary carbon atoms in the isomer, C_4 = number of quaternary carbon atoms, $\Delta P_3 = P_3(\text{isomer}) - P_3(\text{normal})$ (P_3 = total number of pairs of carbon atoms, 3 bonds apart), $\Delta W = W(\text{isomer}) - W(\text{normal})$ (where W = Wiener number), n = number of carbon atoms), P_4' = number of pairs of quaternary carbon atoms separated by one carbon atom, P_4'' = number of pairs (quaternary + tertiary) separated by one carbon atom.

Eqn. (18) makes individual allowance for several aspects of chain branching: the terms in C_3 and C_4, leading to increased stability, correspond to the increased number of Γ terms (Allen's formula) with chain-branching; the terms P_4' and P_4'' allow for the substantial steric repulsion should the molecule contain t-butyl groups interfering with one another

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[50] J. B. Greenshields and F. D. Rossini, *J. Phys. Chem.*, 1958, **62**, 271.

or with s-propyl groups; the term in ΔP_3 is also present in Platt's equation; the term in ΔW is perhaps included because of the success of the simple two-parameter formula of Wiener.[51] (The Wiener number is the sum over all bonds of $N_L.N_R$, where N_L is the number of carbon atoms to the left, and N_R the number to the right, of a given carbon atom.)

(vi) *Group methods.* The idea of expressing thermodynamic properties by an addition of structural group contributions was introduced by Parks and Huffman[52] for free-energy of formation, and for entropy. The application of group methods to heats of formation is straightforward, and several schemes have been put forward.[53]

Applied to paraffins, most group methods begin by listing the contributions from four basic groups, namely $-CH_3$, $-CH_2-$, $>CH-$, and $\geqslant C-$. If nothing further were added, this would be equivalent to Laidler's scheme, but most group methods introduce corrections to allow for steric interactions. Benson and Buss[53] made a correction of 0·7 kcal./mole per 1,4 C–H *gauche* pair, in similar manner to Allen's scheme. Others have applied specific corrections for particular combinations of the basic groups; one of the most successful of these, due to Souders, Matthews, and Hurd,[53] introduces the following steric corrections (kcal./mole): $>CH-CH<$, 0·75; $>CH-C\leqslant$, 2·39; $>CH-CH-CH<$, 2·30; $\geqslant C-C\leqslant$, 4·61; and 0·88 for each $-C_2H_5$ side-chain. Franklin[53] has used a very similar scheme. Benson and Buss,[53] from a discussion of redistribution reactions in terms of the group additivity method, have shown that constancy of bond-energy terms occurs only when the bonds have the same neighbours before and after transfer.

A group method of a somewhat different type, by Anderson, Beyer, and Watson,[53] considers the paraffins as built up by successive substitution of $-CH_3$ into CH_4, the contributions being classified according to the position of substitution. The method lists no less than fourteen substitution parameters for the paraffins, and, although reasonably successful, it can be criticised on this count.

7. **Comparison of Paraffin Bond-energy Schemes.**—The relative merit of these different bond-energy schemes is brought out in Table 3, which lists their errors of prediction of ΔH_a° for the C_3—C_8 paraffins. The schemes of Allen (as modified by Skinner), Tatevskii, Platt, and Souders are most successful, the Greenshields–Rossini scheme rather less so, whilst the Laidler scheme is markedly inferior, especially with respect to highly branched higher paraffins.

[51] H. Wiener, *J. Amer. Chem. Soc.*, 1947, **69**, 17, 2636.

[52] G. S. Parks and H. M. Huffman, "Free Energies of Some Organic Compounds," Chemical Catalog Co., New York, 1932.

[53] S. W. Benson and J. H. Buss, *J. Chem. Phys.*, 1958, **29**, 546. M. Souders, C. S. Matthews, and C. O. Hurd, *Ind. Eng. Chem.*, 1949, **41**, 1048. J. L. Franklin, *Ind. Eng. Chem.*, 1949, **41**, 1070; J. W. Anderson, G. H. Beyer, and K. M. Watson, *Nat. Petrol. News*, 1944, **36**, R476.

TABLE 3. *Errors of prediction of* $\Delta H_a°$ (25°C, *alkanes*).

Molecule	$\Delta H_a°$ (obs.)	L[46]	A–S[44,45]	T[48]	P[49]	G–R[50]	S–M–H[53]
C_3	954·24	0·56	0·35	0·26	−0·04	—	0·23
C_4	1234·65	0·15	−0·05	−0·05	−0·11	—	0·15
iso-C_4	1236·65	0·35	−0·02	0·22	−0·20	0·65	−0·43
C_5	1514·56	0·24	0·03	0·00	0·07	—	−0·03
iso-C_5	1516·50	−0·20	− 0·19	−0·22	−0·11	−0·20	−0·25
neo-C_5	1519·25	0·35	0·90	0·45	0·91	1·47	0·32
C_6	1794·62	0·18	0·00	0·00	−0·01	—	−0·06
2-Me-C_5	1796·32	−0·02	0·00	0·00	0·00	0·02	−0·04
3-Me-C_5	1795·68	0·62	0·01	0·01	0·32	−0·06	−0·09
2,2-Me_2-C_4	1799·01	0·59	0·01	−0·37	0·11	−0·11	−0·05
2,3-Me_2-C_4	1797·15	0·65	0·03	−0·31	0·14	−0·22	0·10
C_7	2074·63	0·17	0·00	0·03	−0·04	—	−0·04
2-Me-C_6	(2076·34)	−0·04	−0·01	0·02	−0·18	−0·05	−0·04
3-Me-C_6	(2085·70)	0·60	0·00	0·03	0·09	0·05	−0·08
3-Et-C_5	2075·08	1·22	0·14	0·02	0·20	0·13	−0·34
2,2-Me_2-C_5	2079·03	0·57	0·00	−0·35	−0·17	−0·06	−0·04
2,3-Me_2-C_5	2077·36	0·44	−0·75	−1·11	−0·79	−1.09	0·23
2,4-Me_2-C_5	2078·04	−0·24	−0·01	0·02	−0·22	−0·08	−0·01
3,3-Me_2C_5	2077·91	1·69	−0·02	−0·33	−0·30	−0·62	−0·52
2,2,3-Me_3C_4	2078·70	2·40	−0·40	−0·43	−0·27	−0·34	−0·38
C_8	2354·64	0·16	0·00	0·06	−0·07	—	−0·02
2-Me-C_7	2356·32	−0·02	0·02	0·08	−0·18	−0·08	0·02
3-Me-C_7	2355·64	0·66	0·07	0·13	−0·01	0·12	0·01
4-Me-C_7	2355·51	0·79	0·20	0·26	0·07	0·47	0·14
3-Et-C_6	2355·22	1·08	0·01	−0·08	−0·29	0·30	−0·45
2,2-Me_2-C_6	2358·53	1·07	0·51	0·19	0·03	0·38	0·49
2,3-Me_2-C_6	2355·95	1·85	0·52	0·34	0·27	0·48	0·67
2,4-Me_2-C_6	2357·26	0·54	0·05	0·21	−0·11	0·09	0·11
2,5-Me_2-C_6	2358·03	−0·23	0·01	0·07	−0·46	−0·21	0·03
3,3-Me_2-C_6	2357·43	2·17	0·47	0·19	−0·22	0·09	−0·01
3,4-Me_2-C_6	2355·73	2·07	0·31	−0·07	0·08	0·01	0·20
3-Et-2-Me-C_5	2355·30	2·50	0·16	0·36	0·22	0·67	0·44
3-Et-3-Me-C_5	2356·20	3·40	0·41	0·32	−0·57	−0·29	0·34
2,2,3-Me_3-C_5	2357·40	3·70	0·35	0·25	−0·02	0·32	0·23
2,3,3-Me_3-C_5	2356·55	4·55	0·27	0·66	−0·10	0·28	0·20
2,3,4-Me_3-C_5	2356·79	2·51	−0·21	0·02	0·02	0·10	0·00
2,2,3,3-Me_4-C_4	2358·81	5·59	−0·59	0·00	−1·44	−0·19	0·00
Av. deviation		±1·19	±0·19	±0·20	±0·23	±0·30	±0·18

Notes: (i) $\Delta H_a°$(obs.) values are based on $\Delta H_f°$ values recommended in the A.P.I. tables,[34] and on $\Delta H_f°$(C, *g.*) = 170·9, and $\Delta H_f°$(H, *g.*) = 52·09 kcal./mole. (ii) L = Laidler; A–S = Allen, as modified by Skinner; T = Tatevskii; P = Platt; G–R = Greenshields and Rossini; S–M–H = Souders, Matthews, and Hurd. (iii) Laidler's scheme was applied using the values (kcal./mole): E_{CC}(alkanes) = 85·0; E_{CH}(p) = 98·3; E_{CH}(s) = 97·5, and E_{CH}(t) = 96·6, recommended by Mackle and O'Hare[54] and also by Cox.[55] (iv) Allen's scheme was applied using values: B_{CC} = 78·84, B_{CH} = 99·29, Γ = 2·58; and Δ = 0·55 kcal./mole. Values of S were taken from Skinner.[45] (v) The formula:

$$\Delta H_a° = 119{\cdot}79 + 277{\cdot}17n + 1{\cdot}57\Sigma f_1 + 0{\cdot}545\Sigma f_2 + 0{\cdot}14\Sigma f_3 - 0{\cdot}12\Sigma f_{11} - 0{\cdot}235\Sigma f_{12} - 0{\cdot}07\Sigma f_{22}$$

was used to test Platt's scheme. Values of Σf_i and Σf_{ij} are given by Platt.[49] (vi) The errors listed = $\Delta H_a°$(calc.) − $\Delta H_a°$(obs.).

[54] H. Mackle and P. A. G. O'Hare, *Trans. Faraday Soc.*, 1961, **57**, 1521.

[55] J. D. Cox, *Tetrahedron*, 1962, **18**, 1337.

The failings of Laidler's scheme are apparently due to the omission of steric repulsion corrections; thus it is possible to transform the Allen eqn. (7) into the form of Laidler's eqn. (8), except for the steric terms, by evaluating Laidler's parameters as follows:

$$\begin{aligned}
E_{\mathrm{CH}}(\text{methane}) &= B_{\mathrm{CH}} \\
E_{\mathrm{CH}}(\mathrm{p}) &= B_{\mathrm{CH}} - \tfrac{1}{2}\Gamma - \tfrac{1}{3}\Delta \\
E_{\mathrm{CH}}(\mathrm{s}) &= B_{\mathrm{CH}} - \Gamma - \Delta \\
E_{\mathrm{CH}}(\mathrm{t}) &= B_{\mathrm{CH}} - \frac{3}{2}\Gamma - 2\Delta \\
E_{\mathrm{CC}}(\text{paraffins}) &= B_{\mathrm{CC}} + 3\Gamma + 2\Delta
\end{aligned}$$

Similarly, the Souders group method reduces to Laidler's formulation if the steric corrections are omitted, and although the Tatevskii scheme does not include specific steric corrections, they are present in disguised form in the composite parameters B_{ij}, when $i \geqslant 2, j \geqslant 3$. The disguise is exposed in the scheme devised by Bernstein[56] which, like that of Tatevskii, requires nine adjustable parameters, five of which contain steric corrections. The Platt scheme, however, has a more complex basis and is not reducible to Laidler's scheme plus steric terms; moreover the physical significance of the cross-terms (a_{ij}) is obscure, although in practice they subtract from the total binding energy and resemble steric terms in this respect.

8. Bond-energy Schemes Applicable to Olefins.—The published bond-energy schemes for olefins are fewer and less varied than for paraffins. Olefins present a more difficult problem partly because the available thermochemical data are less well-established, and because it is not possible to disentangle individual term values for C=C, =C–H, and =C–C without making a prior arbitrary assumption.

In these circumstances, group methods have an initial advantage, not being committed to evaluate individual term values. The group method of Franklin[53] is typical, an olefin being treated as composed of paraffin fragments attached to one of seven olefin fragments, *viz.*, $=\mathrm{CH_2}$, ${}^{\mathrm{H}}{>}\mathrm{C{=}CH_2}$, ${}^{\mathrm{H}}{>}\mathrm{C{=}C}{<}^{\mathrm{H}}$, ${}^{\mathrm{H}}{>}\mathrm{C{=}C}{<}_{\mathrm{H}}$, ${>}\mathrm{C{=}CH_2}$, ${>}\mathrm{C{=}C}{<}_{\mathrm{H}}$, or ${>}\mathrm{C{=}C}{<}$. More recently, Rockenfeller and Rossini[57] have given simple rules for estimating the heats of hydrogenation of mono-olefins, which are based on the seven olefin types listed above, with additional corrections for steric effects according to the nature (straight-chain or branched) of the attached alkyl groups. This method, applied to forty olefins, gave agreement with experiment with an average deviation of ±0·40 kcal./mole and a maximum deviation of 1·2 kcal./mole.

The problem of devising a realistic scheme of bond-energy terms for olefins has recently been tackled in a novel way by Dewar and Schmeising,[58]

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[56] H. J. Bernstein, *Trans. Faraday Soc.*, 1962, **58**, 2285.

[57] J. D. Rockenfeller and F. D. Rossini, *J. Phys. Chem.*, 1961, **65**, 267.

[58] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron*, 1959, **5**, 166; 1960, **11**, 96.

who postulate a relationship between bond-energy and bond-length, expressed by the tractrix equation:

$$r = \frac{1}{b}\,[a \log(a + \sqrt{a^2 - E^2}) - a \log E - \sqrt{a^2 - E^2}] \quad . \ . \quad (20)$$

Values of the parameters a_C, b_C (for C–C bonds) and a_H, b_H (for C–H bonds) were determined empirically, making use of available experimental data on diamond, CH_4, C_2H_6, C_2H_4, and C_2H_2. With the aid of eqn. (20) and chosen "standard" bond-lengths, Dewar and Schmeising arrived at term values for a variety of different types of C–H and C–C bonds, which they classified according to the state of hybridization of the carbon atoms involved; *e.g.*, C–C, sp^3–sp^3, C–C, sp^3–sp^2, C–C, sp^2–sp^2, etc.

The term values suggested by Dewar and Schmeising have aroused controversy,[59] for the adoption of them implies that hyperconjugation[60] does not add to the stability of unsaturated molecules, and that the magnitude of π-electron delocalisation energies in conjugated systems is decidedly less than has been commonly supposed.

Before examining the Dewar–Schmeising scheme critically, it is advantageous to refer to a scheme for olefins by Skinner,[45] devised on the basis of Allen's bond-interaction model. In this, the C–C and C–H bonds were classified in the same way as by Dewar and Schmeising, but despite this common ground, the two schemes lead to different conclusions, *e.g.*, the Allen–Skinner model, correctly, predicts a difference between $\Delta H_a{}^\circ$ for *trans*-but-2-ene and isobutene, whereas the Dewar–Schmeising model does not discriminate between these isomers. To bring the two schemes into conformity requires that the Dewar–Schmeising model be amended to distinguish between secondary ($=CH_2$) and tertiary ($=CH-$) olefinic C–H bonds; in its present form, the Dewar–Schmeising scheme is less able accurately to predict the $\Delta H_a{}^\circ$ of mono-olefins than the Allen–Skinner scheme. This is brought out in Table 4, which lists the errors of prediction of both schemes for thirteen selected mono-olefins: the selection is restricted to olefins for which steric corrections are not usually considered necessary. The errors of Mackle and O'Hare's version[54] of the Dewar–Schmeising scheme, and of the recent scheme due to Bernstein,[56] are also given. The latter does discriminate between secondary and tertiary olefinic C–H bonds, and fits the data quite well.

Evidence for a slight difference in the bond-lengths of secondary and tertiary olefinic C–H is provided by Lide and Christensen's[61] structural investigation of propene, where the mean length in $=CH_2 = 1{\cdot}086 \pm 0{\cdot}003$ Å, compared with $1{\cdot}090 \pm 0{\cdot}003$ Å in $=CH-$. However, the bonds in $=CH_2$ are not equivalent, the C–H *cis* to the methyl group being longer

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[59] R. S. Mulliken, *Tetrahedron*, 1959, **5**, 253; 1959, **6**, 68; 1962, **17**, 247.

[60] R. S. Mulliken, C. A. Rieke, and W. G. Brown, *J. Amer. Chem. Soc.*, 1941, **63**, 41. C. A. Coulson and V. A. Crawford, *J.*, 1953, 2052.

[61] D. R. Lide and D. Christensen, *J. Chem. Phys.*, 1961, **35**, 1374.

than C–H *trans* by 0·010 Å. The authors state that the mean length =CH_2 in propene is determined with high accuracy.

TABLE 4. *Errors of prediction of $\Delta H_a°$ for mono-olefins.*

	A–S	D–S	M–O′H	B
Propene	0·00	0·52	0·14	0·06
But-l-ene	0·02	0·66	0·15	−0·14
trans-But-2-ene	0·07	0·88	1·41	0·15
2-Me-propene	0·00	−0·38	0·04	0·08
Pent-1-ene	0·00	0·47	0·10	−0·06
trans-Pent-2-ene	0·08	1·03	1·41	−0·06
3-Me-but-1-ene	0·09	0·79	−0·32	0·04
Hex-1-ene	−0·05	0·44	0·06	0·03
trans-Hex-2-ene	−0·28	0·52	1·04	−0·30
trans-Hex-3-ene	−0·48	0·56	0·91	−0·77
3-Me-pent-1-ene	0·12	0·83	−0·30	−0·09
4-Me-pent-1-ene	−0·30	1·04	−0·72	−0·51
4-Me-*trans*-pent-2-ene	−0·06	0·95	0·73	−0·09
Av. deviation	±0·11	±0·70	±0·56	±0·18

(i) Error = $\Delta H_a°$(calc.) − $\Delta H_a°$(obs.). (ii) The D–S values refer to 0°K and are based on $\Delta H_f°(0°K)(C + 2H, g.)$ = 273·52 kcal./mole.

9. Criticisms of the Dewar–Schmeising Scheme.—The Dewar–Schmeising scheme, by allotting individual term values to olefinic C=C, C–H, and C–C bonds, attempts more than the Allen–Skinner scheme, and is consequently open to more detailed criticism. Although a focal point for criticism is the validity[56] of the assumed energy–length relationships, it should be realised, irrespective of this issue, that the tractrix equations for C–C, and for C–H in particular, are extremely sensitive to experimental uncertainties in available bond-length data. To illustrate this point, consider the best available structural data on benzene, and on propene: Langseth and Stoicheff[62] obtained r_0(C–C) = 1·397 ± 0·001 Å and r_0 (C–H) = 1·084 ± 0·005 Å in the former, and Lide and Christensen[61] give r_s(C=C) = 1·336 ± 0·004 Å, r_s(C–C) = 1·501 ± 0·004 Å, r_s (C*–H) = 1·091 ± 0·003 Å, 1·081 ± 0·003 Å, and 1·090 ± 0·003 Å, r_s (C–H) = 1·085 ± 0·004 Å and 1·098 ± 0·014 Å (twice), in propene. On substituting these bond-lengths in the Dewar–Schmeising tractrix equations, the heats of atomisation, $\Delta H_a°(0°K)$ may be calculated, *viz.*, benzene 1299·6 ± 10·8, and propene 818·0 ± 14·9 kcal./mole. These are to be compared with the experimental values, as quoted by Dewar and Schmeising of 1307·4 and 812·1 kcal./mole, respectively; the significant point is not the measure of agreement, but the fact that such small uncertainties in the bond-lengths lead to calculated energy uncertainties of these magnitudes.

Dewar and Schmeising, however, did not use the energy–length equations in the manner described above, but only for the limited purpose of evaluating the energies of specific "standard" C–H and C–C bonds.

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[62] A. Langseth and B. P. Stoicheff, *Canad. J. Phys.*, 1956, **34**, 350.

Thus, *e.g.*, the Dewar–Schmeising scheme, applied to propene, gives $\Delta H_a^\circ = 3E(\text{CH, p}) + 3E(\text{C}^*\text{–H}) + E(\text{C–C}^*) + E(\text{C}^*\text{=C}^*)$ (C* represents trigonal C, sp^2), and ignores the fact that the actual C–C and C–H bonds in propene[61] may differ slightly in length from those adopted for "standard" bonds.

The Dewar–Schmeising scheme is badly at fault when applied to allenes; it also has difficulties with the free methyl radical, in which the C–H term value is less than in CH_4, despite the shorter bond-length:[62]

	ΔH_a° (0°K)	Term value	r (Å)
CH_4	392·07	98·02	1·094
CH_3	291·07 (±1)	97·02	1·080

These failings, Bernstein argues,[56] imply that a single-valued energy–length curve cannot be expected to cover all C–C or C–H bonds; the fault may however lie deeper, if, as Long[63] has reasoned, "intrinsic" rather than conventional bond-energy terms should be related to bond-length.

10. Aromatic and Conjugated Hydrocarbons.—The bond-energy treatment of a typical conjugated system such as benzene usually begins with a calculation of the energy of a "Kekulé" form, composed of standard C–H, C–C, and C=C bonds; the difference between the observed and calculated energy is then accepted as the net resonance, or π-conjugation energy. Dewar and Schmeising have criticised this procedure, pointing out that resonance energies so obtained are composite quantities, made up of contributions of which π-conjugation energy is one, and not necessarily the major, component.

In illustration, consider the (hypothetical) redistribution reaction:

$$CH_2{=}CH{-}CH{=}CH_2 + C_2H_6 \rightarrow 2CH_3CH{=}CH_2$$

for which the heat of reaction, $\Delta H^\circ_{(0^\circ K)} = 3{\cdot}48$ kcal./mole, may be calculated from available ΔH_f° data' Applying the Dewar–Schmeising scheme,

$$\begin{aligned}\Delta H_a^\circ(\text{butadiene}) &= 6E(\text{C}^*\text{–H}) + 2E(\text{C}^*\text{=C}^*) + E(\text{C}^*\text{–C}^*) + R_\pi\\ (\text{ethane}) &= 6E(\text{C–H, p}) + E(\text{C–C})\\ (\text{propene}) &= 3E(\text{C–H, p}) + 3E(\text{C}^*\text{–H}) + E(\text{C}^*\text{=C}^*) + E(\text{C}^*\text{–C})\end{aligned}$$

(R_π = net resonance energy), then, since
$\Delta H^\circ = \Delta H_a^\circ(\text{butadiene}) + \Delta H_a^\circ(\text{ethane}) - 2\Delta H_a^\circ(\text{propene})$,
it follows that:

$$R_\pi = 3{\cdot}48 + [2E(\text{C–C}^*) - E(\text{C–C}) - E(\text{C}^*\text{–C}^*)] \quad . \quad . \quad . \quad (21)$$

Thus, R_π has the "conventional" value of *ca.* 3·5 kcal./mole[64] only on condition that the term in square brackets is small or zero.

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[63] L. H. Long, *Quart. Rev.*, 1953, 7, 134.

[64] G. W. Wheland, "Resonance in Organic Chemistry," Wiley, New York, 1955, p. 132.

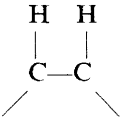
Dewar and Schmeising evaluated the latter, making use of their energy–length relationship for C–C bonds, and assuming C–C = 1·5445 Å, C–C* = 1·517 Å, and C*–C* = 1·489 – 1·479 Å; for the choice 1·479 Å, the term in brackets was calculated to be sufficiently large and negative virtually to reduce R_π to zero.

However, the energy of a bond A–B is almost invariably larger than given by the mean of A–A and B–B, the more so as the electronegativity of A deviates from that of B; it is thus at least arguable that the term in brackets should be positive, specially as estimates indicate[14] a significant electronegativity difference between trigonal and tetrahedral carbon. The problem of the magnitude of the term remains unresolved.

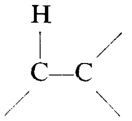
Despite uncertainty as to the "true" value of R_π in conjugated systems (and in benzene in particular), several empirical schemes have been devised which reproduce $\Delta H_a°$ of aromatic systems reasonably well. The alkyl benzenes, *e.g.*, were fitted to Laidler's scheme[46] merely by adding a constant resonance-energy correction of 42·2 kcal./mole. On the other hand, the treatment by Tatevskii, Korolov, and Mendzheretskii[65] makes no direct reference to R_π; instead, the resonance energy is absorbed into the empirical term values, C_{ar}–C_{ar}, of the bonds composing the ring. The same approach was used by Lovering and Nor[66] and by Mackle and O'Hare;[54] in both these schemes, toluene, *e.g.*, is represented by

$$6E(C_{ar}\text{–}C_{ar}) + 5E(C_{ar}\text{–H}) + E(C_{ar}\text{–C}) + 3E(\text{CH}, p).$$

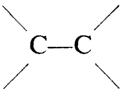
To deal with condensed-ring compounds and polyaryls, Tatevskii *et al.*[65] distinguished between four types of C_{ar}–C_{ar} bond, *viz.*:



(A)



(B)



(C)

and the central C–C bond in biphenyl; thus naphthalene, *e.g.*, is represented: $8C_{ar}$–H + 6(A) + 4(B) + (C). McGinn[67] has used the same system. Bernstein[56] points out that the scheme would lead one to expect three distinct values for the C–C bond-lengths in condensed-ring aromatic compounds, whereas in practice an almost continuous range of values from 1·36 to 1·48 Å is observed. His own scheme for condensed aromatic hydrocarbons relates the energy C_{ar}–C_{ar} to its π-bond order, and to the π-bond orders of the bonds adjacent to it. The justification for this assumption is the success of a similar scheme[68] relating π-bond order with bond-length. Bernstein's derived expression for $\Delta H_a°$ of a condensed aromatic

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[65] V. M. Tatevskii, V. V. Korolov, and E. A. Mendzheretskii, *Doklady Akad. Nauk S.S.S.R.*, 1950, **74**, 743.

[66] E. G. Lovering and O. bin M. Nor, *Canad. J. Chem.*, 1962, **40**, 199.

[67] C. J. McGinn, *Tetrahedron*, 1962, **18**, 311.

[68] H. J. Bernstein, *Trans, Faraday Soc.*, 1961, **57**, 466.

hydrocarbon leads to calculated ΔH_f° values which agree satisfactorily with experiment, except for the last four of the compounds listed:

	ΔH_f° (*g.*), kcal./mole		
	Calc.	Obs.	Ref.
Benzene	19·44	19·81	34
Naphthalene	35·42	36·26	69
Anthracene	52·10	53·47	70
Phenanthrene	48·60	46·40	70
Naphthacene	69·78	67·41	70
Triphenylene	59·58	61·26	70
Chrysene	64·18	62·58	70
1,2-Benzanthracene	65·08	66·69	70
Diphenyl	41·20	42·6	71
3,4-Benzophenanthrene	62·14	69·35	70
9,9′-Bianthryl	102·62	112·99	70
9,9′-Biphenanthryl	95·91	86·68	70
9,10-Diphenylanthracene	90·67	105·41	70

In 3,4-benzophenanthrene, 9,9′-bianthryl, and 9,10-diphenylanthracene, the aromatic rings are prevented for steric reasons from lying in a single plane, thus reducing the effectiveness of π-conjugation in these molecules. The poor agreement in the case of 9,9′-biphenanthryl is inexplicable in these terms, and it may be the experimental ΔH_f° that is here at fault; the condensed-ring compounds are difficult to obtain in a sufficiently pure state for precise measurement of ΔH_f° by combustion calorimetry and moreover their heats of vaporisation have not been directly measured, so that the experimental data are subject to indefinite uncertainty limits.

11. Cycloalkanes and Cycloalkenes.—The bond-energy schemes designed for paraffins and olefins are equally applicable to cycloalkanes and cycloalkenes, and indicate that there is considerable ring-strain in certain cyclic systems. Experimental heats of formation are available for the cycloalkanes, $(CH_2)_n$, for $n = 3$ to $n = 17$ inclusive,[72] and for a few cyclic olefins;[73] these are listed below, together with the apparent ring-strain energies, S_R, calculated by application of the Allen scheme.

The calculated ring-strain in cyclohexane is virtually zero, but as Cottrell[9] has pointed out, there appears to be a small strain-energy when

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[69] D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, 1960, **64**, 1723.

[70] A. Magnus, H. Hartman, and F. Becker, *Z. phys. Chem.*, 1951, **197**, 75.

[71] G. S. Parks and L. M. Vaughan, *J. Amer. Chem. Soc.*, 1951, **73**, 2380. R. S. Bradley and T. G. Cleasby, *J.*, 1953, 1690.

[72] Sj. Kaarsemaker and J. Coops, *Rec. Trav. chim.*, 1952, **71**, 261; H. van Kamp, Dissertation, Free University, Amsterdam, 1957; J. Coops, H. van Kamp, W. A. Lambregts, B. J. Visser, and H. Dekker, *Rec. Trav. chim.*, 1960, **79**, 1226.

[73] R. B. Turner and W. R. Meador, *J. Amer. Chem. Soc.*, 1957, **79**, 4133; J. B. Conn, G. B. Kistiakowsky, and E. A. Smith, *ibid.*, 1939, **61**, 1868; K. J. Wiberg, W. J. Bartley, and F. P. Lossing, *ibid.*, 1962, **84**, 3980.

Cycloalkanes, $(CH_2)_n$

	$\Delta H_f^\circ(g.)$	S_R
C_3	12·72	27·5
C_4	6·35	26·1
C_5	−18·46	6·2
C_6	−29·43	0·1
C_7	−28·52	6·0
C_8	−30·03	9·4
C_9	−32·14	12·2
C_{10}	−37·13	12·2
C_{11}	−43·11	11·1
C_{12}	−55·83	3·3
C_{13}	−59·29	4·8
C_{14}	−68·31	0·7
C_{15}	−72·25	1·7
C_{16}	−77·08	1·8

Cycloalkenes, $(CH_2)_nC_2H_2$

	$\Delta H_f^\circ(g.)$	S_R
C_3	66·6	54·0
C_5	7·73	5·0
C_6	− 1·28	0·9
C_7	− 2·0	5·2
cis-C_8	− 7·0	5·1
trans-C_8	2·0	14·1
cis-C_9	− 8·5	8·5
trans-C_9	− 5·6	11·4
cis-C_{10}	−16·5	4·5
trans-C_{10}	−13·0	9·0

the calculations are based on ΔH_a° at 0°K. The energy difference between the chair and boat forms has been measured[74] as 5·3 kcal./mole.

The large strain-energies in cyclopropane and cyclobutane are due to considerable distortion of the normal valence angles, which have been described in terms of the use of bent or "banana" bonds[75]. For the remaining cycloalkanes, the strains arise from three sources: (a) distortion of normal valence angles, (b) forced adoption of "eclipsed" configurations by neighbouring CH_2 groups, and (c) repulsions due to the close approach (within 2 Å) of hydrogen atoms across the ring. The conformations of the C_9, C_{10}, and C_{12} cycloalkane rings have recently been determined by crystal-structure analyses.[76] In the C_9 and C_{10} rings, the bond-angles are

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[74] W. S. Johnson, J. L. Margrave, V. J. Bauer, M. A. Frisch, L. H. Dreger, and W. N. Hubbard, *J. Amer. Chem. Soc.*, 1960, **82**, 1255.

[75] C. A. Coulson and W. E. Moffitt, *Phil. Mag.*, 1949, **40**, 1.

[76] E. Huber-Buser, J. D. Dunitz, and K. Venkatesan, *Proc. Chem. Soc.*, 1961, 463; J. D. Dunitz and V. Prelog, *Angew. Chem.*, 1960, **72**, 897; R. A. Raphael, *Proc. Chem. Soc.*, 1962, 97.

expanded to 117°; the C_{10} ring has six strong $H \cdots H$ repulsions, due to the approach of hydrogen atoms within 1·8 Å, and the C_9 ring has four of these. The C_9 ring also has a number of "eclipsed" CH_2 groups. In the C_{12} ring, the bond angles are only slightly distorted (112°), all CH_2 groups are "staggered", and although there are eight $H \cdots\cdot H$ repulsions, they are weak (the approach being only to *ca.* 2·0 Å), so that the strain is not severe.

12. Substituted Paraffins.—The bond-energy schemes specifically designed for paraffins can readily be modified, in theory, to cover substituted paraffins, $C_nH_{2n+1}X$, where X is a univalent atom or radical. In practice, the empirical evaluation of the additional parameters arising from the introduction of C–X into paraffins demands that accurate heat of formation data be known for at least a few of the lower members of the RX series, *e.g.*, the additional parameters in the Allen scheme,[45] Γ_X, Δ_X, and B_{CX}, could be obtained given accurate $\Delta H_f°$ values for CH_3X, C_2H_5X, and $(CH_3)_2CHX$ or $(CH_3)_3CX$. Surprisingly, these modest but minimal requirements are currently met for very few substituents X: these include —SH (discussed in relation to the Allen scheme by McCullough and Good[77]) and —OH, Br, and —NH_2 (similarly discussed by Skinner[45]).

The bond-energy scheme of Mackle and O'Hare,[54] designed specifically to derive group energies for >SO and >SO_2 in sulphoxides and sulphones, has recently been extended by Cox[55] to a number of aliphatic and benzenoid compounds containing C–X bonds, where X is F, Cl, Br, I, OH, –O– (ethers), carbonyl, carboxyl, SH, –S–, NH_2, and CN. In deriving empirical C–X bond-energy terms (or C–X group term values), Cox was careful to exclude from consideration thermochemical data for which the overall uncertainty exceeds 1 kcal./mole. In consequence, his scheme is reliable and the best available for RX compounds; moreover, it is economical in the number of parameters required. Mention should also be made of the successful application to a variety of substituted hydrocarbons of the group method by Benson and Buss.[53]

13. Conclusion.—Recent technical developments in experimental thermochemistry[78] make it certain that reliable heat of formation data will gradually become available for a far wider variety of compounds than hitherto; the real test of schemes devised primarily for hydrocarbons is therefore still to come.

Meanwhile, despite the evident promise of the Allen and related schemes, the empirical introduction of "steric corrections" remains an unsatisfactory feature, and much more insight into the nature of non-bonded steric interactions, and of the origin of rotational barriers, is needed to

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[77] J. P. McCullough and W. D. Good, *J. Phys. Chem.*, 1961, **65**, 1430.

[78] "Experimental Thermochemistry," Vols. I and II, ed. F. D. Rossini and H. A. Skinner, Interscience, New York, 1956 and 1962.

progress further. The detailed discussions on the structure of bond energies by Tatevskii and Papulov,[79] and by Allen and Shull[80] have touched on these and other difficulties to be resolved.

APPENDIX

To aid readers wishing to apply Allen's scheme to substituted hydrocarbons, *provisional* values (in kcal./mole) of the necessary parameters are tabulated below. The "effective" bond-energy terms, B_{CX}, are dependent on the values ΔH_f° (X, *g.*) given in Table 1. The heat of atomisation, $\Delta H_a^\circ(298{\cdot}15^\circ\mathrm{K})$, for compounds $\mathrm{R}_n\mathrm{X}$ is given by:

$$\Delta H_a^\circ = nB_{\mathrm{CX}} + n_1B_{\mathrm{CH}} + n_2B_{\mathrm{CC}} + b_3\Gamma + c_4\Delta + b_3'\Gamma_{\mathrm{CCX}} + c_4'\Delta_{\mathrm{CCX}} + b_3''\Gamma_{\mathrm{CXC}} + c_4''\Delta_{\mathrm{CCC}} - [S]$$

where n_1 and n_2 are the numbers of C–H and C–C bonds, b_3 is the number of C–C–C interactions, b_3' the number of C–C–X interactions, and b_3'' the number of C–X–C interactions; c_4 is the number of C_3 trios attached to carbon and c_4' the number of $\mathrm{C}_2\mathrm{X}$ trios attached to carbon; c_4'' is the number of C_3 trios attached to X and [*S*] the total steric repulsion correction.

$B_{\mathrm{CH}} = 99{\cdot}29$	$B_{\mathrm{SiH}} = 77{\cdot}4$	$B_{\mathrm{GeH}} = 69{\cdot}25$
$B_{\mathrm{NH}} = 93{\cdot}45$	$B_{\mathrm{PH}} = 76{\cdot}8$	$B_{\mathrm{SnH}} = 60{\cdot}4$
$B_{\mathrm{OH}} = 110{\cdot}78$	$B_{\mathrm{SH}} = 87{\cdot}35$	
$B_{\mathrm{CC}} = 78{\cdot}84$	$\Gamma_{\mathrm{CCC}} = 2{\cdot}58$	$\Delta_{\mathrm{CCC}} = -0{\cdot}55$
$B_{\mathrm{NN}} = 37{\cdot}85$		
$B_{\mathrm{OO}} = 34{\cdot}26$		
$B_{\mathrm{SiSi}} = 47{\cdot}9$		
$B_{\mathrm{PP}} = 47{\cdot}1$		
$B_{\mathrm{SS}} = 57{\cdot}0$	$\Gamma_{\mathrm{SSS}} = 5{\cdot}3$	
$B_{\mathrm{GeGe}} = 38{\cdot}8$		
$B_{\mathrm{CN}} = 64{\cdot}73$	$\Gamma_{\mathrm{CCN}} = 4{\cdot}1$	$\Delta_{\mathrm{CCN}} = -1{\cdot}0$
	$\Gamma_{\mathrm{CNC}} \sim 5{\cdot}1$	$\Delta_{\mathrm{CCC}}^{\mathrm{N}} \sim -3{\cdot}5$
	$\Gamma_{\mathrm{CNN}} \sim 6{\cdot}1$	
$B_{\mathrm{CO}} = 78{\cdot}15$	$\Gamma_{\mathrm{CCO}} = 5{\cdot}66$	$\Delta_{\mathrm{CCO}} = -1{\cdot}43$
	$\Gamma_{\mathrm{COC}} = 6{\cdot}00$	
	$\Gamma_{\mathrm{COO}} \sim 9$	
$B_{\mathrm{CS}} = 65{\cdot}19$	$\Gamma_{\mathrm{CCS}} = 3{\cdot}30$	$\Delta_{\mathrm{CCS}} = -1{\cdot}20$
	$\Gamma_{\mathrm{CSC}} = 2{\cdot}97$	
	$\Gamma_{\mathrm{CSS}} = 4{\cdot}45$	

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[79] V. M. Tatevskii and Yu G. Papulov, *Russ. J. Phys. Chem.*, 1960, **34**, 115, 231, 335; Yu. G. Papulov and V. M. Tatevskii, *ibid.*, 1962, **36**, 93.

[80] T. L. Allen and H. Shull, *J. Chem. Phys.*, 1961, **35**, 1644.

$B_{\mathrm{CCl}} \sim 78\cdot9$ $\quad \Gamma_{\mathrm{CCCl}} \sim 3\cdot6$ $\quad \Delta_{\mathrm{CCCl}} \sim -0\cdot8$

$B_{\mathrm{CBr}} = 65\cdot9$ $\quad \Gamma_{\mathrm{CCBr}} \sim 4\cdot0$ $\quad \Delta_{\mathrm{CCBr}} \sim -1\cdot4$

$B_{\mathrm{CI}} \sim 52\cdot0$ $\quad \Gamma_{\mathrm{CCI}} \sim 3\cdot0$ $\quad \Delta_{\mathrm{CCI}} \sim -1\cdot0$

$B_{\mathrm{CZn}} + \tfrac{1}{2}\Gamma_{\mathrm{CZnC}} = 38\cdot4$ $\quad \Gamma_{\mathrm{CCZn}} = -2\cdot3$

$B_{\mathrm{CCd}} + \tfrac{1}{2}\Gamma_{\mathrm{CCdC}} = 30\cdot1$ $\quad \Gamma_{\mathrm{CCCd}} = -2\cdot0$

$B_{\mathrm{CHg}} + \tfrac{1}{2}\Gamma_{\mathrm{CHgC}} = 26\cdot5$ $\quad \Gamma_{\mathrm{CCHg}} = -0\cdot1$ $\quad \Delta_{\mathrm{CCHg}} -1\cdot5$

$B_{\mathrm{CB}} + \Gamma_{\mathrm{CBC}} + \tfrac{1}{3}\Delta_{\mathrm{CCC}}{}^{\mathrm{B}} = 82\cdot7$ $\quad \Gamma_{\mathrm{CCB}} \sim 0\cdot7$ $\quad \Delta_{\mathrm{CCB}} -1\cdot1$

$B_{\mathrm{CAl}} + \Gamma_{\mathrm{CAlC}} + \tfrac{1}{3}\Delta_{\mathrm{CCC}}{}^{\mathrm{Al}} = 62\cdot3$

$B_{\mathrm{CP}} + \Gamma_{\mathrm{CPC}} + \tfrac{1}{3}\Delta_{\mathrm{CCC}}{}^{\mathrm{P}} = 62\cdot2$

$B_{\mathrm{CSN}} + \dfrac{3}{2}\Gamma_{\mathrm{CSnC}} + \Delta_{\mathrm{CCC}}{}^{\mathrm{Sn}} = 48\cdot5$ $\quad \Gamma_{\mathrm{CCSn}} = -0\cdot3$

$B_{\mathrm{CPb}} + \dfrac{3}{2}\Gamma_{\mathrm{CPbC}} + \Delta_{\mathrm{CCC}}{}^{\mathrm{Pb}} = 32\cdot9$ $\quad \Gamma_{\mathrm{CCPb}} = -0\cdot60$