851. *An Examination of Allen's Empirical Bond-energy Scheme, and its Application to Paraffins and Cycloalkanes, Olefins, Alkyl Alcohols and Bromides, and Amines.*

By H. A. SKINNER.

The relationship of the empirical bond-energy scheme proposed recently by Allen to the L.C.B.O. molecular-orbital treatment of saturated paraffins used by Brown is pointed out.

Allen's scheme is shown to correlate very well with the heats of formation of gaseous paraffins, from methane to the nonanes, provided that the steric interactions are calculated by the methods here proposed. The scheme is extended to cover mono-olefins (C_2—C_7) as well as a number of cycloalkanes and cycloalkenes. An application of the scheme to the limited data on heats of formation for alcohols, alkyl bromides, and alkylamines is also presented.

1. *Introduction.*—The bond-energy scheme recently proposed by Allen[1] correlates very well with the experimental heats of formation of gaseous paraffin hydrocarbons from methane to the heptanes. McCullough and Good[2] have applied Allen's scheme also to a number of alkanethiols and alkyl sulphides and disulphides: they found that the correlation is remarkably good, the average deviation between calculated and experimental heats of formation being less than the average experimental uncertainty interval.

However, Allen's scheme is less satisfactory when applied to highly branched paraffins containing 8 or more C atoms; *e.g.*, the calculated and the experimental heats of formation of gaseous 2,3,3-trimethylpentane, 2,2,3,3-tetramethylbutane, and 2,2,3,3- and 2,3,3,4-tetramethylpentane differ by 2·16, 3·10, 4·33, and 3·3 kcal./mole, respectively. These deviations are well outside the experimental uncertainty intervals.

A modification of Allen's scheme described by Skinner[3] fits the experimental data for the octanes and nonanes reasonably well, but needs a larger number of empirical parameters than does Allen's scheme. The present paper describes a version which retains the main features of Allen's scheme and differs from it only in the method of evaluating steric hindrances.

2. *Theoretical Basis.*—A basis for Allen's scheme lies in the molecular-orbital treatment of paraffin hydrocarbons given by Brown[4] in 1953, in which the molecular orbitals were represented as linear combinations of bond-orbitals (the L.C.B.O. approximation). The method may be illustrated by reference to methane: the molecular orbitals are written $\psi_i = \sum_{i=1}^{4} c_i\phi_i$, where the C–H bond orbitals, ϕ_i, need not be specified precisely. The energies of the orbitals ψ_i are obtained by solution of the secular determinant:

$$\begin{vmatrix} \alpha\text{-}E & \beta\text{-}SE & \beta\text{-}SE & \beta\text{-}SE \\ \beta\text{-}SE & \alpha\text{-}SE & \beta\text{-}SE & \beta\text{-}SE \\ \beta\text{-}SE & \beta\text{-}SE & \alpha\text{-}E & \beta\text{-}SE \\ \beta\text{-}SE & \beta\text{-}SE & \beta\text{-}SE & \alpha\text{-}E \end{vmatrix} = 0, \qquad (1)$$

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[1] Allen, *J. Chem. Phys.*, 1959, **31**, 1039.

[2] McCullough and Good, *J. Phys. Chem.*, 1961, **65**, 1430.

[3] Skinner, *Anales real Soc. españ. Fís. Quím.*, 1960, **56**, *B*, 931.

[4] Brown, *J.*, 1953, 2615.

where α = coulomb parameter for the CH bond-orbital, β = resonance integral for interaction between two adjacent CH bond-orbitals, and S = overlap integral of adjacent CH bond-orbitals. Writing $\gamma = \beta - S\alpha$, we obtain the roots of expression (1) as:

$$E_1 = \alpha + 3\gamma/(1 + 3S); \qquad E_2 = E_3 = E_4 = \alpha - \gamma/(1 - S);$$

so that the total electronic energy of the eight bonding electrons of methane is

$$\begin{aligned} 2(E_1 + E_2 + E_3 + E_4) &= 8\alpha + 6\gamma[(1 + 3S)^{-1} - (1 - S)^{-1}] \\ &= 8\alpha - 24\gamma S + 48\gamma S^2 - \text{(terms in higher powers of } S). \end{aligned}$$

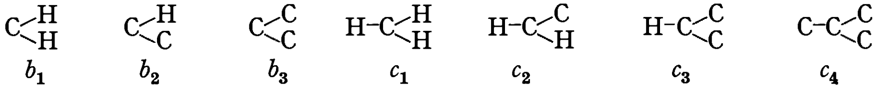
To extend the treatment to ethane and higher paraffins, additional coulombic and resonance integrals are needed, *viz.*:

Coulomb	parameters	Resonance	integrals	Overlap	integrals
CH	α	CH : CH	β	CH : CH	S
CC	$\alpha + h\gamma$	CH : CC	$\theta\beta$	CH : CC	θS
		CC : CC	$\eta\beta$	CC : CC	ηS

Brown derived a general formula for the total electronic energy of the bonding electrons of a paraffin hydrocarbon, C_nH_{2n+2}, in terms of these parameters, as a power series in S:

$$\begin{aligned} E = (6n + 2)\alpha + (2n - 2)h\gamma - 4S\gamma(b_1 + b_2\theta^2 + b_3\eta^2) + 2\gamma S^2\{[(3n - 5)b_2 - 3b'_2]h\theta^2 + \\ [(3n - 7)b_3 - 3b'_3]h\eta^2 + 6(c_1 + c_2\theta^2 + c_3\eta\theta^2 + c_4\eta^3)\} + \\ \text{(terms in higher powers of } S). \quad (2) \end{aligned}$$

In equation (2), b_1, b_2, and b_3 are the numbers of adjacent pairs of bonds, and c_1, c_2, c_3, c_4 the numbers of adjacent trios of bonds in the molecule C_nH_{2n+2}, of the types shown below:



b'_2 and b'_3 are defined by $b'_2 = \sum A_r$, and $b'_3 = \sum B_r$, where A_r, B_r, are properties of the r-th C–C bond, the summations being over all C–C bonds in the molecule C_nH_{2n+2}. A_r is the number of adjacent pairs $\mathrm{C}{<}^{\mathrm{H}}_{\mathrm{C}}$ not involving r, and B_r the corresponding number $\mathrm{C}{<}^{\mathrm{C}}_{\mathrm{C}}$ pairs not involving r.

To shorten equation (2), we make the following substitutions:

E_1 = energy of an isolated C–H bond = 2α;
E_2 = energy of an isolated C–C bond = $(2\alpha + 2h\gamma)$;
P_1 = interaction between the adjacent pair $\mathrm{C}{<}^{\mathrm{H}}_{\mathrm{H}} = -4\gamma S$;
P_2 = ,, ,, ,, ,, ,, $\mathrm{C}{<}^{\mathrm{C}}_{\mathrm{H}} = -4\gamma S\theta^2$;
P_3 = ,, ,, ,, ,, ,, $\mathrm{C}{<}^{\mathrm{C}}_{\mathrm{C}} = -4\gamma S\eta^2$;

$T_1 = 12\gamma S^2$; $\quad X_1 = 2\gamma S^2 h\theta^2$;
$T_2 = 12\gamma S^2\theta^2$; $\quad X_2 = 2\gamma S^2 h\eta^2$
$T_3 = 12\gamma S^2\eta\theta^2$ $\quad x_1 = [(3n - 5)b_2 - 3b'_2]$
$T_4 = 12\gamma S^2\eta^3$ $\quad x_2 = [(3n - 7)b_3 - 3b'_3]$

and recast equation (2) in the form:

$$E = (2n + 2)E_1 + (n - 1)E_2 + b_1P_1 + b_2P_2 + b_3P_3 + c_1T_1 + c_2T_2 + c_3T_2 + c_4T_4 + x_1X_1 + x_2X_2. \quad (3)$$

The scheme is applied to the paraffins C_1 to C_5 in the annexed Table.

The bonding-energy equation (3) can, however, be considerably simplified by introducing the parameters:

$$\begin{aligned} B_1 &= E_1 + \tfrac{3}{2}P_1 + T_1; \\ B_2 &= E_2 - 3P_1 + 6P_2 - 4T_1 + 6T_2 + 6X_1; \\ \Gamma &= P_1 - 2P_2 + P_3 + 2(T_1 - 2T_2 + T_3 - X_1 + X_2); \\ \Delta &= -T_1 + 3T_2 - 3T_3 + T_4. \end{aligned}$$

Paraffin	$(2n + 2)$	$(n - 1)$	b_1	b_2	b_3	c_1	c_2	c_3	c_4	x_1	x_2
C	4	0	6	0	0	4	0	0	0	0	0
CC	6	1	6	6	0	2	6	0	0	6	0
CCC	8	2	7	10	1	2	8	2	0	10	2
CCCC	10	3	8	14	2	2	10	4	0	14	4
C CC C	10	3	9	12	3	3	9	3	1	12	6
CCCCC	12	4	9	18	3	2	12	6	0	18	6
CCCC C	12	4	10	16	4	3	11	5	1	16	8
C CCC C	12	4	12	12	6	4	12	0	4	12	12

The equations for the paraffins C_1 to C_5 given above, expressed in terms of these four parameters, are then as tabulated.

	B_1	B_2	Γ	Δ
C	4	0	0	0
CC	6	1	0	0
CCC	8	2	1	0
CCCC	10	3	2	0
C CC C	10	3	3	1
CCCCC	12	4	3	0
CCCC C	12	4	4	1
C CCC C	12	4	6	4

For the general case of a paraffin, C_nH_{2n+2}, equation (3) transforms into

$$E = (2n + 2)B_1 + (n - 1)B_2 + b_3\Gamma + c_4\Delta, \quad (4)$$

which is the same as Allen's formula, except for the omission of corrections for steric repulsion.

3. *Corrections for Steric Repulsion.*—Allen modified equation (4) when applied to isopentane and branched paraffins containing six or more carbon atoms to allow for steric repulsions in these molecules. The *gauche* configuration of n-butane is known to be less stable than the *trans*-form by *ca.* 0·5 kcal./mole, and may be regarded as sterically weakened by the close approach (to within *ca.* 2 Å) of two hydrogen atoms attached to the

1,4-carbon atoms. Allen therefore subtracted from equation (4) a term 0·5*m*, where *m* is the number of pairs of *gauche* 1,4-C–H bonds present in the molecule C_nH_{2n+2}.

However, the magnitude of a *gauche* 1,4 steric repulsion appears to be more severe than 0·5 kcal./mole in certain cases; *e.g.*, in alkylcyclohexanes, the experimental value is *ca.* 0·95 kcal./mole per 1,4-interaction.[5] We propose therefore to distinguish between different types of 1,4-interaction, the basis for distinction being that some interactions are more " rigid " than others.

The steric repulsion between 1,4-H atoms could be relieved either by twisting the interfering CH_3 groups from " staggered " conformations, or by widening the C–C–C angles of the chain connecting the groups. In Fig. 1, we have represented schematically four types of steric interaction, labelled S_{11}, S_{12}, S_{13}, and S_{22}, which differ in respect of their ability to make use of the twisting release mechanism.

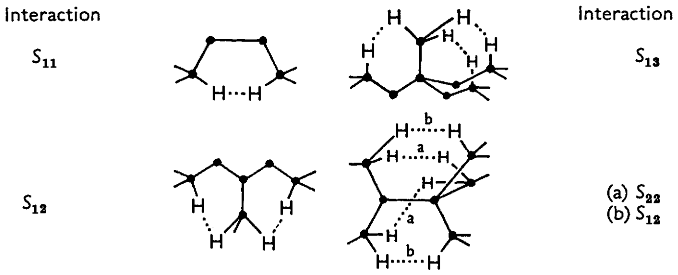


FIG. 1.

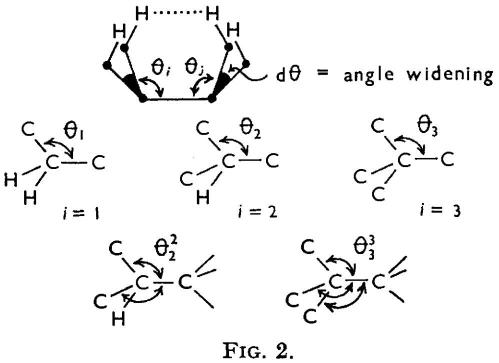


FIG. 2.

The interaction S_{11} could be relieved somewhat by a slight rotation of one or both of the 1,4-CH_3 groups from the staggered towards the eclipsed conformation: only a small angle of " twist " can be considered as a mechanism of release, since the rotational-energy barrier is substantial. Interactions S_{12} and S_{13} are also open to release by twisting, but in both these cases only one of the C–H bonds of an interacting pair brings release on twisting. On the other hand, the interaction S_{22} (and also S_{32}, not shown in Fig. 1) cannot effectively be reduced by slight twisting; *e.g.*, in 2,2,3-trimethylbutane, twisting of terminal CH_3 to reduce S_{22} simultaneously increases S_{12}, so that no net advantage accrues. Hence we accept that $S_{22} = S_{23} > S_{21} = S_{31} > S_{11}$, following the order of ability to use the " twisting " mechanism of release.

The " angle " release mechanism, represented schematically in Fig. 2, may be classified according to the angles θ_i, θ_j. Angle release is limited by the resistance of θ_i, θ_j to deformation: we assume that angle rigidity decreases in the order $\theta_3 > \theta_2 > \theta_1$, and is greater

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[5] Prosen, Johnson, and Rossini, *J. Res. Nat. Bur. Stand.*, 1947, **39**, 173.

when more than one C–C–C angle of a given carbon atom is involved in repulsion interactions, *e.g.*, $\theta_2^2 > \theta_2$.

Accordingly, we propose to characterize 1,4-interactions in respect both of twisting and angle release possibilities, *e.g.*, $S_{11}(\theta_1,\theta_2)$, $S_{12}(\theta_1,\theta_2^2)$: we represent these more simply as $S_{11}(12)$ and $S_{12}(12^2)$.

4. *Application to Paraffins.*—Equation (4), with steric interaction terms added, can be tested against extensive thermochemical data for paraffin hydrocarbons.[6] Strictly, heats of atomization at 0°K, corrected to apply to molecules without zero-point energy, should be used for the test.[7] In practice, the difficulty of evaluating accurately the zero-point energies of all but the simplest of polyatomic molecules renders it impossible to carry out an extensive test in this way: we have used the experimental data appropriate to 25°C. Consequently, the success of the scheme, despite some theoretical justification, rests in part on an empirical approach.

The parameters B_1 and B_2 (equation 4) may be evaluated from the experimental heats of atomization of methane and ethane, giving $B_1 = 99{\cdot}29$ kcal./mole and $B_2 = 78{\cdot}84$ kcal./mole. On substitution of these values, equation (4) may be transformed into the more convenient form, *viz.*:

$$\Delta H^0{}_f(C_nH_{2n+2}, g) = \Delta H^0{}_f(CH_4, g) + (n-1)[\Delta H^0{}_f(C_2H_6, g) - \Delta H^0{}_f(CH_4, g)] - b_3\Gamma - c_4\Delta + \text{steric terms;} \tag{5}$$

or,

$$\Delta H^0{}_f(C_nH_{2n+2}, g) = -15{\cdot}54 - 2{\cdot}35n - b_3\Gamma - c_4\Delta + [S], \tag{6}$$

where $[S]$ measures the total steric repulsion correction in C_nH_{2n+2}.

Experimental heats of formation of paraffins [6,8] are compared with values calculated from equation (6) in Table 1. The parameters Γ and Δ were given the values (in kcal./mole) $\Gamma = 2{\cdot}58$; $\Delta = -0{\cdot}55$. The values chosen for the steric 1,4-interactions are:

	S_{11}	S_{12}	S_{22}		S_{11}	S_{12}	S_{22}		S_{11}	S_{12}	S_{22}
(12)	0·33	0·38	0·43	(2^n2^n)	0·75	0·80	1·00	(3^m3^m)	0·85	0·90	1·25
(12^n)	0·48	0·53	0·58	(2^n3^m)	0·80	0·85	1·10	(22)	0·45	0·50	0·70
(13^m)	0·52	0·57	0·62								

(n = 2 or 3; m = 2, 3, 4, 5, or 6.)

The agreement between the calculated and the experimental $\Delta H^0{}_f$ values is in general excellent, and within the limits of error of determination of the heats of combustion: the deviations are largest for neopentane and 2,3-dimethylpentane, and there may be grounds for re-measuring the heats of combustion of both these compounds.

For 2,2,4-trimethylpentane, and also for 2,2,3,4- and 2,2,4,4-tetramethylpentane, the maintenance of the staggered configuration about each C–C bond results in a prohibitively close H • • • H approach, owing to 1,5-interaction. It seems probable that these molecules will avoid this by twisting away from the staggered towards the eclipsed configuration about one or more of the C–C bonds: as a consequence we cannot calculate the steric repulsion in these cases by the method used for the other hydrocarbons in Table 1. To obtain agreement with the experimental $\Delta H^0{}_f$ values, the terms $[S]$ are, empirically, 4·02 kcal./mole (2,3,3-trimethylpentane), 7·71 kcal./mole (2,2,3,4-tetramethylpentane), and 8·00 kcal./mole (2,2,4,4-tetramethylpentane).

5. *Application to Mono-olefins.*—The bond–bond interaction scheme can be applied to olefins by dividing the interactions into those between σ-bonds, and those involving π- or " quasi-π "-bonds, and summing the contributions from both.

The σ-bond interactions include those already described for paraffins, and additional terms involving the sp^2- or trigonal carbon atoms, C*. We represent the bond energy and

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[6] A.P.I. Tables, Project 44, Carnegie Inst. Technology, Pittsburg, 1953—61.

[7] Cottrell, *J.*, 1948, 1448.

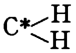
[8] Labbauf, Greenshields, and Rossini, *J. Chem. Eng. Data*, 1960, **6**, 261.

TABLE 1.

Compound	Steric terms	[S]	$-\Delta H^0_f$ (calc.)	$-\Delta H^0_f$ (obs.)	Diff.
Propane	—	—	25·17	24·82	0·35
Butane	—	—	30·10	30·15	−0·05
Isobutane	—	—	32·13	32·15	−0·02
Pentane	—	—	35·03	35·00	0·03
Isopentane	$S_{11}(12)$	0·33	36·73	36·92	−0·19
Neopentane	—	—	40·57	39·67	0·90
Hexane	—	—	39·96	39·96	0·00
2-Methylpentane	$S_{11}(12)$	0·33	41·66	41·66	0·00
3-Methylpentane	$2S_{11}(12^2)$	0·96	41·03	41·02	0·01
2,2-Dimethylbutane	$2S_{12}(13^2)$	1·14	44·36	44·35	0·01
2,3-Dimethylbutane	$2S_{11}(2^22^2)$	1·50	42·52	42·49	0·03
Heptane	—	—	44·89	44·89	0·00
2-Methylhexane	$S_{11}(12)$	0·33	46·59	46·60	−0·01
3-Methylhexane	$2S_{11}(12^2)$	0·96	45·96	45·96	0·00
3-Ethylpentane	$3S_{11}(12^3)$	1·44	45·48	45·34	0·14
2,2-Dimethylpentane	$2S_{12}(13^2)$	1·14	49·29	49·29	0·00
2,3-Dimethylpentane	$S_{11}(2^23^3) + S_{12}(12^3) + S_{12}(2^22^3)$	2·08	46·87	47·62	−0·75
2,4-Dimethylpentane	$2S_{11}(12)$	0·66	48·29	48·30	−0·01
3,3-Dimethylpentane	$4S_{12}(13^4)$	2·28	48·15	48·17	−0·02
2,2,3-Trimethylbutane	$2S_{12}(2^23^3) + 2S_{22}(2^23^3)$	3·90	48·56	48·96	−0·40
Octane	—	—	49·82	49·82	0·00
2-Methylheptane	$S_{11}(12)$	0·33	51·52	51·50	0·02
3-Methylheptane	$2S_{11}(12^2)$	0·96	50·89	50·82	0·07
4-Methylheptane	$2S_{11}(12^2)$	0·96	50·89	50·69	0·20
3-Ethylhexane	$3S_{11}(12^3)$	1·44	50·41	50·40	0·01
2,2-Dimethylhexane	$2S_{12}(13^2)$	1·14	54·22	53·71	0·51
2,3-Dimethylhexane	$S_{11}(2^22^3) + S_{12}(12^3) + S_{22}(2^22^3)$	2·28	51·65	51·13	0·52
2,4-Dimethylhexane	$S_{11}(12) + 2S_{12}(12^2)$	1·39	52·49	52·44	0·05
2,5-Dimethylhexane	$2S_{11}(12)$	0·66	53·22	53·21	0·01
3,3-Dimethylhexane	$4S_{12}(13^4)$	2·28	53·08	52·61	0·47
3,4-Dimethylhexane	$2S_{12}(12^3) + 2S_{12}(2^32^3)$	2·66	51·22	50·91	0·31
3-Ethyl-2-methylpentane	$2S_{12}(12^3) + 2S_{12}(2^22^3) + S_{22}(12^3)$	3·24	50·64	50·48	0·16
3-Ethyl-3-methylpentane	$3S_{12}(13^6) + 3S_{22}(13^6)$	3·57	51·79	51·38	0·41
2,2,3-Trimethylpentane	$S_{12}(2^33^3) + S_{13}(12^3) + S_{13}(2^33^3) + S_{22}(2^33^3) + S_{23}(2^33^3)$	4·43	52·96	52·61	0·36
2,2,4-Trimethylpentane	see text	[4·02]	—	53·37	—
2,3,3-Trimethylpentane	$S_{12}(2^23^5) + S_{22}(13^5) + S_{22}(2^23^5) + S_{23}(13^5) + 2S_{23}(2^23^5)$	5·39	52·00	51·73	0·27
2,3,4-Trimethylpentane	$S_{11}(2^22^3) + S_{12}(2^22^3) + 2S_{13}(2^22^3) + S_{23}(2^22^3)$	4·15	51·76	51·97	−0·21
2,2,3,3-Tetramethylbutane	$6S_{22}(3^33^3)$	7·50	53·40	53·99	−0·59
Nonane	—	—	54·75	54·74	0·01
3,3-Diethylpentane	$8S_{22}(13^4)$	4·96	55·33	55·44	−0·11
2,2,3,3-Tetramethylpentane	$2S_{23}(13^5) + 6S_{23}(3^33^5)$	8·74	57·09	56·70	0·39
2,2,3,4-Tetramethylpentane	see text	[7·71]	—	56·64	—
2,2,4,4-Tetramethylpentane	see text	[8·00]	—	57·83	—
2,3,3,4-Tetramethylpentane	$2S_{12}(2^23^5) + 6S_{23}(2^23^5)$	8·30	56·05	56·46	−0·41

interaction terms involving trigonal carbon atoms (occurring in olefins and alkyl free radicals) by the following symbols:

E_1^* = energy of an isolated C*–H bond
E_2^* = energy of an isolated C*–C bond
E_2^{**} = energy of an isolated C*–C* bond

P_1^* = interaction between the adjacent pair 
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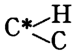
P_2^* = ,, ,, ,, ,, ,, 
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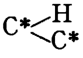
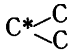
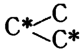
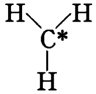
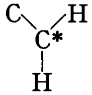
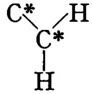
P_2^{**} = ,, ,, ,, ,, ,, 
$\mathrm{C}^*\!\genfrac{}{}{0pt}{}{\diagup \mathrm{H}}{\diagdown \mathrm{C}^*}$

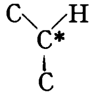
P_3^* = ,, ,, ,, ,, ,, 

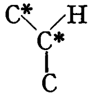
P_3^{**} = ,, ,, ,, ,, ,, 

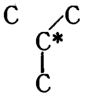
T_1^* = the trio interaction  (present in planar CH_3)

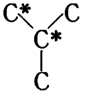
T_2^* = ,, ,, ,,  (present in $CH_3{\cdot}CH_2$)

T_2^{**} = ,, ,, ,, 

T_3^* = ,, ,, ,,  (present in isopropyl radical)

T_3^{**} = ,, ,, ,, 

T_4^* = ,, ,, ,,  (present in t-butyl radical)

T_4^{**} = ,, ,, ,, 

The problem may be simplified by introducing the following composite parameters: †

$$B_1^* = E_1^* + P_1^* + \tfrac{1}{3}T_1^*$$
$$B_2^* = E_2^* - \tfrac{3}{2}P_1 + 3P_2 - P_1^* + 2P_2^* - 2T_1 + 3T_2 - \tfrac{2}{3}T_1^* + T_2^*$$
$$B_2^{**} = E_2^{**} - 2P_1^* + 4P_2^{**} - \tfrac{4}{3}T_1^* + 2T_2^{**}$$
$$\Gamma^* = (P_1^* - 2P_2^* + P_3^*) + (T_1^* - 2T_2^* + T_3^*)$$
$$\Delta^* = -T_1^* + 3T_2^* - 3T_3^* + T_4^*$$
$$\Gamma^{**} = (P_1^* - P_2^* - P_2^{**} + P_3^{**}) + (T_1^* - 2T_2^{**} + T_3^*)$$
$$\Delta^{**} = -T_1^* + 3T_2^{**} - 3T_3^* + T_4^{**}$$

With the aid of these parameters, the σ-contribution to the total bonding energy of an olefin can be expressed by a sum of the relevant " bond-energy terms " (B_1, B_2, B_1^*, B_2^*, B_2^{**}) and bond-interactions (Γ, Γ*, Γ**, Δ, Δ**). The energy equations can be written down very simply from inspection of the molecular formulæ, by counting the number of bonds and C–C–C interactions, *e.g.*:

	B_1	B_2	B_1^*	B_2^*	B_2^{**}	Γ	Δ	Γ*	Γ**	Δ**
$CH_2{=}CH_2$	0	0	4	0	1	0	0	0	0	0
$CH_3{\cdot}CH{=}CH_2$	3	0	3	1	1	0	0	0	1	0
$C_2H_5{\cdot}CH{=}CH_2$	5	1	3	1	1	1	0	0	1	0
$(CH_3)_2C{=}CH_2$	6	0	2	2	1	0	0	1	2	1

---

† Terms corresponding to X_1, X_2 (equation 3) have been omitted in these expressions.

The π-contribution to the total bonding energy includes the energy of the π-component of the C=C bond itself, and the π-hyperconjugation energy arising from the interaction of saturated groups attached to the double-bond with the π-electrons of the double bond. As a simplifying measure, we assume that a grouping R–C=C (where R = alkyl) contributes a quantity h_π to the total hyperconjugation energy. The π-contribution in an olefin is thus expressed by $(x_\pi + mh_\pi)$, where x_π is the contribution in ethylene, and m is the number of C–C* bonds present in the olefin. Accordingly, this scheme gives, for the total bonding energy of an olefin $\mathrm{C}_n\mathrm{H}_{2n+1}\cdot\mathrm{CH{=}CH_2}$:

$$E = (2n+1)B_1 + (n+1)B_2 + 3B_1{}^* + B_2{}^* + B_2{}^{**} + b_3\Gamma + c_4\Delta + \Gamma^{**} + x_\pi + h_\pi; \tag{7}$$

and, for an olefin $(\mathrm{C}_n\mathrm{H}_{2n+1})(\mathrm{C}_m\mathrm{H}_{2m+1})\mathrm{C{=}CH_2}$:

$$E = 2(n+m+1)B_1 + (n+m-2)B_2 + 2B_1{}^* + 2B_2{}^* + B_2{}^{**} + b_3\Gamma + c_4\Delta + \Gamma^* + 2\Gamma^{**} + \Delta^{**} + x_\pi + 2h_\pi. \tag{8}$$

As for paraffins, these equations can be transformed to enable heats of formation to be calculated directly; thus, for example, equation (7) transforms into:

$$\Delta H^0{}_\mathrm{f}(\mathrm{C}_n\mathrm{H}_{2n+1}\cdot\mathrm{CH{=}CH_2},\ \mathrm{g}) = \Delta H^0{}_\mathrm{f}(\mathrm{C_2H_4},\ \mathrm{g}) + n[\Delta H^0{}_\mathrm{f}(\mathrm{C_2H_6},\ \mathrm{g}) - \Delta H^0{}_\mathrm{f}(\mathrm{CH_4},\ \mathrm{g})] - b_3\Gamma - c_4\Delta - \Gamma^{**} - h_\pi - [B_1 - B_1{}^* + B_2{}^* - B_2]; \tag{9}$$

or, on substitution of the experimental $\Delta H^0{}_\mathrm{f}$ values for $\mathrm{C_2H_4}$, $\mathrm{C_2H_6}$, and $\mathrm{CH_4}$, and $\Gamma = 2{\cdot}58$, $\Delta = -0{\cdot}55$ (as in paraffins), into:

$$\Delta H^0{}_\mathrm{f}(\mathrm{g}) = 12{\cdot}50 - 2{\cdot}35n - 2{\cdot}58b_3 + 0{\cdot}55c_4 - A, \tag{10}$$

where $A = \Gamma^{**} + h_\pi + (B_1 - B_1{}^*) + (B_2{}^* - B_2)$.

If the values $A = 5{\cdot}27$, $(\Gamma^* + \Delta^{**}) = 1{\cdot}30$ kcal./mole, are chosen, the following equations apply to olefins $\mathrm{R^1CH{=}CH_2}$, $\mathrm{R^1R^2C{=}CH_2}$, $\mathrm{R^1HC{=}CHR^2}$, $\mathrm{R^1R^2C{=}CHR^3}$, and $\mathrm{R^1R^2C{=}CR^3R^4}$ {the steric corrections (omitted so far) are represented by the term $[S]$}:

(i) $\mathrm{R^1CH{=}CH_2}$ $(\mathrm{R^1} = \mathrm{C}_n\mathrm{H}_{2n+1})$

$$\Delta H^0{}_\mathrm{f}(\mathrm{g}) = 7{\cdot}23 - 2{\cdot}35n - 2{\cdot}58b_3 + 0{\cdot}55c_4 + [S]; \tag{11}$$

(ii) $\mathrm{R^1R^2C{=}CH_2}$ $(\mathrm{R^2} = \mathrm{C}_m\mathrm{H}_{2m+1})$

$$\Delta H^0{}_\mathrm{f}(\mathrm{g}) = 0{\cdot}66 - 2{\cdot}35(n+m) - 2{\cdot}58b_3 + 0{\cdot}55c_4 + [S]; \tag{12}$$

(iii) $\mathrm{R^1CH{=}CHR^2}$

$$\Delta H^0{}_\mathrm{f}(\mathrm{g}) = 1{\cdot}96 - 2{\cdot}35(n+m) - 2{\cdot}58b_3 + 0{\cdot}55c_4 + [S]; \tag{13}$$

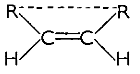
(iv) $\mathrm{R^1R^2C{=}CHR^3}$ $(\mathrm{R^3} = \mathrm{C}_p\mathrm{H}_{2p+1})$

$$\Delta H^0{}_\mathrm{f}(\mathrm{g}) = -4{\cdot}61 - (n+m+p)\,2{\cdot}35 - 2{\cdot}58b_3 + 0{\cdot}55c_4 + [S]; \tag{14}$$

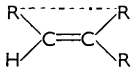
(v) $\mathrm{R^1R^2C = CR^3R^4}$ $(\mathrm{R^4} = \mathrm{C}_q\mathrm{H}_{2q+1})$

$$\Delta H^0{}_\mathrm{f}(\mathrm{g}) = -11{\cdot}18 - (n+m+p+q)\,2{\cdot}35 - 2{\cdot}58b_3 + 0{\cdot}55c_4 + [S]. \tag{15}$$

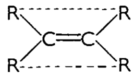
The steric corrections in an olefin may involve terms additional to those already met in paraffins. One of the most important of these is the repulsion between alkyl groups attached *cis* to the double bond. We represent these generally by S_{cis}, and distinguish between different types according to the angles θ_i, θ_j (for angles R–C= and R′–C=, respectively). For an angle C–C=C we have θ_1 in $^{\mathrm{C}}_{\mathrm{H}}\!\!>\!\mathrm{C{=}C}$ (i = 1) and θ_2 in $^{\mathrm{C}}_{\mathrm{C}}\!\!>\!\mathrm{C{=}C}$ (i = 2). Provided neither R nor R′ is tertiary, the repulsion S_{cis} is considered to be due to the close approach (1,4) of hydrogen atoms across the double bond. To some extent, repulsion might be alleviated by angle-widening and by displacements from planarity of the olefinic bonds: in either event, release should be most effective in the case $S_{cis}(11)$, and become increasingly difficult in the more crowded situations represented by $S_{cis}(12)$, $S_{cis}(12^2)$, and $S_{cis}(2^22^2)$.



S_{cis} (11)



S_{cis} (12)



$2S_{cis}$ (2^22^2)

Empirically, we propose the values:

$$S_{cis}(11) = 1{\cdot}0 \text{ kcal./mole}; \quad S_{cis}(12) = 1{\cdot}4 \text{ kcal./mole};$$

$$S_{cis}(12^2) = 1{\cdot}6 \text{ kcal./mole}; \quad S_{cis}(2^22^2) = 2{\cdot}2 \text{ kcal./mole}.$$

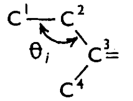
When one or more of the interacting *cis*-groups is tertiary, the steric overcrowding becomes very severe owing to the closeness of approach of the 1,5-carbon atoms. The steric interference is larger than in any of the cases discussed above, and from specific examples quoted in Table 2 the following values are indicated:

$$S_{cis}(11, \text{Bu}^t \cdots \text{R}) = 5{\cdot}8 \text{ kcal./mole};$$

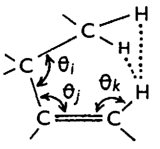
$$S_{cis}(12, \text{Bu}^t \cdots \text{R}) = 6{\cdot}5 \text{ kcal./mole};$$

$$S_{cis}(11, \text{Bu}^t \cdots \text{Bu}^t) = 14{\cdot}5 \text{ kcal./mole}.$$

In addition to S_{cis}, there are two further steric interactions involving the double bond. These are: (1) The repulsion between 1,4-*gauche* C–H bonds of a C_4 chain which includes one olefinic carbon atom, *e.g.*, (A). These interactions (represented by S^*) are comparable with the 1,4-*gauche* interactions in paraffins, but may be weaker because of the widening of the angle 2,3,4 relative to the regular tetrahedral angle. To estimate S^*, we have assumed $S^*(\text{i }2) = S(\text{i }2) - 0{\cdot}10$. (2) The repulsion between 1,4-*gauche* C–H bonds in a C_4 chain which includes both olefinic carbon atoms, *e.g.*, (B). This interaction involves three hydrogen atoms, represented by $S_3^{**}(\text{ijk})$. The magnitude of S_3^{**} should be of the order of twice the interaction $S_{22}(\text{ij})$ in paraffins. For $k = 0$ (*i.e.*, in alk-1-enes) this expectation is reasonably well borne out: when $k = 1$ (*i.e.*, in alk-2- or -3-enes), the S_3^{**} values appear to be larger. The S_3^{**} values used in Table 2 were derived by assuming $S_3^{**}(\text{ij}0) = 2S_{22}(\text{ij})$, and $S_3^{**}(\text{ij}1) = 2S_{22}(\text{ij}) + 0{\cdot}7$ kcal./mole.



(A)



(B)

Table 2 gives a comparison of $\Delta H^0_f(g)$ values for olefins as calculated from equations (11)—(15) with experimental values given in the A.P.I. Tables,[6] by Bartolo and Rossini,[9] and by Rockenfeller and Rossini.[10] The measure of agreement is not as impressive as in the case of the paraffins (Table 1); nevertheless, in most examples there is agreement within the uncertainty of experimental measurement of the heats of combustion, and only in five cases (*cis*-hex-2-ene, 2,3-dimethylbut-1-ene, 3-methyl-*trans*-hex-3-ene, 4,4-dimethylpent-1-ene, 2-ethyl-3-methylbut-1-ene) does the divergence become serious, reaching values of the order 1 kcal./mole.

6. *Application to Cycloalkanes and Cycloalkenes.*—The application of the bond–bond

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[9] Bartolo and Rossini, *J. Phys. Chem.*, 1960, **64**, 1685.
[10] Rockenfeller and Rossini, *J. Phys. Chem.*, 1961, **65**, 267.

Table 2.

Compound	Steric terms	[S]	$-\Delta H^0_f$ (calc.)	$-\Delta H^0_f$ (obs.)	Diff.
Propene		—	−4·88	−4·88	0·00
But-1-ene		—	0·05	0·03	0·02
cis-But-2-ene	$S_{cis}(11)$	1·00	1·74	1·67	0·07
trans-But-2-ene		—	2·74	2·67	0·07
2-Methylpropene		—	4·04	4·04	0·00
Pent-1-ene		—	4·98	5·00	−0·02
cis-Pent-2-ene	$S_{cis}(11)$	1·00	6·67	6·71	−0·04
trans-Pent-2-ene		—	7·67	7·59	0·08
2-Methylbut-1-ene	$S_{11}^*(12)$	0·23	8·74	8·68	0·06
3-Methylbut-1-ene		—	7·01	6·92	0·09
2-Methylbut-2-ene	$S_{cis}(12)$	1·40	10·26	10·17	0·09
Hex-1-ene		—	9·91	9·96	−0·05
cis-Hex-2-ene	$S_{cis}(11)$	1·00	11·60	12·51	−0·91
trans-Hex-2-ene		—	12·60	12·88	−0·28
cis-Hex-3-ene	$S_{cis}(11)$	1·00	11·60	11·38	+0·22
trans-Hex-3-ene		—	12·60	13·01	−0·41
2-Methylpent-1-ene	$S_{11}^*(12)$	0·23	13·67	14·19	−0·52
3-Methylpent-1-ene		—	11·94	11·82	0·12
4-Methylpent-1-ene		—	11·94	12·24	−0·30
2-Methylpent-2-ene	$S_{cis}(12)$	1·40	15·19	15·98	−0·79
3-Methyl-*cis*-pent-2-ene	$S_{cis}(12^2) + S_{11}^*(12^2)$	1·98	14·61	14·86	−0·25
3-Methyl-*trans*-pent-2-ene	$S_{cis}(12^2) + S_{11}^*(12^2)$	1·98	14·61	15·08	−0·47
4-Methyl-*cis*-pent-2-ene	$S_{cis}(11)$	1·00	13·63	13·73	−0·10
4-Methyl-*trans*-pent-2-ene		—	14·63	14·69	−0·06
2-Ethylbut-1-ene	$2S_{11}^*(12)$	0·46	13·44	13·38	+0·06
2,3-Dimethylbut-1-ene	$2S_{12}^*(2^22)$	1·10	14·83	15·85	−1·02
				14·78 [a]	+0·05
3,3-Dimethylbut-1-ene	$S_3^{**}(310)$	0·94	14·51	14·70	−0·19
				14·25 [a]	0·26
2,3-Dimethylbut-2-ene	$2S_{cis}(2^22^2)$	4·40	16·18	16·68	−0·50
				15·91 [a]	0·27
Hept-1-ene		—	14·84	14·89	−0·05
3-Methyl-*cis*-hex-3-ene	$S_{cis}(12^2) + S_{11}^*(12^2)$	1·98	19·54	19·22	0·32
3-Methyl-*trans*-hex-3-ene	$S_{cis}(12^2) + S_{11}^*(12^2)$	1·98	19·54	18·60	0·94
2,4-Dimethylpent-1-ene	$S_{11}^*(12)$	0·23	20·63	20·27	0·36
4,4-Dimethylpent-1-ene	$S_{11}^*(31)$	0·27	20·11	19·20	0·91
2,4-Dimethylpent-2-ene	$S_{cis}(12)$	1·40	22·15	21·44	0·71
4,4-Dimethyl-*cis*-pent-2-ene	$S_{cis}(11, \mathrm{Bu}^t\text{–}\mathrm{Me})$	[5·8]	17·27	17·60	−0·33
4,4-Dimethyl-*trans*-pent-2-ene	$S_3^{**}(311)$	1·64	21·43	21·46	−0·03
2-Ethyl-3-methylbut-1-ene	$S_3^{**}(12^20) + 2S_{12}^*(2^22^2)$	2·56	18·30	19·25	−0·95
2,3,3-Trimethylbut-1-ene	$\mathrm{S}_3^{**}(3^32^20) + 2S_{12}^*(3^32^2)$	3·70	20·67	20·67	0·00
Oct-1-ene		—	19·77	19·82	−0·05
2,2-Dimethyl-*cis*-hex-3-ene	$S_{cis}(11, \mathrm{Bu}^t\text{–}\mathrm{Et})$	5·8	22·20	21·77	0·43
2,2-Dimethyl-*trans*-hex-3-ene	$S_3^{**}(311)$	1·64	26·36	26·16	0·20
3-Ethyl-2-methylpent-1-ene	$2S_{12}^*(22^2)$	1·10	24·69	24·40	0·29
2,4,4-Trimethylpent-1-ene		[2·62]		26·68	
2,4,4-Trimethylpent-2-ene	$S_{cis}(12, \mathrm{Bu}^t\text{–}\mathrm{Me})$	[6·5]	25·49	25·50	−0·01
Dec-1-ene		—	29·63	29·45 [b]	0·18
2,2,5,5-Tetramethyl-*cis*-hex-3-ene	$S_{cis}(11, \mathrm{Bu}^t\text{–}\mathrm{Bu}^t)$	[14·5]	28·90	28·92 [b]	−0·02
2,2,5,5-Tetramethyl-*trans*-hex-3-ene	$2\mathrm{S}_3^{**}(311)$	3·28	20·12	39·43 [b]	0·69

[a] Derived from heats of hydrogenation. [b] ΔH_{vap} values assumed to be the same as for the corresponding paraffins.

interaction scheme to cycloalkanes and cycloalkenes (cyclic paraffins and olefins) is straightforward and involves the interaction parameters which have already been described. There are, however, additional steric terms which need evaluation, the most important being: (1) Ring strain, represented by S_{R}. This may arise from angle deformation (small rings), from the forced adoption of eclipsed (or near-eclipsed) conformations (as in cyclopentanes), or from severe overcrowding (big rings). For present purposes, we propose the values (in kcal./mole):

$$\text{Cyclohexanes, } S_{\mathrm{R}}(6) = 0{\cdot}0; \quad \text{Cyclohexenes, } S_{\mathrm{R}}(6) = 0{\cdot}8;$$

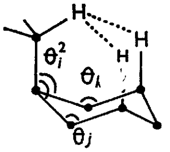
$$\text{Cyclopentanes, } S_{\mathrm{R}}(5) = 6{\cdot}2; \quad \text{Cyclopentenes, } S_{\mathrm{R}}(5) = 5{\cdot}0.$$

TABLE 3.

Compound	Steric terms	$[S]$	$-\Delta H^0_f$ (calc.)	$-\Delta H^0$ (obs.)	Diff.
Cyclohexane		—	29·58	29·43	0·15
Methylcyclohexane		—	36·54	36·99	−0·45
Ethylcyclohexane	$S_{11}(12)$	0·33	41·14	41·05	0·09
Dimethylcyclohexanes:					
1,1-	$S_3(3^21, 3^21)$	1·24	43·74	43·26	0·48
cis-1,2-	$S_3(2^21, 2^22^2) + S_{12}(2^22^2)$	2·38	40·67	41·15	−0·48
trans-1,2-	$S_{11}(22)$	0·45	43·05	43·02	0·03
cis-1,3-		—	43·50	44·16	−0·66
trans-1,3-	$S_3(2^21, 2^21)$	1·16	42·34	42·20	0·14
cis-1,4-	$S_3(2^21, 2^21)$	1·16	42·34	42·22	0·12
trans-1,4-		—	43·50	44·12	−0·62
trans-Decahydronaphthalene		—	42·98	43·54	−0·56
cis-Decahydronaphthalene	$S_4(2^21, 2^22^2, 2^21)$	2·16	40·82	40·45	0·37
Cyclopentane	$S_R(5)$	6·2	18·45	18·46	−0·01
Methylcyclopentane	$S_R(5)$	6·2	25·41	25·50	−0·09
1,1-Dimethylcyclopentane	$S_R(5)$	6·2	33·85	33·05	0·80
Dimethylcyclopentanes:					
trans-1,2-	$S_R(5)$	6·2	32·37	32·67	−0·30
cis-1,2-	$S_R(5) + 2S_{22}(22)$	7·6	30·97	30·96	0·01
trans-1,3-	$S_R(5)$	6·2	32·37	32·47	−0·10
cis-1,3-	$S_R(5)$	6·2	32·37	31·93	0·44
Cyclohexene	$S_R(6)$	0·8	1·42	1·28	0·14
1-Methylcyclohexene	$S_R(6)$	0·8	10·34	10·38	−0·04
1-Ethylcyclohexene	$S_R(6) + S_{11}{}^*(12)$	1·03	15·04	15·20	−0·16
Vinylcyclohexane		—	11·42	11·55 [a]	−0·13
Ethylidenecyclohexane	$S_{cis}(12)$	1·40	14·67	15·09 [b]	−0·42
Cyclopentene	$S_R(5)$	5·0	−7·71	−7·73	0·02
1-Methylcyclopentene	$S_R(5)$	5·0	1·21	1·30	−0·09
3-Methylcyclopentene	$S_R(5)$	5·0	−0·75	−2·07 [b]	1·32
4-Methylcyclopentene	$S_R(5)$	5·0	−0·75	−3·53 [b]	2·78
1-Ethylcyclopentene	$S_R(5) + S_{11}{}^*(12)$	5·23	5·91	4·91	1·00
Vinylcyclopentane	$S_R(5)$	6·2	0·29	−0·73 [a]	0·92
Allylcyclopentane	$S_R(5)$	6·2	5·2	5·95 [a]	−0·73
Methylenecyclopentane	$S_R(5)$	6·2	−2·68	−2·76 [a]	0·08
Ethylidenecyclopentane	$S_R(5)$	6·2	4·94	4·85 [a]	0·09

[a] ΔH_{vap} assumed the same as in the corresponding cycloparaffin. ΔH_{vap} assumed the same as for 1-methylcyclopentene.

(2) The 1,4-interactions of axial methyl (or alkyl) in alkylcyclohexanes. The repulsions involve three hydrogen atoms, represented by $S_3(i^2j, i^2k)$ (cf. C); these are not open to release by "twisting," and hence we have assumed that $S_3(i^2j, i^2k) = S_{22}(i^2j) + S_{22}(i^2k)$.



(C)

A comparison of calculated and experimental ΔH^0_f values for cyclohexanes, cyclopentanes, cyclopentenes, and cyclohexenes is given in Table 3. The experimental data are from A.P.I. tables[6] and from recent papers by Labbauf and Rossini,[11] and by Speros and Rossini;[12] the calculated ΔH^0_f were derived from equations (16—20).

Cycloalkanes:

$$\Delta H^0_f(C_nH_{2n}) = -2{\cdot}35n - 2{\cdot}58b_3 + 0{\cdot}55c_4 + [S]. \qquad (16)$$

1-Alkylcyclohexenes:

$$\Delta H^0_f(C_6H_9{\cdot}C_nH_{2n+1}) = 13{\cdot}28 - (n + 5)2{\cdot}35 - 2{\cdot}58b_3 + 0{\cdot}55c_4 + [S]. \qquad (17)$$

1-Alkylcyclopentenes:

$$\Delta H^0_f(C_5H_7{\cdot}C_nH_{2n+1}) = 13{\cdot}28 - (n + 4)2{\cdot}35 - 2{\cdot}58b_3 + 0{\cdot}55c_4 + [S]. \qquad (18)$$

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[11] Labbauf and Rossini, *J. Phys. Chem.*, 1961, **65**, 476.
[12] Speros and Rossini, *J. Phys. Chem.*, 1960, **64**, 1723.

3- or 4-Alkylcyclopentenes:

$$\Delta H^0_f(C_5H_7 \cdot C_nH_{2n+1}) = 19 \cdot 85 - (n + 4)2 \cdot 35 - 2 \cdot 58 b_3 + 0 \cdot 55 c_4 + [S]. \qquad (19)$$

Decahydronaphthalene:

$$\Delta H^0_f(C_{10}H_{18}) = -7 \cdot 96 - 2 \cdot 58 b_3 + 0 \cdot 55 c_4 + [S]. \qquad (20)$$

The agreement between observed and calculated ΔH^0_f in Table 3 is on the whole good, except in two cases (3- and 4-methylcyclopentene).

7. *Application to Substituted Paraffins*, $C_nH_{2n+1}X$.—For a substituted paraffin $C_nH_{2n+1}X$, the bond interaction scheme leads to:

$$\begin{aligned}\Delta H^0_f(C_nH_{2n+1}X, g) = \Delta H^0_f(CH_3X, g) - \\ (n - 1)2 \cdot 35 - 2 \cdot 58 b_3 - b'_3\Gamma_X + 0 \cdot 55 c_4 - c'_4\Delta_X + [S], \quad (21)\end{aligned}$$

where b'_3 = number of C–C–X interactions, $P_3{}^X$,

c'_4 = number of $C\!-\!C\!\begin{smallmatrix}C\\X\end{smallmatrix}$ trios, $T_4{}^X$

and Γ_X, Δ_X are composite parameters, defined by:

$$\Gamma_X = P_1 - P_2 - P_2{}^X + P_3{}^X + 2(T_1 - T_2 - T_2{}^X + T_3{}^X - X_1 + X_2)$$

$$\Delta_X = -T_1 + 2T_2 + T_2{}^X - T_3 - 2T_3{}^X + T_4{}^X$$

In these equations $P_2{}^X$, $P_3{}^X$ and $T_2{}^X$, $T_3{}^X$, $T_4{}^X$ are derived from P_2, P_3, and T_2, T_3, T_4 on replacing one carbon atom by X.

McCullough and Good[2] have tested equation (21) against experimental data for the alkane-thiols (X = SH) and shown that it fits the facts extremely well. In Table 4 the test is made by using the limited experimental data available for alkyl bromides and alcohols, and amines. Equations (22—24) were used to calculate ΔH^0_f values.

TABLE 4.

Compound *	$-\Delta H^0_f$ (calc.)	$-\Delta H^0_f$ (obs.)	Diff.	Compound *	$-\Delta H^0_f$ (calc.)	$-\Delta H^0_f$ (obs.)	Diff.
Methanol [13]	47·94	47·94	0·00	1-Bromobutane [19]	26·06	26·01	0·05
Ethanol [13]	55·95	56·17	−0·23	2-Bromobutane [19]	28·66	28·66	0·00
Propan-1-ol [14]	60·88	61·07	−0·19	1-Bromo-2-methylpropane [19]	28·09	28·4	−0·31
Propan-2-ol [14]	65·11	65·15	−0·04	2-Bromo-2-methylpropane [17]	31·89	31·2	0·69
Butan-1-ol [15]	65·81	65·81	0·00	1-Bromopentane [19]	30·99	31·13	−0·14
Butan-2-ol [16]	67·83	67·88	−0·05	1-Bromohexane [19]	35·92	35·88	0·04
2-Methylpropan-1-ol [16]	70·05	70·06	−0·01	1-Bromoheptane [19]	40·85	40·69	0·16
2-Methylpropan-2-ol [16]	74·87	74·87	0·00	1-Bromo-octane [19]	45·78	46·26	−0·48
Bromomethane [17]	9·85	9·6	0·25	Methylamine [20]	5·15	5·1	0·05
Bromoethane [18]	16·20	15·3	0·90	Ethylamine [20]	11·6	11·2	0·40
1-Bromopropane [17, 19]	21·13	21·98 [19]	−0·85	Butylamine [21]	21·5	22·3	−0·80
		21·1 [17]	0·03	s-Butylamine [21]	24·8	25·2	−0·40
2-Bromopropane [19]	23·73	23·55	0·18	t-Butylamine [21]	28·7	28·7	0·00

* Superior numerals denote reference footnotes.

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[13] Green, *J. Appl. Chem.*, 1961, **11**, 397.

[14] Snelson and Skinner, *Trans. Faraday Soc.*, 1961, **57**, 212 (ΔH_{vap} from Wadsö, personal communication).

[15] Gundry, Head, and Lewis, *Trans. Faraday Soc.*, 1962, **58**, 1309.

[16] Skinner and Snelson, *Trans. Faraday Soc.*, 1960. **56**. 1776.

[17] Skinner, *Royal Inst. Chem., Monograph* No. 3, 1958.

[18] Lane, Linnett, and Oswin, *Proc. Roy. Soc.*, 1953, *A*, **216**, 361.

[19] Bjellerup, *Acta Chem. Scand.*, 1961, **15**, 231.

[20] Jaffe, Thesis, Univ. Maryland, 1958.

[21] Evans, Fairbrother, and Skinner, *Trans. Faraday Soc.*, 1959, **55**, 399.

Alcohols ($\Gamma_0 = 5{\cdot}66$, $\Delta_0 = 1{\cdot}43$):

$$\Delta H^0{}_f(C_nH_{2n+1}OH, g) = -45{\cdot}59 - 2{\cdot}35n - 2{\cdot}58b_3 - 5{\cdot}66b_3' + 0{\cdot}55c_4 + 1{\cdot}43c_4' + [S]. \quad (22)$$

Alkyl bromides ($\Gamma_{Br} = 4{\cdot}0$, $\Delta_{Br} = 1{\cdot}4$):

$$\Delta H^0{}_f(C_nH_{2n+1}Br, g) = -7{\cdot}5 - 2{\cdot}35n - 2{\cdot}58b_3 - 4{\cdot}0b_3' + 0{\cdot}55c_4 + 1{\cdot}4c_4' + [S]. \quad (23)$$

Alkylamines ($\Gamma_N = 4{\cdot}1$, $\Delta_N = 1{\cdot}0$):

$$\Delta H^0{}_f(C_nH_{2n+1}{\cdot}NH_2, g) = -2{\cdot}8 - 2{\cdot}35n - 2{\cdot}58b_3 - 4{\cdot}1b_3' + 0{\cdot}55c_4 + 1{\cdot}0c_4' + [S]. \quad (24)$$

CHEMISTRY DEPARTMENT, UNIVERSITY OF MANCHESTER,
MANCHESTER, 13.

[*Received, April* 13*th*, 1962.]