236. *Atomic Heats of Formation and Bond Energies.*

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Two important thermochemical generalisations have followed the recently acquired knowledge of interatomic bond energies. In 1932 Pauling (*J. Amer. Chem. Soc.*, 1932, **54**, 3570) showed that the energy of non-polar bonds is probably additive, *i.e.*, that A—B = 1/2 (A—A + B—B), where A—B represents the energy of the non-polar bond between A and B, and further, that the more polar the bond between A and B, the greater the heat evolved in its formation and the greater the divergence from the additive relation. In 1933, Pauling and Sherman (*J. Chem. Physics*, 1933, **1**, 606) demonstrated that for compounds capable of existing in two or more forms not involving appreciable displacement of the constituent atoms, the atomic heat of formation calculated for either structure is less than the observational value. Such compounds evolve an unexpectedly large amount of heat on formation, so that their heats of combustion are correspondingly low. The excess energy evolved on formation, termed the resonance energy of the compound, is associated with the formation of a state intermediate (but not oscillating) between the two forms indicated by the alternative formulæ. The more nearly the states, represented by the alternative formulæ, approach each other in energy, the greater the observed resonance energy of the compound.

The object of work now in progress was to examine the resonance energy in substituted benzenes, with special reference to the known kinetic properties of various groups. For this purpose it is necessary to know the values of the interatomic bond energies concerned

with some degree of certainty. To a first approximation, the bond energy of a particular link is constant, independent of the nature and number of atoms in the molecule. This experimental fact is stated to be in harmony with calculations based on wave mechanics (Pauling, *loc. cit.*), each bond function interacting but slightly with the functions of other bonds. But in many isomeric compounds, *e.g.*, *n*- and *tert.*-butyl alcohol, where the atomic heats of formation are respectively 1243·5 and 1254·8 kg.-cals., discrepancies occur which are not attributable to resonance and result in considerable uncertainty in the value to be assigned to a particular bond. This uncertainty reappears in the calculated resonance energies and prevents more than qualitative comparison in a series of compounds.

It would appear, according to Pauling, that the variation in the bond energy of a particular link may be caused by variations in the polarity caused by the induced effects of vicinal groups. Thus the value for the C—Cl bond falls progressively in the compounds CH_3Cl, CH_2Cl_2, $CHCl_3$, CCl_4, in harmony with its decreased polarity due to the effects of other chlorine atoms. The correlation of increased bond energy with increased polarity of the link breaks down, however, in the paraffin hydrocarbon series. Rossini's recent determinations (*Bur. Stand. J. Res.*, 1934, **12**, 735; **13**, 189) of the heats of combustion of these substances show that the atomic heat of formation of methane is, in comparison with other paraffins, abnormally high, giving a correspondingly high value for the C—H bond. Yet it is in methane that we should expect the C—H links to be least polar and thus of least energy. The values to be assigned to the C—H and C—C bonds are fundamental, and the data obtained by Rossini for the paraffins and for the alcohols are given in Table I.

TABLE I.

Substance.	Q.	H_a.	Increment per CH_2.	Substance.	Q.	H_a.	Increment per CH_2.
CH_4	212·79	374·35		$CH_3 \cdot OH$	182·58	463·56	
C_2H_6	372·81	630·09	255·74	$C_2H_5 \cdot OH$	336·78	725·12	261·56
C_3H_8	530·57	888·09	258·00	$C_3H_7 \cdot OH$	493·20	984·46	259·34
C_4H_{10}	687·94	1146·48	258·39	$C_4H_9 \cdot OH$	649·90	1243·52	259·06
C_5H_{12}	845·27	1404·91	258·43	$C_5H_{11} \cdot OH$	806·75	1502·43	258·91
C_6H_{14}	1002·40	1663·54	258·63	$C_6H_{13} \cdot OH$	963·60	1761·34	258·89
				$CMe_3 \cdot OH$	638·6*	1254·8	270·3

* I.C.T., Vol. 5, 137, 164.

The heats of formation, H_a, shown in this table are calculated from the heats of combustion, Q, of the gaseous compound by the equation, $H_a = 244·38c + 85·69h + 59·0o - Q$, where c, h, and o are the numbers of atoms of carbon, hydrogen, and oxygen in the compound. The equation is based on C (s.) + O_2 (g.) = CO_2 (g.) + 94·38 kg.-cals.; H_2 (g.) + O_2 (g.) = H_2O (l.) + 68·38 kg.-cals.; C (s.) = C (g.) + 150 kg.-cals.; H_2 = 2H + 103 kg.-cals.; O_2 = 2O + 118 kg.-cals. Alteration of the value of C (s.) = C (g.) from 150 to 150 + dQ kg.-cals. alters C—C by $dQ/2$ and C—H by $dQ/4$ kg.-cals. It does not affect the discrepancy between observed and calculated values for the heat of formation of the lower members of the series.

It will be observed that the increment in the heat of formation in successive members, which is due to the formation of one C—C and two C—H bonds, varies from 255·74 to 258·63 in the hydrocarbons and from 261·56 to 258·89 in the alcohols, becoming constant as the series are ascended. If we take 258·80 as the value to be assigned to one C—C and two C—H bonds, we obtain on combination with the heat of formation of the higher hydrocarbons, C—H = 92·39, whence the calculated value for methane becomes 369·56, or 4·8 kg.-cals. less than is observed.

In the crystals of the alkaline chlorides, where the atoms are held together by " electrovalencies," the lattice energies were evaluated (Born, *Ber. deut. physikal. Ges.*, 1919, **21**, 13) by taking into account the coulombic and repulsive forces between the atoms. The correctness of the calculated values was confirmed (Fajans, *ibid.*, p. 542) from heat of solution measurements, and further confirmation was provided by Born (*ibid.*, p. 679), who deduced the affinity of the chlorine atom for an electron from the lattice energies and thermochemical data. Values for this affinity were obtained which were independent of the nature of the alkali metal.

The observed heat of formation of a Na—Cl " bond " from the atoms might thus be regarded as the difference of two electronic affinities (the respective affinities of a sodium and a chlorine atom for an electron), together with the coulombic and repulsive energy of the ion-pair in the position of minimum potential energy. The heat of formation of a covalent bond is, on the other hand, largely due to resonance between the two atoms, together with coulombic terms relating to electrons and nuclei. Good agreement between observation and calculation has been obtained (Eyring and Polanyi, *Z. physikal. Chem.*, 1931, *B*, **12**, 279) for the non-polar hydrogen molecule. When, however, the molecule contains permanent dipoles, it would appear that these will result in the acquirement of molecular dipole potential energy. The bond energies in a molecule should be equated, not to the heat evolved when the molecule is formed from its constituent atoms, but to the sum of this heat and the intramolecular dipole potential energy.

In attempts to evaluate the interatomic coulombic energy in molecules containing polar links, the dipole was at first regarded as located on the surface of the atom forming the covalent link (cf. Smallwood and Herzfeld, *J. Amer. Chem. Soc.*, 1930, **52**, 1919), and its energy evaluated from its known magnitude and direction. This procedure did not give results which would account for the abnormalities in the heats of formation of methane and methyl alcohol. The atoms were then considered as charged spheres. The spherical shell of negative electricity surrounding the nucleus was regarded as increased or decreased in charge when in combination with another atom, according to the time spent by the shared electrons in the respective spherical shells. Since, for coulombic attraction, a charged sphere is equivalent to a charge of the same magnitude at its centre, the dipole moment of a particular bond may be converted into charges situated at the centres of the atoms concerned (cf. Sidgwick, " Covalent Link in Chemistry," 1933, 156). For two such charges q and q', separated by a distance r, the coulombic energy is $qq'/2r = 7\cdot246$ qq'/r kg.-cals. per N pairs, where N is the Avogadro number, q and q' are expressed in 10^{-10} e.s.u., and r is in A. The dipole moments and interatomic distances employed (see *Ann. Reports*, 1931, **28**, 401) are collected in Table II.

TABLE II.

| Distance, A.	$\mu \times 10^{18}$.	Charge on atoms $\times 10^{10}$.	Distance, A.	$\mu \times 10^{18}$.	Charge on atoms $\times 10^{10}$.
C—C = 1·54	0	0	C—Cl = 1·74	1·5	0·86
H—C = 1·14	0·40*	0·35	H—O = 1·07	1·6	1·50
C—O = 1·47	0·74	0·50			

* This value is uncertain; for references see Sidgwick (*op. cit.*, p. 146).

The coulombic energy of the paraffins has been evaluated as the sum of $n(n-1)/2$ terms, where n is the number of atoms in the molecule. It is necessary to consider each individual pair of atoms as the coulombic forces decrease relatively slowly with distance. The repulsive energy, which varies inversely as a high power (*ca.* 8) of the distance apart of the atoms, falls off very rapidly and can be neglected. Even in the crystal lattice of salts, where the atoms are close packed, the repulsive energy is only approximately a quarter of the coulombic energy. Energy of compression or stretching will, however, arise in the covalently linked atoms and can be evaluated from the force constants given by Raman and vibration spectra. In the equilibrium position of the link, where the compression and coulombic forces are equal, *i.e.*, $q_1q_2/r^2 = f.x$, the compression (or extension) energy $\frac{1}{2}f.x^2 = (q_1q_2/fr^3).\frac{1}{2}q_1q_2/r$, and is equal to the coulombic energy times the factor $q_1q_2/f.r^3$. For C—H bonds the compression energy is negligible, and in the alcohols the O—H link has a compression energy of 0·79 kg.-cal., but this energy has no effect on the observed differences in the heats of formation of successive members of the series.

The configurations of the paraffin molecules, for which the coulombic energy has been summed, are shown in Figs. I—VII. The charges on the atoms are shown enclosed in ellipses. Broken lines denote that the bond is lying below the plane of the paper, whilst thick lines lie in the plane of the paper. The results are collected below.

Struc-ture.	No. of terms.	Energy of + terms, kg.-cals.	Energy of − terms, kg.-cals.	Net coulombic energy, kg.-cals.	Struc-ture.	No. of terms.	Energy of + terms, kg.-cals.	Energy of − terms, kg.-cals.	Net coulombic energy, kg.-cals.
I	10	2·88	12·48	− 9·60	V	91	29·12	44·60	−15·48
II	21	11·00	21·24	−10·24	VI	91	31·76	46·76	−15·00
III	21	11·04	21·24	−10·20	VII	136	39·96	57·68	−17·72
IV	55	19·40	32·36	−12·96					

It will be noticed that rotation of the methyl groups in ethane (II and III) has little effect on the interatomic coulombic energy. The two alternative positions considered for butane (V and VI) have potential energies of − 15·48 and − 15·00 kg.-cals. respectively. The lower potential energy has been used.
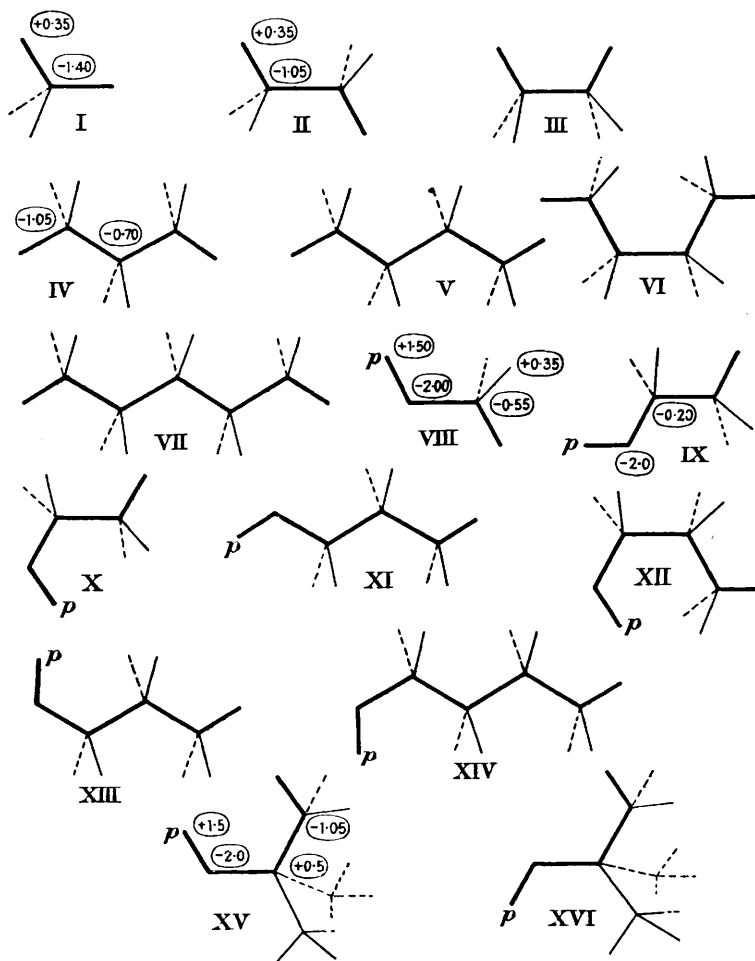
The configurations for the alcohols are shown in Figs. VIII—XVI, *p* representing the hydroxyl hydrogen. The results are collected below.

Structure	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI
Net coulombic energy, kg.-cals.	−22·75	−26·85	−27·41	−28·67	−28·47	−30·70	−33·30	−41·41	−42·76

The lower potential energy of X and XIII shows that the position favoured is that in which the hydroxyl hydrogen lies near to the β-carbon. This is the position for which the coulombic energy of *n*-butyl alcohol has been evaluated (XIV). The position of minimum

potential energy of *tert.*-butyl alcohol is XVI.   The difference in the coulombic energies of *n*- and *tert.*-butyl alcohol is noteworthy, the latter being more stable, according to these calculations, by approximately 9·4 kg.-cals.   This is in harmony with the heats of combustion of the vapours of these alcohols, which are 649·90 and 638·6 respectively.

The negative potential energies calculated for the paraffins and alcohols correspond to an enhanced evolution of energy of formation, and the sums of the bond energies are less than the observed atomic heats of formation by this amount.   The corrections are introduced in Table III.

TABLE III.

Sub-stance.	H_a.	Coulombic energy.	Corrected bond energies.	Increment per CH_2.	Sub-stance.	H_a.	Coulombic energy.	Corrected bond energies.	Increment per CH_2.
CH_4	374·35	− 9·60	364·75	255·1	$CH_3 \cdot OH$	463·56	−22·75	440·81	256·9
C_2H_6	630·09	−10·24	619·85	255·3	$C_2H_5 \cdot OH$	725·12	−27·41	697·71	256·1
C_3H_8	888·09	−12·96	875·13	255·9	$C_3H_7 \cdot OH$	984·46	−30·70	953·76	256·5
C_4HI_{10}	1146·48	−15·48	1131·00	256·2	$C_4H_9 \cdot OH$	1243·52	−33·30	1210·22	258·2
C_5H_{12}	1404·91	−17·72	1487·19		$CMe_3 \cdot OH$	1254·8	−42·76	1212·0	

Comparison with Table I shows that the major part of the variation in the increment due to the formation of one C—C and two C—H bonds is removed by introducing a correction for the interatomic coulombic energy in the molecule.   Taking 256·0 kg.-cals. as the corrected value for one C—C and two C—H bonds, we find the value of C—C and C—H to be 73·4 and 91·3 kg.-cals. respectively.

In almost all homologous series, a progressive increase appears in the bond energy of a particular link.   As a general illustration, the atomic heats of formation of the chloroparaffins (Sidgwick, *op. cit.*, p. 115) are shown below.   The coulombic energies and the corrected bond energies are also given.   The corrected value of C—Cl has been evaluated by using C—C = 73·4, C—H = 91·3 kg.-cals.

Substance.	H_a.	C—Cl, kg.-cals.	Coulombic energy.	Sum of bond energies.	C—Cl (corr.), kg.-cals.
CH_3Cl	355·5	74·7	− 1·7	353·2	79·3
C_2H_5Cl	616·8	77·6	− 7·3	609·5	79·6
C_3H_7Cl	877·9	79·3	− 9·5	868·4	82·5
			(*iso-*) −14·3	863·6	77·7
CMe_3Cl	1142·3*	86·4	−22·1	1120·2	79·8

* Unpublished result obtained by Mr. R. J. Lloyd.

From these results and those for the paraffins and alcohols in Table III, it is suggested tentatively that when bond energies are deduced from atomic heats of formation corrected for interatomic coulombic energy, they have constant values characteristic of the two atoms forming the bond.   Other series of compounds, and isomeric substances showing appreciable differences in their heats of combustion, will be examined later.