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The thermochemistry of carbon: valence states, heats of sublimation and energies of linkage

BY L. H. LONG, D.I.C., PH.D., AND R. G. W. NORRISH, F.R.S.

*Laboratory of Physical Chemistry, Cambridge*

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The controversy which exists at the present time between the figures 125 and 170 kcal./g.-atom for the latent heat of sublimation of carbon into monatomic vapour in the ground state originates largely from the neglect to take into consideration the energy required to raise the carbon atoms from the ground (²P) state to the lowest tetravalent (²S) electronic configuration corresponding to that in which it is normally found in chemical combination. Consideration of the energies of removal of a hydrogen atom from the methane and ethane molecules and of the energies of reorganization of the resulting radicals leads to the figure 190± about 10 kcal. for $L_0$, the heat of sublimation into free atoms in the ²S state. This in turn leads to a satisfactory and unambiguous assignment of values to bond energies (as distinct from dissociation energies) which can now be expressed with an uncertainty of not more than a few kcal. In the light of the valency distinction there remains no sound evidence to maintain the higher value put forward for $L_0$, and 125 kcal. is unquestionably of the right order. There are strong indications that an earlier estimate of 100 kcal. for the energy level of the ²S state above the ²P (ground) state is about 50% in excess of the true value.

The necessity for establishing this branch of thermochemistry on a sound theoretical and experimental footing has long been a very obvious need. The scheme here suggested reconciles points hitherto in apparent conflict, and brings virtually all established experimental knowledge into alignment.
L. H. Long and R. G. W. Norrish

1. Introduction

The dual purpose of this paper is to review critically the divergent values published for the heat of sublimation of carbon and the strengths assigned to certain chemical bonds involving carbon, including the reported variations in bond strength with the length of carbon chain. The two subjects are interdependent, and observations we wish to put forward with respect to the one throw a certain amount of light on the other.

Two prerequisites to the clear understanding of the thermochemistry of carbon and, indeed, of thermochemistry in general, are:

(a) a careful distinction between the different natures of bond energies and energies of dissociation;

(b) a differentiation between the fundamentally different energy levels of each individual element in its various states of valency (being two and four for carbon).

Both distinctions have been ignored by many in the past, and this has been largely responsible for the uncertain and conflicting bond-energy values which have been a feature of the thermochemistry of carbon from its beginning. The stress on the importance of these differences is not new in either instance, but a systematic treatment of this field in the light of these essential distinctions has not been undertaken before, and a reconciliation of many seemingly conflicting facts is here proposed.

2. Measurements and Calculations

It will help to clarify our arguments if we briefly review the methods which are at present available for the determination of the energies associated with chemical linkages. The following methods have been employed, of which the first two have had the widest application:

(a) Thermochemical. The heats of reaction of a number of different types of chemical processes have been measured and employed in the calculation of heats of formation and bond energies. For this purpose the heats of combustion have been found in general to be the most accessible. In the case of binary compounds with only one type of linkage, these can be combined directly with the heats of combustion of the component elements in their normal states, together with the heats of formation of the elements in these states from their monatomic vapours, to give the required bond energies. For example, if the heat of combustion of hydrogen sulphide to sulphur dioxide and water is accepted to be 134·5 kcal./mol., the energy of the S—H bond could be calculated in the following manner:

\[
\begin{align*}
\text{H}_2\text{S} + 1\frac{1}{2}\text{O}_2 & = \text{SO}_2 + \text{H}_2\text{O} \text{ (liq.)} + 134.5 \\
\text{SO}_2 & = \text{S (rhombic)} + \text{O}_2 - 70.91 \\
\text{S (rhombic)} & = \text{S}^{(3P)} - 66.3 \\
\text{H}_2\text{O} \text{ (liq.)} & = \text{H}_2 + \frac{1}{2}\text{O}_2 - 68.32 \\
\text{H}_2 & = 2\text{H} - 104.1 \\
\text{(By addition)} & \quad \text{H}_2\text{S} = \text{S}^{(3P)} + 2\text{H} - 175.1
\end{align*}
\]
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The last process involves only the rupture of two S—H bonds. Thus the average S—H bond energy is 87.6 kcal.

The purpose of providing this simple example is to emphasize that, in the case of polyvalent elements, the value provided by thermochemical data is the average value of the bond energy \((E)\) and not the dissociation energy \((D)\) of any specific linkage.

Heats of combustion are frequently expressed with uncertainties of 3 parts or less in 10,000, but not all thermochemical quantities are known with anything approaching this precision. The most notable example of this is the energy difference between solid carbon and its monatomic vapour in the ground state, that is, the latent heat of sublimation of carbon. Opinions are divided between two values differing by about 30%.

\(b\) Spectroscopic. It is frequently possible to obtain information about energies of dissociation from band spectra. The various ways of doing this are reviewed elsewhere (Herzberg 1937). Where a convergence limit can be observed directly, the required energy may be obtained with considerable accuracy, that is, to within a few tenths of 1%. Accurate values may also be furnished by predissociation limits if the potential energy curves for the products satisfy certain conditions. Otherwise the available methods supply in general only upper limits for dissociation energies.

To obtain energies of dissociation into atoms or radicals in the ground state it is essential to determine the energy levels of the products, if they are not originally formed in that state. Also, for molecules which might dissociate in more than one way, wrong conclusions may be drawn unless evidence for the primary step is obtained by an examination of the products of photodecomposition at the relevant wave-length.

In some cases it has not been possible to decide conclusively between several possible values. This is so in the case of carbon monoxide where it is not known with certainty if the predissociation reported at 9-61 eV is real, accidental, or merely ordinary perturbation. If \(D_0(\text{CO})\) could be unambiguously determined, it would be possible, since the other requisite thermochemical quantities are accurately known, to fix the value for the latent heat of sublimation of carbon.

\(c\) Reaction kinetics. From a knowledge of the kinetics of reactions involving free atoms or radicals, and a determination of the activation energies of the reactions concerned, it is possible to derive information on dissociation energies. This method has been recently applied, for example, to estimate the energies of removal of the first hydrogen atom in methane (Andersen, Kistiakowsky & Van Artsdalen 1942; Andersen & Kistiakowsky 1943; Kistiakowsky & Van Artsdalen 1944) and ethane (Andersen & Van Artsdalen 1944).

\(d\). Electron impact critical potentials. By making certain rather questionable assumptions, Stevenson (1942) has attempted to calculate \(D(\text{CH}_3—\text{H})\) and \(D(\text{C}_2\text{H}_5—\text{H})\) from the critical potentials observed in electron impact experiments. This method has also been successfully employed by others to diatomic molecules.
The results agree reasonably well with those obtained by other methods, allowance being made for the inherent uncertainty of several percent.

(e) Other methods. In the case of reversible reactions, equilibrium data have been much used to calculate energies of dissociation by means of the van’t Hoff isochore. It is also possible to calculate $D$ for a neutral molecule by combining $D$ for an ionized state with ionization energy data. For a few very simple atomic linkages, $D$ has been calculated by exhaustive wave-mechanical or other theoretical treatment, as in the case of the $\text{H} - \text{H}$ bond (James & Coolidge 1933; Cook 1945). Finally, there is a semi-empirical relationship deduced by Sutherland (1938, 1940), for the interdependence of interatomic distance, force constant and dissociation energy, from which a rough value of the latter may be derived if sufficient data are available. These methods do not closely concern us here and need not be discussed further.

In order to avoid confusing the bond energy $E$ with the energy of dissociation $D$, consideration must be given to the precise quantity provided by the method in question. Only for diatomic molecules can $D$ and $E$ sometimes be equated. Although in the case of polyatomic molecules the two quantities may on occasions approximate quite well, it needs to be emphasized that they are not identical and frequently differ by large amounts. It is seen that $D$ depends on the states of the products, whereas $E$, like the bond length, has a fixed value.

3. THE TWO HEATS OF SUBLIMATION OF CARBON

It is of primary importance to remember, when employing heats of formation to calculate the sum of the bond energies in molecules containing di- and tetravalent carbon, that the molecules must be regarded in the two cases as having been built up from carbon atoms initially possessing fundamentally different energy levels (Norrish 1934). The ground state of the carbon atom corresponding to a valency of two is $sp^2$, $3P$, the lowest corresponding to a valency of four being $sp^3$, $5S$, which is at a considerably higher energy level. The energy change in the $5S \rightarrow 3P$ transformation has not been directly determined for C, although the corresponding changes have been observed for $\text{N}^+$ and $\text{O}^{++}$. By an extrapolation method, the value for C has been estimated by Bacher & Goudsmit (1934) to be about 4·3 eV or 100 kcal., but, more recently, Ufford (1938) has placed it at about 73 kcal. If the latent heats of sublimation of graphite into monatomic vapours consisting entirely of atoms in the $3P$ and $5S$ states be designated by $L_1$ and $L_2$ respectively, then, assuming the former figure quoted to be correct, $L_2 - L_1 = 100$ kcal./mol. However, we believe the difference between $L_2$ and $L_1$ to be considerably less than this amount for reasons which will be discussed later.

Neither $L_1$ nor $L_2$ is known with certainty. Whereas some authors support a value for $L_1$ of about 125 kcal./g.-atom (Herzberg 1937, 1939, 1942; Goldfinger & Jeunehomme 1936), others advocate a much higher figure around 170 kcal. (Gaydon & Penney 1945; Kyneh & Penney 1941; Baughan 1941). Clearly, since carbon in most of its compounds is tetravalent, the figure with which thermochemical data are
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normally concerned in the first instance is \( L_2 \) rather than \( L_1 \). This point has escaped many investigators, including Pauling (1939), whose table of bond energies consequently contains values deficient in the case of links involving carbon. For example, if the average bond energy in methane were known, \( L_2 \) could be calculated from the following set of equations:

\[
\begin{align*}
\text{CH}_4 &= \text{C (graphite)} + 2\text{H}_2 - 17.87 \\
2\text{H}_2 &= 4\text{H} - 208.2 \\
\text{C (graphite)} &= \text{C}(^5S) - L_2 \\
\text{CH}_4 &= \text{C}(^5S) + 4\text{H} - (L_2 + 226.1)
\end{align*}
\]

Thus \( L_2 + 226.1 \text{ kcal.} \) could be placed equal to four times the average C—H bond energy and \( L_2 \) evaluated directly.

On the other hand, if one considers the total energy required to rupture the four bonds in methane by successive steps, one would here be primarily concerned with \( L_1 \) if the carbon were able to revert to the divalent state with the rupture of the second bond. That the carbon in \( \text{CH}_2 \) is indeed in the divalent state is indicated by the experimental work of Pearson, Purcell & Saigh (1938) and Barrow, Pearson & Purcell (1939). If the energy absorbed by the four steps were \( a, b, c \) and \( d \) respectively, then

\[
\text{CH}_4 = \text{C}(^3P) + 4\text{H} - (a + b + c + d).
\]

The value of \( a \) has been determined to be 102 kcal. (Andersen & Kistiakowsky 1943; Kistiakowsky & Van Artsdalen 1944). One would expect \( b \) to have the same order of magnitude but for the fact that during the step \( \text{CH}_4 \rightarrow \text{CH}_2 + \text{H} - b \), the carbon changes to the divalent state with the liberation of energy. This energy may be regarded as being divided into three parts: one part is liberated during the removal of the hydrogen atom, which means that \( b \) will be smaller than the mean bond energy in free methyl, whereas the other two parts are absorbed in the weakening of the two remaining bonds. The value of \( d \), the energy of removal of the last hydrogen atom, is known to be 80 kcal., having been recalculated by Herzberg (1939) from published spectroscopic data (Shidei 1936). There is nothing to support the view of Berriman & Clark (1938) that \( d \) is \( \frac{1}{2}(L_2 - L_1) \) less than the mean bond energy in methane. \( c \) would be expected to have about the same magnitude as \( d \), and a theoretical treatment by Voge (1936) indicates that the difference is only about 0.05 eV. Thus, in the calculation of \( L_1 \), \( c \) could be placed equal to \( d \) as a first approximation. If were known, therefore, \( L_1 \) could be determined from the two foregoing equations and the relationship

\[
\text{C}(^5S) = \text{C}(^3P) + L_2 - L_1.
\]

Although \( b \) is not known, it has long been recognized that its value is probably considerably less than \( a \) (Meeke 1930). This is questioned by Baughan (1941), however, who puts forward the following two arguments in support of the higher value 170 kcal. for \( L_1 \):
(a) The first is based on the work of Voge (1936), who calculates that the energy required for the successive removal of hydrogen atoms in methane does not vary by any large amount. Voge's conclusions, however, rest on the quantities 17.0 and 4.0 eV for the atomic heats of formation of CH₄ and CH respectively. Considerable uncertainty must be attached to the former figure, and the latter is now known to be over 0.5 eV less than the value employed (Herzberg 1939). Furthermore, it is now known that the process CH₄ → CH₃ + H requires 101 kcal. or 4.38 eV at absolute zero (Kistiakowsky & Van Artsdalen 1944), and, combining this value with Voge's equations (20) and (22), a new value of 1.16 eV for his integral Nₛₘ is obtained, which in turn leads to the estimates 14.25 and 9.87 eV respectively for the energies of formation of CH₄ and CH₃ from free atoms. These figures lead to a low value for L₁, even if the fact that they include zero-point energy be neglected. Thus Voge's calculations are not compatible with the value 170 kcal. for L₁.

(b) The second argument rests on the observation that the energy exchange in the successive replacement of hydrogen atoms in methane by halogen atoms is approximately constant for any one halogen. This does not seem to us, however, to be a relevant argument, since in every case the carbon atom remains saturated and there are no free valencies or divalent state to consider as in the case in question.

We will now examine the arguments of Kynch & Penney (1941) who also support this value of 170 kcal. for L₁, claiming agreement for several independent methods as follows:

<table>
<thead>
<tr>
<th>Method</th>
<th>L</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) spectroscopic determination of D₀(CO)</td>
<td>168.8</td>
</tr>
<tr>
<td>(ii) rate of sublimation of carbon in vacuo</td>
<td>176*</td>
</tr>
<tr>
<td>(iii) heat of reaction 2CH₄ → C₂H₆ + H₂</td>
<td>170</td>
</tr>
<tr>
<td>(iv) Birge-Sponer extrapolation for CO</td>
<td>~175</td>
</tr>
<tr>
<td>(v) absorption-band limits of (a) butadiene, (b) hexatriene, (c) benzene</td>
<td>168–173</td>
</tr>
</tbody>
</table>

On close examination, however, it becomes apparent that some of these methods provide a value for L₁ and some for L₂.

Methods (i) and (iv) lead to L₁, but the value selected for D₀(CO) is only one of several possible values, others of which, for example, lead to L₁ = 125 or 108.5 kcal. Method (iv), as has been pointed out by Herzberg (1942), usually provides values 20–40% too high for long extrapolations such as are involved here, thus supporting L₁ = 125 kcal. rather than L₁ = 170 kcal.

Method (ii) is due to Marshall & Norton (1933) who determined the rate of loss in weight of carbon at high temperatures in vacuo, and calculated that the conversion of solid carbon to monatomic vapour requires 177 kcal./g.-atom. Since solid carbon is in the tetravalent state, it cannot be assumed that the vapour is produced directly in the ³P state, though doubtless some atoms quickly revert to this. Only, therefore, in a method which permitted the establishment of equilibrium conditions could one feel sure that, allowing for the additional complication of the presence of C₂

* Misquoted by Kynch & Penney. The experimental figure is 177 kcal.
molecules, a measure of \( L_1 \) was being obtained. Here is a dynamic method, which, if the carbon vapour were initially produced in the \(^5S\) state, would provide a value for \( L_2 \). That the vapour, or at least the major part of it, is not initially produced in the \(^3P\) state is indicated by the wide disagreement in values provided by the equilibrium and dynamic methods (§5). The manner in which carbon vapour leaves a solid surface is not known, but several suggestions have been made (Herzberg, Herzfeld & Teller 1937; Herzberg 1937; Kynch & Penney 1941). If Herzberg’s considerations of a ‘potential hill’ apply, then the dynamic method should provide a value between \( L_1 \) and \( L_2 \). It must be concluded, therefore, that in the absence of a precise knowledge of the mechanism of sublimation of carbon, the method of Marshall & Norton cannot provide an experimental value for \( L_1 \), but might be more rightly regarded as furnishing a lower limit for \( L_2 \).

Method (iii) provides an approximation to \( L_2 \). Since \( L_2 \) is numerically equal to twice the energy of the single C—C link in solid barbon (§4), and since this link is rather stronger than the C—C link in ethane (§4), the value 88-2 kcal. calculated for the latter link (Baughan & Polanyi 1940; Baughan 1941) leads to a value for \( L_2 \) nearer 180 than 170 kcal. But for this calculation Baughan tacitly identifies bond energies with dissociation energies as will be discussed in greater detail in the next section.

Likewise, when discussing bond energies, Kynch & Penney fail to realize that the figures they quote refer to \( L_2 \) and not to \( L_1 \). If method (v) is valid, it determines \( L_2 \); but, without stating their reasons, Mulliken & Rieke (1942) consider it to provide no basis for deciding upon the true value of the heat of sublimation of carbon.

In conclusion, therefore, the apparent agreement obtained by Kynch & Penney is seen to be unreal and misleading. Inasmuch as the higher value (170 kcal.) is based on arguments leading to \( L_2 \), there are no grounds in these considerations of Kynch & Penney for regarding this quantity as incompatible with \( L_1 = 125 \) kcal., the value these authors are trying to refute in their belief that \( D_0(\text{CO}) = 11-1 \text{eV} \) and \( L_1 = 170 \) kcal. Nevertheless, though the figure 170 kcal. may be regarded as not altogether an unreasonable estimate for \( L_2 \), in our opinion it still needs some modification to comply with published experimental data (§5).

4. Variation of Bond Strengths in the Normal Paraffin Series

Until 1933, published values for the heats of combustion of the series of straight-chained paraffins showed no irregularities outside the limits of experimental error. There was thus no reason to believe the C—C and C—H bond strengths were other than constant (Sidgwick & Bowen 1931). However, more accurate measurement has indicated a deviation in bond strength towards increased stability of the first five members of the series (Rossini 1934b), the deviation decreasing from methane to \( n \)-pentane.

Van Artsdalen (1942) has calculated the values of

\[ D(\text{CH}_3—\text{CH}_3) \quad \text{and} \quad D(\text{C}_2\text{H}_5—\text{C}_2\text{H}_5), \]
obtaining a difference of about 3 kcal., to which he attaches a qualitative rather than quantitative significance in view of the probable errors. A similar decrease with increasing chain length has been reported by Stevenson (1942). Unfortunately, Van Artsdalen, in common with Baughan (1941), confuses the issue somewhat by identifying the energy of dissociation with the bond strength. In the case of the C—C link in C₅H₅, for example, the dissociation energy differs from the bond strength by six times the difference between the C—H bond strengths in CH₃ and C₂H₅, which may amount to several kcal. The difference between

\[ D(\text{CH}_3-\text{CH}_3) \quad \text{and} \quad D(\text{C}_2\text{H}_5-\text{C}_2\text{H}_3) \]

is reduced to about 1 kcal. when the more recent figure for \( D(\text{C}_2\text{H}_5-\text{H}) \) (Andersen & Van Artsdalen 1944) is employed in Van Artsdalen's calculations. Let us now proceed to investigate the actual variation with chain length of the average values for \( E(\text{C—C}) \) and \( E(\text{C—H}) \).

In both diamond and graphite the carbon is in the tetravalent state, and the sublimation of either solid form into monatomic vapour involves the energy of rupture of two valency links per carbon atom (plus a small \( RT \) term which will be neglected). Thus the average strength of the C—C valency link is \( \frac{1}{2}L_2 \). Since the difference in the heats of combustion of diamond and graphite is negligibly small, being only a few tenths of 1 kcal./g.-atom (Prosen, Jessup & Rossi 1944), the heats of sublimation are almost identical, and the C—C bond strength in diamond may be equated to \( \frac{1}{2}L_2 \) without appreciable error.

The aliphatic C—C bond is known to be slightly weaker than that of diamond, varying values for this difference having been suggested from time to time. The order of this amount is given by some of the later papers dealing with this point at 4 kcal. (Lasareff 1935; Schmid 1936). This figure, however, can be obtained with greater accuracy from the heats of formation of the paraffin series. For this purpose the difference in strength between the central C—C bond in the long-chained paraffins and the C—C bond in solid carbon will be equated to \( x \) kcal. The strength of the aliphatic bond then becomes \( \frac{1}{2}L_2 - x \). The strength of the H—H bond is required for the calculation of absolute values, and this is known accurately. Herzberg (1939) gives it as 103.2 kcal. at 0° K, which is equivalent to 104.1 kcal. at 25° C and constant pressure when the appropriate adjustment of 0.94 kcal. (Giauque 1930) is made.

One cannot, of course, calculate absolute values for the average bond energies while \( L_2 \) remains undetermined, but by combining the foregoing values with the heats of formation of the paraffins it is possible to obtain relative values, the variation being independent of \( L_2 \). The heats of formation of the lower homologues from methane to \( n \)-pentane have been calculated (Rossini 1940) direct from the heats of combustion (Rossini 1931, 1934a). For the higher members of the series, from \( n \)-hexane to \( n \)-dodecane, the heats of formation have been calculated from the heats of combustion in the liquid state (Jessup 1937) and the latent heats of vaporization (Holcomb & Brown 1942). The accuracy will not be quite as high for the liquid paraffins, as the latent heats may be in error by a small percentage, but the error
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thereby introduced in the bond energies will be very small as the latent heats are small compared with the heats of combustion.

The heats of formation of the higher members of the series from \( n \)-hexane upwards show regular increments of 5·45 kcal. per CH\(_2\) group, that is, the heat of formation of the CH\(_2\) grouping is equal to this amount. Removing a CH\(_2\) group from the middle of a chain to leave a molecule containing one carbon atom fewer eliminates one C—C and two C—H bonds. The sum of these bond energies is equal to the energy required to convert the CH\(_2\) grouping into atoms, which may be simply calculated:

\[
\begin{align*}
\text{CH}_2 \text{ (grouping)} &= \text{C (graphite)} + \text{H}_2 - 5\cdot45 \\
\text{C (graphite)} &= \text{C}^{(5S)} - L_2 \\
\text{H}_2 &= 2\text{H} - 104\cdot1
\end{align*}
\]

\[
\text{CH}_2 \text{ (grouping)} = \text{C}^{(5S)} + 2\text{H} - (L_2 + 109\cdot55)
\]

Hence \( E(\text{C—C}) + 2E(\text{C—H}) = L_2 + 109\cdot55 \) kcal. But \( E(\text{C—C}) = \frac{1}{2}L_2 - x \), from which it follows

\[
E(\text{C—H}) = \frac{1}{4}L_2 + \frac{1}{2}x + 54\cdot775 \text{ kcal.}
\]

This value can be compared with the corresponding values for the paraffins themselves. The following set of equations is known for the case of methane (the third place of decimals, although of no significance in the actual bond-energy values, is necessary for the accurate computation of small differences):

\[
\begin{align*}
\text{CH}_4 &= \text{C (graphite)} + 2\text{H}_2 - 17\cdot865 \\
\text{C (graphite)} &= \text{C}^{(5S)} - L_2 \\
2\text{H}_2 &= 4\text{H} - 208\cdot2
\end{align*}
\]

\[
\text{CH}_4 = \text{C}^{(5S)} + 4\text{H} - (L_2 + 226\cdot065)
\]

Thus for methane,

\[
E(\text{C—H}) = \frac{1}{4}L_2 + 56\cdot516 \text{ kcal.}
\]

For the other paraffins allowance must be made for the C—C bonds. If the C—C bond energy, as a first approximation, is assumed constant at \( \frac{1}{2}L_2 - x \), the series of values given in the second column of table 1 is obtained. The difference between the average values of \( E(\text{C—H}) \) and that for the CH\(_4\) group, when multiplied by the number of C—H bonds in the molecule, gives \( \delta \), the total deviation from linearity of the heats of formation of the various hydrocarbons as shown in the third column. Since the deviation for \( n \)-hexane and the higher members is zero, the value of \( x \) is seen to be 0·93 kcal. Still assuming the C—C bond to be constant, the average energies of the C—H bond are compared in table 2. The figures in the third column are derived from the heats of formation at absolute zero as calculated by Pitzer (1940), and are given for comparison. The superscript in the symbol \( L_2^0 \) refers to the absolute temperature. (The heat of vaporization data for the liquid homologues have not been obtained from the same source in columns 2 and 3.)
For the higher members of the series the following relationship holds at \( 25^\circ C \):

\[
E(\text{C—C}) = 2E(\text{C—H}) - 111.4 \text{ kcal}.
\]

This relationship is independent of the heat of sublimation of carbon, and depends solely on accurately known heats of combustion and on heats of vaporization.

The foregoing tables are based on the assumption that the C—C bond strength is constant. It is far more reasonable to suppose that the C—C bonds also make a contribution to the deviation from linearity of the lower homologues. The proportion of the deviation due to each type of bond cannot be assessed with certainty. It seems reasonable to suppose that the variation in bond energy rests mainly in the contribution due to the carbon atoms, since the proportion of primary and secondary carbon atoms varies from molecule to molecule. This would lead one to expect that the variation in the average strengths of the C—C bonds (involving two carbon atoms) would be about twice that of the C—H bonds. On this assumption the mean strengths of the two bond types for the series are compared in table 3. The maximum variation in the average bond strength is seen to be about 1.3 kcal. for the C—H bond and 0.5 kcal. for the C—C bond. For the whole series the C—H bond shows appreciable deviation only in the case of methane. The deviation for ethane is very small, and for the other homologues is negligible (less than 0.1 kcal.). Thus the postulate of the additivity of bond strengths holds very accurately for the normal
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paraffins with the exceptions of methane and, to a lesser extent, ethane. The difference in $E(C—H)$ in CH$_4$ and C$_2$H$_6$ is seen to be about 1 kcal., and the C—C link in C$_2$H$_6$ roughly 0·5 kcal. weaker than in solid carbon. The variation of $D$(C—H) for individual primary, secondary and tertiary hydrogen atoms is dealt with elsewhere (Brackett 1928; Eyring 1932; Conn, Kistiakowsky & Smith 1939; Smith & Taylor 1939).

<table>
<thead>
<tr>
<th>Substance</th>
<th>Average $E$(C—C) at 25°C</th>
<th>Average $E$(C—H) at 25°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_4$</td>
<td></td>
<td>$\frac{1}{2}L_2 + 0.44$</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>$\frac{1}{2}L_2 - 0.74$</td>
<td>$\frac{1}{2}L_2 + 0.51$</td>
</tr>
<tr>
<td>C$_3$H$_8$</td>
<td>$\frac{1}{2}L_2 - 0.86$</td>
<td>$\frac{1}{2}L_2 + 0.54$</td>
</tr>
<tr>
<td>n-C$<em>4$H$</em>{10}$</td>
<td>$\frac{1}{2}L_2 - 0.92$</td>
<td>$\frac{1}{2}L_2 + 0.57$</td>
</tr>
<tr>
<td>n-C$<em>5$H$</em>{12}$</td>
<td>$\frac{1}{2}L_2 - 0.93$</td>
<td>$\frac{1}{2}L_2 + 0.58$</td>
</tr>
<tr>
<td>n-C$<em>6$H$</em>{14}$, etc.</td>
<td>$\frac{1}{2}L_2 - 0.93$</td>
<td>$\frac{1}{2}L_2 + 0.58$</td>
</tr>
</tbody>
</table>

Shortly before going to press there has been published a revised set of values for the heats of formation of the paraffins at 25°C (Prosen & Rossini 1945) and at 0°F (Prosen, Pitzer & Rossini 1945). The most surprising feature about these new figures is that the first five members of the series no longer all deviate towards greater stability as originally indicated (Rossini 1934b). Methane is still given as the most stable, but n-pentane, n-butane and propane deviate towards decreased stability, the bond energies reaching a minimum in the case of propane. This lessening of stability is very slight but seems to exceed the limits of experimental error. With these figures the value of $x$ required is 2.7 kcal. and the maximum variation in the average bond strengths is smaller, being about 0.7 kcal. for the C—H bond and less than 0.1 kcal. for the C—C bond. The value of $E$(C—H) is about 0·7 kcal. stronger for methane than for ethane. If accepted, this revision would not affect materially the conclusions reached in § 5.

5. Evaluation of $L_1$ and $L_2$

It has already been emphasized that $D$ and $E$ are not identical terms. When a polyatomic molecule is split into two parts by the rupture of a chemical link, the molecules or radicals formed reorganize themselves. Whether one or more of the atoms undergo a change in electron configuration with the entailed transference of energy or not, some change in the bond energies of the remaining links is to be expected, and this will also involve the absorption or liberation of energy. For the net effect we shall use the expression energy of reorganization, a term originally defined elsewhere (Norrish 1934). Only if the energy of reorganization is zero will $D$ be equal to $E$.

As already mentioned, the experimental value of $D$(CH$_3$—H) at 25°C is 102 ± 1 kcal. (Andersen & Kistiakowsky 1943; Kistiakowsky & Van Artsdalen 1944). This
implies that $D(\text{CH}_3 - \text{H})$ and $D(\text{H}_2)$ differ but slightly (about 2 kcal.), in good agreement with Patat (1936), who came to the conclusion that the reaction

$$\text{CH}_4 + \text{H} = \text{CH}_3 + \text{H}_2$$

is almost thermoneutral on the grounds that the forward and reverse processes require approximately equal activation energies.

The dissociation energy of the $\text{C}_2\text{H}_5 - \text{H}$ link is about 3 kcal. less than that of the $\text{CH}_3 - \text{H}$ link (Andersen & Van Artsdalen 1944). Since the actual C—H bond strength in the ethane molecule is only about 1 kcal. weaker than in $\text{CH}_4$ (table 3), this implies a difference of about 2 kcal. in the energies of reorganization of the ethyl and methyl radicals. No great quantitative significance should be attached to this figure as it is subject to relatively large experimental error. The value is reasonable, since it implies that $D(\text{CH}_3 - \text{CH}_3)$ is 1.2 kcal. greater than $D(\text{C}_2\text{H}_5 - \text{C}_2\text{H}_5)$, whereas a lessening of 1 kcal. in the reorganization energy difference would make $D(\text{C}_2\text{H}_5 - \text{C}_2\text{H}_5)$ greater than $D(\text{CH}_3 - \text{CH}_3)$, which scarcely seems likely in consideration of the fact that stability decreases rather than increases with increasing chain length. Since it might be expected that the energy of reorganization of the ethyl radical would be larger than that of the methyl radical, the observed difference infers that energy is liberated by these radicals at their formation from ethane and methane. Thus one would expect the energy required to remove the first hydrogen atom from $\text{CH}_4$ to be rather less than the average C—H bond energy, $E(\text{C—H})$ being slightly greater in $\text{CH}_3$ than in $\text{CH}_4$. It follows that the value of 102 kcal. for the energy of removing the first hydrogen atom from the methane molecule may be regarded as a minimum value for $E(\text{C—H})$, corresponding to a minimum figure of 182 kcal. for $L_2$. Since there is no change in the valence state of the carbon atom when one hydrogen atom is removed, and since the difference in electronegativity of carbon and hydrogen is small, no large energy of reorganization for the $\text{CH}_3$ radical is to be expected, and the difference in $E(\text{C—H})$ for $\text{CH}_4$ and $\text{CH}_3$ will be small. Our reasoning that the bond energy is the greater in $\text{CH}_3$ is supported by considerations brought forward by Van Vleck (1934). The actual bond energy in $\text{CH}_4$ cannot be fixed precisely, but it is not likely to differ from the weighted value of 104 kcal. by more than a small number of kilocalories in either direction. This figure leads to 190 kcal. for $L_2$. Since any variation in $L_2$ correspondingly affects $E(\text{C—H})$ by one-quarter of that amount, the uncertainty in $L_2$ is four times that in the C—H bond energy. The permissible limits for $L_2$ will be considered later.

If the estimate of Bacher & Goudsmit (1934) of 100 kcal. for the $^5S \rightarrow ^3P$ conversion is correct, the value here suggested for $L_2$ implies a magnitude of about 90 kcal. for $L_1$. Since this would imply an equilibrium vapour pressure for carbon very much higher than has ever been experimentally indicated, it seems probable that Bacher & Goudsmit's figure is in excess of the true value. Reference has already been made to the alternative figures 125 and 170 kcal. for $L_1$, and it seems impossible to reconcile the higher of these with the foregoing observations; indeed, the value 170 kcal.
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appears to be even less likely than a value lower than 125 kcal. The next lower value possible for correlation with the CO spectrum is 108.5 kcal., but even this value is very difficult to reconcile with the observed vapour pressure of carbon. On the other hand, a dimension of the order of 225 kcal. for \( L_2 \) would necessitate bond-energy values very much higher than those normally assigned to carbon compounds. The difference between \( L_2 \) and \( L_1 \) is therefore in all probability considerably less than 100 kcal., and \( L_1 = 125.0 \) kcal. at 0° K, corresponding to 9.144 eV for \( D_0(\text{CO}) \) (Herzberg 1939) and 27.20 kcal. for the heat of formation of CO at 0° K (Wagman, Kilpatrick, Taylor, Pitzer & Rossini 1945), still seems the most likely.

The employment of electron impact phenomena by Hagstrum & Tate (1941) to determine \( D(\text{CO}) \) has furnished the value 9.6 eV, necessitating about 136 kcal. for \( L_1 \). If the estimated appearance potential of the \( C^+ \) ion is in error it is in all probability high, and the result may be regarded as an upper limit. To reconcile the figure with that advocated by Herzberg from spectroscopic data presupposes an error of 0.5 eV, an amount exceeding that which Hagstrum & Tate are inclined to allow on the grounds that agreement with spectroscopic data is much closer in the case of other molecules: on the other hand, electron impact experiments have elsewhere indicated a somewhat lower value (8.8 eV) for \( D(\text{CO}) \) (Savard 1937): In any case, this evidence weighs decidedly against 170 kcal. as a possible value for \( L_1 \), and even more convincing is the photodecomposition of carbon monoxide by ultraviolet radiation of wave-length 1295 A with a quantum yield of unity (Faltings, Groth & Harteck 1938), which, as pointed out by Herzberg (1942), would appear to set a definite maximum of 135 kcal. on \( L_1 \).

Further confirmation that 125 kcal. is the most probable value for \( L_1 \) is to be found in the observations of Barrow (1940) concerning the linear relationship between \( D_0 \) and the internuclear distance for a series of diatomic molecules, each consisting of one atom in group IV and one in group VI (b subgroups) of the Periodic Table. If this relationship is valid for the whole series, \( D_0(\text{CO}) = 11.11 \) eV, corresponding to \( L_1 = 170 \) kcal., would appear to be far too large to be permissible, 9.14 eV being the most satisfactory value. Undue emphasis is not placed on this point since the linearity is entirely empirical and only six of the values indicated were determined by rotational analysis, but attention is drawn to it as good circumstantial evidence.

The triple point of carbon has been determined by Basset (1939, 1942) who passed an electric current through a thin graphite rod under a varying pressure of argon until it either sublimed or melted. The co-ordinates of the triple point were found to be about 4000°C K and 100 atm. Below this pressure the carbon sublimed without melting. Goldfinger & Jeunehomme (1936) have calculated the vapour pressures of carbon corresponding to each of the three values 107, 124 and 169 kcal. for \( L_1 \). For monatomic vapour the expected pressures at 4000°C K are 151, 20 and 0.065 atm. respectively. The observed value is intermediate between the figures provided by the two lower values of \( L_1 \), agreement being best for \( L_1 = 107 \) kcal., but lies close to the total-pressure curve for \( L_1 = 124 \) kcal. for which the pressure of \( \text{C}_2 \) molecules
has been taken into consideration. It is to be regretted that Basset does not provide an experimental sublimation curve. Presumably maximum temperatures, corresponding to the onset of sublimation, would have been observed at lower pressures, and his apparatus would have been suitable for carrying out the required measurements. Instead, he constructs a provisional phase diagram by combining his result with the readjusted figures obtained from measurements by other workers of the temperatures of the positive crater of the carbon arc at pressures of 1 atm. and below. The sublimation curve suggested cannot be correct, since, as can be demonstrated by the Clausius-Clapeyron relationship, it necessitates a heat of sublimation which increases rapidly with the temperature, reaching an impossibly high value long before the triple point is approached. The same author reports having obtained temperatures in the carbon arc considerably above the sublimation temperature at 22 kg./cm.² pressure, and this supports previous criticisms of the arc method for determining the vapour pressure of carbon, on the grounds that the pressures indicated are considerably lower than the true equilibrium pressures.

Two of the rough measurements of Thiel & Ritter (1923) are derived by essentially equilibrium methods, and also support the intermediate value 125 kcal. for \( L_2 \). All the other experimental data referred to by Goldfinger & Jenehommne (1936) either concern the dynamic method which, for reasons given in §3, cannot be expected to provide direct information about \( L_1 \), or the arc method, in which true equilibrium conditions are not obtained.

The foregoing leads to the conclusion that the order of difference between \( L_2 \) and \( L_1 \) is about 65 kcal. and not 100 kcal. as estimated by Bacher & Goudsmidt (1934). This is in accord with the theoretical calculations of Ufford (1938), who places the excitation energy of the \( ^3S \) carbon atom at about 73 kcal. It is also in accord with the conclusion reached by Burton, Davis, Gordon & Taylor (1941) concerning \( \text{CH}_2 \), namely, that if it has a molecular (unpromoted electron) structure, the heat of formation is only slightly above that of the radical (containing tetravalent carbon). The 65 kcal. liberated by the carbon atom in passing from the latter to the former structure is largely absorbed by the weakening of the two C—H bonds. Having taken \( E(\text{C—H}) \) for \( \text{CH}_4 \) to be 104 kcal. and that for \( \text{CH}_3 \) nearly 1 kcal. stronger, we would expect the two bonds in \( \text{CH}_2 \) to change from about 105 kcal. (or more) to about 80 kcal. (§3), thus absorbing approximately 50 kcal. In consequence, the energy required to raise the \( \text{CH}_2 \) molecule to the radical structure would be only some 15 kcal., in agreement with Burton et al.

Experimental evidence regarding the formyl radical also lends support to our interpretation. \( \text{CHO} \), although not very stable, has been shown to exist at 100°C (Burton 1938). For the process

\[
\text{CHO} \rightarrow \text{H} + \text{CO},
\]

Style & Summers (1946) calculate an activation energy of at least 16 kcal. Elsewhere the actual energy absorbed by this process is given as 26 kcal. (Gorin 1939). Whether these figures can be accepted uncritically or not, there is strong evidence...
that CHO possesses a definite stability which could scarcely be the case if $L_2 - L_1$ were as much as 100 kcal. The value of $E(C-H)$ in CHO is not known with precision, but that it is very probably not more than 100 kcal. is indicated by the following facts. Atomic hydrogen reacts very readily with formaldehyde (Geib 1936) removing a hydrogen atom, but does not react with methane (Bonhoeffer & Harteck 1928), from which it appears that the dissociation energy of the first C—H bond has a smaller value in formaldehyde than in methane. Assuming that no considerable amount of energy is liberated by the reorganization of the CHO radical, it follows that the C—H bond strength in formaldehyde is likewise less than in methane. Since the force constants for the C—H bonds differ by some 10 % in the two compounds (Linnert 1945), being smaller in the case of formaldehyde, this may be regarded as a confirmatory indication that the C—H bond energy in CH$_2$O is appreciably weaker than in CH$_4$. In consequence our assumption that the reorganization of the CHO radical does not liberate more than a small amount of energy appears to be justified. Now the energy of dissociation of the first C—H bond in methane has been fixed at 102 ± 1 kcal. (Kistiakowsky & Van Artsdalen 1944). The foregoing evidence indicates that the corresponding dissociation energy in formaldehyde is somewhat smaller, and we regard it justifiable to assume that it is about 100 kcal. or rather less. Thus since the reorganization energy liberated by the CHO radical is small (or negative), it would also be expected that the values of $E(C-H)$ in both CH$_2$O and CHO do not exceed 100 kcal.

When the hydrogen atom is removed from CHO, not only will energy be liberated by the switch of the carbon atom to the divalent state, but an additional amount released by the change in strength of the C—O linkage. This latter quantity is not small (Pauling 1939) and almost certainly exceeds 20 kcal. That the energy associated with this linkage is greater in CO than in CO$_2$ or the carbonyl group is an accepted fact, and further could be predicted from the shorter bond length, according to the observations of Wrinch & Harker (1940), who regard ‘definite lengths as connoting definite energies’. In addition, Walsh (1946) has drawn attention to the existence of a smooth gradation of properties of the carbonyl bond in the series CO, CO$_2$, CH$_2$O, CH$_3$CHO and the ketones, even though the carbon in CO is divalent. The total variation is considerable. From the foregoing it is clear that if $L_2 - L_1 = 100$ kcal., the total energy available would exceed considerably that required to rupture the C—H bond, and CHO must needs be a very unstable and endothermic substance. But, on the contrary, the process

$$\text{CO} + \text{H} \rightarrow \text{CHO}$$

is very probably exothermic, since it is regarded as a necessary step in the formation of formaldehyde and glyoxal which occurs when mercury-sensitized mixtures of hydrogen and carbon monoxide are subjected to ultra-violet irradiation (Groth 1937; Falttings et al. 1938). The facts are very difficult to reconcile with a value higher than about 75 kcal. for $L_2 - L_1$. Unless $L_1$ has a value other than 125 kcal., this would place an upper limit of about 200 kcal. on $L_2$, in good agreement with our
previous estimate of about 190 kcal. for \( L_2 \). The lower limit, as we have shown, is about 182 kcal. Thus to our figure of 190 kcal. for \( L_2 \) must be attached an uncertainty of some 10 kcal. in either direction. The corresponding value of \( E(C — C) \) is \( 95 \pm 5 \) kcal. in diamond (§ 4) and \( 94 \pm 5 \) kcal. in the normal paraffins (table 3).

Further light on the difference between \( L_2 \) and \( L_1 \) is forthcoming from the relative bond strengths in CO and \( \text{CO}_2 \). That the bond strength is definitely weaker in \( \text{CO}_2 \) is in accord with much experimental evidence, including the known facts regarding force constants, bond lengths and ionization potentials of the \( p\pi \) electrons on the oxygen atom (Walsh 1946). Pauling (1939) explains this difference in terms of resonance energy, but his explanation cannot be accepted as it stands since he has not taken account of the energy difference in the valence states of carbon in the two compounds. Now the value we have accepted to be by far the most probable for \( D_0(\text{CO}) \) is \( 9.144 \text{ eV} \) or \( 210.8 \) kcal. (Herzberg 1939). The heat of combustion of carbon monoxide, corrected to \( 0^\circ \text{K} \), is \( 66.77 \) kcal./mol. (Wagman et al. 1945). These figures can be combined with the value of \( D_0(\text{O}_2) \) (Herzberg 1939) to calculate the mean bond energy in carbon dioxide at \( 0^\circ \text{K} \):

\[
\begin{align*}
\text{CO} + \frac{1}{2}\text{O}_2 &= \text{CO}_2 + 66.77 \\
\text{C}(^3\text{P}) + \text{O} &= \text{CO} + 210.8 \\
\text{O} &= \frac{1}{2}\text{O}_2 + 58.6 \\
\text{C}(^5\text{S}) &= \text{C}(^3\text{P}) + 65 \\
\text{C}(^5\text{S}) + 2\text{O} &= \text{CO}_2 + 401.2
\end{align*}
\]

This is reasonable as it corresponds to an average value of 200.6 kcal. for \( E(C — O) \) in \( \text{CO}_2 \), that is, some 10 kcal. less than in CO. Had we taken \( \text{C}(^5\text{S}) — \text{C}(^3\text{P}) = 100 \) kcal., the bond energy in \( \text{CO}_2 \) would have assumed a mean value of 218.1 kcal., a figure exceeding that for CO. Thus, here again, experimental evidence is definitely against an estimate of 100 kcal. for the energy required by the \( ^3\text{P} \rightarrow ^5\text{S} \) transformation, and indicates that the value 65 kcal. here suggested cannot be more than 10—15 kcal. below the true figure.

In like manner the strength of the carbonyl bond in formaldehyde can be estimated if a mean value is assumed for \( E(C — H) \) in this compound. The heat of formation of gaseous formaldehyde according to Delépine & Badoche (1942) is 25.7 kcal./mol. after a slight readjustment for the most recent data published on the heats of formation of \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) has been effected. The slightly different value 27.7 kcal./mol. can be calculated from the figure for the heat of combustion at constant volume reported by von Wartenberg & Lerner-Steinberg (1925). The former claim greater accuracy, and the value adopted here as the ‘best’ in the absence of more precise data is 26.2 kcal./mol., which becomes 25.3 kcal./mol. at \( 0^\circ \text{K} \) when allowance is made for the change in heat content. Combining this figure with other thermochemical quantities, the atomic heat of formation of formaldehyde at \( 0^\circ \text{K} \) can be calculated as follows:
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\[
\begin{align*}
\text{C (graphite)} + \text{H}_2 + \frac{1}{2}\text{O}_2 & = \text{CH}_2\text{O} \text{ (gas)} + 25.3 \\
\text{O} & = \frac{1}{2}\text{O}_2 + 58.6 \\
2\text{H} & = \text{H}_2 + 103.2 \\
\text{C}(^3P) & = \text{C (graphite)} + 125.0 \\
\text{C}(^5S) & = \text{C}(^3P) + 65 \\
\text{C}(^5S) + 2\text{H} + \text{O} & = \text{CH}_2\text{O} \text{ (gas)} + 377.1
\end{align*}
\]

Taking the value \(\sim 100\) kcal. for the strength of the \(\text{C}–\text{H}\) bonds in formaldehyde, the implied strength of the carbonyl bond is \(\sim 177\) kcal. Again, this is very reasonable, and far more so than the higher value provided by employing the old figure for the \(^5S\rightarrow^3P\) transformation.

Finally, we wish to consider the work of Cherton* on acetylene which has come to our notice since we first deduced that \(L_2\) is about 100 kcal. From a study of the products of decomposition, Cherton (1941) deduced that the \(\text{C}_2\text{H}_2\) molecule initially loses a hydrogen atom in the electric discharge. Subsequently, it was shown that ultra-violet radiation has the same effect (Cherton 1942), and from the wave-length at which continuous absorption commences it was calculated that 121 kcal. are required to remove this hydrogen atom. This figure is reasonable, as here the \(\text{C}–\text{H}\) bond length is considerably shorter than for saturated hydrocarbons. Further, it agrees very well with the value supplied by an extrapolation of vibrational terms according to the method of Rydberg (Funke & Lindholm 1937), but, as might be expected, is considerably lower than that furnished by the Birge-Sponer extrapolation method. From this figure Cherton proceeds to calculate that the heat of sublimation of diamond to free atoms in the \(^5S\) state is 190 kcal. At first sight this might appear to be excellent support for our value of 190 kcal. for \(L_2\), but we are unable to proffer it as such as Cherton’s calculation involves certain tacit assumptions.

First, the atomic heat of formation of acetylene is calculated by adding the dissociation energies of the various linkages, the value taken for the \(\text{C}≡\text{C}\) bond being that derived from predissociation data (Price 1935). Quite apart from the doubt which has been cast \(h\) recent years upon the reliability of dissociation energy values obtained from predissociation in the spectra of polyatomic molecules, the treatment of dissociation energies as additive quantities is unsound. Only if the energies of dissociation are nearly equal to the bond strengths, that is, only if the energies of reorganization of the \(\text{C}_2\text{H}\) and \(\text{CH}\) radicals are small, will the result be a good approximation. Secondly, it is tacitly assumed that Price’s evaluation of the energy required to rupture the \(\text{C}≡\text{C}\) linkage refers to a dissociation in which the carbon remains in the tetravalent state, that is, to the change

\[
\text{C}_2\text{H}_2 = \text{CH}(^4\Sigma) + \text{CH}(^4\Sigma),
\]

and not to

\[
\text{C}_2\text{H}_2 = \text{CH}(^2\Pi) + \text{CH}(^2\Pi)
\]

* We are indebted to M. Cherton for kindly providing us with reprints of his three papers, the original journals being unavailable in this country.
as supposed by Price. It is not impossible that Price's value does refer to the former change, as, allowing for the change in C—H bond strength, the energy level of the \( ^4\Sigma \) state will not exceed that of the \( ^2\Pi \) state by a prohibitively large amount. The energy required for the latter dissociation has been calculated to be 137.9 kcal. (Henkin & Burton 1940).

Thus Chertan's calculation is not rigid and does not provide closer limits for \( L_2 \). As we have shown, however, the figure he puts forward is of the right order, and furthermore, the bond energies calculated from it are compatible with experimental data on the pyrolysis of numerous hydrocarbons, as discussed in a third paper by the same author (Chertan 1943).

### 6. Conclusions

When the energy associated with the tetravalent state of carbon is systematically taken into account and a careful distinction made between bond energies and energies of dissociation, it is possible to bring order out of the relative state of chaos which has been associated hitherto with the thermochemistry of carbon. Practically all the experimental data from a wide variety of sources are now reconciled, and the value \( 190 \pm 10 \) kcal. for \( L_2 \), the latent heat of sublimation of carbon into free atoms at the lowest energy level of tetravalence \( (5S) \), provides a scheme of bond energies for carbon compounds which is compatible with all the more important established quantities. This dimension for \( L_2 \), in combination with a considerable weight of other evidence, rules out the high value contested for \( L_1 \) (170 kcal.), a value supported from erroneous premises by those who fail to take into account the energy absorbed in the \( ^3P \rightarrow ^5S \) conversion. There is very good evidence to indicate that this change involves considerably less than 100 kcal., the figure hitherto accepted, and by far the most probable and satisfactory value for \( L_1 \) is 125-0 kcal. at \( 0^\circ \text{K} \). The evidence may conveniently be summarized as follows:

<table>
<thead>
<tr>
<th>Evidence</th>
<th>Deduction (kcal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Marshall &amp; Norton's vapour-pressure measurements (dynamic method)</td>
<td>( L_2 \ll 177 )</td>
</tr>
<tr>
<td>Voge's calculations and ( D(\text{CH}_3-\text{H}) )</td>
<td>( L_1 \ll 170 )</td>
</tr>
<tr>
<td>Van Vleck's calculations and ( D(\text{CH}_4-\text{H}) )</td>
<td>( L_2 &gt; 182 )</td>
</tr>
<tr>
<td>consideration of ( D(\text{CH}_3-\text{H}), D(\text{C}_2\text{H}_2-\text{H}) ) and energies of reorganization</td>
<td>( L_2 \approx 190, L_1 \ll 170 )</td>
</tr>
<tr>
<td>electron impact measurement of ( D(\text{CO}) )</td>
<td>( L_1 \gg 136 )</td>
</tr>
<tr>
<td>photodecomposition of CO</td>
<td>( L_1 \gg 135 )</td>
</tr>
<tr>
<td>Barrow's empirical relationship</td>
<td>( L_1 \approx 125 )</td>
</tr>
<tr>
<td>triple point of graphite</td>
<td>( L_1 \approx 125 )</td>
</tr>
<tr>
<td>Thiel &amp; Ritter's vapour-pressure measurements (equilibrium method)</td>
<td>( L_1 \approx 130 )</td>
</tr>
<tr>
<td>structure of ( \text{CH}_2 )</td>
<td>( L_2 - L_1 \ll 100 )</td>
</tr>
<tr>
<td>stability of ( \text{CHO} )</td>
<td>( L_2 - L_1 &gt; 75 )</td>
</tr>
<tr>
<td>relative ( E(\text{C}=\text{O}) ) in ( \text{CO}, \text{CO}_2 ) and ( \text{CH}_2\text{O} ) pyrolysis data</td>
<td>( L_2 - L_1 &gt; 80 )</td>
</tr>
<tr>
<td>(spectroscopic determination of ( D(\text{CO}) )</td>
<td>( L_2 \approx 190 )</td>
</tr>
<tr>
<td></td>
<td>( L_1 = 125 )</td>
</tr>
</tbody>
</table>
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The values of C—C and C—H bond energies for the various hydrocarbons, calculated as shown in table 3 assuming \( L_2 = 190 \text{ kcal} \), are, in our view, the most probable values, taking all evidence into account, and must be regarded as superseding bond energies calculated assuming other values for \( L_2 \), as, for example, in the recent paper of Skinner (1945).

Appendix

Considerations arising from the interpretation of the CN spectrum by Schmid, Gerö & Zemplén (1938) have suggested a more precise value for the quantity we have termed \( L_2 \). The CN dissociation limits, which are entirely experimental, having been obtained from short extrapolations, led these authors to the assignment of energy levels for the products of dissociation to agree with the belief that the excitation energy of the \(^5S\) carbon atom is in the neighbourhood of 100 kcal.

In accord with our estimate \((65 \pm 10 \text{ kcal})\) for the excitation energy of \( C(^5S) \), a reassignment of energy levels to the dissociation products of \( \text{CN}(A^2\Pi) \), namely \( C(^3P) + N(^2D) \) has indicated that the \(^5S\) energy level for carbon is situated at about 24,200 cm.\(^{-1}\) or 69.2 kcal. above the ground-level. Further details will be forthcoming in a later paper. These considerations are purely tentative, but, if correct, would provide the improved value \( 194.2 \pm 4 \text{ kcal} \) for \( L_2 \). In round figures this corresponds at \( 0^\circ \text{K} \) to \( 104 \pm 1 \text{ kcal} \) for the mean C—H bond energy in methane and \( 97 \pm 2 \text{ kcal} \) for the single C—C link in solid carbon. The corresponding value for the dissociation energy of the C—C link in cyanogen is about 116 kcal., a very reasonable figure lying between the highly discordant extremes published in the literature. The acceptance of the foregoing brings the spectroscopic determination of \( D(\text{CN}) \) into alignment with Herzberg’s determination of \( D(\text{CO}) \). The calculation of \( D(\text{NC—CN}) \) is based on the old accepted value for the dissociation energy of \( N_2 \) (Herzberg 1939). If, instead, we accept \( D(N_2) = 225.1 \text{ kcal} \), the new value proposed by Gaydon & Penney (1945), the extremely high and unlikely value 171 kcal. results for \( D(\text{NC—CN}) \). We have already shown that the interpretation Gaydon & Penney assign to the CO spectrum is incorrect, and the indication is therefore that the same probably applies to their interpretation of the \( N_2 \) spectrum. Excellent confirmation of the forementioned value 116 kcal. for \( D(\text{NC—CN}) \) is forthcoming from the long wave-length limits of the second regions of continuous absorption at 1600 and 2100 A respectively in the spectra of \( \text{CH}_2\text{CN} \) (Herzberg & Scheibe 1930) and \( \text{ICN} \) (Badger & Woo 1931; Mooney & Reid 1931), these regions corresponding to photo-dissociation in which, as demonstrated by fluorescence, \( \text{CN} \) radicals are produced in the excited \( B^2\Sigma \) state (Neuimin & Terenin 1936; Yakovleva 1938).

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The experimental study of the blast from bombs and bare charges

BY G. GRIME, M.SC. AND H. SHEARD, M.SC.

(Communicated by Sir Edward Appleton, F.R.S.—Received 3 October 1944)

The paper gives an account of investigations on the blast from bare and cased charges of explosive ranging in weight from a few pounds to several thousand pounds.

The measuring technique, involving the use of piezo-electric gauges with cathode-ray oscillographs, is described, and features of theoretical interest or of practical importance are illustrated.

It is shown that, at any rate at distances large compared with the dimensions of the charge, the scale relationship, deduced from simple dimensional theory, holds good over a wide range of charge weight. The importance of this finding in relation to model and full-scale investigations of bomb behaviour is discussed.

Comparisons of the measured velocity of the blast wave with that calculated, by the Rankine-Hugoniot formula, from the maximum excess pressure behind the shock-front show that the recorded values are in good agreement with those deduced theoretically. Observed and calculated rates of decay of maximum excess pressure are also in reasonable agreement.