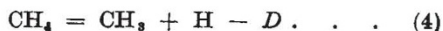Similarly, the formation energy of the methyl radical is given by :

$$W' = 3 E_{CH} - [V(v) - w] - 3 M(H_2), \quad (3)$$

where w is the difference of the promotional energies between CH_4 and CH_3.

The energy D of removal of the first hydrogen atom in methane according to

$$CH_4 = CH_3 + H - D \quad . \quad . \quad (4)$$

is now well known from several experimental studies[10] and is equal to $100 \cdot 8$ kcal. According to (2), (3) and (4), D is not equal to E_{CH}, but is given by

$$D = W - W' = E_{CH} - w - 3 M (H_2). \quad (5)$$

By taking E_{CH} from (2) and W from (1) and introducing them into (5) we obtain

$$D_{CO} = 4 D - 136 \cdot 8 - [V(v) - 4w - 6 M(H_2)].$$

According to Van Vleck[7] and Penney[9], the values for $V(v)$, $6 M(H_2)$ and w are respectively 163, 51 and $15 \cdot 6$ kcal., and we obtain thus :

$$D_{CO} = 217 \text{ kcal., or } 9 \cdot 4 \text{ eV. ; and } L_C = 132 \text{ kcal.}$$

Considering the uncertainty of about 10 per cent, generally admitted for the determination of $V(v)$, $M(H_2)$ and w, the agreement with the spectroscopic value of $9 \cdot 11$ eV. is very satisfactory, and must be considered as an important argument for $L_C = 124 \cdot 4$ kcal.

We wish to emphasize that the above values of D_{CO} and L_C are independent of spectroscopic data on the CO molecule. They would not be changed by a different interpretation of these data, resulting, for example, from the existence of maxima in the potential energy curves of this molecule.

The concept of promotional energy applies as well to other carbon compounds, especially to aldehydes, ketones and acids, as may be easily understood from the work of Goldfinger, Lasareff and Letort[11]. The method sketched above yields for these compounds promotional energies of about 150 kcal., as compared with Van Vleck's theoretical figure of 163 in methane. We hope to go into details of this question by experimental studies on several free radicals, especially CH_2 and CH_3CO.

It is to be noted that Kynch and Penney[12] have given arguments for $L_C = 170$ kcal. by comparing calculated and observed energies of excited states of molecules with conjugated double bonds. It seems, however, that their conclusions are not definitive, since they neglected to consider the removal of degeneracy of the excited states of butadiene and hexatriene. Further calculations might change their results noticeably, as has already been remarked by Mulliken and Rieke[5].

We may conclude that among all the discussed values, the value $L_C = 124 \cdot 4$ kcal. can alone be accepted, being in agreement with (a) spectroscopic data on the CO molecule ; (b) vapour-pressure data on carbon ; (c) removal energy of hydrogen from hydrocarbons and promotional energy of C in organic compounds.

On the other hand, by using the relation between the twisting frequency of the ethylene molecule and L_C, one of us has shown[13] that the value 170 kcal. is very improbable.

Finally, it is also very difficult to explain with this latter value the results of Faltings, Groth and Harteck[14] on the photochemical decomposition of CO,

as well as the results of the studies on ionization of CO by electron impact[15].

Note added in proof. Voge[16] has obtained a value of the energy of the valency state of carbon which is appreciably lower than Van Vleck's estimate. In connexion with our considerations Voge's value (4·5 eV.) would lead to $D_{CO} \cong 12$ eV., a figure considerably higher than even the highest possible spectroscopic value. On the other hand, the relative removal energies of the four hydrogen atoms from methane seem incompatible with Voge's result.

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[1] Gaydon, A. G., and Penney, W. G., *Proc. Roy. Soc.*, A, **183**, 374 (1945). Herzberg, G., *Chem. Rev.*, **20**, 145 (1937). Schmid, R., and Gerö, L., *Z. Phys.*, **105**, 36 (1937). These papers discuss the arguments in favour of each of the values quoted as well as those against the intermediate possible values of 8·4 and 9·6 eV.
[2] Goldfinger, P., and Jeunehomme, W., *Trans. Farad. Soc.*, **32**, 1591 (1936).
[3] Ribaud, G., and Bégue, J., *C.R. Acad. Sci. Paris*, **221**, 73 (1945). Their values for the vapour pressure of carbon are too high for $L_C = 170$ but too low for $L_C = 124$ kcal.
[4] Goldfinger, P., Lasareff, W., and Rosen, B., *C.R. Acad. Sci. Paris*, **201**, 958 (1935).
[5] Mulliken, R. S., and Rieke, C. A., *Rev. Mod. Phys.*, **14**, 259 (1942).
[6] Basset, J., *C.R. Acad. Sci. Paris*, **208**, 267 (1939) ; *J. Phys. Rad.*, **10**, 217 (1939).
[7] Van Vleck, J. H., *J. Chem. Phys.*, **2**, 20, 297 (1934).
[8] Long, L. H., and Norrish, R. G. W., *Nature*, **157**, 486 (1946) : **158**, 237 (1946). Sidgwick, N. V., and Springall, H. D., *Nature*, **156**, 600 (1945). Baughan, E. G., *Nature*, **147**, 542 (1941). Baughan, E. G., and Polanyi, M., *Nature*, **146**, 685 (1940).
[9] Penney, W. G., *Trans. Farad. Soc.*, **31**, 734 (1935).
[10] Andersen, H. C., and Kistiakowsky, G. B., *J. Chem. Phys.*, **11**, 6 (1943). Kistiakowsky, G. B., and Van Artsdalen, E. R., *J. Chem. Phys.*, **12**, 479 (1944).
[11] Goldfinger, P., Lasareff, W., and Letort, M., *C.R. Acad. Sci. Paris*, **200**, 1593 (1935).
[12] Kynch, G. J., and Penney, W. G., *Proc. Roy. Soc.*, A, **179**, 214 (1941).
[13] Duchesne, J., *Physica*, **10**, 817 (1943).
[14] Faltings, K., Groth, W., and Harteck, P., *Z. Phys. Chem.*, B, **41**, 15 (1938).
[15] Hagstrum, H. D., and Tate, J. T., *Phys. Rev.*, **59**, 354 (1941).
[16] Voge, *J. Chem. Phys.*, **4**, 581 (1936).

IN view of the fact that the evidence obtained by Prof. Shenstone in 1939 has not yet been published, and that others have not had an opportunity of considering the conditions under which his spectra were obtained, or of examining the spectra as a whole, we feel that the statement made by Prof. Edlén at the end of his letter cannot be accepted as final. In any event, it would appear to us that his argument by analogy requires further confirmation.

The communication of Messrs. Duchesne, Goldfinger and Rosen provides valuable confirmation for the value $L_1 = 125$ kcal. which on other grounds we have advocated[1] as the most probable value for the reaction

$$C_{solid} \longrightarrow C_{gas} (^3P).$$

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[1] Long and Norrish, *Nature*, **157**, 486 (1946) ; *Proc. Roy. Soc.*, **187**, 337 (1946).