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Attempts to determine the equilibrium constant Kwere made by observing the decrease in the absorbance of the HF polymer band because of the depletion of HF monomer in the formation of the HF·ClF₃. The decrease was small. The equilibrium constant was estimated to be about 1×10^{-5} /mm at 21°, so that the partial pressure of the HF·ClF₃ never exceeded 1 mm Hg by any large amount.

The wavelength of this HF · ClF₃ band is the shortest of any fundamental vibration ever observed, with the exception of the fundamental HF vibrational band itself, so that without doubt the vibration is a H-F stretching vibration. Its displacement from the HF fundamental is much smaller than the separation between the HF monomer and polymer absorption. This suggests that this complex involves a bonding of the F of the HF to the ClF₃, rather than a hydrogen bond. Rogers and Katz,¹ in interpreting F¹⁸ exchange rates between HF and ClF₃, postulated a complex.

The 3.51 μ band of DF · ClF₃ has also been observed as coincident with the long wavelength branch of the DF band in mixtures of DF and ClF₃.

¹ M. T. Rogers and J. J. Katz, J. Am. Chem. Soc. 74, 1375 (1952).

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Ionization and Dissociation by Electron Impact; Methylene, Methyl, and Methane

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The appearance potentials of C^+ , CH^+ , and CH_2^+ in the mass spectra of methylene, methyl, and methane are found to be mutually consistent and when combined with the spectroscopic value of the ionization potential of the carbon atom (11.26 ev) lead to 15.5 ± 0.5 ev/molecule for the heat of atomization of methane. This value (15.5) when further combined with the heat of formation of methane (-0.78 ev/molecule) and the dissociation energy of H₂ (4.48 ev/molecule) yields 5.76 ev/atmos or 133 kcal/mole for the heat of sublimation of graphite.

The set of appearance potentials confirmed the spectroscopic value for the heat of dissociation of CH^+ (3.6 ev/molecule) and yield the following additional energetic quantities: $D(CH_2-H)=3.7_{b}\pm0.3$ ev/molecule, $D(CH-H) = 3.99 \pm 0.3 \text{ ev/molecule}, D(CH_3^+-H) = 1.34 \pm 0.1 \text{ ev/molecule}, D(CH_2^+-H) = 5.54 \pm 0.2 \text{ ev/m$ molecule, and $D(CH^+-H) = 3.3_7 \pm 0.2$ ev/molecule. Earlier determinations of $I^z(CH_4)$, $I^z(CH_3)$ and $D(CH_3-H)$ are confirmed (within the experimental error) and the ionization potential of the methylene radical, $I^{z}(CH_{2})$, is found to be $11.7_{5}\pm0.1$ ev/molecule.

Combination of the appearance potentials of CH_2^+ in the methane and diazomethane mass spectra gives 46 ± 6 kcal/mole for the heat of formation of diazomethane.

INTRODUCTION

HE spacing of the energy levels of the various states of combination of four hydrogen atoms with one carbon atom has been a subject of speculation and experimentation¹⁻³ for many years. Although the dissociation energies, $D(CH_3-H)^{4-6}$ and $D(C-H)^7$ appear to be well established,⁸ such is not the case for $D(CH_2-H)$ and D(CH-H). Furthermore the sum of these four dissociation energies, the heat of atomization of methane, $A_t(CH_4)$, is intimately related to that continuing subject of debate, the heat of sublimation of graphite, through the accurately known heat of formation of methane and dissociation energy of hydrogen.

With the objective of obtaining information on the

- ¹ J. H. Van Vleck, J. Chem. Phys. 2, 20, 297 (1934). ² H. H. Voge, J. Chem. Phys. 4, 581 (1936); 16, 984 (1948). ³ Glockler, Discussions Faraday Soc., Hydrocarbon 10, 26 (1951). ⁴ D. P. Stevenson, J. Chem. Phys. 10, 291 (1942). ⁵ Anderson, Kistiakowsky, and Van Artsdalen, J. Chem. Phys. ² 205 (1942).
- 10, 305 (1942)

EXPERIMENTAL METHODS AND RESULTS

A special ion source for this study was constructed for a 90° sector analyzer mass spectrometer.^{11,12} The features of the source were the following:

¹² Hipple, Grove, and Hickam, Rev. Sci. Instr. 16, 69 (1945).

 ⁶ Butler and Polanyi, Trans. Faraday Soc. 39, 19 (1943).
 ⁷ Douglas and Clark, Can. J. Research A20, 71 (1942).

⁸ See reference 3 for contrary opinion re D(C-H).

unknown quantities mentioned above there was undertaken a mass spectrometric study of the ionization and dissociation by electron impact of methane, methyl, and methylene.9 Although methane has been the subject of several previous such studies¹⁰ it was deemed desirable to include its study in order to assure self-consistency of the measurements on the various molecules that were to be intercombined to derive the quantities of interest.

⁹ A preliminary report of the measurement of the ionization

<sup>A preliminary report of the measurement of the ionization potential of methylene was made several years ago. Langer and Hipple, Phys. Rev. 69, 691 (1946).
¹⁰ (a) L. G. Smith, Phys. Rev. 51, 263 (1937); (b) M. B. Koffel and R. A. Lad, J. Chem. Phys. 16, 420 (1948); (c) J. J. Mitchelland F. F. Coleman,</sup> *ibid.* 17, 44 (1949); (d) R. E. Honig, *ibid.* 16, 105 (1948); (e) Geerk and Neuert, Z. Naturforsch. 5A, 502 (1950); (f) McDowell, and Warran. Discussion: Faraday, Soc. Hudroenborg McDowell and Warren, Discussions Faraday Soc., Hydrocarbons **10**, 53 (1951). ¹¹ J. A. Hipple, J. Appl. Phys. **13**, 551 (1942).

(1) the use of double slits for entries to and exits from the ionization chamber of both electrons and positive ions in order to minimize external field penetration;

(2) the use of an indirectly heated oxide-coated platinum cathode, and

(3) the use of a hemicylindrical ion repeller that was considerably longer than the positive ion exit slit from the ionization chamber. The cathode heater consisted of a tubular ceramic with imbedded tungsten heater wires. The electron trap was always maintained 6 volts positive with respect to the ionization chamber in order to trap secondary electrons emitted from the platinum collector plate.

The gases for study were admitted to the ionization chamber through a 1-mm i.d. quartz tube that ended at a suitable hole in the top center of the ion repeller. The quartz tube could be heated over the 4-cm length immediately preceding its end by means of a close winding of tungsten wire surrounded by a radiation shield. The temperature of the quartz tube was determined by means of a "platinum" thermocouple

TABLE I. Mass spectrum of diazomethane \sim 75°C, 75 ev.

M/q	Relative intensity	
42	0.010	
29	0.024	
28	1.00	
27	0.50	
26	0.44	
25	0.062 }	$C_{2}H_{2}$??
24	0.020	
14	0.020	$A(CH_2^+) = 12.7 \pm 0.3 \text{ ev}$
13	0.007	、 <u>-</u> ,
12	0.002	

inserted through a hole in the radiation shield and placed in contact with the quartz ca 1 cm from its end.

The gases, methane, lead tetramethyl, or diazomethane admixed with argon, entered the quartz tube through a pinhole leak in a platinum foil from a light shielded reservoir. Ohio Chemical Company methane was used without treatment. The lead tetramethyl was from the generous gift of the Ethyl Corporation.¹³ Linde Company spectroscopically pure argon was employed.

Diazomethane was prepared by the reaction of hydrazine and chloroform in absolute alcohol in the presence of potassium hydroxide. A stream of argon was employed to sweep the diazomethane from the reaction vessel as it was formed and carry it over potassium hydroxide pellets at -30 °C to remove entrained alcohol. The diazomethane was condensed from the argon stream by passage through a trap chilled with liquid air and stored in this trap maintained at this low temperature. As vaporized from the trap into the gas reservoir of the mass spectrometer no evidence of either ethanol or chloroform could be found in the mass spectrum of the diazomethane.





FIG. 1. CH_3^+ from Pb(CH₃)₄ as a function of furnace temperature —electron energy ~11 volts (corrected).

The mass spectrum of diazomethane characteristic of 75 volt ionizing electrons at 75°C is given in Table I.

The appropriate furnace temperature for measurements on methyl and methylene radicals were chosen as the temperatures at which the methyl and methylene ion currents from lead tetramethyl and diazomethane, respectively, had approximately their maximum values. There is shown in Fig. 1 the dependence of methyl ion current in the mass spectrometer on furnace temperature for constant lead tetramethyl flow. The data in Fig. 1 confirm the previously reported observation¹² and fix the temperature (indeterminant in the earlier work) of maximum methyl yield at $850\pm50^{\circ}$ C. Similarly 780° C was chosen as an appropriate furnace temperature for methylene formation from diazomethane. The variation of CH₂⁺ with furnace temperature for constant CH₂N₂ flow is shown in Fig. 2.

In the appendix to this paper further experimental results on the pyrolysis of other substances are summarized.

The appearance potentials of the various ions in the mass spectra were determined from the ion yield ionizing electron energy curves by means of the vanishing current method.^{10(a),14} The additive constant in the voltage scale was determined by association of the



FIG. 2. CH₂⁺ from CH₂N₂ as a function of furnace temperature-electron energy \sim 11 volts (corrected).

¹⁴ T. Mariner and W. Bleakney, Phys. Rev. 72, 807 (1947).

TABLE II. Appearance potentials of ions CH_{4}^{+} in the mass spectra of CH_{4} , CH_{3} , and CH_{2} .

ev				
Ion	CH₄	CH3	CH_2	
CH4+	13.10 ± 0.1			
CH ₃ +	14.30 ± 0.1	9.85 ± 0.1		
CH_2^+	15.5 ± 0.2	15.30 ± 0.1	11.90 ± 0.1	
CH^+	23.4 ± 0.2	16.2 ± 0.2	17.1 ± 0.2	
C+	27.0 ± 0.2	17.8 ± 0.2	18.0 ± 0.2	

appearance potential of A^+ in the mass spectrum of the simultaneously admitted argon with the spectroscopically determined ionization potential of argon, 15.76 ev.¹⁵

The appearance potentials determined from five or six series of measurements on each ion are summarized in Table II. The repeatability of determination varied from ± 0.05 ev in the cases of ions of high probability of formation, CH₄⁺ and CH₃⁺ from CH₄, CH₃⁺ from CH₃, and CH₂⁺ from CH₂ to ± 0.2 ev in the cases of ions of low probability of formation as C⁺ from CH₄. No search was made for "higher" appearance potentials such as have been found^{10(a),(f)} for CH₂⁺ in the methane mass spectrum.

DISCUSSION

The discussion of the appearance potentials summarized in Table II will be divided into two parts. In the first part the data will be examined ion by ion for mutual compatability and assignment of state to the ions, and the nature of the accompanying neutral products. Only differences between appearance potentials are used in this section, and thus the quality of the absolute calibration of the ionizing electron energy scale will not affect the arguments other than in the comparison of our results with those of previous investigations. For the purposes of this first section it will be presumed that the dissociation energies, $D(CH_3-H)$ = 4.42 ± 0.04 ev, $D(C^+-H)=3.61$ ev, and D(C-H)= 3.47 ev are reliable. The conclusions reached in the first part of the discussion are summarized in Table III.

In the second part of the discussion the appearance potentials (Table II) are combined with data from other sources by means of conclusions of the first part (Table III) to derive a self-consistent set of dissociation energies, $D(CH_m-H)$ and $D(CH_m^+-H)$ ($0 \le m \le 3$) and the heats of atomization of CH_{m+1} and C^+H_{m+1} where the heat of atomization, $A_t(CH_j)$, of CH_j is the energy required for the reaction,

$$\mathrm{CH}_{j}^{(\mathrm{gas})} = \mathrm{C}^{(\mathrm{gas})} + j \cdot H.$$

Part I

$$CH_4^+$$

The appearance potential of CH_4^+ , $A(CH_4^+)=13.1 \pm 0.1$, in the methane mass spectrum is in excellent, agreement with all previously reported determinations of this quantity, viz. 13.2 ± 0.4 , $^{10(a)}$ 13.0 ± 0.2 , $^{10(b)}$ 13.04 ± 0.03 , $^{10(a)}$ 13.3 ± 0.3 , $^{10(e)}$ and $13.1_2\pm0.03$, $^{10(e)}$ This agreement lends confidence to the reliability of the calibration of our voltage scale and thus to the significance of the results of calculations in which our data are combined with data from other sources. This appearance potential is to be associated with the vertical ionization potential of methane, and it will be assumed that the difference between the vertical and adiabatic ionization potentials is no larger than the uncertainty of the determinations.

CH_{3}^{+}

The appearance potential, $A_1(CH_3^+) = 14.3 \pm 0.1$, in the methane mass spectrum is in essential agreement with the literature values, namely, 14.5 ± 0.4 ,^{10(a)} 14.4 ± 0.3 ,^{10(b)} $14.5_2 \pm 0.05$,^{10(c)} 14.5 ± 0.3 ,^{10(e)} and $14.3_9 \pm 0.02$.^{10(f)} The appearance potential of this ion in the methyl mass spectrum, $A_2(CH_3^+) = 9.8_5 \pm 0.1$ is 0.22 ev lower than the previous measurement by the mass spectrometric method, $10.0_7 \pm 0.1$.¹³ This difference is coincident, with the difference between the present determination of $A_1(CH_3^+) = 14.3 \pm 0.1$ and the value found in the earlier study of the methyl radical, $A_1(CH_3^+) = 14.5_0 \pm 0.1$.^{10(a),13} Thus this research leads to the same value for $D(CH_3 - H)$ as the earlier one¹³ when this dissociation energy is associated with the difference $A_1(CH_3^+) - A_2(CH_3^+) = 4.4_5 \pm 0.1$ ev.

In order for the association of $A_1(CH_3^+) - A_2(CH_3^+)$ with $D(CH_3 - H)$ to be valid, it is necessary that the methyl ion in both processes of formation be in the same electronic state and that in the case of methane the

TABLE III. Energetic quantities to be associated with the appearance potentials, $A(CH_m^+), 0 \ge m \le 4$ listed in Table II.

	CH4	CH3	CH ₂
$\overline{ \begin{array}{c} CH_4^+ \\ CH_3^+ \end{array} }$	$I_{v^{z}}(CH_{4}) \ge I_{ad}^{z}(CH_{4})$ $I^{z}(CH_{3}) + D(CH_{3} - H)$	$I_{v^{z}}(CH_{3}) \cong I_{ad^{z}}(CH_{3})$	
CH_2^+	$I^{*}(CH_{2})+D(CH_{3}-H)$ + $D(CH_{2}-H)-D(H-H)$	$I^{z}(\dot{\mathbf{CH}}_{2})+D(\dot{\mathbf{CH}}_{2}-\dot{\mathbf{H}})$	$I_{v^{z}}(\mathrm{CH}_{2})\cong I_{ad^{z}}(\mathrm{CH}_{2})$
CH+	$I^{z}(CH) + A_{t}(CH_{4}) - D(C-H)$ = $I^{z}(CH) + D(CH_{3}-H)$ + $D(CH_{2}-H) + D(CH-H)$	$I^{t}(CH)+E_{CH}+(A^{1}\Pi)+D(CH_{2}-H)$ +D(CH-H)-D(H-H) =I^{t}(CH)+E_{CH}+(A^{1}\Pi)+A_{t}(CH_{3}) -D(C-H)-D(H-H)	$I^{z}(CH)+E_{CH}+(A^{1}\Pi)+D(CH-H)$ = $I^{z}(CH)+E_{CH}+(A^{1}\Pi)$ + $A_{t}(CH_{2})-D(C-H)$
C+	$I^{z}(\mathbf{C}) + A_{t}(\mathbf{CH}_{4})$	$I^{z}(C) + A_{t}(CH_{s}) - D(H-H)$	$I^{z}(\mathbf{C}) + A_{t}(\mathbf{CH}_{2})$

¹⁵ Moore, Natl. Bur. Standards. Circ. No. 467, U. S. Government Printing Office, Washington, D. C. (1949).

formation of CH_3^+ proceed through transitions to levels of CH₄⁺ above the dissociation limit of the attractive state. If we associate the appearance potential of CH_{3}^{+} in the methyl mass spectrum with the vertical ionization potential of methyl and assume negligible difference between vertical and adiabatic ionization potential, it follows that the difference between $A(CH_4^+)$ and $A_1(CH_3^+), A_1(CH_3^+) - A(CH_4^+) = 1.2 \pm 0.1$ is to be associated with the dissociation energy, $D(CH_3^+-H)$. This is a consequence of our assumption that identical CH_3^+ ions are formed from CH_4 and CH_3 . Justification for the validity of this assumption is to be found in the consistency of direct and indirect electron impact determinations of $D(CH_3-H)^{16}$ and the agreement with the values found by entirely independent methods.^{5,6}

The value found for $D(CH_3^+-H)$, 1.2 ev is but onefourth that of $D(CH_3-H)$. This appears to be a remarkably larger weakening of a bond to be associated with a change from a one electron-pair bond to a threefourths electron-pair bond, when it is noted that in the cases of H_2 and H_2^+ the change from an electron-pair bond to a one-electron bond reduces the dissociation energy by less than a factor of 2, visa 4.48 to 2.65 ev. This qualitative reasoning suggests that there may be a significant difference between the vertical and adiabatic ionization potentials of methane.

CH_2^+

The appearance potentials of this ion in the methane mass spectrum $A_1(CH_2^+) = 15.5 \pm 0.2$, lies between two of the previously reported values of this quantity, i.e., $15.8 \pm 0.5^{10(a)}$ and $15.3_0 \pm 0.05^{10(f)}$ A third much higher value 16.5 ± 0.3 has also been reported.^{10(e)} There have been no previously reported values for the appearance potential of this ion in the mass spectra of methyl, $A_2(CH_2^+) = 15.3 \pm 0.1$; methylene, $A_3(CH_2^+) = 11.9$ ± 0.2 ; or diazomethane, $A_4(CH_2^+) = 12.7 \pm 0.3$.

If it is assumed that the same state of CH_2^+ obtains for its formation from the three species, CH₄, CH₃, and CH₂; then values may be calculated for the dissociation energy, $D(CH_2-H)$, if the formation of CH_2^+ is associated with the reactions;

$$CH_3 + \epsilon^{-} \rightarrow CH_2^{+} + H + 2\epsilon^{-} \quad A_2(CH_2^{+}), \qquad (1)$$

$$CH_4 + \epsilon^- \rightarrow CH_2^+ + H_2 + 2\epsilon^- A_1(CH_2^+).$$
 (2)

From $A_2(CH_2^+) - A_3(CH_2^+)$ there is found

$$D(CH_2 - H) = 3.4 \pm 0.2$$

while,

$$A_1(CH_2^+) - A_3(CH_2^+) = 3.6 = D(CH_2 - H) + D(CH - H) - D(H - H).$$

Taking $D(CH_3-H) = 4.42$ and D(H-H) = 4.48 one obtains the second value, $D(CH_2-H)=3.7\pm0.2$. The essential agreement between these semi-independent

¹⁶ Stevenson, Discussions Faraday Soc. Hydrocarbons 10, 35 (1951).

determinations of $D(CH_2-H)$ shows the consistency of the assumptions made in the derivation of the values, namely the identity of the state of CH_2^+ in the three modes of formation and the accompanying formation of H_2 molecules in the case of methane.

The appearance potential in the methylene mass spectrum, $A_3(CH_2^+)$, is naturally associated with the vertical ionization potential of the free radical that should be very little different from the adiabatic ionization potential in the species with unshared electrons. The consistency of $A_1(CH_2^+)$ and $A_2(CH_2^+)$ with $A_3(CH_2^+)$ found above, leads us to believe that the CH₂⁺ formed from both methane and methyl are in their ground state.

The differences between the appearance potentials of CH_{2}^{+} and CH_{3}^{+} in the mass spectra of methane and methyl are related to the difference $D(CH_2^+-H)$ -D(H-H) and $D(CH_2+-H)$, respectively. Thus from $A_1(CH_2^+) - A_1(CH_3^+) = +1.2, D(CH_2^+ - H) = 5.7$, while $A_2(CH_2^+) - A_2(CH_3^+) = 5.45 = D(CH_2^+ - H).$

It should be noted that Voge² and Field¹⁷ have both used the difference $A_1(CH_2^+) - A_3(CH_2^+)$ to estimate the energy of formation of CH_2 from methane.

If the heat of formation of diazomethane from its elements were known, the appearance potential of CH2⁺ in the diazomethane mass spectrum, $A_4(CH_2^+) = 12.7$ ± 0.3 would provide another datum relative to the energy of CH_2^+ with respect to methane. Since this heat of formation is not known, it is of interest to calculate a value for this quantity by combination of the appearance potential of CH_2^+ in the mass spectrum of methane, $A_1(CH_2^+)$, with that in the diazomethane mass spectrum, $A_4(CH_2^+)$, the heat of formation of methane (-0.78 ev/molecule) and the plausible assumption that the process of formation of CH_2^+ from diazomethane by electron impact is,

$$CH_2N_2 \rightarrow CH_2^+ + N_2 + \epsilon^-, A_4(CH_2^+) = 12.7.$$

Then, since

$$CH_{4} \rightarrow CH_{2}^{+} + H_{2}^{+} \epsilon^{-}, \quad A_{1}(CH_{2}^{+}) = 15.5;$$

$$C_{gr} + 2H_{2} = CH_{4} \qquad \Delta H_{f} = -0.78;$$

$$C_{gr} + H_{2}^{+} + N_{2}^{-} = CH_{2}N_{2} \quad \Delta H_{f} = -0.78 + 15.5 - 12.7$$

$$= 2.0 \text{ ev/molecule}$$

$$= 46 \text{ kcal/mole.}$$

That this is a reasonable value may be seen from the following argument. Following Pauling:18

$$\begin{split} \Delta H_f(CH_2N_2) &= -2H_{C-H} - 2H_{C-N} + \frac{1}{3}H_N \equiv N + H_{H-H} \\ &+ L_c + \text{strain energy} \\ &= -2(87.3) - 2(48.6) + \frac{1}{3}(170) + 103.4 \\ &+ 124.3 + \text{strain energy} \\ &= 12.5 + \text{strain energy. kcal/mole.} \end{split}$$

¹⁷ F. H. Field, J. Chem. Phys. **19**, 793 (1951). ¹⁸ Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1939), pp. 53 et seq.

The strain energy of cyclopropane is 34.2 kcal¹⁹ and it would be expected to be greater in diazomethane in view of the nitrogen-nitrogen double bond in the ring. Thus it would be expected that,

$$\Delta H_f(CH_2N_2 \text{ gas}) \ge 47 \text{ kcal},$$

and we see that the estimate from the appearance potentials of CH_2^+ in the methane and diazomethane mass spectra is quite acceptable.

 CH^+

The present determination of the appearance potential of CH⁺ in the methane mass spectrum, A_1 (CH⁺) = 23.4±0.2 is in excellent agreement with the earlier value due to Smith^{10(a)} (23.4±0.6) and approximately one electron volt higher than the determinations by Geerk and Neuert^{10(e)} (22.5±0.5) and MacDowell and Warren^{10(f)} (22.4±0.1). The last named authors^{10(e),(f)} employed a different technique in determining the appearance potential from the ion yield-ionizing electron energy curve than that employed by Smith and ourselves and this may be the source of the discrepancy noted. No previous values have been reported for the appearance potentials of CH⁺ in the mass spectra of methyl, A_2 (CH⁺)=16.2±0.2 and methylene, A_3 (CH⁺) =17.1±0.2.

If it is assumed that the CH⁺ ions formed from methylene and methyl are in the same electronic state, the lower value of A_2 (CH⁺) than of A_3 (CH⁺) requires in the case of methyl the process

$$CH_3 + \epsilon^{-} \rightarrow CH^+ + H_2 + 2\epsilon^{-},$$
 (3)

since in the case of methylene the process must be

$$CH_2 + \epsilon^{-} \rightarrow CH^+ + H + 2\epsilon^{-}.$$
 (4)

With assumption of identical states for the CH⁺, the difference

$$A_2(CH^+) - A_3(CH^+) = -0.9 = D(CH_2 - H) - D(H - H),$$

or since D(H-H) = 4.48, $D(CH_2-H) = 3.6$, in excellent agreement with the values deduced from appearance potentials of CH_2^+ . This agreement may be taken as confirmation of the validity of the assumption of identity of state of CH^+ from CH_3 and CH_2 .

The appearance potential of CH⁺ in the methane mass spectrum, A_1 (CH⁺)=23.4, is to be associated with either the process

$$CH_4 + \epsilon^- \rightarrow CH^+ + 3H + 2\epsilon^-,$$
 (5)

or

$$CH_4 + \epsilon^{-} \rightarrow CH^+ + H_2 + H + 2\epsilon^{-}.$$
 (6)

If the state of CH^+ from methane is identical with that formed from methyl then if (5) obtains,

$$A_1(CH^+) - A_2(CH^+) = 7.2 = D(CH_3 - H) + D(H - H),$$

¹⁹ Golmov, J. Gen. Chem. (U.S.S.R.) 11, No. 5-6, 405 (1940).

or

or

$$D(\mathrm{CH}_3-\mathrm{H})=2.7,$$

while if (6) obtains

$$A_1(CH^+) - A_2(CH^+) = 7.2 = D(CH_3 - H)$$

Neither of these alternatives leads to a value of $D(CH_3-H)$ that is compatible with the accepted value of this quantity 4.42.

If it were assumed that the process of formation of CH⁺ in the methane mass spectrum is represented by (6) with the ion in the first excited state $A^{1}\Pi$, with $E_{CH^{+}}(A^{1}\Pi) = 2.99$,²⁰ while the common identical state for this ion in the cases of methyl and methylene is the ground state, $X^{1}\Sigma$; then

$$A_1(CH^+) - A_2(CH^+) = 7.2 = D(CH_3 - H) + E(A^{1}\Pi),$$

$$D(CH_3-H)=4.2$$
,
that is equal, within experimental uncertainty to the
accepted 4.42.

An alternate assumption might be that (5) represents the formation of CH⁺ in its ground state from methane while the common state of CH⁺ formed from CH₃ and CH₂ is the $A^{1}\Pi$. If this is taken, then

$$A_1(CH^+) - A_2(CH^+) = 7.2 = D(CH_3 - H)$$

+ $D(H - H) - E(A^1\Pi),$
 $D(CH_3 - H) = 5.7.$

a value that is in poor agreement with the accepted value. However, as will be shown later, there is strong evidence that (5) represents CH^+ formation from methane and that the excited state of CH^+ is the one common to this ion in its formation from CH_3 and CH_2 .

 C^+

The present determination of the appearance potential of C⁺ is the methane mass spectrum, $A_1(C^+)$ = 27.0±0.2 agrees quite well with the Smith^{10(a)} value, 26.8±0.8, and is greater than the value due to McDowell and Warren,^{10(f)} 26.2±0.2, by an amount about equal to the difference in the case of $A_1(CH^+)$. The value of $A_1(C^+)$ due to Geerk and Neuert,^{10(e)} 21.5±1 ev, appears to be in error. No previous determinations have been reported for the appearance potentials of this ion in the mass spectra of methyl, $A_2(C^+)=17.8\pm0.2$, or methylene, $A_3(C^+)=18.0\pm0.2$.

If it is assumed that the C^+ formed from each of the three molecules, CH_4 , CH_3 , and CH_2 are in the same state and that the processes are representable by the expressions

$$CH_4 + \epsilon^- \rightarrow C^+ + 4H + 2\epsilon^-,$$
 (7)

$$CH_3 + \epsilon^- \rightarrow C^+ + H_2 + H + 2\epsilon^-,$$
 (8)

$$CH_2 + \epsilon^{-} \rightarrow C^{+} + 2H + 2\epsilon^{-}; \qquad (9)$$

²⁰ Herzberg, *Molecular Spectra and Molecular Structure*. I. (D. Van Nostrand Company, Inc., New York, 1950), second edition.

we find from (8) and (9),

$$A_2(C^+) - A_3(C^+) = 0.2 = D(CH_2 - H) - D(H_2),$$

 $D(CH_2 - H) = 4.3,$

and from (7) and (8),

$$A_1(C^+) - A_2(C^+) = 9.2 \text{ ev} = D(CH_3 - H) + D(H_2),$$

 $D(CH_3 - H) = 4.7.$

The value of $D(CH_2-H)$, 4.3, from the combination of Eqs. (8) and (9) is not incompatible with the value deduced above that ranged from 3.4 to 3.7, and similarly the value of $D(CH_3-H)$, 4.7, from Eqs. (7) and (8) is in reasonable agreement with the accepted value, 4.42. Thus Eqs. (7), (8), and (9) are self-consistent with the assumption of the identity of the states of the C⁺ in the three processes.

If we assume in addition that the C^+ is in its ground state, then from Eqs. (3) and (8),

$$A_2(C^+) - A_2(CH^+) = 1.6 = D(C^+ - H),$$

while from (4) and (9)

$$A_3(C^+) - A_3(CH^+) = 0.9 = D(C^+ - H)$$

values that are incompatible with the spectroscopic value of Douglas and Clark, $^7 D(C^+-H)=3.6$.

On the other hand, from Eqs. (5) and (7):

$$A_1(C^+) - A_1(CH^+) = 3.6 = D(C^+ - H)$$

if the CH⁺ formed from methane is in its ground $X^{1}\Sigma$ state. Similarly, if it is assumed that the CH⁺ formed from CH₃ and CH₂ by processes (3) and (4), respectively, are in the $A^{1}\Pi$ state, then,

 $A_2(C^+) - A_2(CH^+) = 1.6 = D(C^+ - H) - E(^{1}\Pi),$

or

$$D(C^+ - H) = 4.6,$$

and

 $A_3(C^+) - A_3(CH^+) = 0.9 = D(C^+ - H) - E(^{1}\Pi),$

or

$$D(C^+-H) = 3.9.$$

These assumptions lead to reasonable agreement between the spectroscopic value of $D(C^+-H)$ and that from $A_3(C^+) - A_3(CH^+)$, and even better (within possible experimental error) agreement in the case of $A_2(C^+)$ $-A_2(CH^+)$. Thus we believe Eq. (5) represents the formation of CH⁺ in its ground state from CH₄ and that the common state of formation of CH⁺ from CH₃ and CH₂ is $A^1\Pi$ with the processes represented by Eqs. (3) and (4).

The conclusions with respect to the formal energetic significance of the appearance potentials of the ions CH_m^+ in the mass spectra of methane, methyl, and methylene summarized in Table II are given in Table III.

Part II

The ionization potential of the carbon atom is $I^{z}(C) = 11.264 \text{ ev}^{15}$ for the formation of C⁺ in its ground state, $2P_{i}^{0}$. If it is assumed that the C⁺ ions formed from CH₄, CH₃, and CH₂ are in the ground state, then from the appearance potentials $A_{i}(C^{+})$ one calculates by means of the expressions of Table III:

$$A_t(CH_4) = A_1(C^+) - I^z(C) = 15.7,$$

$$A_t(CH_3) = A_2(C^+) - I^z(C) + D(H-H) = 11.0,$$

$$A_t(CH_2) = A_3(C^+) - I^z(C) = 6.7.$$

Taking $I^{z}(CH) = 11.13$ and D(C-H) = 3.47 from Douglas and Clark⁷ and the assignments of Table III:

$$\begin{aligned} A_t(CH_4) &= A_1(CH^+) - I^z(CH) + D(C - H) = 15.7, \\ A_t(CH_3) &= A_2(CH^+) - I^z(CH) - E_{CH^+}(A^{1}\Pi) \\ &+ D(C - H) + D(H - H) = 10.0, \\ A_t(CH_2) &= A_3(CH^+) - I^z(CH) - E_{CH^+}(A^{1}\Pi) \\ &+ D(C - H) = 6.5. \end{aligned}$$

Since $D(CH_3-H)=4.42$, these values so found for $A_t(CH_3)$ correspond to $A_t(CH_4)=15.4$ from $A_2(C^+)$ and 14.4 from $A_2(CH^+)$. Either value of $A_t(CH_2)$ leads to $A_t(CH_4)=11.0+D(CH_2-H)$.

The dissociation energy of carbon monoxide found by Hagstrum²¹ from electron impact measurements on carbon monoxide, oxygen, nitric oxide and nitrogen, D(CO)=9.6 ev., when combined with the heats of formation of methane, carbon monoxide and the dissociation energies of oxygen and hydrogen give for the heat of atomization of methane,

$$A_t(CH_4) = -\Delta H_f(CH_4) + \Delta H_f^0(CO) + D(CO) - 1/2D(O_2) + 2D(H-H) = 0.775 - 1.147 + 9.60 - 2.56 + 8.96 = 15.63 \text{ ev.}$$

The values of $A_t(CH_4)$ from $A_1(C^+)$, $A_1(CH^+)$, and $A_2(C^+)$, 15.7, 15.7, and 15.4, respectively, are in excellent agreement with this value of Hagstrum's, as well as the earlier deduction of Smith^{10(a)} based on the appearance potentials of H⁺ and C⁻ in the methane mass spectrum. The values of $A_t(CH_4)$ deducible from $A_2(CH^+)$ as well as $A_3(C^+)$ and $A_3(CH^+)$ are all less than or equal to 15.6 ev. Thus all the present electron impact data that may be interpreted in terms of the heat of atomization of methane and thus the heat of sublimation of graphite are only consistent with the so-called low value 136 kcal/mole.

The recent work of Goldfinger and co-workers²² that indicates the accommodation coefficient of carbon atoms in graphite to be very small ($<10^{-3}$) makes it possible to reconcile the electron impact values of the heat of atomization of methane and dissociation energy of

²¹ H. D. Hagstrum, Revs. Modern Phys. 23, 185 (1951).

²² Doehaerd, Goldfinger, and Walbroeck, J. Chem. Phys. 20, 757 (1952).

carbon monoxide with the apparent heat of sublimation of graphite found from the effusion or evaporation experiments of Brewer, et al.23 and of Marshall and Norton.²⁴ Thus it is reasonable to take the Hagstrum value for the heat of atomization of methane, 15.63 ev, along with the presumably reliable $D(CH_3-H)=4.42$ and D(C-H) = 3.47 to fix the sum of $D(CH_2-H)$ and D(CH-H) as

$$D(CH_2-H)+D(CH-H)=15.63-4.42$$

-3.47=7.74 ev.

It was found above (Part I) that the three appearance potentials of CH₂⁺ lead to the two semi-independent determinations of $D(CH_2-H)$, 3.4 and 3.7 ev. The appearance potentials of CH⁺ in the methyl and methylene mass spectra give $D(CH_2-H)=3.6$, while those of C⁺ in the same radicals give 4.3 and thus the unweighted mean of the values is $D(CH_2-H)=3.75\pm0.3$. From the sum, $D(CH_2-H)++D(CH-H)=7.74$, we then have, $D(CH-H)=3.9_9\pm0.3$. With methane, CH_4 , as the ground state, the energy levels of CH_i $+(4-j)H(0 \le j \le 4)$ and the heats of atomization $A_{l}(CH_{j})$ are:

$CH_j + (4-j)H$	Energy-ev/molecule	$A_t(\mathrm{CH}_j),$
CH_4	0.00	15.63,
CH_3+H	4.42 ± 0.03	11.21,
$CH_2 + 2H$	$8.1_7 \pm 0.3$	7.4_{6} ,
H + 3H	$12.1_{6} \pm 0.3$	3.47,
C + 4H	$15.6_3 \pm 0.1$	• • • • .

It may be noted that the energy level of CH_2+2H with respect to methane $8.1_7 \pm 0.3$ ev/molecule corresponds to 3.69 ev/molecule for the endothermicity of the reaction,

$$CH_4 = CH_2 + H_2$$

The value 3.6₉, for the heat of this reaction lies at the extreme of the range, 3.0 ± 0.7 ev/molecule, deduced by Long²⁵ from consideration of the activation energy of the homogeneous pyrolysis of methane, the long wavelength limit of the photodecomposition of ketene and other kinetic considerations.

It may be further noted that the suggestion of Long that an estimate of the heat of formation of diazomethane (2.0 ev/molecule, see foregoing) in combination with the long wavelength limit of the first continuum of the diazomethane absorption spectrum 4710 A according to Kirkbridge and Norrish²⁶ does not provide useful confirmation of the energy level of CH_2+H_2 with respect to methane. This method of calculation gives for

 $CH_4 \rightarrow CH_2 + H_2$, $\Delta H < 5.4 \text{ ev.}$

The inequality contains an unknown and at present unestimatable electronic excitation of CH₂, visa

$$CH_2N_2 + h\nu(4710 \text{ A}) \rightarrow CH_2 + N_2$$

The two determinations of the ionization potential of the methyl radical have given 10.07 and 9.85 ev. The best value is then $9.9_6 \pm 0.1$ and the energy of $CH_3^+ + H$ with respect to methane is $14.3_8 \pm 0.1$. The three appearance potentials of CH_2^+ , $A_1(CH_2^+)$, $A_2(CH_2^+)$, and $A_3(CH_2^+)$, when recalculated according to the relations of Table III, give for the level of CH_2^+ +2H with respect to CH_4 , the values, 19.98, 19.72 and 20.07, respectively, or 19.92 ± 0.14 as the best value. This corresponds to the best value for the ionization potential of methylene equal to 11.7₅. The three appearance potentials of CH^+ , $A_1(CH^+)$, $A_2(CH^+)$, and $A_3(CH^+)$, according to the assignments of Table III, give for CH^++3H with respect to CH_4 , 23.4 ± 0.2 , 22.1 ± 0.2 , and 22.3 ± 0.2 , or 22.6 ± 0.5 that is to be compared with the best value that may be presumed to be the sum of the spectroscopic value of the ionization potential of CH, $I^{z}(CH) = 11.13$ and the level of CH+3H with respect to methane given above, $12.1_{6}\pm0.3$, or CH⁺+3H at $23.2_{9}\pm0.3$. It is of interest to note that the level of CH^++3H deduced from $A_2(CH^+)$ and $A_3(CH^+)$ and the assignments of Table III is in agreement with the appearance potential of CH⁺ in the methane mass spectrum found by McDowell and Warren,^{10(f)} and Geerk and Neuert,^{10(c)} 22.4 and 22.5, respectively, rather than the higher value, 23.4 found by Smith^{10(a)} and ourselves.

The best value for the level of C^+ +4H with respect to CH_4 is the sum of the heat of atomization of methane, $A_t(CH_4) = 15.6_3$ plus the spectroscopic value of the ionization potential of the carbon atom, 11.26,14 or 26.89. The three appearance potentials of C⁺, A_1 (C⁺), $A_2(C^+)$ and $A_3(C^+)$ corrected according to the assignments of Table III give for this level 27.0, 26.7, and 26.2, respectively, or 26.6 ± 0.3 . It may be noted that whereas the value for this level deduced from the appearance potential of C⁺ in the methyl mass spectrum, 26.7 is in agreement with the energy of this level according to both Smith's^{10(a)} and our determination of the appearance potential of C⁺ in the methane mass spectrum, the value from the appearance potential in the methylene mass spectrum 26.2 agrees with the energy from the McDowell and Warren10(f) determination of the appearance potential of C⁺ in the methane mass spectrum.

There are summarized in Table IV the successive dissociation energies of CH_j and CH_j^+ according to the best values of the energy levels of $CH_j + (4-j)H$ and $CH_{j}^{+}+(4-j)H$ with respect to CH_{4} given above. In

TABLE IV. Dissociation energies of CH_i and CH_i^+ ev/molecule.

	CH₄ Electron impact Vogeª		CH₄+ Electron impact	
$\begin{array}{c} D(\mathrm{CH_3-H})\\ D(\mathrm{CH_2-H})\\ D(\mathrm{CH-H})\\ D(\mathrm{C-H}) \end{array}$	$\begin{array}{c} 4.4_{2}\pm0.03\\ 3.7_{5}\pm0.3\\ 3.9_{9}\pm0.3\\ (3.47)^{\mathrm{b}}\end{array}$	4.54 4.14 3.46	$ \begin{array}{r} 1.3_4 \pm 0.1 \\ 5.5_4 \pm 0.2 \\ 3.3_7 \pm 0.2 \\ (3.60)^{\mathrm{b}} \end{array} $	

*Reference 2 calculated under assumption that $A_t(CH_i) = 15.6$ ev and D(C-H) = 3.47. b Spectroscopic value, reference 7.

 ²³ Brewer, Gilles, and Jenkins, J. Chem. Phys. 16, 797 (1948).
 ²⁴ Marshall and Norton, J. Am. Chem. Soc. 72, 2166 (1950).
 ²⁵ Long, Proc. Roy. Soc. (London) 198, 62 (1949).
 ²⁶ Kirkbridge and Norrish, J. Chem. Soc. 119 (1933).

this Table IV there are also given for comparison the dissociation energies of CH₄ calculated by Voge.² Contrary to an opinion expressed elsewhere by one of authors,²⁷ the electron impact data do not support Voge's calculations other than in the case of $D(CH_3 - H)$, except when the extreme range of uncertainty of $D(CH_2-H)$ and D(CH-H) are taken, i.e., $D(CH_2-H)$ $=3.7_{5}+0.3=4.0_{5}$ and $D(CH-H)=3.9_{9}-0.3=3.6_{9}$. Professor E. B. Wilson has remarked²⁸ that the more or less monotonic variation of $D(CH_j - H)$ with j, causes the comparison of the experimental values with those of Voge's calculations to be an insignificant test of the quality of the calculations since the latter are essentially interpolations. Thus a comparison of calculations of the dissociation energies of CH_{i}^{+} with the experimental values given in Table IV would be of considerable interest in view of the marked alternation of their magnitude.

APPENDIX

In addition to lead tetramethyl two other substances, mercury dimethyl and dimethyl disulfide, were found to be potentially useful sources of methyl radicals by pyrolysis in our furnace, while a number of others, azomethane, methyl sulfide, methyl iodide, trimethylamine, ethane, methylether, and silicon tetramethyl gave no evidence of pyrolysis to methyl at temperatures less than 1000°C. In Figs. 3 and 4 there are shown the intensity of methyl ion in the mass spectrometer for constant flow rate of mercury dimethyl and dimethyl disulfide, respectively, as a function of furnace temperature. Like lead tetramethyl, the yield of methyl from mercury dimethyl has a maximum value between 700 and 800°C and then decreases rapidly, presumably due to a different mode of decomposition. The rate of decrease with temperature above the maximum yield temperature is too rapid to be accounted for by 100 percent decomposition of the metal alkyl and the normal decrease of mass spectrometer sensitivity with increasing gas temperature.29









²⁹ D. P. Stevenson, J. Chem. Phys. 17, 101 (1949).



FIG. 4. CH_3^+ current as a function of temperature for constant CH₃SSCH₃ flow—electron energy ~ 11 volts (corrected).

In contrast to the behaviour of the metal alkyls, it will be seen in Fig. 4 that the yield of methyl radicals by pyrolysis of dimethyl disulfide is still increasing rapidly at 1000°C, the nominal maximum attainable temperature of the inlet furnace.

OTHER DATA ON CH₂+

In addition to the four substances discussed previously the appearance potential of the ion CH_{2}^{+} has been measured in the mass spectra of ethylene, ethane, methyl cyanide, methanol, and ethanol. It is of interest to examine the compatability of these data with the conclusion based on the measurements on methylene, methyl, and methane. The four substances, ethane, methyl cyanide, methanol, and ethanol can be written as



with X equal to methyl, cyanide, hydroxyl, and CH₂OH respectively. Thus the lowest energy process for the formation of CH₂⁺ from these four substances will be

$$H_2CHX + \epsilon^- \rightarrow CH_2^+ + HX + 2\epsilon^-$$

and this type of process seems very probable in view of the fact that CH_2^+ formation from methane (at the first appearance potential) proceeds by the process

$$H_2CH_2 + \epsilon^- \rightarrow CH_2^+ + H_2 + 2\epsilon^-$$

The heats of formation from the elements in their standard state of H_2CHX (gas) and HX are (ev/ molecule)

	$\Delta \mathrm{H}_{f}^{0}(\mathrm{H}_{2}\mathrm{CH}X)$	$\Delta \mathbf{H}_f^0(\mathbf{H}X)$
H_2CHCH_3	-0.88	-0.78
H ₂ CHCN	+0.91	+1.36
H_2CHOH	-2.09	-2.51
H ₂ CHCH ₂ OH	-2.44	-2.09.

If the heat of the reaction

(

$$CH_4 = CH_2 + H_2$$

		$\Delta H_f(HX) + \Delta H_f(CH_4) - \Delta H_f(H_2CHX) + \Delta H_x + I^z(CH_2)$			
	H_2CHCH_3	-0.78	-0.78	+0.88	$+\Delta H_x + I^z(CH_2)$
	H ₂ CHCN	+1.36	-0.78	-0.91	$+\Delta H_x + I^z(CH_2)$
	H_2 CHOH	-2.51	-0.78	+2.09	$+\Delta H_x + I^z(CH_2)$
	H_2CHCH_2OH	-2.09	-0.78	+2.44	$+\Delta \mathbf{H}_{\mathbf{x}}+I^{\mathbf{z}}(\mathbf{CH}_{2}),$
or					
		A_{m}	$_{in}(CH_{2}^{+})$	$A_{\min}(CH_{2}^{+})$	$A_{obs}(CH_2^+)$
	H_2CHCH_3	$-0.68+\Delta H_x+I^z(CH_2)$		14.76	16.3 ± 1
	H ₂ CHCN	-0.33+4	$\Delta H_x + I^z(CH_2)$	15.11	$15.6_2 \pm 0.04$
	H_2CHOH	-1.20+4	$\Delta H_x + I^z (CH_2)$	14.24	15.4 ± 0.5
	H ₂ CHCH ₂ OH	-0.43+4	$\Delta H_x + I^z (CH_2)$	15.01	16.5 ± 0.5 .

is called ΔH_z , then the heats of the four reactions of formation of CH_2^+ are

The $A_{\min}(CH_2^+)$ given in the third column are calculated from the second column taking for $\Delta H_x + I^z(CH_2)$ the "best value" found above, 15.44 ev.

The observed appearance potentials, given in the fourth column, range from 0.5 to 1.5 ev greater than the calculated values, $A_{\min}(CH_2^+)$. In the first three cases any fragmentation of the neutral particle HX would require in excess of 3.5 ev, thus the process as written must be the correct one. The difference between the calculated and assumed values suggest that extra energy, either as kinetic energy or electronic excitation of the fragment is required for the formation of CH_2^+ , or that the value assigned to $\Delta H_x + I^z(CH_2)$ is *low*. This latter possibility seems unlikely in view of the excellent agreement between the various measurements of the first appearance potential of CH_2^+ in the methane mass spectrum.

In the case of ethanol the difference between the calculated and observed energy of formation of CH_2^+ can again signify an extra energy requirement in the form of kinetic energy or electronic energy of the fragments or that the process is more disruptive of the molecule than the assumed process. It requires +0.89 ev to dissociate methanol into hydrogen plus formaldehyde or 0.95 ev to dissociate methanol into two hydrogen molecules plus carbon monoxide. Thus the minimum energies for the reactions

$$C_{2}H_{5}OH + \epsilon^{-} \rightarrow CH_{2}^{+} + H_{2} + H_{2}CO + 2\epsilon^{-},$$

$$C_{2}H_{5}OH + \epsilon^{-} \rightarrow CH_{2}^{+} + 2H_{2} + CO + 2\epsilon^{-},$$

are 15.9_0 and 15.9_6 ev, respectively, both significantly less than the observed appearance potential of CH_2^+ in the ethanol mass spectrum, 16.5 ± 0.5 ev. No final assignment of process can thus be made for CH_2^+ formation from ethanol.

In the case of ethylene we may write

$$C_{2}H_{4}+2H_{2}=2CH_{4}, \qquad \Delta H=-2.10,$$

$$\epsilon^{-}+CH_{4}=CH_{2}^{+}+H_{2}+2\epsilon^{-}, \quad \Delta H=\Delta H_{x}+I^{z}(CH_{2}),$$

$$CH_{4}=CH_{2}+H_{2}, \qquad \Delta H=\Delta H_{x},$$

or

$$C_2H_4 + \epsilon^- = CH_2^+ + CH_2 + 2\epsilon^-,$$

$$A_{\min}(CH_2^+) = 2\Delta H_x + I^z(CH_2) - 2.10$$

or since

$$C_{2}H_{4}: A_{min}(CH_{2}^{+}) = \Delta H_{4} + 13.3_{4} \text{ ev.}$$

 $\Lambda H + I^{z}(CH_{o}) = 15.44$

The best value assigned to ΔH_x is 3.69 ev thus, C₂H₄; $A_{\min}(CH_2^+)=17.0_3$ ev, that is to be compared with the observed

$$C_2H_4$$
; $A(CH_2^+) = 19.3 \pm 0.3$ ev.

Since further disruption of CH_2 to CH+H or $C+H_2$ would require 3.9₉ or 2.9₈ ev we may conclude that neutral CH_2 accompanies CH_2^+ formation from ethylene and that the fragments share the order of 2 ev kinetic energy or one or both of the fragments is (are) electronically excited.