

Ionization and Dissociation of Polyatomic Molecules by Electron Impact. I. Methane¹

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The first of a series of mass-spectrograph studies of the products of ionization of polyatomic molecules by low speed electrons is described. The following are the positive ions detected in methane together with their appearance potentials in volts: CH_4^+ (13.1 ± 0.4); CH_3^+ (14.4 ± 0.4); CH_2^+ (15.7 ± 0.5 , 22.9 ± 0.8); CH^+ (23.3 ± 0.6); C^+ (26.7 ± 0.7); H^+ (22.7 ± 0.5 , 29.4 ± 0.6); H_2^+ (27.9 ± 0.5); and H_3^+ (25.3 ± 1.0). The following negative ions were also observed: CH_2^- ; CH^- ; C^- ; and H^- . From the higher appearance potential of H^+ and the appearance potentials of C^+ and C^- three independent upper limits are calculated for the heat of dissociation of CH_4 to normal atoms which lead, respectively, to the following three upper limits for the heat of sublimation of carbon: $L(\text{C}) \leq 6.1 \pm 0.6$ volts or 141 ± 14 kcal.; $L(\text{C}) \leq 5.7 \pm 0.7$ volts or 131 ± 16 kcal.; $L(\text{C}) \leq 6.0 \pm 0.9$ volts or 139 ± 21 kcal. Thus of the three values of $L(\text{C})$ recently proposed from data on predissocia-

tion in CO, these results are inconsistent with the value $L(\text{C}) = 168.8$ kcal. but are quite consistent with the value $L(\text{C}) = 123.6$ kcal. Correlations of known ionization energies with the best obtainable data on the relative energies of the possible stable states of a carbon and four hydrogen atoms give reasonable interpretations of all observed appearance potentials. Upper limits for the ionization potentials of CH_3 , CH_2 , and CH are deduced. These are: $I(\text{CH}_3) \leq 9.9$ volts; $I(\text{CH}_2) \leq 12.0$ volts; $I(\text{CH}) \leq 11.7$ or 16.2 volts. Two general conclusions are drawn. The first is that most ions are only formed when the parent molecules are broken into as many parts as possible. The second is that interpretations of all but four appearance potentials are possible on the assumption that the total excitational and kinetic energy of products formed in an electron impact from a CH_4 molecule be less than two volts.

INTRODUCTION

ONE of the important physical tools for studying molecular structure is the mass spectrograph wherein ions are formed by impacts of electrons of known energy with molecules. With this instrument one can determine in most cases what ions are produced from molecules of a particular variety through approximate measurements of the mass-to-charge ratios of the ions. Also, one can determine for ions of each kind: the relative probabilities for formation under different conditions in the ion source; the appearance potential or the minimum energy required to produce them; and, possibly, the kinetic energies with which they are formed. The first two types of information are of interest chiefly in themselves and can seldom be compared with results obtained by other means either experimental or theoretical. The appearance potential of undissociated ions or the ionization potential of the molecule under investigation is also important *per se* and often checks or supplements spectroscopic or theoretical results. In-

terest in the appearance potentials and kinetic energies of other ions lies not so much in the quantities measured as in the dissociation and ionization energies which can in some cases be calculated therefrom by use of data from other sources. Since these ionization and dissociation energies comprise the most important contributions of a mass spectrograph to the field of molecular structure, a brief review of how they are obtained and of the chief sources of uncertainty involved in their calculations will probably not be out of place here.

The appearance potential of an ion which lacks one or more of the atoms of the parent molecule is the sum of three quantities: a dissociation energy; an ionization energy; and the total minimum excitational and mutual kinetic energy with which the products can dissociate. (The ionization energy in the case of a negative ion is an electron affinity—with negative sign—and if both a positive and a negative ion are produced, it is the algebraic sum of an ionization energy and an electron affinity.) Provided one knew what all the products of dissociation are, how much kinetic energy each has, and in what excited state each is formed, he could calculate the dissociation energy from the appearance potential and a knowledge of the ionization energy or *vice versa*.

¹The results on positive ions formed in methane were discussed briefly in a paper by W. Bleakney, E. U. Condon and L. G. Smith which was presented at the Symposium on Molecular Structure held at Princeton, N. J. under the auspices of the American Chemical Society (Dec. 31, 1936–Jan. 2, 1937) and which has been published in the *Journal of Physical Chemistry*.

Unfortunately, if more than one atom of the parent molecule is missing in the ion, there are at least two possibilities for the states of aggregation of the missing atoms, and the reaction occurring can only be determined through considerations of energy relations. Furthermore, the kinetic energies of unionized products of dissociation cannot be calculated from that of the ion if more than one of the former is produced from a molecule. Finally, *a priori* knowledge of the states of excitation of the products is never at hand. Conclusions drawn from combinations with other data of the appearance potential and kinetic energy of an atomic ion formed from a diatomic molecule are subject only to uncertainties in the electronic states of the products of dissociation. In the case of the appearance potential of an ion lacking but one of the atoms of a parent polyatomic molecule, conclusions are also subject to uncertainties with regard to vibrational energy of the ion. In general, where there are more than two products of dissociation of a single molecule, not only electronic and vibrational energy but kinetic energies of the products as well as their states of aggregation are uncertain. Here the best one can hope to do is to determine the reaction occurring and from this to determine a value of either the dissociation or the ionization energy involved plus the total excitational and kinetic energy of the products. It is evident that such a value is an upper limit for the true dissociation or ionization energy (or a lower limit for the true electron affinity). Additional factors complicating the interpretation of results obtained by the electron impact method are: experimental errors in these results (which are seldom less than 1 percent and often as high as 4 or 5 percent); and uncertainties in quantities obtained from other sources. The latter uncertainties, however, add importance to any conclusions which may be drawn even if it is possible to determine only upper or lower limits for the true values.

The results for diatomic molecules obtained by the electron impact method have in many cases corroborated and supplemented spectroscopic and thermochemical data. Also they have given experimental evidence in support of the Franck-Condon principle and the repulsive electronic states of such molecules predicted by quantum

mechanics. Results for the triatomic molecules that have been studied (H_2O , H_2S , N_2O , NO_2 , SO_2 , CO_2 and CS_2) have also in some cases checked and added to thermochemical and spectroscopic data. However, little attempt has been made to interpret in the light of other data results for the more complex molecules which have been studied (NH_3 , C_2N_2 , CH_4 , CH_3Cl , C_3H_8 , C_4H_{10} , C_8H_{18} , C_2H_2 , C_6H_6). Good reviews of all this work have been prepared by Smyth,² and more recently by de Groot and Penning,³ and by Sponer.⁴

The mass spectrograph analysis of methane, results of which are reported in this paper, is the first of a series of such analyses to be undertaken in this laboratory. The results for methane yield some information regarding unknown and uncertain quantities. It is to be hoped that with the accumulation of further data for other molecules more such information will be obtained.

APPARATUS AND PROCEDURE

The mass spectrograph used to study ionization processes in methane is of the type described by Bleakney⁵ and by Tate, Smith, and Vaughan.⁶ A detailed description of the instrument, the gas-handling system, the electrometer-tube amplifier used to measure the ion current, and the device for recording automatically this current as a function of the potential applied to accelerate either the ions or the electrons will be found in a recent paper.⁷

Fig. 1 shows a typical mass spectrum obtained with the automatic recorder of the positive ions with m/e values from 12 to 16 formed in methane by electrons with an energy of 50 electron volts. When this record was obtained the magnetic field was kept constant at about 550 gauss (as in all work on methane), and the potential applied to the electron gun was fixed at 50 volts, while a variable potential accelerating the ions was applied by the drum potentiometer which is a

² H. D. Smyth, *Rev. Mod. Phys.* **3**, 347 (1931).

³ de Groot and Penning, *Handbuch der Physik*, Vol. 23/1 (J. Springer, Berlin, 1933).

⁴ H. Sponer, *Molekulspektren* (J. Springer, Berlin, 1935, 1936).

⁵ W. Bleakney, *Phys. Rev.* **40**, 496 (1932).

⁶ J. T. Tate, P. T. Smith, and A. L. Vaughan, *Phys. Rev.* **48**, 575 (1935).

⁷ W. W. Lozier, P. T. Smith, L. G. Smith, and W. Bleakney, *Rev. Sci. Inst.* **8**, 51 (1937).

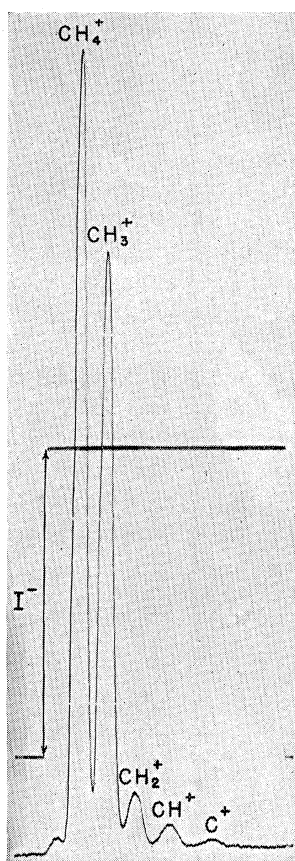


FIG. 1. Mass spectrum of the heavier positive ions formed in methane. Ordinates represent ion currents and abscissae analyzer voltage or e/m values. I^- is the electron current recorded simultaneously with the ion current. The small peak to the left of the CH_4^+ peak corresponds to ions with $m/e=17$ which can only be $\text{C}^{13}\text{H}_4^+$ ions. The ratio of the heights of these two peaks is $\sim 1/100$ which is approximately the abundance ratio $\text{C}^{13}/\text{C}^{12}$.

part of the recorder. The height of a peak is assumed to be proportional to the intensity of the corresponding ionization or number of ions of the given kind formed per second per unit volume.⁸ The pressure of methane in the mass spectrograph when Fig. 1 was obtained was $\sim 4 \times 10^{-5}$ mm of Hg.⁹

⁸ The deflection of the galvanometer is strictly proportional to the ion current arriving at the collector. This fact coupled with the fact that peaks for ions with m/e as high as 6 are flat topped indicates that even for ions with $m/e=16$ this assumption should not be far from the truth.

⁹ Pressures were estimated by calculation from the absolute values of electron and total positive ion currents, the geometry of the ion source, and the value given by J. T. Tate and P. T. Smith (Phys. Rev. 39, 270 (1932)) for the cross section of common gas molecules for ionization which was assumed to be correct for methane. Such estimates of pressures should not be in error by more than factors of two.

Fig. 2 illustrates the method of determining the appearance potential of an ion (in this case H^+ formed from CH_4). Curve 1 was taken with the ion-accelerating potential fixed so that H^+ ions passed through the exit slit of the analyzer and with the variable potential from the drum applied in series with a fixed potential to accelerate the electrons. Curve 2 was taken in similar fashion with the analyzer set to record He^+ ions formed in helium gas which was admitted into the apparatus simultaneously with the methane. The curve for He^+ serves to correct the recorded electron energies for contact potentials in the instrument. It will be observed that the upward break of curve 2 from its horizontal portion is more abrupt than that of curve 1 and that to the right of the break, curve 2 is nearly a straight line while curve 1 has considerable upward curvature.¹⁰ Hence in de-

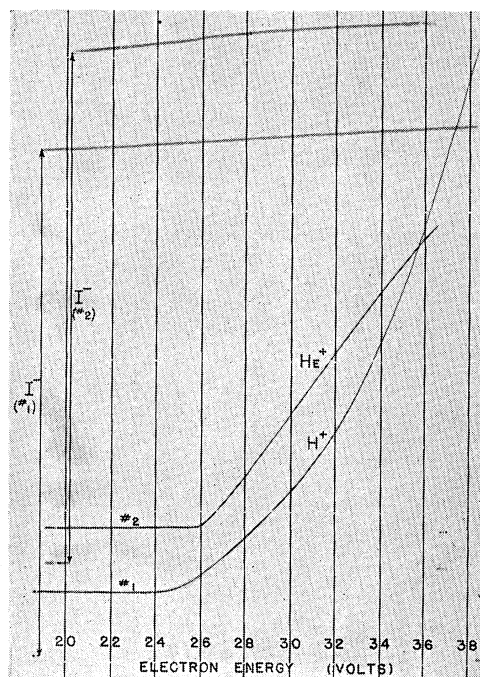


FIG. 2. Appearance potential curves for H^+ ions formed in methane and He^+ ions formed in helium. Ordinates represent ion currents. I^- is the electron current recorded in each case simultaneously with the ion current.

¹⁰ This effect is characteristic of the appearance potential curves for all ions from methane and has been noted by others who have measured the appearance potentials of molecular ions. The effect is presumably due first to the fact that at room temperature a gaseous molecule may exist in one of a larger number of energy states than a gaseous atom. Secondly, it is due to the fact that a molecu-

termining the lowest appearance potential of H^+ ions it was not feasible to attempt to fit curves 1 and 2 together, nor could one extrapolate to zero current any linear portion of curve 1 to the right of the upward break. It seemed best in this as in all other cases to use the method of selecting the appearance potential for each ion as the lowest electron energy at which the corresponding ion current was detectable. This method is open to several objections, the chief of which is that the value obtained depends somewhat on the sensitivity used in obtaining the corresponding curve. This source of error was reduced as far as possible by adjusting the sensitivity of the

lar ion may be formed in one of a much larger number of closely spaced energy states within a range of a few volts above the lowest state.

amplifier and the relative pressures of methane and the calibrating gas so that in each case the curve for ions from methane had roughly the same slope to the right of its upward break as the curve for ions formed in the calibrating gas. With the total pressure of impurities about 5×10^{-8} mm of Hg, the pressures of methane used in determining the appearance potentials of positive ions ranged from about 5×10^{-6} to about 5×10^{-5} mm of Hg, while the pressure was about 1×10^{-4} mm of Hg when similar determinations were made for negative ions.⁹ An equipotential, oxide-coated cathode was used in obtaining all appearance potentials. Because of the smaller range of the speeds with which electrons leave such a source, the upward breaks in curves like those of Fig. 2 were more sharply defined when

TABLE I. Ions formed in methane.

OBSERVED ION	% OF TOTAL IONIZATION (ELECTRON ENERGY 50 VOLTS)	OBSERVED APPEARANCE POTENTIALS (VOLTS)	PROBABLE PROCESS $CH_4 \rightarrow$:	CALCULATED MINIMUM ENERGY (VOLTS)	ADDITIONAL ENERGY REQUIRED OR IONIZATION ENERGY DEDUCED (VOLTS)
Positive ions					
H^+	3.0	22.7 ± 0.5	$H^+ + CH_2 + H$ (1) or $H^+ + CH + H_2$ (2) $H^+ + C + 3H$ (3) $H_2^+ + C + 2H$ (4) $H_3^+ + C + H$ (5) or $H_3^+ + CH^-$ (6) $C^+ + 4H$ (7) $CH^+ + 3H$ (8) or $CH^+ + H_2 + H$ (9) $CH_2^+ + H_2$ (10) $CH_2^+ + 2H$ (11) $CH_3^+ + H$ (12) CH_4^+ (13)	21.6 20.6 28.6 26.0 $24.1 - D(H_3^+)$ $20.6 - D(H_3^+) - E(CH)$ 26.3 $11.6 + I(CH)$ $7.1 + I(CH)$ $3.7 + I(CH_2)$ $8.1 + I(CH_2)$ $4.5 + I(CH_3)$ $I(CH_4)$	1.1 2.1 0.8 1.9 $1.2 + D(H_3^+)$ $4.7 + D(H_3^+) + E(CH)$ 0.4 $I(CH) \leq 11.7$ $I(CH) \leq 16.2$ $I(CH_2) \leq 12.0$ ≤ 2.8 $I(CH_3) \leq 9.9$ $I(CH_4) = 13.1$
$H_2^+ *$	0.3	29.4 ± 0.6 27.9 ± 0.5			
$H_3^+ *$	0.005	25.3 ± 1.0			
C^+	0.6	26.7 ± 0.7			
CH^+	1.7	23.3 ± 0.6			
CH_2^+	4.2	15.7 ± 0.5 22.9 ± 0.8			
CH_3^+	39.5	14.4 ± 0.4			
CH_4^+	50.7	13.1 ± 0.4			
Negative ions					
H^-	0.04	6.1 ± 0.3 6.9 ± 0.8 7.3 ± 1.0 18.0 ± 0.6	$H^- + CH_3$ (14) $H^- + CH + H_2$ (15) $H^- + CH_2 + H$ (16) $H^- + CH^+ + H_2$ (17) or $H^- + CH_3^+$ (18) $C^- + H^+ + 3H$ (19) $CH^- + 3H$ (20) $CH^- + H^+ + 2H$ (21) or $CH^- + H_3^+$ (22) $CH_2^- + 2H$ (23) $CH_2^- + H^+ + H$ (24) or $CH_2^- + H_2^+$ (25)	3.8 6.4 7.4 ≤ 18.1 ≤ 13.7 26.7 $11.6 - E(CH)$ $25.1 - E(CH)$ $20.6 - D(H_3^+) - E(CH)$ $8.1 - E(CH_2)$ $21.6 - E(CH_2)$ $19.0 - E(CH_2)$	2.3 0.5 ~ 0 ~ 0 4.3 0.7 $E(CH) \geq 1.4$ ≥ 0.8 $3.9 + D(H_3^+) + E(CH)$ $0.8 + E(CH_2)$ $1.8 + E(CH_2)$ $4.4 + E(CH_2)$
C^-	0.003	27.4 ± 0.6			
CH^-	0.005	10.2 ± 0.3 24.5 ± 0.5			
CH_2^-	0.002	8.9 ± 0.3 23.4 ± 0.6			

* The results for H_2^+ and H_3^+ ionization in methane are of interest in connection with attempts to produce helium of mass three by bombardment of deuterium with canal rays from an intense, high voltage discharge in deuterium. (Phys. Rev. 46, 81 (1934); Phys. Rev. 47, 800(A) (1935).) Samples of the treated gas were allowed to stand over hot copper oxide and a liquid-air trap to remove the hydrogen in the form of water. In the residual gases admitted to the mass spectrograph later used for obtaining the present results on methane, ions were found with $m/e = 3$ whose appearance potential was approximately equal to the ionization potential of He (24.5 volts). These were at first believed to be He^+ ions, but it was later found that the rate of diffusion through a capillary of the gas from which they were formed was smaller than that of ordinary helium. It was then suggested that the ions might be formed from some hydrocarbon gas like methane. The present results indicate: (1) that they were probably not HD^+ ions formed from deuteromethane since their appearance potential was too low; and (2) that only very few of them could have been H_3^+ ions from ordinary methane.

such a source was used than when a tungsten filament supplied the electrons.

EXPERIMENTAL RESULTS

A list of all ions, both positive and negative, which were observed, their approximate relative intensities for an electron energy of 50 volts, and their appearance potentials will be found in the first three columns of Table I. The errors quoted in column three are estimated probable errors. Helium served as the calibrating gas in determining the appearance potentials of the negative ions and H^+ ions, while argon and a slight impurity of hydrogen were used in the cases of the other ions. In all cases the calibrating gas was in the instrument along with methane. No multiply charged ions could be detected at electron energies as high as 80 volts.

The positive ions were all observed when either a tungsten filament or an oxide-coated cathode, operating at considerably lower temperature, was used as an electron source. Their relative intensities were the same within experimental error in the two cases indicating that few, if any, ions were formed by ionization of products of thermal dissociation at either cathode. In Table II are given the results of three independent measurements of the relative intensities of the heavier positive ions showing the constancy of these quantities at widely different pressures and electron currents. Constancy of the relative intensities of H_3^+ , H_2^+ , and H^+ ionizations at different pressures is shown by Fig. 3 in which are plotted the intensities of H_3^+ and H_2^+ as functions of the intensity of CH_4^+ and the intensity of H^+ as a function of that of H_2^+ . Measurements of the intensity ratios H_3^+/CH_4^+ , H_2^+/CH_4^+ , and H^+/CH_4^+ at electron currents ranging from 3.1 to 60, from 0.52 to 32, and from 0.52 to 60 microamperes, respectively, gave results which in

TABLE II. Percents of total ionization at various pressures and electron currents.

APPROXIMATE PRESSURE (MM OF Hg)	ELECTRON CURRENT (MICROAMP.)	CH_4^+	CH_3^+	CH_2^+	CH^+	C^+
1×10^{-6}	0.53*	52.3	39.2	3.4	1.3	0.6
4×10^{-6}	4.3*	52.0	38.8	3.8	1.6	0.6
2×10^{-6}	61.0†	49.0	41.0	4.3	1.9	0.7

* Electrons supplied by oxide-coated cathode.

† Electrons supplied by tungsten filament.

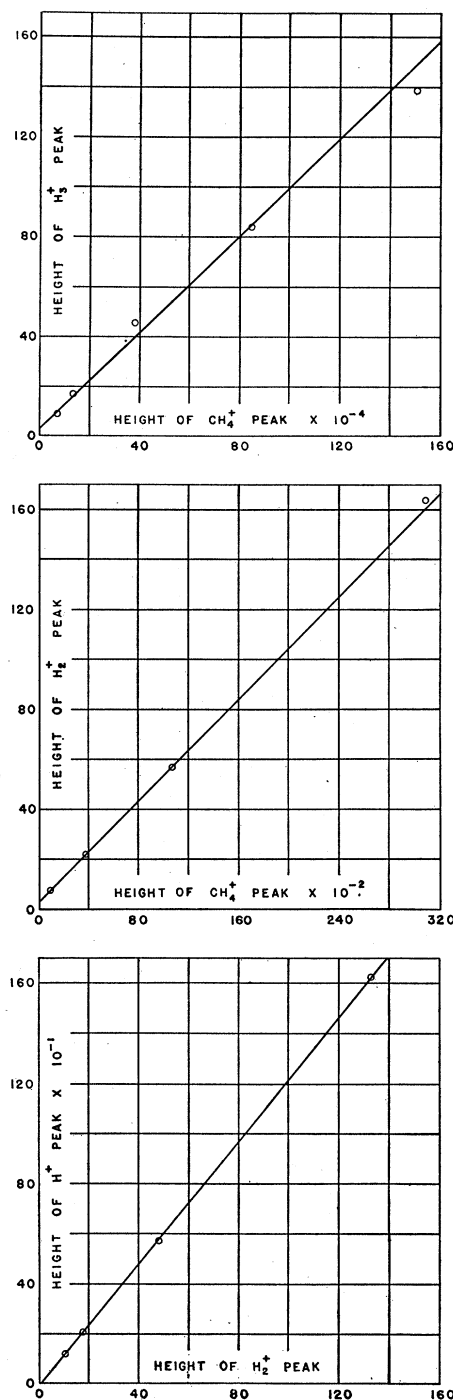
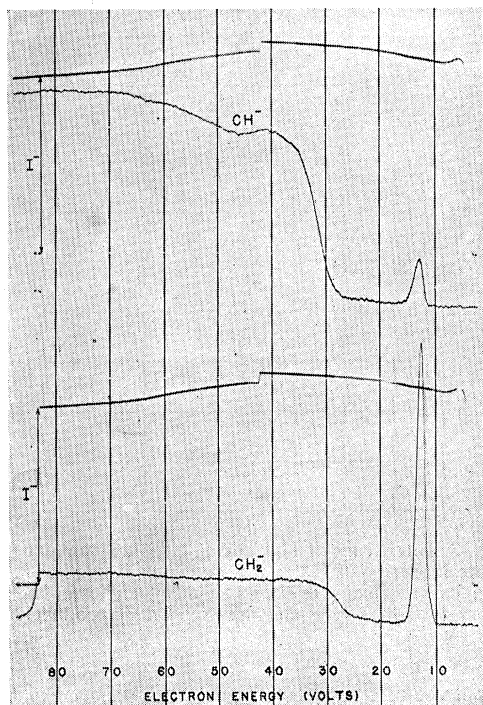
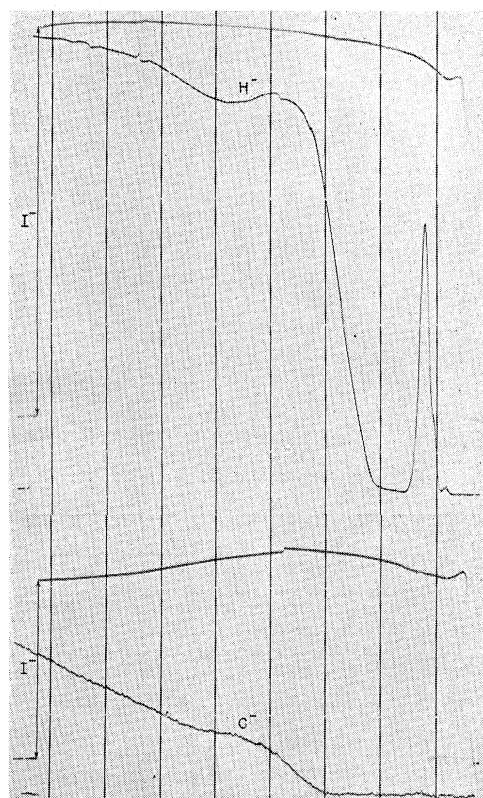


FIG. 3. Intensities of H_3^+ and H_2^+ as functions of CH_4^+ and the intensity of H^+ as a function of that of H_2^+ . The linearity of these curves shows that H^+ , H_2^+ , and H_3^+ ions are formed from CH_4 molecules as primary products.

no case disagreed with the ratios obtained from the curves of Fig. 3 by more than a factor of two.



From all these facts we may be sure that each positive ion is formed as the result of a single impact between an electron and a CH_4 molecule.

The heights of the negative ion peaks were not measured as functions of pressure or electron current, nor were these peaks looked for when a tungsten filament was being used as a source of electrons. However, the absence of secondary processes in the formations of any of the positive ions together with the fact that the ion current *vs.* electron energy curves for all the negative ions observed in methane (Fig. 4) are of the same character as those obtained by various investigators for other negative ions which are formed in single electron impacts leads one to assume that all negative ions from CH_4 molecules are formed in the same manner.

COMPARISONS WITH OTHER ELECTRON IMPACT RESULTS FOR METHANE

The ionization potential of CH_4 was measured prior to 1929 by several workers using instruments which could not separate ions according to their mass-to-charge ratios. These results are summarized in Table III. Using a mass spectrograph, Hogness and Kvalnes¹¹ found that when a tungsten filament supplied electrons CH_4^+ , CH_3^+ , CH_2^+ , CH^+ , C^+ , H_2^+ , and H^+ ions were produced in methane, but that with an oxide-coated cathode as source of electrons only CH_4^+ and CH_3^+ appeared in about equal numbers at minimum electron energies of 14.5 and 15.5 volts, respectively. They therefore ascribed the forma-

TABLE III. *Early results on the ionization potential of CH_4 .*

OBSERVER	REFERENCE	IONIZATION POTENTIAL (VOLTS)
Mayer	Ann. d. Physik 45 , 1 (1914)	13.5
Hughes and Dixon	Phys. Rev. 10 , 495 (1917)	9.5
Hughes and Klein	Phys. Rev. 23 , 450 (1924)	13.9
Pietsch	Dissert. Berlin p. 534 (1926)	12.5 ± 0.5
Glockler	J. Am. Chem. Soc. 48 , 2021 (1926)	14.4 to 15.2
Pietsch and Wilke*	Zeits. f. Physik 43 , 342 (1927)	14.58 ± 0.05
Morris	Phys. Rev. 32 , 942 (1928)	14.4

* Pietsch and Wilke also found a second critical potential for ionization at 15.40 ± 0.05 volts which was later interpreted by Hogness and Kvalnes, reference 11, as the appearance potential of CH_3^+ .

¹¹ Hogness and Kvalnes, Phys. Rev. **32**, 942 (1928).

FIG. 4. Ionization efficiency curves for negative ions formed in methane. Ordinates represent ion current. I^- is the electron current recorded in each case simultaneously with the ion current. The electron energy increases from right to left.

tions of the other ions to ionization of the products of thermal dissociation at the tungsten filament. Hipple and Bleakney,¹² analyzing methane with a mass spectrograph of the same type as, but less sensitive than, that used in the present work, observed the ions CH_4^+ , CH_3^+ , CH_2^+ , CH^+ , C^+ , and H^+ at the minimum electron energies 13.7, 14.7, 15.7, 23, 27 and 31 volts, respectively. Pressure, electron current, and pumping speed variations showed these all to be primary products. In addition, an H_2^+ peak was observed about 10^{-4} as high as the CH_4^+ peak.

Because of the use of lower pressures made possible by improved vacuum technique and greater sensitivity of the device for measuring ion currents, it is believed that the author's values for the appearance potentials of CH_4^+ and CH_3^+ are more reliable than those of Hogness and Kvalnes or those in Table III. All the results of Hipple and Bleakney agree within experimental error with those of the author excepting their values of the relative intensity of H_2^+ ionization and the appearance potential of H^+ ions. Evidently H^+ ionization in their apparatus was too weak to enable them to detect its appearance at 22.7 volts, and their 31-volt value probably corresponds to the author's value of 29.4 volts for the second appearance potential of H^+ ions.

The value 12.72 ± 0.05 volts for the ionization potential of CH_4 reported by Smith and Bleakney¹³ was determined by a method to which several objections have been raised. The value given in Table I was obtained by the method described above.

INTERPRETATION AND DISCUSSION

In the discussions below the following abbreviations will be used:

$A(\text{X}^+) \equiv$ Appearance potential of X^+ ions formed by electron impact in methane;

$I(\text{X}) \equiv$ Ionization potential of X;

$E(\text{X}) \equiv$ Electron affinity of X;

$D(\text{X}) \equiv$ Heat of dissociation of X to normal atoms in the gaseous state;

$Q(\text{X}) \equiv$ Energy evolved in the formation of a gram mole of X from its elements in the

¹² J. A. Hipple, Jr. and W. Bleakney, Phys. Rev. **47**, 802(A) (1935).

¹³ L. G. Smith and W. Bleakney, Phys. Rev. **49**, 883(A) (1936).

states in which they exist at room temperature and atmospheric pressure;

$L(\text{C}) \equiv$ Heat of sublimation of carbon (energy absorbed by a gram mole of carbon in changing from diamond to a gas consisting of atoms in the 3P normal state).

Here X stands for the chemical symbol of a molecule, a radical, or an atom. All these quantities will correspond to reactions taking place at the absolute zero of temperature.¹⁴ Whenever energy values have a direct bearing on thermochemical data they will be given both in volts (meaning electron volts per molecule) and in kcal. (meaning kcal. per mole). The conversion factor is: 1 volt = 23.054 kcal.

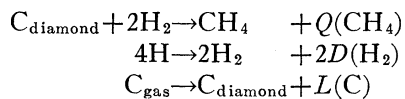
STATE	ENERGY		
$\text{C}+4\text{H}$	---e---	15.1 VOLTS	: 348 KCAL.
$\text{CH}+3\text{H}$	---d---	11.6 "	: 268 "
$\text{C}+2\text{H}+\text{H}_2$	---e'---	10.6 "	: 246 "
CH_2+2H	---c---	8.1 "	: 187 "
$\text{CH}+\text{H}+\text{H}_2$	---d'---	7.1 "	: 164 "
$\text{C}+2\text{H}_2$	---e''---	6.2 "	: 142 "
CH_3+H	---e---	4.5 "	: 104 "
CH_2+H_2	---c'---	3.7 "	: 84 "
CH_4	---a---	0 "	: 0 "

FIG. 5. Energies of the possible stable states of combination in which a carbon atom and four hydrogen atoms may exist referred to the state CH_4 as zero.

Fig. 5 shows the energies of the possible stable states of combination in which a carbon atom and four hydrogen atoms may exist, referred to the state CH_4 as zero. These energies are in accord with what seem to be the most reliable data available, though considerable uncertainty

¹⁴ Dissociation and ionization energies obtained spectroscopically, since they involve only considerations about two energy states of a single molecule, correspond to reactions, from the standpoint of thermochemistry, at absolute zero. According to the Franck-Condon principle an electron striking a molecule cannot change directly either the translational or rotational kinetic energies of the nuclei. Hence an appearance potential determined by the electron impact method is simply the energy difference between a vibrational level of an upper electronic state and one of a lower electronic state and is thus the minimum energy required for a reaction at absolute zero.

exists as to their validity. Levels c' , d' , e' , and e'' must lie below levels c , d , e , and e' , respectively, by $D(\text{H}_2) = 4.46 \pm 0.04$ volts or 102.9 ± 0.9 kcal.¹⁵ The position of the level e is determined by means of the following cycle:



This shows that $D(\text{CH}_4) = Q(\text{CH}_4) + 2D(\text{H}_2) + L(\text{C})$, which yields

$$D(\text{CH}_4) = \left\{ \begin{array}{l} 224.5 \pm 1.9 \text{ kcal.} \\ 9.84 \pm 0.08 \text{ volts} \end{array} \right\} + L(\text{C}) \quad (1)$$

on substitution of the above value of $D(\text{H}_2)$ and the value $Q(\text{CH}_4) = 18.66$ kcal. or 0.81 volts.¹⁶

There is considerable uncertainty concerning the true value of $L(\text{C})$. Bichowsky and Rossini¹⁷ after reviewing all data published prior to Jan. 1, 1934 set the value at $170 - a$ kcal., "where a is an unknown whose value at the present writing may be as much as +60 kcal." Recently data on predissociation in CO have set three possible values: $L(\text{C}) = 168.8 \pm 0.5$ kcal., 123.6 ± 0.5 kcal., or 107.2 ± 0.5 kcal. These data cannot, however, decide which is the correct value since they do not reveal in what electronic states the C and O atoms are formed in a predissociation process. Goldfinger and Jeunehomme,¹⁸ using these values to calculate vapor pressure *vs.* temperature curves for carbon, conclude that experimental curves, inaccurate as they may be, quite definitely rule out the lowest value and seem to favor the highest. However, their final conclusion is that the balance of evidence is in favor of the value $L(\text{C}) = 123.6 \pm 0.5$ kcal. or 5.36 ± 0.02 volts. (2)

Adopting this value one obtains from Eq. (1)

$$D(\text{CH}_4) = 348.1 \pm 2.0 \text{ kcal. or } 15.10 \pm 0.10 \text{ volts.} \quad (3)$$

¹⁵ Richardson and Davidson, Proc. Roy. Soc. **A125**, 23 (1929).

¹⁶ This quantity was obtained from the value, reference 18, for the corresponding reaction under constant pressure at 18°C by correcting for the thermal energies of the reactants.

¹⁷ Bichowsky and Rossini, *Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, N. Y., 1936).

¹⁸ P. Goldfinger and W. Jeunehomme, Proc. Faraday Soc. **32**, 1591 (1936). In this paper will be found an excellent bibliography of recent papers on this subject.

The location of level b in Fig. 5 at 4.5 volts above a is in agreement with the estimate of Norrish¹⁹ from thermal and spectroscopic data. It also agrees with the results of Trenner, Morikawa, and Taylor²⁰ which show that the energy required for the reaction $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ at constant pressure and room temperature is almost certainly greater by a small amount than the heat of dissociation of hydrogen measured under the same conditions. Correcting the latter quantity¹⁷ for the thermal energies of the reactants CH_4 and $\text{CH}_3 + \text{H}$, one concludes that the level b must be slightly more than 102.4 kcal. or 4.44 volts above zero. Further evidence on this point is afforded by Vogé's²¹ theoretical calculations of the energies of formation, measured from the minima of the potential surfaces, of CH_4 , CH_3 , CH_2 , and CH from normal carbon and hydrogen atoms. From the normal frequencies²² of these molecules the author has calculated their zero-point energies to be: 1.17 volts, 0.82 volts, 0.46 volts, and 0.18 volts, respectively. If now for the energy of formation of CH_4 the value 16.27 volts (quantity (3) + 1.17 volts) is used in Vogé's equations, a new value for the energy of formation of CH_3 may be obtained which, when corrected by the zero-point energy of CH_3 and subtracted from (3), gives 4.40 volts or 101.4 kcal. as the height at which level b should be set above zero.

Level d must be below level e by $D(\text{CH})$ for which the value 3.5 volts⁴ has been adopted. Level c was located by adding the zero-point energy of CH_2 to Vogé's result for the energy of formation of CH_2 based on the above value of $D(\text{CH})$ and subtracting the result from $D(\text{CH}_4)$ (3).

(a) Positive ions

H^+ .—The dissociation energy plus the total kinetic and excitational energy involved in the higher of the two appearance potentials of H^+ ions is $29.4 - 13.5 = 15.9 \pm 0.6$ volts, where 13.5 volts = $I(\text{H})$. The dissociation process therefore

¹⁹ R. G. W. Norrish, Trans. Faraday Soc. **30**, 106 (1934).

²⁰ N. R. Trenner, K. Morikawa and H. S. Taylor (paper soon to appear).

²¹ H. H. Vogé, J. Chem. Phys. **4**, 581 (1936).

²² Frequencies of CH_4 and CH as well as those of the methyl halides from which those of CH_3 were estimated are given by Spomer, reference 4. The frequencies of CH_2 are given by Sutherland and Dennison (Proc. Roy. Soc. **A148**, 250 (1935)).

could be that represented by a transition from level a (Fig. 5) to any one of the higher levels except c' and e'' . If this higher level is e the total excitational and kinetic energy which an H^+ ion, three H atoms, and a C atom must have when formed is $15.9 - 15.1 = 0.8 \pm 0.6$ volts; if it is any level lower than e at least 4.3 volts must be assigned to kinetic and excitational energy of the products of dissociation. It seems reasonable, therefore, to assume that the reaction wherein H^+ ions are formed at a minimum energy of 29.4 volts is: $CH_4 \rightarrow H^+ + C + 3H$. Subject to the validity of this assumption, the following upper limits may be set:

$$\left\{ \begin{array}{l} D(CH_4) \leq 15.9 \pm 0.6 \text{ volts or } 366 \pm 14 \text{ kcal.} \\ L(C) \leq 6.1 \pm 0.6 \text{ volts or } 141 \pm 14 \text{ kcal.} \end{array} \right\} \quad (4)$$

This conclusion, if correct, cannot be reconciled with the value 168.8 ± 0.5 kcal.¹⁸ for $L(C)$.

Subtracting $I(H) = 13.5$ volts from 22.7 volts, one sees from Fig. 5 that the dissociation process involved in the formation of H^+ ions at 22.7 volts minimum energy must be one of the three represented by transitions from a to c , d' , or b . The total kinetic and excitational energy of the products in these cases would be: $9.2 - 8.1 = 1.1$ volts; $9.2 - 7.1 = 2.1$ volts; or $9.2 - 4.5 = 4.7$ volts. Since the latter value seems high it is probable that these ions are produced either in the reaction $CH_4 \rightarrow H^+ + CH_2 + H$ or the reaction $CH_4 \rightarrow H^+ + CH + H_2$.

H_2^+ .—It is evident from Fig. 5 that the dissociation energy involved in $A(H_2^+)$ is that required for one of the reactions whereby a CH_4 molecule is transformed to one of the four states e' , d' , e'' , or c' . Since the dissociation plus kinetic and excitational energy is $27.9 - 15.4 = 12.5 \pm 0.5$ volts (where 15.4 volts = $I(H_2)$) it seems likely that the dissociation is to level e' rather than to a lower level, and hence that H_2^+ ions are formed in accordance with the reaction $CH_4 \rightarrow H_2^+ + C + 2H$. The products must possess at least $12.5 - 10.6 = 1.9 \pm 0.5$ volts of kinetic energy or energy of excitation.

H_3^+ .—If we let $D(H_3^+)$ stand for the unknown energy absorbed in the reaction $H_3^+ \rightarrow H_2 + H^+$ we have as the energy of the dissociation of CH_4 to a state involving three H atoms plus the total kinetic and excitational energy involved in $A(H_3^+)$: $A(H_3^+) + D(H_3^+) + D(H_2) - I(H)$

$= 16.3 \pm 1.0$ volts $+ D(H_3^+)$. In accordance with previous reasoning this state must be either d or e of Fig. 5. This would indicate that H_3^+ ions are probably formed in the reaction $CH_4 \rightarrow H_3^+ + C + H$, the energy required to excite or give kinetic energy to the products being $\{16.3 + D(H_3^+)\} - 15.1 = 1.2 \pm 1.0$ volts $+ D(H_3^+)$. However, it appears that in the case of these ions one should consider the possibility that products of dissociation formed along with a positive ion may be negatively charged as well as neutral. A consideration of the negative ions (see below) shows that possibly an H_3^+ ion is formed together with a CH^- ion (but that negative ions need not be considered in the interpretations of the observed appearance potentials of any other type of positive ion).

C^+ .—There are three transitions $a \rightarrow e''$, $a \rightarrow e'$, and $a \rightarrow e$ (Fig. 5), the energy required for which could be the dissociation energy involved in $A(C^+)$. Subtraction of $I(C) = 11.2$ volts from 26.7 ± 0.7 volts yields 15.5 ± 0.7 volts as the sum of this dissociation energy and any kinetic or excitational energy with which the products may be formed. It therefore seems most reasonable to assume that C^+ ions are formed according to the reaction $CH_4 \rightarrow C^+ + 4H$, the total kinetic and excitational energy of $C^+ + 4H$ being $15.5 - 15.1 = 0.4 \pm 0.7$ volts. If this assumption is correct the observation $A(C^+) = 26.7 \pm 0.7$ volts leads to the conclusion:

$$\left\{ \begin{array}{l} D(CH_4) \leq 15.5 \pm 0.7 \text{ volts or } 357 \pm 16 \text{ kcal.,} \\ L(C) \leq 5.7 \pm 0.7 \text{ volts or } 131 \pm 16 \text{ kcal.} \end{array} \right\} \quad (5)$$

Here again we have fairly strong evidence against the value $L(C) = 168.8 \pm 0.5$ kcal.¹⁸

CH^+ .—There are two possible reactions which could account for the production of CH^+ ions from CH_4 molecules: (a) $CH_4 \rightarrow CH^+ + 3H$; and (b) $CH_4 \rightarrow CH^+ + H + H_2$. If (a) is correct $I(CH) \leq A(CH^+) - \{D(CH_4) - D(CH)\} = 11.7 \pm 0.6$ volts (according as the products of dissociation are formed with or without excitational and kinetic energy), while if (b) is correct $I(CH) \leq 11.7 + D(H_2) = 16.2 \pm 0.6$ volts. No data on $I(CH)$ which might enable one to choose between (a) and (b) exist.²³

²³ In a previous paper, reference 1, the value 150 kcal. was calculated for $L(C)$ from the difference between $A(CH^+)$ and the appearance potential of CH^+ ions formed in acetylene. The reasonableness of this value was

CH_2^+ .—Since there are two appearance potentials for CH_2^+ ions and only two reactions whereby they may be formed it seems quite probable that 15.7 ± 0.5 volts is the minimum energy required for the process $\text{CH}_4 \rightarrow \text{CH}_2^+ + \text{H}_2$ while 22.9 ± 0.8 volts is that required for the process $\text{CH}_4 \rightarrow \text{CH}_2^+ + 2\text{H}$. Thus, from the energies required for the corresponding dissociations without ionization (Fig. 5), we may conclude that $I(\text{CH}_2) \leq 15.7 - 3.7 = 12.0 \pm 0.5$ volts, and hence that the products of the reaction requiring 22.9 volts must dissociate with at least $22.9 - (8.1 + 12.0) = 2.8$ volts of kinetic and excitational energy.²⁴

CH_3^+ .—Simple considerations show that 14.4 ± 0.4 volts is the minimum energy required to produce CH_3^+ ions according to the reaction $\text{CH}_4 \rightarrow \text{CH}_3^+ + \text{H}$. This means that $I(\text{CH}_3) \leq 14.4 - 4.5 = 9.9$ volts according as the CH_3^+ ions and H atoms are formed with or without energy. This is not in very good agreement with either Fraser and Jewett's value of 11.1 ± 0.5 volts²⁵ obtained by direct measurement on free CH_3 radicals or with Mulliken's theoretical estimate of 8.5 volts.²⁶

(b) Negative ions

The curves shown in Fig. 4 are characteristic of ion current *vs.* electron energy curves for negative ions formed in various substances. The interpretation which is at present accepted of such curves²⁷ is that a peak at low electron energies indicates the formation of a negative ion through dissociation of a molecule and capture of the impacting electron, while the rising of a curve to a broad maximum at higher energies corresponds to the dissociation of molecules into pairs of positive and negative ions. No explanation of the apparent upward breaks at ~ 47 volts, 50 volts, and 45 volts in the curves of Fig. 4 for H^- , C^- , and CH^- , respectively, has been attempted. It is

taken to be evidence in favor of reaction (a). However, on the assumption that reaction (b) is correct and that CH^+ ions are produced from C_2H_2 molecules in the process $\text{C}_2\text{H}_2 \rightarrow \text{CH}^+ + \text{CH}$ one obtains by a similar calculation $L(\text{C}) = 128$ kcal.

²⁴ The conclusions with regard to CH_2^+ ions in a previous paper, reference 1, were less definite because of doubt as to the reality of the appearance potential at 22.9 volts. This doubt has since been largely dispelled.

²⁵ R. G. J. Fraser and T. N. Jewett, *Phys. Rev.* **50**, 1091 (1936).

²⁶ R. S. Mulliken, *J. Chem. Phys.* **1**, 492 (1933).

²⁷ W. W. Lozier, *Phys. Rev.* **46**, 268 (1934).

quite possible that these are due to some peculiarity of the apparatus and not to the formations of negative ions according to reactions different from those requiring lower energies.

H^- .—Taking $E(\text{H}) = 0.7$ volt,²⁸ we see from Fig. 5 that the following are the four possible processes requiring least energy according to which H^- might be formed by dissociation and capture:

- (a) $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}^-$ -3.8 volts;
- (b) $\text{CH}_4 \rightarrow \text{CH} + \text{H}_2 + \text{H}^-$ -6.4 volts;
- (c) $\text{CH}_4 \rightarrow \text{CH}_2 + \text{H} + \text{H}^-$ -7.4 volts;
- (d) $\text{CH}_4 \rightarrow \text{C} + \text{H} + \text{H}_2 + \text{H}^-$ -9.9 volts.

The observation that H^- ions are formed in three different processes all requiring less energy than (d) suggests rather strongly that (a), (b) and (c), respectively are the reactions occurring at the observed minimum energies 6.1 ± 0.3 volts, 6.9 ± 0.8 volts, and 7.3 ± 1.0 volts. This interpretation requires that the total kinetic and excitational energies of the products formed be at least $6.1 - 3.8 = 2.3$ volts in reaction (a), $6.9 - 6.4 = 0.5$ volt in reaction (b), and $7.3 - 7.4 \cong 0$ volts in reaction (c).

If we take $I(\text{CH}) = 11.7$ volts and $I(\text{CH}_2) = 12.0$ volts Fig. 5 indicates that the 18.0-volt appearance potential of H^- can only be the minimum energy for one of the reactions $\text{CH}_4 \rightarrow \text{H}^- + \text{CH}_3^+$ or $\text{CH}_4 \rightarrow \text{H}^- + \text{CH}^+ + \text{H}_2$. The energy required for the first of these would be 14.4 volts (that needed for the reaction $\text{CH}_4 \rightarrow \text{H} + \text{CH}_3^+$) $- E(\text{H})$ or 13.7 volts plus the kinetic and excitational energy of $\text{H}^- + \text{CH}_3^+$. Hence the latter energy would be 4.3 volts. The energy required for the second reaction, aside from the kinetic and excitational energy of $\text{H}^- + \text{CH}^+ + \text{H}_2$, would be 7.1 volts $+ I(\text{CH}) - E(\text{H})$ or 18.1 volts. Thus if H^- ions are produced according to this process the products can be formed in their normal states with practically no mutual kinetic energy. Because of the relatively strong CH_3^+ ionization and unresolved ion current at $m/e = 13$ produced at minimum energies less than 18.0 volts, neither the CH_3^+ ions, if formed in the first reaction, nor the CH^+ ions, if formed in the second reaction, at 18.0 volts minimum energy could have been detected.

²⁸ Hylleraas, *Zeits. f. Physik* **65**, 208 (1930).

C^- .—The striking feature of the curves shown in Fig. 4 for C^- ions is the absence of a detectable peak at low electron energies. From this it appears that a C^- ion is only formed along with a positive ion. This ion may be H^+ , H_2^+ , or H_3^+ . The assumption that the reaction $CH_4 \rightarrow C^- + H + H_3^+$ occurs at a minimum energy of 27.4 ± 0.6 volts seems distinctly unreasonable on the grounds that the additional H_3^+ ionization would have been detected in the appearance potential curve for that ion. It is quite possible that 27.4 ± 0.6 volts may be identified with the 27.9 ± 0.5 volt appearance potential of H_2^+ ions. The fact that at an electron energy of 50 volts H_2^+ ionization is about 80 times as intense as C^- ionization shows that most of the H_2^+ ions are formed according to some reaction (a) other than (b) $CH_4 \rightarrow C^- + 2H + H_2^+$. From the discussion of $A(H_3^+)$ it is evident that probably (a) is the reaction $CH_4 \rightarrow C + 2H + H_2^+$. The minimum energy required for (b) should, except for differences in the kinetic and excitational energies of the products, be less than that required for (a) by $E(C) = 1.9 \pm 0.7$ volts.²⁹ However, in the appearance potential curve for H_2^+ there is no abrupt change of curvature at electron energies above 27.9 volts showing that if both (a) and (b) take place the minimum energies required are about the same and hence that $C^- + 2H + H_2^+$ must possess about 1.9 volts more energy when formed than $C + 2H + H_2^+$.

A simpler and more likely explanation of the formation of C^- ions is provided by the assumption that they are accompanied by H^+ ions. The intensity of H^+ ionization is $\sim 10^3$ times that of C^- ionization at 50 volts electron energy. Hence we should not expect to detect the appearance of the relatively small H^+ ionization produced in the process $CH_4 \rightarrow C^- + 2H + H^+$ at 27.4 volts minimum energy. Without allowance for excitational and mutual kinetic energies of the products the minimum energy for this process should be $D(CH_4) + I(H) - E(C) = 26.7 \pm 0.7$

²⁹ The author estimated the value $E(C) = 1.9 \pm 0.7$ volts by plotting the square roots of the ionization potentials of N , O^+ , and F^{++} vs. their atomic numbers and extrapolating to atomic number six. Glocker (Phys. Rev. **45**, 111 (1934)), by a similar extrapolation, has obtained the value 1.37 volts for $E(C)$. Use of this value instead of 1.9 volts lowers the total excitational and kinetic energy of products as well as the upper limits (6) for $D(CH_4)$ and $L(C)$ by 0.5 volts or 12 kcal.

volts. Hence on this assumption we may conclude that the products possess at least $27.4 - 26.7 = 0.7 \pm 0.9$ volts of energy, or that $D(CH_4) \cong A(C^-) + E(C) - I(H)$ and hence that²⁹

$$\left. \begin{aligned} D(CH_4) &\leq 15.8 \pm 0.9 \text{ volts or } 364 \pm 21 \text{ kcal.} \\ L(C) &\leq 6.0 \pm 0.9 \text{ " or } 139 \pm 21 \text{ " } \end{aligned} \right\} (6)$$

The latter conclusions like (4) and (5) provides fairly strong evidence against the value 168.8 kcal.¹⁸ for $L(C)$.

CH^- .—The first appearance potential of CH^- ions may readily be explained as the energy required for the process $CH_4 \rightarrow CH^- + 3H$. This yields the result that $E(CH) \cong 11.6 - 10.2 = 1.4$ volts according as the products are formed with or without energy. The other reaction ($CH_4 \rightarrow CH^- + H + H_2$) which could account for these ions demands that the products be formed with an energy of 2.1 volts $+E(CH)$. The second appearance potential of CH^- ions could be the minimum energy for the reaction $CH_4 \rightarrow CH^- + H_3^+$. This interpretation is indicated by the agreement of $A(CH^-) = 24.5 \pm 0.5$ volts with $A(H_3^+) = 25.3 \pm 1.0$ and by the fact that the intensities of H_3^+ and CH^- ionizations are approximately equal at all electron energies at least as high as 60 volts. Again using $D(H_3^+) \rightarrow H_2 + H^+$, we see from Fig. 5 that only 20.6 volts $-E(CH) - D(H_3^+)$ should be required to break a CH_4 molecule apart into a CH^- ion and an H_3^+ ion in their normal states without mutual kinetic energy. Hence if this be the correct interpretation the amount of the impacting electron's energy which must go into kinetic and excitational energy of the two ions is 3.9 volts $+E(CH) + D(H_3^+)$.

The process whereby a CH^- ion and other products of a CH_4 molecule could be formed with the least total kinetic and excitational energy is $CH_4 \rightarrow CH^- + 2H + H^+$. Here we see from Fig. 5 that this energy would be $(24.5 - 25.1)$ volts $+E(CH)$ and is $\cong 0.8 \pm 0.6$ volts if we take $E(CH) \cong 1.4$ volts as indicated in the previous paragraph.

CH_2^- .—When a CH_2^- ion is produced by dissociation of a CH_4 molecule and capture of the impacting electron, the other atoms of the original molecule may dissociate as $2H$ or as H_2 . The energy required to excite or give kinetic

TABLE IV. Values calculated for $D(\text{CH}_4)$ and $L(\text{C})$.²⁹

BASIS OF CALCULATION	$D(\text{CH}_4) \leq$	$L(\text{C}) \leq$
$A(\text{H}^+) = 29.4 \pm 0.6$ volts	15.9 ± 0.6 volts or 366 ± 14 kcal.	6.1 ± 0.6 volts or 141 ± 14 kcal.
$A(\text{C}^+) = 26.7 \pm 0.7$ volts	15.5 ± 0.7 volts or 357 ± 16 kcal.	5.7 ± 0.7 volts or 131 ± 16 kcal.
$A(\text{C}^-) = 27.4 \pm 0.6$ volts	15.8 ± 0.9 volts or 364 ± 21 kcal.	6.0 ± 0.9 volts or 139 ± 21 kcal.

energy to the products formed would be 0.8 volts $+E(\text{CH}_2)$ in the first case or 5.2 volts $+E(\text{CH}_2)$ in the second case. Since the latter value seems high it is probable that the reaction occurring is $\text{CH}_4 \rightarrow \text{CH}_2^- + 2\text{H}$. The formation of a CH_2^- ion at energies greater than 23.4 ± 0.6 volts must proceed according to one of the two reactions $\text{CH}_4 \rightarrow \text{CH}_2^- + \text{H} + \text{H}^+$ or $\text{CH}_4 \rightarrow \text{CH}_2^- + \text{H}_2^+$. Aside from the excitational and mutual kinetic energies of the products, the minimum energies for these two reactions are respectively: 21.6 volts $-E(\text{CH}_2)$; and 19.0 volts $-E(\text{CH}_2)$. Thus the total kinetic and excitational energies of the products must be: 1.8 volts $+E(\text{CH}_2)$; or 4.4 volts $+E(\text{CH}_2)$. It is unlikely that the positive ions formed in one or the other of these processes would be sufficiently numerous to be distinguishable from those formed in other ways.

SUMMARY AND CONCLUSION

A summary of the conclusions which were drawn in the above discussions from the values of dissociation energies given in Fig. 5 will be found in the last three columns of Table I. The values in column five are calculated by adding ionization energies to these dissociation energies. They represent minimum energies for the corresponding reactions exclusive of the total kinetic or excitational energy products must have when formed by electron impact. Values of the latter quantities are given in column six where possible and are obtained by subtraction of the values of column five from the corresponding appearance potentials in column three.

It should be emphasized that the quantities of Fig. 5 are not certain and that hence some of the interpretations may be incorrect. One cannot be completely sure at present of any reaction except (12) and (13). However, it is a fact of considerable significance that a reasonable explanation for every observed appearance potential exists. Attention should be drawn specifically to the fact that in all cases except $A(\text{CH}_2^+) = 22.9$ volts,

$A(\text{H}^-) = 6.1$ volts, and probably the appearance potentials of H_3^+ and CH_2^- , interpretations are possible which require that the total excitational and kinetic energy of products formed by electron impact from CH_4 molecules be less than two volts.

It will be noted that the ions H_2^+ , H_3^+ , C^+ , C^- , CH^- , and CH_2^- are not produced unless in each case the energy of the electrons is at least slightly greater than the largest of the calculated minimum energies for possible processes. This may be true of CH^+ ions as well. The higher of the two appearance potentials of H^+ and the higher appearance potential of CH_2^+ also satisfy this condition. The only type of ion for which an appearance potential satisfying this condition was not detected is H^- . These facts seem to indicate that at least in most of the cases mentioned, the possible processes which require the largest calculated minimum energies are the ones which actually take place: i.e., that most ions are only formed when the parent molecules are broken into as many parts as possible. This conclusion gives one some reason to prefer the reactions (5), (8), (21), and (24) to the reactions (6), (9), (22), and (25) (column four of Table I).

This conclusion also adds weight to the relations (4), (5), and (6) which are gathered together in Table IV. These relations are based on the assumptions that the appearance potentials in column one of Table IV are minimum energies for the reactions (3), (7), and (19) in column four of Table I. The values quoted are in each case less than or equal to the true values of $D(\text{CH}_4)$ and $L(\text{C})$ according as the total excitational and kinetic energies of the products is greater than or equal to zero. Thus as a further conclusion, we may say that of the three values of $L(\text{C})$ determined from a predissociation limit in CO^{18} , the results for methane provide good evidence against the value 168.8 kcal. and are completely consistent with the value 123.6 kcal. They are also consistent with the lower of the two possible

values (136 kcal.) obtained by Lozier²⁷ from data on the products formed by electron impact in CO.

In closing the author wishes to thank Professor Walker Bleakney, under whose direction this work was done, and Professors E. U. Condon and H. D. Smyth for many helpful suggestions. He

also would like to express appreciation to Drs. W. Wallace Lozier and Philip T. Smith who, with Professor Bleakney, designed and constructed the apparatus with which this work was done and to Mr. Kiyoshi Morikawa of the chemistry department of Princeton University for supplying samples of very pure methane.

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Thermionic Emission into Dielectric Liquids

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The presence of thermionic emission at ordinary temperatures for cathodes in contact with dielectric liquids is demonstrated. The current voltage relation is shown to obey the law $I = I_0 e^{(\epsilon(\epsilon F D)^2 / kT)}$, where I is the current, F the field, and D the dielectric constant of the liquid. This is a modification of the Schottky law in vacuum. The effects of adsorbed hydrogen and oxygen, of surface irregularities, and of work function are discussed. The formation of a wax by electron bombardment of the liquid is also reported.

A. INTRODUCTION

MANY theories have been advanced to explain the mechanism of current conduction in pure dielectric liquids in the region of high field strengths. A good resume of these may be found in Nikuradse's book.¹ The most generally accepted of these is the process of ionization by collision, in analogy to gaseous conduction. It is assumed that ions are initially present in the liquid which are the current carriers at low field strengths. These are supposed to be formed by some ionizing agent such as x-rays or cosmic rays, or from ordinary electrolytic dissociation. At intermediate field strengths this ion current saturates and becomes independent of field until such a value is reached that the ions (or electrons) attain sufficient velocity to form new ions by collision. New ions are formed at such a rate that the current becomes an exponential function of the voltage $I = I_0 e^{\sigma V}$ which is found to agree fairly well with experiment, considering I_0 and C as adjustable constants. Most published data available to the authors are not sufficiently accurate, however, to distinguish this relation from $I = I_0 e^{\sigma \sqrt{V}}$, for example.

In contrast to the above view, the results

obtained in our investigation prove that, in the case of the liquid investigated (pure toluene), at least, the only important means of current conduction is by electrons emitted from the cathode thermionically.

This mechanism was first proposed in tangible form by H. Edler and O. Zeier² who found the temperature variation of the current to correspond to the Richardson equation for thermionic emission. Although they did not derive the current voltage relation given in this paper they found the current to vary less rapidly with voltage than $I = I_0 e^{\sigma V}$.

L. Inge and A. Walther³ also disagree with the mechanism of ionization by collision and invoke instead the cold cathode effect, which would require a current voltage relation of the form $I = I_0 V^2 e^{-\sigma/V}$. They plot essentially $\log I/V^2$ against $1/V$ and obtain not a straight line, but a curve which they believe to be approaching a straight line in its high voltage portion. However, if their data are replotted as $\log I$ against \sqrt{V} , a straight line is obtained in verification of the formula $I = I_0 e^{\sigma \sqrt{V}}$ of the present paper.

² H. Edler and O. Zeier, *Zeits. f. Physik* **84**, 356 (1933).

³ L. Inge and A. Walther, *Tech. Phys. U. S. S. R.* **1**, 539 (1935).

¹ A. Nikuradse, *Das flüssige Dielektrikum*, pp. 135-136.

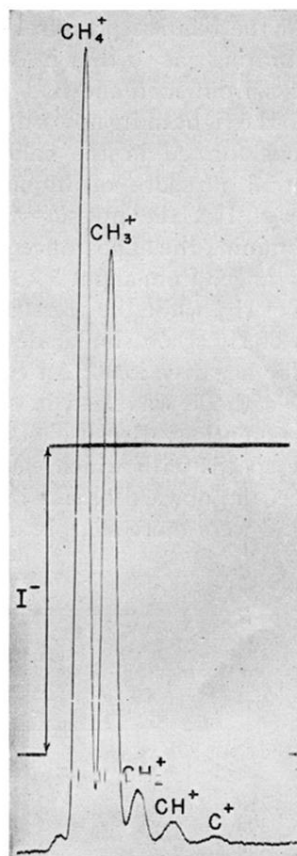


FIG. 1. Mass spectrum of the heavier positive ions formed in methane. Ordinates represent ion currents and abscissae analyzer voltage or e/m values. I^- is the electron current recorded simultaneously with the ion current. The small peak to the left of the CH_4^+ peak corresponds to ions with $m/e=17$ which can only be $C^{13}H_4^+$ ions. The ratio of the heights of these two peaks is $\sim 1/100$ which is approximately the abundance ratio C^{13}/C^{12} .

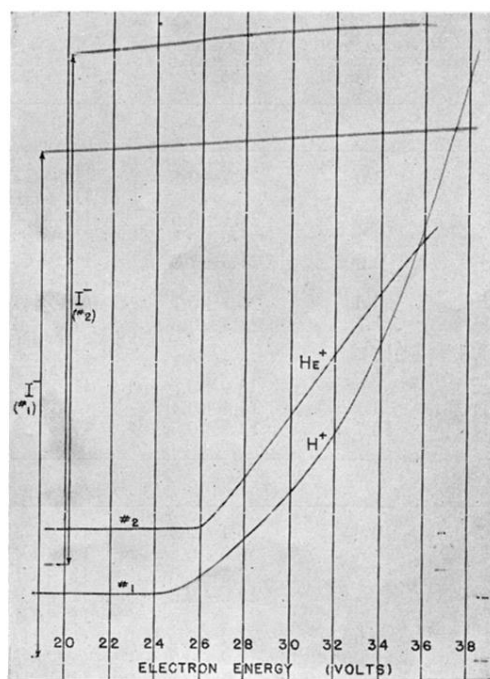


FIG. 2. Appearance potential curves for H^+ ions formed in methane and He^+ ions formed in helium. Ordinates represent ion currents. I^- is the electron current recorded in each case simultaneously with the ion current.

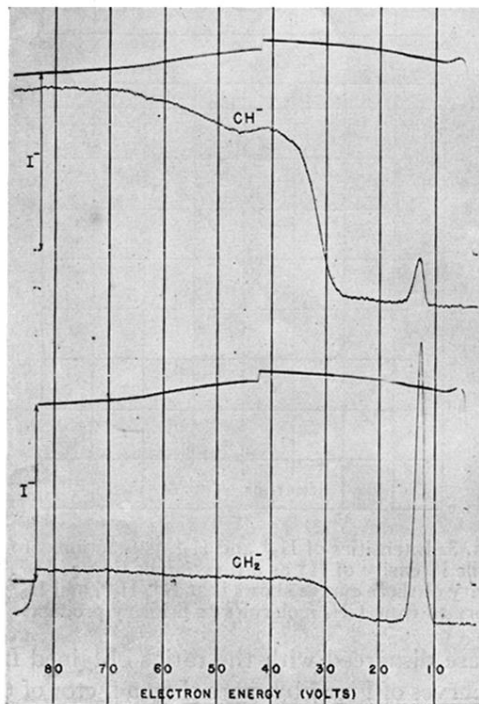
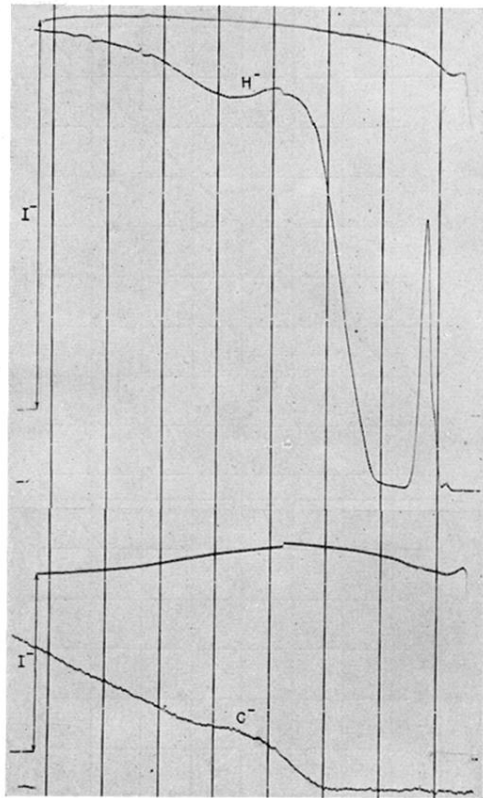


FIG. 4. Ionization efficiency curves for negative ions formed in methane. Ordinates represent ion current. I^- is the electron current recorded in each case simultaneously with the ion current. The electron energy increases from right to left.