# THE IONIZATION PROCESSES IN METHANE INTERPRETED BY THE MASS SPECTROGRAPH

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ABSTRACT

The ionization processes occurring when $CH_4$ molecules are ionized by controlled electron impact have been determined with the aid of the mass spectrograph. $CH_4^+$ and $CH_3^+$ are the only ions formed, and by a study of their relative intensities under different conditions of pressure and voltage, it was found that both these ions are formed directly by the electron impact. The ionization processes are: $CH_4 = CH_4^+ + E^-$ (14.5 volts); $CH_4 = CH_3^+ + H + E^-$ (15.5 volts).

**Isotopes of neon.**—It has been definitely determined that besides the two isotopes of neon, $Ne_{20}$ and $Ne_{22}$, there exists a third isotope with a mass of 21.

THE work here described was undertaken with the hope of obtaining the bonding energy between the $CH_3$ radical and the hydrogen atom in methane. The dissociation or bonding energy of diatomic molecules can be obtained from the data of positive ray analysis[1] and by applying the same methods to polyatomic molecules, it should be possible to determine the bonding energies of these molecules as well. If $H^+$ were produced directly from $CH_4$ by electron impact and if the minimum potential applied to the impact electron to produce $H^+$ from methane were known, the bonding energy could be determined by simply subtracting the ionization potential of the hydrogen atom (13.5 volts) from this minimum potential.

Unfortunately the $H^+$ ion is not produced by electron impact with $CH_4$ and, because of this, the principal object of the work has not been attained, but the processes that do occur when methane is ionized by impact electrons have been successfully interpreted.

The apparatus, with the exception of a few changes in minor details, and the method of analysis were the same as those employed by Hogness and Lunn.[2]

In the first experiments, tungsten filaments were used and under these conditions the ions $CH_4^+$, $CH_3^+$, $CH_2^+$, $CH^+$, $C^+$, $H_2^+$, and $H^+$ were found to be present. The intensity of the ions $CH_2^+$, $CH^+$, $C^+$, $H_2^+$ and $H^+$ were, under all conditions, very small and it was suspected that these ions were produced by ionization of the products of thermal dissociation of the methane by the filament. The tungsten filament was then replaced by a nickel-platinum oxide-coated filament which, at a much lower temperature, gave the same electron emission as that of the tungsten filament. With this new filament, only the ions $CH_4^+$ and $CH_3^+$ were obtained. Under no conditions was it now possible to get any evidence whatsoever of the $H^+$ ion.

To determine whether the $CH_3^+$ resulted from spontaneous dissociation accompanying the ionization of the $CH_4$ molecule or whether a collision of

[1] For references, see Hogness and Harkness, Phys. Rev. **32**, 784 (1928).

[2] Hogness and Lunn, Phys. Rev. **26**, 44 (1925).

the $CH_4^+$ ion with a neutral $CH_4$ molecule was necessary for the production of the $CH_3^+$ ion, the usual method of studying the relative intensities of these two ions as a function of the pressure in the ionization chamber was employed. In twenty-three determinations with the pressure varying all the way from $3\times10^{-5}$ to $380\times10^{-5}$ mm, the ratio of $CH_3^+$ to $CH_4^+$ was $1\pm0.1$ and since no variation of this ratio with pressure was found, it must be concluded that the $CH_3^+$ ion is produced directly upon ionization of the $CH_4$ molecule by electron impact. The two processes which occur may be represented by the following equations:

$$CH_4 = CH_4^+ + E^- \quad (1)$$

$$CH_4 = CH_3^+ + H + E^- \quad (2)$$

When an electron of sufficient energy ionizes a $CH_4$ molecule, it may do so in one of two ways; it may produce the stable $CH_4^+$ ion, or an unstable $CH_4^+$ ion which dissociates spontaneously into a stable $CH_3^+$ ion and a neutral

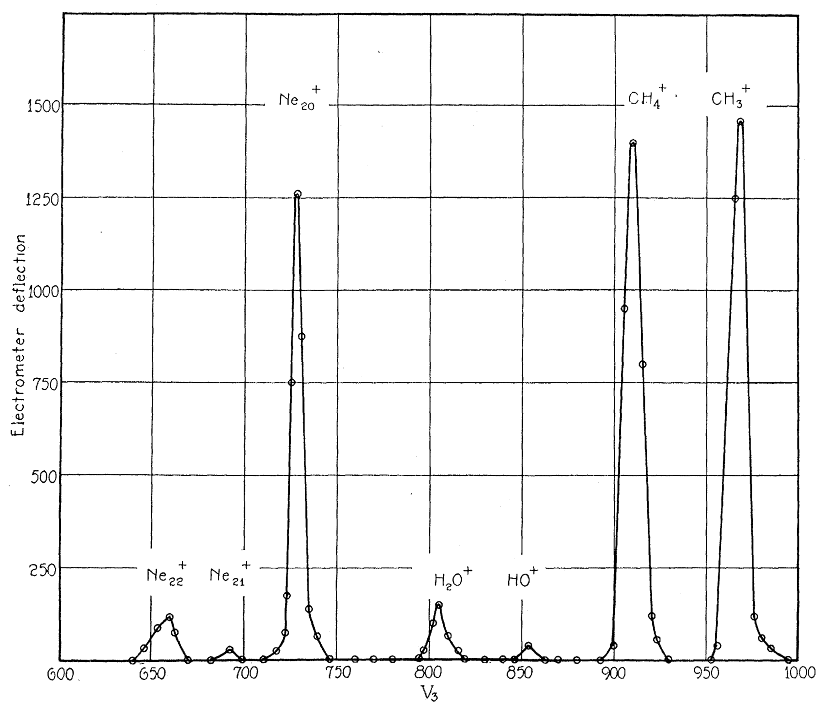


Fig. 1. Mass spectrograph curves for $CH_4$ together wih the curves for neon used for calibration.

hydrogen atom, but any $CH_4^+$ ion produced by electron impact cannot dissociate into a $CH_3$ radical and an $H^+$ ion. Furthermore, the probabilities for the occurrence of processes (1) and (2) are about equal. This constant ratio between the $CH_4^+$ and $CH_3^+$ ions was also maintained in mixtures of neon and methane. If any of the $CH_4^+$ or $CH_3^+$ ions were produced by impact of the $CH_4$ molecule with the $Ne^+$ ion, the probabilities of the formation of either of these ions was also the same under these conditions. The accompanying figure shows this fact graphically and also shows the resolution which was obtained with the instrument. In this figure, the ordinates represent electrometer deflections and the abscissas the analyzing voltage applied to the positive ions. The $m/e$ values from which the various ions were identified were calculated from $e/m = 2V_3/H^2r^2$ where $H$ is the magnetic field strength and $r$ the radius of curvature (5 cm), of the path of the positive ions in the magnetic field.

The ionization potentials of each of the two processes was determined by the usual method of lowering the voltage applied to the impact electrons until the peak of the particular ion just disappeared. To correct for initial velocities, contact potentials and instrument sensitivity neon was used as the calibrating gas. The ionization potential of neon was taken to be 21.5 volts[3] and referred to this the ionization potentials obtained in four different determinations are given in Table I. The value, 14.5 volts, of the second column represents the energy change in process (1) and that of the third column, 15.5 volts, that of process (2).

TABLE I. *Ionization potentials for $CH_4^+$ and $CH_3^+$.*

| Expt. No. | $CH_4^+$ | $CH_3^+$ |
|---|---|---|
| 1 | 14.45 volts | 15.50 volts |
| 2 | 14.50 | 15.50 |
| 3 | 14.50 | 15.50 |
| 4 | 14.50 | 15.83 |
| Average | 14.5 | 15.5 |

Mayer[4] obtained a value of 13.5 volts for the ionization potential of methane, Hughes and Dixon[5] 9.4 to 9.6 volts, and Hughes and Klein[6] 13.9 volts, Glockler[7] was unable to obtain a sharp break in the current potential curves obtained with methane and believed that but one process was taking place which had an ionization potential between 14.4 and 15.2 volts. Pietsch and Wilcke[8] obtained two distinct values of the ionization potential of methane, one at $14.58 \pm 0.05$ volts and one at $15.40 \pm 0.05$ volts. The first of these they interpreted correctly to be that of our process (1). The second value, however, they ascribed to the complete dissociation of $CH_4$ into gaseous atoms without ionization. The correct interpretation of this second value is that of process (2).

[3] Hertz and Kloppers, Zeits. f. Physik **31,** 463 (1925).
[4] Franz Mayer, Ann. d. Physik **45,** 1 (1914).
[5] Hughes and Dixon, Phys. Rev. **10,** 495 (1917).
[6] Hughes and Klein, Phys. Rev. **23,** 455 (1924).
[7] Glockler, J. Am. Chem. Soc. **48,** 2021 (1926).
[8] Pietsch and Wilcke, Zeits. f. Physik **43,** 342 (1927).

No negative ions, doubly charged positive ions or positive ion clusters were found.

## Isotopes of Neon

The calibrating gas, neon, gave the positive ions, $Ne_{20}^+$ and $Ne_{22}^+$ in the ratio of ten to one as found by Aston[9] and by Barton and Bartlett.[10] There was, in addition to these ions, a small peak for $Ne_{21}^+$, which was always found when neon was in the apparatus (see Fig. 1) but was never obtained in the absence of neon. When pure neon was run at such conditions as to give greatest intensity of the $Ne_{20}^+$ ion, it was found that the intensity of the $Ne_{21}^+$ ion corresponded to about 2 percent of the sum of the intensities of the three ions of neon. In early work by Aston,[11] reference was made to finding a line in neon corresponding to $Ne_{21}^+$, and from its intensity he estimated its concentration in neon as being less than one percent by volume. In a later work by Aston,[9] no line for $Ne_{21}^+$ was found, but since poor results are claimed for $Ne_{22}^+$, it may be that the increased resolution of the apparatus which was used cut down the sensitivity for $Ne_{21}^+$ to such an extent that it could not be detected. Such effects are very pronounced in the apparatus used in the present work. The fact that Aston only finds $H_2O^+$ during the first few days after pumping out the apparatus likewise indicates that the absence of $Ne_{21}^+$ is a matter of intensity since $H_2O^+$ is always present in the type of apparatus used here.

The plot of the curve for the ions of neon published by Barton and Bartlett shows that the peak for $Ne_{22}^+$ starts at 20.7 so that any $Ne_{21}^+$ present would not be resolved.

If the peak for mass twenty-one were due to a hydride of $Ne_{20}$, then there should be a peak for mass twenty-three corresponding to the hydride of $Ne_{22}$. The calculated intensity for this peak is 1.6 scale divisions under the conditions referred to before, which is detectable when a specific search is made for such an intensity. No such peak was found, however. There are then three isotopes of neon of masses, twenty, twenty-one and twenty-two, respectively.

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[9] F. W. Aston, Proc. Royal Soc., **115A**, 487 (1927).
[10] Barton and Bartlett, Phys. Rev. **31**, 822 (1928).
[11] F. W. Aston, Phil. Mag. **39**, 449 (1920).