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# A CRITICAL POTENTIAL OF METHANE AND ITS ABSORPTION IN THE ULTRA-VIOLET

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In a previous paper[1] it was stated that the maximum in the current potential curve found in a *three*-electrode tube with methane must be due either to a resonance potential of methane or to a large transparency for slow electrons. It was further pointed out that the interpretation of maxima in current-potential curves obtained in *four*-electrode tubes must also take into account the possibility of abnormal transparency at certain velocities. In the meantime Brode[2] has as a matter of fact found a variable mean free path for electrons in methane using the method of Ramsauer,[3] which presumably accounts for the maximum, since it occurs at about the expected velocity. Nevertheless, the whole problem is of such importance that it seemed wise to make a further investigation to see if, in addition to the effect due to transparency, there might not also be a resonance potential occurring in the same neighborhood, accounting for part of the effect. The possibility must also be considered of a critical potential (as distinguished from a resonance potential) at which the molecule assumes a metastable state, without immediate re-emission as in the case of a resonance potential. (The hypothesis of a metastable state has been made before for instance in the case of helium by Franck and Knipping;[4] and, since nothing is known concerning the energy-levels of methane, this possibility must also be considered.)

In this paper experimental work is described which shows that no part of the maximum obtained in three or four-electrode tubes filled with methane can be due to a resonance potential. The work does not eliminate, however, the possibility of a non-radiating critical potential occurring at the voltage in question. The experiments consist in the measurement of the absorption of methane for ultra-violet light and in the study of Lenard photo-electric curves in methane. Before describing them the current-potential curves obtained by the resonance method will be given.

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*The Experiments in Four-Electrode Tubes.*—The current-potential curves obtained in methane in a four-electrode tube are shown in figure 1. The method of obtaining these curves is fully described by K. T. Compton.[5] A large number of such curves were taken and they all show the maximum. Pressures from 0.2 to 0.9 mm. Hg were used, sometimes a tungsten and sometimes a Pt(CaO) filament being employed. The usual interpretation of such curves would ascribe the maximum to a resonance potential at about five volts (corrected for initial velocity). However, these curves did not show a second maximum at about 10 volts, as might have been expected from the conditions of experiment and from analogy with similar curves in mercury and other substances.[6] This lead to the belief that the maximum was not due to a resonance-point, but to large transparency for slow electrons.

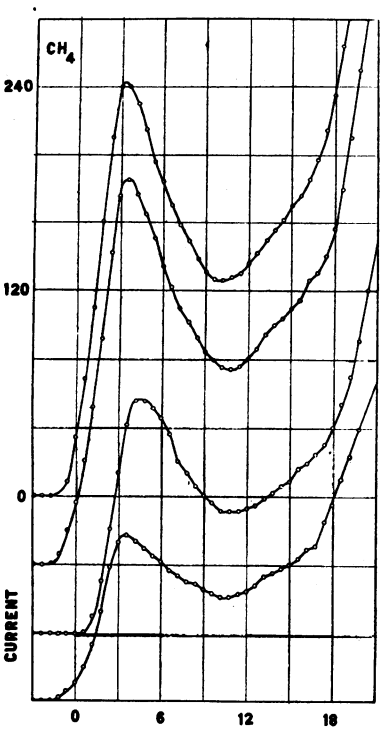

FIGURE 1

If it were possible to get spectroscopic data for methane, this question could easily be decided; for methane should show a line or band spectrum in the region of 5 volts or 2400Å. The reason that no spectroscopic data exist is that the substance decomposes under the conditions maintained in an ordinary discharge tube. However, absorption measurements are of course possible; and, in coöperation with Dr. Richard M. Badger of this laboratory, they have been carried out as described below.

*The Absorption of Methane for Ultra-Violet Light.*—The light from an aluminum spark under water was sent through a layer of methane 54 cm. long into a Hilger quartz spectrometer, for the use of which we wish to thank Prof. R. A. Millikan. The gas was at atmospheric pressure. Figure 2 shows that no absorption could be detected in the region around 2400Å. For comparison benzene at 0.13 atmosphere was placed in the tube, and its absorption was easily shown. Although it may be argued that a thicker layer of methane or the gas at higher pressure might show absorption, yet it is felt that the conditions were stringent enough to make it very improbable that absorption exists. If it be admitted that the experiment indicates *no* absorption in the ultra-violet region, then methane has no

radiation potential at five volts. Additional proof of the correctness of this inference is afforded by the following Lenard experiments.

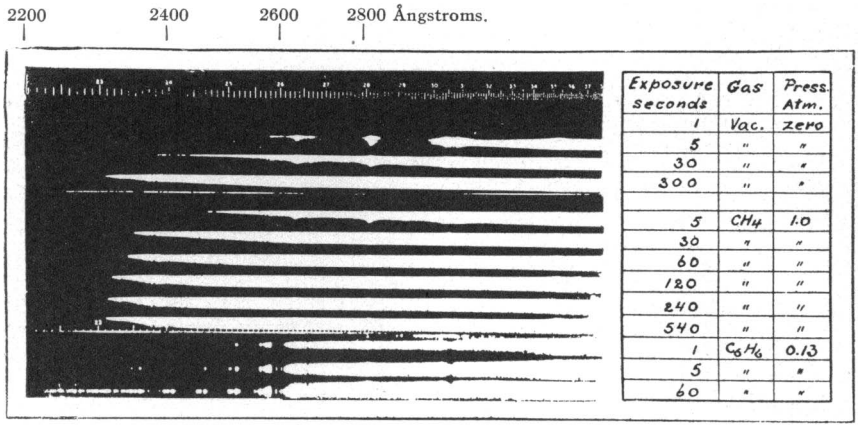


FIGURE 2

*The Lenard Photo-Electric Experiments in Methane.*—These experiments were carried out on the basis of the following considerations. If methane has a radiation potential at five volts, the light of wave-length 2400Å. should liberate photoelectrons from the platinum receiving plate, and a photo-current beginning at five volts should be detected in analogy with the same type of experiment in mercury by Franck and Einsporn,[7] and in nitrogen by Brandt.[8] However, the curves in figure 3 A show that no positive current is detected below 17 volts, and this is undoubtedly due not to electrons, but to positive ions reaching the plate, as may be judged in the usual way from the magnitude of this current. From the very pronounced maximum in the resonance curve it would be expected that enough photo-electrons would be liberated from the plate at five volts to be detected; especially since

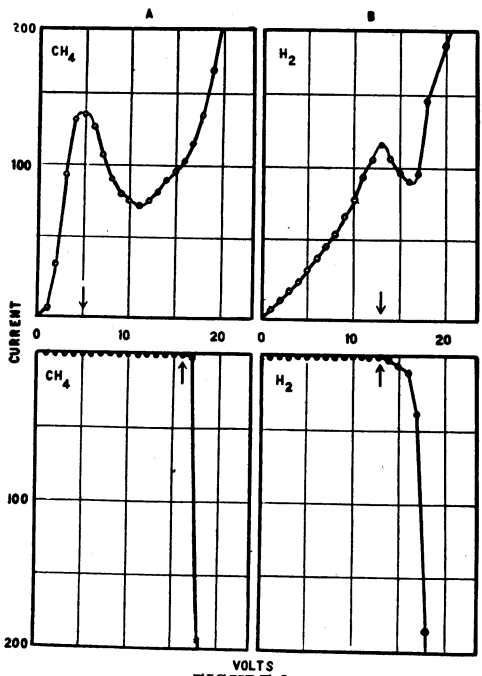


FIGURE 3

similar experiments in hydrogen showed that the photo-electric curves (shown in figure 3 B) start at 13 volts—the same voltage at which the maximum in the resonance curve appears.

*Conclusions.*—These experiments, it is believed, prove that five volts is not a resonance potential of methane. But it cannot be argued that the maximum is due solely to transparency for slow electrons, if we draw, as is customary, a distinction between a resonance and a critical potential of a gas. At the *resonance potential* the impinging electron excites the atom or molecule which gives out radiation on subsequent return to normal. At a *critical potential* the impinging electron brings the atom or molecule into a metastable state from which the system may reach its normal state without necessarily giving out its energy as radiation, but returning perhaps by some sort of impact of the second kind. If we make this hypothesis, the maximum under discussion may in part be due to such a critical potential for in that case the absorption results and the Lenard curves would be as found.

Summarizing the results of these experiments and the earlier ones in three-electrode tubes it may be said that a maximum in the current may be due to the following causes: (1) a true resonance potential of the gas; (2) a possible critical potential; (3) variable mean free path of the electron; (4) dissociation of the molecule; (5) thermal decomposition by the hot filament. In particular it is to be pointed out that critical potentials obtained by the resonance method are not easily interpreted for a substance for which no spectroscopic data exist.

It is a pleasure to thank Professor Richard C. Tolman for suggestions received.

[1] G. Glockler, *Proc. Nat. Acad. Sci.*, **10**, 155 (1924).
[2] *Physic. Rev.*, **23**, 664 (1924).
[3] *Ann. Physik*, **64**, 513 (1921).
[4] *Zt. Physik.*, **1**, 320 (1920).
[5] Critical Potentials, *Bull. Nat. Res. Council No.* **48**, vol. 9, pt. 1, page 9.
[6] *Ibid.*, pages 8 and 19.
[7] *Zt. Physik.*, **2**, 18 (1920).
[8] *Ibid.*, **8**, 32 (1921).