$$\rho = \left((2\rho_0/\sqrt{\pi})\int_0^y e^{-\beta^2}d\beta = \left(2\rho_0/\sqrt{\pi}\right)\left(y - \frac{1}{3}y^3 + \frac{1}{5.2}y^5 - \ldots\right)\right.$$

Since for the vertical tube $dp = \rho g dx$, an integration gives $p = (2x\rho_0 g/\sqrt{\pi})(y/2 - y^3/12 + y^5/60 - \ldots)$. Putting $x\rho_0 g = p_0$ and recalling that $p/p_0 = s/s_0$ and that the tube length of $x = l$, the equation solved for a reads

$$a = \frac{1}{\sqrt{\pi}}\frac{s_0}{s}\frac{l}{2\sqrt{t}}\left(1 - l/24a^2t + l^4/480a^4t^2 - \ldots\right)$$

seeing that an approximate a sufficies in the corrections. Hence s_0 would be the initial ($t = 0$ sec.) and s the final ($t = 300$ sec.) fringe displacement as given by figure 2; but as in this experiment diffusion takes place at *both* ends of the tube (two tubes each of length $l/2$) the equation becomes finally

$$a = \frac{1}{\sqrt{\pi}}\frac{s_0}{s}\frac{l}{4\sqrt{t}}\left(1 - l^2/96a^2t + l^4/7680\,a^4t^2 - \ldots\right).$$

Data for Diffusion.—Inserting the data of figure 2

$$t = 0,\ s_0 = 168;\quad t = 300 \text{ sec.},\quad s = 83;\quad l = 68.4 \text{ cm.}$$

the first term is .6508, so that a'^2 would be .4236. The first correction $-l^2/96a^2t = -.1278$; the second correction $l^4/8680a^4t^2 = .0196$ whence $a = .580$ and $a^2 = .337$. This datum is again a hit of the right order of value, but in need of the modifications already instanced. In particular diffusion from both ends not strictly identical is objectionable.

THE BEHAVIOR OF LOW VELOCITY ELECTRONS IN METHANE GAS

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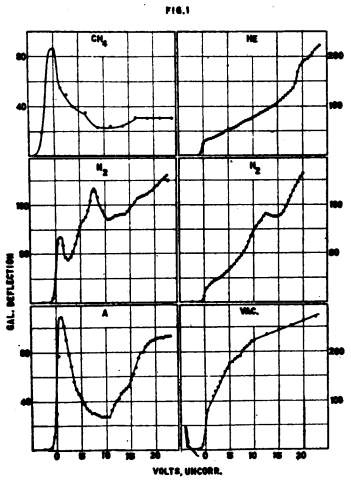
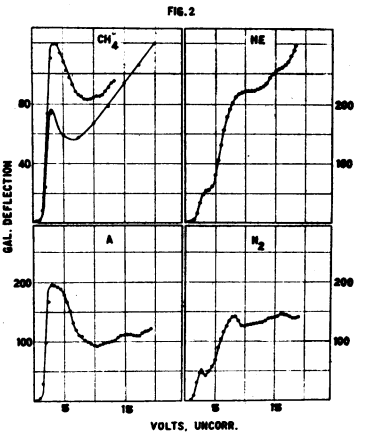
The radiation and ionization potentials of most of the monatomic vapors have been determined[2] experimentally. The natural extension of such research would be the determination of these constants for molecules. The simple molecule hydrogen has been investigated extensively[3] and the results can be reasonably well interpreted in terms of modern atomistics. When atoms and molecules for which no spectroscopic data exists are investigated by the current-potential method, it must be born in mind that not only a radiation-potential but also the phenomenon of trans-

parency as known in argon[4] gives a maximum in the current-potential curves as shown by Minkowski and Sponer in a three-electrode tube. Hence in interpreting results obtained by the current-potential method the occurrence of a maximum cannot be taken as conclusive evidence of a radiation potential.[5]

The specific object of this research is to show that there is a current maximum in methane gas which is not considered to be due to a resonance





potential of the gas, nor its dissociation, nor its thermal decomposition by the filament, but is presumably due to transparency of the methane molecule for electrons of low speed.

Experiments in a Three-Electrode Tube.—Argon, helium, hydrogen, methane and nitrogen were investigated in a three-electrode tube shown in figure 3, and some of the current-potential curves obtained are reproduced in figures 1 and 2. The experiments shown in figure 1 were carried out with a Tungsten filament and those shown in figure 2 were performed with a Platinum-(CaO) filament.

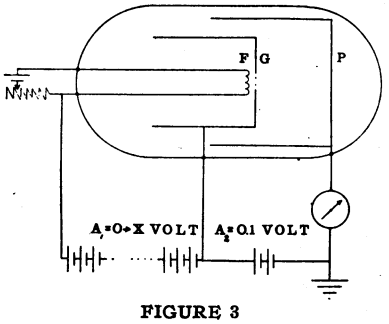


FIGURE 3

Argon[6] prepared by the General Electric Company and helium from the Government were not further purified. Electrolytic hydrogen was freed from oxygen by Pd-asbestos and dried over phosphorus pentoxide. Methane from natural gas was fractionally distilled over liquid air. Nitrogen was made from ammonium nitrite and purified by liquid air and phosphorus pentoxide.

The tube shown in figure 3 has three electrodes: a Tungsten or Platinum-(CaO) filament F; a copper cylinder G, having a 3 mm. hole covered with copper gauze of 31 mesh per inch, at a distance of 1 mm. from the filament and surrounding it; a copper receiving cylinder P with its bottom 2.5 cm. from the gauze and surrounding the other electrodes.

The accelerating field between the gauze G and the cylinder P was kept constant at 0.1 volt and the accelerating field between the filament and gauze G was varied in steps of 0.25 volt.

Discussion of the Experimental Results.—Various pressures and heating currents were employed and a portion only of the data is given in figures 1 and 2; the maxima in the current-potential curves in the case of argon and methane are always very definite. However, no such maxima occurred when hydrogen or helium were in the tube.

By analogy with the interpretation given by Minkowski and Sponer[4] to their results in argon, it is to be inferred that methane also shows the phenomenon of abnormal transparency to low speed electrons.

That the phenomenon in methane is not due to the dissociation of the molecule is probable for the following reason. Dissociation of the methane molecule cannot be caused by electrons, though they have sufficient energy, as is seen from the analogous case of the hydrogen molecule. Three volt electrons do not dissociate the hydrogen molecule though they have sufficient energy. Moreover this is what one would expect from an application of the laws of conservation of energy and momentum to the impact of a three volt electron and hydrogen molecule. By applying the same arguments to the case under consideration it is seen that the maximum observed cannot correspond to the dissociation of the methane molecule.

It was thought possible that the thermal dissociation of the gas by the hot filament might cause the maximum in the current-potential curve. It will be demonstrated below that this was not the case.

The maximum might, however, be due to a radiation-potential. It is seen that it occurs between zero and one volt and would correspond to a band in the red, or to a change in the state of oscillation of the methane molecule. This would mean that an impinging electron can cause this change. It is true that band-spectra of the oscillation-rotation type have thus far been observed in absorption and in emission only by Paschen[7] at high temperatures. However, it is possible that such bands might be excited by electron impact and it cannot be concluded that the phenomenon is not due to a radiation-potential. This must be kept in mind in the present case of methane for which no spectroscopic data exists.

Minkowski and Sponer[4] point out that argon and helium show an increase in current at their radiation potentials of 11.55 and 19.75 volts, respectively. The same effect was also observed in these experiments as is seen from figures 1 and 2 and is presumably due to the abnormal trans-

parency of argon and helium to the low velocity electrons which are produced by collision at the radiation potential. Nitrogen and hydrogen, however, show a decrease at their radiation potentials of 8.2 and 13.5 volts. This would apparently be in conflict with the idea that they show transparency. If these gases have no low radiation potentials, then it would almost seem necessary that the maximum near zero volts in nitrogen and the change in increase of current in hydrogen must be ascribed to a slight transparency of these molecules.

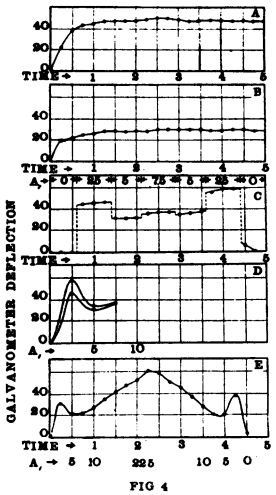


FIG 4

Thermal Decomposition of Methane by the Hot Filament.—It might be supposed that the thermal decomposition of the gas is responsible for the maximum obtained in methane for as hydrogen is created near the filament and carbon is deposited on it in accordance with the reaction $CH_4 \rightarrow C + 2H_2$ the emission of the filament might be affected. Moreover, using the high temperature Tungsten filaments definite evidence of such decomposition was afforded by rise in pressure. With oxide-covered filaments, however, there is no evidence of such decomposition.

This conclusion was further tested with the three-electrode tube in the following manner. The deflections of the galvanometer were noted during five minute intervals with constant accelerating field A_1 and the curves in figure 4 were obtained. It will be noted that with the oxide-covered filament used there is no appreciable change in pressure.

TABLE I

CURVE	A_1 (VOLTS)	HEATING AMPS.	HEATING VOLT	PRESSURE, MM. HG. START	PRESSURE, MM. HG. FINISH	REMARKS
A	2.5	1.7	0.87	0.45	0.46	A_1 constant at 2.5 volts
B	5.0	1.7	0.88	0.45	0.46	A_1 constant at 5.0 volts
C	2.5	1.7	0.88	0.45	0.45	A_1 changed to various values as shown
	5.0					
	7.5					
D	2.5	1.7	0.88	0.45	0.45	Data of curve C plotted against A_1
	5.0					
	7.5					
E	variable	1.7	0.87	0.46	0.47	A_1 changed every 15 seconds by 2.5 volts

Curve A gives the deflections during five minutes with a constant accelerating field of 2.5 volts from the time the heating current was turned on. Curve B similarly gives the deflections with a larger accelerating field of 5.0 volts. It is seen that the current in both runs is quite constant after

the first minute had elapsed, which period was necessary for the filament to get to temperature. Curve *C* gives again the current plotted against time, but with different accelerating voltages as shown in the figure. The applied accelerating voltage is, therefore, shown to have a decided effect on the magnitude of the current. It should be noted that the accelerating voltage was both increased and decreased. Curve *D* shows the galvanometer deflections of Curve *C* plotted against the accelerating voltage. The maximum is clearly brought out. Curve *E* shows a complete run of five minutes duration with the accelerating field increased during the first two and one-half minutes, and decreased the rest of the period. These curves fully demonstrate that the maximum is a function of the accelerating voltage applied to the tube.

Interpretation of Results in a four Electrode Tube.—Special attention should be called to the bearing of the above experiments on the interpretation of the results obtained with four-electrode tubes, when these are used for the determination of radiation-potentials. As a matter of fact, working with a four-electrode tube, an attempt was made to determine the radiation-potentials of methane. It was found, however, that the same maximum obtained with methane in the three-electrode tube was also present in the four-electrode tube, and might easily have been erroneously ascribed to a radiation-potential. It is evident that great circumspection must be used in the interpretation of work with four-electrode tubes.

Summary.—Methane shows a maximum in the current-potential curve obtained in a three-electrode tube. This maximum is shown not to be due to its dissociation, nor its thermal decomposition by the hot filament, but may be due to a low radiation-potential of the gas or its transparency for slow electrons.

By analogy with similar curves in argon, it is thought that the maximum is due to an abnormal transparency of methane for low velocity electrons.

Gases that exhibit the phenomenon of *great* transparency for low velocity electrons show an increase in current at their radiation-potentials, while in others the current decreases at their resonance points.

Conclusions.—A maximum in a current-potential curve as usually obtained when studying resonance potentials may be due to (1) a true resonance point of the gas; (2) abnormal transparency for low velocity electrons. The last point mentioned must be taken into account in interpreting resonance curves.

It is a pleasure to thank Prof. Richard C. Tolman and Dr. James H. Ellis for suggestions received.

[1] NATIONAL RESEARCH FELLOW in Chemistry.

[2] Hughes, Research Bulletin, National Research Council, No. 10.

[3] For instance, see Olmstead and Kompton, *Physic. Rev.*, **22**, 559 (1923).

[4] Minkowski and Sponer, *Zt. Physik*, **15**, 403 (1923).

[5] Foote and Mohler, "*The Origin of Spectra*," page 189.

[6] I wish to thank Prof. Millikan for the supply of Argon, the Mt. Wilson Observatory for the helium, and the Midway Gas Company of Taft, Calif., for the natural gas, which contained 95% methane.

[7] Paschen, *Ann. Physik*, **53**, 336 (1894).