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THE IONIZATION POTENTIAL OF METHANE

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The ionization potentials of several hydrocarbons have been determined by Hughes and Dixon[2] and by Boucher.[3,4] These investigators found that these ionization potentials are all in the neighborhood of 10 volts. At present it is believed that the ionization potential of a molecule corresponds to the removal of an electron from the molecule and therefore to the production of a mole-ion, rather than to dissociation of the molecule and ionization of one of the parts.

In this research we have determined the ionization potential of methane by the usual methods of electron impact and have found it to be between 14.4 and 15.2 volts. We have further predicted this quantity from Eve's rule.[5] Our prediction is based on the belief that methane has a rare-gas structure and that the reaction leading to ionization consists in the removal of an electron, in accordance with the equation $CH_4 = CH_4^+ + E^-$.

The Physical Properties of Methane.—The belief that methane has the rare-gas arrangement of electrons is readily justified. When a comparison is made of the physical properties of methane and the rare gases, which are not dependent on molecular weight, it is seen from Table I that methane fits in between argon and krypton. We shall also see from this investigation that the ionization potential of methane lies between the ionization potentials of argon and krypton.

TABLE I

COMPARISON OF PHYSICAL PROPERTIES OF THE RARE GASES AND METHANE

Property	Ne	A	CH_4	Kr
Critical temperature, °K.	44.40	150.66	190.1	210
Critical pressure, atm.	26.86	47.99	54.9	54.3
van der Waals' constant, $a \times 10^5$	42.2	268	449	462
van der Waals' constant, b, cm.^{3}	17.0	32.2	35.6	39.6
Radius from critical data, Å.	1.19	1.47	1.56	1.58
Molecular refractivity P_0 in cm.^{3}	1.0	4.18	6.36	10.2
Ionization potential, volts	21.5	15.4	14.4–15.2	13.3

Another interesting property which shows the similarity of methane and argon most strikingly is the mean free path of electrons in these gases. The curves connecting the mean free path of electrons in the rare gases

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[2] Hughes and Dixon, *Phys. Rev.*, **10,** 495 (1917).

[3] Boucher, *ibid.*, **19,** 189 (1922).

[4] For a summary see *Nat. Res. Council Bull.*, No. **48,** 123 (1924).

[5] Eve, *Nature,* June 30, **1921.**

and their energies are known from the work of Ramsauer.[6] The curves for methane and argon are identical in shape, while the curve for neon differs from that obtained for methane.[7,8] The theory of this phenomenon has been given by Zwicky.[9]

The Predicted Ionization Potential.—Eve's rule states: "The product of the ionization potential of an atom and its radius is a constant." This rule is not an exact one, but it serves well when applied to the rare gases, and we have used it to predict the ionization potential of niton,[10] and now we wish to apply it to methane. It may be questioned whether or not this rule can be applied to molecules. It is certainly believed at present that methane has the rare-gas arrangement of its outer electrons. This belief is the very foundation of our modern theory of chemical combination as advanced by G. N. Lewis.[11] We may, therefore, plot the ionization potential of the rare gases as determined by Hertz[12] against their kinetic-theory diameters obtained from critical data on viscosity, and obtain the curve shown in Fig. 1. The predicted ionization potential of methane is 13.7 volts.

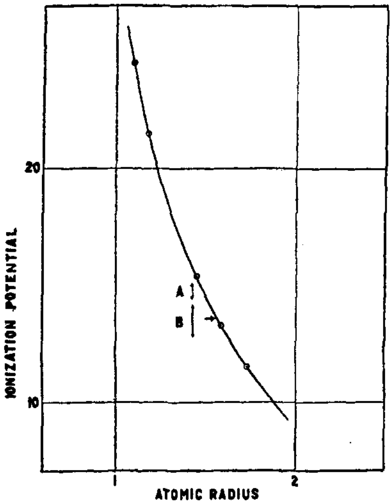

Fig. 1.—Ionization potentials in volts, plotted against atomic radii in Ångström units. *A*, experimental value, and *B*, predicted value of the ionization potentials.

Table II

Comparison of Radii and Ionization Potentials

Gas	Radii, Å. From viscosity	Radii, Å. From critical data	Ionization potential Volts	Eve's constant
He	0.94	1.13	24.5	25.4
Ne	1.18	1.19	21.5	25.5
A	1.42	1.42	15.4	21.8
Kr	1.56	1.59	13.3	20.8
Xe	1.74	1.71	11.5	19.9
CH_4	1.56	1.57	(13.7)	21.4

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[6] Ramsauer, *Ann. Physik*, **64**, 513 (1921).

[7] Glockler, *Proc. Nat. Acad.*, **10**, 155 (1924).

[8] Brode, *Phys. Rev.*, **25**, 636 (1925).

[9] Zwicky, *Phys. Z.*, **24**, 171 (1923).

[10] *Phil. Mag.*, **50**, 997 (1925).

[11] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., **1923**.

[12] Hertz, *Z. Physik*, **31**, 463 (1925).

The Experimental Value of the Ionization Potential.—The Lenard method was used to determine the ionization potential. Full description of the method is found in several places.[4] The experimental tube used is described by Hertz[13] and is shown in Fig. 2. We shall mention only the points to which particular attention has been paid in order to work with methane.

Methane was prepared from the gas issuing from the gas wells of the Midway Gas Company at Taft, California. The gas is said to be 98% methane. It was purified by fractional distillation at liquid-air temperatures. We wish to thank the Midway Gas Company for the supply of methane.

It is important to avoid thermal decomposition of the gas by the hot filament. It is known[7] that a calcium-oxide covered platinum filament does not cause decomposition if used at a low temperature. Furthermore, in our experiments the pressure was always measured at the beginning and end of a run, and it was found that no change of pressure resulted during an experiment. If the hot filament had decomposed the gas according to the equation $CH_4 = 2H_2 + C$, an increase in pressure would have occurred. Since the pressure did not increase, we believe that this reaction did not take place.

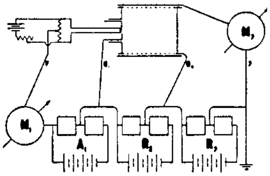

Fig. 2.—Wiring diagram.

Helium was used as a calibrating gas, and the experiments were performed in a mixture of helium and methane. In Table III are given the data of eight experiments.

Table III

Experimental Data on the Ionization Potential of Methane

Pressure in mm. of Hg						
CH_4	He	Total	Total press. / CH_4 press.	Liq. air	Point where current first rises (Fig. 3) Volts	Large rise in current (Fig. 3) Volts
0.031	0.249	0.280	9.1	No	14.45	15.35
.036	.203	.239	6.6	No	14.70	15.10
.021	.189	.210	10.0	No	14.80	15.25
.040	.252	.292	7.3	No	14.30	15.05
.039	.227	.266	6.7	No	14.13	14.88
.044	.283	.327	7.4	No	14.20	14.92
.031	.233	.264	8.6	Yes	14.25	15.35
.030	.157	.187	6.2	Yes	14.12	15.31
				Av.	14.4	15.2

A retarding field of 2.0 volts was applied in the second condenser ($G_1 - G_2$ in Fig. 2) to help the positive ions diffuse to the plate and a large retarding field of 30 volts in the third condenser ($G_2 - P$ in Fig. 2) prevented the electrons from the filament from reaching the plate. The filament carried 4.5 amperes at a drop of 1.4 volts.

[13] Hertz, *Proc. Roy. Soc. Amsterdam*, **25**, 179 (1922).

Discussion of Results.—It may be questioned whether we have actually determined the ionization potential of methane or a radiation potential since the rise in positive current to the plate might be due to photoelectrons, and then we would be measuring a radiation potential. However, the rise in positive current is large compared to the photo-currents usually obtained in such experiments, although the curve in helium alone does show a large current rise at the radiation potential near 20 volts. It is, of course, well known that the methods of critical potentials must be combined with the methods of mass-spectroscopy, in order to make sure at what voltage positive ions actually occur. But combining our results with the prediction from Eve's rule, it seems reasonably certain that we have actually measured the ionization potential. Furthermore, we do not find a second rise in current in pure methane after 14.4 volts, as we have found in pure helium at 24.5 volts and, this fact also is in favor of the view that ionization in methane sets in near 15 volts. The positive current actually starts to rise at 14.4 volts and, as usual, we have a small rise in current in a region of 0.8 volt (between 14.4 and 15.2 volts). This may be due to the velocity distribution of the impinging electrons and to efficiency of impact. However, in our calibration we have taken the point where the current *first* rises due to helium impacts, and it might seem more reasonable to have taken the *first* appearance of positive current (14.4 volts) as the ionization potential. We may certainly say from our experiments that methane has a *critical* potential between 14.4 and 15.2 volts, and that this is presumably the *ionization* potential.

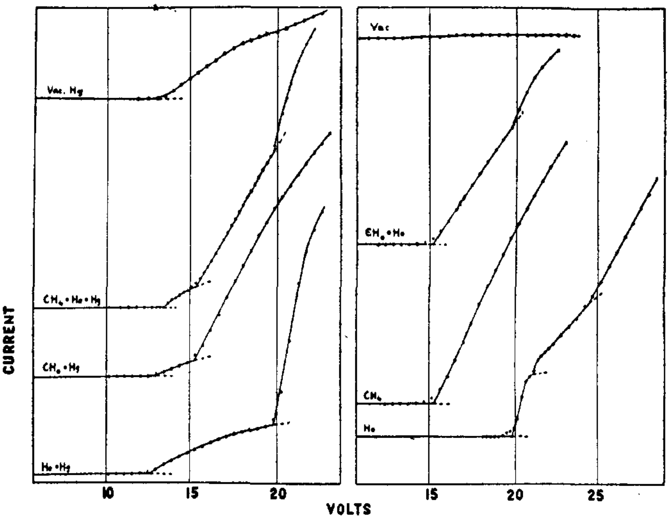

Fig. 3.—Current-potential curves in methane, helium and methane-helium mixture, with liquid-air trap off and on.

If we compare this result with the measurements of others[2] we find that our value is much higher. From Fig. 3 it is seen that when mercury vapor is present (no liquid air) the current rises at about 12 volts. This rise in positive current must be due to ionization of mercury vapor, because we can also obtain it in an ordinary vacuum, and it does not occur when the mercury vapor is removed by means of liquid air. However, the ionization potential of mercury is known to be 10.4 volts, so that positive mercury ions should appear at that voltage. They may appear in our apparatus at 12.0 volts because at the small vapor pressure of mercury at room temperature (0.001 mm.) only a few mercury ions are produced at 10.4, and only at 12.0 volts are enough ions produced to be measured by our galvanometer. The appearance of positive current depends then on the gas pressure used, the efficiency of ionization, and the sensitivity of the galvanometer used. In the case of methane and helium we believe we had a high enough pressure to detect the rise in positive current very near to the critical potentials, because the pressures of helium and methane in the mixtures used are of the same order of magnitude, and we know from the work of Hughes and Klein[14] and Dymond[15] on the efficiency of ionization of methane and excitation of helium that the former is much larger than the latter. If, therefore, we can detect the resonance potential of helium, we feel sure that the same apparatus will show the critical potential of methane at approximately the correct voltage.

We therefore believe that the lower results in the earlier experiments on methane have possibly been due to mercury vapor.

Referring now to Fig. 1 we see that the predicted value of the ionization potential and the experimental value check satisfactorily. Therefore, we believe that it is not unreasonable to take this agreement as additional experimental proof of the rare-gas structure of methane. On our modern view of atomic structure[11] we should believe that methane is like neon. Grimm[16] has brought out this relation very strikingly. He considers methane as a pseudo-atom of neon, since the carbon and hydrogen nuclei together have the total atomic number of ten, as has neon. In neon, however, the total charge is situated at one point while in methane the positive carbon center (the carbon atom with its two K-electrons) and the four protons take up a larger volume. We must, therefore, expect that the methane molecule is larger than the neon atom and that its ionization potential is less than the ionization potential of neon. We see that methane is more like argon in size and that their ionization potentials are very nearly equal. We should, therefore, be inclined to draw the electron orbits in methane so as to include the hydrogen nuclei rather than to imagine that

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[14] Hughes and Klein, *Phys. Rev.*, **23**, 460 (1924).

[15] Dymond, *Proc. Roy. Soc.*, **107A**, 291 (1925).

[16] Grimm, *Z. Elektrochem.*, **31**, 474 (1925).

pairs of electrons are situated between the carbon center and the hydrogen nuclei. This makes the methane molecule more rare-gas-like when looked at from a distance.

In conclusion we wish to thank Professor R. C. Tolman for the interest he has shown in this research.

Summary

We have measured a critical potential in methane at 14.4–15.2 volts, which we believe to be the ionization potential. Using Eve's rule we have predicted the ionization potential to be 13.7 volts. Special attention has been paid to the possible thermal decomposition of the gas by the hot filament, and it has been avoided. We have also taken care of the effect of mercury vapor in interpreting our current-potential curves.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, NO. 174]

ELECTROMOTIVE-FORCE MEASUREMENTS IN AQUEOUS SOLUTIONS OF HYDROCHLORIC ACID CONTAINING SUCROSE[1]

BY GEORGE SCATCHARD

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Solutions of sucrose in water have long occupied a prominent position in the study of the properties of solutions, and particularly in the study of reaction rates. With the correlation of reaction rates with activities, electromotive-force measurements in solutions containing sucrose have become important. All the measurements so far reported, however, have been made in cells containing liquid junctions, and with those junctions made by dipping a small tube containing the lighter liquid into a larger one containing the heavier. Most of them have been made with a hydrogen electrode.

This paper describes an attempt to study the problem in more detail by dividing it into two parts: a study of the effect of sucrose on the liquid-junction potential between hydrochloric acid and saturated potassium chloride, and a study of the effect of sucrose on the potential of the hydrogen electrode. The measurements do not agree with those in the literature, and they disclose three sources of errors which probably account for the discrepancies. They give a more precise knowledge of the ion activities in sucrose solutions, and they comprise the first experimental study, so far as I am aware, of the effect of a non-electrolyte solute on liquid-junction potentials.

[1] Reported to the Physical-Inorganic Division of the American Chemical Society at Los Angeles, August 7, 1925. The experimental work was carried out in 1924 during the tenure of a National Research Fellowship.