

[CONTRIBUTION FROM THE HUMBLE OIL AND REFINING COMPANY, RESEARCH AND DEVELOPMENT DIVISION, BAYTOWN, TEXAS]

Reactions of Gaseous Ions. X. Ionic Reactions in Xenon-Methane Mixtures

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A study has been made of the ionic and excited atom reactions occurring between xenon and methane in the ionization chamber of a mass spectrometer. The reactions found are

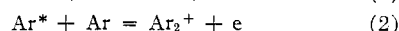
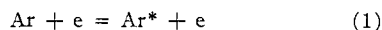


The ions XeC^+ and XeCH^+ are also formed but by unknown reactions. In Reaction 1 Xe^* represents an Xe atom excited to an energy about 0.5 volt beneath the Xe ionization energy. This reaction is similar to that observed both in this work and other work for the formation of dimers of the rare gas ions, *viz.*

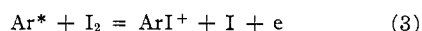


Ionization efficiency curves were determined for the several ions, and those for Xe_2^+ and XeCH_4^+ exhibit a sharp maximum about 2 volts above onset. This is compatible with the formation of these ions from an excited neutral reactant; that is, the ionization efficiency curve is an excitation function. Rate constants were determined for the formation of XeH^+ , XeCH_3^+ and XeCH_2^+ , and the values are 3.8×10^{-11} , 2.2×10^{-12} and 4.5×10^{-13} cc./mole sec., respectively. Relative rate constants for the formation of Xe_2^+ and XeCH_4^+ were also obtained. Xe^* reacts with Xe nine times more rapidly than it does with CH_4 . No net charge exchange between xenon and methane was observed, but no reason can be advanced for this somewhat unexpected behavior. A preliminary report of observations of reactions between xenon and O_2 , C_2H_2 , and H_2O is given.

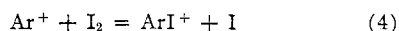
As a result of studies of ion-molecule reactions in the mass spectrometer, a chemistry of rare gas ions and excited atoms is emerging. The formation of the diatomic molecule-ions has been known for a considerable length of time.¹⁻³ Hornbeck and Molnar in particular have observed the dimeric ions of all the rare gases except radon, and they have shown that the dimer is formed by the reaction of an excited neutral atom with an atom in the ground state, *e.g.*



Morris⁴ has observed mass spectrometrically the formation of the rare gas dimeric ions in an electric discharge. Norton⁵ has reported the formation of the rare gas hydride ions, and Stevenson and Schissler⁶ have also observed these ions and have measured the rates of the reactions by which they are formed. Melton and Rudolph⁷ have observed the formation of $\text{Xe}(\text{CN})_2^+$, and Henglein and Muccini⁸ have observed reactions between the argon and iodine and krypton and iodine to form the ions ArI^+ and KrI^+ . They postulate the occurrence of reactions such as



and



For the reactions of the positive ions with I_2 cross-sections of about 50\AA^2 are observed. Fuchs and Kaul⁹ have produced in a mass spectrometer the heteronuclear rare gas molecule ions NeAr^+ and

(1) O. Tüxen, *Z. Physik*, **103**, 463 (1936).

(2) F. L. Arnot and M. B. M'Ewen, *Proc. Roy. Soc. (London)*, **A171**, 106 (1939).

(3) J. A. Hornbeck and J. P. Molnar, *Phys. Rev.*, **84**, 621 (1951).

(4) D. M. Morris, *Proc. Phys. Soc. (London)*, **A68**, 11 (1955).

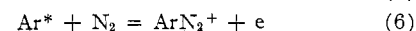
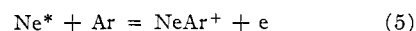
(5) F. J. Norton, *Nature*, **169**, 542 (1952); *Natl. Bur. Standards Circ.*, No. 522, 201 (1953).

(6) D. P. Stevenson and D. O. Schissler, *J. Chem. Phys.*, **23**, 1353 (1955); *ibid.*, **29**, 282 (1958); and D. O. Schissler and D. P. Stevenson, *ibid.*, **24**, 926 (1956).

(7) C. E. Melton and P. S. Rudolph, *ibid.*, **33**, 1594 (1960).

(8) A. Henglein and G. A. Muccini, *Angew. Chem.*, **72**, 630 (1960).

ArKr^+ and the nitrogen-argon ions ArN_2^+ and ArN^+ .¹⁰ The reactions deduced from appearance potential measurements are



and



Of particular interest is the fact that the energy of the excited state of neon which serves as reactant in reaction 5 is about 16.5 volts, which is not only about 5 volts lower than the ionization potential of neon (21.56 volts) but also about a volt higher than the ionization potential of argon (15.76 volts). The excited state of N_2^+ involved in reaction 7 lies about 6.6 volts above the ground state of the ion.

We have scanned the mass spectra of relatively high pressure mixtures of xenon and several gases, and we have been rewarded by observing compound ions of xenon with oxygen, water, methane, acetylene and fragments from these substances. The paper is a report of the detailed study of the compounds formed between xenon and methane.

Experimental

The measurements were made with the Humble chemical physics mass spectrometer (12" radius of curvature, 60° deflection) previously described.¹¹ Separate sets of measurements were made with each of two ion sources of quite different dimensions and somewhat different configurations. Source 1 comprises an ionization chamber 7.0 mm. in length, planar ion repeller electrodes separated by a 3 mm. gap and a set of four electron gun electrodes placed between the filament and the entrance to the ionization chamber. The slits in these electrodes have the dimensions 3.0×0.5 mm., and the electrodes serve various functions when the equipment is used to make appearance potential measurements using the retarding potential difference technique. Source 2 comprises an ionization chamber 20.0 mm. in length, U-shaped ion repeller electrodes separated by a 0.5 mm. gap, and only an electron drawout electrode is placed between the filament and the entrance to the ionization chamber. The ionization chamber pressure attainable in

(9) R. Fuchs and W. Kaul, *Z. Naturforschung*, **15a**, 108 (1960).

(10) W. Kaul and R. Fuchs, *ibid.*, **15a**, 326 (1960).

(11) F. H. Field, *J. Am. Chem. Soc.*, **83**, 1523 (1961).

Source 1 without encountering appreciable difficulties is greater than that attainable in Source 2. On the other hand, the behavior of Source 2 at low pressures is more conventional than that of Source 1 in that in Source 1 a high ion repeller voltage (repeller field strength of 50–100 volts/cm.) is needed to extract the ions from the ionization chamber.

We mention in passing that we have evidence that this difficulty is the result of a deep potential depression in the electron beam. This depression is thought to result in turn from the narrow slits defining the electron beam, for because of them a relatively high current density is associated with the passage of an ionizing current of a given magnitude. Trouble was particularly observed with currents greater than 3–5 microamp.

Studies with methane-xenon mixtures were made with both sources. Using Source 1 studies were made holding the pressure of xenon constant and varying the methane pressure, and *vice versa*. In general the pressure of the constant pressure component was held at 40×10^{-3} mm. and that of the variable pressure component was 0 to 50×10^{-3} mm. The ionizing electron current was maintained at 1.0 microamp., and the pressure studies were made at a nominal ionizing voltage of 70 volts. Using Source 2 the methane source pressure was maintained at 12.5×10^{-3} mm. and the xenon source pressure varied in the range of 0 to 14×10^{-3} mm. The ionizing electron current was maintained at 3.0 microamp., and pressure studies were made at nominal ionizing voltages of 10 and 70 volts. In both sources the field strength in the ionization chamber was 12.5 volts/cm. (ion repeller voltage = 5.0 volts), and the distance from the mid-line of the electron beam to the ion-exit electrode was 2.0 mm.

Gas pressures in the ionization chamber were determined by means of a McLeod gage attached to the gas inlet line at a point about 15 inches upstream from the ionization chamber. For the two component studies involved in this work, the variable pressure component was introduced into one of the gas handling reservoirs of the instrument in such quantity as to give the desired pressure in the ionization chamber. The constant pressure component then was introduced into the other gas handling reservoir, and the amount charged was equal to that known from an independent experiment to give the desired pressure in the ionization chamber. In short, it is assumed that pressure interactions between the two components of the mixture do not occur to a significant extent, and evidence has been obtained showing that this assumption is largely valid.

The pressures in the ionization chamber when Source 2 was used were obtained by the usual technique of determining the total ionization collected by the ion repeller when negatively biased.^{11,12} However, one calculates that if one passes a beam of electrons through an ionization chamber of length 20 mm. and filled with gas of ionization cross-section 6×10^{-18} cm.² (rough mean of cross-sections for CH₄ and Xe)¹³ at a pressure of 25×10^{-3} mm. about 45% of the incident electrons undergo collisions resulting in ionization. We have found that more reasonable total ionization results can be obtained with Source 2 if the measurements are made with a constant ionizing current incident on the ionization chamber rather than with the conventional technique of maintaining a constant current to the electron collector. That this is the case is doubtless the consequence of the large fraction of the incident electrons causing ionization. We approximated a constant incident ionizing current by maintaining a constant total electron emission from the filament. Ionization chamber concentrations were calculated from equation 8

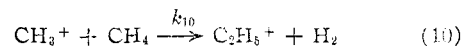
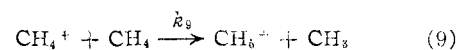
$$N = \ln \left(\frac{I_e^0}{I_e^0 - I_i} \right) / kQ \quad (8)$$

where N = number molecules/cm.³, Q = ionization cross-section from ref. 13, $l = 1.80$ cm., the length of the ion repeller, I_e^0 = incident electron current (0.50 microamp.) and I_i = collected ion current. At the ionization chamber temperature of 200°, pressure is related to concentration by the equation P_s (microns) = $5.0 \times 10^{-14} N$.

The relation for Source 2 between the source pressure (P_s) and the McLeod manometer pressure (P_m) has been

determined for methane and xenon. In the pressure range with which we are concerned in these measurements (up to about 30×10^{-3} mm.) the $P_s - P_m$ relationship is identical for the two gases. Since the gas flow is for the most part molecular in the pressure region considered, the lack of dependence of the source pressure on the identity of the gas is not unexpected, but it is none the less nice to have it confirmed experimentally.

It is possible to make an independent check on the $P_s - P_m$ relation for methane from the extent of occurrence of known ion-molecule reactions at various McLeod gage pressures. To make this experiment we measured the intensities at masses 15, 16, 17 and 29 at values of P_m for methane up to 300×10^{-3} mm. The reactions producing the mass 17 and 29 ions are¹²



and for the general reaction $\text{A}^+ + \text{B} \xrightarrow{k_A} \text{C}^+ + \text{D}$ the relation between measured ion currents and the ion source concentration of B is

$$N = \ln \left(1 - \frac{I_{C^+}}{I_{A^+}} \right) / k_A \tau_{A^+} \quad (11)$$

Where I_{A^+} is calculated by summing the observed ion currents of A^+ and C^+ , k_A is the rate constant for the reaction, and τ_{A^+} is the residence time of ion A^+ in the ionization chamber. The relationship P_s (Microns) = $5.0 \times 10^{-14} N$ still obtains. Equation 10 can be derived easily from equation 11 of ref. 11. Values of k_9 and k_{10} were taken from reference 12; namely, at ionization chamber field strength = 12.5 volts/cm. $k_9 = k_{10} = 8.5 \times 10^{-10}$ cc./mole sec. The ion source methane pressure values deduced from the intensities at masses 15 and 29 and from masses 16 and 17 are for practical purposes identical, and when a plot of P_s vs. P_m was made both sets of points defined one line. As a matter of interest we compare in Table I the methane source pressures obtained from the ion-molecule reactions in methane with those obtained from the total ionization in methane. The excellent agreement shown in Table I is encouraging from a number of different points of view, and in our opinion the most significant is that concerned with the absolute accuracy of rate data in ion-molecule reactions and the transferability of such data from one mass spectrometer to another. The rate constants for the methane reactions reported in Reference 12 were obtained with a Consolidated Electrodynamics Corporation Model 21-620 cycloidal path mass spectrometer. The difference in ion source configuration, dimensions and operating conditions between the CEC instrument and that used for the present work is about as great as will be encountered in mass spectrometry, and consequently we believe as a result of the agreement in Table I that the error remaining in the values of these rate con-

TABLE I
METHANE SOURCE PRESSURE CALIBRATION
(PRESSURE IN MICRONS)

P_m	P_s Total ionization	P_s Ion-molec. react.	% Difference
20	1.1	1.6	40
40	2.4	3.2	28
60	3.8	4.7	22
80	5.4	6.3	16
100	7.2	7.9	9
120	8.9	9.5	6
140	10.8	11.2	4
160	12.8	13.1	2
180	14.5	15.3	5
200	17.0	17.3	2
220	19.5	19.6	1
240	22.5	22.0	2
260	25.0	24.7	1
280	28.5	27.9	2

Average = 10

(12) F. H. Field, J. L. Franklin and F. W. Lampe, *J. Am. Chem. Soc.*, **79**, 2419 (1957).

(13) F. W. Lampe, J. L. Franklin and F. H. Field, *ibid.*, **79**, 6129 (1957).

stants is that coming from any error which may exist in the absolute value for the ionization cross-section for argon, the quantity on which the ionization chamber pressures are ultimately based.

The intensities of the ions at masses 15, 16, 17 and 29 may be used to check on the methane ionization chamber partial pressures in xenon-methane mixtures. The mass 15 and 29 ions are the more useful because we believe that the CH_3^+ ion will be neither produced nor consumed in reactions with xenon. This question will be discussed more fully later. We find in the methane-xenon studies at 70 volts ionizing voltage that the ratio $I_{29}/(I_{15} + I_{29})$ exhibits a variation as the xenon pressure is varied which pessimistically might be interpreted as indicating a variation in the methane pressure. Adopting this latter point of view for the sake of argument, the pressure trend represented in one run is from $P_s(\text{CH}_4) = 11.4 \times 10^{-3}$ to 9.2×10^{-3} mm. The nominal methane source pressure based on the McLeod gage pressure is 11.8×10^{-3} mm. If one considers the ratio $I_{17}/(I_{16} + I_{17})$ one finds that the methane pressure trend is in the opposite direction to that exhibited by the ratio $I_{29}/(I_{15} + I_{29})$. In view of these contrary indications we calculate our kinetic quantities using the nominal methane source pressure of 11.8×10^{-3} mm. It is clear that the methane and xenon source pressures are to a satisfactory extent independent of each other, as we remarked earlier.

The $P_s - P_m$ relationship for Source 1 was taken to be the same as that obtained in a previous study of ethylene.¹¹

The identities of the reactions yielding the product ions observed were deduced as usual from appearance potential measurements. In xenon-methane mixture studies equal amounts of the two components were used. In measurements using Source 1 the total pressure was maintained at about 90×10^{-3} mm. but with Source 2 the total pressure was changed from one experiment to another, as will be discussed later. At the high pressures involved in these experiments it is impractical to use a separately added substance to calibrate the electron voltage scale, but fortunately the $^{124}\text{Xe}^+$ ion can be used for this purpose.

Results

A. Mass Spectra.—The intensities of selected ions from the mass spectra of a mixture of approximately equal amounts of methane and xenon determined with Source 2 are given in Table II. The total pressure in the source was 24×10^{-3} mm. and measurements were made at nominal ionizing voltages of 70 and 10 volts. As is indicated in Table II, the ions with masses from 141 to 152 can result from several combinations of carbon, hydrogen and the different xenon isotopes, and it is desirable to calculate spectra monoisotopic in xenon for the various ionic species. Such a monoisotopic spectrum is given in Table III. In making the calculation the small xenon isotopes at masses 124, 126 and 128 were neglected, which made it possible to do only the $^{129}\text{XeC}^+$ species.

Elementary mass considerations dictate the conclusion that the ions with mass greater than 136 are formed by secondary processes in the ionization chamber of the mass spectrometer, and as corroboration it is found that the intensities of these ions vary linearly with either the methane pressure or the xenon pressure, except for the Xe_2^+ ion, the intensity of which varies with the second power of the xenon pressure. The ratios of the intensities of the product ions to the intensity of xenon ion at constant methane pressure are listed in Table IV, which illustrates the degree of constancy (except, of course, for $\text{Xe}_2^+/\text{Xe}^+$) which is experimentally observed.

To our knowledge the existence of the ions XeCH_n^+ , $n = 0-4$, has not been reported previously.

TABLE II
PARTIAL MASS SPECTRUM OF XENON-METHANE MIXTURE
 $P_s(\text{CH}_4) = 12 \times 10^{-3}$ mm. = $P_s(\text{Xe})$; Source 2

Mass	Ion	Intensity (div.) ^a	
		e.v. = 70 v.	e.v. = 10 v.
15	CH_3^+	10,000	3400
16	CH_4^+	11,000	6800
17	CH_5^+	2,300	1100
29	C_2H_5^+	1,330	550
136 ^b	$^{136}\text{Xe}^+$	3,670	3150
137	$^{136}\text{XeH}^+$	138	77
141	$^{129}\text{XeC}^+$	5	0
142	$^{129}\text{XeCH}^+$, $^{130}\text{XeC}^+$	3	0
143	$^{129}\text{XeCH}_2^+$, $^{130}\text{XeCH}^+$, $^{131}\text{XeC}^+$	9	4
144	$^{129}\text{XeCH}_3^+$, $^{130}\text{XeCH}_2^+$, $^{131}\text{XeCH}^+$, $^{132}\text{XeC}^+$	27	14
145	$^{129}\text{XeCH}_4^+$, $^{130}\text{XeCH}_3^+$, $^{131}\text{XeCH}_2^+$, $^{132}\text{XeCH}^+$	11	17
146	$^{130}\text{XeCH}_4^+$, $^{131}\text{XeCH}_3^+$, $^{132}\text{XeCH}_2^+$, $^{134}\text{XeC}^+$	22	15
147	$^{131}\text{XeCH}_4^+$, $^{132}\text{XeCH}_3^+$, $^{134}\text{XeCH}^+$	25	26
148	$^{132}\text{XeCH}_4^+$, $^{134}\text{XeCH}_3^+$, $^{135}\text{XeC}^+$	8	17
149	$^{134}\text{XeCH}_3^+$, $^{136}\text{XeCH}^+$	9	6
150	$^{131}\text{XeCH}_4^+$, $^{136}\text{XeCH}_2^+$	3	6
151	$^{135}\text{XeCH}_3^+$	7	4
152	$^{135}\text{XeCH}_4^+$	1	4
263 ^c	$^{129}\text{Xe}^{131}\text{Xe}^+$, $^{131}\text{Xe}^{132}\text{Xe}^+$	12	49

^a 1 div. = 1×10^{-15} amp. ^b From the known xenon isotope distribution one can write $\sum_n I_n \text{Xe}^+ = 10.63 I^{136}\text{Xe}^+$. ^c Xenon molecule ions of significant intensity range in mass from 256 to 272. From the known xenon isotope distribution one can write $\sum_n \sum_m I_n \text{Xe}_m \text{Xe}^+ = 5.65 I^{263}\text{Xe}_2^+$.

TABLE III
PARTIAL MONOISOTOPIC MASS SPECTRUM OF XENON-METHANE MIXTURE

$P_s(\text{CH}_4) = 12 \times 10^{-3}$ mm. = $P_s(\text{Xe})$; Source 2

Ion	Intensity (div.)	
	E.v. = 70 v.	E.v. = 10 v.
Xe^+	39,000	33,500
XeH^+	1,460	820
XeC^+	19	0
XeCH^+	7	0
XeCH_2^+	18	13
XeCH_3^+	74	51
XeCH_4^+	9	46
Xe_2^+	67	274

TABLE IV
ION INTENSITY RATIOS AT SEVERAL XENON PARTIAL PRESSURES

$P_s(\text{CH}_4) = 11.8 \times 10^{-3}$ mm.; Source 2

$P_s(\text{Xe})$	E.v. = 70			
	$\text{XeCH}_2^+/\text{Xe}^+$ $\times 10^3$	$\text{XeCH}_3^+/\text{Xe}^+$ $\times 10^3$	$\text{XeCH}_4^+/\text{Xe}^+$ $\times 10^3$	$\text{Xe}_2^+/\text{Xe}^+$ $\times 10^3$
2.2	0.39	1.35		0.33
3.6	.44	1.68	0.16	.44
5.2	.32	1.65	.26	.68
6.8	.42	1.72	.24	.82
8.3	.48	1.89	.20	1.32
9.8	.42	1.81	.17	1.32
12.2	.46	1.88	.24	1.71

Since Xe^+ is isoelectronic with iodine, the formation of XeCH_3^+ , XeCH_2^+ , etc., may be looked upon as analogous to the formation of CH_3I , CH_2I , etc., but XeCH_4^+ has no iodine analog. However, this ion may be looked upon as a substituted CH_5^+ ion, albeit a rather unexpected one.

B. Reaction Mechanism Determinations.—The reactions by which the several product ions are formed were determined by the usual methods of matching appearance potentials of products and postulated reactants and/or calculating ratios of

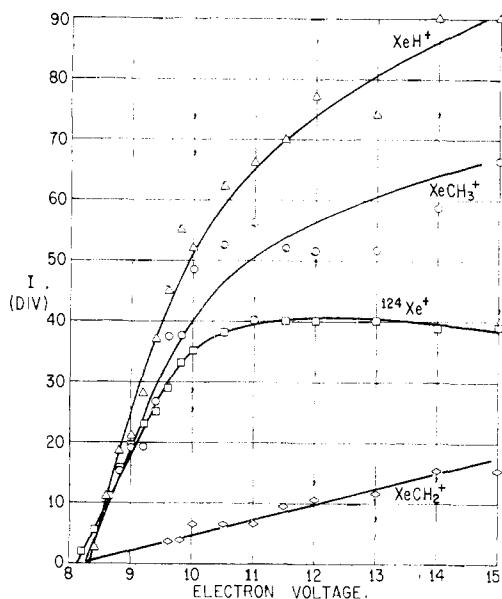


Fig. 1.—Ionization efficiency curves.

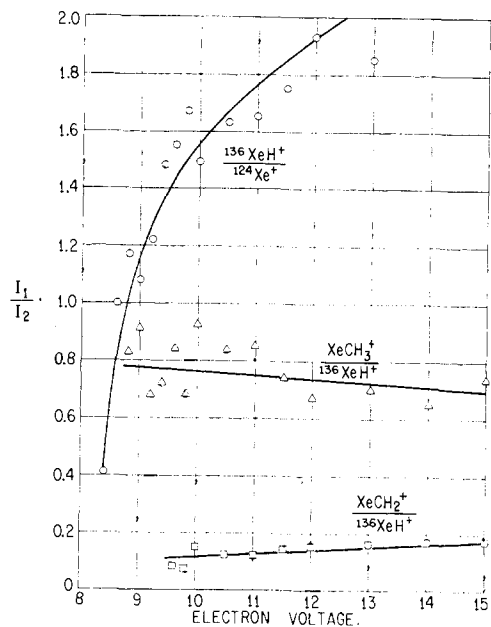
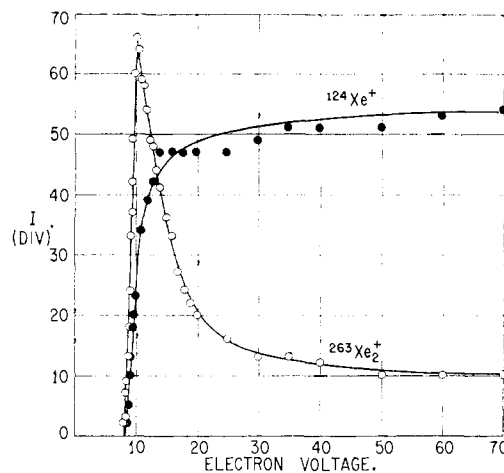
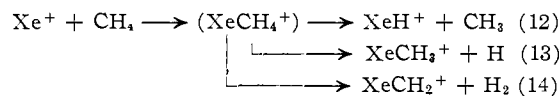


Fig. 2.—Ion ratio plots.

intensities of product ions and postulated reactant ions at different electron energies. From experiments in both Source 1 and Source 2 one obtains the results that within experimental error the appearance potentials of the ions Xe^+ , XeH^+ , XeCH_2^+ and XeCH_3^+ are equal. Ionization efficiency curves illustrating this equality are given in Fig. 1, the data for which were obtained in Source 2 at total pressure in the ionization chamber of 20×10^{-3} mm. One concludes that the three product ions have a common reactant ion, namely, Xe^+ . If this be strictly the case, the ratios of the intensities of the four kinds of ions should be independent of the ionizing electron energy. Such ratios are plotted in Fig. 2, and it may be seen that the ratios on the product ion intensities are for practical pur-

Fig. 3.— Xe^+ and Xe_2^+ ionization efficiency curves.

poses constant. However, the ratios of the product ion intensities to the $^{124}\text{Xe}^+$ intensity vary quite sharply with the ionizing energy, which behavior is not compatible with the postulate that Xe^+ is the reactant ion. We are forced to choose between the conflicting evidence, and we believe that more weight should be given to the appearance potential data. Thus we postulate that the reactions involved are



The XeCH_4^+ is a transient intermediate in this process which we believe is not observable. We have no direct evidence for postulating in equation 14 the formation of H_2 rather than 2H , but H_2 would require significantly less energy and is thus more likely.

In evaluating the significance of the non-constancy of the ratios of the intensities of product ions and alleged reactant ion, it should first be said that it is quite possible that the behavior constitutes an experimental artifact, for at these pressures the conditions in the ionization chamber are complicated and have been observed to give rise to unexpected behavior. However, as will be pointed out later, an unexpected variation in the current ratio of XeH^+ and Xe^+ similar to that shown in Fig. 2 is observed in pressure studies at low ionizing voltage, and this leads us not immediately to dismiss the matter as experimental error. The intensity ratio evidence and the appearance potential evidence can be reconciled if one postulates that an appreciable fraction of the products observed is produced from the upper state ($^2P_{1/2}$) of the Xe^+ doublet, but this is just speculation.

The ionization efficiency curves for Xe_2^+ and XeCH_4^+ are identical in form and quite different from the ionization efficiency curves usually encountered for electron impact processes. Figure 3 shows the ionization efficiency curves for $^{263}\text{Xe}_2^+$ and $^{124}\text{Xe}^+$ between onset and 70 volt, and Fig. 4 shows the initial portions of the curves on an expanded scale. For this run the Xe source pressure was 9×10^{-3} mm.

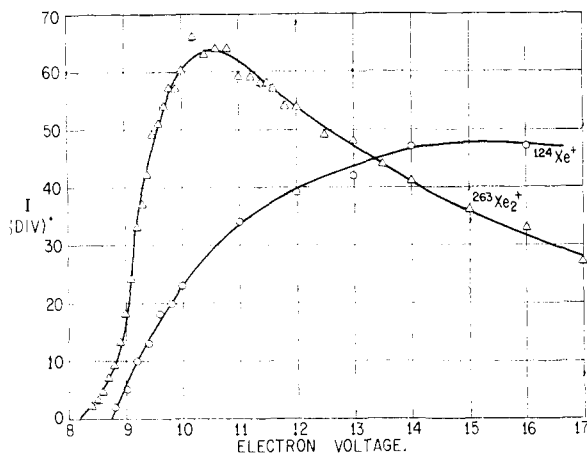
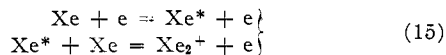


Fig. 4.—Xe⁺ and Xe₂⁺ ionization efficiency curves.

It may clearly be seen from Fig. 4 that the appearance potential of Xe₂⁺ is 0.5 volt lower than that of ¹²⁴Xe⁺; that is, $A(\text{Xe}_2^+) = 11.7$ volts. Thus Xe₂⁺ is formed by the reaction of an excited xenon atom.



This finding is what one would expect from Hornbeck and Molnar's³ results for the lighter rare gases (see equations 1 and 2, for example). The ionization efficiency curve observed for Xe₂⁺ is really an excitation function, and it is very similar in form to the curves given for the lighter rare gases in the paper of Hornbeck and Molnar.

It may be seen from Fig. 4 that the Xe₂⁺ ionization rises to its maximum value at only 2 volts above onset, and since the electron beam contains the usual energy spread, the Xe* excitation function must rise very sharply from onset. However, caution must be exercised in drawing conclusions from the shape of the curve, for we have observed that the shapes can be markedly influenced by experimental conditions. In particular we find that the sharpness of the onset for the formation of Xe₂⁺ and XeCH₄⁺ in Source 2 is very dependent on the source pressure. In an experiment with xenon at a source pressure of about 35×10^{-3} mm. the Xe₂⁺ intensity increased from a residual value of 75 divisions to its maximum value of 3370 divisions when the ionizing electron voltage was increased from 7.9 to 8.0 volts. We should also mention that increasing the pressure changed the energy scale for the ionizing electrons, for at higher pressures all ions appeared at lower voltages. The very sharp rise in ionization with electron energy at the higher pressures clearly is the result of the operation of some kind of cooperative phenomena, but we are at a complete loss to characterize it further. The data included in Figs. 3 and 4 were obtained at a low enough pressure so that we observed no discontinuous effects. Furthermore, an experiment with xenon at the lowest pressures at which Xe₂⁺ measurements could be made (5×10^{-3} mm.) gave results identical with those depicted in Figs. 3 and 4.

Higher pressures are needed in mixtures of xenon and methane to achieve measurable intensities of the XeCH_n⁺ ions, and consequently we have not

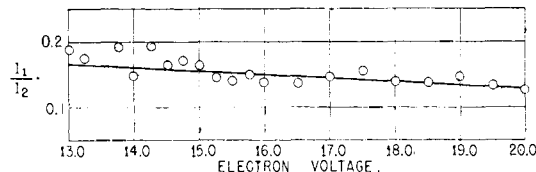
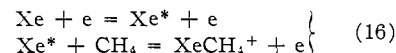


Fig. 5.—Ion ratio plot $\frac{\text{XeCH}_4^+}{\text{Xe}_2^+}$.

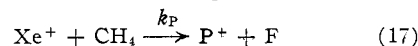
succeeded in obtaining in Source 2 a value of the appearance potential of XeCH₄⁺ which is above suspicion. However, the XeCH₄⁺ ionization efficiency curve is of the same form as that of Xe₂⁺, passing through a sharp maximum about two volts above onset. The ratio of intensity of XeCH₄⁺ to that of Xe₂⁺ does not vary with the ionizing electron voltage, as is shown in Fig. 5. These data were obtained with Source 1, and it should be noted that with this source the onset of ionization is at about 13 volts, as compared with 8.5 volts in Source 2 (cf. Fig. 4). Finally, in mixtures of xenon and methane the appearance potentials of XeCH₄⁺ and Xe₂⁺ are identical. We feel sure that XeCH₄⁺ ion is formed by an excited atom or molecule reaction, and while we cannot be sure that excited methane is not involved, this seems unlikely. Thus we postulate



The energy of the excited state(s) of xenon involved here is close or identical to that involved in the formation of Xe₂⁺.

No serious attempt has been made to measure the appearance potentials of the XeC⁺ and XeCH⁺ ions observed in the mass spectrum at 70 volts, but it has been noticed in the course of making other appearance potential measurements that these ions vanish at electron voltages 5–10 volts above Xe⁺, XeH⁺, etc., appearance potentials, and thus they are formed from rather highly excited reactants.

C. Rate Constant Determinations.—For the reactions 12–14 written in the general form



the rate expression is

$$\ln \left(1 - \frac{(\text{P}^+)}{(\text{Xe}^+)_0} \right) = -k_p(\text{CH}_4)\tau_{\text{Xe}^+} \quad (18)$$

which for small amounts of reaction reduces to

$$\frac{(\text{P}^+)}{(\text{Xe}^+)} = \frac{I_{\text{P}^+}}{I_{\text{Xe}^+}} = k_p(\text{CH}_4)\tau_{\text{Xe}^+} \quad (19)$$

τ_{Xe^+} is the ion chamber residence time of the reactant Xe⁺ ions at the ionization chamber repeller field strength of 12.5 volt/cm. used in these experiments. Residence time can be calculated from the relation $\tau = (2dM/eE)^{1/2}$, d = distance from electron beam to ion exit electrode, M = mass and E = ionization chamber field strength. To calculate the rate constants, the ion current ratios obtained at the different reactant partial pressures (Table IV, for example) are averaged and substituted along with the appropriate value of τ into equation 19.

For the kinetics of XeCH₄⁺ formation one writes by analogy to equation 19 the relation

$$\frac{(\text{XeCH}_4^+)}{(\text{Xe}^*)} = k_{\text{XeCH}_4^+}(\text{CH}_4)\tau_{\text{Xe}^*} \quad (20)$$

Unfortunately, at the present, we have no information concerning the concentration of Xe^* atoms in the ion source, and so a rate constant cannot be calculated. However, it is reasonable to think that the concentration of Xe^* will parallel that of Xe^+ , so we can write

$$(\text{Xe}^*) = \alpha(\text{Xe}^+) \quad (21)$$

$$\frac{(\text{XeCH}_4^+)}{(\text{Xe}^+)} = \frac{I_{\text{XeCH}_4^+}}{I_{\text{Xe}^+}} = \alpha k_{\text{XeCH}_4^+}(\text{CH}_4)\tau_{\text{Xe}^*} \quad (22)$$

The residence time τ_{Xe^*} is calculated from

$$\tau_{\text{Xe}^*} = \frac{d}{\bar{v}} = d \sqrt{\frac{8RT}{\pi M}} \quad (23)$$

The residence time calculated from equation 23 is the maximum time. If the excited state(s) of xenon (Xe^*) involved in the formation of XeCH_4^+ can undergo optically allowed transitions to lower states with the emission of radiation, τ_{Xe^*} will be the relaxation time for dipole radiation, *i.e.*, about 10^{-8} sec. On the other hand, if the xenon excited states are metastable, the relaxation time for radiation can be on the order of 10^{-4} to 10^{-3} sec.; the excited atoms will have time to diffuse out of the ionization chamber from their thermal motion; and an approximation to the value of τ_{Xe^*} can be obtained from Eq. 23.

The rate expression for the formation of Xe_2^+ is analogous to that for XeCH_4^+

$$\frac{I_{\text{Xe}_2^+}}{I_{\text{Xe}^+}} = \alpha k_{\text{Xe}_2^+}(\text{Xe})\tau_{\text{Xe}^*} \quad (24)$$

Pressure studies which serve for the determination of rate constants have been made at electron voltage (e.v.) = 70 volts in both Source 1 and Source 2 for the ions XeH^+ , XeCH_3^+ and XeCH_2^+ . In addition studies have been made in Source 2 at e.v. = 70 volts and 10 volts for XeCH_4^+ and Xe_2^+ . The purpose of the e.v. = 10 volt runs was to provide rate data for the excited neutral reactions at conditions where the formation of the excited reactant was close to its maximum. The studies in Source 2 were all made holding the pressure of the methane constant and varying the pressure of the xenon. In the Source 1 studies the converse experiments (methane varied) were also made.

Replicate experiments were made in all cases. The agreement between replicate results was generally satisfactory. No difference in results could be observed between runs in which the methane pressure was held constant and the xenon pressure varied, and *vice versa*. However, the rate constants from experiments conducted with Source 2 were uniformly about a factor of 2 higher than those obtained with Source 1. The relative magnitudes of the rates for the several different ions fortunately are the same for both sets of measurements. We are unable to explain this discrepancy, and since we have no reason to choose one set of results in preference to the other, we have used all of the experimental values to calculate average rate constants for the several reactions investigated. These average rate constants are given in Table V.

By adding together the e.v. = 70 volt rate constant for the ions XeH^+ , XeCH_3^+ and XeCH_2^+ given in Table V, we obtain a value of about 4.0×10^{-11} cc./mole sec. for the rate constant for the for-

TABLE V

AVERAGE RATE CONSTANTS AT $E = 12.5$ VOLT/CM.

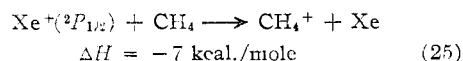
Reaction	k^a (cc./mole sec.)	
	e.v. = 70 v.	e.v. = 10 v.
$\text{Xe}^+ + \text{CH}_4 \rightarrow \text{XeH}^+ + \text{CH}_3$	3.8×10^{-11}	
$\text{Xe}^+ + \text{CH}_4 \rightarrow \text{XeCH}_3^+ + \text{H}$	2.2×10^{-12}	
$\text{Xe}^+ + \text{CH}_4 \rightarrow \text{XeCH}_2^+ + \text{H}_2$	4.5×10^{-12}	
$\text{Xe}^* + \text{CH}_4 \rightarrow \text{XeCH}_4^+ + \text{e}$	$1.1 \times 10^{-14}/\alpha$	$9.4 \times 10^{-14}/\alpha$
$\text{Xe}^* + \text{Xe} \rightarrow \text{Xe}_2^+ + \text{e}$	$9.2 \times 10^{-14}/\alpha$	$8.9 \times 10^{-13}/\alpha$

^a $\alpha = (\text{Xe}^*)/(\text{Xe}^+)$ formed in ionization chamber.

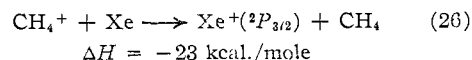
mation of the intermediate complex XeCH_4^+ written in equations 12-14. To make comparisons with other reactions, it is convenient to convert this rate constant to a reaction cross-section, Q , using the relation¹⁴ $Q = k/(eEd/2M)^{1/2}$. One thus finds that the 12.5 volt/cm. cross-section is $Q_{12.5} = 4.2 \times 10^{-16}$ cm.² This corresponds to a rather slow ion-molecule reaction when compared with relatively fast reactions such as $\text{Ar}^+ + \text{H}_2 = \text{ArH}^+ + \text{H}$, $Q_{10} = 111 \times 10^{-16}$ cm.²; $\text{Kr}^+ + \text{H}_2 = \text{KrH}^+ + \text{H}$, $Q_{10} = 42.5 \times 10^{-16}$ cm.², $\text{CH}_4^+ + \text{CH}_4 = \text{CH}_5^+ + \text{CH}_3$, $Q_{10} = 61.0 \times 10^{-16}$ cm.², etc. (all cross-section values taken from ref. 14).

From Table V one can see that in the decomposition of the XeCH_4^+ intermediate the loss of a methyl radical to produce XeH^+ ion is about 10 times as probable as the complementary process, namely, loss of hydrogen atom to produce XeCH_3^+ . Loss of H_2 ($2\text{H}^?$) to form XeCH_2^+ is in turn about 10 times less probable than loss of H. Also from Table V one can see that the reactivity of Xe^* with methane is about 9 times smaller than the reactivity with Xe. The rate constants at e.v. = 70 and 10 volts reflect the fact that the excitation cross-section for Xe passes through a sharp maximum close to onset. It is to be hoped that these excitation cross-sections can be determined experimentally, which will permit the calculation of rate constants for reactions involving the excited atoms.

D. Charge Exchange.—One might expect that one of the most likely ionic reactions between methane and xenon would be charge exchange. For example, Melton¹⁵ has observed charge transfer between Ar^+ , Kr^+ and CH_4 , and we have in this Laboratory studied charge exchange reactions between rare gas ions and ethylene.¹⁶ The ionization potential of CH_4 by electron impact is 13.12 volts,¹⁷ and the energies of the two components of the Xe^+ ground state doublet are 12.13 and 13.44 volts.¹⁸ Then one anticipates the occurrence of the following exothermic reactions



and



In Fig. 6 we plot the quantity $(I_{16} + I_{23})/(I_{17} + I_{16})$ as a function of the ionization chamber partial

(14) F. W. Lampe and F. H. Field, *Tetrahedron*, **7**, 189 (1959). See equation 11.

(15) C. E. Melton, *J. Chem. Phys.*, **33**, 647 (1960).

(16) J. L. Franklin and F. H. Field, *J. Am. Chem. Soc.*, **83**, 3555 (1961).

(17) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

(18) C. E. Moore, *National Bureau of Standards Circ.*, No. 467, Vol. III (1958).

