Table I gives the thermodynamic values we obtained for the 1,2 water equilibrium at propane pressure equal to 2.5 Torr, and for comparison we also give the values obtained in this laboratory previously at propane pressure equal to 0.8 Torr[1] and the values of Kebarle and coworkers.[2] The value of K_{300} obtained in the present work is a factor of 2 larger than our earlier value, and it is now clear that experimental limitations forced us to make our previous experiments at a propane pressure which was a little too low. Our new value for $\Delta G°_{300}$ reflects this increase in the value of K_{300}, but our new and old values of $\Delta H°$ and $\Delta S°$ are in effect identical. A very large discrepancy remains between our thermodynamic values and those of Kebarle and coworkers. We have considered these discrepancies at some length previously,[1,3] and the discussion will not be repeated. The present results enable us to add the statement that except for a trivial factor of 2 uncertainly coming from the effect of the repeller field, the discrepancy does not result from the existence of nonequilibrium conditions in our ionization chamber.

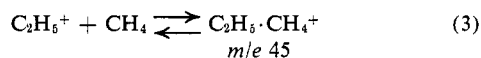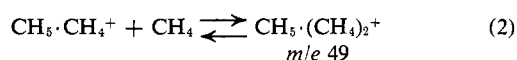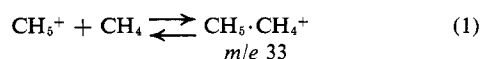# Reversible Reactions of Gaseous Ions. V. The Methane–Water System at Low Temperatures

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Contribution from The Rockefeller University, New York, New York 10021. Received January 5, 1972

**Abstract:** The mass spectra of methane–water mixtures have been determined at several subambient temperatures. The $H_3O \cdot CH_4^+$ ion (m/e 35) is formed in an equilibrium reaction with H_3O^+ and CH_4. The $H_3O \cdot (CH_4)_2^+$ ion (m/e 51) is formed in an equilibrium reaction between $H_3O \cdot CH_4^+$ and CH_4. The equilibrium constants for these reactions were determined at several temperatures, and the following thermodynamic values were obtained. For the formation of $H_3O \cdot CH_4^+$, $K_{300} = 25$, $\Delta G°_{300} = -1.9$ kcal/mol, $\Delta H° = -8$ kcal/mol, and $\Delta S° = -20.4$ eu. For the formation of $H_3O \cdot (CH_4)_2^+$ the corresponding values are 7, -1.2 kcal/mol, -3.4 kcal/mol, and -8.1 eu. Classical electrostatic calculations are made to determine the energy of interaction of the $H_3O \cdot CH_4^+$ ion and the $CH_5 \cdot CH_4^+$ ion produced in pure methane at low temperatures. From these calculations we conclude that the experimentally observed interactions can be adequately accounted for in terms of ion-induced dipole interactions. Differences in the observed interactions in the $H_3O \cdot CH_4^+$ ion and the $CH_5 \cdot CH_4^+$ ion are also accounted for by the calculations.

In a previous study in this laboratory of the gaseous ionic reactions in methane at subambient temperatures (down to liquid nitrogen temperature) we found[1] that the following reversible gaseous ionic reactions occur.

$$CH_5^+ + CH_4 \rightleftharpoons \underset{m/e\ 33}{CH_5 \cdot CH_4^+} \qquad (1)$$

$$CH_5 \cdot CH_4^+ + CH_4 \rightleftharpoons \underset{m/e\ 49}{CH_5 \cdot (CH_4)_2^+} \qquad (2)$$

$$C_2H_5^+ + CH_4 \rightleftharpoons \underset{m/e\ 45}{C_2H_5 \cdot CH_4^+} \qquad (3)$$

Equilibrium constants, free energies, enthalpies, and entropies were determined for the reactions.

It is virtually impossible completely to exclude water from a mass spectrometer, and in the course of this study ions with m/e 19 and 35 were always observed with small intensities. The m/e 19 ion is, of course, H_3O^+, and in a system containing just methane and water the m/e 35 ion with little uncertainty may be taken as the association complex between H_3O^+ and methane formed by the reaction
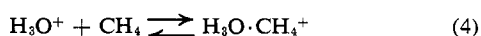
$$H_3O^+ + CH_4 \rightleftharpoons H_3O \cdot CH_4^+ \qquad (4)$$

We have undertaken to study the low temperature water–methane system, and in this paper we report our results. We have also made classical electrostatic calculations in an attempt to explain the binding in ions such as $CH_5 \cdot CH_4^+$ and $H_3O \cdot CH_4^+$, and we also give the results of these calculations.

Experimental Section

The apparatus used for these studies was the Esso Chemical Physics mass spectrometer described previously.[2,3] It was equipped with the ion source designated previously[3] as source III, which can be heated to 270° and cooled to approximately liquid nitrogen temperature. A 200 line per in. wire screen (maintained at focus electrode potential) is located between the focus electrode and the analyzer entrance slit, and the distance between this screen and the ion exit slit of the source is relatively large (12 mm). Thus one is assured that little or no penetration of the ion acceleration voltage (3000 V) into the source region occurs. The repeller and the focus electrodes were maintained at minimum operating potentials (typically 5 V repeller and 5 V focus) needed to achieve a usable sensitivity. The electron collector electrode and the electrode in the electron gun immediately in front of the ionization chamber were both maintained at ionization chamber potential. These are the conditions previously referred to as approximate field-free conditions,[3] and with them the ions in the ionization chamber and downstream of the ion exit slit for a distance of 12 mm are

(1) F. H. Field and D. P. Beggs, *J. Amer. Chem. Soc.*, **93**, 1585 (1971).

(2) F. H. Field, *ibid.*, **83**, 1523 (1961).
(3) D. P. Beggs and F. H. Field, *ibid.*, **93**, 1567 (1971).

subjected to the weakest electric fields compatible with attaining an adequate sensitivity of the equipment. Our experience has been that the occurrence of collision induced dissociations in the ion gun is manifested by distortions of the peak shape of the ion produced by the dissociation, and consequently the shapes of the various peaks of importance in the water-methane system were kept under continuous surveillance during the course of the work. No distortion of the peak shapes was observed. The electron accelerating voltage used throughout the study was 220 V.

The materials used were distilled water and Matheson ultra high purity methane (99.97% CH_4). Traces of water in the methane were significantly reduced in magnitude by passing the methane through a coil submersed in liquid nitrogen.
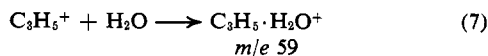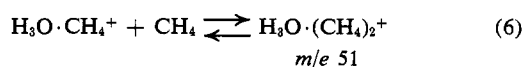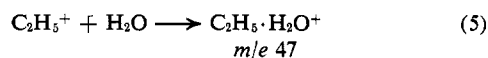
Experimental Results

We give in Table I the mass spectra observed in the

Table I. Mass Spectra in Methane-Water System[a,b]

m/e	Ion	Rel intensity, $I_i/\Sigma I_i$ at t =			
		+76°	−9°	−44°	−97°
17	CH_5^+	0.231	0.188	0.166	0.188
19	H_3O^+	0.190	0.200	0.157	0.051
28	$C_2H_4^+$	0.044	0.038	0.042	0.033
29	$C_2H_5^+$	0.430	0.343	0.282	0.321
31	$C_2H_7^+$	0.009	0.007	0.009	0.014
33	$CH_5 \cdot CH_4^+$		0.002	0.003	0.024
35	$H_3O \cdot CH_4^+$	0.001	0.027	0.054	0.047
37	$H(H_2O)_2^+$	0.007	0.090	0.128	0.127
41	$C_3H_5^+$	0.057	0.051	0.053	0.055
43	$C_3H_7^+$	0.015	0.017	0.021	0.024
45	$C_2H_5 \cdot CH_4^+$		0.001	0.001	0.005
47	$C_2H_5 \cdot H_2O^+$	0.014	0.023	0.034	0.038
49	$CH_5 \cdot (CH_4)_2^+$		0.001	0.004	0.008
51	$H_3O \cdot (CH_4)_2^+$			0.003	0.020
55	$H(H_2O)_3^+$	0.001	0.007	0.032	0.030
59	$C_3H_5 \cdot H_2O^+$	0.002	0.002	0.003	0.004
73	$H(H_2O)_4^+$		0.001	0.007	0.009
91	$H(H_2O)_5^+$			0.001	0.002

[a] $P_{CH_4} = 1100 \mu$, $P_{H_2O} = 0.5 \mu$. [b] Ions due to ^{13}C content omitted from tabulation.

methane-water system at four temperatures. One observes ions formed by the reaction of ions from methane with methane molecules (m/e 17, 28, 29, 31, 41, 43, 45, and 49) and ions formed by reaction of ions from water with water molecules (m/e 19, 37, 55, 73, and 91). In addition, one observes other ions which must be formed by reactions involving both water and methane, namely, m/e 35 ($H_3O \cdot CH_4^+$), 47 ($C_2H_5 \cdot H_2O^+$), 51 ($H_3O \cdot (CH_4)_2^+$), and 59 ($C_3H_5 \cdot H_2O^+$). It is this latter group of ions that concerns us here. The formulas written for these ions are deduced from the stoichiometry implicit in the m/e values and the fact that the mass spectrometer contains only water and methane. We have already postulated reaction 4 for the formation of the m/e 35 ion, and we postulate the following reactions for the other three methane-water ions.

$$C_2H_5^+ + H_2O \longrightarrow C_2H_5 \cdot H_2O^+ \qquad (5)$$
$$m/e \ 47$$

$$H_3O \cdot CH_4^+ + CH_4 \rightleftharpoons H_3O \cdot (CH_4)_2^+ \qquad (6)$$
$$m/e \ 51$$

$$C_3H_5^+ + H_2O \longrightarrow C_3H_5 \cdot H_2O^+ \qquad (7)$$
$$m/e \ 59$$

The intensities of all four methane-water ions increase as the temperature of the ion source is decreased, but the magnitude of the effect of temperature is significantly greater for the $H_3O \cdot CH_4^+$ and $H_3O \cdot (CH_4)_2^+$ ions than
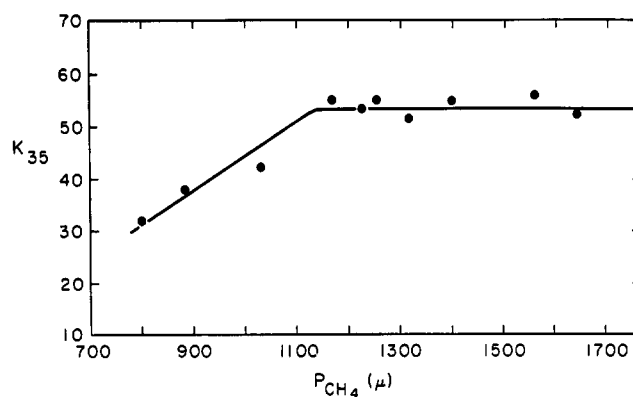
Figure 1. Equilibrium constant $vs.$ CH_4 pressure for H_3O^+ + $CH_4 \rightleftharpoons H_3O \cdot CH_4^+$. $P_{H_2O} = 0.5 \mu$, $T = 28°$.

for the $C_2H_5 \cdot H_2O^+$ and $C_3H_5 \cdot H_2O^+$ ions. Such behavior immediately leads one to think that reversible reactions are at hand and to consider the possibility that equilibrium conditions may be achieved. We have considered these possibilities for the $H_3O \cdot CH_4^+$, $C_2H_5 \cdot H_2O^+$, and $H_3O \cdot (CH_4)_2^+$ ions, and our conclusions may be anticipated from the fact that we write reactions 4 and 6 as reversible reactions, but reaction 5 as a unidirectional reaction. We have not seriously investigated the reaction producing $C_3H_5 \cdot H_2O^+$ because of the small intensity of the m/e 59 ion, and in reaction 7 we arbitrarily represent it as being formed by a unidirectional reaction.

We consider in detail first the formation of m/e 35 ($H_3O \cdot CH_4^+$). If the ion is indeed produced by reversible reaction 4, and if the reaction is assumed to have achieved equilibrium, we may write an equilibrium constant for the reaction

$$K_{35} = (I_{35}/I_{19})(1/P_{CH_4}) \qquad (8)$$

This constant should be independent of the concentrations of both reactants. Figure 1 illustrates the effect of varying the pressure of methane on the value of K_{35}, and one sees that the value of the equilibrium constant rises as the pressure is increased to about 1.1 Torr and then is sensibly constant up to about 1.6 Torr, which was the upper limit of pressure at which the mass spectrometer could be operated. This behavior is that to be expected for a reversible reaction which achieves equilibrium above some minimum pressure. It should be kept in mind that in this system the methane acts both as a reactant and a third body, and our past experience with other systems has been that reversible reactions in the mass spectrometer achieve equilibrium at third-body pressures of approximately 1 Torr.

Figure 2 illustrates the effect of water pressure on the value of K_{35}. The equilibrium constant decreases rapidly as the water pressure increases. The solid rectangles along the left-hand ordinate represent the values of K_{35} obtained when the water content of the mass spectrometer was the irreducible background contribution. This comprises a low but unknown pressure. Decreases in equilibrium constants with pressure of reactants have been observed previously in this laboratory for reversible reactions,[1,3] and they have been attributed to the occurrence of reactions which consume the product of the reversible reaction under consideration. A mathematical analysis of the phenomenon
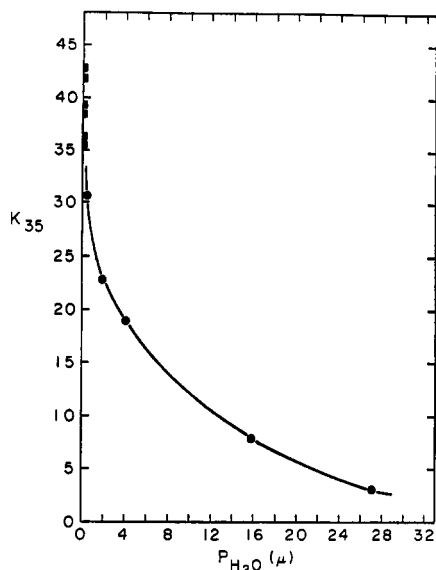
Figure 2. Equilibrium constant $vs.$ H_2O pressure for H_3O^+ + $CH_4 \rightleftharpoons H_3O \cdot CH_4^+$. $P_{CH_4} = 930 \mu, T = 28°$.

Figure 3. Equilibrium constant $vs.$ CH_4 pressure for CH_5^+ + $H_2O \rightleftharpoons CH_5^+ \cdot H_2O$. $P_{H_2O} = 0.5 \mu, T = 28°$.

has been given,[4] and the phenomenon may briefly be described by saying that under time-limited conditions for the attainment of equilibrium, which is the situation obtaining in the ionization chamber of our mass spectrometer, time is not available for the establishment of simultaneous equilibria in a system consisting of several consecutive reversible reactions. We postulate that the reaction which consumes $H_3O \cdot CH_4^+$ and produces the rapid diminution in K_{35} shown in Figure 2 is

$$H_3O \cdot CH_4^+ + H_2O \longrightarrow H_3O \cdot H_2O^+ + CH_4 \qquad (9)$$
$$m/e \ 37$$
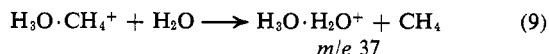
We have no experimental evidence for the occurrence of this reaction because the m/e 37 ion is produced directly in significant abundance by the reaction

$$H_3O^+ + H_2O \rightleftharpoons H_3O \cdot H_2O^+ \qquad (10)$$
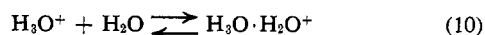
and the small increment in the m/e 37 intensity produced by (9) is not observable. However, from the known values of the equilibrium constant for reaction 10 and the much lower value for K_{35} obtained in this work (*vide infra*) we conclude that reaction 9 is strongly exothermic, and thus since it is a gaseous ionic reaction it doubtless proceeds with the high rate constant typical of this type of reaction. Because of the occurrence of this reaction (and analogs of it for other methane-water ions) all of the quantitative studies in the methane-water system were performed with the presence in the ionization chamber of the smallest quantity of water possible, namely, $P_{H_2O} = 0.5 \mu$ at room temperature. From Figure 2 it may be concluded that equilibrium constant values obtained in this way are slightly low because of the effect of reaction 9 on the equilibrium, but we have no alternative but to accept the error involved. We think that this is small enough so that our thermodynamic results are meaningful.

A problem which immediately presents itself in considering the origin of the m/e 35 ion is that in addition to reaction 4, stoichiometry allows with equal likeli-
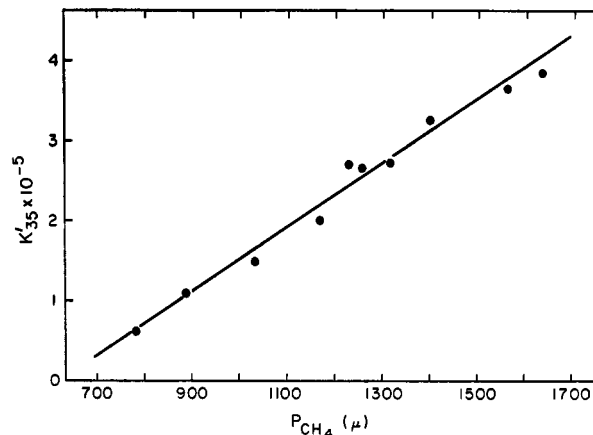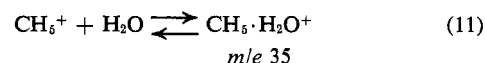
hood the possibility that the reaction producing the ion is

$$CH_5^+ + H_2O \rightleftharpoons CH_5 \cdot H_2O^+ \qquad (11)$$
$$m/e \ 35$$

We have not been successful in conceiving of a way of distinguishing between reactions 4 and 11 using isotopes or any other direct means, and consequently we are obliged to use indirect arguments. The first is that the proton affinity of water $(PA(H_2O) = 164 \text{ kcal/mol}[5])$ is much greater than that of methane $(PA(CH_4) = 127 \text{ kcal/mol}[6])$, and thus one would expect that the formation of the complex $CH_5 \cdot H_2O^+$ would immediately lead to a transfer of the proton from CH_5^+ to the H_2O, and the large exothermicity of this reaction would effect the dissociation of the complex. That this process does occur extensively is beyond question, for H_3O^+ is formed in copious amounts when water is added to methane in a mass spectrometer operated under chemical ionization conditions.[6] Secondly, if the m/e 35 ion is indeed formed by reaction 11, the expression for the equilibrium constant would be

$$K'_{35} = (I_{35}/I_{17})(1/P_{H_2O}) \qquad (12)$$

The behavior we would predict for K'_{35} as the methane pressure is increased is that it should rise initially because of the third-body role played by the methane, but at some minimum pressure of methane the value of K'_{35} should become independent of methane pressure. That is, a plot of the form of Figure 1 should be obtained. Figure 3 shows the observed dependence of K'_{35} upon methane pressure, and it may be seen that K'_{35} rises monotonically over the whole range of methane pressure available to us with our equipment. We take this behavior as indicating that reaction 11 and the equilibrium constant expression associated with it (12) are not applicable to our system.

Values of K_{35} (eq 8) were determined as a function of the temperature of the ion source. The methane pressure was adjusted to about 1250μ at room temperature, and no further changes in the controls determining the flow of methane through the mass spectrometer were made over the course of the experiment. Under these circumstances the pressure of methane in the ion

(4) D. P. Beggs and F. H. Field, *J. Amer. Chem. Soc.*, **93**, 1576 (1971).

(5) J. Long and B. Munson, *J. Chem. Phys.*, **53**, 1356 (1970).

(6) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **87**, 3294 (1965). Value of PA(CH₄) quoted recalculated from these data.

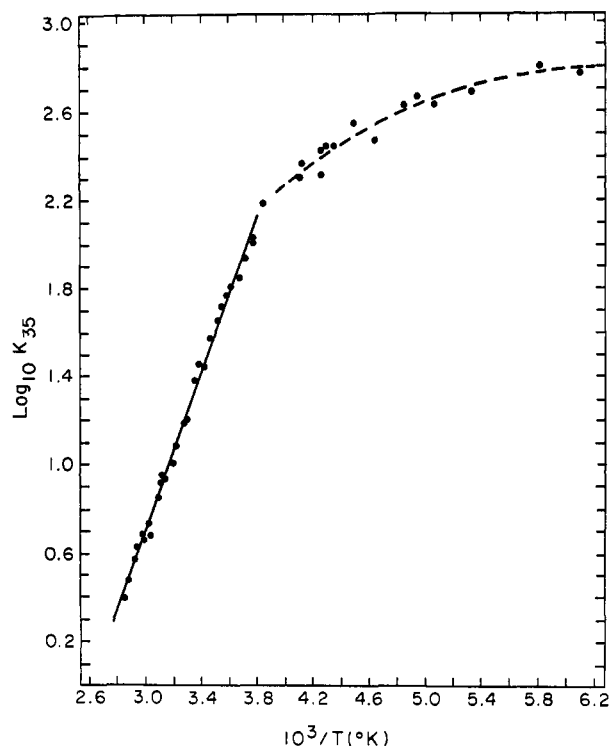Figure 4. Van't Hoff plot for $H_3O^+ + CH_4 \rightleftharpoons H_2O \cdot CH_4^+$
Standard state $= 1$ atm, $P_{CH_4} = 1250 \mu$, $P_{H_2O} = 0.58 - 0.40 \mu$.

Figure 5. Equilibrium constant $vs.$ CH_4 pressure for $H_3O \cdot CH_4^+ +$. $CH_4 \rightleftharpoons H_3O \cdot (CH_4)_2^+$. $P_{H_2O} = 0.35 \mu$, $T = -60°$.

Figure 6. Van't Hoff plot for $H_3O \cdot CH_4^+ + CH_4 \rightleftharpoons H_3O \cdot (CH_4)_2^+$. Standard state $= 1$ atm, $P_{CH_4} = 900 \mu$, $P_{H_2O} = 0.40 - 0.30 \mu$.

source varies somewhat with the temperature of the source, and the value of the methane pressure used in the equilibrium constant expression 8 was always the value determined experimentally at the temperature in question. Water was added to give a partial pressure of about 0.5μ in the source, a new charge of water being made at each temperature. After the addition of water the spectrum was scanned. Duplicate experiments involving measuring the spectra over the total temperature range were made on separate days, and excellent agreement between the duplicate experiments was obtained.

A van't Hoff plot for K_{35} is given in Figure 4. The plot is linear from 75° to $-20°$, but a nonlinear behavior sets in at temperatures below $-20°$. Such nonlinear behavior at low temperatures is a phenomenon which has generally been encountered in our mass spectrometric equilibrium studies. From our mathematical analysis[4] of these systems, we believe that the explanation for the curvature in the van't Hoff plots results from time limitations on the establishment of equilibrium in the ionization chamber of the mass spectrometer. The behavior predicted by these calculations has been observed in this system; namely, the nonlinear behavior sets in when the product to reactant ion ratio is greater than about 10%.

Taking the various observations made into account, we are of the opinion that the reaction producing the m/e 35 ion is reaction 4 and that equilibrium is largely established under conditions producing an equilibrium constant independent of methane pressure and a linear van't Hoff plot. A small uncertainty in the absolute magnitude of the equilibrium constant exists because of the occurrence of reaction 9, but we have tried to minimize this effect by keeping the pressure of water as low as possible.
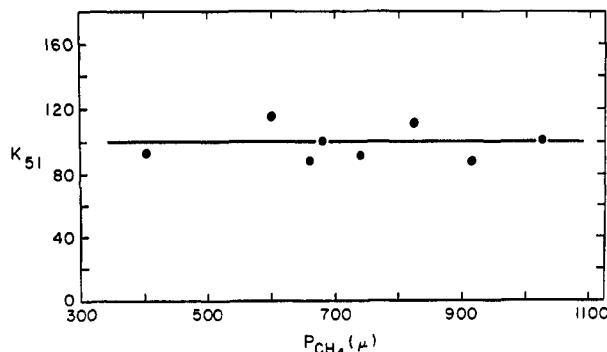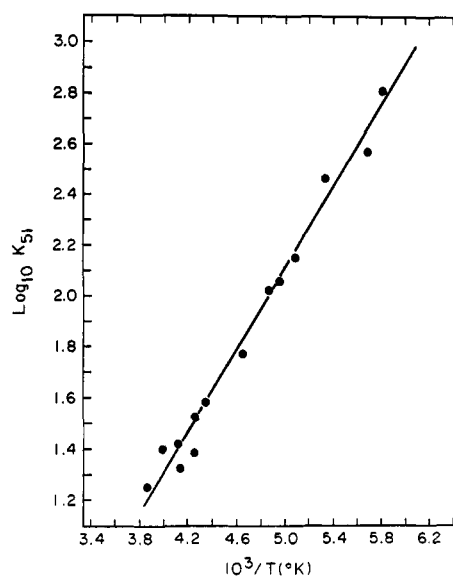
From stoichiometric considerations the reaction producing the m/e 51 ion must be reaction 6 and the evidence available indicates that it is at equilibrium. The equilibrium constant expression corresponding to this reaction is

$$K_{51} = (I_{51}/I_{35})(1/P_{CH_4}) \qquad (13)$$

and Figure 5 shows the effect of methane pressure upon the value of K_{51}. The constancy observed occurs at significantly lower pressures than the pressures over which K_{35} becomes constant (Figure 1). Perhaps this is the result of the larger number of degrees of freedom in the m/e 51 ions and the weaker binding forces holding it together. The van't Hoff plot of K_{51} is given in Figure 6. It is linear from -20 to $-100°$, at which temperature the water condenses in the source. No curvature is observed in this plot because the ion is only formed at quite low temperatures and its intensity always remains quite small.

From stoichiometry the ion with m/e 47 must be formed from reaction 5, and if this reaction were a reversible reaction at equilibrium its equilibrium constant would be

$$K_{47} = (I_{47}/I_{29})(1/P_{H_2O}) \qquad (14)$$

Table II. Experimental Thermodynamic Quantities

Reaction	K_{300}[a]	$\Delta G°_{300}$, kcal/mol	$\Delta H°$, kcal/mol	$\Delta S°$, eu
(4) $H_3O^+ + CH_4 \rightleftharpoons H_3O \cdot CH_4^+$	25	-1.9	-8.0	-20.4
(6) $H_3O \cdot CH_4^+ + CH_4 \rightleftharpoons H_3O \cdot (CH_4)_2^+$	7	-1.2	-3.4	-8.1
(1) $CH_5^+ + CH_4 \rightleftharpoons CH_5 \cdot CH_4^+$ [b]	2.1^c	-0.45^d	-4.14	-12.4
(2) $CH_5 \cdot CH_4^+ + CH_4 \rightleftharpoons CH_5 \cdot (CH_4)_2^+$ [b]	0.32^c	$+0.69^d$	-1.47	-7.2
(3) $C_2H_5^+ + CH_4 \rightleftharpoons C_2H_5 \cdot CH_4^+$ [b]	0.76^c	$+0.16^d$	-2.39	-8.6

[a] Standard state = 1 atm. [b] From ref 1. [c] Given in ref 1 as K_{298}. [d] Given in ref 1 as ΔG_{298}.

However, three pieces of evidence lead strongly to the conclusion that the reaction is indeed not at equilibrium. First, the value of K_{47} rises monotonically as the methane pressure is increased up to 1700 μ giving a plot of the form of Figure 3. Secondly, one would expect from the outset that the interaction of $C_2H_5^+$ with H_2O would result in proton transfer to the water. The proton affinity of ethylene is less than that of water (159 kcal/mol as compared with 164 kcal/mol), and, indeed, such proton transfer has been experimentally observed to occur under chemical ionization conditions.[7] Thirdly, the equilibrium constant calculated from eq 14 shows only a small temperature coefficient, which superficially corresponds to an enthalpy change of -2 kcal/mol. If reaction 5 were an equilibrium reaction, the product ion formed would doubtless be protonated ethanol. From known values of proton affinities, one can calculate that the heat of reaction for the formation of protonated ethanol from $C_2H_5^+$ and H_2O is about -40 kcal/mol, and the discrepency between this energy and the small energy of -2 kcal/mol corresponding to the observed temperature coefficient for the formation of the m/e 47 ion indicates strongly that the m/e 47 ion must be a very highly excited association complex between ethyl ion and water.

We give in Table II the thermodynamic values obtained from least-squares fits of the linear portions of the van't Hoff plots for reactions 4 and 6. For comparison we also include thermodynamic values obtained for reactions 1, 2, and 3 observed[1] in the pure methane system. Comparing reaction 4 with reaction 1, both reactions involve the formation of an association complex with a methane molecule, but the binding for the complex in reaction 4 is stronger than that of the complex in 1. Thus the enthalpy change for 4 is twice as great as that for 1, and the equilibrium constant is approximately 12 times greater. An obvious experimental manifestation of the stronger binding in reaction 4 is the fact that the $H_3O \cdot CH_4^+$ ion begins to appear in the mass spectrum of a methane–water mixture at 50–75°; whereas the $CH_5 \cdot CH_4^+$ ion does not appear in the spectrum of pure methane at temperatures above about $-40°$. The entropy for reaction 4 is 8 eu more negative than that of 1. In our opinion the significance of this difference is not clear.

Reactions 6 and 2 involve the addition of second methane molecule to the product ions formed reactions 4 and 1. Again the binding in the ion produced in the methane–water system is stronger than that in the pure methane ion, which is physically manifested by the fact that the $H_3O \cdot (CH_4)_2^+$ ion appears in the mass spectrum at a much higher temperature than does the $CH_5 \cdot (CH_4)_2^+$. The enthalpy change for the reaction

in the methane–water system is again about twice as large as that in the pure methane system. The entropy change for adding a second methane is lower than that for adding the first methane in both the methane–water and the pure methane systems. The consistancy in this behavior leads us to think that it may be real, in which case we conclude that the complexes containing two methane molecules are looser than those containing only one methane molecule. Such behavior is perhaps not unexpected, especially in view of the fact that the energy binding the second methane is smaller than that for the first.

Since the addition of $C_2H_5^+$ to water in an equilibrium reaction does not occur, we have no reaction in the methane–water system with which to compare reaction 3.

Electrostatic Calculations

From the results given in Table II it is seen that several different kinds of ions form association complexes with methane, and, furthermore, the binding energies are different for the different ions. We are particularly struck by the difference in binding energies for the association with methane of CH_5^+ and H_3O^+. Consequently, it is of interest to attempt to determine the nature of the forces holding the complexes together and to explain the differences in energy observed. Since the complexes all involve ions and neutral molecules, we have undertaken calculations to investigate whether classical ion-induced dipole interactions can account for the observed energies.

Conway[8] has made classical electrostatic interaction calculations for clusters of oxygen ions and molecules using a calculational technique devised by Rowell and Stein[9] to calculate internal fields and polarizabilities of hydrocarbons. We have used portions of these procedures to calculate the electrostatic interaction energies between CH_5^+ and CH_4 and between H_3O^+ and CH_4.

Considering the jth bond in a molecule with $\mathbf{a}_j$ as a unit vector along the jth bond axis subjected to an electric field $\mathbf{E}_j$ at its midpoint, we write as a first approximation for the x component of the induced dipole m_{xj}

$$m_{xj} = (\alpha_{jl} - \alpha_{jt})(\mathbf{E}_j \cdot \mathbf{a}_j)a_{xj} + \alpha_{jt}E_{xj} \qquad (15)$$

E_{xj} is the x component of $\mathbf{E}_j$, α_{jl} is the polarizability of the bond j parallel to the bond axis, and α_{jt} is the bond polarizability transverse to the bond axis. Analogous expressions may be written for the y and z components of the induced moment. In our calculation the field $\mathbf{E}_j$ is considered to arise from a system of point

(7) M. S. B. Munson and F. H. Field, *J. Amer. Chem. Soc.*, **87**, 4242 (1965).

(8) D. C. Conway, *J. Chem. Phys.*, **52**, 2689 (1970).
(9) R. L. Rowell and R. S. Stein, *ibid.*, **47**, 2985 (1967).

charges located on the atoms of a polarizing ion, and thus we write

$$E_j = \sum_\alpha \delta_\alpha r_{\alpha j} r_{\alpha j}^{-3} \qquad (16)$$

In this expression δ_α is the charge on atom α, and $r_{\alpha j}$ is the vector between the nucleus of atom α and the center of bond j. After the induced dipole has been calculated from (15) and its y and z analogs, the polarization energy of the bond is calculated from the expression

$$V_{pj} = -\tfrac{1}{2} m_j \cdot E_j \qquad (17)$$

The total polarization energy of the molecule is obtained by summing (17) over the j bonds.

The calculation described by Rowell and Stein[9] includes an extensive portion devoted to the determination of the reciprocal polarization of bonds in the ion and in the molecule by induced dipoles. We applied a simplified version of this procedure to our problem, and we arrived at the conclusion that the contribution to the total energy of this back polarization constituted only a few per cent of the total. This is negligible for our purposes, and consequently this type of calculation was not routinely made, and we shall not take the space to reproduce the equations used.

Obtaining the polarization energy from eq 15–17 constitutes a modest exercise in applied vector analysis, and for this purpose a Fortran program was written and the calculations were made on a DEC PDP 15 computer. We found that it was also feasible, although somewhat more time consuming, to do the calculation on our programmable desk calculator (Wang 100). The value of the polarizabilities needed in eq 15 were taken from Denbigh,[10] namely, $\alpha_l = 0.79 \times 10^{-24}$ cm^3 and $\alpha_t = 0.58 \times 10^{-24}$ cm^3.

The polarization energy calculations were made by assuming models for the complexes deemed to be appropriate. We consider first the $CH_5 \cdot CH_4^+$ complex. Lathan, Hehre, and Pople[11] give a structure for CH_5^+ based on molecular orbital calculations, and this structure was used here. The model used for the complex
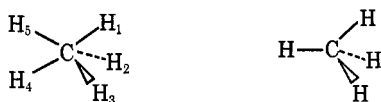
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where the bond distances and angles in CH_5^+ were taken essentially as given in ref 11 is shown by **1**. However, as a harmless simplification for our calculation we took the C–H distances for H_1, H_2, and H_3 to be equal at 1.10 Å, and similarly the C–H distances for H_4 and H_5 to be equal at 1.37 Å. The methane was taken to have the normal C–H distance of 1.09 Å and tetrahedal angles. The calculations were made as a function of the distance between the carbon atoms in CH_5^+ and CH_4.

Lathan, Hehre, and Pople do not give any information about the charge distribution in CH_5^+, and consequently we made calculations for several assumed distributions. These distributions differed only in the fraction of the charge borne by the carbon atom and

by the five hydrogen atoms. A fixed distribution of charge over the hydrogen atoms was assumed, namely, the charges on H_1, H_2, and H_3 were equal, and the charges on H_4 and H_5 were also equal. However, the sum of the charges on the first three hydrogen atoms was taken to be twice as large as that on the second two. This arbitrary assumption of charge distribution was made to keep the calculational problem within manageable bounds. We give in Table III an example of

Table III. Electrostatic Interaction Energy in $CH_5 \cdot CH_4^+$ for Different Charge Distributions [a]

δ_{C^+}	V_P, kcal/mol
1.0	−4.81
0.9	−4.67
0.8	−4.53
0.7	−4.40

[a] $r_{C-C} = 3.2$ Å.

the relatively mild dependence of the electrostatic interaction energy, V_p, upon the charge on the carbon atom, δ_{C^+}. The C–C distance for which these calculations apply is 3.2 Å. Over the range of δ_{C^+} tabulated the polarization exhibits a small monotonic decrease.

The total energy of interaction between the CH_5^+ ion and the CH_4 molecule consists of the electrostatic polarization interaction calculated from eq 15–17 and the van der Waals attractive and repulsive interaction. These last quantities were obtained by use of the Lennard–Jones potential function

$$V_{L-J} = 4\epsilon[(\sigma/r)^{12} - (\sigma/r)^6] \qquad (18)$$

The quantity σ is the value of r for which the potential is zero, and ϵ is the depth of the potential well. σ is the distance of closest approach of two molecules which collide with zero initial relative kinetic energy, and as such it is a measure of the size of the colliding molecules.

Hirschfelder, Curtiss, and Bird[12] tabulate values of ϵ/k, where k is the Boltzmann constant, and as a necessary but not unreasonable approximation we use in this calculation the value of ϵ/k for neutral methane, namely, 148°K. We consider σ to be an unknown, and we calculate the total energy of the interaction (electrostatic polarization plus van der Waals) for several values of σ.

However, as we pointed out above, the electrostatic energy (and thus the total energy) depends to a small extent upon the charge distribution in CH_5^+, and thus the calculation contains this unknown along with the value of σ. Fortunately, electronegativity considerations provide some guidance concerning the charge distribution, although uncertainties in these considerations exist. The charge distribution in CH_5^+ depends upon the relative magnitudes of the electronegativities of hydrogen and charged carbon, but unfortunately, the two most widely accepted electronegativity scales, namely, those of Pauling and Mulliken,[13] have the relative electronegativities of C and H just reversed. Opinions and evidence supporting each set of values can be found, but we develop the impression from the

(10) K. G. Denbigh, *Trans. Faraday Soc.*, **36**, 936 (1940).
(11) W. A. Lathan, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.*, **93**, 808 (1971).

(12) J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York, N. Y., 1964.
(13) For a review of electronegativity, see H. O. Pritchard and H. A. Skinner, *Chem. Rev.*, **55**, 745 (1955).

literature that contemporary opinion tends to favor the Mulliken electronegativities, which make hydrogen somewhat more electronegative than sp^3 carbon. However, in CH_5^+ we are dealing with charged carbon, and Pauling[14] points out that the electronegativity of a charged atom is greater than that of the neutral atom by $^2/_3$ of the increment in electronegativity in passing to the next higher element in the periodic table. Taking this into account, we estimate that the electronegativity for C^+ is approximately equal to that for H, and thus we adopt the point of view that all or a very large fraction of the formal charge in CH_5^+ resides on the carbon atom.

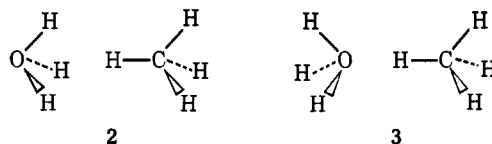We give in Table IV the values of the total energy of

Table IV. Calculated Total Interaction Energy for $CH_5 \cdot CH_4^{+ a}$

| r, Å	$\sigma = 3.30^b$	$\sigma = 3.35$	$\sigma = 3.40$	$\sigma = 3.45$	$\sigma = 3.50$
			E_T, kcal/mol		
3.6	−3.20	−3.18	−3.16	−3.12	−3.07
3.4	−3.88	−3.81	−3.71	−3.60	−3.45
3.2	−4.53	−4.32	−4.07	−3.76	−3.38
3.0	−4.75	−4.22	−3.57	−2.78	−1.84

$^a \delta_{C^+} = 1.0.$ ^{b} All σ values in Å.

interaction, E_T, calculated for $\delta_{C^+} = 1.0$ as a function of the C–C internuclear distance, r, for a series of values of σ. The experimental enthalpy change for the formation of $CH_5 \cdot CH_4^+$ is −4.14 kcal/mol (Table II), and we look in Table IV for a value of σ which will give a minimum value of E_T equal to the experimental enthalpy. The value $\sigma = 3.40$ Å produces a minimum E_T value of about −4.1 kcal/mol at $r = 3.2$ Å. We have calculated tables such as Table IV for other values of δ_{C^+}, and for comparison we cite the results that for $\delta_{C^+} = 0.9$, a minimum energy of −4.1 is obtained at $r = 3.2$ Å for $\sigma = 3.37$ Å; for $\delta_{C^+} = 0.8$, the corresponding values are $r = 3.1$ Å and $\sigma = 3.34$ Å; and for $\delta_{C^+} = 0.7$, the corresponding values are $r = 3.0$ Å and $\sigma = 3.30$ Å. We examine these values for reasonableness. The quantity σ is a measure of the distance of closest approach of the ion and the molecule were no electrostatic attractive force operating, and this perhaps is the quantity to be used for comparing these results with those obtained in neutral systems. The value of σ given by Hirschfelder, Curtiss, and Bird[12] for the CH_4–CH_4 system is 3.8 Å. We have made estimates of the distance of closest approach for our model using Dreiding atomic models taking into account the van der Waals radii for hydrogen, and we estimate a value of 3.2–3.4 Å. Thus our calculated value of 3.3–3.4 Å is of the right order of magnitude.

We have assumed a number of possible models for the $H_3O \cdot CH_4^+$ ion. Our first estimate was that H_3O^+ has a pyramidal structure. For simplicity and as a kind of extreme case we assumed that the hydrogens are arranged tetrahedrally with respect to the oxygen, i.e., the H–O–H angle is 109° 28′. We further assume that the O–H bond distance is 1.00 Å, that is, slightly larger than the value in H_2O (0.96 Å). We have made calculations for the following assumed structures for $H_3O \cdot CH_4^+$.

(14) L. Pauling, "The Nature of the Chemical Bond," 2nd ed, Cornell University Press, Ithaca, N. Y., 1944, pp 65–66.

2 3

Newton and Ehrenson[15] report the results of molecular orbital calculations on the structure of H_3O^+, and they suggest that this ion is planer with H–O–H of 120°. Consequently we have made calculations for models **4–6** of $H_3O \cdot CH_4^+$.

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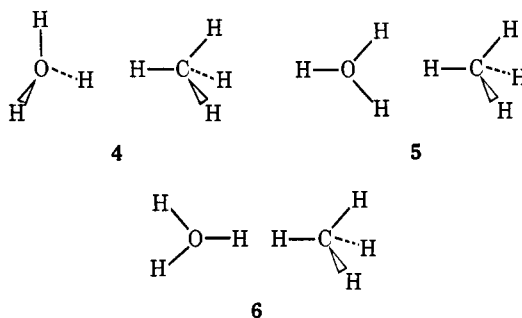
Concerning the problem of the charge distribution in H_3O^+, both the Pauling and Mulliken electronegativity scales make oxygen more electronegative than hydrogen. For consistency with our $CH_5 \cdot CH_4^+$ calculations we place more emphasis on the Mulliken electronegativities, and using this scale we estimate $X_{O_3^+} - X_H = 1.2$. From the Pauling[14] correlation between electronegativity and partial ionic character this corresponds to about 30% partial ionic character in the O–H bonds in H_3O^+, and thus we estimate that the oxygen will carry little or none of the formal positive charge.

Calculations for the total energy, E_T, were made for all the models for several values of σ and δ_{O^+}. The value of ϵ used in the Lennard–Jones equation was the geometric average of the ϵ values given by Hirschfelder, Curtiss, and Bird[12] for methane and water. The values of σ and r giving values of the total energy equal to the experimental enthalpy for reaction 4, i.e., $\Delta H° = -8.0$ kcal/mol, were determined. Typical values obtained are given in Table V. Calculations were

Table V. σ and r Values for $H_3O \cdot CH_4^+$

Model	δ_{O^+}	σ, Å	r, Å
2	0.0	2.9_2	2.8
	0.5	2.9_0	2.8
3	0.0	2.2_3	2.2
	0.5	2.6_2	2.5
4	0.0	2.5_5	2.4
	0.5	2.7_5	2.6
5	0.0	2.8_4	2.8
	0.5	2.8_4	2.8
6	0.0	3.1_9	3.0
	0.5	3.0_7	2.8

made for values of δ_{O^+} other than 0.0 and 0.5, but they have not been tabulated. The value for $\delta_{O^+} \cong 0$ is most appropriate for this system.

To obtain an idea concerning the reasonableness of these values, we compare them with values for neutral

(15) M. D. Newton and S. Ehrenson, *J. Amer. Chem. Soc.*, **93**, 4971 (1971).

analogs. From Hirschfelder, Curtiss, and Bird[12] the value of σ for H_2O is 2.5 Å, and that for CH_4 is 3.8 Å, and for a mixed complex between H_2O and CH_4 it is appropriate to take the arithmetical average of these values, which is 3.2 Å. We found for the $CH_5 \cdot CH_4^+$ ion that the value of σ for the ion was about 0.4 Å smaller than σ for the neutral analog, that is, the CH_4–CH_4 complex. If a similar difference in σ exists for $H_3O \cdot CH_4^+$ and H_2O–CH_4, we would expect a σ value for $H_3O \cdot CH_4^+$ on the order of 2.8 Å. If we adopt the reasonable point of view that the structure of H_3O^+ is similar to that of NH_3, we may compare the value of σ for $H_3O \cdot CH_4^+$ with the arithmetical average of σ values for NH_3 and CH_4. The values of σ for NH_3 is 3.15 Å,[12] and the average of this value with that for CH_4 is 3.4 Å. Again postulating some contraction in the ion, we would predict a value of 3.0 Å for $H_3O \cdot CH_4^+$. From Table V one sees that the σ values for models **2, 5,** and **6** lie in the expected range around approximately 2.9 Å. The σ values for model **3** seem to be too small, and the model is not very reasonable *a priori*. We think it can be rejected as a real possibility. Model **4** has a σ value which is rather low on the basis of these considerations. This low value of σ means that its binding energy is relatively weak, and we think it reasonable to reject this model in favor either of model **5** or **6**.

We have also made experiments with Dreiding models to estimate distances of closest approach for H_3O^+ and CH_4. However, since the hydrogen atoms in H_3O^+ carry a significant fraction of the formal charge, their van der Waals radii will be smaller than the radii in a neutral compound by some unknown amount. By assuming that the hydrogen van der Waals radius decreases in proportion to the amount of positive charge carried by the hydrogen, we arrived at a crude estimate that the distance of closest approach is about 3.0 Å for models **2** and **5**. By contrast, the value obtained for model **6** is about 4 Å. We are inclined to the opinion that models **2** and **5** are the most reasonable ones for $H_3O \cdot CH_4^+$.

We will not belabor the obvious crudeness of these calculations and the simplicity of the models upon which they are based. Nevertheless, we believe the calculations have enough validity to indicate that the forces holding together the $CH_5 \cdot CH_4^+$ and $H_3O \cdot CH_4^+$ ions are either largely or completely classical electrostatic polarization forces. Furthermore, using reasonable models for $CH_5 \cdot CH_4^+$ (model **1**) and $H_3O \cdot CH_4^+$ (models **2, 5,** and perhaps **6**) we can account for the observed factor of 2 difference in the enthalpy change involved in the formation of these two ions. The greater enthalpy change observed for $H_3O \cdot CH_4^+$ may be attributed to the combined effects of the greater charge residing on the hydrogen atoms of H_3O^+ than on those of CH_5^+, the possibility for closer approach in the $H_3O \cdot CH_4^+$ ion, and the larger attractive inter-

action parameter in the Lennard–Jones equation for the $H_3O \cdot CH_4^+$ ion. Finally, experiments and calculations of this type offer an opportunity for obtaining crude but perhaps valuable information concerning the relative sizes of ions such as CH_5^+, H_3O^+, etc., from mass spectrometric measurements.

$C_2H_5^+$ also interacts with CH_4, and the experimental enthalpy change is -2.39 kcal/mol (Table II). We have considered the problem of applying our calculational technique to this system and have made a preliminary calculation, but without encouraging results. Lathan, Hehre, and Pople[11] gave a structure for $C_2H_5^+$ calculated from molecular orbital theory, and this structure is not very much different from the classical structure for $C_2H_5^+$ as a methyl ion with one of the hydrogens replaced by a methyl radical. If all of the formal change is concentrated on the methylene carbon atom, the electrostatic interaction with a nearby methane molecule will be about equal to that calculated for the $CH_5 \cdot CH_4^+$ ion for $\delta_{C^+} = 1.0$. This is not in agreement with the experimental finding that the enthalpy for $C_2H_5 \cdot CH_4^+$ formation is approximately half that for $CH_5 \cdot CH_4^+$.

For an unsymmetrical entity such as $C_2H_5 \cdot CH_4^+$ the interaction energy will depend rather strongly upon the charge distribution in $C_2H_5^+$, and the lower interaction energy found may be the result of an extensive distribution of formal charge over the $C_2H_5^+$ ion. Alternatively, the distance of closest approach between $C_2H_5^+$ and CH_4 may be much larger than one would predict on the basis of the postulated structure for $C_2H_5^+$; that is to say, the postulated structure is not appropriate. The heat of formation of ethyl ion is significantly lower than that of methyl ion, and this is generally attributed to the inductive effect and/or hyperconjugation. With both of these phenomenon the energy lowering is effected by distributing the charge over a larger volume, which would account for our low interaction energy. However, we have been unable to arrive at reasonable quantitative estimates of the charge distribution and to account quantitatively for the observed enthalpy change. We are of the opinion that the inherent complexity of the $C_2H_5 \cdot CH_4^+$ system exceeds the capacity of our naive electrostatic calculational formalism, and we do not think that our failure with this system casts doubt upon our results for the $CH_5 \cdot CH_4^+$ and $H_3O \cdot CH_4^+$ systems.

In somewhat the same vein, one can observe from Table II that both $CH_5 \cdot CH_4^+$ and $H_3O \cdot CH_4^+$ ions add a second molecule of methane, but because there is no hope for guessing at structures for these ions, no electrostatic calculations have been attempted.